Part two:

Environmental Assessment

1. INTRODUCTION

The scope document for this arsenic wood treatments review indicates that environmental concerns regarding timber treatments mainly relate to the potential contamination of sites where timber has been treated and where disposal of treated timber occurs. CCA has been extensively used in the past as a timber treatment and there are sites that have potentially been contaminated due to leaks and spills from treatment plants or drips from freshly treated timbers. Other possible areas of concern are where treated timbers have been slowly degraded and CCA components released into the ground, with possible subsequent mobility to other areas and effects on non-target organisms. The burning of CCA-treated timber is of environmental concern as the smoke and ash contain high levels of copper, chromium and arsenic, all of which can be toxic to the environment.

The NSW EPA submission regarding CCA timber treatments (including comments on behalf of the Environment Protection Heritage Council Waste Working Group) raises issues pertaining to:

- the design and management of wood preservation sites, both in regard to environmental protection at the site and proper treatment and fixation of CCA;
- impacts from arsenic leaching during use, with those from uses such as structures around houses and playgrounds perceived more as a concern for human health, while potential environmental effects are seen as more of an issue from uses such as boardwalks and other structures in National Parks, jetties and other structures in marine and freshwaters, and possibly electricity poles;
- the problems arsenic-treatment creates for the management of waste timber, eg contamination of compost, emission problems if the waste is used for energy recovery, and potential long-term problems if waste is directed to landfill.

A submission from K Loveridge of the Croydon Conservation Society claims that the viticulture industry is the largest user of treated pine products in Australia. NSW EPA also raised the specific issue of the large number of CCA-treated posts now being used by the viticulture industry, and the large disposal problem this may lead to in the future. With expansion of the viticulture industry over recent years to 33,000 ha in NSW, and 400-800 posts used per hectare, there are 13.2-26.4 million posts in vineyards. With up to 15% of posts replaced each year due to breakage etc, disposal of CCA-treated timber posts is potentially a large-scale problem. The Department of the Environment and Heritage is aware that this issue is also concerning the South Australian EPA. Similar problems have presumably arisen in other states due to the expansion of the wine grape industry.

NSW State Forests noted in its submission that there are potential implications for the use and availability of forest resources. CCA-treated plantation softwood timber products are now being used in many applications where durable hardwoods (eg tallowwood and ironbark) were used previously. This has been important because of the significant reduction in availability of naturally durable timber that has followed the major reduction in logging of native forests in the past 10 years. Better use has also been made of the available hardwood forest resource by using CCA to treat the sapwood component of finished products, particularly heavy timber such as poles, piles and girders. The submission by Osmose (Australia) Pty Ltd also suggests that extending the life of timber by wood preserving techniques reduces the number of trees that may otherwise need to be harvested, and that there are savings in energy and other resources by using treated wood instead of steel, concrete or plastic.

WHO (2001) observes that arsenic (and other arsenicals) is produced from arsenic trioxide, a by-product of metal smelting operations, and that it has been estimated that 70% of world arsenic production is used in timber treatment as CCA, 22% in agricultural chemicals, and the remainder in glass, pharmaceuticals and non-ferrous alloys. Thus there may be significant implications for world demand for arsenic from falling agricultural and timber treatment use. An increasing proportion of arsenic mined as a by-product with other minerals would then be likely to become mining and smelting waste. Australia has produced arsenic in the past, mainly as a by-product of Western Australian gold mines and a Queensland (Stanthorpe) mine, with some production also in NSW, Victoria and South Australia (in some cases, mines were operated solely for arsenic production, and a major purpose was for production of herbicide to control prickly pear). Since 1952 all of the nation's requirements have been imported, as it has not been economic to continue mining or processing ore for arsenic production in Australia (Internet http://www.minerals.nsw.gov.au/minfacts/22.htm).

This review will concentrate on environmental exposure arising from the wood treatment/fixation process, use in terrestrial situations, and disposal of treated material. Attention will be given to all three elemental components of CCA, though most emphasis will be on the arsenic component. The review will not consider the potential environmental impacts of non-arsenic alternatives to CCA or arsenic trioxide.

Information sources which have been used include conference papers, reviews and scientific papers, some website sources and some unpublished reports (often summaries only) of standard ecotoxicity studies. These have largely been provided by the product registrants, with some supplied with public submissions, and some obtained directly for this assessment.

2. CHEMICAL IDENTITY

2.1. COPPER CHROME ARSENATE

Common names	CCA Copper Chrome Arsenate Chromated Copper Arsenate
Chemical name	CCA is not a single one substance, but a mixture in water solution of inorganic components containing the elements copper (II), chromium (VI) and arsenic (V). Various ratios of these elements in the form of oxides or salts have been or are still available (Section 4.1).
CAS Registry number	There appears to be no CAS number for CCA, but CAS numbers are listed below for the individual components used in Australian CCA formulations (Table 1).

Table 1. Individual active components used in CCA formulations in Australia.

Active	Chemical form	CAS Number
Copper	Copper (II) oxide [CuO] Copper sulphate (anhydrous) [$CuSO_4$] Copper sulphate pentahydrate [$CuSO_4.5H_2O$]	1317-38-0 7758-98-7 7758-99-8
Chromium	Chromium trioxide [CrO_3] Sodium dichromate [$Na_2Cr_2O_7$]	1333-82-0 7778-50-9
Arsenic	Arsenic acid [H_3AsO_4] Arsenic pentoxide [As_2O_5]	7778-39-4 1303-28-2

It is possible that both sodium dichromate and arsenic pentoxide are the dihydrates (this should have no effect on the content of chromium or arsenic provided the water of hydration is considered during the manufacturing process).

2.2. ARSENIC TRIOXIDE

Common name:	Arsenic trioxide, arsenous oxide, white arsenic
Chemical names:	Arsenic (III) oxide
CAS Registry number:	1327-53-3
Molecular formula:	As_2O_3
Structural formula:	As_4O_6

3. PHYSICAL AND CHEMICAL PROPERTIES

3.1. COPPER CHROME ARSENATE COMPONENTS

As indicated above, CCA is a mixture of inorganic components containing the elements copper, chromium and arsenic. Lebow (1996) explains that the primary role of chromium is in CCA fixation, through a complex series of reactions driven by its reduction from the hexavalent state to the trivalent state after it is applied to the wood. Copper and arsenic provide the efficacy of the preservative, copper primarily as a fungicide, and arsenic more for its activity as an insecticide, and also for activity against copper-tolerant fungi. Cookson (2001) claims that while arsenic was originally thought to be needed for insect control, the latest theory is that arsenic is more useful in controlling copper-tolerant brown rotting fungi. Details of the individual substances used in Australian formulations follow.

3.1.1. Copper

Compounds of the metal copper usually have a valence of 2+ (II, cupric) under oxidised conditions or 1+ (I, cuprous) under reducing conditions. Only substances with the divalent (2+) form are used in CCA formulations, as listed in Table 2.

Table 2. Properties of copper containing substances used in various CCA formulations.

Active	Properties	Species in solution
Copper (II) oxide	Formula: CuO Molecular Weight: 79.54 % copper (Cu): 79.9% Form: Black to brown solid Decomposition: 1326 ºC Solubility: Insoluble in water, soluble in acidic solutions. Stability: Stable at room temperature under normal storage conditions	$Cu(OH)_2$
Copper sulphate (anhydrous)	Formula: $CuSO_4$ Molecular Weight: 159.50 % copper (Cu): 39.8% Form: White or grey hygroscopic powder Decomposition: 600 ºC Solubility: Very soluble in water Stability: Stable	Cu^{2+} and SO_4^{2-}
Copper sulphate pentahydrate	Formula: $CuSO_4.5H_2O$ Molecular Weight: 249.50 % copper (Cu): 25.5% Form: Blue crystalline solid Decomposition: Loss of water of hydration begins at 30 ºC, becomes anhydrous by 250 ºC Solubility: Very soluble in water Stability: Stable	Cu^{2+} and SO_4^{2-}

3.1.2. Chromium

The metal chromium (Cr) occurs in each of the oxidation (valence) states from –2 to +6, but only the 0 (elemental), +2, +3 and +6 states are common. Divalent (+2 or II) chromium is unstable in most compounds, as it is readily oxidised to the trivalent (3+ or III) form by air. The trivalent (chromous) and hexavalent (6+ or VI, chromic) oxidation states are those most relevant to the environment, each having very different properties and biological effects on living organisms (WHO, 1988). The following chromium-containing components of CCA formulations (Table 3) all contain chromium in the hexavalent form. Once wood is treated with CCA, the form of chromium present is largely trivalent.

Table 3. Properties of chromium containing substances used in various CCA formulations.

Active	Properties	Species in solution
Chromium trioxide	Formula: CrO_3 Molecular Weight: 99.99 % chromium (Cr): 52.0% Form: Dark red deliquescent solid Decomposition: 197 ºC Solubility: 63 g/100 g water at 20 ºC Stability: Stable under ordinary conditions of use and storage. Moisture sensitive, strong oxidiser	Species are pH dependent. pH 2-6: $HCrO_4^- \leftrightarrow Cr_2O_7^{2-}$ pH < 1: $H_2CrO_4^-$
Sodium dichromate	Formula: $Na_2Cr_2O_7$ Molecular Weight: 261.9 % chromium (Cr): 39.7% Form: Orange to red crystals Decomposition: 400 ºC Solubility: Very soluble in water Stability: Stable under normal conditions. Incompatible with combustible materials	Initially: Na^+ and $Cr_2O_7^{2-}$, but is pH dependent (see chromium trioxide)

3.1.3. Arsenic

Arsenic (As) is an element with metalloid properties. Although not strictly a metal, scientific and technical reports commonly include arsenic in discussions of CCA components and heavy metals in the environment. Arsenic can exist in four valency states: -3, 0, +3 and +5. Under reducing conditions, arsenite (As^{3+}[III] – AsO_2^-) is the dominant form, while arsenate (As^{5+}[V] – AsO_4^{3-}) is generally the stable form in oxygenated environments (WHO, 2001). Substances containing arsenic in the pentavalent form are used in CCA formulations (Table 4), whereas arsenic termite treatments use arsenic trioxide, which contains arsenic in trivalent form.

Table 4. Properties of arsenic containing substances used in various CCA formulations.

Active	Properties	Species in solution
Arsenic acid (80% solution)	Formula: H_3AsO_4 Molecular Weight: 141.90 % arsenic (As): 52.8% Form: Aqueous solution (slightly yellow) Decomposition: 206 ºC, boils at 128 ºC Solubility: Completely miscible Specific gravity: 2.00 g/mL Stability: Stable at normal conditions (avoid reducing agents)	$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+$, is pH dependent.
Arsenic pentoxide	Formula: As_2O_5 Molecular Weight: 229.8 % arsenic (As): 65.2% Form: Amorphous white solid Decomposition: 315 ºC Solubility: 65.8 g/100 mL water at 20 ºC Stability: Stable	See arsenic acid.

3.2. ARSENIC TRIOXIDE

Molecular weight:	197.8
% arsenic (As)	75.7%
Appearance:	White powder, transparent crystals
Melting point and boiling point:	315 ºC; 465 ºC; sublimes freely at >135°C
Density:	3.74 g/cm^3
Vapour pressure:	66.1 mm Hg at 315 ºC
Solubility in water:	3.7 g/100 mL at 20 ºC

4. FORMULATIONS

4.1. COPPER CHROME ARSENATE FORMULATIONS

4.1.1. CCA formulation types

There are two preferred mixtures for the formulations, described as CCA oxide or salt formulations (Table 5).

Table 5. Active components of CCA oxide and CCA salt formulations.

Formulation I – oxides	Copper (II) oxide, chromium trioxide, arsenic acid
Formulation II - salts	Copper sulphate (anhydrous or pentahydrate), sodium dichromate, arsenic acid or arsenic pentoxide

The Australian Standard™ Specification for Preservative Treatment, Part 1: Sawn and round timber (AS 1604.1-2000) specifies that the composition of CCA formulations shall fall in the limits copper 23-25%, chromium (hexavalent) 38-45% and arsenic (pentavalent) 30-37% in solution. This appears in Appendix B (p 32) of the document, described as “normative”, ie “an integral part” of the Standard.

Three types of formulation are specified in the USA AWPA standards (1994), and these are tabulated below (Table 6). Two of the formulations first used for large scale treatments of utility poles in the USA (from ~1938) were CCA-A, and CCA-B was in use by 1967 (Arsenault, 1975). Arsenault (1975) found field test evidence confirming earlier laboratory studies that showed CCA-B was not as resistant to leaching as CCA-A and CCA-C, where the proportion of chromium to each of the other elements is higher. Lebow (1996) indicates that the vast majority of treatment in the USA uses CCA-C - the use of CCA-B is currently confined to field and remedial treatments, while relatively few pressure treatment facilities use CCA-A.

Table 6. Composition of US AWPA CCA formulation types.

Active	**CCA-A (% m/m)**		**CCA-B (% m/m)**		**CCA-C (%m/m)**	
	Nominal	**Range**	**Nominal**	**Range**	**Nominal**	**Range**
CuO	18.1	16.0-20.9	19.6	18.0-22.0	18.5	17.0-21.0
CrO_3	65.5	59.4-69.3	35.3	33.0-38.0	47.5	44.5-50.5
As_2O_5	16.4	14.7-19.7	45.1	42.0-48.0	34.0	30.0-38.0

There are currently two main types of CCA approved for use in the United Kingdom. Type 1 and 2 formulations are set out in “Wood preservation by means of copper/chromium/arsenic compositions British Standard 4072: Part 1:1987”, and are tabulated below (Table 7).

Table 7. Composition of CCA formulation types in the United Kingdom.

Actives	UK Type 1 (% m/m)		UK Type 2 (% m/m)	
	Nominal	Minimum	Nominal	Minimum
$CuSO_4.5H_2O$	32.6	29.5	35.0	31.5
$Na_2Cr_2O_7$	41.0	37.0	45.0	40.5
As_2O_5	26.4	23.5	20.0	18.0

Table 8 compares the proportions of copper, chromium and arsenic and mole ratios in various US and UK formulation types with those under the Australian Standard. It appears that the Australian Standard is comparable with the US type CCA-C and the UK type 2.

Table 8. Proportions and mole ratios of the active elements in CCA formulation types in the United States and United Kingdom compared to those with the Australian Standard.

Country	Formulation type/Standard	Proportion Cu/Cr/As by weight			Mole ratios[1]	
		copper	chromium	arsenic	Cr/Cu	Cr/As
Australia	AS 1604.1-2000	0.23-0.25	0.38-0.45	0.30-0.37	1.86-2.39	1.48-2.16
United States	*CCA-A*	0.24	0.58	0.18	2.87	4.59
	CCA-B	0.25	0.29	0.46	1.43	0.90
	CCA-C	0.24	0.40	0.36	2.04	1.60
United Kingdom	*CCA-Type 1*	0.22	0.38	0.40	2.11	1.38
	CCA-Type 2	0.25	0.44	0.31	2.16	2.00

[1] Mole ratios have been presented for nominal values for the USA and UK, calculated from values presented in HSE (2001).

4.1.2. Formulations of CCA currently registered in Australia

There are currently nine CAA timber treatment products registered within Australia. Table 9 lists these, together with their active ingredient content, proportions of copper, chromium and arsenic, and the mole ratio of chromium to copper and chromium to arsenic. All these formulations appear to meet the Australian Standard.

Table 9. Copper Chrome Arsenate (CCA) formulations currently registered in Australia.

Product Number	Product Name	Active element and form present			Proportion Cu/Cr/As by weight	Molar ratio	
		Copper	Chromium	Arsenic[1]		Cr/Cu	Cr/As
30691	Tanalith CP Wood Preservative Paste	75.7 g/kg (as cupric sulphate)	135.2 g/kg (as sodium dichromate)	95.8 g/kg (as orthoarsenic acid)	0.25/0.44/0.31	2.18	2.03
39884	Tanalith O Type C Oxide Wood Preservative	86 g/L (as cupric oxide)	147.9 g/L (as chromium trioxide)	132.7 g/L (as orthoarsenic acid)	0.23/0.40/0.36	2.10	1.61
40092	Impretect CS	52 g/L (as cupric sulphate)	98 g/L (as sodium dichromate)	67 g/L (as orthoarsenic acid)	0.24/0.45/0.31	2.30	2.11
41482	Impretect CO Timber Preservative	163 g/L (as cupric oxide)	306 g/L (as chromium trioxide)	211 g/L (as orthoarsenic acid)	0.24/0.45/0.31	2.29	2.09
41680	Sarmix 3 CCA Salts[2]	88.9 g/kg (as cupric sulphate)	158 g/kg (as sodium dichromate)	112 g/kg (as orthoarsenic acid)	0.25/0.44/0.31	2.17	2.03
41681	Sarmix Oxcell C-680 for Timber Treatment	161 g/L (as cupric oxide)	274 g/L (as chromium trioxide)	245 g/L (as orthoarsenic acid)	0.24/0.40/0.36	2.08	1.61
51821	A & C CCA Salt Wood Preservative	53.5 g/L (as cupric sulphate)	95.9 g/L (as sodium dichromate)	67.9 g/L (as orthoarsenic acid)	0.25/0.44/0.31	2.19	2.06
51822	A & C CCA Oxide Wood Preservative	87.5 g/kg (as cupric oxide)	148.9 g/kg (as chromium trioxide)	133.1 g/kg (as orthoarsenic acid)	0.24/0.40/0.36	2.08	1.61
55939	Timtech C Oxide Wood Preservative	160 g/L (as cupric oxide)	300 g/L (as chromium trioxide)	210 g/L (as orthoarsenic acid)	0.24/0.45/0.31	2.29	2.06

[1] Even if added to the mix as arsenic pentoxide, the arsenic will be in the form of orthoarsenic acid in solution (Section 3.1.3); [2] The copper sulphate is packaged separately to the other ingredients, and the label indicates that 320 kg blue ($CuSO_4.5H_2O$ – four X 80 kg packs) + 400 L (720 kg – 2 X 200 L drums) red/white per batch of 900 kg (nominal) CCA salts.

4.2. Arsenic trioxide termite treatments

Formulations of arsenic trioxide termite treatments currently registered in Australia are shown in Table 10.

Table 10. Arsenic trioxide formulations currently registered in Australia.

Product number	Product name	Active ingredient
48410	Aldi Arsenic Trioxide Termite Dust	489 g/kg arsenic as arsenic trioxide
48909	Garrard’s Termite Powder Insecticide	379 g/kg arsenic as arsenic trioxide
51234	One Bite Arsenic Trioxide Termite Treatment	500 g/kg arsenic as arsenic trioxide

5. ENVIRONMENTAL EXPOSURE

5.1. Application/treatment methods

5.1.1. Copper Chrome Arsenate

5.1.1.1. Treatment process and fixation of CCA

5.1.1.1.1. Overall comments

The general treatment process involves the timber being placed under vacuum to remove air and water from the wood cells. The timber is then pressure treated with the CCA mixture to refill the wood cells with the CCA mixture. The CCA solution is orange, but turns green on fixation to give treated timber its familiar light green colour. The fixation process (loosely defined as the series of chemical reactions that occur to minimise the leaching of the preservative components) is complex and not fully understood (although it has been extensively studied). However, it is considered that important reactions occur during the first few hours of treatment, corresponding to the time during and immediately following treatment. There are no standard treatment procedures (temperature, length of treatment time, pressure, etc.) specified for CCA treated wood. The conditions during treatment and fixation (temperature, length of treatment time, pressure, etc.), composition and concentration of the CCA solution, wood characteristics may have an influence on the extent of fixation and subsequent leachability of CCA, as well as the time for fixation to occur (hence time wood needs to be kept on the drip pad) and other quality and performance aspects of the treatment (depth of penetration, retention rate of CCA in the wood, depth and uniformity of colour etc).

Various internet websites provide some explanation of the main processes used for wood preservation treatment (http://eppserver.ag.utk.edu/pat/PATinfo/C11/pdf/Chapter06.pdf; http://fcg.cof.orst.edu/rc/rc15.pdf; http://www.umass.edu/bmatwt/publications/articles/preservative_treated_wood.html). Brudermann (1999) provides a more detailed description of CCA application procedures commonly used in Canada. The treatment process described above is the "full cell" or "Bethell" pressure method, used for most CCA treatments. It maximises uptake and penetration of the preservative and tends to leave the cell lumina (interior of the cells) filled with preservatives. With "empty cell" ("Lowry" and "Rüping") pressure methods, preservative is pumped in without a preliminary vacuum applied and without air being allowed to escape. Once the pressure is released, air compressed in the cells of the wood (assisted by a vacuum stage at the end) tends to force excess preservative out of the cell lumina, leaving less preservative within them. Thus more preservative than required is applied and the excess removed. These empty cell methods are not commonly used with CCA, but are common with creosote. In the modified Bethell process, which is used with CCA, a lower initial degree or period of vacuum is applied, leaving more air in the cells and rejecting more preservative when the pressure is removed. Use of higher CCA concentrations can then achieve comparable retention of CCA to the standard process, with less water retained. Pearson et al (2001), Pendlebury et al (1997) and Nasheri et al (1998) describe an experimental Multiple-Phase Pressure (MPP) Process, a one stage empty cell CCA treatment and fixation process using hydraulic pressure to inject the preservative solution, replaced by pneumatic pressure which is maintained during a shortened fixation period.

The procedures used, conditions and other parameters may influence CCA recycling and waste streams during treatment, primary fixation and storage. The relative quantities of different solutions produced and the need for processing before recycling or disposal vary between methods. Under some conditions, chemical reactions can form a sludge that cannot be reused directly for processing (affected by temperature effects, acidity changes, wood extractives, iron contamination, minerals in the water – Australian/New Zealand Standard for Plant Operation, AS/NZS 2843.2:2000). Steam heating treatments during fixation may greatly shorten fixation time, reducing the extent of loss of CCA onto drip pads or other treated wood storage areas, and lowering the likelihood that wood may leave the plant yard before fixation is satisfactorily complete. Condensate which contains residues of CCA is then produced and needs to be recycled or may need processing due to sludge formation (Peek and Willeitner, 1988; Willeitner and Peek, 1988). However, accelerated fixation processes are unlikely to be in use in Australia, as fixation occurs satisfactorily under ambient conditions.

5.1.1.1.2. Changes in composition of CCA components during fixation

In a scientific review article, Hingston et al (2001) described the fixation of CCA as a complex and active process, not simply a process of CCA being taken up and deposited in the cells of the wood. Material is taken up and deposited on the cell walls, with deposits of mainly copper on cellulose microfibrils. The highest metal concentrations have been found in porous ring tissues of the wood, and granular precipitates have been observed in tracheids (the main type of cell in softwood). Hingston et al (2001) cite work by Pizzi (eg Pizzi, 1982b), who undertook studies such as the reaction of CCA components with the constituents of wood (lignin, cellulose etc). They state:

"The reaction of Cr^{VI} was considered to take place in a series of consecutive reactions, involving an initial adsorption by carbohydrates, 'in-situ' reduction and the formation of various complexation reactions such as $CrAsO_4$ with lignin, Cu^{2+} precipitation and complexation with lignin and cellulose and CrO_4^{2-} complexation with lignin. CCA-C was considered to have only ±10% of the total chromium remaining in the hexavalent form, which was totally and irreversibly bound to wood and unable to leach. Cr^{III} was considered to be leachable, slowly, along with arsenic. Later work highlighted the presence of chrome arsenates that may be weakly adsorbed or simply precipitated on wood carbohydrates or lignin. Wood extractives (substances that can be extracted from wood by solvents, such as simple sugars, triglycerides, resin acids, free fatty acids and sterols) have also been suggested as a potential site for CCA fixation."

Hingston et al (2001) add that modern techniques have allowed further identification of chemical species and complexes bound to specific sites in the wood anatomy, eg evidence suggests that oxidation of hydroxyl groups on cellulose or lignin and decarboxylation of carbonyl and carboxyl groups occurs during fixation. They note that the continuing longer-term reactions, and the effects these have on the distribution of metal species, are not so well understood. It has also been shown that copper can fix to wood in the absence of chromium. Copper is known to adsorb strongly to organic matter in general.

Hingston et al (2001) provide the following general scheme for CCA fixation (Table 11). Dahlgren (1975c) notes various other substances that are formed during the fixation process, but which are not present among the final equilibrium products: eg some chromium is temporarily fixed to the wood present as a chromato-chromium complex ($[Cr(CrO_4)_3]^{3-}$) in the early stages of fixation, and some as chromium chromates at a later stage.

Table 11. General scheme for CCA fixation reactions (Hingston et al, 2001).

Reaction	Description	Products
Initial – rapid (minutes)	Cu^{2+}, CrO_4^{2-} adsorption to wood	Cu^{2+}/wood Cr^{6+}/wood
Main (hours/days)	Cr^{6+} reduction	$CrAsO_4$ $Cu(OH)CrAsO_4$ $CuCrO_4$ $Cr(OH)_3$ Cr^{6+}/wood complexes Cr^{3+}/wood complexes Cu^{2+}/wood complexes
Long term (weeks/months)	Fluctuating pH	Unknown

There is an instant extensive increase in pH from CCA preservatives coming in contact with wood or sawdust. This increase continues to a maximum and then fluctuates over a period of several months at room temperature (Dahlgren, 1972, 1975c; Plackett, 1983). There are also fluctuations in electrical resistance in solid wood during fixation which may also reflect the chemical changes going on (Evans and Nossen, 1989).

Cooper et al (2000b) noted that the fixation process has at least two distinctly different zones. There is a fast "initial reaction" characterised by a rapid increase in pH (ie from the low initial pH of wood immediately after treatment with CCA) and a decrease in hexavalent chromium (Cr^{VI}). While this may effectively occur while the wood is still in the treating vessel, it may extend a significant time at low temperatures. Cooper et al (2000b) added that the second or main reaction proceeds until the Cr^{VI} in the wood voids is completely reduced to the trivalent form (Cr^{III}). According to Cooper et al (2000b), this point can be used as a definition of "complete fixation." They developed a mathematical model to predict the extent of fixation based on the temperature history of the treated wood following pressure treatment.

Van den Broeck et al (1997) summarised research by Pizzi (1982) and others published in scientific journals as showing that "CCA interacts mainly with the lignin and cellulose compounds of the wood structure, resulting in complexation, precipitation or adsorption. The fundamental reaction during the fixation process is the oxidation of wood components by Cr^{VI} resulting in the reduction of Cr^{VI} to Cr^{III}. This can be described as an interaction of CCA with the functional groups (carbonyl, carboxyl, methoxyl and phenylhydroxyl groups) of the wood components, during which chromium is reduced, arsenic and copper are fixed and some wood components are oxidised."

5.1.1.2. Australian Standards pertaining to application and use

5.1.1.2.1. Recently developed standards

CCA is applied to wood in specially designed facilities so application and fixation conditions can be controlled and to minimise and contain release of the product or waste material to the environment. Labels for CCA products generally provide very limited information on application of the product to wood, some not even indicating rates, though labels and the corresponding Material Data Safety Sheets (MSDSs) carry some general environmental protection advice.

However, the Australian/New Zealand Standard™ Timber Preservation Plant Safety Code, Part 1: Plant design (AS/NZS 2843.1:2000) and Part 2: Plant operation (AS/NZS 2843.1:2000) has been prepared to promote the safe operation of wood preservation treatment plants using CCA and other preservatives, and to reduce environmental and occupational hazards. The standard refers to and incorporates information from the Australian Guidelines for Copper Chrome Arsenate Timber Preservation Plants (ANZECC/TPAA, 1996). A further document (AS/NZS 1605:2000) describes methods for sampling and analysing timber preservatives and preservative-treated timber.

Australian or Australian/New Zealand Standards also provide guidance on use for various types of timber. Standards for Specification for Preservative Treatment include Sawn and Round Timber (AS 1604.1:2000), Reconstituted Wood-based Products (AS/NZS 1604.2:2002), Plywood (AS/NZS 1604.3:2002), Laminated Veneer Lumber (AS/NZS 1604.4:2002), and Glued Laminated Timber Products (AS/NZS 1604.5:2002).

Australian Guidelines for Copper Chrome Arsenate Timber Preservation Plants (ANZECC/TPAA, 1996) and the Australian Standards for Specification for Preservative Treatment (AS 1604) do not specify any methods to be used for fixing CCA in timber. The Australian Standard for Plant Design (AS/NZS 2843.1:2000) indicates that treated timber shall not be moved from the drip pads until the timber surface is dry, and in the case of CCA-treated timber, no sooner than 48 h after treatment, with the comment that this time period may need to be longer in cooler climates. The same document indicates that CCA-treated timber must be held in the treatment plant yard until the preservative is well fixed. However, information on how to assess this is informative rather than normative: an appendix suggests a diphenylcarbazide test kit used with wood samples shaken in water as an appropriate method for assessing fixation, by measuring chromium concentrations in the water extract, and states that (under the test conditions) well-fixed timber should give a result of <0.5 ppm. The Australian Standard AS1604 documents also set out requirements for penetration and retention of the preservative under each hazard class, methods for testing penetration and compliance, and requirements for marking timber to indicate the treatment plant, treatment used and hazard class (penetration and retention results are required if a certificate of treatment is requested).

5.1.1.2.2. Relevance to environmental protection

Various requirements of the Australian Environmental Guidelines and the above Standards seek to protect the environment by minimising and containing leakage, spillage and other means of environmental contamination from CCA, and ensuring that spillages, sludge or contaminated material are collected and recycled or treated and disposed of according to regulatory authority requirements. Guideline requirements pertinent to environmental protection are outlined below:

Plant site

- avoidance of steeply sloping sites (slopes should be < 1:10);
- soil types from loam to clay (>15% clay), with approved protective measures if soils are permeable or located over aquifers;
- located with a buffer distance (though this may be reduced by site factors such as topography) between the plant and any watercourse or water supply storage of 100 m and 800 m, respectively;
- located in an area subject to floods not more than once in 100 years.

Treatment plant layout

- appropriate stormwater management for different parts of the plant – external water (uncontaminated, eg from the plant roof) diverted away from the plant and monitored to ensure it is not contaminated if released offsite, surface water not to build up in the treatment plant yard (eg where drip-free treated timber is stored) and water leaving the yard to comply with relevant environmental guidelines (ie emission limits), plant water to be collected in a sump and either used in the treating process or tested for contamination before disposal, uncontaminated water may be directed to stormwater drains so it does not enter sullage or preservative spillage collection tanks or areas;

- bunding of the plant site/individual vessels located and designed so as to collect leakage and contain a safety margin above the maximum total volume of timber preservative solution in use and/or in storage;
- impervious concrete paving of the treatment plant site (including vessels, pumps, tanks and other chemical storage vessels, chemical unloading areas and freshly treated timber pads), surrounded by a ≥200 mm integrally constructed bund and draining to collection sumps, with an impermeable membrane beneath all concrete on new plants and all joints appropriately sealed;
- installation of leak detection systems, including a test well at the lowest point, and additional test wells to detect contamination under the impermeable membrane;
- the ability to collect and store any contaminated rainwater from exposed surfaces;
- all stored concentrates to be held in a bunded, roofed and secure compound;
- in plants where dry chemicals are processed, provision to contain the contaminated dust (eg filtered exhaust ventilation in a closed plant, with filtered contaminants recycled or disposed of as hazardous waste);
- provision of drip pads with sufficient capacity to hold freshly treated timber until the surface is dry (and no sooner than 48 h after treatment with CCA), with facilities to collect and recycle solution which has dripped;
- provision for subsequently holding treated wood until the CCA preservative is well fixed.

Treatment plant operation

- emergency planning precautions – signs and labels, staff training etc;
- operational training, controlled access etc;
- appropriate design and maintenance of pressure vessels, vacuum pumps etc, including condensing traps to catch preservatives contained in their exhausts;
- spill management procedures – containment to prevent spills flowing into drains and watercourses or blowing away, eg placement of soil levee banks and the use of absorbent material (sand, sawdust etc) and/or stabilising agents (90% lime and 10% sodium metabisulphite mixture for large spills of CCA which cannot be recycled);
- wherever practicable, spilt material, washings etc should be collected and returned to the treatment process;
- chemical sludge can be formed from CCA components under some conditions, but there is a recovery process for this from CCA chemical suppliers, hence this type of sludge can and should be recycled;
- waste which cannot be used should be drummed, labelled and disposed of at a site approved for acceptance of such waste, or after appropriate treatment according to relevant regulatory authority requirements;
- if a Toxicity Characteristic Leaching Procedure (TCLP) test shows copper, chromium and arsenic levels in excess of 100, 5 or 5 mg/L, respectively, there may be regulatory requirements to treat CCA-contaminated material by washing any free CCA chemicals from the contaminated material, immobilising the insoluble residue into a concrete-type matrix, and containing the treated waste in concrete pipes or steel drums;
- wastes should not be disposed of on site.

Decommissioning phase

- land that has previously been used for timber preservation plants should not be used for a more sensitive land use, unless a detailed site assessment has been conducted and the results assessed by the relevant environmental protection and/or planning authority.

5.1.1.2.3. Past use and current adherence to these standards

The Australian Environmental Guidelines document (ANZECC/TPAA, 1996) explains that the guidelines were developed jointly by the Australian and New Zealand Environment and Conservation Council (ANZECC) and the Timber Preservers Association of Australia (TPAA) to generate an Australian national standard for the design of new treatment facilities and for the upgrading of existing plants. CCA was introduced commercially into Australia in 1957. Initial plants had minimal or non-existent containment facilities, with discharge of leaks onto the ground. Progressive improvements were made over succeeding decades. There were limited containment facilities in plants built over the 1960s and 1970s, with treated timber still stored on bare ground, and some ground contamination still noticeable. Plants built in the 1980s had an effective bunding system to contain spills and leaks from the cylinder, tanks and equipment, and retained collected liquids for use in plant operations, but the adequacy of measures for drip pads was variable. Some more recent plants conform to an earlier Australian Standard developed in 1985 (AS 2843.1 – SAA Timber Preservation Safety Code: Plant Design), with an appropriately designed drip pad area as well as provision of bunding etc to retain and re-use contaminated plant water.

ANZECC/TPAA (1996) indicates that new plants are expected to comply with these guidelines immediately and existing plants (where presumably there may in some cases be contaminated areas from inadequate plant design and operation in the past) within two years (ie presumably by September 1998). Whether due to inadequacies in plant design or in plant operation, it appears that full compliance with the guidelines/standards cannot yet be replied upon: the submission for this review from NSW EPA notes gaps which were found through audits of a number of NSW timber treatment facilities which included a review of best environmental management practices. A survey by the Timber Preservers Association of Australia (see Section 5.2.1) produced 28 out of 29 respondents indicating that they treated wood in accordance with the requirements of AS 1604 series of Standards, but 3 out of 29 respondents indicated that their plant did not conform to AS 2843 or similar specifications.

The NSW EPA submission also notes that the Standards contain most, but not all of the best environmental management practices used within the industry worldwide. They indicate that they have asked the industry to consider a review of the Standards to address the gaps. One aspect that may need reinforcement is to specify particularly that wood, sawdust and shavings treated with CCA shall not be incinerated at all with currently available facilities - the current recommendation is that this shall not be carried out except in plants specifically designed for that purpose, but it is uncertain whether or not available facilities would have adequate provisions to prevent release of volatilised arsenic to the atmosphere. Also, current facilities may not have adequate provisions for managing ash and particulate recovery. The Standards do not seem very clear on how the treatment plant yard used for holding CCA-treated timber should be constructed, though the ANZECC Guidelines indicate that impervious treated timber storage areas may need to be provided in cooler areas where fixation times may be extended in winter. Another aspect which could be considered is the use of the chromotropic acid test (Section 6.3.1.3.2) as an alternative means of assessing fixation to that indicated under AS/NZS 1605-2000.

There may also be other material such as manuals to guide use available from different sources, including product suppliers, treatment companies and state environmental agencies. Guidance on the design and operation of wood preservation facilities is also available overseas, such as that prepared for Environment Canada by Bruderman (1999).

5.1.1.3. Application rates

Through the description of various hazard classes and specifications for their use, guidance is provided in the Australian Standards to ensure efficacy while avoiding unnecessarily high rates. Indications of the selection criteria used and typical uses for sawn and round timber are summarised in Table 12, obtained directly from the published standards. Table 13 indicates the retention rate and penetration requirements specified for sawn and round timber under the same standards (ie specifically AS 1604.1 – 2000). The same hazard classes, exposure situations, service conditions, biological hazards and retention rates essentially apply to other timber product types and necessary information can simply be adapted for use on product labels, as is the case with the one current product label providing this information. However, typical uses and penetration requirements differ between sawn and round timber and other timber products (ie reconstituted wood-based products, plywood, laminated veneer lumber and glued laminated timber products (AS/NZS 1604.2-1604.5), and the higher hazard classes are not relevant to some timber products. The differences in penetration requirements and complexity of descriptions for these make this information in particular more difficult to add to the label. No current label carries it.

Table 12. Selection criteria and typical uses for sawn and round timber for Hazard Classes under Australian Standards (AS 1604-2000).

Hazard class	Exposure	Specific service conditions	Biological hazard	Typical uses
H1	Inside, above ground	Completely protected from the weather and well ventilated, and protected from termites	Lyctids	Susceptible framing, flooring, furniture and joinery
H2	Inside, above ground	Protected from wetting, nil leaching	Borers and termites	Framing, flooring and similar, used in dry situations
H3	Outside, above ground	Subject to periodic moderate wetting and leaching	Moderate decay, borers and termites	Weatherboard, fascia, pergolas (above ground), window joinery, framing and decking
H4	Outside, in-ground	Subject to severe wetting and leaching	Severe decay, borers and termites	Fence posts, greenhouses, pergolas (in ground) and landscaping timbers
H5	Outside, in-ground contact with or in fresh water	Subject to extreme wetting and leaching and/or where the critical use requires a higher degree of protection	Very severe decay, borers and termites	Retaining walls, piling, house stumps, building poles, cooling tower fill
H6	Marine waters	Subject to prolonged immersion in sea water	Marine wood borers and decay	Boat hulls, marine piles, jetty cross-bracing, landing steps and similar

Australian application rates are specified on a mass/mass basis (ie kg/kg wood dry weight) as total CCA elements (copper + chromium + arsenic) for most hazard classes, and as arsenic only for hazard class H1. However, the units generally used in the technical and scientific literature for timber treatment are kg/m^3 (or pcf – pounds per cubic foot), evidently as CCA oxides, though UK rates are specified in kg product/m^3. Furthermore, the density of wood varies widely between species, especially softwoods to hardwoods, hence care is necessary in relating Australian rates to those overseas or in the literature. Tabulated data in Bootle (1983) indicate that dry densities of wood range from ~400 to ~1140 kg/m^3, with the dry density of radiata pine ~480-510 kg/m^3, whereas hardwoods like ironbark and tallowwood are in the range 990-1140 kg/m^3.

Table 13. Minimum retention and preservative penetration zone requirements for sawn and round timber for Hazard Classes under Australian Standards (AS 1604-2000).

Hazard class	Retention requirement (% m/m)[1]	Preservative penetration zone
H1	Not less than 0.035 as elemental arsenic	Evidence of distribution of the preservative in the sapwood
H2	0.320 as Cu + Cr + As	Penetration of all sapwood if timber is in natural durability class 1 or 2 (penetration of heartwood not required), plus additional requirements for durability classes 3 and 4 based on dimensions (≥5 mm if lesser dimension ≤35 mm, ≥8 mm penetration if >35 mm) or on the proportion of untreated heartwood for sawn timber, or ≥8 mm from the surface in round timber
H3	0.380	As for H2
H4	0.630 in softwood and 0.700 in hardwood	As for H2, but additional penetration required with durability classes 3 or 4 in sawn timber (10 mm from all surfaces unless heartwood proportion falls below specified limits) and round timber (≥10 mm from the surface)
H5	1.00 in softwood and 1.20 in hardwood	As for H4, except that the penetration should be ≥20 mm from the surface instead of 10 mm, with specific requirements for poles supporting overhead lines
H6	2.00 in softwood and 1.20 in hardwood; creosote must also be used in northern waters	Penetration of all sapwood if the timber is a hardwood of durability class 1 (turpentine only in northern waters), plus additional requirements of a minimum of 20 mm penetration in sawn timber unless heartwood proportion falls below specified limits, and a minimum penetration of 15 mm from the surface for round timber.

[1] % mass/mass based on the oven-dried mass of the treated wood, as total elements except for H1..

Broadly similar hazard classes and retention rate requirements are specified in the USA and UK, but with five rather than six hazard classes (Table 13 and Table 14). To convert Australian rates to kg/m^3 as CCA oxides, a wood density of 500 kg/m^3 has been assumed for softwoods and 1000 kg/m^3 for hardwoods, and a ratio of 1.63 for CCA oxides relative to CCA total elements. To compare the UK rates with these figures, it has been assumed that a typical product contains ~70% CCA oxides. The results are summarised in Table 15, showing a broad similarity in rates, though possibly somewhat lower for equivalent uses in Australia than the United States. The US is in the process of changing their system to a range of usage classes (Norton, personal communication, 4 November 2003), but the older system has been presented as it relates to the available scientific and technical literature discussed in this assessment report.

Table 14. CCA timber treatment requirements for US hazard classes (based on Lebow, 1996).

US Class	Retention levels (as CCA oxides)		Typical purposes
	pcf	kg/m^3	
I	0.25	4.0	laminates, plywood & timber used for above-ground applications
II	0.40	6.4	agriculture & building posts, highway fences, signs, ie ground or freshwater contact uses
III	0.60	9.6	load bearing wood components such as utility, agriculture & building poles
IV	0.80	12.8	load bearing wood components such as saltwater piles with dual treatment, building poles
V	2.50	40	wood foundations and saltwater applications - saltwater lumber, saltwater piles with severe borer hazard

Table 15. CCA timber treatment requirements for UK hazard classes (from HSE, 2001).

UK Class	Approximate retention levels (kg CCA product/m^3)	Purpose
I	8	Out of ground contact (dry) – insect risk only
II	8	Out of ground contact (occasional wetting)
III	10.5	External timbers exposed to wetting by rain but not in ground contact
IV	12-20	Timbers in ground contact or in fresh water
V	20-32	Timbers in the marine environment

Table 16. Comparison between Australian CCA treatment rates and those in the USA and UK.

AUSTRALIA	% kg/kg oven dry weight as total elements	kg/m^3 if wood 500-1000 kg/m^3 oven dry weight as elements[2]	kg/m^3 if wood 500-1000 kg/m^3 oven dry weight as CCA oxides[3]	US	kg/m^3 wood as CCA oxides	UK	Approximate retention levels (kg CCA product /m^3)	Approximate retention levels as CCA oxides (assuming these are ~70% of the product weight)
H1	0.11	0.55-1.1	0.9-1.8	**H1**	4.0	**I**	8	5.6
H2	0.32	1.6-3.2	2.6-5.2					
H3	0.38	1.9-3.8	3.1-6.2	**H2**	6.4	**II**	8	5.6
H4	0.63 (softwood) 0.7 (hardwood)	3.15-7.0	5.1-11.4	**H3**	9.6	**III**	10.5	7.4
H5	1.0 (softwood) 1.2 (hardwood)	5-12	8.2-19.6	**H4**	12.8	**IV**	12.0-20	8.4-14
H6	1.2 (hardwood) 2 (softwood)[4]	6-10	16.3-19.6	**H5**	40	**V**	20-32	14-22.4

[1] The H1 retention rate is actually specified as 0.035% m arsenic/m wood); [2] 500 kg/m^3 assumed where Australian Standard 1604 refers to softwoods, and 1000 kg/m^3 where it refers to hardwoods (ie in H4-H6); [3] rate as oxides calculated as 1.63 X rate as total elements; [4] note that while a higher retention level is specified in the Standard for hardwoods than softwoods in hazard classes H4 and H5, the reverse is the case for H6.

5.1.2. Arsenic trioxide

Product labels indicate that formulations of arsenic trioxide for the control of termites may be used both in the interior and exterior of buildings, and outside buildings in logs, stumps, poles or living trees suspected of harbouring termites. Australian Standard 3660-2000 applies to the use of such products - AS 3660.2-2000 and AS 3660.3-2000 appear most relevant, ie Termite management - In and around existing buildings and structures - Guidelines and Termite management - Assessment criteria for termite management systems, respectively, whereas 3660.1-2000 is Termite management - New building work. The dust is applied into the termite workings by a hand blower, gaining access by prising a splinter from the surface or drilling holes through which the dust may be gently puffed. The labels stress that only a small amount should be applied, with the indicated rate being 1-2 g per infestation. This rate is the same for all three products, though the amount of active ingredient in each varies slightly (379-500 g arsenic/kg - Table 10, p 16). Thus pack sizes of 100-500 g enable a large number of infestations to be treated.

In practice, the quantity used in an infestation is somewhat dependent on the level of infestation, and the size of an infestation or the area that needs to be treated may vary widely. An infestation is likely to be located some distance from the main colony/nest, linked by a series of subterranean tunnels, and there may be several other infestations from the same colony. There may also be more than one infestation affecting a structure, eg with termites from another species.

The labels note that excessive use of arsenic trioxide dust could lead to termites sealing off galleries, and that with living trees, care should be taken to avoid contamination of the sapwood. One approved label indicates that openings made in workings should be taped up so there is minimum disturbance of the colony, but it appears that the access holes are not always sealed by the operator. This label adds that after treatment the treated areas should be left undisturbed for 10-20 days, then reopened and areas still occupied by termites retreated, which may need to recur several times before complete control is achieved. Thus any sealing by the operator that does occur is likely to be temporary, both because holes are simply sealed with tape, and because they are likely to be reopened in any case to inspect the workings for any remaining activity.

A submission from the Australian Environmental Pest Managers Association Ltd explains that dissemination of the dust throughout the termite galleries and contact with the queen is assisted by the slow (hours to days) toxic action of the poison. The powder adheres to the bodies of worker and soldier termites as they move through parts of the nest reached by the dust and is then passed from termite to termite by grooming and cannibalism. They note that success depends on using minute quantities (usually ≤2 g per colony) of ultra fine powder propelled by relatively large quantities of air, with minimum disruption of the termite workings. Colony elimination usually takes from 14-28 days.

A submission from Ensystex Australasia claims that while in theory only small amounts need to be used, significantly greater amounts of dust are actually applied (they suggest comparison with the total amount sold and claim instances of heavy cumulative application and of gross misuse). This submission also notes (from the aspect of worker and homeowner exposure) that the fine dust may billow through or out of the timber, and that it may sometimes be used unnecessarily, eg where termites are not active. However, these are issues of misuse, as the label instructions clearly indicate the maximum rate and general method which should be used. If the label directions are followed, the risks to the environment should be acceptable. Two of the three product labels for arsenic timber treatments stipulate “For sale to, and use by, licensed pest control operators only (One Bite Arsenic Trioxide Termite Treatment) or “For use by licensed pest control operators only" (Garrard's Termite Powder Insecticide"), while the ALDI label bears the sentence "treatment by licensed pest manager as assessed as competent to National Pest Management Industry Competency Standards, Certificate II" under the use instructions.

The Plywood Association of Australasia Ltd (PAA) in its submission noted that for 35 years PAA members have been using arsenic trioxide as a glueline termiticide, as indicated under Australian/New Zealand Standard AS/NZS 1604.3 – Specifications for Preservative Treatment, Part 3: Plywood, and AS/NZS1604.4 – Specification for Preservative Treatment, Part 4: Laminated Veneer Lumber. Arsenic trioxide is added to plywood adhesives at a dosage of 800 g/m^3, and it is suggested that the arsenic remains encapsulated within the phenolic resin matrix of the glue and is therefore not released into the surrounding environment of the plywood product. The standards only provide glueline specifications for hazard class 2 of plywood or laminated veneer lumber, for which the specified arsenic retention is 0.13% mass/mass based on the oven-dried mass of the test sample. None of the Australian labels provided refers to this use.

5.2. Environmental release

5.2.1. Copper Chrome Arsenate

Copper chromium arsenate is applied to wood in special treatment facilities. The treated timber is then transported for wholesale and retail sale. It may then be used to construct timber structures on site, or for the manufacture of timber products. CCA-treated wood in structures is likely to remain *in situ* for a prolonged period (of the order of 10-50 years), depending on the nature and purpose of the structure. It might then be re-used, recycled or disposed of in various ways. Release of CCA components to the environment may therefore occur as a consequence of manufacture, transport and storage of the CCA product, treatment, transport and storage of the treated wood, and construction, service and disposal of the structure.

Crumière et al (2002 – source indicated as Greaves, 2002 personal communication) and OECD (2003) reported estimates that the present annual use of CCA in Australia is 6500 tonnes. OECD (2003 – sources indicated as communications from Graves [presumably Greaves] and Hawkins, 2001) indicates that in Australia there are estimated to be a total of 109-121 vacuum-pressure plants applying non-creosote preservatives, plus 4 applying creosote/heavy oil. Of the former, there are 90-100 vacuum-pressure plants applying CCA, 8-10 applying copper-based alternative waterborne preservatives, and applying 11 light organic solvent preservative (LSOP).

The Timber Preservers Association of Australia (TPAA) is the peak association representing the treatment plant operators producing treated timber in Australia. The TPAA has provided the results of a survey of its members. Twenty nine responses were received, a 60% response rate, though evidently one response was rather incomplete. The results show that operations range from wood processing (sawmill) operations in conjunction with treatment facilities (15), to specialist treated timber only producers (11), treatment service providers (3), and unspecified other operations (8). Twenty two of 28 responses indicated that they do brand /tag/label/mark their treated product so that the consumer knows what they have purchased and where it may be used. Responses suggest that the majority of timber treated was hazard classes H3 to H5:

- H1 - 2400 m^3 treated per year by 1 plant;
- H2 – no responses listed;
- H3 – average 6138 (range 600-30,000) m^3 treated per year by 15 plants;
- H4 – average 3594 (range 1200-23,000) m^3 treated per year by 18 plants;

- H5 – average 4120 (range 500-1,600) m^3 treated per year by 5 plants;
- H6 – 60 m^3 treated per year by 1 plant.

5.2.2. Arsenic trioxide

Arsenic trioxide dust blown into termite cavities is not fixed to the wood and will sooner or later be released to the environment. It is presumed that unless exposed to moisture or other action, the arsenic will remain in the form of arsenic trioxide. Treatment occurs to widely dispersed, confined areas where termites are present in structures and nearby trees. Hence secondary dispersal is likely to be in the vicinity of the treated material, and/or destinations of the treated material during disposal when the structure is modified or removed.

6. ENVIRONMENTAL FATE

6.1. Fate of copper, chromium and arsenic in the environment

6.1.1. GENERAL FATE AND BEHAVIOUR

6.1.1.1. Arsenic

Battacharya et al (2002) summarise the literature to state that under the range of redox potential and pH in soil compartments, arsenic normally occurs in the +III and +V oxidations states. As^{III} (H_3AsO_3 or $H_2AsO_3^-$) dominates under reducing conditions and As^V ($H_2AsO_4^-$ or $HAsO_4^{2-}$) is more prevalent under oxidising conditions. As^{III} is the more toxic and mobile form. Preferential sorption of As^V may occur on clay minerals at pH 2 to <8, while As^{III} sorbs preferentially at pH 8 to 10. The geochemical behaviour of As^V and phosphorus are very similar, eg adsorbing to Al and Fe oxides.

WHO (2001) states that under reducing conditions arsenite (As^{III}) dominates in soil, but that elemental arsenic and arsine (the gas AsH_3) may also be present. In well-drained soils, arsenic would be present as $H_2AsO_4^-$ if the soil was acidic or as $HAsO_4^{2-}$ if alkaline. Reactions involving arsenic commonly occurring in soil include oxidation, reduction, adsorption, dissolution, precipitation and volatilisation. WHO (2001) indicates that the amount of arsenic sorbed from solution increases as the free iron oxide, magnesium (presumably actually manganese) oxide, aluminium oxide or clay content of the soil increases (oxalate can be used to remove amorphous iron and aluminium components and hence reduce the arsenic sorption capacity of the soil). Iron oxides/hydroxides appear to be the soil colloids most commonly involved in arsenic adsorption in both acidic and alkaline soils. Aluminium oxides/hydroxides and clay may also adsorb arsenic, but only in acidic soils. Carbonate minerals may contribute to adsorption in calcareous soils, at high pH. Precipitation (eg iron arsenate or sulphides of arsenite) may also assist arsenic removal from soil. Phosphate may suppress arsenic adsorption in soil. Many soil organisms are capable of converting arsenate and arsenite to substances such as methylated arsines, which may be volatile. Some investigators have claimed that total losses of arsenic from soil through volatilisation of alkylarsines are as high as 14-15% or even 17-35% per year, affected by soil nutrient levels and soil microbial activity.

Peters et al (1996) estimated the residence time of arsenic in terrestrial soils as approximately 2400 years, due primarily to the stability and insolubility of the complexes that arsenic forms in this compartment, though arsenic tends to be slightly more mobile in sandy environments, particularly at higher pH levels, and where phosphate competes for binding sites. They also noted that dimethylarsine and trimethylarsine do not adsorb to soil like other forms of arsenic and are not leached downward, and may allow arsenic loss from soil to the atmosphere (amounting to 12-15% per year). However, they add that loss of arsenic from soil is not a major source of arsenic input into the atmosphere (<0.01% of atmospheric input). The global tropospheric atmospheric residence time of arsenic is thought to be ~9 days, due to natural flushing of residues in air by precipitation (also dry deposition) as well as chemical conversions (Peters et al, 1996). It appears that while loss of arsenic from soil to the atmosphere can occur at a significant rate, a 2400 year residence time suggests that generally volatile loss occurs at a low rate.

WHO (2001) comments that dissolved forms of arsenic in the water column include arsenate, arsenite, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Various complex processes may occur in the water column and sediment, including oxidation and reduction, adsorption to clay surfaces, iron oxides, aluminium hydroxides and organic matter, methylation and demethylation, with microbial action and transport by turbulence and convection, as discussed in more depth by WHO (2001).

WHO (2001) states that leaching is not considered to be a major route of arsenic loss from soil. However, Smedley and Kinniburgh (2002) note aspects of arsenic's behaviour that contribute to its presence as a common trace contaminant in groundwaters. Most trace metals occur in solution as cations (eg Cu^{2+}) which at near-neutral pHs in soil are precipitated or coprecipitated as an oxide, hydroxide, carbonate or phosphate mineral, or adsorbed strongly to hydrous metal oxides, clay or organic matter. In contrast, most oxyanions (including arsenic) can persist in solution at relatively high concentrations at near-neutral pH. Furthermore, compared to other oxyanion forming elements, arsenic is relatively mobile under reducing conditions, and can be found at concentrations in the mg/L range when other oxyanions are present in the µg/L range. For example, while it may be present as an oxyanion (Cr^{VI}) under oxidising conditions, chromium is likely to be present in the Cr^{III} form as a cation, and is relatively immobile at near-neutral pH. Suitable reducing conditions are likely to be uncommon in agricultural topsoils, and the conclusion that leaching of arsenic is unlikely to be significant appears valid for many situations, though not necessarily in flooded soils (note that many studies of arsenic movement have evaluated soil levels subsequent to lead arsenate use as a pesticide).

6.1.1.2. Copper

Battacharya et al (2002) indicate that the solubility of copper in soil is governed by pH and redox reactions in the pH range 5.4-6.5, where copper is distinctly more soluble under oxidising conditions than reducing conditions. Copper is complexed by organic ligands, especially carboxylic and phenolic groups. They note that as the solubility of organic matter increases with pH, the dissociation of Cu-organic matter complexes can result in the leaching of copper to groundwater.

WHO (1998) comments that factors influencing the fate of copper in soil include the nature of the soil itself, its pH, the type and distribution of organic matter, the soil redox potential, the presence of oxides, the base status of the soil and its cation exchange capacity (CEC), the rate of litter decomposition and the proportions of clay to silt to sand particles. Most copper deposited on the soil is strongly adsorbed to the upper few centimetres of soil, being especially bound to organic matter, as well as being adsorbed by carbonate minerals and hydrous iron and manganese oxides. Greatest leaching of copper occurs from sandy soils rather than clays and peats, while acidic conditions favour leaching to groundwater. Processes influencing the fate of copper in aquatic systems include complexation to inorganic and organic ligands, sorption to metal oxides, clays and particulate organic matter, bioaccumulation and exchange between sediment and water.

Van Eetvelde et al (1998b) examined the effect of soil characteristics on copper adsorption in an adsorption study with six soils and various copper-based preservative products (not specified, but two were water-borne copper-salt preservatives and two were copper-organic products). The CEC and pH of a soil were found to be the pre-eminent parameters for adsorption of copper, and there were also differences between copper-salt and copper-organic formulations in soils high in clay or organic matter.

6.1.1.3. Chromium

Battacharya et al (2002) indicate that the Cr^{III} and Cr^{VI} oxidation states govern the mobility of chromium in soil. The prevalent species of Cr^{III} are $CrOH_2^+$ at pH 2 to 6, $Cr(OH)_3$ at pH 6.5-11.5, and $Cr(OH)_4^-$ at pH >11.5. Battacharya et al (2002) add that in the presence of Fe^{III} in geological environments, the solubility of Cr^{III} is controlled by interaction with iron hydroxides. The adsorption of Cr^{VI} increases with decreasing pH.

In a review of the mobility and bioavailability of chromium in soil, James (2002) noted that Cr^{III} has a strong affinity for negatively charged ions and colloids in soils, plants, microorganisms and animals, and as a result, is relatively immobile and non-toxic in these environments and organisms. Soluble chromium concentrations in equilibrium with $Cr(OH)_3$ are $<10^{-9}$ M (<0.05 ppb) in water at pH 6 to $<10^{-15}$ M at pH 8, but the solubility increases significantly with pH values <5.5 (as Cr^{III}) and >8 (as $Cr(OH)_4^-$). Organic acids can co-ordinate with Cr^{III} cations to form organic acid-metal complexes which may affect the solubility and bioavailability of Cr^{III}. In contrast, Cr^{VI} is generally more soluble, mobile and bioavailable, and also more toxic than Cr^{III}. It is present as an anion rather than cation in most soil environments, as the bichromate ($HCrO_4^-$) between pH 1 and 6.4, and as chromate (CrO_4^{2-}) at higher pH values. The dichromate ($Cr_2O_7^{2-}$ - as may be used in CCA formulations) may be present in acidic conditions, but reverts to the bichromate or chromate when diluted or neutralised. Under certain conditions (eg with high levels of manganese oxides/hydroxides present, freshly precipitated forms of Cr^{III}, and pH $\geq$ 7) a proportion of Cr^{III} may be oxidised to Cr^{VI}. James (2002) discusses an approach termed the Potential Chromium Oxidising Score (PCOS) to assess the potential for oxidation of Cr^{III} to Cr^{VI} under specific soil conditions with chromium waste.

6.1.2. Volatility

Arsenic trioxide sublimes at >135°C and thus becomes volatile under combustion conditions, pertinent therefore to disposal of CCA and arsenic treated wood (pp 110-114). Under some conditions (including strongly reducing conditions and biotransformation), arsenic may form compounds which are gaseous under ambient conditions, including arsine (AsH_3) and alkylarsines (CH_3AsH etc). Biotransformation is unlikely to occur generally in treated wood in service, but this may be a means by which arsenic leaching to soil may be lost in some circumstances (Section 6.1.1.1, p 28). The volatility of arsenic trioxide has important ramifications for the fate of arsenic in the event that treated timber or treated waste is burnt (Section 6.8.2, pp 110-114). The salts or oxides of copper and chromium present in CCA formulations, treated wood or treated wood on burning are unlikely to volatilise.

6.1.3. FATE AND BEHAVIOUR OF ELEMENTS ADDED TO SOIL AS CCA OR CCA LEACHATE

6.1.3.1. General overviews

Battacharya et al (2002) note that the bioavailability of copper, chromium and arsenic in contaminated soils may vary according to pH, redox conditions and the quantity of organic matter in the soils. They state that the mobility of these elements is generally controlled by precipitation, diffusion, volatilisation and dissolution of unstable minerals, besides other surface complexation processes. The sorption of arsenic, an anion, differs significantly from that of copper and chromium, which are cations (ie when chromium is Cr^{III}, rather than Cr^{VI}, when it is likely to be an oxyanion), with different influences of soil pH and redox conditions.

Bergholm (1990) explained that when surface soils are directly contaminated with CCA solution, the active constituents are precipitated as different forms of copper and chromium arsenates or other salts due to the rise in pH when the acidic solution reaches the soil. Initially the occurrence of copper, chromium and arsenic in the soil is the same as in the preservative solution. Subsequent dissolution of the precipitated salts may then lead to differing redistribution of these elements down the soil profile, owing to differences in their mobility. Arsenic and chromium may be leached from the surface soil, while copper is often retained. The elements may also become more stable in the soil as insoluble complexes. In contrast, leachate from stored wood has a different composition to the original solution: arsenic is more mobile (for the CCA formulations he was discussing, ~8 X more arsenic than copper can be leached from freshly treated wood by rain or melting snow, while chromium is even less mobile from wood), hence a portion of the arsenic may combine with leached copper and chromium, while the remainder complexes with other soil components or is leached through the soil profile.

Bergholm (1990) noted that factors in soil influencing the mobility of copper, chromium and arsenic include soil pH and the content of organic matter, clay and iron oxides. A low soil redox potential increases the mobility and toxicity of arsenic through reduction of As^V to As^{III}. The chemical properties of As^V, the most common form in aerated soils, are very similar to phosphorus in soil – eg precipitation as strong complexes with iron and aluminium in acid soils and with calcium in calcareous or limed soils. Complexes can also be formed with other elements, such as manganese, and above pH 7, with cadmium and lead.

6.1.3.2. Artificial contamination of synthesised soils with CCA

Balasoiu et al (2001) artificially contaminated nine soils synthesised from differing amounts of peat (0.5-15%), kaolinite (5-30%), sand (30-69.5%) and silt (all 25%) with a commercial CCA-C solution. This was added to soil with a soil/solution ratio of 1:3 and the slurry agitated for 24 h, followed by a further 120 h contact without agitation. The application rate was 2573 mg CCA (605 mg copper, 984 mg chromium and 984 mg arsenic) per kilogram dry soil. The mixture was then centrifuged, the supernatant removed and the soil air dried at room temperature. The soil samples were then digested and subjected to a sequential extraction procedure (SEP) for total copper, chromium and arsenic and arsenic speciation determinations, and to determine the nature in which the metals were held in the soil. SEP groups heavy metals into the following five fractions:

- F1: soluble and exchangeable (extracted in $MgCl_2$ solution);
- F2: bound to carbonates or specifically adsorbed (extracted in acetic acid/acetate buffer);

- F3: bound to reducible Al, Fe and Mn oxides (extracted with hydroxylamine hydrochloride);
- F4: bound to oxidisable matter (released by nitric acid, hydrogen peroxide and ammonium acetate);
- F5: residual metal fraction (dissolved by acid attack with nitric acid, hydrogen fluoride and $HClO_4$).

The authors stated that the contamination level was intended to be realistic and compatible with copper, chromium and arsenic concentrations possibly found in contaminated soils close to wood treated poles in service or at timber treatment facilities. However, as the composition of CCA leachate differs greatly from that of the original solution and the contamination levels are high, the data clearly relate more to contamination at a treatment facility.

Copper retention in the soils varied between 47-97% (283-585 mg/kg), increasing strongly as the organic matter content increased. Copper retention was also correlated with CEC, which was dominated by the organic matter rather than kaolinite clay content, and in mineral soils (0.5% peat) retention increased with increasing kaolinite content. Chromium retention in the soils varied between 19-86% (191-852 mg/kg), being low in mineral soils and increasing strongly as the organic matter content increased. chromium retention was not related to kaolinite content, consistent with previous reports that CEC and soil surface area (clay content) do not significantly influence Cr^{VI} retention. The presence of arsenate was also likely to have reduced chromium sorption to iron oxide-coated sand, due to competition for adsorption sites and electrostatic effects. Total arsenic retention behaved quite differently to copper and chromium, with similarly high retention in mineral and organic soils (71-81%, 700-795 mg/kg). The authors suggested that high arsenic retention was favoured by the slightly acidic pH (5.5) and presence of organic matter and kaolinite. No influence of sand content was evident under the test conditions.

Analyses suggested that in mineral soils, a higher proportion of the copper was present in a soluble or an exchangeable form, whereas binding to oxidisable matter became more important with increasing organic matter content. The level of chromium found in reducible form was relatively high and constant between soils (50-66% of the chromium present was in F3), suggesting that about half the chromium present remained as Cr^{VI}. Strong binding of chromium to oxidisable matter was indicated, with little chromium present in soluble or exchangeable form at ≥7.75% organic matter. Thus the amount of copper and chromium present in soluble or exchangeable form was 138-222 mg/kg and 54-61 mg/kg, respectively, in mineral soils, but this fell for chromium particularly, to 33-99 mg/kg and 1-3 mg/kg in organic soils.

Arsenic was present both as As^V (arsenate) and As^{III} (arsenite), but principally as As^V (69-95%). As^V content was highest in mineral soil (90-95%), decreasing as the soil organic matter content increased. The presence of As^{III} indicates that pentavalent arsenic was reduced once the CCA solution was added to the soil. The authors suggested that this could have been caused by microbial action, as well as chemical actions.

6.1.3.3. Mobility of CCA components from direct spillage onto soil in Belgium

The mobility of CCA components in four soils (a sand, loam, clay and high organic matter content potting mix) was examined in pot trials (soil 55 cm deep) reported by van Eetvelde et al (1998b). A direct leakage of CCA-C-solution (3.5%) to the surface of the soil was simulated, followed by simulated rain. High downward mobility of chromium was evident, consistent with it being present as Cr^{VI}. Copper and arsenic moved downwards to a much lesser extent. Downward movement of chromium was least in the potting mix. Movement of the ions was possibly affected by various soil characteristics, including those to do with moisture dynamics. The investigators concluded that dripping of the product from freshly treated wood or spillage around dipping tanks and treatment vessels might cause severe copper and arsenic pollution of upper soil layers, whereas the evident mobility of Cr^{VI} in soil may potentially lead to groundwater contamination. They noted that these results are consistent with those of previous investigators and confirm the need for measures such as collection of run-off water and reuse of the filtrate in a closed system at treatment plants to care for the environment.

6.1.3.4. Cr^{VI} leaching from large lysimeters in New Zealand following CCA application

To investigate the behaviour in soil of CCA spillage and leaching (eg with up to 10% w/v solutions frequently stored at timber treatment plants prior to dilution to 2% working solutions), Carey et al (2002) undertook a study with large undisturbed soil lysimeters. A simulated CCA timber preservative solution (7:9:4 mixture of $Cu_2SO_4.5H_2O$:$NaCrO_7.2H_2O$:As_2O_5, pH 1.8) was applied to the top of pre-watered sandy loam soil in four lysimeters (500 mm diameter X 700 mm high). After an initial equilibrium period of 3 days, water was applied to leach the CCA solution, using a mixture of mini-sprinkler irrigation and rainfall. The morning after each leaching event, the volume was recorded and a subsample taken for analysis by AAS for total copper, chromium and arsenic. It was assumed that chromate would comprise the vast bulk of any mobile chromium, hence no specific analyses were made for Cr^{VI}. After completion of the leaching experiment, the lysimeter soils were sampled in 20 mm increments to 100 mm and 50 mm increments thereafter. Soils were analysed by AAS after a digestion procedure claimed to determine metals in “bioavailable” form, without extracting significant quantities of background heavy metals in soil minerals.

Total water applied to each lysimeter was ~800 mm over the 102 days of the study, of which 700-780 mm was collected in drainage from each lysimeter. Concentrations for arsenic and copper in leachates from all the lysimeters were negligible (<0.05 mg/L), indicating that they had been retained within the soil profile. Peak concentrations of chromium reached ~27-52 mg/L, with a yellow colouration suggesting that virtually all chromium present was chromate (Cr^{VI}). Mean peak chromium concentration was ~31 mg/L, dropping to ~5 mg/L after 102 days. Characteristics of peak breakthrough time and soil pore volumes indicated that soil physical and chemical processes were slowing peak breakthrough and solute transport in general. The total quantity of chromium leached was ~26% of that applied.

Soil sampling showed that the distribution of retained copper, chromium and arsenic was heavily weighted towards surface layers. 30% of chromium was extracted from the first 50 mm of soil and ~71% in the top 200 mm, with minimal retention in the subsoil (>350 mm). Some 87.5% of the applied copper and 79.7% of the arsenic was recovered from the 0-200 mm depth range, with total recoveries from soil approaching 100%. There were some overestimations in total recovery, thought to be due to sample errors, use of soil core rather than soil layer sampling, and difficulties in sampling the surface layers due to root growth.

A subsidiary experiment was then conducted to examine rates of reduction and sorption of Cr^{VI} over time using soil from the same location used to collect the lysimeters. Small cores were obtained at various depths and sealed in small containers with a quantity of 10% CCA solution equivalent to that applied to a corresponding area of the lysimeter surface. These were maintained at field capacity and aerated conditions before extraction after various time intervals up to 102 days. Reduction of dichromate/chromate anions ($Cr_2O_7^{2-}/CrO_4^{2-}$) to the strongly sorbed cation Cr^{III} was shown to be greatest in surface layers where organic matter contents were largest. After 102 days, <1% of the added Cr^{VI} was still extractable in 0-50 mm cores, compared to ~60% in cores from 400-450 mm or deeper after the same period.

The data were modelled and the conclusion made that there exists a significant potential for Cr^{VI} to be a serious threat to groundwater in the event of a large uncontained spillage of a concentrated CCA solution, heightened in soils with low organic matter contents, where leaching occurs soon after spillage, and with high water input conditions. Once present in the subsoil, a slow rate of reduction would be likely to leave Cr^{VI} anions mobile for a considerable period of time. The authors noted that previous research had shown copper to be particularly well sorbed in this soil, with arsenic added as arsenate less strongly sorbed than copper, but having far less potential for leaching beyond 700 mm than Cr^{VI}.

6.1.3.5. Composition of CCA leachate and effects of passage through soil in New Zealand

The composition of CCA leachate from lysimeters over an 18 month period was evaluated in this New Zealand study reported by Gifford, Marvin and Dare (1997). Lysimeters (300 mm diameter, 600 mm deep, half buried in soil) were set up with washed sand, untreated timber pieces or CCA-treated timber pieces above a 25 mm layer of sand and a 200 mm layer of soil (silty/sand, 7.7-13.3% organic matter, pH 4.9-5.3, CEC 18.7-25.1 meq/100 g). An additional lysimeter contained CCA-treated chips without soil, and one was empty (to monitor rainwater). Radiata pine chips were used, with a CCA type C salt formulation applied via a commercial Bethell full cell process, treating to H3 standards, ie ~6 kg/m^3 salts or 0.22 pcf oxides (pp 23-26). The chips were weathered for 2 months prior to placement into the lysimeters to ensure fixation was complete and that readily soluble CCA salts had been washed off. Wood chips were used to allow material to be satisfactorily packed into the lysimeters, to represent wood waste rather than timber, and to accelerate the rate of leaching. Leachate resulting from natural rainfall was composited over two month intervals. The authors noted that this was a dynamic leaching test, as the leaching solution was continually replaced, and that the leachant to solids ratio was ~40:1.

Highest concentrations of copper, chromium and arsenic (measured by ICAP – inductively coupled argon plasma spectroscopy) were found in leachate from the lysimeter with CCA-treated chips and no soil: the maximum copper, chromium and arsenic concentrations were respectively, 0.17 mg/L, 0.25 mg/L and 0.98 mg/L. The data provided show copper, chromium and arsenic were present in leachate from the second sampling period, 4 months after the study commenced. From this point, there was a more or less consistent decline over the study period in copper concentration and quantity leached per two month increment. In contrast, chromium concentration and quantity leached declined to reach a minimum after 10-12 months and then increased to a secondary peak at 16 months. Concentrations and quantities leached of arsenic reached a minimum at 12 months and then increased substantially, to reach maxima at the end of the study period above peak levels early in the study. The authors suggested that factors contributing to these trends may have included seasonal variation in rainfall and temperature affecting wetting and drying cycles, and a progressive change in the availability of each component.

The presence of soil reduced the concentrations of these elements in leachate, with the greatest reduction (25 X) being for arsenic. Maximum concentrations for each element in CCA-leachate which had passed through soil were ~0.04 mg/L. While the graphs provided suggest residues of copper, chromium and arsenic were slightly higher in leachate from lysimeters with CCA-treated wood than untreated wood or sand on at least some sampling occasions, the authors stated that no statistically significant differences were found in concentrations of these elements in leachate between the treatments where soil was present.

The pH of the leachate was generally ~6-7. During the first 8 months, total dissolved solids (TDS) of the leachate was highest for the lysimeters containing CCA-treated wood (with or without soil), possibly due to leaching of soluble solids originating from the wood and CCA-treatment (Ca and K evidently from the wood and sodium from the CCA formulation). There was some evidence of greater total organic carbon (TOC) in leachate from the CCA-wood/soil lysimeters, possibly because of lower microbial fixation of organic carbon leaching from the treated wood. Leachates from treatments containing treated or untreated wood were found to be low in toxicity or non-toxic by a Microtox® test, with lower toxicity when leachate had passed through soil and highest toxicity (cause unknown) in leachate from the empty lysimeter.

Thus over the 18 month period of the study, a 200 mm depth of the soil used significantly attenuated the leachate concentration of copper, chromium and arsenic. The authors therefore concluded that there would be substantial capacity to adsorb copper, chromium or arsenic which might be leached from CCA treated material in well constructed landfills using clay capping layers.

6.1.3.6. Effect of soil physical and chemical characteristics on adsorption

Stefanovic and Cooper (2003) undertook a study with leachate from CCA-treated wood and three soils (clay, sandy and organic) to investigate the effect of soil characteristics on adsorption of CCA components. Leachate was obtained by extended leaching of treated sawdust in water (1.5 kg treated wood/20 kg water for 3 weeks). Adsorption studies were conducted at ~21°C using a range of leachate concentrations and shaking for 48 hours (cf a standard adsorption isotherm study), with the supernatant sampled for analysis several times over the shaking period. An additional 7 soils were treated similarly, but the supernatant sampled only at 48 hours. The amounts of adsorbed copper, chromium and arsenic were calculated by difference from the amount added initially and that present in supernatant. The authors stated that even though leachate from treated wood does not contain high levels of copper, chromium or arsenic, these elements can accumulate to high levels in soil due to their slow mobility through the soil profile and their stability in upper horizons, and this behaviour helps prevent contamination of ground water. They noted that copper, chromium and arsenic do not have the same behaviour in interacting with soil when present combined in solution as the individual elements.

Sandy soil showed much lower capacity for adsorption of all three elements than clay or organic soil. Adsorption equilibrium appeared not to have been reached by 48 hours for arsenic in the clay or organic soil or chromium in the organic and sandy soils. The amounts of CCA components adsorbed in soil at 48 hours increased with increased concentration of leach water, but with considerable variability. However, the concentrations of the components in leachate were low, and adsorption of copper, chromium and arsenic did not follow a Langmuir adsorption isotherm model. Partitioning coefficients relating the amounts of each element adsorbed to soil to the (supposed equilibrium) concentration at 48 hours varied considerably among the ten soils. Attempts to relate these ratios to soil characteristics (pH, clay, silt and organic matter contents, CEC, and iron and manganese oxide concentrations) showed no statistically significant trends. CEC, organic matter and clay content were thought to be dominant contributing factors to arsenic adsorption, CEC, organic matter and silt content to copper adsorption, and organic matter, CEC and silt content to chromium adsorption.

6.1.4. Summary and conclusions regarding fate and behaviour of copper, chromium and arsenic in CCA and CCA leachate once it reaches soil and water

Arsenic (atomic symbol As) is an element with metalloid properties. Arsenic in soil may be present in the trivalent As^{III} form (arsenite) or the pentavalent As^{V} form (arsenate). In well-drained soils it is normally present in the form of arsenate because of the oxidising conditions likely to be present. However, in reducing conditions (soil saturated with water and poorly oxygenated), it is present largely as arsenite. Arsenite is generally more mobile in soil and more toxic to terrestrial organisms than arsenate. Arsenic may be adsorbed to various soil colloids, most importantly iron oxides/hydroxides (in acidic and alkaline soils). Arsenic may also adsorb to clay, organic matter, aluminium oxides/hydroxides (acidic soils) and carbonates (calcareous soils). Precipitation as relatively insoluble substances may also occur (eg iron arsenate or sulphides of arsenite). Arsenate behaves similarly to phosphate in soils, with phosphate competing to suppress arsenic adsorption. Soil organisms may convert arsenate and arsenite to substances such as methylated arsines, which are volatile and can be lost from the soil to the atmosphere. In natural waters, the dissolved forms of arsenic present include arsenate, arsenite, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Various complex processes may occur in the water column and sediment, including oxidation and reduction, adsorption to clay surfaces, iron oxides, aluminium hydroxides and organic matter, methylation and demethylation, with microbial action important and transport occurring by turbulence and convection.

Compounds of the metal copper usually have a valence of 2+ (II, cupric) under oxidised conditions or 1+ (I, cuprous) under reducing conditions. As a cation, copper can exchange with other cations on clay and organic matter Most copper deposited onto soil is strongly adsorbed to the upper few centimetres of soil, being especially bound to organic matter, as well as being adsorbed by carbonate minerals and hydrous iron and manganese oxides. Greatest leaching of copper occurs from sandy soils rather than clays and peats, while acidic conditions favour leaching to groundwater. Under some conditions, copper can also be transported bound to soluble organic matter. Processes influencing the fate of copper in aquatic systems include the formation of inorganic and organic complexes, sorption to metal oxides, clays and particulate organic matter, bioaccumulation and exchange between sediment and water.

In natural soils and waters, the metal chromium (Cr) occurs mainly in the trivalent (Cr^{III}, chromous) and hexavalent (Cr^{VI}, chromic) forms. Cr^{III} interacts strongly with negatively charged ions and colloids in soil and as a result, is relatively immobile. In contrast, Cr^{VI} is generally more soluble, mobile and bioavailable, and also more toxic than Cr^{III}. Cr^{VI} is present as bichromate or chromate (ie as an anion) rather than as a cation in most soil environments. Though some Cr^{VI} can be formed in some soils, in general chromium is present in soil as Cr^{III} unless added as such to the soil.

The active ingredients in CCA treatment solution or wood treated with CCA are not themselves volatile, but arsenic compounds may be volatilised during burning of treated wood, and the formation of volatile compounds is a possible route for arsenic-containing substances in soil. Arsenic trioxide in termite and plywood glueline treatments may also be volatilised if the wood is burnt.

Various studies have examined the mobility of copper, chromium and arsenic in soil when surface soils are directly contaminated with CCA solution. Depending on soil characteristics such as pH and the content of organic matter, clay and iron oxides, differing redistribution of the elements may occur down the soil profile, owing to differences in their mobility. A low soil redox potential increases the mobility and toxicity of arsenic through reduction of As^{V} to As^{III}. One study showed that the amount of copper and chromium present in soluble or exchangeable form was higher in mineral soils, but fell for chromium particularly in organic soils. Arsenic was present both as As^{V} and As^{III}, but principally as As^{V}. However, As^{V} content was highest in mineral soil, decreasing as the soil organic matter content increased, possibly due to microbial action, as well as chemical actions after the CCA solution was added to the soil.

A lysimeter study in New Zealand with CCA solution added to the soil surface indicated the potential for Cr^{VI} to leach in some soils. Chromium as Cr^{VI} could be leached to groundwater in the event of a large uncontained spillage of a concentrated CCA solution, particularly in soils with low organic matter contents, where leaching occurs soon after spillage, and with high water input conditions. Once present in the subsoil, a slow rate of reduction would be likely to leave Cr^{VI} anions mobile for a considerable period of time. Another New Zealand lysimeter study examined leaching from CCA-treated wood mulch. This study showed the substantial capacity of a soil high in organic matter to adsorb copper, chromium or arsenic leached from CCA treated material. Hence they suggested CCA elements in leachate could be retained in well constructed landfills using clay capping layers.

6.2. Reports of environmental contamination from CCA

6.2.1. Studies pertaining to treatment facilities

6.2.1.1. Mobility of arsenic, copper and chromium in CCA-contaminated soil beneath Swedish preservation plants

Bergholm (1990) noted that CCA wood preservatives had been used in Sweden since 1950 and that in the early years soils at preservation plants were strongly polluted with arsenic, copper, and chromium from either wood preservative solutions and waste directly, or from leachate from stored preserved wood. The arsenic content in surface soil at preservation plants was recorded as attaining levels as high as 10,000-20,000 ppm, though levels of a few hundred ppm to 1000 ppm were more common.

CCA contaminated soils from six Swedish preservation plants were investigated by Bergholm (1990). Soil samples were taken near the surface only (17 samples, 0-5 to 0-20 cm) at some sites, and to greater depths (9 samples, as deep as 40-60 cm in one case) at others. Individual soil samples varied widely in pH (pH in $CaCl_2$ solution = 4.4-7.6), clay content (3-79%) and organic carbon content (0.3-13%). All 26 samples were analysed for the total extractable content of arsenic, copper and chromium (extracted in 2 M hydrochloric acid at 100°C for 2 h). Measurements were also obtained of the pH-dependent solubility of these elements, and of water-soluble amounts present when in a saturation extract of soil samples conditioned with distilled water for 4 and 8 days. Arsenic content was also determined in an equilibrium solution of soil and water (1:2 by weight) conditioned for 1 and 3 days. arsenic, copper and chromium were also monitored in leachate from soils leached with artificial rain at pH 3.5, 4.5 and 5.5 (adjusted by sulphuric acid) for 322 days. Adsorption isotherms for arsenic were determined on unpolluted clay soil, marsh peat soil and fine sand soil. Fixation of arsenic by Fe^{II}, Fe^{III} and aluminium dissolved in ammonium acetate solution, and by calcium hydroxide, was also determined.

The total extractable arsenic content varied between 33 and 9350 mg/kg in topsoil and 11-502 in samples from subsurface layers. The arsenic content always decreased with depth, and concentrations <100 mg/kg were generally from deeper layers, except for four topsoil samples. The total extractable copper content was 28-3109 mg/kg in topsoil samples and 3-249 mg/kg in deeper layers. Bergholm (1990) noted the low mobility of copper, evident by its sharp decrease with depth towards background levels of <10 mg/kg. While the copper content was often lower than that of arsenic, in some surface samples it was as high as the arsenic levels due to stronger fixation. The total extractable chromium content was 26-4906 mg/kg in topsoil samples and 8-1928 mg/kg in deeper layers. Bergholm (1990) noted that chromium content did not decrease with depth towards background levels (<20 mg/kg) as rapidly as copper. This possibly reflects contamination with the more mobile Cr^{VI} form (as in CCA formulations), whereas Cr^{III} is the form expected in aerated soils. The highest soil concentrations of all three elements occurred in a topsoil sample near a preservation shed, and some other high levels were encountered in 0-15 cm and 15-30 cm samples in a soil high in organic matter content.

The solubility of arsenic was pH dependent (minimum solubility at pH 6.5, solubility increasing above and below pH 6-7). At the same total arsenic content, release of arsenic was higher from a sandy soil than a clay soil. The solubilities of copper and chromium were also pH dependent, but to a lesser extent. Tests were conducted to estimate the concentrations of the elements present in the soil solution at the preservation plants. Estimated soluble arsenic content varied between 0.1 and 1.6% (average 0.7%) of the total content in soil samples, whereas copper was less soluble (<0.1% of the total content) and the release of chromium was less than that of copper.

Tests showed that the amounts of the elements leached from contaminated soils were influenced by the total amounts present and pH of the soils, and not by the pH of artificial precipitation (range 3.5-5.5). In leaching studies, with the exception of one soil column, release of arsenic occurred at a steady rate with continuing leaching, indicating that dissolved arsenic was in equilibrium with stable arsenic compounds in the soil (eg copper and chromium arsenates). In one case a high increase in arsenic release developed, possibly due to stagnation in the column leading to reducing conditions and hence formation of more mobile arsenite from arsenate. Leaching was distinctly higher in one soil, possibly due to higher pH increasing the solubility of arsenates. Copper and chromium behaved similarly to arsenic, except that copper was fixed in surface soils which had been limed, and chromium was partially or completely fixed in two of the soils. From the data, Bergholm (1990) noted that the total content of arsenic in soils may not exceed 100-200 mg/kg if the WHO limit value for drinking water of 50 µg/L is not to be exceeded. However, this level was reached by 50-80 cm depth, and there may be further dilution in ground water.

6.2.1.2. Contamination at another Swedish site

Bhattacharya et al (2002) investigated the occurrence of CCA components in the soil at an abandoned wood preservation unit in Sweden. It had operated between 1940 and 1968, and was destroyed by fire in 1974. Early CCA formulations used at the site also had zinc added. Arsenic had been detected in an adjacent drinking water well, hence remediation of the site was also under consideration. A detailed investigation of the 0.5 ha site was conducted. Soil pH was in the range 4.5-7.3 and redox potential –134 to +18 mV, ie conditions were often acidic and reducing (anoxic).

Highest concentrations of contaminant elements were found in the vicinity of the concrete platform on which the chemical tank was located. Average element concentrations in contaminated mineral soils were 26 (range 10-74), 29 (range 3-153) and 186 (range 10-1067) mg/kg, respectively, for copper, chromium and arsenic. Most of the contamination was present in the <0.125 mm soil fraction, though this fine grained portion constituted an average of only 10% of the soil. Average element concentrations in contaminated organic fills (wood chips) were 42 (range 6-88), 83 (range 25-148) and 237 (range 98-465) mg/kg, respectively, for copper, chromium and arsenic. Average element concentrations in contaminated stream sediments were 1092 (range 139-1772), 1335 (range 23-2647) and 632 (range 103-1681) mg/kg, respectively, for copper, chromium and arsenic. Average concentrations of arsenic were also relatively high (higher than the level of arsenic in average glacial till) in material described as “reference soils”, ie areas away from the main contaminated area surrounding the site of the concrete platform: average levels were 25 (range 10-47), 13 (range 4-37) and 119 (range 6-190) mg/kg, respectively, for copper, chromium and arsenic. The authors suggested that possible sources of contamination for this area included aerosol release when the pressure vessel was opened, storage of treated wood products, and handling of wastes such as sawdust. Another indication that the reference soils areas were contaminated is the range in values obtained, particularly for arsenic.

The paper presented data for two soil profiles to show the pattern of element concentrations with depth. The concentrations of copper, chromium and arsenic decreased somewhat to 30 cm, then increased in the B horizons (peak concentrations for copper, chromium and arsenic generally in the 40-50 cm layer). The authors suggested that pH and redox changes with depth interacted to affect the form of arsenic present and hence mobility, and the overall acidity of the soil favoured mobility of copper and chromium.

6.2.1.3. Mobility of arsenic, copper and chromium in CCA-contaminated soil beneath a Turkish preservation plant

Tests of soil copper, chromium and arsenic levels from CCA use in a wood preserving plant in Turkey were reported by Erdin et al (1997). Samples of soil were obtained at various locations in the plant, at depths of 0-5, 10-20, 30-40 and 50-60 cm. Soil was extracted with 2 M hydrochloric acid at 100°C for 2 h and analysed by AAS.

Soil arsenic levels ranged from 1-513 mg/kg. The highest soil concentration was obtained from surface soil near the impregnation cylinder (falling to 11.8 and 3.1 mg/kg with increasing depth, then rising to 19.6 mg/kg at 50-60 cm). The second highest concentration was from surface soil beneath a nearby tree, with concentrations falling to 0.9-3.8 mg/kg at depth. Soil arsenic concentrations beneath a pile of treated logs were low (1.7 mg/kg at the surface and 3.5 mg/kg at 50-60 cm). Total copper concentration in surface soil ranged between 306-1945 mg/kg near the impregnation cylinder, 135-154 mg/kg beneath the pile of treated logs, and 14.0-105 mg/kg beneath the tree or elsewhere away from the cylinder or woodpile. Total chromium concentration in surface soil ranged between 744-2400 mg/kg near the impregnation cylinder, 212-333 mg/kg beneath the pile of treated logs, and 23.6-134 mg/kg beneath the tree or elsewhere away from the cylinder or woodpile. Concentrations of copper and chromium were in most cases lower beneath the surface (copper concentration 6.2-84.2 mg/kg at 30-40 cm or 50-60 cm, and chromium concentration 21.2-146 mg/kg, with chromium movement to 50-60 cm clearly evident near the impregnator, suggestive of direct contamination with the preservative). Thus there was evidence of surface contamination of all three elements near the impregnation cylinder, but only of copper and chromium contamination beneath the wood piles. It is unclear why leaching of arsenic was not detected beneath the treated wood piles when both copper and chromium had evidently leached.

6.2.1.4. Contamination at sites in the United Kingdom

Grant and Dobbs (1977) presented data from a 1969 study of heavy metal levels in soils at and around CCA treatment sites. There were some areas of gross contamination (>5% of individual metals in the soil, even in off-site soil from areas of natural drainage from treatment sites (Table 17).

Table 17. Levels of copper, chromium and arsenic in soils at CCA treatment plants in the UK (Grant and Dobbs, 1977).

Location	Concentration (mg/kg)		
	copper	chromium	arsenic
Surface layer (0-5 cm) from area used to stack freshly treated timber	590-82,000	530-37,000	960-73,000
Surface layer (0-5 cm) from near preservative solution mixing tanks	6400-38,000	4500-24,000	6900-37,000
Surface layer (0-5 cm) from random on-site areas	370-1600	420-2200	940-1200
Surface layer (0-5 cm) from off-site soil from area of natural drainage from site	22-58,000	22-45,000	16-66,000

6.2.1.5. Contamination of soil beneath a Norwegian treatment facility

A site in southern Norway which had been used for over 30 years to preserve wood with CCA (mainly a 14.8% CuO, 26.6% CrO_3, 34% As_2O_5 formulation) was investigated by Andersen and Rasmussen (1998). Soil samples (5-25 cm depth) were taken from an area used as a drying pad for treated wood. Soil solution collectors (tension lysimeters) were installed at the site to sample soil water during unsaturated conditions and during rain events. Soil was digested in *aqua regia* and analysed by ICP-AES, and water samples by AAS.

The most polluted area had total soil concentrations of ~18,000 ppm arsenic, 21,000 ppm copper and 5000 ppm chromium. The highest observed soil solution concentrations were 80 ppm arsenic, 8 ppm copper and 10 ppm chromium. Despite a tenfold range in concentrations, there was no evident relationship between total soil concentration and toxicity assessed by the Microtox® technique (inhibition of luminescence of *Vibrio fischeri*), suggesting that total soil concentrations are a poor predictor of toxicity. Evaluation by the same technique of soil solution samples collected in a rain event showed that elevated concentrations of these elements in the soil solution were associated with increased toxicity. Arsenic concentrations in the soil solution increased with precipitation, whereas copper levels were highest at the onset of rainfall.

6.2.1.6. Release to the aquatic environment from the above facility

Rasmussen and Andersen (1999) reported an investigation of the release of CCA components into a river adjacent to the above timber plant, which they note had been closed for 7 years, cleared and levelled. As an experimental technique, the aquatic moss *Fontinalis antipyretica* was transplanted into the river in 8 cages, one located upstream, one downstream, and 6 adjacent to the site. This plant had been tested as a plant bioindicator in fresh water and found to give reliable results as a trace metal accumulator. Samples of moss were collected during a rainfall event following a dry spell. The samples were analysed by ICP or AAS after rinsing, drying and digestion in nitric acid under reflux.

Concentrations of arsenic increased during the rainfall event, consistent with increasing dissolution of arsenic from the soil as rainfall persisted. Copper and chromium concentrations in the moss increased initially, but tended to decrease as rainfall progressed due to increased dilution towards the end. It was proven that leaching of copper, chromium and arsenic from the wood processing plant increased during the rain event. However, the investigators made various criticisms of the technique in regard to use in this brackish (tidal) water situation, differences in the affinities of these three elements to soil and to the moss (eg presence of arsenic as an anion), and the difficulties of quantifying leaching when the concentrations of the elements are continuously changing.

6.2.1.7. Fate and bioavailability of CCA components in sediments near an old Finnish sawmill site

Lyytikäinen et al (2001) investigated levels of CCA components (also chlorophenols) in sediments in the vicinity of an old sawmill site in Finland, where CCA had been used prior to its closure in the 1980s. The sawmill was among the largest in Scandinavia and was located by a river which ran into a lake a short distance downstream of the mill. The sawmill study area was over 70 ha, with an estimated volume of contaminated soil of 70,000 m^3. In addition to surface run-off, the authors noted two additional sources of aquatic contamination: leaching from the pool used for storing logs prior to sawing, which had large amounts of CCA elements in the sediment and was separated from the river only by a gravel wall, and from a brook running through an old landfill area into the river. For this study, samples of sediment (generally 5 cm increments to at least 15 cm) were taken from various locations in the river (just downstream and upstream of the sawmill, and from the upper part of the river near a paper mill site), lake (two points in the lake were chosen as they were “supposed major sedimentation areas”, and the other was near where the river entered the lake), log pool and brook. These were analysed for copper, chromium and arsenic by AAS techniques (limits of detection respectively, 1.3, 1.0 and 0.2 µg/g dw in sediment and 26.1, 20.3 and 4.6 µg/L in water). Wet sediment was also used for a 28 day bioaccumulation study with the oligochaete worm species *Lumbriculus variegatus*.

In sediments from the sawmill area (log pool), concentrations of copper, chromium and arsenic were high (mean values respectively, 167-788, 81-563 and 306-829 µg/g dw) in the three depth layers tested (0-5, 5-10 and 10-15 cm). Arsenic levels in particular were also elevated (but in the surface layer only) in the brook (copper, chromium and arsenic concentrations 72, 31 and 306 µg/g dw) and confluence of the brook and river (43, 28 and 66 µg/g dw). The arsenic concentration at one of the supposed major sedimentation areas was also slightly elevated (mean 0-7 cm and >7 cm arsenic concentrations = 18 µg/g dw and 8 µg/g dw, respectively). Concentrations of copper, chromium and arsenic in sediment were in the ranges 8-25.4, 9-39 and 1.1-8 at the other sampling points, either downstream or upstream. A sample of water also taken from the brook contained mean concentrations of copper and arsenic of 50 and 59 µg/L, respectively, but no chromium was detected (ie <20.3 µg/L). The authors noted that according to Canadian Environmental Quality guidelines (1995) in freshwater sediments, the probable effects level for copper, chromium and arsenic are 197, 90 and 17 µg/g dw, respectively. The concentrations in the pool exceeded these levels. That of arsenic was also exceeded in the brook, and just exceeded at one point in the lake.

Lyytikäinen et al (2001) suggested that the presence of elevated copper and arsenic levels in the brook water and of arsenic in surface layers of sediment at some points downstream indicated that arsenic and copper may have been mobilised by the anoxic conditions prevailing in the study area and transported away from the sawmill area by the brook (eg As^{III} was likely to have been the prevailing form). Nonetheless, they concluded that transportation of CCA from the sawmill area to its surroundings was "fairly low."

In the worm study, arsenic was the only element found to bioaccumulate, in the worst case reaching levels of 362 µg/g dw in tissue of the worms exposed to brook sediment for 28 days (measured copper, chromium and arsenic concentrations respectively 36, 30 and 170 µg/g dw in sediment, nd [not detectable], nd and 126 µg/L in pore water, nd, nd and 24 µg/L in surface water, and 17, nd and 362 µg/g dw in tissue). Copper was found in all tissues, but chromium was not detected (ie < 6 µg/g dw). The experimenters noted that the study conditions favoured the mobilisation of arsenic from sediment to pore water and deduced that the main route of bioaccumulation was likely to have been pore water.

6.2.1.8. Release to the aquatic environment from a preservative facility in Georgia, USA

Neary et al (1993) summarised research on transport of CCA in a watershed in northern Georgia USA which received surface run-off from a wood preservative facility. Stream and pond bottom sediments contained significant quantities of CCA (up to 148 mg/kg). Elevated levels of CCA were still detected 4 km downstream, though levels evidently peaked in natural (beaver ponds) and artificial impoundments, retaining CCA largely in the headwaters. Levels of chromium were highest (up to ~140 mg/kg), with copper and arsenic concentrations in the sediment similar (peak ~70 mg/kg).

6.2.2. Off site contamination during service

There are a large number of papers discussing localised contamination in terrestrial situations (Sections 6.4.1-6.6), but little discussion of larger scale contamination with arsenic from CCA-treated timber during service. The following discusses arsenic contamination in a suburban lake through wooden structures surrounding the lake and suburban run-off.

Rice et al (2002) evaluated and modelled copper, chromium and arsenic concentrations in a 10.9 ha lake (Lake Anne) which was created in 1964 in suburban northern Virginia. The 235 ha catchment is densely populated and heavily developed, with dwellings surrounding the lake shoreline. There are two tributaries contributing to the lake, one of which drains another dammed lake. It was claimed that no copper sulphate had been used to treat algal growth on the lake. CCA-treated wood had been used in the construction of decks and docks in and near Lake Anne and as a bank stabilisation material along approximately 75% of the shoreline. Some aspects of the study and its interpretation were not fully explained or presented.

The authors calculated a mass balance for total copper and arsenic for the lake using 1998 data for precipitation, stream flow (including road run-off), stream outflow, and contributions from leaching lumber. This approach considered natural as well as anthropogenic inputs and outputs of each element for the catchment, with the premise that input to the lake minus export from the lake was equal to the contribution to the lake sediments. Samples obtained of lake sediment indicated dryweight concentrations of arsenic and copper at the top of the sediment cores of 18-28 µg/g arsenic and 105-137 μg/g copper, stated to be up to 23 and 5 times their respective background concentrations. Concentrations of arsenic and copper in precipitation were very low, and those in baseflow samples indicating geologic contributions via groundwater were also relatively low. The major source of inflow contributions was road run-off (stormflow), said to indicate mobilisation of arsenic from sources such as soil near decks and copper more from roadways (from various sources relating to vehicles). Contributions from CCA-treated timber surrounding the lake were estimated based on measured leaching rate data obtained by the authors in a procedure simulating a flushing type environment (various kinds, types and ages of timber placed in lake water for 1 week of static leaching, after which the solution was changed and the process repeated for a total of 14 weeks) and estimated treated areas of decks and docks on the lake and wood in pilings and retaining walls in contact with the lake.

Results of the study indicated that a greater mass of arsenic and copper was input into the lake than was exported in the study year. The majority was derived from anthropogenic sources within the catchment. With atmospheric deposition a relatively insignificant source, the major source of copper to the lake was road run-off. For arsenic, leaching of CCA-treated lumber around the lake was an important contributor, together with stream inflow, the latter also evidently predominantly carrying arsenic from anthropogenic sources. The mass balance approach showed reasonable agreement with measured levels in lake sediment for arsenic, though less so for copper and the authors discussed possible reasons for this and considered various adjustments to their modelling. Overall, they concluded that CCA-treated lumber and road run-off could be significant non-point sources of arsenic and copper, respectively, in suburban catchments.

However, the mass balance approach used has been criticised by Saxe and Beck (2003). They noted various deficiencies in the data used, such as inadequate sample numbers, sample location and targeting, leaching rate data etc, and in the presentation of the data used. They also questioned some estimations and assumptions made, such as how CCA-treated wood was identified without confirmatory tests. They also noted that other potential arsenic sources were not considered, such as areas which had been treated with arsenic pesticides. The study focuses on exposure from timber in docks, decks and bank stabilisation structures directly on and around the lake rather than run-off from treated wood elsewhere within the suburban catchment. Full details of the data already obtained would be necessary to fully understand the authors' arguments regarding the extent and sources of arsenic inputs into the lake from urban run-off, and further sampling in time and space appear necessary to elucidate this.

6.2.3. Summary and conclusions regarding reports of environmental contamination with CCA

There are several published reports from overseas of contaminated sites where CCA treatment has occurred or is still occurring, in some cases with demonstrated off-site movement into streams or lakes. These generally refer to treatment plants that are old and have been abandoned or decommissioned. Hence they were likely to have been in use before modern environmental standards were adopted. However, they do indicate the extent to which environmental contamination may occur if suitable facilities and management practices are not in place. There are likely to be many more such published and unpublished reports, presumably including some for treatment sites in Australia. Evidently, there may also be data available regarding leachate from landfill sites containing CCA-treated timber.

The available studies show that soil concentrations of arsenic, copper and chromium may accumulate to high levels in the area of CCA treatment plant facilities, particularly in soil near the impregnation cylinder or concrete pad on which the cylinder stood, and also in areas where wood piles had stood for fixation and drying. Contamination of some areas was also suspected to be due to sources such as aerosol release during the application process, leaching from stored wood, and disposal of contaminated sawdust. UK data indicated high contamination of off-site soil through natural drainage. Maximum measured concentrations of arsenic, copper and chromium in the surface soil at different sites ranged from 513-73,000 ppm, 74-82,000 ppm and 153-37,000 ppm, respectively. Concentrations of these elements generally fell with increasing soil depth, but soil concentrations were sometimes still clearly elevated below the surface and in one case concentrations rose in the soil B horizon. The rate of decline differed between the elements and was affected by the soil type, consistent with the known behaviour of each element in soil. In more than one case mobility of chromium was clearly evident (to as deep as 50-60 cm), presumably because it reached the soil in the more mobile form of Cr^{VI}. Estimations of arsenic concentrations in the soil solution at one site were ~0.7% (range 0.1-1.6%) of the total arsenic content, whereas copper and chromium present in that soil were less soluble. At the site where arsenic concentrations reached as high as 18,000 ppm in soil, peak observed soil solution concentrations of arsenic, copper and chromium were 80 ppm, 8 ppm and 10 ppm, respectively. In some situations levels of CCA elements declined towards background levels at soil depths well above groundwater and tests of groundwater showed no accumulation. However, the reason for evaluating one site was that arsenic had been detected in an adjacent drinking well.

Mobilisation off site of arsenic, copper and chromium residues from contaminated soil at former treatment plants has been shown to have occurred. In one case, testing with an aquatic moss known to accumulate trace metals indicated some movement of arsenic, copper and chromium to an adjacent river had occurred during a rain event. In another case, sampling of a brook flowing through an old site showed elevated arsenic and copper levels (59 µg/L and 50 µg/L, respectively). Sediment concentrations (0-5 to 10-15 cm depths) of arsenic, copper and chromium were high in a pool formerly used to hold treated logs (306-829 ppm, 167-788 ppm and 81-563 ppm, respectively). Surface sediment concentrations of arsenic in particular were also elevated in the brook (306 ppm), confluence of the brook and a river (66 ppm) and at a sampling point near where the river entered a lake downstream (18 ppm). The latter point was noted as just exceeding the Canadian Environmental Quality guideline for arsenic in freshwater sediments (18 ppm). A US study showed transport of CCA components had occurred to as far as 4 km downstream in a watershed which received surface run-off from a wood preservative facility, in this case with transport of chromium most evident (maximum sediment concentrations nearer the facility were ~70 ppm for arsenic and copper and 140 ppm for chromium).

A study of a suburban lake in the USA indicated that a greater mass of arsenic and copper was input into the lake than was exported in the study year. For arsenic, leaching from CCA-treated timber in docks, decks and bank stabilisation structures directly on and around the lake was likely to have been an important contributor, together with stream inflow, the latter also evidently predominantly carrying arsenic from anthropogenic sources. One source of arsenic in stream flow may have been leaching from treated wood elsewhere within the suburban catchment, but there were inadequate data presented to confirm this. The major source of copper to the lake was road run-off.

Thus, heavy contamination of CCA treatment sites has clearly occurred from past practices. At the sites where data have been evaluated, the heaviest soil contamination was generally confined to areas near likely sources of CCA treatment solution, with leaching of CCA components deeper into the soil reflecting soil characteristics and the extent of contamination, potentially reaching groundwater in some situations. Mobilisation of CCA elements off-site through run-off and/or leaching has also been found, with arsenic accumulating in downstream sediments. No conclusive data are available regarding off-site movement of arsenic leached from wood in service, except for situations where treated wood is directly in contact, above or adjacent to a waterbody. However, it is likely that a proportion of arsenic or other heavy metals in run-off would accumulate in downstream sediments, particularly where affected waters do not reach the ocean.

6.3. Release of CCA components from CCA-treated timber

6.3.1. Fixation and leaching of CCA components

6.3.1.1. Definitions of fixation and leachability

Fixation of wood preservatives such as CCA refers to the series of chemical reactions that render the preservative largely non-leachable during service. Dahlgren (1972) drew a distinction between the terms “fixation” and “leachability”, suggesting that the term “fixation” be used for the process of precipitating or otherwise rendering active elements resistant to removal from the wood, and “leachability” as a measure of how resistant the active elements are to removal by the action of a specified solvent (eg water). Hence, as noted by Lahiry (1997), leaching rates are dependent on proper fixation.

6.3.1.2. Importance of achieving adequate fixation

Results of a study in the UK by Warburton and Cornfield (1991) make it clear why it is important to achieve adequate fixation while wood is on a surface where drips or leachate can be collected and recycled or disposed of appropriately, and preferably under cover or with accelerated fixation to minimise leaching due to rain. Fencing timbers were treated with CCA-C (salts), divided into four stacks and each stack subjected to a simulated rainfall leaching treatment after differing degrees of fixation. With fixation levels of 30% (freshly treated), 80%, 91% and 99%, the amount of chromium (total) removed in leachate was 7545, 740, 321 and 10.5 mg per stack, respectively. Correspondingly losses of copper were 4078, 117, 33 and 13.4 mg per stack, and of arsenic, 4321, 12.4, 5.6 and 1.2 mg per stack. Thus a high level of fixation is required before potential losses in leachate fall to low levels, particularly as much of the chromium lost before fixation is complete is likely to be the more toxic and mobile form, Cr^{VI}.

6.3.1.3. Methods of assessing fixation and leachability

There are various methods for assessing CCA fixation and leachability from CCA-treated wood. Their appropriateness varies with the purpose of measurement (ranging from scientific monitoring of fixation development or relationships with subsequent leaching, to quantitative or qualitative checking by applicators). The relative merits and disadvantages of these methods have been discussed by various investigators.

6.3.1.3.1. Evaluating fixation using expressate from moist wood

McNamara (1989a) described a method of monitoring fixation by measuring chromium, copper and arsenic using atomic absorption spectrophotometry (AS) in liquid expressed from blocks of treated wood. The expressate was obtained by squeezing the blocks to approximately half their thickness in an hydraulic press. The technique cannot be used once the wood has dried.

6.3.1.3.2. Comparison of other methods to assess fixation with expressate evaluation

Cooper et al (1994) and McNamara (1989b) have reported comparisons of several methods for assessing fixation. Monitoring showed that the copper and arsenic contents of leachate from wood borings during fixation dropped much faster than that of chromium, while total chromium and Cr^{VI} (assessed by inductively coupled plasma [ICP] analysis and the diphenylcarbazide method, respectively) concentrations conformed relatively closely. This confirmed that total chromium or Cr^{VI} should be used as the indicator of fixation, since it is the last of the components to be stabilised (there are, however, arguments based on ecotoxicity for using copper as the fixation standard for marine environments – Walley et al, 1996b). The chromotropic acid spot test on wood borings gives only a qualitative "go/no go" indication of the presence or absence of Cr^{VI} residues (corresponding to Cr^{VI} concentration as low as 10-15 ppm in expressate obtained by squeezing treated wood). Measurement of expressate pH was not an acceptable indicator, as pH levels off before complete reduction of Cr^{VI} has occurred. There was a relatively strong relationship between Cr^{VI} concentration in acid or water leachate from small borings and that in expressate. Water extraction is the more sensitive technique, though requiring longer agitation and being sensitive to the extraction time. With suitable AAS or ICP analysis facilities, water leachate can also be used for analysis of copper, chromium ($Cr^{III} + Cr^{VI}$) and arsenic (eg for scientific evaluation and technical development). The water leachate/diphenylcarbazide method described is similar to the test recommended in Australian Standard AS/NZS 2843.1:2000.

Cooper et al (1995) evaluated the relationship between chromium fixation in CCA-treated wood (determined by Cr^{VI} analysis of solution expressed from the wood) and the leaching of copper, chromium, arsenic and Cr^{VI} in a simulated rain test using jack pine (*Pinus banksiana*) board or red pine (*Pinus resinosa*) pole sections in Canada. The levels of all contaminants dropped to very low levels while there were still significant levels of unreduced chromium (Cr^{VI}) in the expressate (98-99% chromium fixation). The authors concluded that fixation monitoring methods that depend on Cr^{VI} monitoring (including the chromotropic acid spot test) are somewhat conservative and that following them guarantees that leaching losses are minimal.

6.3.1.3.3. What level of fixation is "adequate"?

A further issue in using such techniques to monitor fixation in a treatment plant is determination of an acceptable level of fixation. The above standard states that (under the test conditions) well-fixed timber should give a result of <0.5 ppm chromium (ie Cr^{VI} by the particular test). Walley et al (1996) noted that it has been suggested that Australia should apply a CCA fixation requirement of 99% as the standard for fixation prior to removal from the drip pad. However, they noted that significant levels of unreduced chromium may still be present in expressate from timber at this level of fixation and that a much higher level of fixation may be needed (perhaps even 99.999%). They added that in any case, the amount of chromium (or other components) that may be leached per m^3 of treated timber increases with increasing hazard class, ie as a function of preservative retention. Thus they argued that it is not logical to provide a standard fixation percentage for specifying maximum levels of chromium or copper for this purpose. They proposed the alternative of using existing guidelines for groundwater and soil contamination and give examples of how this might be used to calculate the maximum allowable concentration per m^3 of wood: possibly such an approach has been used to arrive at the allowable test concentration in the Australian Standard). They also summarised current fixation and/or contamination guidelines for overseas countries, showing the general lack of uniformity in these (there are some explanations for this variability – eg whether or not CCA is registered along with other timber preservatives, and where low ambient temperatures are more likely to increase the duration of fixation).

6.3.1.3.4. Assessment of fixation using shower tests

Measurement of chromium in leachate from “minipacks” of wood by simulated rainfall or shower tests provide a more realistic assessment of potential preservative leaching than measurement of borings using a diphenylcarbazide method (Walley et al, 1996b; Homan, 1994). There is a large variation within timber, such as the occurrence of high localised surface concentrations (“hot spots”), the effect of which is minimised by use of larger timber samples. However, the shower test is time consuming and relatively expensive, and is considered unsuitable for frequent process control. Hence an “on site” test protocol using several bore samples from different boards and places along the boards in each stack was developed, but tests showed that this only provides an indicative test (Homan, 1994). On the other hand, there is also a need to standardise the techniques used for shower testing (eg the volume of water used), so new products and processes can be compared around the world (Walley et al, 1996b).

6.3.1.3.5. Influence of surface area effects in fixation and leaching rate tests

Techniques where various timber sizes or small pieces of wood or shavings of timber are shaken in water or subjected to simulated rainfall are sensitive to surface area effects, ie the surface area of the timber relative to its volume. For example, Yamamoto, Motegi and Inai (2000) undertook tests of CCA leaching from treated wood specimens varying in size from 10 X 10 X 25 cm to 2 X 10 X 25 cm and with or without the end grain sealed. They found that there was a positive relationship between the surface area to volume ratio and the leaching amount per unit wood volume. The influence of wood sampling method used as well as the dimensions of the material exposed was examined by Evans and Edlund (1993). In studies with CCA-treated stakes, a coring method indicated substantially less remaining preservative than a method using a whole stake section, which is explained by the lower exposed surface area to volume ratio of the core of wood compared to the whole section. The study by Lebow et al (2000) also clearly indicates the extent of surface area effects on leaching of CCA components (Section 6.7).

6.3.1.3.6. Need to standardise leaching rate test methods and practical interpretation of results

Hingston et al (2001) noted that there are a number of standard laboratory protocols for evaluating leaching of wood preservatives, such as block tests specified by the American Wood Preservers Association and British Standards Institute. Researchers have also used various other original tests using different parameters. Hence comparison of results is difficult and recommendations for harmonisation towards a single protocol have been made. Various methods have differing advantages and disadvantages, and various improvements have been suggested (eg Cornfield et al, 1991). It is important to recognise that such tests may be useful to compare preservative types etc, but not to predict losses from commercial sizes of timber or practical situations (eg Jin and Preston, 1993; Yamamoto et al, 1999).

6.3.1.3.7. Losses in laboratory, 9 month soil bed and 12 months above ground depletion tests at different CCA retentions in the USA

Jin and Preston (1993) compared evaluations of CCA component losses by a standard two week laboratory leaching test (presumably with small blocks), 12 month above ground exposure test (19 X 19 X 450 mm stakes), and 9 month soil bed exposure test (50 X 19 X 150 mm stakelets) and five CCA retention levels (1.0 kg/m^3 to 9.6 kg/m^3 – the CCA formulation type was not indicated). There was reasonably close correspondence in arsenic losses between these methods, showing a clear effect of initial CCA retention level on % loss (72.8-90.1% to 4.7-15.8% loss with CCA retentions of 1.0 kg/m^3 to 9.6 kg/m^3). A similar pattern was evident with data for copper and chromium, particularly with the laboratory data. However, losses of copper and chromium were consistently lower with the laboratory study than found by the other exposure methods (eg at 4 kg/m^3 retention, copper loss was 2.6% by the laboratory test, 7.8% at 12 months above ground, and 19.6% at 9 months in the soil bed, while chromium loss was respectively, 0.8%, 13.6% and 14.2%). The authors suggested that this may have been associated with wetting/drying cycles that occur under field conditions, and in the case of copper but not chromium, effects due to soil contact allowing cation exchange. Thus tests designed to test leaching for fixation assessment or other treatment comparison purposes may not reflect actual real world leaching losses.

6.3.1.3.8. Losses in an outdoor above ground exposure test with pegs compared to a laboratory test

Yamamoto et al (1999) compared leaching from CCA-B impregnated specimens of Japanese cedar wood in a 10 day laboratory accelerated leaching test and a 6 month outdoor leaching test. In the laboratory, 2 cm X 2 cm X 1 cm blocks were leached according to a standard Japanese test. In the outdoor test, 25 cm X 10 cm X 1 cm specimens were placed in exposure tanks draining to leachate collection tanks. The samples were exposed to natural rainfall over the test period (average temperature 14.3° C, pH of rain 4.0-5.8, 979 mm). Results are summarised in Table 18. With CCA retention increased from 3.3 kg/m^3 to 6.6 kg/m^3, amounts of copper and arsenic leached in the laboratory test increased greatly, whereas chromium leaching changed very little. Total leaching of copper, chromium and arsenic after 6 months was much less in the outdoor study, with relatively minor differences between CCA retention levels and no leaching detected for chromium. Thus, in contrast to the results for above ground exposure in the above study, the accelerated leaching test in the laboratory greatly over-estimated the amount of leaching occurring in the 6 month time frame of the outdoor study. Concentrations of arsenic in leachate exceeded Japanese environmental standards for arsenic for human health (0.01 mg/L).

Table 18. Leaching of copper, chromium and arsenic in laboratory and field tests in Japan (Yamamoto et al, 1999).

Retention	Element	10 d laboratory test			6 month field test		
		Amount leached ($\mu g/cm^3$ of specimen)			Amount leached ($\mu g/cm^3$ of specimen)		Concentration in leachate (mg/L)
		Day 1	Days 2-4	Total days 1-10	Initial month	Total	
3.3 kg/m^3 (3.7 kg/m^3 in field test)	Cu	15	13	41	8	11	0-0.17
	Cr	8	4	15	0	0	0
	As	177	121	392	66	126	0.22-1.46
6.6 kg/m^3	Cu	64	159	391	11	16	0-0.25
	Cr	2	6	19	0	0	0
	As	269	377	1074	97	180	0.33-2.16

6.3.1.3.9. OECD test recommendations for environmental assessment purposes

The OECD has recently prepared a set of emission scenario documents for wood preservatives to provide guidance on how the emissions of active substances and other relevant substances from wood preservatives to the environment can be estimated during product application and storage of wood prior to shipment, and from treated wood in service (OECD, 2003). Part 3 of this set of documents provides general requirements for leaching test methods and protocols to enable emissions via leaching to be estimated for any particular preservative (not specifically CCA, in fact the ESD would generally be used to evaluate alternatives to CCA). These stress that the test used must be able to provide an average daily flux value for input into the models used, ie the average quantity of a preservative component that is leached out daily per treated wood surface area and time (eg kg/m^2/day). While, in principle, the test should be performed using the contact medium and/or the receiving environmental compartment of the scenario under consideration, it is considered acceptable for most scenarios that calculations can be based on a single laboratory test with wood in direct and continuous contact with water (generally deionised, pH 5.5-5.8 unless seawater exposure needs to be considered). Tests with soil exposure are recommended for conditions such as the bottom portion of utility poles or fence posts.

Standardised conditions are recommended in regard to the species and quality of wood used for tests (100% softwood, no heartwood, free of damage etc), dimensions of wood blocks and amount of water to wood (general recommendations wood area/wood volume = 40 m^2/40 m^3, wood area/water volume = 40 m^2/m^3), duration of the test and number of measurements (standard 60 days, with leachate solution changed and analysed on days 1, 2, 4, 6, 8, 10, 20, 30, 40, 50, and 60). Curves of fluxes versus time are used to make long term predictions of the quantities of preservatives leached, recognising that preservative-treated products may be in service for many years and that in many cases the initial leaching rate slows to reach a constant “steady state” leaching rate. Extension of the leaching test to allow this point to be reached is recommended if necessary.

Thus some of the data available from various studies is reasonably consistent with this guidance, but many results are shorter in duration or use material such as sawdust and therefore need more careful interpretation if they were to be used for prediction of leaching. Following the development of the ESD, the OECD is currently considering draft test guidelines for emissions from preservative-treated wood stored outside at the preservative treatment site or used in commodities where the wood or wood-based product is not covered and not in contact with the ground, and for emissions from preservative treated wood in contact with the ground, fresh water or seawater. However, there may be no need to rely on such tests to predict leaching of CCA because its long, extensive existing use enables more direct measurements to be made. Thus, with CCA there are data available where leaching has been evaluated under semi-realistic scenarios (from stakes exposed out doors above or below ground to model decks with natural rainfall) and under actual use conditions. There are also situations where the impact of leaching from treated wood has been evaluated in nearby soil and soil water. An alternative approach has been to estimate leaching loss by evaluating the amounts of CCA components remaining in wood after use. Results for these various types of data are discussed later in this assessment.

6.3.1.3.10. Towards estimation of potential leaching rate from wood in service using test data

Waldron et al (2003) noted that estimation of the leaching properties of preservative components is greatly affected by the leaching test method, since not all methods equally consider the physical components responsible for leaching. They proposed that these physical components included:

- wetting of the wood and penetration of the water (affected by dimensions, amount of end grain, permeability, duration and nature of water exposure);
- solution of preservative components into available moisture (affected by component solubility, wood moisture content, temperature etc);
- diffusion of components out of wood (affected by product dimensions, permeability, direction of movement, moisture content, temperature, nature of the diffusing species, etc); and
- re-drying of the wood between moisture exposures (possibly wicking components to the wood surface).

Waldron et al (2003) suggested that aggressive leaching of finely ground wood provides a measure of the ultimate amounts of preservative components available for leaching, while analysis of the equilibrium dissociation or solubility of components in free water in the wood (by re-impregnating treated wood cubes with water by vacuum/pressure and obtaining expressate at different times provides information on their effective concentration, which drives the diffusion process). This could be combined with a simple diffusion test to allow the estimation of potential risk from leaching over a wide range of specified conditions. Derived parameters were used to estimate copper leaching from a CCA-treated deck continuously exposed to rainfall for a 1 year period in Canada, assuming all leaching was coming from the top face of the board. The model predicted that about 2/3 of the dissociated copper (which had been estimated at 4.3% of initial retention) would be lost, but the authors noted that the loss may be an underestimate, as further dissociation of additional leachable copper may occur above the initial dissociation level.

6.3.1.3.11. Comparison of standard leaching protocols and sample particle size effects in regard to waste disposal

Townsend et al (2001b) undertook a comparison of five standard leaching test methods as part of recycling and landfill disposal evaluations for CCA-treated wood. The test methods were:

- the Toxicity Characteristic Leaching Procedure (TCLP) – used to determine whether or not a waste is hazardous due to its toxicity characteristic within US legislation (the Resource Conservation and Recovery Act [RCRA]) – the solvent used simulates the acidic conditions found inside a municipal solid waste landfill, with an acetic acid solution adjusted to pH ~5, eg a 100 g sample in a 20:1 liquid to solid ratio rotated for ~18 hours - failure to meet the federal toxicity characteristic (TC) limit of 5 mg/L for arsenic or chromium means the waste must be disposed of in a hazardous waste landfill;
- the Synthetic Precipitation Leaching Procedure (SPLP) – generally applied to an environment outside of a landfill where leaching may occur, eg land application of recycled waste material such as ash or compost – the leaching fluid simulates acid rainfall (nitric acid + sulphuric acid solution at pH 4.2), eg a 100 g sample in a 20:1 liquid to solid ratio rotated for ~18 hours – leachate concentrations are compared to Groundwater Guidance Concentrations (GWGCs), which in Florida are 0.05, 0.1 and 1 mg/L, respectively, for arsenic, chromium and copper;
- EP Tox – an older technique under the US RCRA, requiring periodic opening of the vessel during extraction for addition of acid and extended extraction until the solution falls to pH 5 - replaced by the TCLP;
- the Waste Extraction Test (WET) – leaching procedure used by the State of California, similar to the TCLP except that citric acid buffered to pH 5 is used, with similar regulatory limits for arsenic and chromium – eg a 100 g sample in 1 L solution rotated for 24 hours;
- the Multiple Extraction Procedure (MEP) – a sequential batch leaching test used to predict worst case long term leaching characteristics of wastes placed in a landfill, but not for regulatory purposes as such – eg a 60 g sample with 24 h extraction in acetic acid solution, followed by 7 subsequent extractions of the solid material in nitric acid/sulphuric acid solution at pH 3, each with rotation of a 20:1 liquid to solid ratio for 24 h, with leachate from each 24 h period analysed to show the trend in time.

The researchers compared the TCLP and SPLP for a range of commercial products and sample particle sizes (sawdust, chipped wood, 20 g blocks, 100 g blocks). The results showed that TCLP tends to extract more (~3 X more on average) copper than SPLP, but both tests extracted similar amounts of arsenic and chromium. This was ascribed both to the greater buffering capacity in the TCLP, maintaining a lower pH over time, and the ability of acetic acid to form metal-acetate complexes with copper, resulting in greater extraction of metals into solution. As expected, there was also a clear effect of sample particle size.

Comparisons of all five tests were also conducted for one brand of timber using the different sample particle sizes. For each particle size, arsenic was leached at approximately the same level for the TCLP and EP Tox tests, with the SPLP resulting in similar but slightly lower concentrations and the WET method resulting in much higher metal concentrations. The same trend occurred with copper and chromium (10 X greater extraction of chromium with the WET method than the other four methods). Result for the MEP method showed a decreasing trend throughout the extraction period for each element, with chromium leached least and copper most, though the initial rate of loss was greatest for arsenic.

In comparison to regulatory requirements, TCLP leachates from sawdust exceeded the TC for arsenic in 8 out of 10 samples, compared to 6 out of 10 samples for SPLP leachate, but the TC for chromium was not exceeded. The authors concluded that the standard requirement of a small particle size (<0.95 cm) for the TCLP was appropriate, as the test is not designed to be predictive of actual leachate concentrations that may result, but was a rapid test to provide a conservative estimate of maximum potential leachability to distinguish wastes requiring greater care. Leachate from sawdust exceeded the Florida GWGC levels for arsenic, chromium and copper by both the SPLP and TCLP, and even for leachate from the largest particle size all samples exceeded the Florida GWGC levels for arsenic and chromium.

6.3.1.4. Summary and conclusions regarding fixation and leaching assessment

Fixation refers to the process of chromium reduction and related reactions that render the active elements resistant to removal from the wood. Until fixation is almost complete, the copper, arsenic and particularly chromium in the more toxic Cr^{VI} form are much more susceptible to leaching. Various countries therefore recommend or require that fixation be monitored and treated wood not moved from the drip pad until fixation has reached an adequate level, as do the relevant Australian standards.

Fixation can be monitored by various techniques. Evaluation of Cr^{VI} levels is most critical, as complete conversion of Cr^{VI} in the application solution to Cr^{III} in the timber can be considered as indicating fixation is complete, though further changes may continue at a slow rate. Specification of an acceptable level of fixation is not straightforward: eg significant leaching of Cr^{VI} may still occur if a 99% fixation level is used, and the amount of leaching is then directly related to the retention level of CCA in the timber. The standard against which techniques can be compared is determination of Cr^{VI} and total copper, chromium and arsenic concentration in liquid expressed from treated wood by a hydraulic press. Useful techniques for evaluating fixation for process control appear to be determination of Cr^{VI} in leachate from small borings of treated wood by a diphenylcarbazide colorimetric technique (such a technique is described in the Australian standards, with guidance as to what concentration in the tests can be considered to indicate well-fixed timber), and a chromotropic acid spot test on wood borings. The latter gives only a qualitative indication of the presence or absence of Cr^{VI} residues, but the limit of detection of the test has been considered to be adequately sensitive by various investigators. More realistic evaluation of the extent of fixation using the shower test method with minipacks of wood helps overcome sampling and variability problems with methods using borings, but is more expensive and time consuming.

A diverse range of laboratory and field leaching test methods have been used with CCA treated wood to compare the effects of different CCA treatment processes, evaluate influences of soil and climatic conditions, or to predict worst case or realistic losses in use or upon disposal. Several aspects of the way such tests are conducted affect their outcome, eg the surface area to volume ratio of the wood material, duration of the test, composition and replenishment of the leaching solution, nature of exposure to the leaching solution (continuous or intermittent shower or rain, bathed in liquid which is static or shaken), contact with soil, etc. Hence the methods used need to be considered in interpreting test data, and choice of method is important when planning tests. Various standardised test methods have now been described for evaluation of CCA treated wood in practice (American Wood Preservers Association and British Standards Institute methods), prediction of worst case leaching rates for environmental assessment purposes (OECD emission scenario document for wood preservatives) and prediction of worst case leaching rates for environmental regulation or management purposes with waste material (eg the Toxicity Characteristic Leaching Procedure to characterise waste in regard to landfill, or Synthetic Precipitation Leaching Procedure to evaluate material where land application occurs outside landfill situations). Some research has been undertaken towards combining leaching rate data with that from other tests to estimate potential leaching rates in service, but in general, laboratory methods are useful for exploratory, comparative and regulatory purposes rather than realistic prediction.

6.3.2. Factors influencing fixation and subsequent leachability of CCA components during treatment, fixation and drying of wood (ie prior to use)

6.3.2.1. Managing CCA treatment for optimum economy, efficiency and performance

Various experiments have shown that many factors potentially interact to affect the time taken for fixation to occur and effectiveness and quality of treatment, though several of these are not practically important under normally used conditions. Dahlgren (1972) commented that under practical conditions fixation takes place simultaneously with drying, which is sometimes carried out at an elevated temperature. Much research has been undertaken by applicators to take advantage of the great reduction in fixation time that can be obtained by such practices (which can greatly reduce the time treated timber needs to remain in special facilities on site), and to determine what factors are important to controlling the whole process.

6.3.2.2. Application process

The procedures used may also influence penetration and retention of CCA. Increasing the pressure treatment period may reduce the proportion of copper, chromium and arsenic on the wood surface and hence possibly also reduce leaching, while increasing the length of the vacuum stage may have a converse effect (Hingston et al, 2001).

6.3.2.3. Composition of the CCA solution

Smith and Williams (1973a,b) found that maximum fixation of arsenic occurred with a Cr/As ratio (as salts) of ≥1.9, and for copper with a Cr/Cu ratio (as salts) of ~1.7 (eg the CCA-C formulation – pp 14-15). Maximum effectiveness occurred with the area of maximum fixation of arsenic, but with some loss of copper. Earlier work cited by Hingston et al (2001) proposed a Cr/As ratio of 1.0-1.3 as optimum. The presence of electrolytes such as sodium sulphate (ie from CCA salt formulations) does not affect leachability but may influence the pH (Dahlgren, 1975c). Pizzi (1982) suggests that the use of oxide formulations may be slightly more effective for softwoods and salt formulations more effective for hardwoods. Salt formulations may lead to sodium sulphate leaching slowly to the wood surface to form a white deposit in the months after treatment (Read, 2003).

6.3.2.4. pH and concentration of the CCA solution used during treatment

A correlation has also been found between the final wood pH and leachability in fresh water of copper and arsenic (Dahlgren, 1975c). Pizzi (1982) discussed possible consequences of the chemical mechanism of CCA fixation to wood. He indicated that while relatively minor compared to the effects of temperature: a decrease in pH of the treating solution moderately accelerates the fixation of the preservatives, and decreasing pH to pH ≤2.4 increases the amount of CCA linked to cellulose; increasing the solution concentration accelerates fixation and favours distribution of CCA linked to lignin. He suggested choice of factors such as these could be manipulated to optimise economy and effectiveness, but Plackett (1983) has criticised some of Pizzi et al's arguments.

6.3.2.5. Initial retention

Jin and Preston (1993) found that CCA component losses measured by a two week laboratory leaching test, 12 month above ground exposure test, and 9 month soil bed exposure test were affected by the initial retention level of the preservative. There were very high arsenic losses at low retention levels (4.7%, 9.5%, 17.7%, 35.8% and 87.1%, respectively, by the laboratory leaching test at CCA retention levels of 9.6, 6.4, 4.0, 2.0 and 1.0 kg/m^3). The explanation proposed was that at normal commercial retention levels, sufficient copper and chromium is still available following the primary reaction mechanisms of the copper and chromium directly with the wood to allow for the secondary fixation mechanisms which provide arsenic complexation. In contrast, at low active ingredient retentions, the copper and chromium are consumed by primary fixation mechanisms on the wood and the secondary fixation involving the arsenic component does not take place, leaving unfixed arsenic susceptible to loss from the wood through leaching. Similar results were reported by Archer and Jin (1994) in a study of soil CEC influences on leaching, but Taylor and Cooper (2001) found differing results and noted that other researchers had reported mixed effects of CCA loading on absolute and % leaching (see below). Arsenault (1975) also reported instances where apparent loss of CCA components from treated posts was greater where initial retention was low.

6.3.2.6. Temperature during treatment and fixation

Higher temperatures during treatment and/or fixation may greatly reduce the time for fixation to occur (eg McNamara, 1989a). Hence various methods of increasing temperature are used or have been tested, particularly where ambient conditions become cold. Such methods include accelerated steam fixation (Willeitner and Peek, 1988; Peek and Willeitner, 1988), moderately elevated (50-60° C) temperatures (Cooper and Ung, 1989), and even microwave heating (Fang and Ruddick, 1999; Torgovnikov et al, 2000). Homan et al (1993) outlined the results of a comparison of natural fixation (held under cover at ambient conditions for 14-38 days), a controlled climate room (91 hours at 30-35° C and 75% relative humidity), and steam fixation (~2 hours at 72° C). Overall, steam fixation gave the lowest leaching figures, particularly for chromium.

However, such treatments may undesirably affect various aspects of effectiveness, eg Dahlgren (1975a) and van Eetvelde et al (1995a) observed that elevated drying conditions led subsequently to increased leaching of copper, though decreasing leaching of chromium. Pizzi (1982) summarised research which showed that temperature (during contact with the treating solution rather than during fixation) affects the rate of fixation of chromium to lignin and cellulose to different extents, with higher temperatures increasing the proportion of CCA products fixing to cellulose. Waldron and Cooper (2001, 2002) developed a mathematical diffusion and reaction model which could predict leaching of CCA components from unfixed CCA-treated wood under various temperature conditions.

Lebow and Tippie (2001) indicated the approximate time required to achieve fixation in CCA-treated wood as a function of temperature (Table 19). The authors noted that increasing amounts of time are needed to gain additional degrees of fixation as the process proceeds, eg that ~43 hours are required to progress from 90% to 95% fixation at 21°C, but an additional 100 hours are required to reach 99% fixation at the same temperature.

Table 19. The approximate time required for various degrees of fixation to be achieved in CCA-treated wood at different temperatures (Lebow and Tippie, 2001).

Wood temperature (°C)	90%	95%	99%
4	32.9 days	42.8 days	65.8 days
10	18.2 days	23.6 days	36.3 days
16	10.3 days	13.4 days	20.5 days
21	5.9 days	7.7 days	11.9 days
24	4.5 days	5.9 days	9.1 days
27	3.5 days	4.5 days	7.0 days
32	2.1 days	2.8 days	4.2 days
38	1.3 days	1.7 days	2.6 days
52	10 hours	13 hours	19 hours
71	2.3 hours	2.9 hours	4.5 hours
104	0.3 hours	0.3 hours	0.5 hours

6.3.2.7. Relative humidity, air circulation and sunlight

Important factors for uniformity of the CCA treatment in the wood being treated with elevated temperature treatments are good air circulation and steam supply, to maintain high relative humidity and ensure lumber deep within the wood pile reaches a similar temperature (Taylor and Cooper, 1996). Drying of the wood surface and exposure to sunlight before primary fixation is complete can affect the depth and uniformity of colour, and drying of the wood can also slow the reaction rate if the moisture content falls sufficiently that ion transport is affected (Dahlgren, 1975c; Lahiry, 1997). Arsenault (1975) suggested that as well as the presence of water over the time period where reactions are occurring being important for maximum fixation to occur, too rapid removal of water can also decrease the rate of crystal growth, thus increasing solubility of finely dispersed particles. Van Eetvelde et al (1995a,b) observed higher initial leaching of copper from wood with steam fixation from high levels of copper on the wood surface, though the metals were otherwise effectively fixed.

6.3.2.8. Wood species, wood quality and seasoning

Holmes (1996) reported that at ambient diurnal temperatures of 12-26 C, 99% CCA-C (oxide) fixation was achieved in 6 days (128 h) with spotted gum poles, compared to <24 hours in blackbutt and ironbark species. Important wood properties noted by Dahlgren (1975a,b,c) are the ion-exchange capacity for copper, natural pH, chemical composition (lignin, cellulose and extractives), and anatomy. Lahiry (2001) reported problems with the use of hardwood poles in

Bangladesh due to inadequate retention of CCA during treatment rather than more rapid subsequent loss compared to softwood poles. Arsenault (1975) also noted that experience had shown the necessity of adequate seasoning before treatment with waterborne preservatives, due to poor sapwood penetration in green, steam conditioned poles.

6.3.2.9. Heartwood vs sapwood

Kennedy and Palmer (1994) showed that successful penetration of CCA into heartwood of Queensland plantation-grown slash pine (*Pinus elliottii*) could be achieved (though it is generally considered impermeable). However, they indicated that caution was necessary as arsenic concentrations in heartwood leachate approached the allowed maximum by the TCLP test of 5 ppm under current Australian guidelines for disposal in landfill.

6.3.2.10. Summary and conclusions regarding factors influencing fixation and leaching during treatment

A large number of factors pertaining to the CCA treatment process influence the rate at which fixation occurs, quality of the product produced and subsequent leachability of CCA components. These include:

- The composition of the CCA formulation – there is an optimal range in the relative proportions of chromium to copper and chromium to arsenic present to achieve a satisfactory balance between maximum efficacy together with minimum leachability. Too low a Cr:As ratio results in a higher level of arsenic leaching, as has been evident with the US CCA-B formulation;
- Retention rate of CCA in the treated timber – while the amount of copper, chromium and arsenic present in the wood and potentially available for leaching increases with increasing retention, leachability may be significantly worse with very low retention rates (~1-2 kg/m^3), possibly due to incomplete fixation of arsenic;
- The pH and concentration of the CCA solution used during treatment – this may affect the leachability of the product in service, and there is a correlation between the final pH of the wood after treatment and leachability of copper and arsenic;
- Temperature during treatment and fixation – this greatly affects the rate at which reactions occur, hence particularly where ambient temperatures are low, various higher temperature or steam processes may be used to reduce the time wood needs to be kept under protected conditions or on drip pads, but in most areas of Australia available data suggest that ambient temperatures for much of the year allow fixation to occur within a few weeks (eg at 16-24°C wood temperature, 99% fixation is estimated to take about 9-21 days);
- Factors such as air circulation (hence stacking, steam supply etc), relative humidity and sunlight – these may also affect the uniformity of treatment and fixation and quality of the product (eg colour), eg, it may be necessary with some treatment systems to maintain adequate relative humidity to prevent excessive drying, as this can arrest the fixation process;
- Wood species, wood quality, seasoning and the presence of heartwood vs sapwood – these may affect the performance of CCA treatments in regard to subsequent leachability, may alter process requirements to achieve the desired penetration and retention level and may limit the success of treatment;

Thus CCA treatment appears to be a highly skilled task requiring thorough knowledge and experience if timber is to be appropriately treated to the desired penetration and retention, while maintaining suitable quality and environmental standards. There are choices in the composition of treatment solution and timber to be treated and strategies and application process which affect leachability of CCA components in treated wood in service. Regarding actions which might relate to product registration or product labels, Australian Standard AS-1604 2000 appears to provide a satisfactory ratio of Cr:As to minimise leaching of arsenic, being similar to US formulation type CCA-C. The lowest retention rates recommended in Australia equate to ~0.9-1.8 and 2.6-5.2 kg/m^3 as CCA oxides, respectively. However, timber treated to the lowest hazard classes (H1 and H2) are intended for inside, above ground use where there is no exposure to wetting, and should therefore not be exposed to leaching during service. Aspects such as the choice of timber to be treated and process conditions would be expected to be strongly influenced by the knowledge and experience of the applicators and nature of the facilities available.

6.3.3. Redistribution and disproportionation of CCA components

6.3.3.1. “Disproportionation” of CCA components

Preferential retention of chromium in the surface layer of wood has been reported in several studies examining residues of CCA components in wood. This is generally attributed to chromatographic-like separation of the components due to faster reaction of chromium as the preservative penetrates the wood, and the degree of disproportionation depends on the species of wood being treated (Dahlgren, 1975c). For example, Cooper and Ung (1997) found that Cr^{VI} concentration in expressate taken immediately after pressure treatment with CCA fell linearly with increasing depth in the pole (~20% decline in concentration from 0 to 70 mm depth, 6 mm increments). Similarly, in a study by Cooper et al (2001) the outer 5 mm of freshly treated wood contained copper, chromium and arsenic in the ratio 14:52:35, compared to 18:46:36 in the treating solution.

6.3.3.2. Migration of CCA components within the wood

Drysdale (1983) reported evidence of migration of CCA components occurring in treated wooden stakes in New Zealand during a 12 week leaching treatment and/or subsequent air drying. Ten stakes (500 X 50 X 25 mm) were treated with a commercial CCA product (Tanalith NCA). After a two week fixation and drying period, five stakes were leached for 12 weeks (evidently static in 9 times their own volume of water, with leaching water changed 3 times per week). The other 5 stakes were left as unleached controls. Before the start of the leaching period, one 50 X 500 mm radial longitudinal face (face A) of each stake was planed off to 0.2 mm and 2-4 mm and analysed, and the face sealed with waterproof resin. After leaching, the opposite side (face B) was planed off and analysed at depths of 0-2, 2-4 and 4-6 mm. The results are summarised in Table 20. Compared to the calculated retention and measured retention in face A, total CCA retention fell in the 4-6 and 2-4 mm sections of face B, but rose in the surface 2 mm section. This migration towards the unsealed surface during leaching was most evident with copper and arsenic. A similar effect on copper migration had been reported previously in marine piles in seawater, where it has been proposed that redistribution was caused electrolytically (Hingston et al, 2001).

Table 20. CCA retentions in leached and unleached stakes (Drysdale, 1983).

Leaching treatment	Calculated retention (kg/m^3)	Mean retention (kg/m^3) in face A (prior to leaching period) at a depth of		Mean retention (kg/m^3) in face B (after leaching period) at a depth of		
		0-2 mm	2-4 mm	0-2 mm	2-4 mm	4-6 mm
No leaching	15.1	14.9	14.5	15.1	14.5	14.1
12 weeks	14.9	15.1	15.0	18.5	13.5	13.3

6.3.3.3. Redistribution of CCA components into untreated wood

Choi et al (2001) found evidence of redistribution of copper into “checks” (imperfections which develop in the wood) and sawn ends in Canada, and hypothesised that this had contributed to protecting wood from decay where surfaces which had not been penetrated by the original treatment were exposed (ie in CCA-refractory timbers where penetration was relatively shallow). They also showed movement of CCA components (copper and chromium – arsenic had not been analysed at the time the paper was presented) into untreated timber in contact with treated wood. Thus there is evidence that partial absorbance of CCA components (at least copper) in water leaching treated wood may occur into wooden surfaces in the path of the water. Many other studies show decreased overall retention and retention in different depths in the wood of CCA elements, and changes in the ratio between elements, showing some movement of CCA elements within treated wood and loss out of the wood over time.

6.3.3.4. Summary and conclusions regarding disproportionation, migration and redistribution of CCA components

Disproportionation (higher chromium levels in the surface layer of wood) is a factor which needs to be born in mind when considering the results of measurements of component levels in treated timber. There is evidence of copper and arsenic migration within the wood during a leaching treatment (constant soaking), confirming that CCA components are not completely immobilised in treated wood. There is also evidence that some protective effect may be gained in untreated wood in contact with treated wood, through movement of copper in leachate into the untreated wood. Thus untreated wood in a structure could potentially be contaminated with copper from CCA-treated wood, but the concentrations of copper, chromium or arsenic that might result would presumably be very low relative to treated wood and also very limited in extent.

6.3.4. Factors affecting leaching during use

6.3.4.1. pH 3.5-5.5 and presence of organic acids

Cooper (1991) undertook a study in Canada to further explore reports of high copper, chromium and arsenic leaching from wood exposed to buffered acidic conditions. Pole sections of four timber species were treated with CCA-C (retentions ~11.5-20 kg/m^3 depending on the species) and stored indoors for 3 months. Specimens 10 mm square by 40 mm long were taken. The initial copper and arsenic content of each specimen was analysed by non-destructive neutron activation analysis of the whole specimen and the chromium content estimated from the ratio of copper to chromium in the CCA-C solution used. The samples were leached using a modified version of an AWPA procedure (initial vacuum impregnation with the leaching solution, followed by repeated changing of the leaching solution over the subsequent 13 days). The leaching solutions used were a NaOH/citric acid buffer solution at pH 5.5, and water adjusted to pH 5.5, 4.5 and 3.5 using a sulphuric acid/nitric acid solution. At each water change, the copper, chromium and arsenic content (by AAS) and pH of the leach water were determined and the cumulative element losses calculated.

Leaching was consistently higher in the citrate buffer than the mineral acid acidified water, and the buffer preferentially extracted copper (cumulative leaching for the four species = ~53-81% for copper, ~7-11% for chromium, and ~27-47% for arsenic). There was no consistent effect of pH on extraction in the mineral acid solutions, where similar percentages of copper and arsenic were leached (cumulative leaching = ~1-10% for copper, ~0.2-1.4% for chromium, and ~3-7% for arsenic). In all cases chromium was leached to the lowest extent. Monitoring of leachate pH showed that it rose during the initial 6 hour impregnation period and then plateaued at pH ~5.5-6.5 due to buffering from the wood.

The investigators confirmed that the effect of the citric acid buffer was due to its composition rather than it buffering capacity by conducting a brief follow-up test with NaOH/citric acid buffer at pH 7 and acidified water maintained at pH 3.5 and 4.5 by periodic addition of sulphuric acid/nitric acid solution. The citrate buffer again leached the most copper and arsenic, showing that the effects on depletion were not due to maintenance of a low pH, but to the buffer itself.

6.3.4.2. pH 2-6.4 and different CCA formulations

Kim and Kim (1993) evaluated leaching of CCA components from western hemlock (*Tsuga heterophyla*) blocks which had been treated with CCA-B (oxide) and CCA-C (oxide and salt) formulations to retention levels of 4.0 and 6.4 kg/m^3 and left to fix for 3 weeks in a Korean study. The blocks were leached according to a modified AWPA method similarly to the above study, but with 14 days total leaching. The leaching solutions used were water adjusted to pH 2.0, 3.0, 4.0 using a sulphuric acid/nitric acid solution, and tap water at pH 6.8. Biological efficacy of leached wood samples was then evaluated by 12 weeks exposure to a fungal culture or by burial in soil for 20 weeks.

There was a clear effect of pH on leaching, which was greatly increased for all three elements at pH 2.0 (cumulative leaching of copper, chromium and arsenic respectively, ~43-65%, 17-34% and 26-53%) and somewhat increased for copper and arsenic at pH 3.0 (cumulative leaching of copper, chromium and arsenic respectively, ~17-36%, 1.2-4.4% and 5-17%). There was little difference in leaching of copper or arsenic between pH 4.0 and 6.8 (cumulative leaching of copper, chromium and arsenic respectively, ~0.8-3.2%, 0.1-0.6% and 1.9-13.0% at pH 4.0, 0.2-1.4%, 0.1-0.3% and 2.3-11.0%). Thus chromium was leached strongly at pH 2.0, but only to a minor extent at higher pHs. Copper was leached to a greater extent than arsenic at pH 2.0 and 3.0, and arsenic at pH 4.0 and 6.8. Leaching of all components was greater with the CCA-B formulation, presumably due to an insufficient ratio of chromium to arsenic (it is thought that insufficient chromium is left over after initial reactions with the wood components for reactions to precipitate insoluble arsenic compounds), and also tended to be higher with CCA-C (salt) than the CCA-C (oxide) treatments. Decay and soft rot tests showed weight loss >0.5% in the pH 2.0 and 3.0 treatments, but not at higher pH, suggesting some loss in efficacy due to copper loss at pH 2.0 and 3.0.

Thus low pH in leaching water may increase depletion of CCA components without the presence of organic acids such as citric acid, with greatly accelerated loss of chromium as well as copper and arsenic at pH 2.

6.3.4.3. Acid rain

Acid rain (pH < ~5.0) has been detected down to pH 3 and even lower in the short term in many parts of northern Europe, and more commonly at pH ~4.0-4.5. It is considered a major environmental problem and arises through contact with oxides of sulphur and nitrogen in the atmosphere. Normal, unpolluted rain has a pH of ~5.6 through contact with atmospheric carbon dioxide (Bunce, 1994; Hudson and Murphy 1997). However, acid deposition (in precipitation or as dry deposition) is not a widespread phenomenon in Australia, though it might occur in regions surrounding significant individual and regional sources (Department of the Environment Sport and Territories, 1996 - http://www.ea.gov.au/soe/soe96/pubs/chap05.pdf).

Because of known effects of acid rain on leaching of some metals in soils, Murphy and Dickinson (1990) considered it may also influence leaching rates of CCA components from treated wood. They evaluated three CCA formulations in a study in the United Kingdom, CCA-B (oxide) and CCA-C (oxide) (AWPA classifications), and BS4072/1 (salt) (UK type 1 – pp 14-15). Small pine sapwood stakes (20 mm X 20 mm X 150 mm) were treated to give CCA retentions of 15.0-18.6 kg/m^3 and allowed to fix for two weeks before testing. Three simulated rainfall acidities were prepared by adjusting with sulphuric acid/nitric acid solution: pH 5.6 (uncontaminated rainfall), pH 4.1 (characteristic of much of southern England), and pH 3.0 (short term rainfall incidents in many parts of Northern Europe).

A preliminary experiment was conducted using small blocks of wood (10 mm X 20 mm X 20 mm) cut from treated stakes. These were leached by exposure to the pH 3.0 or 5.6 test water in a standard procedure (9 changes of leaching medium over a 2 week period). Leaching was evaluated in the blocks by X-ray fluorescence, rather than by evaluating the leachate. By this method, with the pH 3.0 treatment considerable losses of copper (~40%) were evident with all three formulations, while losses of the other elements varied with formulation (arsenic loss was 24%, 12% and not evident with the CCA-B formulation, BS4072/1 formulation and CCA-C formulation, respectively; chromium loss was only evident with BS4072/1, at 6%). No loss was evident of any element with the pH 5.6 treatment, except for arsenic with CCA-B (20% loss), with the other formulations showing an apparent gain in chromium of 5% and 12% (a gain was stated to be an indication of variability between replicates for analysis before and after leaching).

Leaching from treated stakes was then evaluated using three soil types (a sandy soil, peat soil, and clay soil). The treated stakes were embedded vertically so they were just covered in soil in test bottles which were then leached regularly over a six week period, to an extent representing approximately two years of average annual rainfall in the UK. Leachate samples were analysed by AAS, and the content of copper, chromium and arsenic in the soils at the end of the experiment determined by AAS after appropriate digestion procedures.

Simulated rainfall pH had no evident effect on arsenic leaching, whereas arsenic leaching was greater with CCA-B than the other formulations, and for that formulation was much greater in sand (~22 ppm arsenic in leachate) than the peat or clay (1.9-4.3 ppm, 0.2-1.0 ppm in the other treatments). Very little chromium was detected in leachate (≤0.3 ppm), though there were nonetheless statistically significant differences. The concentration of copper was not influenced by any of the factors investigated (0.1-0.3 ppm in leachate). Most of the soil samples showed clear increases in copper, chromium and arsenic due to leaching from treated wood (copper, chromium and arsenic concentration in soil = 15.3-43.4 ppm, 0.0-5.7 ppm and 3.1-71.8 ppm, respectively above background in exposed soil, which was 2.4-19.0 ppm, 5.4-15.2 ppm and 1.9-10.5 ppm, respectively, in the same soils). There was no evidence for an effect of rainfall pH on soil levels of any of these elements. Most noteworthy was that of the three formulations, increases in arsenic concentration were lowest with CCA-C (3-9 ppm compared to ~11-19 ppm with BS4072/1 and ~24-91 ppm with CCA-B), and that there was a much larger increase in arsenic concentration with CCA-B formulation in clay and peat soil (72 ppm and 91 ppm, respectively, compared to ~24 ppm in sand).

Thus, in the absence of soil there was a considerable effect of acid rain at pH 3.0, with a conspicuous loss of copper, very low loss of chromium, and intermediate loss of arsenic, which was affected more by formulation. Rainfall pH had no detectable influence on leaching of wood exposed in soil, presumably due to buffering of pH by the soil. In soil, soil type and CCA formulation together affected leaching. Best overall performance in terms of environmental risk was given by the CCA-C formulation, and worst performance by the CCA-B formulation (lowest Cr:As ratio and highest retention). Soil type evidently affected the extent to which elements leached from the wood were held in soil, eg sand adsorbed high levels of arsenic poorly and all three soils adsorbed copper and chromium well over the concentration range present.

6.3.4.4. Water temperature

Van Eetvelde et al (1995a,b) observed that metal loss ratios were much higher at standard leaching temperature conditions of 20ºC than at 8ºC, both in laboratory and shower tests, which suggests that water temperature may potentially affect the rate of leaching in the field.

6.3.4.5. pH 3.5-8.5 in soil-water extracts

Venkatasamy and Okwara (2003) reported a study where Kenyan-grown *Eucalyptus saligna* was treated with CCA-C (oxide – 25.4 kg/m^3 retention, 14 days fixation) and leached for 3-18 days. Treated wooden blocks (10 cm X 5 cm X 3 cm) were subjected to accelerated leached in plastic tanks holding 10 L of leaching water which was agitated slowly by paddles. The leaching water was obtained by mixing 5 kg of different soil types with nominal pH 3.5, 4.5, 5.5, 7.5 and pH 8.5 with 10 L water and decanting the liquid after settling. The pH of the water was then adjusted to represent that of the soil used in each case. Tap water (pH 6.8) was used as a neutral pH control. At the end of each leaching period, leachate was analysed for copper, chromium and arsenic by AAS, expressed as ppm in the leachate.

Leaching of all three elements was generally highest under acidic conditions (copper, chromium and arsenic concentration at 18 days = 60.8 ppm, 51.3 ppm and 53.8 ppm, respectively, at pH 3.5), lower under alkaline conditions (copper, chromium and arsenic concentration at 18 days = 1.9 ppm, 2.4 ppm and 1.4 ppm, respectively, at pH 8.5), and lowest at neutral pH (copper, chromium and arsenic concentration at 18 days = 0.15 ppm, 0.25 ppm and 0.42 ppm, respectively, at pH 6.8). Maximum leaching tended to occur between 12 and 15 days, changing little thereafter. The authors acknowledged that in addition to pH, other soil chemical, physical and microbiological properties may have influenced the results and discussed the possible impact of various soil properties. They noted the minor increase in leaching under alkaline conditions as possibly relevant to poles and posts in alkaline soils. They also noted a lack of information on CCA leaching from treated eucalypts and discussed the issue of whether CCA-treatment is appropriate from an environmental perspective for hardwoods such as the eucalypts, given that fixation of CCA in hardwoods is poor, especially in species high in tannins.

6.3.4.6. Humic acids

Cooper et al (2000a, 2001b) reported studies in Canada to examine the effect of natural humic acids on leaching of CCA components from treated wood (measured on ground samples by X-ray fluorescence spectroscopy). Sapwood cubes (19 mm) cut from a new red pine pole section which had been pressure treated with a CCA-C formulation (initial retention 7.2-8.0 kg/m^3) were exposed to leaching solution over a period of two weeks (solution replaced at set intervals, according to AWPA Standard E-11-97). Compared to distilled water, samples of leaching solution from natural water (swamp or beaver pond overflow) or solutions of commercial humic acids (1000-10,000 ppm) generally had significantly higher chromium and copper due to losses from the wood, with increasing loss with increasing humic acid content. Copper was the component which was most affected. The arsenic content in leachate was slightly higher with natural waters, but not commercial humic acids.

6.3.4.7. Cation exchange capacity (CEC)

Archer and Jin (1994) reported soil bed studies in the USA using natural soil and modified soil media which provide some indications of the influence of soil Cation Exchange Capacity (CEC) on CCA-C depletion from treated wood (retention rates 4.0, 6.4 and 9.6 kg/m^3 in small southern yellow pine [*Pinus* spp] stakes, left to fix for 14 days after treatment). The context was to assist the interpretation of results from soil bed studies where preservative depletion is accelerated. Soil CEC is an estimate of the soils ability to attract, retain, and exchange cations (eg Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+) via negative charges on clay minerals and organic matter. CEC was seen as potentially influencing CCA depletion, as soils with high CEC values are known to have strong binding power for metallic ions such as Cu^{2+}, and *vice versa*. For the tests, a range of CEC conditions (8 to >95 meq/100 g) was obtained through the use of soil (CEC = 19 meq/100 g), vermiculite or peat alone (CEC respectively = 45 meq/100 g and >95meq/100 g), or soil amended with silica, clay, vermiculite or peat (CEC ranging from 8.0-31.0 meq/100 g). The stakes were exposed for 12 months in plastic containers of the soil media, watered every second day until water ran out the drainage holes. Retention was measured in the stakes by ICP analysis of digested material.

Chromium losses showed no clear trend with increasing initial retention levels, but with the exception of the soil + silica treatment, depletion of copper and arsenic was greater at 4.0 kg/m^3 than at the higher initial retention levels. At each retention level, depletion of copper and arsenic was highest in peat (68.4-84.5% depletion of copper and 23.8-60.7% depletion of arsenic). Despite having the second highest CEC, the vermiculite only treatment tended to have among the lowest depletion levels for copper and arsenic (9.4-19.4% and 14.6-30.4%, respectively), comparable to the soil + silica treatment (19.0-24.6% and 18.6-30.9%). Thus CEC alone was not responsible for variations in the depletion of CCA components. The authors suggested that while the low pH of peat possibly contributed, the reason for excessively high depletion in peat was that copper complexes with humic acids present in peat, hence assisting the extraction of copper from the treated wood (see below). However, the 1:1 soil:peat mixture did not show a consistent difference in retention behaviour from unamended soil (27.0-44.1% depletion of copper and 17.0-40.9% depletion of arsenic in soil:peat, compared to 27.0-40.1% and 24.0-44.3%, respectively, in unamended soil).

6.3.4.8. Inorganic salt solutions

Plackett (1984) reported a study of the influence of various inorganic salt solutions on CCA component leaching from wood which had been treated with a CCA-C formulation or a formulation lower in chromium content (the latter was the one more recently used in New

Zealand, a possible contributing factor being analytical requirements for arsenic and copper concentrations in CCA-treated wood driving the nature of formulations [Hedley et al, 2000], rather than minimisation of leaching). The study was conducted as part of research examining potential causes of premature decay of posts used in vineyards in New Zealand. *Pinus radiata* sapwood stakes were treated to give CCA retentions of ~10 kg/m^3. These were cut into sections and ground. Using ground wood was recognised to be a very artificial test, but was chosen as it would maximise leaching losses and amplify treatment differences. Ground wood was leached in a laboratory procedure and the leachate analysed for copper, chromium and arsenic by AAS. Four different types of inorganic salt solution were used for leaching, each at a range of concentrations. The solutions were calcium chloride (0.06-1.00 M), calcium nitrate (0.03-0.25 M as less soluble), magnesium nitrate (0.06-1.00 M), and a 1:1 mixture of dipotassium hydrogen orthophosphate (K_2HPO_4) and potassium dihydrogen orthophosphate (KH_2PO_4) (0.025-0.75 M for each). The chemicals were chosen to cover elements representative of those present from fertilisers added to horticultural soils, and the concentrations were designed to enable comparisons based on the ionic strength of the leaching solution (ie the sum of the molalities for each cation and anion in the solution, taking account of both concentration of each ion [molarity] and the size of its valency).

Results were provided for copper leaching, with no comment given on leaching of arsenic or chromium (presumably effects of the salt solutions were relatively minor for these elements, but the focus of the paper was loss of efficacy, hence copper was the element of concern). Low concentrations of each solution caused a significant increase in copper leaching compared with that induced by distilled water. Increasing the concentration of each solution increased leaching loss, but the manner in which this occurred differed between salts. Leaching loss was generally greater from the lower chrome content formulation than the CCA-C formulation with the calcium and magnesium salts, but comparable with the potassium phosphates. The author indicated that in particular, calcium concentrations in field horticultural soils in New Zealand are likely to be at concentrations sufficient to cause enhanced copper leaching from posts, but that the possibility that there may be pockets of soil with elevated magnesium, phosphorus or potassium levels in contact with posts cannot be excluded.

6.3.4.9. Effect of US soil physical and chemical characteristics on leaching

In a study by Wang et al (1998), 100 mm long sections of wooden stakes (15 X 15 mm) which had been treated with a CCA-C formulation were inserted into pots of moist soil so that the end of the stake was flush with the soil surface. Five soils differing widely in clay and organic matter content (hence drainage), to a small extent in pH (3.4-5.3), and widely in cation exchange capacity (CEC) were used. The pots were watered with distilled water to maintain a high moisture content without through drainage for a period of 12 weeks, after which half of each stake was sampled and the remainder returned for a further 14 weeks of exposure. Similarly treated stakes were exposed to distilled water without soil. Analyses of wood samples for copper and arsenic (but not chromium) were made by X-ray fluorescence spectroscopy. Little leaching of copper occurred in water compared to soil (0.9% compared to 1.8-36.5% in soils at 26 weeks), whereas the extent of leaching of arsenic in water was more comparable to that in soil (6.7% compared to 2.1-8.7% in soil at 26 weeks). Copper depletion from wood in an organic soil (36.5% leaching at 26 weeks, ~80% organic matter) was particularly high relative to the other soils (1.8-15.5% leaching at 26 weeks, ~1.2-3.6% organic matter). Considering the latter soils, leaching of copper and arsenic was lowest in a soil with a high clay content (~2% leaching of each element at 26 weeks in a soil with ~73% clay, compared to ~8-16% and ~5-7% leaching for copper and arsenic, respectively, in soils ranging in clay content from 9.4-23.1%). Within this very limited set of data, factors such as soil pH and CEC appeared unimportant, but there were indications of a possible effect of exchangeable cation concentration and soil copper content (copper tended to leach less with higher exchangeable cation and soil copper levels).

6.3.4.10. Summary and conclusions regarding factors affecting leaching from timber during use

It is reasonable to expect that the amount of rain, irrigation or other sources of water to which treated timber is exposed will affect the leaching rate. The nature of rainfall is also thought to affect leaching rate, eg in one study short heavy showers did not produce as much leaching as the equivalent mm of steady rain, presumably due to a longer wetting period and deeper water penetration with the latter (Section 6.4.2.1). A greater surface area to volume ratio of the treated timber is likely to increase leaching rate, as shown by numerous laboratory and field trials discussed elsewhere (eg Section 6.3.1.3.5, Section 6.7) A number of other site factors may also affect the rate of CCA leaching from timber in use, including:

- water pH (eg acid rain);
- the presence of organic acids such as citrate, acetate or COOH groups in humic acid (organic matter);
- soil pH and buffering capacity;
- inorganic salt in soil, particularly phosphates;
- soil cation exchange capacity;
- surface area of soil particles (amount of clay present, soil texture);
- iron, aluminium and manganese oxide or hydroxide complexes;
- water temperature.

Thus there are situations such as in silage pits where materials other than CCA-treated timber could be used to avoid excessively high component leaching rates, though the example of silage pits pertains more to leaching of copper than arsenic or chromium. Accelerated leaching due to acid rain is unlikely to be a problem in Australia, hence it may be that leaching rates are lower in Australia than areas where acid rain occurs frequently.

6.3.5. Effects of surface coatings, water repellents and cleaning methods

6.3.5.1. Effect of coating materials on leaching of CCA in Thailand

Veenin and Veenin (2001) treated rubber wood (*Hevea brasiliensis*) blocks (20 mm X 20 mm X 20 mm) with CCA (formulation type not stated). After a two week fixation period and air drying they were brush coated with wood stain, polyurethane, varnish or polyethylene glycol (PEG) 1000, or left uncoated. After a 7 day drying period the treated blocks, and similarly coated untreated blocks, were exposed to a leaching test. The latter was modified from a standard British test and involved immersion in water for 15 days at ambient conditions with 5 changes of water. Leachates were analysed by AAS, and leached blocks also analysed, for copper only in both cases. Blocks were also used for laboratory decay tests where they were placed into cultures of two different fungi on agar (brown rot [*Gloeophyllium sepiarum*] and white rot [*Pycnoporus sanguineus*]) and left for up to 12 months.

The amount of copper leached per cm^3 for CCA-treated blocks after 15 days was greatly reduced by the wood stain, polyurethane and varnish (most effective), and slightly reduced by the PEG (total copper leached in 15 days = 90.4-143 $\mu g/cm^3$, 402 $\mu g/cm^3$ and 546 $\mu g/cm^3$, respectively).

Most of the loss with PEG and uncoated wood occurred in the first day of exposure. Concentrations of copper remaining in the wood reflected the results in leachate, with PEG and uncoated wood showing higher copper losses.

Weight loss measurements in the agar-block decay tests showed treated and untreated wood blocks coated with PEG were less durable to attack of both fungi than coated wood, and stained wood lost durability after the first 4-8 months of exposure. The authors suggested that the PEG 1000 may have increased rather than reduced moisture absorption in the wood, leading to greater fungal destruction, and that a higher molecular weight PEG (eg PEG 3000) may have been more effective. In each case, untreated wood had greater weight loss than CCA-treated wood with the same coating treatment.

Thus varnish, polyurethane and wood stain coatings reduced copper leachability into water under laboratory conditions.

6.3.5.2. Above ground leaching from structural timber – species, CCA loading and water repellent coating in Canada

Taylor and Cooper (2001) examined leaching of CCA-C from 20.3 cm (8 inch) sections cut from CCA-treated 5.1 cm X 15.2 cm (2 inch X 6 inch) lumber with above ground exposure under ambient conditions in Toronto, Canada. Three wood species were tested, southern yellow pine (*Pinus* spp), jack pine (*Pinus banksiana*) and black spruce (*Picea mariana*). Southern yellow pine is permeable, allowing deep penetration of CCA, whereas jack pine has moderate permeability and black spruce has low permeability. Two preservative concentrations were used (1% and 3%), and the difference in permeability is evident in the resulting retentions (for southern yellow pine, jack pine and black spruce, retention was 5.5, 2.6 and 1.7 kg/m^3 with a 1% solution, and 13.9, 6.5 and 5.4 kg/m^3 with a 3% solution). To avoid end grain effects on penetration and leaching, the ends of the blocks were sealed before treatment and again after 36 h accelerated fixation and two weeks conditioning. The effect of a water repellent treatment on leaching was examined by applying a brush coat of a commercial water repellent on some blocks prior to leaching exposure. The trial was a factorial design of the wood species, preservative concentration and repellent use, with three replicates.

For leaching exposure, blocks were suspended on spikes above individual plastic trays and exposed to ambient weather conditions. Samples of leachate in each tray were taken after each precipitation event over a 183 day period (40 rain and 1 snow, ~750-800 mm total) and the collection tray emptied after measurement of the leachate volume. Copper, chromium and arsenic were determined in leachate by ICP analysis. The data were presented both on the basis of loss per unit area of wood surface (μg/cm^2) and % loss based on initial CCA retention.

Mean leaching of copper was significantly greater from southern yellow pine (0.98 μg/cm^2) than from jack pine and black spruce (0.75-0.77 μg/cm^2), but differences between species for leaching of chromium (0.22-0.26 μg/cm^2) and arsenic (0.77-0.89 μg/cm^2) were not statistically significant. Mean leaching of chromium was 37% greater at the lower preservative loading than the higher loading (0.30 and 0.19 μg/cm^2, respectively), but leaching of arsenic was not significantly affected (0.79 and 0.83 μg/cm^2) and that of copper was 28% less at the lower loading (0.69 and 0.97 μg/cm^2). The authors noted that other researchers had reported mixed effects of CCA loading on absolute and % leaching. The commercial water repellent resulted in 45%, 39% and 31%, respectively, reduction in leaching of copper, chromium and arsenic.

In terms of % loss, southern yellow pine performed significantly better than the other species (mean % loss of copper, chromium and arsenic in 183 days = 0.019%, 0.002% and 0.013%, respectively in southern yellow pine, and 0.042-0.049%, 0.011-0.013% and 0.033-0.035% in the other species). In these terms, there was 56% greater copper leaching, 88% greater chromium leaching and 66% greater arsenic leaching with the lower preservative loading than the higher, consistent with laboratory studies on the influence of retention on leaching (p 27). Water repellent application resulted in ~50% less leaching. In general, percent loss of copper was greatest and that of chromium least. Overall average leaching losses from all treatment combinations over the 183 days were 1.51% for copper, 0.38% for chromium and 1.10% for arsenic, but in the worst case (black spruce with 1% CCA-C and no water repellent) losses were substantially greater (4.28%, 1.33% and 3.04%, respectively).

Copper had a leaching rate that was initially high and then declined to a more stable rate after the first month of exposure, and the chromium leaching rate behaved similarly, stabilising at a low level. In contrast, the leaching rate of arsenic did not decline over the test period. A longer study period would be necessary to clarify whether there were any impacts of climatic variables (temperature, amount of rainfall per event etc) on these patterns. The paper noted that the trial was continued for a further 6 months, but no subsequent report has been provided.

6.3.5.3. Above ground leaching from structural timber – water repellents applied during or after CCA treatment in Canada

Cooper et al (1997) reported studies with a water repellent treatment applied to CCA-treated spruce-pine-fir timber by brush, and with two water repellents applied in conjunction with the CCA treatment. Fence boards (2.5 cm X 15 cm) and decking boards (5.1 cm X 15.2 cm) were treated with 2% CCA-C or 2% CCA-C with 0.5% of two different commercial water repellents (WR A and WR B). The boards were fixed either at 21° C or at 60° C and high humidity. Some CCA-treated fence boards were brush-coated with a commercial water repellent product (TWS). The boards were then leached for 12 cycles of accelerated spray exposure, during which the concentration of CCA components was monitored. The boards were then made up into fence or deck units equipped with water collecting traps and exposed to natural weather conditions. Collected drip water was analysed for copper, chromium and arsenic concentrations in leachate during the first four months of exposure and after 2 years exposure (it was not clear what collection duration the 4 month and 2 year samples were actually taken over).

In the accelerated leaching part of the study, concentrations of CCA components were lowest in leachate from the TWS coated lumber. Results for the CCA WR additives were inconsistent, sometimes leading to higher concentrations of an element in leachate and sometimes lower. Overall, copper was the most readily leached element, then arsenic, with chromium giving the lowest leachate concentrations. In most cases, but not always, leachate concentration was lower with the high temperature fixation.

In the fence units, TWS coated boards led to a significant reduction in CCA component concentrations in trapped rain drip water after both 4 months and 2 years exposure. There were also some reductions in CCA component concentrations with the CCA WR additives, with WR B the more effective and those from WR A generally not statistically significant, though almost always lower than CCA only. Concentrations of copper, chromium and arsenic in drip water from fence boards at 4 months ranged from 0.9-5.0 ppm, 0.4-1.2 ppm and 0.5-2.8 ppm, respectively, and at 2 years 0.6-3.7 ppm, 0.3-1.9 ppm and 0.1-3.1 ppm. In CCA (only) treated boards without coating, copper concentrations were lower at 2 years than 4 months, chromium concentrations slightly higher, and arsenic concentrations similar.

In the deck units, results for the CCA WR additives were in most cases lower than those for CCA only, but the differences were generally not statistically significant. However, on the deck units there was a clear decrease in CCA component concentrations in drip water between 4 months (copper, chromium and arsenic concentrations 1.3-1.9 ppm, 0.4-0.7 ppm and 1.0-1.7 ppm, respectively) and 2 years (0.2-0.8 ppm, 0.2-0.5 ppm and 0.3-1.7 ppm, respectively).

The authors concluded that brush on water repellents such as the product tested can reduce the concentration of CCA components in rain drippage from products in service, thereby reducing *in situ* impacts of the wood treatment. The effect was still evident 2 years after treatment. Water repellent additives to the CCA solution were somewhat effective at the 0.5% concentration used, and the authors suggested that application at the manufacturer's recommended concentrations of 1-2% would be more effective. Levels of all CCA component elements dropped with time in leachate from deck units, but only copper levels dropped with the fence units.

6.3.5.4. Above ground leaching from structural timber – water repellents applied during CCA treatment in the USA

Cui and Walcheski (2000) treated southern yellow pine boards (5 cm X 15 cm X 52 cm, end-sealed with an epoxy sealer) with CCA (1%) or CCA (1%) in combination with commercial water repellent additives (UW, WR A or WR B at 0.8% or 1.2%). After fixation and drying, boards were placed on small supports in plastic boxes designed to collect run-off but keep the boards above water. The boards were then exposed to the weather for 14 natural rainfalls. Leachate was collected after each rain event, weighed, and analysed by ICP. In a pine wafer swelling test, UW and WR B were shown to have similar water repellency, with WR A less water repellent.

The data suggested that the type and amount of water repellent coating had a significant impact on CCA leaching (there was no statistical analysis). During a two month period with ~206 mm of rain, the CCA boards without water repellent additive leached out 43 mg copper, 15.3 mg chromium and 42.5 mg arsenic. The CCA/0.8% UW treatment leached out 39.9 mg copper, 20 mg chromium and 30.3 mg arsenic. Results were similar for the WR B treatment, whereas the WR A treatment resulted in higher arsenic and copper leaching (copper, chromium and arsenic leaching 60.4 mg, 20.8 mg and 46.8 mg, respectively).

For the 1.2% additive comparison, different sets of end-matched boards were used (hence there was a different set of CCA only results). In the same two month period, CCA boards without water repellent additive leached out a total of 50.6 mg copper, 22.8 mg chromium and 74.5 mg arsenic. UW and WR B treated boards leached out less arsenic (42.2-47.1 mg). Chromium leaching was similar for all four treatments (21.7-26.8 mg). Copper leaching was lower with UW (30.6 mg) than the other treatments (46.2-55.8 mg).

However, the effect of water repellent on component leaching was not consistent between individual rain events, in some cases water repellent treated boards leaching more than CCA only boards, and sometimes less. The investigators considered that this was related to the amount and severity of the rain and the absorption and run-off behaviour of the rain on the different surfaces: eg without water repellent, the boards absorbed much of the rainwater, whereas small puddles formed on the repellent treated boards before running off. Another result of interest was that the amount of arsenic leached out per square centimetre of deck surface was unrelated to the absolute rain amount.

All three water repellent products were described as oil-in-water type emulsions, with different types and amounts of surfactants. The authors suggested possible effects of the ingredients on fixation of CCA in wood, eg that WR A causes significant reduction of Cr^{VI} in CCA solution, and that polyethylene glycol segments of the surfactants may complex with metals.

6.3.5.5. Leaching from small deck units in Canada – effects of deck washes and brighteners

Taylor, Cooper and Ung (1999) prepared 16 small (1 metre square) deck units from southern pine lumber which had been treated with CCA-C to a loading of 6.4 kg/m^3. The wood was fixed at high temperatures and all the chromium reduced before assembly. The decks were placed outdoors in New Brunswick, Canada. Rainwater drippage on each deck was collected by a polyethylene drape under each deck. The water was measured for volume and analysed for copper, chromium and arsenic by AAS for each of five rain events over a 6 week study period. Two decks (controls) were scrubbed clean with 8 L of water and the water drippage collected for analysis. The remaining 14 decks were treated with seven commercial deck wash or brightener treatments (2 decks/treatment) according to manufacturers' recommendations and then rinsed with 8 L of water, which was collected and analysed.

The average amount of water collected per deck per rain event was 21 L (ie 2.1 cm over 1 m^2), containing an average concentration of 3.8 ppm copper, 0.9 ppm chromium and 2.8 ppm arsenic, or 81 mg of copper, 19 mg of chromium and 59 mg of arsenic. A number of the treatments had adverse influences on the amount of CCA components in rinse water compared to normal water (it was not clear how the values for "normal" water were obtained, as they differ for each treatment rather than being a common value for the two water only decks). As evident in Table 21, this was particularly the case for copper with acid treatments and chromium with hydroxide/bleach and percarbonate treatments. Furthermore, the latter were sufficiently strong as oxidising agents to convert some of the Cr^{III} present in the treated wood to Cr^{VI}, which is more mobile and more toxic. When the amount of each element released in a single 8 L wash is compared with that in a single rain event, the amounts of each element were of the same magnitude or lower (Table 22).

Thus the deck wash/brightening products differed in the extent to which they released CCA components according to their active constituents, with high copper extraction by acid formulations and higher chromium extraction by strongly oxidising formulations. Even so, the amount of copper and arsenic leached in a single wash was comparable to that from an average rainfall event in the area, and the total amount of chromium released in a wash was ~1.5-2.3 X that in a rain event. However, release of Cr^{VI} by sodium hydroxide, sodium hypochlorite and (presumably sodium) percarbonate is of concern, hence the authors recommended that these products should not be used on CCA-treated wood.

Table 21. Ratio of concentration of CCA components in deck wash water compared to normal water.

Treatment constituents	Ratio of leached element compared to water			Cr^{VI} concentration (ppm)
	copper	chromium	arsenic	
Phosphoric acid	37	10	0.3	0.07
Oxalic acid	20	4.5	4	0.42
Citric acid	14	2	1.2	0.1
Borate	1	0.5	1	0
NaOH	5	15	1.1	0.75
NaOH/NaOCl	4	60	5	4.37
Percarbonate (oxygen bleach)	4	50	4	3.64

Table 22. Ratio of leached CCA components in deck wash water compared to a natural rain event.

Treatment constituents	Ratio of contaminants leached in wash/rinse water to that in an average rainfall event		
	copper	chromium	arsenic
Phosphoric acid	1.11	0.23	0.02
Oxalic acid	0.44	0.39	0.14
Citric acid	0.63	0.26	0.07
Borate	0.04	0.03	0.03
NaOH	0.15	0.74	0.03
NaOH/NaOCl	0.11	2.26	0.22
Percarbonate (oxygen bleach)	0.04	1.53	0.14

6.3.5.6. Summary and conclusions regarding the effects of water repellent treatments, coatings and cleaning methods on leaching

Water repellent treatments to reduce checking, splitting, warping and twisting of timber such as decking and stains can be pressure incorporated into the wood at the same time CCA is applied. Studies suggest that some factory applied water repellent treatments do reduce leaching of CCA components. However, there were indications of differences between products, effects of rates, reactions between some water repellent formulations and CCA treatment solutions, and inconsistent results possibly associated with the nature of individual rainfall events. Hence further data and experience appear necessary to clarify the impacts of factory applied water repellent treatments on CCA leaching rates.

Various types of surface coatings and stains are commonly applied after construction and studies have shown that these may also reduce CCA leaching, by as much as ~50%. However, such coatings are likely to need relatively frequent replacement to maintain their water repellent effect. In sensitive environments there may be environmental contamination considerations regarding dripping or spillage during application, and surface preparation for recoating may also release particles containing CCA components.

An evaluation of the effect of various deck washing and brightening treatments indicated that products differed in the extent to which they released CCA components according to their active constituents, with high copper extraction by acid formulations and higher chromium extraction by strongly oxidising formulations. In general, the amount of copper and arsenic leached in a single wash was comparable to that from a rainfall event. While not a problem with the other products tested, release of Cr^{VI} by the alkalis and oxidising agents sodium hydroxide, sodium hypochlorite and (presumably sodium) percarbonate was of concern. Hence the authors recommended that products of this type should not be used on CCA-treated wood.

Thus the use of some water repellent treatments incorporated at the time of CCA treatment may have beneficial effects in reducing CCA leaching, but further research is necessary to clarify what treatments work best. Various coatings and stains applied to timber which has already been treated with CCA may in some cases greatly reduce CCA leaching, but need to be reapplied regularly. Washing a deck with various types of cleaning and brightening products is generally likely to be similar to a rain event, except that products containing sodium hydroxide, hypochlorite or percarbonate should not be used as they enhance release of Cr^{VI} from CCA-treated wood.

6.4. Field and semi-field investigations

6.4.1. Leaching from stakes, poles and posts in trials and actual use situations

6.4.1.1. Leaching from test stakes in ground contact and above ground in Norway

Evans, Nossen and Edlund (1994) reported a study with exposure of CCA-treated field test stakes at two sites in Sweden for up to 28 years ground contact, where the stakes were examined at the time they were rejected due to decay, or 7 years above ground exposure (still sound when examined). The test stakes were Scots pine, with dimensions 20 X 50 X 500 mm, treated with a CCA-B to a retention of 18 or 28 kg/m^3 sapwood. Analyses were conducted by AAS on milled wood digested in a mixture of concentrated sulphuric, nitric and perchloric acid with hydrogen peroxide.

There was a gradient in the concentration of preservatives in unexposed stakes, with greater retention in the ends of the stakes (~1.5 X), and ~20% greater retention in the outer part of stakes compared to the inner. Leaching from stakes exposed for 2-28 years in ground contact (vertically, with ground level at 250 mm) differed between the two sites. Least preservative was found in the end grain and there were also indications of redistribution from the inner part of stakes to the outer part. At the wetter site (sandy soil, pH ~4.5, ~1000 mm precipitation/year), approximately 50% of the expected arsenic, 10% of the copper and practically all the chromium remained in the upper 5 mm of test stakes, approximately 70-80% of the arsenic, 50% of the copper and all the chromium remained at the lowest 5 mm, and approximately 60-70% of arsenic and copper remained in intermediate sampling points. At the drier site (clay soil, higher pH than the other site, ~500 mm precipitation/year), retention was approximately 100% of the expected copper, 80-90% of the arsenic and 100% of the chromium in the outer part of the stakes, and approximately 80-90% of the copper and 70-90% of the arsenic in the inner part. The authors suggested that less acidic pH, together with iron and aluminium combining with arsenic to form insoluble compounds, reduced leaching with ground contact at the drier site. They also hypothesised that aluminium may migrate into the stakes and fix the arsenic.

Leaching from the end grain in stakes exposed horizontally above ground for 7 years (precipitation ~500 mm/year) was very high, with approximately 80% of the copper, 20% of the chromium and 50% of the arsenic evidently leached. In the rest of the stake, leaching from the upper surface was higher than the lower, presumably because of greater exposure to rain, and possibly with redistribution towards the lower part. Leaching from stakes exposed horizontally above ground was not less than from stakes in ground contact.

6.4.1.2. Loss of CCA components from treated stakes into soil in the UK

Hudson and Murphy (1997) examined movement of CCA components from Corsican pine stakes (600 X 50 X 50 mm) which had been treated with a CCA UK Type 2 formulation (retention ~6.25 and 12.5 kg/m^3) and had been buried vertically to a depth of 270 mm for 41 years. Sections of wood were sampled from above, below and at ground level. Soil samples were taken at distances of 0, 20, 100 and 300 mm from treated and control stakes at ~30 mm below the soil surface. Ground wood was digested in acid-peroxide mixture, and soil extracted using *aqua regia* (total element present) or ammonia-EDTA solution (available element). Extracts were analysed by AAS.

No appreciable loss of chromium from the stakes was evident, but large falls occurred from the estimated original retained levels of arsenic and copper in the upper portion of the stakes, with some evidence of arsenic loss below the groundline. Consistent with these results, while chromium was found in the highest concentration of the three elements in treated wood, it occurred in the lowest concentration in surrounding soil (average total concentration at 0 mm was 19 ppm and 8 ppm with 1% and 2% treatment solutions, respectively, and 5-10 ppm at greater distances, with significantly lower available chromium levels, in the range 1-3 ppm). Soil concentrations of total and available copper and arsenic decreased with increasing distance from the stake, with arsenic concentrations higher than those of copper (average total arsenic and copper concentrations at 0 mm were 132-184 ppm and 35-84 ppm, respectively). Copper concentrations declined more sharply with distance (average total arsenic and copper concentrations at 20 mm were 76-153 ppm and 17-26 ppm, respectively, declining to 17-42 ppm and 5-8 ppm at 100-200 mm). The investigators suggested that this was due to copper exchanging for other cations such as sodium (Na) in the soil (they note that Cu^{2+} is more electropositive and has a lower hydrated radius than Na^+ and is therefore likely to replace Na^+), whereas arsenic is leached in the pentavalent (As^V) form as anions (eg H_2AsO_4), which are more mobile in soil (repelled by the net negative surface charge of clay particles, optimum adsorbance of As^V occurs at pH ~5, by displacement of hydroxyl ions on clay particles). While the majority of copper and arsenic present at 0 and 20 mm from the stake was available, available copper and arsenic was significantly lower than the total amount present in soil at 100 and 200 mm (average available arsenic and copper concentrations at 0-20 mm were 18-110 ppm and 6-89 ppm, respectively, falling to 3-8 ppm and 2-4 ppm at 100-200 mm).

6.4.1.3. Leaching of CCA from exposed wooden stakes in Mississippi

DeGroot et al (1979) conducted a study of lateral and vertical migration of CCA metal residues near ten 50 X 101 mm southern pine stakes which had been treated with CCA-A at 10.6 kg/m^3 or CCA-B at 8.8 kg/m^3, inserted into soil to a depth of ~23 cm and exposed for 30 years to an annual rainfall of 160 cm in a subtropical climate (Saucier, Mississippi). The soil was an acidic (pH 4.9) sandy loam. The stakes were removed and soil samples taken from the bottoms and sides of the holes where the stakes had been and at distances of 7.6, 15.2 and 22.8 cm laterally at various depths. The samples were digested in hydrochloric acid and analysed by AAS (copper and chromium on half the samples only). Background metal levels in the soil were 4.0-6.6 ppm (minimum in the surface 15.2 cm and maximum at 30.5-45.7 cm) for copper, 3.8-9.2 ppm (minimum in the surface 15.2 cm and maximum at 61.0-76.2 cm) for chromium, and 0.6-1.4 ppm (reasonably uniform) for arsenic.

The results are summarised in Table 43. Arsenic levels were much higher with the CCA-B formulation (know to leach more arsenic than type A or C formulations), and greater leaching within the soil was evident with this formulation. Copper and chromium levels were slightly higher with the CCA-A formulation (also applied to a higher retention level). Arsenic levels were as high as 183 ppm in surface soil adjacent to the stakes and 108 ppm in the first 15.2 cm (six inches) of soil immediately beneath the stakes. Copper levels were up to 56.6 ppm in surface soil adjacent to the stakes and 75.8 ppm immediately beneath the stakes. Chromium levels were up to 45.9 ppm in surface soil adjacent to the stakes and 25.1 ppm immediately beneath the stakes. Relative to background levels there was evidence of arsenic leaching from the CCA-B formulation deeper into the soil, but no clear evidence for deeper leaching of copper or chromium with either formulation. Arsenic did not appear to leach into the 30.5-45.7 cm (twelve to eighteen inch) sample zone beneath the stakes. Lateral movement of residues in the soil surrounding the stakes appeared to be largely limited to the zero and 7.6 cm (three inch) sampling areas surrounding the treated stakes. The only statistically significant results at 7.6 cm were arsenic from CCA-B and chromium from CCA-A (the results for copper were relatively variable). No results were statistically significant at greater lateral distances, though arsenic concentrations at 15.2 and 22.8 cm look slightly elevated with the CCA-B formulation. Thus there was leaching of copper, chromium and arsenic from the stakes over the 30 years they were in the ground, but little lateral movement occurred and no leaching beyond 30 cm below the bottoms of the stakes was detected.

Table 23. Results of a study of CCA-component levels in soil surrounding and beneath treated stakes (DeGroot, 1979).

Soil sample location	Copper (ppm)		Chromium (ppm)		Arsenic (ppm)	
	CCA-A	CCA-B	CCA-A	CCA-B	CCA-A	CCA-B
Background levels	4.0-6.6		3.8-9.2		0.6-1.4	
Depth beneath stakes [cm (inches)]						
0-15.2 (0-6)	56.6	48.3	25.1	22.9	18.9	108.1
15.2-30.5 (6-12)	6.9	8.2	8.2	7.4	1.6	21.4
30.5-45.7 (12-18)	5.7	6.4	9.2	6.2	1.2	1.1
45.7-61.0 (18-24)	3.6	4.1	9.4	7.1	1.7	1.1
Surface 0-15.2 cm (6 inches), lateral distance from stake [cm (inches)]						
0 (adjacent)	75.8	47.9	45.9	24.2	73.2	183.2
7.6 (3)	11.8	15.3	9.4	8.2	5.6	117.7
15.2 (6)	5.6	4.9	4.7	6.4	1.3	7.0
22.8 (9)	12.3	7.2	6.2	5.3	1.5	4.9

6.4.1.4. Residual CCA levels in treated poles removed from service in Canada

Cooper, Jeremic and Taylor (2001) reported a study where CCA treated pine poles removed from service 1 to 50 years after installation were evaluated for distribution and mass balance of copper, chromium and arsenic (measured in sawdust by X-ray fluorescence spectroscopy) in above ground and below ground zones (+/- 30 cm of ground level; 0-5 mm, 0-20 mm, 20-40 mm and 40-60 mm depths into the wood). The CCA formulations used had varied over the years, between CCA-A initially, CCA-B until the last 15-20 years, then CCA-C. All poles still had CCA retentions at or above the toxic threshold retention for most decay fungi (~2.9 kg/m^3) at a depth of 40 mm into the wood. There was little difference in CCA component retention or mass balance between the above and below ground wood samples except for copper, where there was some evidence that copper may be preferentially leached from the pole surface in the below ground zone. Arsenic was evidently leached more than the other components, independent of depth into the wood. In all cases, the poles removed from service showed similar trends to freshly treated wood in that mass balances of chromium were higher and those of copper and arsenic lower near the pole surface, hence some of the apparent losses of arsenic and copper from the surface may have been due to the disproportionation effect (p 56). The interpretation of data showing differences associated with the age of the pole was made difficult by lack of data on the original CCA treatment applied.

6.4.1.5. Evaluation of wood, soil and run-off water from poles in service in Canada

A study in Canada by Cooper and Ung (1997) evaluated levels of copper, chromium and arsenic at different depths and distances from CCA-C treated utility poles, most also treated with PEG (polyethylene glycol). The authors note that potential environmental implications of CCA treated wood use include contamination of soil to unacceptable levels and contamination of ground or surface water. Soil contamination could lead to unacceptable intake of CCA components by food plants or to a health risk to those in contact with the soil, while contamination of ground or surface water could affect aquatic environments, or potentially reach water used for humans or livestock.

Samples of wood were taken from each of the 53 poles examined (5 mm deep from the above and below ground surfaces). Soil samples were obtained at different depths (0, 0.5, 1.0, 1.5 m sometimes 2 m) and distances (0, 0.25, 0.5, 1.0 and 25 m from the pole) around red pine (*Pinus resinosa*) and jack pine (*Pinus banksiana*) utility poles with a range in ages in service from 1-2 to 13 years. Some poles were fitted with water traps to collect rainwater that dripped down the poles. In situations which allowed, ground water samples were collected from next to the poles. Soil samples were extracted with 4N nitric acid. Analyses for copper, chromium and arsenic were conducted by X-ray fluorescence spectroscopy for ground wood samples and ICP for soil and water samples.

Retention of CCA at the pole surfaces was high, and similar between red pine and jack pine (~10-33 kg/m^3 and 7-20 kg/m^3 respectively), generally with no significant differences between above ground and below ground levels. Ratios of the active elements varied greatly within and between poles, but in most cases the Cr/Cu and Cr/As ratios were higher than the expected values of 2.57 and 1.40. It is expected that in freshly treated wood these ratios may be somewhat higher due to the disproportioning of chromium near the wood surface. However, the investigators commented that in many cases, there was relatively more chromium near the surface than would be expected, suggesting some preferential loss of copper and arsenic relative to chromium.

The level of soil contamination dropped rapidly with distance from the poles, with soil levels approaching background levels within 0.25 m from the pole. In comparison to background levels, generally copper levels were highest, followed by arsenic, then chromium. The authors stated that this is consistent with the known relative leaching tendencies of the three elements from CCA treatment, and is despite copper having the lowest concentration and chromium the highest concentration in the preserving solution. Canadian soil remediation criteria are shown in Table 24. Copper concentrations often exceeded the 100 ppm (residential/parkland) or 150 ppm (agriculture) criteria at ground level near the pole, and less often at depth, with a peak soil concentration ~995 ppm. Arsenic concentrations occasionally exceeded the 20 ppm (agriculture) criterion at ground level near the pole and more rarely, in the deeper sampling zones next to the poles (most notably in wet soils), with a peak concentration ~325 ppm. Chromium concentrations never exceeded the 750 ppm (agriculture) criterion, with a peak concentration ~280 ppm. Contaminant levels increased with age in service and were generally highest in wet organic soils, possibly reflecting greater leaching (elevated concentrations at depth were often evident), and also potentially the presence of organic acids accelerating leaching.

Table 24. Soil and water remediation criteria used in Canada (Source: Cooper and Ung, 1997).

Medium	Criteria	Units	Concentration objectives for			
			Cr (total)	Cr^{VI}	Cu	As
SOIL	Background	µg/g	20	2.5	30	5
	Agricultural		750	8	150	20
	Residential/Park		250	8	100	30
	Commercial/Industrial		800	8	500	50
WATER	Background	µg/L	15	-	25	5
	Freshwater aquatic		2-20	-	2-4	50
	Irrigation		100	-	200-1000	100
	Livestock watering		1000	-	500-5000	500-5000
	Drinking water		50	-	<1000	25

Soil concentrations were highest at the ground line, adjacent to the poles, consistent with contaminated rainwater running down the poles being the major source and relatively minor lateral movement in soil. This was confirmed by more detailed examination of soil at 5 cm increments in the 0-25 cm zone from poles in wet sites or which had been in service a long time. Concentrations of copper and arsenic were usually >150 ppm and 20 ppm, respectively, in soil in contact with the pole, but in most cases, concentrations of these contaminants dropped rapidly to approach background levels within 10 cm of the poles (levels were elevated for 30-40 cm from the pole with one 2 year old pole in standing water). The investigators calculated a “mixing radius” for each pole, ie the distance around the pole that the soil would have to be uniformly tilled to acceptably reduce the arsenic levels in the soil for agricultural use: they estimated an annulus 0.90 thick around the pole would need to be mixed (depth not specified) in the worst case, and 0.3-0.7 m in the other cases.

Rain water trapped from the pole surfaces had concentrations of all three elements well above the Canadian aquatic and drinking water standards. Average yearly values for the poles ranged from 2-16 ppm for copper, 0.7-2.5 ppm for chromium, and 0.9-7.7 ppm for arsenic. The pH of trapped rainwater was generally ~5-6, higher than the pH of rain in the sampling area due to buffering by the wood, and above levels in acid rain that might lead to abnormal levels of extraction. There was no obvious drop in contaminant content in water that dripped down the poles relative to the age of the poles, in contrast to studies on roof shingles, other solid products and freshly treated laboratory samples. The investigators noted that any effect of age may have been obscured by variation in treatment quality, pole size, rainfall patterns etc, but hypothesised that a steady state leaching equilibrium is reached which is controlled by the solubility of the fixed CCA components, resulting in minimal decreases from year to year in the time frame investigated in this study.

Ground water samples from next to the poles occasionally had detectable CCA components above aquatic and drinking water standards in Canada for all three elements. Levels detected of chromium ranged from <0.01 to 0.57 ppm, those of copper were <0.01 to 1.46 ppm, and those of arsenic <0.03 to 0.59 ppm, with pH in the range 5.7 to 7.8. Mean levels (assuming 0.01 or 0.03 ppm where values were below the limit of determination) were 0.35 ppm for copper, 0.08 ppm for chromium, and 0.13 ppm for arsenic. These samples were only taken on sites classified as wet or clay soil, as the watertables were below sampling depth (1.5-2 m) at all the sand and sandy loam sites. The investigators noted that additional sampling would be required to determine how far from poles increased levels in water could be detected. They concluded that a water well sited near a pole would draw water from a much larger area, resulting in substantial dilution, but that it would be wise to locate CCA treated poles at least several metres from drinking water wells.

6.4.1.6. Loss from poles, piling, posts and stakes treated with CCA in the USA

Arsenault (1975) provided some history of CCA use in the USA, following the original patent in India in 1933 and the first large scale use in the USA in 1938 by Bell Telephone System. The author reviewed the literature and discussed various new evaluations which had been conducted with utility poles, posts, stakes and marine piles by measurement of copper, chromium and arsenic remaining in the wood (retention levels at different depths in the wood and above and below ground, and element balances). In many cases, no significant loss of any component was claimed, but the emphasis of much of the discussion was on demonstrating continuing preservative performance after long time spans in service. Evidence was described of instances where some decay was evident due to problems such as shallow penetration (hence internal decay) and lower than intended initial retention. Greater leaching of arsenic, but not copper, was evident in posts treated with CCA-B than was found with CCA-A and CCA-C, though there was no evident effect on service life.

The author described evaluations of soil surrounding CCA-A treated utility poles in North Carolina (clay soil, poles treated 32 years previously) and CCA-A and CCA-B treated posts in Florida (sandy soil, poles treated 17 years previously). Samples were taken at various distances out from the poles or posts (0-5.1 cm, 5.1-10.2 cm and 10.2-15.2, plus 27.9-33.0 cm for the poles), with control samples from 305 cm away for the poles and 46 m away for the posts. For the poles, samples were taken at a depth of 30.5 cm, while for the posts, they were taken at 15.2 cm as well as 30.5 cm. Presumably the posts and poles were buried more deeply than these sampling depths. Only the arsenic concentrations in the sampled soil were analysed.

The results showed clear evidence of arsenic leaching into the soil from CCA-A treated poles and CCA-B treated posts, but that lateral movement from the poles and posts was generally very limited (Table 25). The author noted that leaching was lower with the CCA-A treated posts as they were only 1.83 m high, whereas the posts treated with CCA-B were 2.54 m high and were larger in diameter, hence there was a greater surface area for leaching. The author made some interesting comparisons between the arsenic levels present in these soil samples and literature reports for the upper concentration for arsenic normally found in US soils (40 ppm), arsenic concentrations in shrimp along the southeastern and northeastern coast of the US (up to 42 ppm) and in large-mouthed black bass from the southeastern waters of the US (as much as 40 ppm), and to arsenic concentrations in soils where arsenicals had been used for horticulture (the level of 300 ppm next to a post was no greater than that commonly found in the soils of apple orchards in Washington, New York and Maryland). However, the more salient point are the limited overall contamination likely from arsenic leaching due to the limited lateral movement of arsenic evident from the available data for the poles and posts evaluated.

Table 25. Arsenic analyses of soil samples taken from the base of CCA treated poles and posts (Arsenault, 1975).

	Distance from surface of wood				
	0-5.1 cm	**5.1-10.2 cm**	**10.2-15.2 cm**	**27.9-33.0 cm**	**Control**
	Arsenic content (ppm)				
North Carolina poles (CCA-A treated)					
Pole 33	109	57.4	24.0	25.3	18.1
Pole 34	33.1	23.6	22.5	12.9	10.6
Pole 35	23.9	29.1	28.9	15.6	-
Pole 37	46.0	34.4	14.9	11.5	13.8
Average	53.0	36.1	22.6	16.3	14.2
Florida posts (CCA-A treated, 1.83 m)					
15.2 cm depth	14.2	10.1	7.0		11.6
30.5 cm depth	11.4	6.7	14.5		7.4
Florida posts (CCA-B treated, 2.54 m, pole thickness)					
Post 1761, 15.2 cm	306.9	38.5	22.3		
Post 1761, 30.5 cm	196.8	25.5	14.6		
Post 1763, 15.2 cm	302.8	115.8	41.9		
Post 1763, 30.5 cm	289.7	16.9	8.5		

6.4.1.7. CCA-C depletion of utility poles in Georgia

In a study by Osborne and Fox (1995) there were no statistically significant differences in CCA-C retentions between above ground and below ground sections of southern yellow pine utility poles after exposure for 6 years in Georgia. The investigators noted similar findings by Arsenault (1975) with CCA-A southern pine poles after 15-17 years service in South Carolina. They hypothesised that below ground retentions should be lower than the corresponding above ground retentions based on the premises that wood in ground contact is subject to a higher leaching potential than wood above ground. From their results, they concluded that little to no depletion had occurred in the time frame. However, there are several other reports where there were little or no differences between above and below ground retention of copper, chromium and/or arsenic in poles, yet evidence such as comparison with assumed initial retentions, increased residues in soil, and residues in pole run-off clearly indicate that loss has occurred.

6.4.1.8. Leaching of CCA-B from Finnish poles in service and levels in soil

Nurmi (1990) reported the results of measurements of CCA-B retention in utility poles after up to 10 years service in Finland, following treatment with a CCA-B oxide product to an initial retention level of ~10-13 kg/m^3. Samples of wood were taken at various distances from the butt end before installation and at 1.5 m from the top, 1 m above ground, ground level, and 0.5 m below ground after 2, 4 and 10 years service. Soil samples were collected systematically around the poles after 2 and 10 years service (depths and distances from the poles were not indicated). copper, chromium and arsenic in borings and in 6 M hydrochloric acid acid-water extracts of soil were analysed by an AAS method.

Determination of moisture content in the wood indicated that the poles were “constantly well over saturation point” at ground level, “wet” at 0.5 m below the ground, and above 20% moisture content above ground level. Substantial quantities of metallic elements were leached from the poles, comparison with laboratory leaching tests suggesting increased leaching due to acid rain.

Average total loss of copper, chromium and arsenic after 10 years compared to estimated initial retention of each element was respectively, 18.8, 2.7 and 25.5% at 0.5 m below ground, 21.8, 24.0 and 33.6% at ground level, 20.0, 12.0 and 25.8% at 1 m above ground, and 11.2, 18.8 and 21.6% at 1.5 m from the top of the pole. Thus leaching was greatest at ground level, but still significant above and below this level. Loss of copper and arsenic was approximately as expected from laboratory results, noting that loss of copper depends strongly on pH (increased leaching with increased acid). However, loss of chromium was unexpectedly high, particularly at ground level.

The average amount of arsenic in soil samples was 180 mg/dm^3 (120 mg/kg, assuming a soil bulk density of 1.5 g/cm^3), varying from 42 to 420 mg/dm^3 (28-280 mg/kg). These levels are considerably above background levels, normally ~1 to 5 mg/dm^3 (0.7-3.3 mg/kg). Copper and chromium were found at lower soil concentrations, 14 to 130 mg/dm^3 (9-87 mg/kg - average 79 mg/dm^3 for copper and 65 mg/dm^3 for chromium). The investigators concluded that this trial together with laboratory tests showed that the decision to move from higher arsenic content CCA-B formulations to CCA-C formulations in Finland was justified.

6.4.1.9. CCA depletion from treated poles in Canada and levels in soil water

CCA-C-treated red pine utility poles in service for 1-15 years and located at wet sites in Canada were identified and sampled by Cooper et al (2000c, 2001a), together with control poles of similar ages from nearby dry sites. Samples to a depth of 5 mm in the wood were taken 30 cm above and below the ground. Where possible at the wet sites, groundwater samples were obtained from immediately adjacent to the poles (copper, chromium and arsenic analysed by ICP, with detection limits of 0.01-0.02 ppm). The pH of soil samples ranged from 5.6-8.4, and the humic acid content from 0.4-104 µg/mL, much lower than in a corresponding laboratory test (Section 6.3.4.6, p 61).

Concentrations of copper, chromium and arsenic in water collected near 26 poles ranged from 40-970 µg/L for copper, 10-280 µg/L for chromium, and 20-1400 µg/L for arsenic. Concentrations of each element increased with increasing humic acid content and decreasing pH, but were not significantly affected by age of the pole. Evaluation of CCA component retentions and mass balances showed that copper and arsenic were leached significantly from the portions of the poles in contact with water in wet sites, whereas chromium leaching did not appear to be affected by location in the pole or by site. From the wood sample data, losses of arsenic appeared to increase with age of the pole compared to the other components. Statistical analyses showed that the concentrations of CCA components in water near poles in wet sites increased with higher natural humic acid concentrations and lower water pH, but interpretation of this together with results for the wood samples suggested that higher losses in samples of wood from below ground in wet locations were due more to constant exposure to water than to specific water characteristics at the sites.

6.4.1.10. Long term mobility of CCA from posts in Florida

Huffman and Morrell (2003) evaluated CCA retention in and soil levels around and below southern pine posts which had been treated to a retention of 8 or 12 kg/m^3 with a CCA-B type formulation in 1954 (8 posts at each rate). Prior to installation in the test site the posts were air seasoned for 90 days after treatment to a moisture content of 20% to ensure maximum fixation had occurred. Thus the posts had been in place for 47 years after application of a formulation leaching arsenic at a relatively high rate, except that in some cases the poles had been temporarily removed (stolen) and then replaced back where they had been, resulting in some soil disturbance and 7 months shorter exposure.

Soil around each post was sampled with a soil auger immediately adjacent to the wood and at 15 and 30 cm out from the post, to depth zones of 0-2.5, 15-17.5, 30-32.5 and 45-47.5 cm (three combined samples per post). On average the posts were ~90 cm apart in rows, but some were closer together. Two posts were carefully removed and samples taken from directly underneath the posts and 30 and 120 cm below where the bottom of the post had been. As well as the post sampling, leaching from four stakes (~5 X 10 X 45 cm) treated to 23-24 kg/m^3 (a very high rate for non-marine use) and installed in 1957 was evaluated by removing the stakes and collecting soil samples immediately below and at depths of 45, 90 and 135 cm below where the end of the stake had been. Soil samples were extracted in 0.025 M diethylenetriamine-pentaacetic acid (DTPA) for 2 hours on a mechanical shaker and analysed by ICP. Wood samples were analysed by ICP after digestion using a microwave/nitric acid-hydrogen peroxide procedure.

The soil A and E horizons (0-10 and 10-50 cm) were described as a very friable or loose, extremely acidic (surface pH 4.5), dark grey or grey sands. The Bh horizon (50-65 cm) was dark brown sand and was described as absorbing a significant amount of trace metals due to the colloidal iron and aluminium oxides present. The E1 horizon (65-150 cm) was described as having little iron retention capacity, but the Bt horizon (150-180 cm) was silt/clay that absorbs metals due to its high surface area. Copper levels were 0.40 ppm in the surface 2.5 cm and 0.10 ppm in deeper sampling depths (30-32.5 to 120-122.5 cm). Chromium levels in native soils were <0.02 ppm throughout the soil profile, except they were 0.04 ppm at 60-62.5 cm. Arsenic levels in native soils were 0.13, <0.05, 0.21, 0.38 and <0.05 ppm at 0-2.5, 30-32.5, 60-62.5, 90-92.5 and 120-122.5 cm, respectively.

Examination of the posts showed that they were still sound and serviceable, ie that adequate protection was still being provided by the CCA treatment. Preservative levels in the posts were higher in the outer 12 mm of the posts than in the next 37 mm, but none of the levels approached the original target retention (total CCA retentions 2.24-3.60 and 2.0-5.4 kg/m^3, 15 cm below ground and 30 cm above ground, respectively, and 3.34-9.43 and 4.30-11.09 kg/m^3 below and above ground at an original 12 kg/m^3 retention). The authors argued that the presence of elevated preservative levels on the surface suggested that extensive depletion of CCA components had not occurred, since depletion is most likely to occur nearer the wood surface, but that the differences between above and below ground exposure suggest that some depletion had occurred over the prolonged exposure period. Presumably data were not available to indicate what the initial retention levels had in fact been.

Results for soil sampling around the posts are summarised in Table 26. Copper levels were highest adjacent to the post and near the surface and declined rapidly with distance out from the post and between the surface and deeper layers adjacent to the post and 15 cm out. The authors suggested that the lack of a further decline with depth at 30 cm out from the posts may reflect the close proximity of the posts and that particularly as some posts were closer, it is possible that chemical migration from one post may have overlapped with that of an adjacent post. Chromium levels were generally low for all of the soil locations and decreased to background levels 15 and 30 cm out from the posts, but were little affected by depth at each distance. Arsenic levels were elevated adjacent to the posts and near the surface, and declined with distance out from the post and with depth in samples taken adjacent to the post.

Results for soil samples taken below the posts and stakes are summarised in Table 27. The results clearly indicate that while copper, chromium and arsenic levels were elevated immediately beneath posts and stakes, in both cases concentrations declined with depth, to background levels by the deepest sampling points. The authors concluded that, while some leaching below the poles and stakes had clearly occurred, all three component elements were unlikely to leach into groundwater.

Table 26. Copper, chromium and arsenic concentrations in soil around CCA-treated posts after prolonged exposure in Florida (Huffman and Morrell, 2003).

		Adjacent to post (0-2.5 cm)		15 cm away from post		30 cm away from post	
Retention	**Sampling depth (cm)**	**Original**	**Disturbed**	**Original**	**Disturbed**	**Original**	**Disturbed**
COPPER							
8 kg/m^3	**0-2.5**	254	144	17.9	7.8	1.5	1.6
	15-17.5	39.5	36.0	1.5	5.7	1.1	3.8
	30-32.5	31.0	30.0	1.0	2.4	2.8	5.6
	45-47.5	25.9	32.0	1.5	4.9	1.2	5.9
12 kg/m^3	**0-2.5**	301	201	3.2	19.5	2.2	1.0
	15-17.5	28.5	33.7	1.3	3.0	0.3	<0.1
	30-32.5	28.0	41.2	0.9	2.3	1.5	0.4
	45-47.5	15.8	24.6	2.0	5.8	0.9	1.4
CHROMIUM							
8 kg/m^3	**0-2.5**	0.47	0.54	0.09	0.09	0.03	0.06
	15-17.5	0.94	0.77	0.05	0.15	0.05	0.06
	30-32.5	0.76	0.70	0.07	0.05	0.05	0.04
	45-47.5	0.85	1.02	0.11	0.07	0.03	0.04
12 kg/m^3	**0-2.5**	0.50	0.46	0.04	0.08	0.04	0.03
	15-17.5	0.40	0.72	0.05	0.03	0.03	0.02
	30-32.5	0.36	0.62	0.07	0.03	0.03	0.02
	45-47.5	0.27	0.44	0.03	0.08	0.05	0.03
ARSENIC							
8 kg/m^3	**0-2.5**	8.19	1.41	0.50	0.31	0.21	0.20
	15-17.5	3.59	0.91	0.17	0.18	0.16	0.13
	30-32.5	2.06	0.94	0.20	0.11	0.24	0.34
	45-47.5	2.88	3.07	0.39	0.67	0.18	0.27
12 kg/m^3	**0-2.5**	7.16	2.18	0.45	0.77	0.35	0.15
	15-17.5	2.19	3.09	0.43	0.09	0.26	0.09
	30-32.5	1.74	2.19	0.68	0.15	0.80	0.06
	45-47.5	3.34	1.76	0.37	0.49	0.32	0.16

Table 27. Residual metal levels beneath southern pine posts (12 kg/m^3 of CCA) and southern pine sapwood stakes (23-24 kg/m^3 CCA) after prolonged (44-47 years) exposure.

Depth beneath post or stake (cm)	Residual metal level (ppm)		
	Copper	Chromium	Arsenic
Posts			
0	18.3	0.60	1.09
30	5.5	0.41	2.41
120	0.3	<0.02	<0.05
Stakes			
0	71.4	1.75	0.22
45	6.5	0.24	0.32
90	1.7	0.12	0.06
135	0.1	<0.02	<0.05

6.4.1.11. CCA-component levels in soils around poles in Florida

Chirenje et al (2003) reported investigations of CCA component levels in soil around CCA-treated utility poles in Gainesville, Florida (there were several obvious errors and omissions evident in this paper, some of which are sufficiently serious to call into question its reliability). The soil around each structure/pole was described as very sandy, typical of the area. Their texture is due to their formation from well-weathered sandy marine sediments and they have very low levels of organic matter and clay and a lack of fine particles in the topsoil particularly. Samples were digested using a nitric acid/microwave procedure and analysed for total copper, chromium and arsenic using AAS. The sampling procedures and results obtained are summarised below.

Utility poles varying in age by ~12 years were evaluated, with surface (0-5 cm) soil samples taken at distances of 30 cm, 60 cm and 1.5 m away from the pole, and soil profile samples collected next to the pole at depths of 0, 15, 30 and 60 cm, plus background samples at least 5 m away but in the vicinity of each pole; wood scraps were also collected from each pole to determine remaining CCA concentrations in the pole. Results are summarised in Table 28.

Soils around poles up to 5 years old showed the highest concentrations of copper, chromium and arsenic. A trend of declining concentrations with depth in younger soils was not as evident with the aged poles. The authors noted that the sandy soil had a very low capacity to retain added chemicals, and suggested that rather than concentrations increasing with time due to cumulative effects, concentrations surrounding older poles were lower due to lower leaching rates as the poles aged and loss of initial additions to the soil to greater depths in the soil. There was a general trend of declining concentrations of arsenic with distance out from the poles, with mean levels respectively ~22, 7, 3 and 1.5 mg/kg at 0, 30, 90 and 150 cm out from the poles.

Table 28. Changes in element concentrations with depth in sites adjacent to utility poles (Chirenje et al, 2003).

Age of pole (years)	Concentration in pole[1] (mg/kg)	Background soil concentration (mg/kg)	Mean concentration (mg/kg) in soil at sampling depth shown (range shown in parentheses)			
			0 cm	**15 cm**	**30 cm**	**60 cm**
Arsenic						
0-2 years (3 poles)	5860 (4880-6430)	4.75 (0.53-11.5)	17.0 (4.04-31.9)	10.6 (2.34-23.2)	4.54 (1.40-7.65)	3.70 (1.47-5.03)
2-5 years (2 poles)	6140 (6030-6250)	1.49 (1.20-1.78)	2.74 (1.47-4.01)	2.79 (0.91-4.66)	3.21 (1.17-5.25)	2.25 (1.30-3.74)
5-10 years (5 poles)	2890 (11-5000)	1.04 (0.77-1.73)	2.64 (0.95-4.60)	1.99 (0.90-3.38)	1.57 (0.89-2.51)	1.62 (0.48-3.79)
Overall mean	4430	2.20	6.97	4.43	2.78	2.42
Copper						
0-2 years (3 poles)	2.54 (2.03-2.95)	26.6 (1.50-74.6)	63.8 (19.6-124)	57.0 (11.9-128)	22.8 (4.53-58.0)	12.0 (4.20-24.0)
2-5 years (2 poles)	3.33 (3.25-3.40)	8.14 (5.28-11.0)	19.9 (16.0-23.8)	20.4 (19.8-20.9)	5.20 (4.27-6.13)	11.3 (7.56-15.0)
5-10 years (5 poles)	1.67 (0.02-3.48)	12.4 (1.29-28.1[2])	27.3 (3.95-92.0)	28.0 (3.84-83.7)	19.6 (4.68-48.8)	15.9 (2.26-47.8)
Overall mean	2.51	16.2	36.8	35.1	17.7	13.8
Chromium						
0-2 years (3 poles)	6.69 (5.55-8.33)	9.74 (3.42-15.5)	17.0 (5.23-23.1)	26.5 (11.9-53.0)	16.7 (5.81-28.8)	15.0 (5.72-30.8)
2-5 years (2 poles)	6.23 (5.65-6.90)	22.3 (11.4-33.2)	71.0 (6.03-136)	60.1 (4.34-116)	49.7 (4.60-94.8)	33.2 (5.25-61.1)
5-10 years (5 poles)	2.96 (0.04-5.40)	9.77 (2.71-22.4)	14.5 (6.94-31.5)	13.0 (5.00-37.5)	11.4 (4.16-35.0)	7.39 (0.04-21.1)
Overall mean	4.74	12.2	26.5	26.5	20.6	14.8

[1] The 1000 fold difference in concentration between arsenic and the other two elements in the poles is unexpected and is not consistent with the levels in soil – it appears that the results for copper and chromium residues in the poles are not in the same units; [2] there was also value of 261, determined to be an outlier and not included in the mean.

6.4.1.12. Summary and conclusions regarding studies of CCA-treated poles, posts and stakes

Several investigators overseas have evaluated CCA component concentrations in surface soil and different soil depths at points adjacent to and at various distances out from CCA treated stakes, posts or poles, and in two cases, in soil below treated items. In some cases, data available for retention of CCA in the wood was available to indicate the extent of loss from the wood. Some data were also obtained for concentrations in water running off poles and for concentrations in soil water. The results of these studies are summarised below. It should be noted that surface area effects mean that leaching is relatively high for stakes used for test purposes, and that in some environments acid rain may have exacerbated leaching.

Test stakes and posts:

- Leaching from CCA-B treated test stakes (18-28 kg/m^3) standing in soil at a wet site for 2-28 years led to losses of ~30-40% of initial retentions of arsenic and copper, with higher losses from the top and bottom ends of the stakes, but with little loss of chromium evident. Losses of arsenic and copper at a drier site were much less, ~10-30% for arsenic and 10-20% for copper. Differences in retention over time between the sites may also have been due to differences in soil characteristics. Leaching in stakes held horizontally above the ground for 7 years indicated very high loss of arsenic and copper (50% and 80%) from the end grains, and as might be expected, greater loss from the more exposed upper surface than the lower.

- Low loss of chromium from CCA (UK Type II, 6.25-12.5 kg/m^3) treated stakes was also found in another study standing in soil in the field. Soil concentrations of arsenic and copper declined sharply with distance from the stakes, from 132-184 ppm and 35-84 ppm, respectively, 0 cm from the stakes, to 17-42 ppm and 5-8 ppm at 100-200 mm. A high proportion of total arsenic in soil near the stakes was available, but only a small proportion was available at 100-2000 mm.
- One study investigated lateral and vertical distributions of CCA elements in soil beside and below stakes treated with CCA-A (10.6 kg/m^3) or CCA-B (8.8 kg/m^3), inserted 23 cm deep in the soil. Arsenic levels were much higher with the CCA-B formulation despite a slightly lower retention rate. With CCA-B, mean soil concentrations of arsenic with lateral sampling of the surface 15.2 cm declined from 183 ppm adjacent to the stake to 118 ppm at 7.6 cm, 7 ppm at 15.2 cm and 4.9 ppm at 22.3 cm. With sampling directly beneath the stake (ie from ~23 cm below the soil surface), mean concentrations of arsenic declined from 108 ppm in the first 15.2 cm below the tip of the stake, to 21.4 ppm at 15.2-30.5 cm and 1.1 ppm at 30.5-45.7 cm and deeper. Similar patterns occurred with CCA-A, but at lower concentrations (peak 73.2 ppm at the surface adjacent to the stake and 18.9 ppm immediately below the stake). Broadly similar trends also occurred with copper and chromium, except that their mean maximum concentrations were higher with CCA-A than CCA-B (48.3-56.6 ppm at the surface and 47.9-75.8 ppm immediately below the stakes for copper, 22.9-25.1 ppm and 24.2-45.9 ppm for chromium).
- Concentrations of arsenic and copper in soil adjacent to CCA-B treated posts (8-12 kg/m^3) in place in a test site for 47 years fell with increasing depth, but significant leaching downwards in the sandy soil was evident for all three elements. With posts in undisturbed situations, surface concentrations of arsenic, copper and chromium adjacent to the posts declined from 7.2-8.2 ppm, 254-301 ppm and ~0.5 ppm, respectively, compared to 2.9-3.3 ppm, 15.8-25.9 ppm and 0.3-0.9 ppm, respectively at 45-47.5 cm. Concentrations of all three elements fell rapidly with increasing lateral distance from the posts at all depths (0.2-0.8 ppm, 0.3-2.8 ppm and 0.03-0.05 ppm, respectively, over all sampling depths at 30 cm from the posts). Sampling of soil concentrations immediately below posts showed a decline from elevated levels immediately below the posts to background levels by 120 cm below them.

Posts and poles in actual service:

- Measurements of CCA retention in utility poles after removal from 1-50 years service indicated arsenic was leached more that the other components. There was some evidence for relatively greater leaching of copper from the below ground pole surface.
- One study investigated lateral and vertical distributions of CCA elements in soil in the vicinity of utility poles treated with CCA-C (7-33 kg/m^3, in service from 1-13 years). Soil concentrations fell rapidly with increasing distance from the poles, in most cases approaching background levels within 25 cm or even 10 cm from the pole. Maximum concentrations of arsenic, copper and chromium were respectively, 325 ppm, 995 ppm and 280 ppm. In this study, leaching of copper evidently occurred to the greatest extent relative to background levels, with concentrations often exceeding 100 or 150 ppm at ground level near the poles or occasionally at depth (0.5, 1 or 1.5 m) near or 25 cm away

from the pole. Arsenic concentrations occasionally exceeded 20 ppm at the ground surface near the poles and occasionally at depth. Contaminant levels increased with age in service and were generally highest in wet organic soils. Measurements of element concentrations in rainwater running down treated poles indicated concentrations of 0.9-7.7 ppm arsenic, 2-16 ppm copper and 0.7-2.5 ppm chromium. Concentrations in rainwater were not related to pole age, leading the authors to suggest that a steady state equilibrium is reached in leaching rate.

- Another study showed a clear decline in arsenic concentration with lateral distance from treated posts and poles, in surface soil at least. Leaching of arsenic from 17 years old CCA-B treated posts was high (soil arsenic concentrations at depths of ~15 and 30 cm at 0-5 cm from the posts = 303-307 ppm and 197-290 ppm, respectively, falling to 22.3-41.9 and 8.5-14.6 ppm at 10-15 cm from the posts). Soil concentrations were much lower in smaller, 17 years old CCA-A treated posts in the same soil (7.0-14.5 ppm), and in 32 year old CCA-A treated poles in a different area (surface concentrations 23.9-109 ppm at 0-5 cm from the poles, falling to 11.5-25.3 ppm 28-33 cm from the poles).
- A study of CCA-B treated utility poles after 2, 4 and 10 years service indicated average losses of arsenic, copper and chromium from various vertical portions of the poles were 22-34%, 11-22% and 3-24%, with greatest losses occurring at ground level. Soil concentrations ranged from ~28-280 ppm (average ~120 ppm) for arsenic (considerably above background levels of ~0.7-3.3 ppm), and ~9-87 ppm for copper and chromium (averages ~79 ppm and 65 ppm), showing high leaching of arsenic from the CCA-B formulation. Chromium leaching was greater than expected, which the author suggested was possibly due to acid rain effects.
- Evaluations of element retention in CCA-C-treated utility poles in service for 1-15 years in wet and dry sites showed that copper and arsenic were leached significantly from the portions of the poles in contact with water in wet sites, whereas chromium leaching did not appear to be affected by location in the pole or by site. Concentrations of arsenic, copper and chromium in soil water collected near 26 poles ranged from 20-1400 μg/L for arsenic, 40-970 μg/L for copper and 10-280 μg/L for chromium.
- In another study, surface soil concentrations in soil adjacent to CCA-treated utility poles averaged 17.0 ppm for arsenic, 63.8 ppm for copper and 71.0 ppm for chromium for poles in place 0-2 years, with a clear trend of declining concentration with depth. However, soil concentrations were quite different for poles in service for 2-5 or 5-10 years (2.7 and 2.6 ppm for arsenic, 19.9 and 27.3 ppm for copper and 14.5 and 71.0 ppm for chromium, respectively), with a less clear trend in concentration with depth. The authors related these differences to the very sandy soil at the site, with poor retention of added chemicals leading to loss of initially high leaching increments to lower depths in the soil.

Thus several studies available of soil metal concentrations in the vicinity of CCA-treated stakes, poles and posts show that arsenic, copper and chromium do leach from the treated wood, but that lateral movement is very limited in dry sites, and unless the water table is very shallow, leaching downwards in the soil is unlikely to carry these elements to groundwater. Data indicated maximum soil concentrations generally occurred at the surface adjacent to the post or pole, consistent with the prime source of soil contamination being leachate from rainfall running down the pole into the soil. Measured concentrations of arsenic, copper and chromium near posts and poles at this point ranged from ~7-325 ppm, ~9-995 ppm and ~0.5-280 ppm, respectively. The highest levels of arsenic were from CCA-B formulations, with the highest concentrations near CCA-A treated poles being 109 ppm. Measurements of CCA retention in wood confirm that over time, a proportion of the arsenic, copper and chromium in the wood is lost through leaching and that some redistribution of these elements may occur in the wood. Measurements of element concentrations in rainwater running down treated poles in one experiment indicated concentrations of 0.9-7.7 ppm arsenic, 2-16 ppm copper and 0.7-2.5 ppm chromium. Measurements of groundwater surrounding poles in wet sites indicated concentrations of 20-1400 µg/L for arsenic, 40-970 µg/L for copper and 10-280 µg/L for chromium. The results indicate a wide spread in peak soil concentration, which could have arisen through various factors associated with the timber (including formulation type, initial retention, age and dimensions) and site (soil characteristics affecting leaching from the wood and mobility in the soil, climate, and potentially acid rain).

6.4.2. Leaching from structures such as decks, fences, playground equipment and walkways

6.4.2.1. Leaching from simulated deck units in Queensland and interactions of leachate with soils

Kennedy and Collins (2001) treated radiata pine decking stock (90 X 22 X 450 mm, end-sealed) with CCA using conventional and modified Bethel schedules (600 L/m^3 and 250 L/m^3 wood respectively), with the concentrations of preservative adjusted to give Australian standard H3 (above ground) retention in both cases. The CCA used had a copper, chromium and arsenic content of 86 g/kg, 147.9 g/kg and 132.7 g/kg, respectively (ie meeting Australian Standard AS 1604 2000). This was followed by a one week fixation and 4-6 week air drying period, ensuring thorough fixation and drying. Sections were removed from the boards and cut into 19 mm cubes for accelerated laboratory leaching tests, which were extended from the standard 14 days to 50 days, as the leaching rate was still rising sharply at 14 days. Boards 300 mm long were then end-sealed, leaving a few ends unsealed so that an average 2.4 m deck length could be simulated when four short boards were placed side by side over a collection tray. Decks were exposed to the weather in Brisbane for ~300 days, during which cumulative rainfall reached ~600 mm. Run-off water was collected after each of 48 rain events for analysis, determination of volume, and collection of an aggregate sample for soil column leaching studies with three different soils (using the OECD Test Guideline, presumably No. 107).

Evaluation of the laboratory and deck leaching data suggested a possible effect of the treatment process on leaching, with the full Bethel process increasing the leaching of copper and decreasing that of chromium compared to the low uptake, modified Bethel process (Table 29). Increasing the duration of the laboratory leaching study increased the leaching of arsenic by 41-43% and of chromium by 16-20%, but only increased copper leaching by 2-9%. However, even just the 14 day laboratory test produced much more leaching from the 19 mm blocks than occurred with the decks over the full test period (Table 29).

Table 29. Comparison of relative leaching between laboratory and simulated deck tests (Kennedy and Collins, 2001).

Component leached	**% of component leached during exposure period**			**Time in lab test to reach deck leach %**
	300 days deck	**14 days lab**	**50 days lab**	
Full Bethel				
copper	1.2	4.9	5.0	<8 h
chromium	0.9	4.1	4.9	~10 h
arsenic	4.4	19.1	27.0	~18 h
Modified Bethel				
copper	1.3	6.5	7.1	~9 h
chromium	1.2	2.5	2.9	~24 h
arsenic	4.0	18.9	27.0	~32 h

The rate of loss of copper declined over time, from 1.54-1.88 mg/m^2/day over the first 21 days, to 0.51-0.64 mg/m^2/day over days 0-90, and 0.34-0.52 mg/m^2/day over days 0-300. The rate of chromium loss was relatively high initially (1.05-1.112 mg/m^2/day), but similar over 0-90 days and 0-300 days (0.41-0.58 mg/m^2/day). That for arsenic was similar for 0-21 days and 0-300 days (1.47-3.14 and 1.40-2.10 mg/m^2/day), and lower at 0-90 days (0.75-1.64 mg/m^2/day). Thus while % leaching of copper and chromium were similar, the higher content of chromium in the formulation led to greater leaching in absolute terms.

Plotting the deck data for each element against cumulative rainfall produced a smoother trendline than plotting simply against time, but it was evident that different rainfall events behaved differently. For example, short heavy showers did not produce as much leaching as the equivalent mm of steady rain, presumably due to a longer wetting period and deeper water penetration with the latter (Choi et al, 2001 also noted that when there was light rain, the water was absorbed by the CCA treated timber rather than running off, which they suggested allowed the CCA components to move around the wood rather than leaching out; Lebow, Brooks and Simonsen, 2002 also noted that in a study comparing rainfall rates of 2.5, 8.3 and 25.4 mm per hour for an equivalent total amount, leaching was greatest at the slowest rainfall rate). Leaching models fitted to the data relating loss of each component per unit area of deck to mm of rain are shown in Table 30.

Table 30. Leaching models for CCA component loss from pine decking (Kennedy and Collins, 2001).

Component[1]	**Bethel process**		**Modified Bethel process**	
Copper	$y = 3.265x^{0.5540}$	$r^2 = 0.98$	$y = 2.152x^{0.6873}$	$r^2 = 0.99$
Chromium	$y = 0.771x^{0.8316}$	$r^2 = 0.98$	$y = 0.5486x^{0.8955}$	$r^2 = 0.99$
Arsenic	$y = 1.529x^{0.9467}$	$r^2 = 0.99$	$y = 0.326x^{1.1180}$	$r^2 = 0.99$

y = mg of component lost per m^2 of deck; x = cumulative mm of rainfall since first exposed.

[1] The author has confirmed that the equations were misidentified in the published paper: those shown are correct.

Composite leachate samples used for the column leaching studies contained 0.39-0.43 mg/L copper, 0.27-0.32 mg/L chromium, and 0.54-1.20 mg/L arsenic, comparable to the results in a deck leachate collection study (Section 6.4.2.5) and study with water repellent and CCA treatments (Section 6.3.5.3). After conduct of the column leaching test, chemical evaluation of soil layers in the columns and column effluent fractions did not detect any increases relative to the amounts already present in the respective soils. The authors concluded that the deck leachates contained insufficient of all components to make a measurable difference to concentrations in soil.

Using the above models, predicted cumulative copper, chromium and arsenic losses per square metre of deck over 600 mm of rainfall (ie the test duration) are respectively, 113 mg/m^2, 158 mg/m^2, and 652 mg/m^2. Extrapolating to 7300 mm of rainfall (ie ~10 years at similar rates to the study period), cumulative losses would be respectively, 451 mg/m^2, 1258 mg/m^2, and 6947 mg/m^2. These levels are not insubstantial, even if it is assumed that the water from a square metre of deck is distributed across a similar area of soil rather than concentrated near run-off points. If a soil bulk density of 1.4 g/cm^3 and mixing depth of 15 cm are assumed, leaching from the initial 600 mm (10 months) would give estimated soil concentrations due to the leaching of 0.54 ppm (mg/kg) copper, 0.75 ppm chromium and 3.1 ppm arsenic. If extrapolation to 7300 mm (~10 years in Brisbane) were correct, estimated cumulative soil concentrations due to the leaching would be 2.15 ppm (mg/kg) copper, 5.99 ppm chromium and 33.1 ppm arsenic. Clearly, a longer period of measurement would be necessary to extend these models to longer time scales, eg the author expects that the rate of arsenic leaching would eventually start to curve over, as was already evident in the data for copper, somewhat reducing the cumulative loss of arsenic on a ten year timescale (pers comm. Michael Kennedy, 23 October 2003).

6.4.2.2. CCA-component levels in soils below decks in Connecticut

Stilwell and Gorny (1997 –cited by Townsend et al, 2001a,b - original not seen) reported elevated levels of metals in soil in the vicinity of treated wood decks in Connecticut, as summarised in Table 31.

Table 31. Results of soil sampling for CCA residues below decks in Connecticut (Stilwell and Gorny, 1997 – cited by Townsend et al, 2001a,b).

Element	Level below treated decks	Background level
Copper	Average 75 mg/kg	Average 17 mg/kg
Chromium	Average 43 mg/kg	Average 20 mg/kg
Arsenic	Average 76 mg/kg (range 3-350 mg/kg)	Average 3.7 mg/kg (range 1.3-8.3 mg/kg)

6.4.2.3. CCA-component levels in soils below structures in Florida – initial study

Townsend et al (2001) commented that of the estimated 15.3 million m^3 (540 million cubic feet) of CCA-treated wood in use in Florida in 2001, ~36% is associated with outdoor decks (the authors used this term to embrace decks in structures such as footbridges and playground equipment). They estimate that this translates to an area of soil in Florida covered by decks of ~10,120 ha (25,000 acres). The authors estimated that if contamination extended to a depth of 20.3 cm (8 inches), this implied that approximately 60 million tons (54.4 million tonnes) of Florida soil would be impacted, but this was based on a very high soil bulk density figure of 2.65 g/cm^3: 33 million tonnes would seem a more reasonable estimate (bulk density ~1.65 g/cm^3). Hence they were interested to determine the impacts of CCA treated decks on the surrounding environment. This first short term study was to evaluate whether or not enough metals leach from CCA-treated decks to increase the concentrations in soil above background levels.

Soils below nine decks in public structures throughout Florida (three each in Gainesville, Miami and Tallahassee – see Table 32) were sampled. In each case, surface samples (within the top 2.5 cm of soil) were taken in a grid pattern (8-9 points per site), plus a soil core sample (~18 cm long, though data were then presented to a depth of ~30 cm) and control samples (upstream of the sample grid by 15-30 m). Soil samples were digested using a standard US EPA method with nitric acid and hydrogen peroxide, and analysed for copper, chromium and arsenic concentrations by AAS. These were then compared to background concentrations for the site and to Florida regulatory guidelines, with an emphasis on arsenic. Testing of the deck timber with a stain test confirmed that eight of the decks had been treated with CCA and that one had not (construction plans indicated the support columns may have been pressure treated).

Table 32. Summary of decks sampled for the initial Florida CCA soil residues study (Townsend et al, 2001a,b).

City	Site code	Description	Age of deck at sampling (years)	Results from stain tests for CCA	CCA Retention level (kg/m^3)
Gainesville	BP	Walkway	14	Positive	7.6
	BR	Footbridge	5	Positive	12.1
	PP	Deck	~15	Positive	3.3
Miami	AD	Playground	9	Positive	4.2
	TP	Lifeguard station	6	Positive	3.3
	OP	Deck	14	Positive	0.1-8.7
Tallahassee	TB	Footbridge	2	Positive	4.0
	MG	Deck	4	Positive	6.6
	LT	Footbridge	19	Negative	0.1

Surface soil analysis data are summarised in Table 33. Arsenic was detected in all surface soils sampled below decks, though its concentration was occasionally below the detection limit (0.25 mg/kg) in control samples. Copper and chromium concentrations were occasionally below the detection limits (0.5 and 0.25 mg/kg, respectively) in some sample points below decks as well as some in control samples. In all cases, the mean data in Table 33 are for values above the detection limit only (ie a slight overestimate). The results are consistent with leaching from treated decks being the source of elevated copper, chromium and arsenic levels in the soil beneath those decks. No leaching was evident beneath deck T/LT, where CCA treatment had not occurred or was very limited. Statistical testing confirmed that arsenic levels were significantly higher (95% confidence level) than control levels for all 8 treated decks, and for 6 decks in the case of copper and chromium. The authors noted that within a site characterised by elevated chromium concentrations in the deck soils, the deck soil concentrations were generally correlated with arsenic concentrations, generally in correspondence with the stoichiometric ratio of CCA-C. In contrast, while copper concentrations also appeared correlated with arsenic concentrations within a particular site, the correlation did not appear to be related to the stoichiometric ratio of copper and arsenic. They concluded that either copper is preferentially leached from CCA-treated decks, or that copper was less mobile in the soil whereas some arsenic had leached to a greater depth in the soil.

Table 33. Surface soil arsenic, copper and chromium concentrations below decks in Florida, compared to corresponding control values (Townsend et al, 2001a,b).

City/site code	Arsenic concentration (mg/kg)		Copper concentration (mg/kg)		Chromium concentration (mg/kg)	
	Mean (range) in soil below decks	Mean for controls	Mean (range) in soil below decks	Mean for controls	Mean (range) in soil below decks	Mean for controls
Sites where CCA use in timber was confirmed						
G/BP	41.6 (15.6-87.9)	2.61	106.3 (53.0-155.5)	9.46	59.7 (30.8-113.5)	3.53
G/BR	10.7 (4.05-33.2)	0.46	20.1 (7.50-37.0)	8.58	23.4 (10.6-48.6)	10.1
G/PP	9.56 (3.54-18.1)	1.03	15.2 (9.0-26.0)	4.60	15.3 (7.80-28.6)	19.2
M/AD	33.9 (15.5-81.2)	1.98	44.5 (16.5-128.5)	7.92	39.5 (13.8-113.6)	12.7
M/TP	4.30 (1.18-7.47)	1.13	9.75 (8.50-11.0)	8.38	6.19 (5.35-6.85)	9.01
M/OP	79.1 (31.7-217)[1]	0.66	68.1 (18.5-216.0)[1]	4.63	71.1 (32.0-198.5)[1]	4.82
T/TB	17.2 (8.59-31.0)	2.31	18.9 (10.0-34.0)	7.30	16.4 (6.90-32.4)	8.80
T/MG	34.0 (5.09-48.8)	1.42	21.8 (12.0-36.0)	3.95	22.9 (14.3-44.3)	7.95
Average	28.5 (1.18-217)	1.53	40.0 (7.50-216.0)	6.66	34.0 (5.35-198.5)	9.82
Sites where CCA use in timber was NOT confirmed						
LT	0.48 (0.25-0.62)	0.47	<0.50	3.31	<0.25	4.58

1 High levels at two points in the grid for this site accounted for the relatively large range – these points appeared to be related to a particular drip point from the intersection of two joists in the deck.

Soil core data indicated that leaching from CCA-treated decks impacted down to the upper 7.6 cm (3 inches) of soil for copper and chromium, and to as deep as 20.1 cm for arsenic. Maximum concentrations of arsenic occurred in the top 5.1 cm of all cores (range 4.97-67.6 mg/kg for the different sites), and in almost all cases minimum concentrations of arsenic occurred below 12.7 cm (range 0.25-3.64 mg/kg). For chromium, maximum values ranged from 16.9-65.1 mg/kg and minimum values from 0.56-8.35 mg/kg. The maximum values for chromium occurred at 0.6 or 1.9 cm in cores below 6 of the CCA-treated decks, but in two cases chromium concentrations were at a maximum deeper in the profile (32.1 mg/kg at 29.2 cm below the G/BR deck, 47.0 mg/kg at 16.5 cm below the T/MG deck, evidently with lower concentrations above these depths in both cases – no explanation was offered for these patterns). For copper, maximum values ranged from 4.71-108 mg/kg and minimum values from 0.10-2.39 mg/kg. The maximum values for copper occurred at 0.6 or 3.2 cm in cores below 7 of the CCA-treated decks, but at 24.1 cm in the T/MG deck.

The authors noted that on average, leaching from CCA-treated wood increased soil concentrations by ~2000% for arsenic, 6 fold for copper, and 3-3.5 fold for chromium. They noted that in addition to contaminating soil below the decks, there was potential for contaminated run-off to be discharged to nearby surface water bodies. Their greater concern was the large quantity of treated wood which would ultimately need to be disposed of.

The arsenic concentration in all of the 65 surface soil samples collected below CCA-treated decks exceeded the Soil Cleanup Target Level (SCTL) for residential direct exposure to arsenic in Florida, ie 0.8 mg/kg. Indeed, many of the control soils naturally exceeded this level. 62 of the 65 soil samples also exceeded the Florida industrial SCTL of 3.7 mg/kg. A total of 24 soil samples also exceeded the SCTL for leaching to groundwater, of 29 mg/kg. However, these SCTL are very low relative to typical background concentrations in Australia (Section 8.1.2), evidently because many soils in Florida are very sandy and may not retain arsenic well in surface layers subject to leaching (see below), and because Florida's population relies heavily on groundwater for drinking water, hence protection of groundwater to drinking water standards is a very important issue (Townsend et al, 2001).

6.4.2.4. CCA-component levels in soils below decks and fences in Florida

Chirenje et al (2003) reported investigations of CCA component levels in soil below CCA-treated residential timber decks and fences in Gainesville, Florida. The same paper reported results for utility poles (see Section 6.4.1.11, p 79 for more details). The sampling procedures and results obtained are summarised below.

6.4.2.4.1. Fences

Eleven fences ranging in age from new to 20 years were evaluated, with composite soil samples from a soil depth of 0-5 cm taken from underneath the fence and 30 cm from the fence, and from at least 5 m away in the vicinity of the fence for background samples. Concentrations of copper, chromium and arsenic under CCA-treated fences were highly variable (ranges for copper, chromium and arsenic respectively, ~3-37, ~4-28 and ~2-36 mg/kg), but were all significantly higher than background soils (levels not stated), and generally higher than corresponding samples collected at 30 cm (~2-21, ~1-18 and ~1-20 mg/kg – not significantly higher than background levels).

The authors stated that the residential and commercial Soil Clean-up Target Levels (SCTLs) in Florida were 0.8 and 3.7, respectively, for arsenic, while the SCTL for arsenic in Connecticut was 10 mg/kg, the differences being a function of different soil types and regulatory criteria. They noted that even the background concentrations of arsenic in the fence areas were higher than both the Florida SCTLs (see pp 85-88). However, mean copper and chromium concentrations even under the fences were below the Florida SCTL for these elements.

6.4.2.4.2. Decks

Seven decks ranging in age from ~1-12 years were evaluated, with composite soil samples from a soil depth of 0-5 cm taken from all exposed sides (3 sides in most cases) within 15 cm of the extent of the deck (25 samples), from under the deck (often very low to the ground, hence sampling was limited by access difficulties – 8 samples only), and from in the vicinity but at least 5 m away for background samples. Mean background concentrations of copper, chromium and arsenic were 13, 15 and 1.9 mg/kg, respectively. Results are summarised in Table 34. Mean arsenic concentrations near and under decks were significantly higher than mean background concentrations, whereas mean copper and chromium concentrations were slightly lower than mean background concentrations.

Table 34. Element concentrations underneath and 15 cm from decks in residential areas (Chirenje et al, 2003).

	Arsenic (mg/kg)		Copper (mg/kg)		Chromium (mg/kg)	
	Below deck	**15 cm from deck**	**Below deck**	**15 cm from deck**	**Below deck**	**15 cm from deck**
Mean	14.1	11.5	6.21	12.4	8.17	9.21
Standard deviation	7.17	8.80	3.29	22.2	5.05	4.93
Range	2.52-23.4	1.56-38.4	2.04-10.8	1.74-119	2.77-16.4	2.77-23.4
Background	1.9		13		15	

6.4.2.5. Decks constructed over a leachate collection system in Florida

Solo-Gabriele et al (2003) provided a summary of progress with a comparison between two decks, each constructed over a separate leachate collection system. One of the decks was made of

CCA-treated wood (presumably CCA-C) and the other of untreated wood. Each was 2 m by 2 m in surface area and was housed inside a 2.4 m X 2.4 m untreated wooden enclosure containing ~0.5 m depth of sand. Part of the leachate collection system enabled collection of direct run-off from the decks, and another part of the system collected leachate from below the 0.5 m of sand. Samples have been collected from these systems since September 2002, ie ~7-8 months, evidently under the weather conditions prevailing at the time in Florida.

The author stated that results to the date of writing (mid May 2003) indicate that the mean concentration of arsenic in direct run-off from the CCA-treated deck was 1.4 mg/L (range 0.8-1.8 mg/L), whereas for the untreated deck concentrations were below the limit of detection of 0.001 mg/L. The primary arsenic species detected in the direct run-off was As^{V}, although low levels of As^{III} were also detected. Forty three samples had been analysed of water which had infiltrated below the sand. Of these, 39 were at or above the detection limit. For the treated deck the average concentration for those samples above the detection limit = 0.003 mg/L. For the untreated deck all infiltrated water was below the detection limit, except for 6 samples at the 0.001 mg/L detection limit. The author indicated that concentrations in the infiltrated water were too low for speciation analysis. Thus results at the time had indicated that measurable concentrations of arsenic were found in run-off from the CCA-treated deck and in water infiltrating through 0.5 m of sand.

6.4.2.6. CCA-treated playground equipment in Virginia and California

Pirnie (2002) sampled base material (soil or wood chips) beneath two sets of CCA-treated playground equipment (presumably CCA-C) in Virginia and two in California using a grid pattern to assess site-wide concentrations of CCA constituents (16 samples over the entire playground for each site). Samples were also taken in a linear pattern in the general direction of water run-off from the structures (total of 12 samples per site, 6 at each of two poles, with two sets of 3 samples at 15.2, 30.5 and 91.5 cm out from the pole, running in a down gradient). Control samples (4 per site) were taken at areas outside the areas considered subject to impact from treated wood structures, ensuring that similar soil to that in the main playground area was sampled. In each case, samples were taken from 0-5.1 cm deep. All the samples were analysed for total copper, chromium and arsenic and for Cr^{VI}, using ICP following extraction in nitric acid/hydrogen peroxide. Some samples were also analysed for water soluble arsenic, subjecting the sample to the Synthetic Precipitation Leaching Procedure (SPLP) extraction method (extracted in pH 5 water) and analysing for arsenic concentration in the leachate by ICP. The author does not state how it was determined that wood in playground equipment had in fact been treated with CCA.

Site 1 was Fort Fun Park in Newport News, Virginia, a large area of wooden equipment constructed in 1992 (~9 years old). The ground surface was a combination of cobble/gravel, sand and wood chips (sand and wood chips sampled for analysis). Results are summarised in Table 35. Mean site wide arsenic and copper (but not chromium) levels were greater than background levels, and arsenic, copper and chromium levels in the leachate drainage area also appeared somewhat elevated, particularly near the monitored poles. Water soluble arsenic was not detectable (<5.0 μg/L) in background samples and ranged between 6-46 μg/L (3.3-28.5% of the total arsenic content) in the other samples tested.

Table 35. Surface soil total arsenic, copper and chromium and Cr^{VI} concentrations in Fort Fun Park, Virginia (Pirnie, 2002).

	Mean concentration and range (mg/kg)			
Sampling location	**Arsenic**	**Copper**	**Chromium**	**Chromium VI**
Background	nd (<4.3-<17.6)	3.4 (1.3-4.9)	8.6 (<1.7-23.3)	nd (<2.2-<5.1)
Site wide	6.4 (<3.5–16.5)	10.3 (1.4-22.4)	9.5 (<2.6-25.2)	nd (<2.1-<5.6)
15.2 cm from support pole	17.8 (<3.6–32.1)	36.2 (16.2-62.1)	34 (15.1-60.6)	nd (<2.2-<6.1)
30.5 cm from support pole	17.5 (5.2-30.7)	18.1 (10.4-27.6)	27.4 (11.2-60.2)	nd (<2.3-<6.3)
91.5 cm from support pole	10.9 (<3.2–21.8)	30.4 (21.8-36.1)	23.8 (9.9-32.4)	nd (<2.3-<6.5)

nd: analyte not detected above the detection limit given in parentheses – note that the detection limits varied widely between samples.

Site 2 was Cedar-Rose Park in Berkeley, California, consisting of open space with one set of wooden playground equipment and one of plastic and metal construction. The CCA-treated wood equipment was constructed in 1978 (~23 years old) and was described as weathered and spalling. The ground surface was sand. Results are summarised in Table 36. Mean site wide arsenic, copper and chromium levels were similar to background levels, possibly because many of the sampling points were not in the vicinity of treated wood. However, maximum values in the site appear slightly greater than background levels, and these higher values occurred near the wooden equipment. Similarly, arsenic, copper and chromium levels in the leachate drainage area also appeared slightly elevated, particularly near the monitored poles. Water soluble arsenic was not detectable (<10 μg/L) in background samples and ranged between not detected (<10 μg/L) and 18-38 μg/L (30-100% of the total arsenic content) in the other samples tested.

Table 36. Surface soil total arsenic, copper and chromium and Cr^{VI} concentrations in Cedar-Rose Park, California (Pirnie, 2002).

	Mean concentration and range (mg/kg)			
Sampling location	**Arsenic**	**Copper**	**Chromium**	**Chromium VI**
Background	nd (<0.91-<0.93)	2.2 (<1.8-2.2)	1.7 (1.2-2.2)	nd (<1.9-<1.7)
Site wide	0.7 (<0.90–1.6)	1.5 (<1.9-2.8)	1.5 (<1.9-2.8)	nd (<1.7-<2.2)
15.2 cm from support pole	3.3 (1.9-6.7)	4.8 (2.6-8.1)	4.8 (2.6-8.1)	nd (<1.8-<1.9)
30.5 cm from support pole	1.3 (<0.93-2.5)	2.2 (0.9-4.8)	2.2 (0.9-4.8)	nd (<1.7-<1.9)
91.5 cm from support pole	1.2 (<0.94–3.0)	3.2 (1.0-4.3)	3.2 (1.0-4.3)	nd (<1.7-<1.9)

nd: analyte not detected above the detection limit given in parentheses – note that the detection limits varied between samples.

Site 3 was Lakeside Park in Oakland, California. This playground was erected in 1996 (~5 years old) and consisted of CCA-treated wood supports with plastic attachments. The base material was sand. Results are summarised in Table 37. Mean site wide arsenic, copper and chromium levels were similar to background levels, as were levels in the leachate drainage areas from the monitored poles. Water soluble arsenic was not detectable (<10 μg/L) in background samples and all other samples tested.

Table 37. Surface soil total arsenic, copper and chromium and Cr^{VI} concentrations in Lakeside Park, California (Pirnie, 2002).

	Mean concentration and range (mg/kg)			
Sampling location	**Arsenic**	**Copper**	**Chromium**	**Chromium VI**
Background	0.9 (<0.91-1.3)	0.9 (<1.8-1.8)	5.5 (3.1-9.1)	nd (<1.9-<2.0)
Site wide	1.1 (<0.85–2.3)	1.2 (<1.8-2.1)	5.7 (3.1-10)	nd (<2.0-<2.1)
15.2 cm from support pole	0.89 (<0.91-1.5)	nd (<1.8-<2.0)	3.4 (2.4-4.3)	nd (<1.9-<2.0)
30.5 cm from support pole	1.1 (<1.0-1.8)	nd (<1.8-<2.0)	3.4 (2.5-4.3)	nd (<1.9-<2.0)
91.5 cm from support pole	0.92 (<0.93-1.6)	nd (<1.8-<2.0)	5.4 (2.4-7.7)	nd ((<1.8-<2.0)

nd: analyte not detected above the detection limit given in parentheses – note that the detection limits varied between samples.

Site 4 was Kids Cove in Virginia Beach, Virginia. This playground was erected in 1992 (~9 years old). The ground surface was partially asphalt and the remainder covered with wood chips, which was the material sampled. Sieving of the chips through 2.36 mm and 0.25 mm sieves indicated that an average of 22.3% (range 3.5-43.8%) of the material was <2.36 mm in size and the proportion of dust was 0-1.4%. Analyses were conducted on both material prior to sieving, and the material passing through the 2.36 mm sieve. Results for material which passed through the sieve are summarised in Table 38. These were on average 25% greater than those for unsieved wood chips. Mean site wide arsenic, copper and chromium levels appeared higher than background levels. Metal levels in the leachate drainage areas from the monitored poles also appeared slightly elevated. Water soluble arsenic was not detectable (<10 µg/L) in background samples and ranged between not detected (<10 µg/L)and 19-22 µg/L (8.6-19% of the total arsenic content) in the other samples tested.

Table 38. Surface soil total arsenic, copper and chromium and Cr^{VI} concentrations in material passing through a 2.36 mm sieve at Kids Cove, Virginia (Pirnie, 2002).

	Mean concentration and range (mg/kg)			
Sampling location	**Arsenic**	**Copper**	**Chromium**	**Chromium VI[1]**
Background	2.1 (1.0-3.8)	3.7 (2.4-5.4)	2.8 (<1.0-9.1)	0.7 (0.68-0.82)
Site wide	11.7 (<0.91–66.0)	6.1 (<1.8-18)	6.3 (<0.91-41.0)	nd (<0.39-<0.40)
15.2 cm from support pole	5.4 (2.2-21.0)	3.4 (1.8-5.8)	3.4 (<0.91-20.0)	0.5 (<0.39-1.8)
30.5 cm from support pole	3.4 (2.2-6.4)	3.6 (2.5-6.6)	2.1 (<0.91-6.3)	0.4 (<0.39-<0.87)
91.5 cm from support pole	4.1 (2.2-7.8)	4.9 (2.6-8.3)	3.3 (<0.91-8.8)	0.4 (<0.40-1.1)

nd: analyte not detected above the detection limit given in parentheses – note that the detection limits varied between samples. [1] The results for Cr^{VI} were affected by poor spike recoveries, presumably due to reduction of chromium in the wood chip material.

Thus elevated CCA metal levels were present in three of the four playground sites tested. Mean site levels were elevated in those three playgrounds due to individual sampling points with elevated levels, rather than a more general increase. Higher concentrations than background levels were also evident in sampling points downstream from treated poles. While water soluble arsenic was never detected in background samples, it was found at several of the points where elevated total arsenic concentrations had been found. CCA metals were comparable to background levels in a fourth playground, where wood was used for the support posts only. Thus the limited amount of treated wood has not significantly affected soil arsenic, copper or chromium concentrations, if indeed the wood had been treated with CCA (no confirmation was given that this was the case).

The authors related the data to background element concentrations on a regional basis for California and Virginia (copper, chromium and arsenic 9.1-96.4, 23-1579 and 0.6-11.0, respectively, in California, and 5.0-100, 7.0-300 and 0.7-18.4 in Virginia). Thus, while surface medium concentrations associated with CCA-treated playgrounds showed localised contamination relative to the background levels in the same area, they were nonetheless generally within regional background levels.

6.4.2.7. Soil levels below CCA-treated playground equipment in Sweden

Lahiry (1997) summarised data from a paper by Henningsson and Carlsson (1984) (original not seen) for a study of sand near/in playground equipment (sand boxes and playground supports) near Uppsala, Sweden. The wood was treated with CCA-B. The data presented by Lahiry (1997) are reproduced below (Table 39). Lebow (1996) states that Henningsson and Carlsson (1984) noted that the proportion of arsenic in the treated wood was 20-25% less than it should have been if the wood was treated according to Swedish standards. This implies 25% loss, but the initial retention was not known to confirm the extent of loss. Arsenic levels in sand adjacent to the timbers was more than five times that found 0.5 m from the timbers, although copper and chromium levels in the sand were not significantly elevated. Nonetheless, compared to natural arsenic levels recorded in this type of sand and that in various soils (i.e. 1–40 mg/kg), the results for arsenic in the contaminated sand were still within the range considered normal (internet document http://europa.eu.int/comm/enterprise/chemicals/legislation/markrestr/arsenic/ind/wptf2.pdf).

Table 39. Summary of published data (Henningsson and Carlsson, 1984 – cited by Lahiry, 1997) on the CCA component content of soil near treated wood in a playground situation in Sweden.

Source material	**Description of exposure conditions**	**Soil concentration (ppm)**		
		Cu	**Cr**	**As**
Sand boxes 2-4 years in service	Fine sand, at surface near wood	1-13	5-7	1-9
	Fine sand, 0.2 m down near wood	8-12	3-9	1-13
	Fine sand, at surface 0.5 m from wood	9-11	3-6	0.1-2
	Fine sand, 0.2 m down 0.5 m from wood	1-11	4-7	0.3-0.9
Playground supports, 2-4 years	Coarse sand, at surface near wood	7-18	4-9	1-10
	Coarse sand, 0.2 m down near wood	7-13	4-12	0.5-8
	Fine sand, at surface 0.5 m from wood	6-10	4-6	0.4-0.8
	Fine sand, 0.2 m down 0.5 m from wood	5-12	3-6	0.2-0.6

6.4.2.8. Levels of CCA components in the basement sump of a treated structure

Arsenault (1975) reported analysis results for copper, chromium and arsenic of water in the basement sump (which is discharged to the sewer) of a CCA-treated wood foundation office building in Georgia. Copper, chromium and arsenic concentrations in groundwater at the time of building construction in May 1974 were respectively, 0.13 mg/L, <0.01 mg/L and <0.01 mg/L. In June 1974, September 1974 and January 1975, copper and chromium levels were in each case <0.01 mg/L, while arsenic concentrations were respectively, 0.11, 0.08 and 0.02 mg/L. The data are very limited in extent and duration and it is not clear to what extent leach water from the treated timber may enter the sump or what the pattern of rainfall was. However, the data suggest some initial leaching of arsenic occurred from the foundation timbers, which may then have slowed. The author used the data to indicate that initial leaching was insignificant and quickly stopped.

6.4.2.9. Tasmanian walkway study

Comfort (1993) reported studies conducted to determine the safety of using CCA-treated wood for the construction of raised walkways ("duckboards" with boards running transversely across the walkway, or "boardwalks" where the boards are parallel) in Tasmanian wilderness areas. Soils in this area have a high organic matter content and are usually acidic. Ten study sites were chosen for leaching studies to cover a range of plant communities, soils, altitudes, track ages and construction techniques. Moorland and alpine sites received the greatest attention. Six sample points were located at each site, three immediately adjacent to the track ("trackside", within a 10 length and within 150 mm of a section of track where the structure was in contact with the ground), and three acting as controls positioned at least 2 m from the track. The structures ranged in age from 1 to 14 years. Annual precipitation in the area is high (it can exceed 2700 mm) and many tracks are constructed through waterlogged and acidic bogs and moorlands, though it seems that none of the sampled sites was waterlogged. Soil was extracted by boiling with concentrated hydrochloric acid for one hour, and analysed by AAS. The amount of sampling and analysis was limited by the funds available.

Mean concentrations of copper, chromium and arsenic in trackside samples were 9.6 µg/g (maximum 49 µg/g), 3.0 µg/g (maximum 87.5 µg/g), and 1.25 µg/g (maximum 9.1 µg/g) in the surface 10 cm, and 2.8, 8.7 and 1.0 µg/g, respectively, at a deeper sampling depth (still within the A horizon). Mean concentrations of copper, chromium and arsenic in control samples were 1.2 µg/g, 8.8 µg/g, and 0.13 µg/g in the surface 10 cm, and 1.5, 6.9 and 1.1 µg/g, respectively, with deeper sampling. Statistically, there were significant effects of location, depth and location X depth interaction for copper concentration, and significant effects of location for chromium. Arsenic concentrations did not differ significantly with either location or depth. A transact study at one point with chromium showed that chromium concentration fell rapidly with distance from the track, from 4.1 and 75.5 µg/g at 0-50 mm distance from the track, to 4.5 and 0.1 µg/g at 55-105 mm and 1.0 and ≤0.05 µg/g at 156 mm. Thus no leaching of arsenic, but some leaching of copper and chromium was detected. Very limited sampling suggested there was little downward movement of copper or chromium, and little lateral movement of chromium. The apparent absence of significant arsenic leaching when both copper and chromium have evidently leached is puzzling. Possible explanations are that the extraction procedure was not adequate (boiling hydrochloric acid, in contrast to sulphuric acid/hydrogen peroxide, or *aqua regia*, or nitric acid digestion procedures in most other studies, though 2 M hydrochloric acid at 100°C for 2 h was used in some studies – eg pp 37-40), or that arsenic may have moved in a fashion that was not detected by the limited sampling procedure.

6.4.2.10. Summary and conclusions regarding levels of CCA components in the vicinity of structures such as decks, fences, playground equipment and walkways

Several investigators overseas have evaluated CCA component concentrations in surface soil directly under, adjacent to or in the vicinity of various types of structures. All these studies dealt with relatively recent structures that appear to have been treated with formulations similar to the CCA-C type. Background levels were generally assessed from samples obtained a few metres away from areas influenced by treated wood. Mean surface levels of arsenic, copper and chromium in the most exposed areas (directly under or adjacent to CCA-treated surfaces) in investigations of structures such as fences and public decks, walkways and footbridges in various US states were 11.5-79.1 ppm (range 1.6-350 ppm), 6.2-43 ppm (range 1.7-216 ppm) and 8.2-71.1 ppm (range 2.8-199 ppm), respectively. Background levels were <1-3.7 ppm for arsenic, <1-17 ppm for copper and <1-20 ppm for chromium. In two studies, mean arsenic concentrations in exposed areas were ~20 fold higher than mean background levels, while mean copper concentrations were ~4.4-6 fold higher and mean chromium concentrations ~2.2-3.5 fold higher. Mean arsenic concentrations were ~7 fold higher than mean background levels in a third study, where mean copper and chromium concentrations were generally similar to or slightly lower than mean background levels.

Limited data in one study indicated similar to slightly higher arsenic levels below decks compared to 15 cm from the edge of the decks. In the one study examining CCA-treated fences, concentrations of arsenic, copper and chromium 30 cm from the fences were generally lower than directly under the fences. Limited data in a study with eight CCA-treated structures suggested arsenic leached to a slightly greater depth (up to 20 cm) than copper or chromium (up to 7.6 cm). Preliminary results for a study where leachate from miniature decks exposed outdoors in Florida was collected, leachate from a CCA-treated deck contained an average arsenic concentration of 1.4 mg/L (range 0.8-1.8 mg/L). Other studies have shown concentrations in drip water from CCA-treated decks of 1.0-1.7 ppm arsenic, 1.3-1.9 ppm copper and 0.4-0.7 ppm chromium four months after installation, and 0.3-1.7 ppm, 0.2-0.8 ppm and 0.2-0.5 ppm, respectively, after 2 years.

An Australian study evaluated leaching from model deck sections exposed over a 300 day period to a total of ~600 mm natural rainfall in Brisbane. Concentrations of arsenic, copper and chromium in composite leachate samples were ~0.5-1.2 mg/L, 0.4 mg/L and 0.3 mg/L, respectively. Over the test period, losses of the arsenic, copper and chromium initially retained were ~4%, 1% and 1%, respectively. Extrapolation of mathematical models fitted to the data to a similar rainfall rate over a 10 year period gives estimates of cumulative losses of arsenic, copper and chromium of 6947, 451 and 1258 mg/m^2 deck, respectively. If distributed into the surface 15 cm of soil below a treated deck, this could increase soil arsenic concentration by ~33 ppm, a comparable level to that found in the field measurement studies discussed above. In a study of a walkway in a Tasmanian wilderness area, no leaching of arsenic, but some leaching of copper and chromium was detected from CCA treated wood at sample points adjacent to the track compared to samples >2 m away. Limited sampling suggested there was little downward movement of copper or chromium, and a very rapid decline in chromium concentration with lateral distance from the track, to background levels at ~15-30 cm. That leaching of arsenic was not detected when copper and chromium were found to leach is surprising and may indicate that there were inadequacies in sampling or sample extraction procedures.

Evaluations of arsenic concentrations in base material (the surface layer of soil, sand or wood chips) beneath playground equipment indicate localised increases in arsenic and sometimes copper and chromium levels in the playground area, eg in the vicinity of support poles or near the structure of sand boxes. In one study, sites were evaluated on a grid pattern and also near selected support poles. Measured concentrations of arsenic in three playgrounds where it appears clear that CCA-treated wood was present ranged from ~1-66 ppm (site wide means 0.7, 6.4 and 11.7 ppm, background <1-4 ppm). Measured concentrations of copper in the playground areas ranged from ~1-62 (site wide means 1.5, 10.3 and 6.1 ppm), and those of chromium from ~1-61 (site wide means 1.5, 9.5 and 6.3 ppm). In a study of sand near wood in sandboxes or near playground supports, there was a more than five-fold decline in surface concentrations of arsenic (but not copper or chromium) between sand adjacent to the wood and 50 cm away from it. The available data also suggest some downward movement of arsenic to 20 cm near the wood.

Thus studies with miniature decks indicate concentrations in drips or run-off from the decks during rainfall were ~0.3-1.9 mg/L for arsenic, ~0.2-1.9 mg/L for copper , and ~0.2-0.7 mg/L for chromium. Mean arsenic concentrations in soil beneath or adjacent to a range of structures were increased by ~7-20 fold compared to mean background concentrations, to ~12-79 ppm, though individual sample points ranged as high as 350 ppm. Copper and chromium concentrations in soil were increased by up to ~3-6 fold, but one study detected no increases for either element, although arsenic concentrations did increase. Available studies indicate measured arsenic concentrations in surface cover in playground areas of 1-66 ppm, with the higher values localised to areas such as the vicinity of support poles or treated wood surfaces in sand pits.

6.5. SURFACE RESIDUES

6.5.1. Introductory comments

Surface-dislodgeable residues of CCA components that might be picked up by an organism through brief periods of surface contact are likely to be of very minor relevance to exposure of non-target organisms, though more pertinent to human exposure. Residues leached into soil and water are considered more environmentally relevant, but dislodgeable residues of CCA components on or near the surface of treated timber are presumably more susceptible to leaching at any particular time than those deeper in the wood. Some results for surface wipe tests conducted for human health assessment purposes are therefore summarised below.

6.5.2. Original Australian study

Johanson and Dale (1973) reported tests of surface residues on *Pinus radiata* rounds (60 cm lengths cut from 75-110 mm diameter posts) treated commercially with CCA (retention of CCA salt ~12-15 kg/m^3, arsenic content ~10-12%, from different plants in Australia, all unweathered and treated as recently as 7 days before). The end surfaces were washed and gently scrubbed with a soft nail brush in 300 mL tap water for 2 minutes, repeated with fresh water at two minute intervals for 10 minutes. The washings were analysed for total and soluble arsenic and total copper. After drying for several days to weeks, the round surfaces were washed in similar fashion.

Total residues from the round surface of various pine rounds from the five washings ranged from 0.75-4.17 mg/100 cm^2 for arsenic and 0.67-3.19 mg/100 cm^2 for copper (area washed ~1430-2070 cm^2), compared to 12.4-26.3 mg/100cm^2 for arsenic and 5.92-24.1 mg/100 cm^2 for copper in the intact end areas (~45-95 cm^2 washed). The major proportion of total arsenic in washings was insoluble. The amount of arsenic removed (particularly the insoluble fraction) and of copper gradually tapered off as washing progressed. Soluble arsenic concentrations from the five washings ranged from 0.06-0.20 mg/100 cm^2 from the round surface and 0.12-0.90 mg/100 cm^2 from the end areas. Thus total arsenic and copper in washings were similar in concentration. Losses to washings were greater from the end area of the rounds, which was, however, only a small proportion of the total surface area. The soluble fraction represented only a small proportion of the arsenic removed by washing.

This older, Australian study differs in two particular respects from the following studies. It used unweathered, freshly treated poles, whereas other studies have examined commercially purchased wood, exposed wood over time, or wood in service, ie with a longer duration following treatment.

It also used a repeated, prolonged washing period, whereas other tests have used a simple wiping procedure with a systematic technique using polyester wipes, or even by human hands which were then exhaustively washed. As noted by Arsenault (1975), the above results are far greater than those obtained by less exhaustive wipe test methods (below).

6.5.3. Measurements using actual hand wiping

Arsenault (1975) reported initial tests conducted in Ohio in 1973 to determine the amount of exposure that might arise from a child wiping its hands on the interior surface of wood foundations using treated plywood. Initial tests used laboratory tissues and cellulose sponge, wiping a 2 foot square area (~60 cm X 60 cm) of treated plywood, after which the tissue or sponge was digested and analysed for arsenic content. Six existing homes were tested, with the result that 80% of the 12 tests conducted found <0.5 mg/ft^2 (<53.8 µg/100 cm^2), with an average value of 0.244 mg/ft^2 (26.3 µg/100 cm^2) and standard deviation of 0.134 mg/ft^2 (14.4 µg/100 cm^2).

Further testing was conducted in 1974 because it was realised that tiny splinters of wood were caught in the sponge and hence digested and analysed. CCA treated ½ inch plywood that was recently treated and kiln dried were cut into 2 foot square sections and wiped with either a normally dry hand or one that had been freshly wetted with distilled water to simulate a damp condition. After some testing, the approach used was to wipe the surface, wash the hand with a detergent, scrub the hand with a toothbrush, and wash the hand with distilled water. Since it was considered that the dry plywood might contain surface dust, the effect of rain or washing was simulated by hosing the surface. After drying and oxidising of the organic matter, samples were analysed by the silver diethyldithiocarbamate colorimetric method for arsenic and AAS for chromium.

Tests of background levels on hands found average levels of <0.1-0.7 µg arsenic and <0.02 µg chromium per hand. Results from wipe tests on the wood are summarised in Table 40. There was a reduction of 2-3 fold in the levels of arsenic removable after hosing, and a much larger difference with the dry hand and wet hand wipe. This method appears rather difficult to reproduce reliably, but the results are on a similar scale to typical results from standardised wipe tests (below). Surprisingly, surface residues were apparently higher in the older wood, rather than that which had been recently treated.

Table 40. Amounts of elemental arsenic and chromium removable from the surface of southern pine plywood treated with CCA-C (Arsenault, 1975).

Condition	Sample	Dry hand wipe		Wet hand wipe	
		As (µg/100 cm^2)	Cr (µg/100 cm^2)	As (µg/100 cm^2)	Cr (µg/100 cm^2)
Unhosed					
2-year old	1	0.9	4.3	56.9	67.3
	2	0.05	-	27.4	-
New (2 weeks)	1	2.6	4.5	29.9	30.7
	2	0.8	-	12.4	-
MEAN		1.1	4.4	31.7	49.0
Hosed					
2-year old	1	1.6	-	19.9	-
	2	0.5	-	10.4	-
New (2 weeks)	1	0.1	-	8.8	-
	2	0.05	-	7.6	-
MEAN		0.6	-	11.7	-

6.5.4. Surface arsenic levels on CCA-C treated lumber by a brushing method

McNamara et al (1980) evaluated surface levels of southern pine dimension lumber that had been commercially treated with CCA-C (retention rate not stated). The investigators sprayed the surface of southern pine dimension lumber with distilled water and then brushed the surface with a test tube brush that had been wetted with distilled water. The wood surface and brush were then rinsed with distilled water, and the rinsate collected. The rinsate was filtered, the insoluble material determined after oven drying and the filter digested and analysed for total arsenic by the silver diethyldithiocarbamate colorimetric method. Arsenic in the filtrate was analysed by the same technique. The results indicated total surface arsenic levels of 12-511 µg/100 cm^2, only 0.9-23.5% of which were soluble. Only 0.41% of surface residue was arsenic, the remainder presumed to be comprised of dirt, wood fibres and wood sugars, along with copper and chromium residues.

6.5.5. Surface arsenic levels on CCA-C treated lumber by a simple tissue wipe test method

Kiekbusch (1983, 1984) investigated surface levels on CCA-C treated pine boards and hardwood dowels obtained from a commercial playground equipment manufacturer. The technique used was a gentle wipe over a 100 cm^2 area using a wet tissue paper technique which had been described by the Californian Department of Health Services. The tissues were acid-digested and analysed for arsenic by AAS. Levels of total arsenic removed by the wipes ranged from 5.0-8.2 µg As/100 cm^2 (mean = 6.3 µg/cm^2) in one test of 10 samples (test blank = 0.34 µg As/100 cm^2), and 0.6-23.8 µg As/100 cm^2 (mean = 7.8 µg/cm^2) in a second set of 20 samples (test blank = 1.6 µg As/100 cm^2).

6.5.6. A systematic polyester wipe method to test surface copper, chromium and arsenic levels on treated timber

Stilwell et al (2003) used a systematic wipe method to determine surface residues of copper, chromium and arsenic on 2.5 m long, 3 cm X 15 cm or 5 cm X 20 cm pine boards that had been treated commercially with CCA at 6.4 kg/m^3 and purchased at lumber yards. The boards were cut into 30 or 60 cm samples and placed on racks outside, with periodic testing over one or two years. Three of the six sets of boards tested had been pressure-treated with both CCA and a water repellent (WR), as are commonly used for decking in the USA. The boards were tested using a weighted wooden block assembly, based on a protocol described by the US Consumer Product Safety Commission (CPSC, 1990 – original report not seen). Polyester wipes moistened to 1.5 X their weight with deionised water were used. A wipe was attached to an 8 cm X 13 cm wood block and drawn across the test surface in a standardised fashion using the weighted block assembly, for a total of five times. The wipe was then removed, digested in nitric acid and analysed by ICP (the procedure used was thoroughly tested and verified).

Samples were only taken when the wood surface appeared dry. Average surface-dislodgeable concentrations of copper, chromium and arsenic were respectively, 23 µg/100 cm^2, 56 µg/100 cm^2 and 37 µg/100 cm^2 (Table 41). Arsenic concentrations tended to follow a similar pattern over time during the two years of observation - ie those samples tending to have a relatively high or low level of dislodgment tended to continue to do so throughout the exposure period, though highly fluctuating. The authors suggested that this approximate steady state could result from a balance between the amount on the surface washed off by rain, countered by an increase in surface preservative caused by diffusional and erosion effects. Such rejuvenation could continue indefinitely, meaning that arsenic residues could remain on the wood surface for a number of years.

Table 41. Summary of copper, chromium and arsenic dislodged from CCA-treated wood coupons over a 1-2 year observation period in a study in Connecticut (Stilwell et al, 2003).

Element	Concentration (µg/100 cm^2)						
	Range	Average ± standard deviation	Percentile				
			10th	20th	50th	75th	90th
Copper	3-69	23±12	9	14	21	30	42
Chromium	4-231	56±38	17	26	47	74	108
Arsenic	5-122	37±22	13	20	32	50	68

Note: The total number of samples was 316.

6.5.7. Surface arsenic levels on CCA-C treated lumber by a systematic wipe test method

Williams (1991) used a test based on the same CPSC (1990) protocol to examine 24 boards of different sizes purchased from 14 different lumberyards and home improvement centres. In this case a 10 cm square lintless nylon cloth was used, with 8 cm^2 of the cloth loaded with a 1 kg weight and drawn across the surface to sample a total area of 400 cm^2. The cloths were extracted with dilute hydrochloric acid and analysed for metal content by AAS. The boards had been treated with CCA at four different manufacturers, to penetrations of 50-100% (most ≥80%) and retention levels of 4.7-9.7 kg/m^3. Surface arsenic levels averaged 16.8 µg arsenic/100 cm^2 (standard deviation 12.3, range 6.2-28.7 µg/100 cm^2). The author noted that this indicated a 95% probability that if another board were sampled, the surface levels of arsenic would be between 15 and 18 µg/100 cm^2. He noted that the average level of arsenic obtained in his study was significantly lower than that measured by the CPSC on commodity lumber, ie 68 µg As/100 cm^2. No correlation could be found between properties such as moisture content, preservative retention etc and the arsenic residues on the surface of the wood. Preservative fixation was shown to have been complete by the absence of detectable Cr^{VI} in the wood. The author noted that testing had shown very low levels of arsenic on treated surfaces, but that the amount of residue can vary widely on different areas of a treated board, or between different boards.

6.5.8. Australian playground equipment tests – public submission

A public submission to this CCA review by K Loveridge of the Croydon Conservation Society Inc presented the following results (Table 42), obtained on Australian playground equipment using a polyester wipe method based on that of Stilwell et al (2003). The results indicate greater residues levels on the surface of vertical poles, which could possibly reflect differences in retention levels in vertical supports that might be in contact with the ground, and/or leaching down the vertical surfaces from higher up the poles. The level of arsenic on the NE vertical No. 2 surface was significantly higher than those reported by Stilwell et al (2003). Total arsenic concentration was also determined in soil below the NE corner of the equipment, showing some increase above field background (single samples only, 16 mg/kg below the playground structure and 10 mg/kg in field background). No information is available on the retention level of CCA present in the wood, or age of the structure.

Table 42. Total dislodgeable copper, chromium and arsenic concentrations on Australian playground equipment treated with CCA (K Loveridge, Croydon Conservation Society, information for submission to APVMA on arsenic timber treatments).

Sampling location	Total Cu (µg/100 cm^2)	Total Cr (µg/100 cm^2)	Total As (µg/100 cm^2)
North horizontal	22	20	21
South horizontal	23	22	24
MEAN - horizontals	**22.5**	**21.0**	**22.5**
SW vertical	190	88	91
NE vertical 1	630	140	140
NE vertical 2	310	670	710
MEAN - verticals	**399**	**320**	**336**

6.5.9. Summary and conclusions regarding levels of CCA components on the surface of treated wood

Regarding environmental exposure, it is likely to be residues of CCA components on or near the surface of treated timber that would be most susceptible to leaching at any particular time. Several studies have been conducted of surface dislodgeable residues for the purposes of human health assessment, with the emphasis on arsenic. Overseas studies using techniques where CCA-treated wood was wiped with a moist tissue or pad have indicated mean surface levels of arsenic of 6.3-37 µg/100 cm^2 (range 0.6-122 µg/100 cm^2). A higher mean of 68 µg/cm^2 was cited for a further study for which no details were available. A study where surface residues on treated wood were evaluated by measuring levels removed by wiping with a moist human hand indicated similar levels, with mean arsenic levels of 31.7 µg/100 cm^2 on unwashed surfaces and 11.7 µg/100 cm^2 on surfaces which had been hosed. However, levels were much lower when the surface was wiped with a dry hand (mean 1.1 µg/100 cm^2 for unwashed timber).

An Australian evaluation of residues on playground equipment using a wipe test method indicated comparable levels of arsenic on horizontal wood surfaces (21 and 24 µg/100 cm^2) to those in similar overseas studies, but much higher levels on vertical surfaces (140, 336 and 710 µg/100 cm^2), possibly because the uprights being in soil were treated to a higher hazard class, or because of accumulation through movement in leachate from further up the vertical posts. In this study and the few others where copper and/or chromium have been measured, the levels of these elements were similar in magnitude to the levels of arsenic present on the same surface (overall range 3-630 µg/100 cm^2 for copper and 4-670 µg/100 cm^2 for chromium).

A technique using a test tube brush indicated mean surface arsenic levels of 120 μg/100 cm^2 (range 12-511 μg/100 cm^2) on treated lumber, of which only 0.9-23.5% (0.8-5.9 μg/100 cm^2) was in soluble form. The highest surface levels have been reported in a study where repeated (5 rinses) gentle scrubbing with a soft brush was used: surface levels of arsenic on the round surface of treated wood were 0.75-4.17 mg/100 cm^2 for arsenic, compared to 12.4-26.3 mg/100 cm^2 in the intact end areas of treated posts.

Thus as might be expected, surface residues detected appear to be influenced by the severity of the wiping/washing process. Surface residues may possibly also be influenced by factors such as the CCA retention rate in the wood, lack of previous exposure of the surface, whether the surface was vertical (perhaps influenced to a greater degree by leachate running downwards or a higher retention rate to suit soil contact) or horizontal, and by end grain effects. One study showed that arsenic levels on the surface of a particular piece of treated timber tended to occur at similar levels over time, though highly fluctuating. This approximate steady state could result from a balance between the amount on the surface washed off by rain, countered by an increase in surface preservative caused by diffusional and erosion effects. Such rejuvenation could continue indefinitely, meaning that arsenic residues could remain on the wood surface (and leaching continue) at a similar level for a number of years. Surface dislodgeable levels of CCA components may also be related to leachability under the same conditions, but this does not appear to have been examined.

6.6. Plant uptake and leaching in garden and agricultural situations

6.6.1. General comments on plant uptake from arsenic in soil

A review by Peters et al (1996) stated that most plants take up arsenic either through the roots or foliage with root uptake dominating. Uptake varies with the ambient level in the soil as well as soil characteristics that affect complexation (eg more arsenic accumulation may occur in sandy soils). They indicated that because most arsenic species are complexed in soils the rate of uptake by plants is low. Arsenic levels tend to be greatest in the roots (much of it concentrated near the skin, evident in the peel of various root vegetables), followed by stems and foliage. Levels are lowest in fruits. Tobacco plants are known to absorb large amounts of arsenic, both from soil and foliage spray. Peters et al (1996) add that the level of arsenic present in soil generally has to be very high (200-300 mg/kg) before the level in most edible plants reaches 1 mg/kg (fresh weight), but that there are notable exceptions in eggplant and beet roots (1-2 mg/kg fresh weight [20 mg/kg dry weight] from 40 mg/kg and 116 mg/kg in soil, respectively). They cite the report by Levi et al (1974) of grapes not accumulating arsenic when grown next to arsenic-treated wood, but also cite a 1971 report that treatment of grapes with arsenic pesticides (evidently herbicides) increased their residue levels two- to fivefold.

Stehouwer (2001) also reviewed this issue in an advisory note on garden use of treated lumber. He noted that low concentrations of arsenic, chromium and copper occur naturally in plants and that plants vary widely in their uptake and tolerance of these metals. On a dry weight basis normal concentrations of copper, chromium and arsenic in plants are 5-30 mg/kg, 0.1-0.5 mg/kg and 0.01-1.5 mg/kg, respectively, while toxic tissue concentrations for most plants are in the ranges 20-100 mg/kg, 1-20 mg/kg and 5-20 mg/kg, respectively. In general, most metals remain in the roots, although leafy green vegetables such as lettuce, spinach and mustard greens also tend to move arsenic from roots to leaves. The amount of leaching of CCA components is related to the surface area of treated wood in contact with water, soil or compost. Soil acidity and the presence of organic acids in compost or silage may also increase leaching. Stehouwer suggested various steps to reduce risks from garden uses of CCA-treated wood, such as using alternatives, shielding the soil from the treated wood with plastic, not growing plants close to the border, and washing and peeling root vegetables.

6.6.2. Leaching from wood in contact with compost in Canada

In a study in Toronto, Canada by Cooper and Ung (1992, 1995), wood blocks (25 mm cubes of jack pine) were vacuum-treated with a 1.8% CCA-C oxides solution to approximately 6.4 kg/m^3 (1.4% by mass), the retention normally specified for ground contact exposure in Canada. After two weeks of aging at 22°C and saturated relative humidity to ensure complete fixation, blocks were exposed to various conditions for a 12 month period, viz. submerged in distilled water at 22°C with monthly water replacement, burial outdoors in garden soil, exposure to exterior weathering conditions, or burial in an outdoors home garden composter. At 3, 6 and 12 months, sample blocks were ground and analysed for copper, chromium and arsenic by X-ray fluorescence spectroscopy. The 1995 report added data for blocks left for 3 years under the same conditions.

Data up to 12 months

In the first 12 months, CCA losses at each occasion were considerably higher for samples exposed to compost (% loss relative to estimated initial retention in terms of the analytical method used were 11.7-12.7% with exposure to compost, and 1.3-8.3% in the other treatments). The results were variable over time, rather than showing a clear effect of exposure duration. The authors suggested this was due to normal variation inherent with wood and in the approach used to estimate initial retention. Changes in mass balance of the CCA components after 12 months indicated that copper was preferentially extracted. This result was considered to be consistent with the formation of water-soluble copper chelates with high molecular weight organic acids in compost. The authors noted losses were minor compared to those that have been found with exposure to silage, where anaerobic bacterial activity results in greater amounts of organic acids than occurs with aerobic conditions ideally present in a compost heap. Presumably, anaerobic conditions in a badly managed compost bin could potentially lead to greater leaching than occurred in this study. Levels in the compost were not monitored.

Data after 3 years

At 3 years, the calculated loss of CCA was still only 12.4% in blocks exposed in compost, and was 5.4-6.9% with soil burial or exposed to natural weathering and outdoor exposure. Blocks in the compost were extensively degraded by soft rot and other fungi, which was thought to be a consequence of high copper losses, whereas blocks buried in soil or exposed to natural weathering had not biodeteriorated. The authors considered the calculated loss of CCA for the blocks buried in compost to be an underestimate due to a greater volume of wood being compressed into the pellets used for analysis with the lower density, decayed wood. Mass balances of copper, chromium and arsenic showed copper was greatly reduced relative to unleached wood, whereas the proportion of chromium was increased. Leaching of arsenic was intermediate between that of copper and chromium.

Test compost bin made from CCA-treated wood

Cooper and Ung (1995) also reported a test conducted with a 1 m X 1 m X 1 m compost bin constructed of CCA-treated wood. The bin was used for 12 months for composting household vegetable wastes. Samples were taken from the interior surfaces of the box initially and (after washing) at the end of the study for analysis by X-ray fluorescent spectroscopy. Fully composted matter was collected at various distances from the wooden floor or walls, as well as from a control plastic composter. Compost samples were subjected to a digestion procedure and analysed for copper, chromium and arsenic by ICP (expressed as µg/g dry mass basis).

Results for the bin analyses were frustrated by variation in CCA retention values among and within boards before and after exposure. There were no statistically significant differences in retention, but the mass balance for copper was significantly reduced by exposure in all boards, whether continuously or intermittently exposed to compost, or not exposed (bottom surface of the lid). The results suggested greater loss of copper in continuously exposed boards. Compost samples adjacent to CCA-treated boards had higher concentrations of chromium at 0-10 mm from the sides (18.2 µg/g compared to 6.2-9.2 µg/g in other samples [ie including the plastic composter]) and arsenic at 0-10 mm and 0-25 mm from the sides (39.1 and 22.3 µg/g, compared to 7.1-10.2 µ/g in other samples). Copper levels were more variable (maximum 25.7 µ/g at 300 mm from the bottom, 19.1 µ/g at 0-10 mm and 21.3 µ/g at 0-25 mm from the sides, 12.1-17.0 in other samples).

Conclusions

Regarding the possible use of CCA-treated wood as a construction material for domestic compost bins, the authors noted that in practice, only one side of the treated wood would be exposed to the compost, and that with blocks there was a relatively large surface area and high proportion of end grain exposed. On the basis of the first 12 months of data, the authors suggested that losses would be sufficiently low that loss of preservative efficacy and contamination of the compost with chromium and arsenic would not be significant enough to prevent use of CCA-C treated wood for household compost bins. However, it was evident in both the extended block experiment and the bin study that there was increased depletion of CCA components, particularly copper, from treated wood in contact with compost. Based on this and the loss of decay protection evident after 3 years of exposure of the blocks, the authors changed their conclusions to recommend against the use of CCA treated wood for compost bins.

6.6.3. Arsenic levels in garden beds in Twin Cities, Minnesota

Alamgir et al (2001) reported a study of arsenic concentrations in established garden beds (≥10 years old) bordered by CCA-treated wood. Details of the wood were not provided. There were six sites, three on soils classified as loamy sand (pH 6.2-6.8, organic matter [OM] 6.8-13.2%, phosphate by the Bray [acid-fluoride] method 66.6-366 ppm) and three on sandy loams (pH 6.4-7.3, OM% 5.5-6.3, Bray-phosphate 49.6-231 ppm). Vegetation in the beds when sampled ranged from evergreens to grass, flowering plants or vegetables. Soil core samples were taken with a 2.5 cm (1 inch) soil probe to a depth of 15.2 cm (6 inches), at three distances from the wood, approximately 0-2.5 cm (0-1 inches), 7.6-10.2 cm (3-4 inches) and 30.5-33 cm (12-13 inches). Control samples were taken from outside the bed (~1.52 m/5 feet) away. Samples were processed by microwave digestion in concentrated nitric acid and analysed for arsenic by ICP. A separate part of the study examined plant uptake (p 100).

The results showed very clearly that arsenic in CCA-treated wood leached into soil in raised garden beds, but that concentrations declined rapidly with increasing distance from the wood. Mean total arsenic concentrations were highest 0-2.5 cm from the wood, ranging from ~24-55 ppm in the loamy sands, and 12-46 ppm in the sandy loams (approximate estimates from the graphical data provided). At 7.5-10 cm, mean concentrations ranged from ~7-18 ppm in the six sites, falling to ~4-8 ppm at 30.5-33 cm and 3-7 ppm at 152 cm. Statistically, as well as a significant distance effect, there were significant differences between beds and a significant bed X distance interaction. However, the trend of high arsenic concentration near the wood and a decrease in concentration further away was consistent in all six sites. The background levels in these soils were comparable to the range of 3.6-8.8 ppm cited by the authors from McBride (1994).

The authors noted that arsenic levels in the two soils with the highest concentration (46 and 55 ppm) exceeded the value of 40 ppm estimated as not posing toxicological hazard to organisms or causing environmental risk by Dudka and Miller (1999). The highest value also exceeded the maximum permissible arsenic concentration in arable soils (50 pm) accepted in the UK, according to Dudka and Miller (1999). The maximum acceptable value for arable land in Denmark (20 ppm – Helgesen and Larsen, 1998) was exceeded in four of the beds. However, in all six soils, arsenic concentrations were below 20 ppm by 7.5 cm from the wood.

6.6.4. Exposure via leaching from garden borders

Alamgir et al (2001) also reported a plant uptake study using soils obtained from the two soils most highly contaminated with arsenic in their garden bed study (mean levels in small samples 46 and 55 ppm - above). Approximately 45 kg of soil was sampled from inside each of the two beds, 0-2.5 cm away from the treated wood. Control soil was collected approximately 1.5 m away from the wood. Soil A was a sandy loam, with an arsenic concentration of 39.7 ppm, pH 7.4, OM% 6.5 and Bray-phosphate 60.5 ppm in the contaminated soil, and 10.4 ppm arsenic, pH 7, OM% 9.2 and Bray-phosphate 46 ppm in the control soil. Soil B was a loamy sand, with an arsenic concentration of 49.9 ppm, pH 6.7, OM% 4.2 and Bray-phosphate 26 ppm in the contaminated soil, and <3.1 ppm arsenic, pH 5.6, OM% 4.4 and Bray-phosphate 51 ppm in the control soil. Four crop species (carrots [*Daucus carota*], spinach [*Spinacia oleracea*], bush beans [*Phaseolus vulgaris*] and buckwheat [*Fagopyrum esculentum*]) were grown in a greenhouse pots of soil fertilised with an NPK fertiliser. After 8 weeks the plants were harvested (presumably therefore they were immature), dried and ground to produce samples which were analysed by hydride generation for ICP-Atomic Emission Spectroscopy.

Results on a dry weight basis are summarised in Table 43. All plants gown in soils collected at 0-2.5 cm from the wood had significantly higher arsenic concentrations than those grown in control soils. Higher arsenic concentrations in plants grown in soil B presumably reflected higher arsenic levels in the soil, though other differences may also have contributed (eg soil pH and OM%). On a fresh weight and dry weight basis, bean leaves and stems accumulated the highest arsenic concentrations, but bean pods had low arsenic concentrations. Carrot peel clearly contained higher arsenic levels than the remaining root tissue. Buckwheat was included as it is known to be a phosphate accumulator and therefore potentially also an accumulator of arsenate, an analogue of phosphate. The authors noted that buckwheat did show some ability to transport arsenic to the shoot, but that accumulation of arsenic in buckwheat was relatively low. While the authors concluded that the edible portions of all the crops remained below recommended US Public Health Service limits and Canadian statutory limits for human consumption, there was a relatively high content in stems and leaves which could be eaten by other organisms or may end up in compost etc. However, the overall impact of such exposure would be expected to be minimal as the contamination is confined to such a localised area.

The authors suggested that to reduce arsenic accumulation in crops, plants should be grown at least 38 cm (15 inches) away from the treated wood in raised beds (ie sufficient distance to minimise the proportion of roots penetrating into contaminated soil near the edge of the bed). For plants with extensive root systems, they suggested a plastic barrier inside the bed to a depth of 15 cm (6 inches) located ~30 cm (1 foot) away from the wood. They made the further suggestion was to line the inside portions of the treated wood with plastic when making a new bed or replacing old soil in an existing bed.

Table 43. Arsenic concentrations in crops grown in soils sampled at different distances from CCA-treated wood (the higher concentrations were from 0-2.5 cm from the garden border, and the lower from ~1.5 m distant).

Soil used and arsenic level	Arsenic concentration in plant tissue (ng/g or ppb)			
	Soil A		Soil B	
	39.7 ppm	10.4 ppm	49.9 ppm	<3.1 ppm
Crop				
Carrots (whole)	378	92	606	49
Carrots (peel)	1633	307	2950	165
Carrots (without peel)	186	55	283	30
Spinach	358	72	1475	65
Beans	318	<9	360	<6
Bean leaves and stems	6831	682	10,984	105
Buckwheat	565	54	1966	37

6.6.5. Use as wood mulch or soil amendment

Townsend et al (2003) examined leaching from material obtained from processed wood piles at construction and demolition waste facilities from various sources, known to contain CCA-treated wood residues. The greater surface area of mulched wood was expected to greatly increase the leaching rate of CCA components from the wood, a potential concern if the wood were to be used for landscape purposes. Hence samples of the mulch were tested using the standard Synthetic Precipitation Leaching Procedure (SPLP – Section 6.3.1.3.11). Eighteen of 22 samples leached arsenic at concentrations greater than Florida's groundwater cleanup target level (GWCTL) for arsenic of 50 µg/L (mean 153 µg/L, maximum 558 µg/L). One of two coloured mulch samples purchased from a retail outlet leached arsenic above 50 µg/L, whereas the other coloured mulch and mulch obtained from virgin materials did not leach detectable levels of arsenic (<5 µg/L). The authors used a mass balance approach to estimate the potential copper, chromium and arsenic concentrations (mg/kg mulch) that would result from CCA-treated wood being present in wood mulch. Their analysis showed that only a very low percentage of CCA-treated wood could be present to avoid exceeding various regulatory standards or guidelines for soil.

6.6.6. Exposure via soil amendment with CCA-treated sawdust

Speir et al (1992a) reported a pot trial assessment of the feasibility of using CCA-C treated sawdust (measured retention 11 kg/m^3 – ie 2000 ppm Cu, 6000 ppm Cr and 2800 ppm As) as a soil amendment. Beetroot, white clover and lettuce were grown in soil both at pH 5 and pH 7, with comparisons between unamended soil as a control, and soil amended with either 10% (v/v) CCA-treated sawdust or 10% untreated sawdust. Amendment with treated sawdust was calculated to increase soil concentrations of copper, chromium and arsenic by 45, 136 and 63 mg/kg, respectively. They noted that these additions were within recommended maximum permissible additions of elements in sewage sludge to uncontaminated soils for copper and chromium, but not for arsenic (100, 140 and 140 ppm for copper, 100, 500 and 600 ppm for chromium and 25, 5 and 10 ppm for arsenic in German, UK and New Zealand regulations in 1983-1986). Much of the copper was present in extractable form, whereas extract concentrations of chromium and arsenic were below detection limits with the standard soil extractant used (ie diethylenetriaminepentaacetic acid [DTPA]). The second paper evaluated effects on soil biochemical or biological properties (see Section 7.8).

Seeds germinated in all the pots, and the CCA-treated sawdust had no negative effect on any of the plants at either pH. However, yield depression occurred with untreated sawdust, which was attributed to oxygen depletion and/or nutrient immobilisation by the decomposing untreated sawdust (visual inspection at the end of the trial found no evidence for decomposition of CCA-treated sawdust). Plant roots in the CCA treatment, especially beetroot fibrous roots, concentrated copper, chromium and arsenic to high levels, with uptake of these elements generally higher at pH 5 than pH 7. However, the above ground parts of the plants and beetroot storage root (ie normal edible portions) had very much lower concentrations. The authors stated that although copper was concentrated to some extent in beetroot and clover, the concentrations were below animal toxicity levels, especially at the higher soil pH. The treatments had no important effects on the uptake of major and minor nutrient elements by the plants and did not adversely affect clover nitrogen fixation. The authors indicated a need for tests on a wider range of edible plants before it could be concluded that amendment with CCA-treated sawdust was acceptable. They also stated that the possibility of increased bioavailability of the heavy metals in the long term should also be considered.

6.6.7. Exposure via leaching from vineyard trellis posts

Levi et al (1974) analysed fruit, leaf and stem tissues from grapevines planted ~7.6 cm (3 inches) from CCA-C treated southern yellow pine posts (~12.7 cm minimum diameter) 1, 2 and 3 years after installation ~46 cm into the ground. The posts were treated to a retention of 9.6 kg/m^3. Half the posts were kiln dried immediately after treatment and half were placed in the ground without drying. New leaves and stems were removed for analysis in all three years, and fruit was sampled in the latter two years. After drying and ashing, samples were extracted in 6 N hydrochloric acid and subsequently analysed using AAS. No evidence of uptake and translocation of CCA in plant tissue was found. Amounts of copper in the leaf/stem tissue and fruit ranged from 4.9-10.5 ppm for plants next to CCA-treated posts and 4.7-11.6 ppm for untreated (black locust) posts, comparable also to known levels for grape leaves in the same US state (presumably the results were not confounded by the use of copper fungicides). The arsenic content of leaf/stem and fruit tissue was below 0.5 ppm in all cases. As well as concluding that CCA components are not concentrated in plants growing near treated wood, the authors used their results to suggest that CCA components in the wood are not readily leached. However, there were no analyses of soil or wood in the posts to determine the extent to which leaching had occurred. Most likely, little lateral movement of CCA components occurred from whatever residues were present near the treated posts, and despite the close proximity of the plants to the treated posts in this trial, their roots would have largely been growing in uncontaminated soil. In Australia, grapevines are usually planted ≥0.5 m from trellis posts, hence their roots would be expected to have very limited exposure to localised CCA contamination of soil near the posts.

6.6.8. Exposure via leaching from support posts and stakes in pots

Zhaobang et al (2003) examined the use of CCA-treated eucalyptus stakes (6-8 cm X 4-5 m long; CCA-C retention ~7.5 kg/m^3) to support banana plants in China. Data from 4 years of monitoring bananas collected from the plots were stated as indicating that arsenic levels were not significantly higher than the levels found in plants supported by untreated stakes (results were not statistically analysed). Similar results were obtained from a trial of tomatoes and garden peas supported by treated eucalypts and bamboo posts in pots.

6.6.9. Bioavailability and speciation of arsenic in carrots grown in CCA-contaminated soil from a Danish wood preservation site

The bioavailability and speciation of arsenic in carrots grown in CCA-contaminated soil was investigated by Helgesen and Larsen (1998), using soil obtained from a "hot spot" at a former industrial wood preservation site. Contaminated soil (a loamy sand low in organic matter) was mixed with uncontaminated soil (a loamy sand rich in organic matter) from a nearby site and placed into cylinders which were positioned in field plots. There were 7 mixtures, four of which were loamy sands high in OM% and loose in structure (soils A-D, 6.5-338 µg As/g dry soil and 11.0-251 µg Cu/g, A being the uncontaminated soil), and three of which were denser due to a higher proportion of contaminated soil (soils E-G, 406-917 µg arsenic µg/g, copper up to 811 µg/g). Carrots were sown in the cylinders and grown for 17 weeks.

As discussed in Section 7.9.2, pronounced depression in carrot growth was evident as arsenic and copper content increased from soil A to soil D, and no carrots grew in soils E-G. The harvested carrots were separated from the tops. Soil and root samples were analysed for total arsenic and copper content, for extractable arsenic (in calcium nitrate solution for soil and 10% methanol:water for carrots), and for arsenic species. The soil extraction procedure was intended to indicate the fraction of arsenic available to the roots and not to affect arsenic speciation, while that for the roots was to optimise extraction without affecting speciation.

The concentration of total arsenic in carrot roots (peel and core) increased with increasing soil concentration, from <0.1 µg/g dry weight in uncontaminated soil to 1.85 µg/g in whole roots from soil D. The arsenic content in peels was ~3 X greater than that in the corresponding cores. Copper concentration in the roots was not significantly affected by increasing soil concentrations, despite a 23 fold increase in measured soil Cu concentrations. As^{III} and As^{V} were present in all soils, with As^{V} higher in concentration than As^{III} in plots C and D, and the reverse in plots A and B. However, As^{III} was present at similar concentrations to As^{V} in carrot flesh. Microbial activity evidently explained the presence of trimethylarsine oxide in soils A and B. The soil to carrot uptake rate (bioavailability) of arsenic was ~0.5% of the arsenic content in soils A-D.

6.6.10. Copper, chromium and arsenic levels in vegetables and grasses grown in contaminated soil

Grant and Dobbs (1977) grew dwarf French bean, carrots and tomatoes in potting compost spiked with CCA at various levels. The study also examined germination and growth of these crop plants (see Section 7.9.1). Samples for elemental analysis in the harvested produce were taken after 27 days (for beans), 91 days (carrots) or 105 days (tomatoes). The control (treatment A) contained total copper, chromium and arsenic at 37, 25 and 14 ppm, respectively. Treatments B, C, D and E contained total Cu, Cr and As concentrations of 37, 28 and 10 ppm, 52, 53 and 24 ppm, 250, 380 and 200 ppm, and 1900, 3100 and 1700 ppm, respectively.

With beans, levels of arsenic appeared substantially higher in treatment C compared to the control (0.29 ppm fresh weight, ~15 X the control), though copper and chromium levels appeared similar between the control and treatments B and C. With carrots, there were significant correlations between the levels of copper, chromium and arsenic in the soil and in the crop, with arsenic levels in treatment D 1.94 ppm fresh weight, ~40 X those in the control. With tomatoes, there were significant correlations between soil and crop levels for chromium and arsenic, but not copper, and the extent of increase was lower than in carrots (0.20 ppm fresh weight, ~1.5 X for arsenic). Presumably higher levels of these elements were present in leaf and stem tissue of beans and tomatoes.

Grant and Dobbs (1977) also noted that arsenic levels in grasses growing in arsenic-enriched soils can be very high indeed, eg 3500 ppm dry weight has been detected in *Agrostis tenuis* growing on mine waste, and that the development of heavy metal tolerance in grasses is well known. The authors also state that a thriving colony of horsetail (*Equisetum arvense*) was observed growing in contaminated soil adjacent to a CCA mixing tank at a treatment facility (presumably in the UK). When analysed, the soil and plant material contained 7000, 4500 and 6900 mg/kg soil and 1200, 1600 and 1400 mg/kg dry weight of copper, chromium and arsenic respectively. The authors noted that the evolution of ecotypes of grasses accumulating high levels of heavy metals or arsenic could present a potential hazard to grazing animals.

6.6.11. Summary and conclusions regarding leaching from CCA treated wood in garden and agricultural situations and plant uptake from contaminated soil

Leaching of CCA from wooden blocks has been shown to occur more rapidly when they are buried in compost than when buried in soil or stored in water. Preferential extraction of copper occurred, consistent with the presence of organic acids in compost and leading to failure to protect the wood from fungi by the end of the three year study, whereas the other blocks remained protected. When CCA-treated wood was used to construct compost bins, it was found that after one year, compared to compost elsewhere in the bin or in a plastic composter, compost close to the sides of the bin had higher concentrations of arsenic (~39 and 22 ppm at 0-10 and 0-25 mm, compared to ~7-10 ppm elsewhere) and chromium (~18 ppm at 0-10 mm, compared to 6-9 ppm elsewhere). Results for copper were more variable (12-26 ppm, with no clear pattern), yet it is copper that is likely to have leached most (suggested also by analyses of CCA retention in the boards). Studies of established raised garden beds to investigate the use of CCA-treated timber for garden borders indicated very clearly that arsenic leached into the soil, but that concentrations resulting in the soil fell rapidly with distance (12-55 ppm at 0-2.5 cm, 7-18 ppm at 7.5-10 cm, 4-8 ppm at 30.5-33 cm and 3-7 ppm at 152 cm, background levels 3.6-8.8 ppm). Pot trials using soil with high arsenic levels obtained from soil near the garden edges (~40 and 50 ppm) compared to soil collected from ~1.5 m away (~10 and 3 ppm) indicated that some plants in contaminated soil had higher concentrations of arsenic (eg 378-606 ppm in whole carrot roots) than in the uncontaminated soil (49-92 ppm in whole carrot roots).

Arsenate is an analogue of phosphate and may be taken up by plant roots. The extent of uptake of arsenic by plants and its concentration in plant tissue vary with the plant species, the concentration in soil and soil characteristics affecting availability. One study showed increasing concentration of arsenic in carrot roots with progressive increases in arsenic concentration in soil prepared by mixing various ratios of contaminated soil from a former CCA preservation plant with and uncontaminated soil (arsenic <0.1-1.85 ppm in carrot roots from soil containing 6.5-338 ppm). Another study showed correlations between arsenic levels in compost spiked with CCA and those in plant tissue. Plants vary widely in their uptake and tolerance of arsenic. High levels of arsenic may accumulate in tolerant species, eg 1400 ppm arsenic was found in a plant growing in CCA-contaminated soil containing 6900 ppm arsenic.

Testing of wood mulch prepared with the standard Synthetic Precipitation Leaching Procedure (SPLP) indicated mean arsenic levels in leachate of 153 μg/L (maximum 558 μg/L), exceeding regulatory standards to avoid groundwater contamination in Florida. Other research indicated no negative effects on seed germination or yield from sawdust from CCA-treated wood used as a soil amendment. However, various tissues in the plants accumulated relatively high concentrations of arsenic, copper and chromium. Thus, the use of soil amendments or mulches from wood containing CCA is likely to lead to increases in soil arsenic, copper and chromium concentrations and these would be likely to be reflected in higher concentrations in plant tissues.

No evidence of elevated arsenic uptake was found in studies with vineyard trellis posts and grapevines (fruit, leaf and stem tissues), possibly because leaching from the posts affects only soil close to the pole, and because despite the test vines being planted close to the posts, most root ramification presumably occurred in uncontaminated soil. Another study claimed there was no evidence of enhanced arsenic uptake in bananas exposed to CCA treated support posts for four years, nor to vegetables with stakes in pots.

Thus, garden edges or structures containing CCA-treated timber may leach arsenic and other CCA components into soil. In general, leached arsenic is likely to remain in soil or compost close to the wood, but it may be taken up by plants growing predominantly in the affected soil, resulting in elevated plant levels. Similarly, soil amendments or mulches containing CCA-treated wood residues may leach arsenic and other components into soil, which may then be taken up by plants. Presumably, plants growing in soil close to decks or fences could also take up elevated levels of arsenic, copper or chromium in leachate from treated timber. However, as with garden borders, in most situations the affected zone of soil is likely to be very limited. Studies investigating plants growing near CCA-treated posts have failed to find elevated CCA-component concentrations in plant tissue, possibly because the plant roots grew largely in uncontaminated soil.

6.7. TIMBER WASTE DURING CONSTRUCTION

Lebow et al (2000) reported a study to investigate CCA losses from construction debris. Wooden boards as used for timber decking were treated with CCA-C (measured retention after a fixation period 5.9-8.6 kg/m^3). Samples were obtained from the treated boards of sawdust from a chain saw and a circular saw, shavings from a wood boring spade bit, and small wooden blocks (40 X 38 X 140 mm). Particle sizes tended to be finer with the circular saw than the chain saw, while the spade bit produced more large particles. Samples were placed in jars of water and shaken for 50 days, with frequent collection and replacement of leachate. Copper, chromium and arsenic were analysed in leachate by AAS.

The release rate of copper, chromium and arsenic from CCA-C treated sawdust and shavings was found to be many times higher per unit weight of wood than from solid wood samples immersed in water (with copper, the average release rate was initially >20 X greater). This gap narrowed with time, but the release rate remained several times greater than for solid wood after 50 days. However, more rapid depletion of the available reservoir of available CCA-C within the particles should ultimately slow the rate of release below that for solid wood. Release rates from the shavings tended to be slightly lower than from sawdust, but there was surprisingly little difference in release rates among the sawdusts and shavings, despite the differences in their particle sizes. The authors compared these results with those for their study (Lebow and Evans, 1999) with long specimens cut from the same boards, which were exposed to artificial rainfall (198 mm over 28 d) rather than immersed in water. The total amount of CCA-C released from the decking specimen was many times lower than from any of the types of samples in the construction debris study, due to intermittent wetting rather than continuous immersion, as well as the large difference in relative surface area.

To assess the risk to the environment from construction debris, the authors then considered a hypothetical wetland boardwalk construction project (ie where the water below the structure was contaminated by wood debris as well as by leaching from the structure). Because of the much smaller available reservoir of CCA in debris compared to the structure, the contribution from debris to overall release was estimated to be only minor in the first few months after construction, and much less in following years. However, the authors noted that the distribution of construction debris may create localised pockets of contamination where they are deposited only a small fraction of the total release. Similarly, leaching from decking is not really uniform, eg following specific flow paths. They recommended steps in construction practice which should effectively reduce environmental contamination by debris. These include cutting to size or fabrication of the lumber prior to treatment with CCA, and as far as practicable where field fabrication is necessary, doing so away from sensitive environments, and collecting and containing debris generated during construction (eg by constructing over tarpaulins or plastic).

Thus, a study showed that surface area to volume effects lead to much more rapid leaching of CCA components from construction debris such as sawdust, wood shavings and small off-cuts, with the rate of leaching increasing with decreasing particle size. On a construction site the reservoir of CCA contained in such debris is relatively small compared to the wood in the structure, but debris can cause localised contamination of soil or water in the areas it has fallen. The author argued that contamination of a sensitive site by CCA-treated wood debris can be avoided by construction elsewhere or by collection and removal of debris at the time of construction.

6.8. Disposal of CCA-treated wood, wood waste and other material containing CCA residues

6.8.1. Overview

Solo-Gabriele et al (2003) gave a general overview of disposal issues for CCA-treated wood in Florida, including the disposal quantities, disposal pathways that needed to be avoided or controlled (disposal in unlined landfills, recycling as wood fuel, recycling as mulch), chemical species present in unburned wood (early results indicate that unburned wood leaches arsenic primarily as As^{V} and chromium as Cr^{III}, but that a larger proportion of As^{III} is observed in weathered wood), chemical speciation in ash (variable, some significant amounts of more toxic As^{III} and Cr^{VI}). They also discussed possible solutions, including using alternative chemicals free of arsenic and alternative disposal management options. They considered that recovery of copper, chromium and arsenic from ash looks uneconomical, but that wood cement composites could be interesting as the chromium in CCA-treated wood improves the bond between the wood and cement, and the cement encapsulates the CCA components within the concrete. It will be necessary to develop procedures to separate CCA-treated wood from the wood waste stream (eg dye or X-ray tests) so that the latter can be used most effectively. However, in relation to environmental issues in Florida, it should be recognised that SCTLs for arsenic are very low, as are typical Florida soil levels, that sandy soils in Florida tend not to hold heavy metals, and that in Florida protecting groundwater from contamination is particularly important, due to the extent of its use for drinking water (Sections 6.4.1.10, 6.4.2.3 and 6.4.2.4).

Solo-Gabriele and Townsend (2000) also discussed several of these issues. Solo-Gabriele and Townsend (1999) provided a useful summary of management options for CCA-treated wood waste in the USA, which is reproduced below. Cooper (1990) has made similar comments in a review of CCA treated wood disposal in Canada, and Smith and Shiau (1998) reviewed the issue. Some further discussion of disposal options follows, with emphasis on the fate of CCA residues if timber is burnt.

“Waste minimisation
Alternative structural materials: plastic lumber, concrete, steel, aluminium, fibreglass, brick, stone, and wood species with a natural resistance to decay.
Alternative chemical preservatives: creosote, pentachlorophenol, alkaline copper quat, copper naphthenate, borates, phytoalexins, etc.
Increase service life: supplemental treatments, chemical re-treatment, and wood treatment process enhancement.

Reuse
Reuse for new applications: fence posts, landscape timber, parking lot bumpers, guardrail posts, composting bins, planter boxes, shipping crates, picnic tables, walkway edging, etc
Reuse for same application: splicing intact portions of spent utility poles.

Recycling
Recovery of untreated portions of treated wood products: clean wood portions used for many different applications.
Wood-based composites: flakeboard, oriented strand board, particleboard.
Wood-cement composites: fire-resistant panels and highway sound barriers.
Other composite materials: wood gypsum composites that can be used for fire-resistant panels (indoor applications only), plastic wood composites currently under development.
Mulching and composting (unburned wood): viewed with caution due to potential for metals leaching.

Energy recovery and wood as fuel
Cement kilns: advantages include stabilisation of the metals in cement matrix; air emissions may create a problem.
Cogeneration: requires shredding wood waste and disposal of ash residual; excessive quantities of CCA-treated wood in fuel stream may cause ash disposal problems.

Disposal
Incineration without energy recovery: some CCA-treated wood may be commingled in trash or wood fuel; excessive CCA-treated wood may cause air emissions and ash disposal problems.
Landfills: currently accepted at construction and demolition landfills and municipal solid waste landfills in the USA.
Ash disposal: wood ash has many recycling opportunities; however, elevated metals concentrations from excessive amounts of CCA may greatly limit these recycling opportunities.”

6.8.2. Burning and pyrolysis

6.8.2.1. Effect of CCA retention and oxygen supply

Dobbs and Grant (1978) investigated the volatilisation of arsenic from burning CCA treated wood in the United Kingdom. The wood had been treated with 0.75%, 1.5% or 3% solutions of CCA (BS4072 Type 2), giving approximate concentrations of 5, 10 and 20 kg salt/m^3. Treated wood planks were fixed and dried, then split and milled to produce particles >2 mm for the study. The wood was burned under laboratory conditions, with the fumes from combustion drawn by suction through wash bottles containing sodium hydroxide solution. Samples of wood, ash and the collection solution (to which washings from tubing etc were added) were analysed by AAS and other means. One control with untreated wood was burnt, two samples were burnt at each retention rate, and one burn was run with the 3% treatment with additional oxygen supplied to the burning wood. Wood treated with 3% solution contained mean levels of 2.34 mg/g copper, 4.57 mg/g chromium and 3.15 mg/g arsenic. The arsenic balance was within ±10% for all eight burns, meaning that volatile arsenic was adequately captured.

The mean arsenic evolution ratio was 16%, 22% and 24%, respectively, for the 0.75%, 1.5% and 3% treatments burnt in air. Hence the proportion of arsenic evolved increased slightly with increasing retention of CCA in the wood. This difference was judged to be too small to be of practical importance. However, there was a much greater proportion of arsenic evolved when CCA-treated wood was burnt in oxygen-enriched air: 59% with oxygen-enriched air, compared to 24% in air. The weight of ash produced tended to increase with CCA salt concentration.

6.8.2.2. Combustion conditions

Pasek and McIntyre (1993) noted that arsenic pentoxide is easily reduced to the trioxide, which can sublime at temperatures below the combustion temperature of wood. The fate of arsenic during burning of arsenic-treated wood is not a new issue, having attracted research attention since the first study of it in 1953. Results of various studies in the scientific literature had shown that in the presence of excess air, between 10% and 80% of arsenic is volatilised, with little or no loss of copper or chromium. The amount of arsenic lost has been found to be directly proportional to the combustion temperature, the time at temperature and the oxygen partial pressure in the air, and to also be affected by the amount of air flow during combustion. Research with arsenic in other feedstocks had shown that low oxygen partial pressure favoured As^{III} and thus volatilisation, but this was evidently not the case with CCA-treated wood.

Pasek and McIntyre (1993) conducted additional experiments with a high CCA retention (36.88 kg/m^3; 1.04% Cu, 1.57% Cr and 1.44% As) in the USA. Wood samples were burnt in a tube furnace under controlled temperature (degrees and duration) conditions. Essentially no copper or chromium were found in gas traps, whereas 3.3-20.9% arsenic volatilisation was indicated for the various study conditions. Volatilisation was maximal at 60°C and fell with increasing temperature, ie an opposite effect to that found in all previous studies. The authors suggested that the formation of transition metal (presumably copper and chromium) arsenides was the reason for these results.

6.8.2.3. Thermodynamic investigations and minimising arsenic volatilisation losses

CCA component behaviour during the pyrolysis of CCA treated wood waste has been investigated and previous research reviewed by Helsen and van den Bulck (2000) and the same authors in an internet web document (http://www.mech.kuleuven.ac.be/tme/research/combust/topics/pyrolysis/default_en.phtml, accessed September 2003). Arsenic is released even at temperatures between 300°C and 400°C. They suggested that chromium (III) arsenate ($CrAsO_4$) is the major arsenic compound in CCA-treated wood (precipitated on cellulose or complexed with lignin), and that decomposition of this probably results in the formation of water and solid chromium trioxide (Cr_2O_3) and arsenic pentoxide (As_2O_5). The latter dissociates to form arsenic trioxide (As_2O_3) and oxygen. The arsenic trioxide (in equilibrium with the gaseous form As_4O_6) sublimes and is emitted to air as gas, ie with arsenic in the trivalent form (As^{III}). This gas is stated to be very difficult to capture and therefore rarely detected (perhaps contributing to poor recovery in some studies). Arsine (AsH_3) is not present in the gas exhaust as it decomposes at 300°C, but decomposition of wood products may give rise to methylated arsine products at temperatures below 300°C. Arsenic in the pentavalent form (eg arsenates) may be released as particulates or aerosols, which can be captured by scrubbing and filtering. In one reviewed study, virtually all the volatilised arsenic was recovered in the particulate form, consisting of both arsenites and arsenates. In their internet report, Helsen and van den Bulck suggest that low temperature pyrolysis (<500°C) offers a means of minimising the loss of arsenic through arsenic trioxide sublimation and discuss research into managing the process. They note that the critical temperature above which reduction of arsenic pentoxide occurs is 327°C.

6.8.2.4. Equilibrium distribution of toxic elements in the burning CCA impregnated wood

Sandelin and Backman (2001) discussed the above and other research and concluded that theoretical arguments confirm that chromium and copper in CCA-treated wood are unlikely to volatilise at practical combustion temperatures (0.05% of the chromium and 0.51% of the copper estimated to be in the gas phase at 1200°C, compared to 86.9% of the total arsenic present – greater copper volatilisation may occur at higher temperatures, and the formation of gaseous copper chloride may also increase copper volatilisation; <5% of chromium is predicted to be in gaseous phase at 1600°C). However, various other reactions may reduce the amount of arsenic volatilised, eg arsenic may form non-volatile compounds with metal compounds and may dissolve in the slag phase of the ash.

6.8.2.5. Characteristics of ash from CCA-treated wood

Solo-Gabriele et al (2002) conducted standard leaching tests (the toxicity characteristic leaching procedure [TCLP] and synthetic precipitation leaching procedure [SPLP]) with ash prepared from CCA-treated wood. Ten different solvents were also tested for their ability to extract copper, chromium and arsenic. Results indicated that the concentration of copper + chromium + arsenic can be as high as 36% of the ash by weight for treated wood samples containing high retention levels (40 kg/m^3) of CCA. Ash samples from 100% CCA-treated wood at various retention levels (4-40 kg/m^3) and weathered CCA-treated wood leached arsenic at 51-561 mg/L in the two tests. The authors noted the consequences of this under US hazardous waste regulations. Concentrated nitric acid was the most effective solvent tested, removing 70-100% of the copper, 20-60% of the chromium and 60-100% of the arsenic for samples with low CCA retention levels.

6.8.2.6. Determination and analysis of copper, chromium and arsenic in pyrolysis residues

Van den Broeck et al (1997) used an inductively coupled plasma mass spectrometry method to compare the total amount of copper, chromium and arsenic in wood and its pyrolysis residues, using three different leaching and dissolution procedures (2.5 M sulphuric acid/hydrogen peroxide; aqua regia/hydrogen fluoride; and reflux with nitric acid) to obtain the samples for analysis from both wood and pyrolysis residue. The three methods produced similar results for copper and arsenic in both materials and chromium in wood, but a slightly lower result for chromium in pyrolysis residue. Copper concentrations in the wood and pyrolysis residues were 3390-3680 ppm (µg/g) and 8260-8560 ppm, respectively. The corresponding arsenic residues were 8350-8590 ppm (µg/g) and 19,980-20,140 ppm, and those for chromium were 9200-9490 ppm and 18,170-22,720 ppm.

The pyrolysis was a low temperature thermal degradation process producing a solid residue (charcoal), liquid product (pyrolysis liquid) and a gaseous product (pyrolysis gas).

Approximately 98% of the copper and chromium was present in the solid residue, compared to 82.3% for arsenic. Most of the remaining arsenic was present in gas (14.7%), with 2.9% in the liquid product, where some copper but no chromium was also present. A sequential analysis procedure applied to the pyrolysis residue showed that arsenic and copper were bound in forms which were likely to leach from it, whereas chromium behaved differently and was unlikely to pose problems of leaching. Partial reduction of As^V to As^{III} was demonstrated to have occurred during the pyrolysis process used.

6.8.2.7. Industrial scale trials of CCA waste wood incineration in Finland

Nurmi (1996) reported an industrial scale trial for disposal of CCA treated waste wood by combustion in Finland. CCA-treated utility poles (272 m^3, 62.7 t) were chipped and incinerated in a gasification heating plant in Finland, the ashes from which were then passed through a copper refinery line. Overall, the whole batch of chips contained 57 kg copper, 95 kg chromium and 76 kg arsenic. During the 56 h combustion trial, measured arsenic emission to air was 76 g in total, with less than 1 g emission of copper and chromium. The total content of arsenic in condensing water from different parts of the flue gas cooling system was 44.2 kg (300-650 g/L), with ~0.3 kg copper and a few grams only of chromium. Calculated amounts of arsenic, copper and chromium in ash collected for up to 2 weeks after the trial were 8.8 kg, 34 g and 40 kg. Hence recovery was only ~30% for arsenic, 60% for copper and 42% for chromium. The authors noted that evaluation of the ash was one source of error (subsampling from 8820 kg of unmixed ash), but that it was likely that arsenic continued to emit to air after the fuel was changed from the wood flakes to the standard peat fuel, and that residues of the CCA components remained in the gasification heating plant. They suggested that to minimise pollution, treated wood could be burnt shortly before annual cleaning of the plant.

Syrjänen (1999) and Lindroos (1999) discussed possibilities for recycling CCA impregnated timber through combustion. CCA impregnated wood (270 m^3, 61.3 t) was chipped and incinerated in a gasification heating combustion plant. Condensate waters were transferred to a CCA production plant and utilised in the manufacturing process, and ash was treated at a copper smelter. The element balances resulting during combustion were calculated to be as follows: total copper, chromium and arsenic contents in the wood were respectively, 71, 99 and 100 kg. Most of the copper and chromium residues were found in the ash (66 and 99 kg), with minor to very small amounts in condensate water (0.03 and 0.1 kg), flue dust from cleaning equipment (2.3 and 2.2 kg) and plant gases (1.1 and 0.3 kg) – total recoveries 69 and 102 kg, respectively. Recovery of arsenic was less complete (79 kg), with significant amounts in condensate water (28.6 kg), ash (30 kg), fuel dust (12.5 kg) and plant gases (7.7 kg).

6.8.2.8. Possible formation of dioxins and furans

An Australian study by Tame et al (2003) indicates that in addition to considerations regarding copper, chromium and arsenic residues in ash, consideration should be given to the possible presence of dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Their experiments showed total average PCDD/F toxic equivalent (TEQ) levels of 35 ng TEQ/kg in the bottom ash from fires of CCA-treated wood, compared to 0.05 ng TEQ/kg in untreated pine ash samples. It is thought that heavy metal residues (principally Cu^{II}) remaining in the smouldering material after flaming combustion act as a catalyst for the formation of PCDD/Fs.

6.8.2.9. Incineration in a copper smelter in Finland

Nurmi and Lindroos (1994) provided a brief report of a preliminary trial where CCA-treated wood was used as fuel in a copper smelter. The authors claimed that almost a full recovery of both copper and arsenic in the wood was achieved (presumably with the smelted copper and arsenic trapped from gases), the recovered elements being utilised in CCA manufacturing. Chromium residues could not be recovered, but underwent a treatment process leaving them insoluble in the smelter slag. Energy was recovered from the wood for the smelting process and the burning gases were fed to a sulphuric acid plant, presumably recovering sulphur from CCA salt formulations.

6.8.2.10. Australian research into combustion of CCA-treated wood

A submission from the University of Sydney Department of Chemical Engineering to this review notes that a project is currently underway there to investigate the combustion of CCA treated timbers under a range of conditions and examine suitable conditions to deliver both high energy recovery and manageable by-products.

6.8.3. Landfill

6.8.3.1. Lysimeter studies in Florida

Jambeck et al (2003) reported an ongoing lysimeter (30.5 cm diameter, 6.1 m tall) study modelling various landfill scenarios, in each case with a matching control lysimeter with similar waste, but no CCA-treated wood:

- a wood monofill, containing 50:50 construction:demolition waste (50% freshly CCA-treated, 50% aged CCA-treated);
- a construction and demolition (C&D) facility, containing 5.1% new and 5.1% old CCA-treated wood by volume, plus other such debris, including metals, cardboard, concrete and untreated wood; and
- municipal solid waste (MSW), containing 1% old and 1% new CCA-treated wood by volume, plus other MSW (plus added food to ensure microbial health and untreated wood).

Redox conditions in all the CCA-lysimeters are reducing. Early results indicate that leachate from the wood mono-fill constituted hazardous waste and would be expensive to dispose of, containing >20 mg/L of arsenic, ~10 mg/L chromium and somewhat lower levels of copper. Leachate from the C&D lysimeter (2% CCA-treated wood by mass) contained arsenic and chromium levels ~1 mg/L initially, rising to 3 mg/L and 1.7 mg/L, respectively. Leachate from the MSW lysimeter was initially 3.8 mg/L and 4.2 mg/L for chromium, despite the low percentage of CCA-timber (~8% less than in the C&D lysimeter). These levels have dropped below 0.5 mg/L since the pH increased and methane began forming.

The authors concluded that while neither the C&D nor MSW waste was classified as hazardous under local regulations, it is clear that the co-disposal of CCA-treated wood in both situations has influenced the arsenic, copper and chromium concentrations in the leachate. Further monitoring was continuing. The authors discussed the large and growing disposal problem for CCA-treated wood in Florida, noting points such as that in Florida aesthetic reasons rather than lack of soundness played a major role in deciding when CCA-treated timber decks were removed, that this lifetime was in the range 10-20 years, that only minor recovery of treated timber was achieved (it was cheaper to demolish than deconstruct and recovery facilities were lacking), and that C&D facilities (which are generally unlined) were the most common method for CCA-treated wood disposal due to greater costs at MSW facilities.

Huffman and Morrell (2003) cited previous research with arsenic contamination in soil adjacent to cattle dip tanks in Florida. This showed that even where movement down this (probably sandy) soil profile occurred, movement of arsenic waste into aquifers was prevented by adsorption to clay and organic matter at depths of 1.8-2.4 m. The authors argued that lined landfills may not always be required for disposal of CCA treated wood.

6.8.3.2. Small scale burial in soil in Japan

Suzuki and Sonobe (1993) investigated the implications for soil copper, chromium and arsenic levels of burying CCA treated wood as a means of disposal, in a study conducted in a soil with pH 6 near Tokyo, Japan. Logs (50 cm long, evidently from the end which had been buried in soil – “short end”) were cut from utility poles which had been treated with CCA-A and had been in service 3-17 years. Four logs from each of four poles were buried parallel to the ground in soil to approximately 15 cm. A fifth log from each pole was cut into chips (~5 X 20 mm to 30 X 30 mm) and placed in boxes with wire mesh bottoms buried to a depth of 20 cm. Soil samples were taken 6 months and 6 years after burial from soil just under the specimens (0-5 cm and 5-10 cm down from the specimens’ faces), in contact (0-5 cm) from the ends of the logs, and at a distance considered to represent background levels. After digestion in acid, samples were analysed by AAS for total chromium and copper, and arsenic and hexavalent chromium by chromo-spectrophotometric means.

Tests of the initial leachability of samples from the poles by a laboratory test (50 g wood flakes shaken for 6 h in 500 mL distilled water at pH 5.8-6.3) indicated leachability of <0.05 mg/L for Cr^{VI}, below the relevant environmental limit of 1.5 mg/L in Japan. Though leachability of arsenic was relatively higher for two of the four logs (0.32-0.44 mg/L compared to <0.05 mg/L), this was again in each case below the relevant Japanese environmental limit. Background levels of total copper, total chromium and total arsenic were respectively, ~60-70 mg/kg and 111-127 mg/kg and 4.9-6.2 mg/kg initially. There was an apparent increase in background levels of chromium and arsenic at 6 years (respectively 72-138 mg/kg and 10-12 mg/kg), but not copper (100-110 mg/kg).

After 6 months and 6 years, all soil samples were found to contain <0.05 mg/L Cr^{VI} (ie below the environmental limit). Relative to levels 5-10 cm under the logs or chips, total copper levels were slightly elevated near the ends or immediately beneath the specimens (114-133 mg/kg compared to 111-116 mg/kg at 6 months, 104-175 mg/kg compared to 96.1-108 mg/kg at 6 years). Similar results were found with chromium (72.9-109.3 mg/kg compared to 64.9-87.8 mg/kg at 6 months, 72.1-192 mg/kg compared to 68.0-103 mg/kg at 6 years) and arsenic (6.4-16 mg/kg compared to 5.7-6.4 mg/kg at 6 months, 12-33 mg/kg compared to 10-12 mg/kg at 6 years). The logs behaved differently, with two logs showing greater arsenic release. The investigators suggested that the data for arsenic were affected by differences in the acid extraction method between sampling times.

The results were interpreted by the investigators as showing that after 6 years of soil contact, concentration levels of copper, chromium and arsenic under treated logs or chips did not significantly exceed those in non-contaminated soil in the same area, and that contamination from these elements could in practice be ignored. While the soil was slightly contaminated in the immediate vicinity (0-5 cm) of treated wood, the contamination remained highly localised in soil under the prevailing conditions and duration of the study. However, the trial was conducted on a very small scale.

6.8.3.3. CCA treatment plant sludge

Gayles and Aston (1993) discussed a solidification process for the treatment of CCA treatment plant wastes in the UK, ie mixing material such as sludge with cement to immobilise copper, chromium and arsenic residues as far as possible prior to disposal to landfill.

6.8.4. Re-use as landscape mulch or soil amendment

Speir et al (1992a,b) examined the use of CCA-C treated sawdust as a soil amendment. Levels of copper, chromium and arsenic in the soil were increased significantly by a 10% amendment. However, on the basis of measured plant uptake (Section 6.6.5) and a lack of significant harmful effects on soil biochemical or biological properties (Section 7.8), the authors recommended “cautious acceptability” of amendment with CCA-treated sawdust, though further studies with different edible crops were essential and it was necessary to consider long term bioavailability of the elements as the sawdust broke down. However, it should be noted that the authors also commented that the amount of arsenic added at this amendment rate would lead to additions of arsenic (though not copper and chromium) above maximum permissible additions to uncontaminated soil in the form of sewage sludge, though the sewage sludge criteria may not be appropriate because of differences in bioavailability of the elements in treated sawdust.

Townsend et al (2003) also examined leaching from mulched CCA-treated timber with a view to its possible use for landscape purposes. Hence samples of the mulch were tested using the standard Synthetic Precipitation Leaching Procedure (SPLP) standard synthetic precipitation leachate procedure. The great majority of samples tested leached arsenic at concentrations greater than Florida’s stringent groundwater cleanup target level (GWCTL) for arsenic of 50 µg/L. There was evidence of such contamination occurring in commercially available mulch. Calculations showed that only a very low percentage of CCA-treated wood could be present to avoid exceeding various regulatory standards or guidelines for soil in Florida.

6.8.5. Other options for the disposal of waste wood and effluent

The list below points to some of published investigations of other means of handling CCA-treated wood at the end of its service life (full reference details are listed in the bibliography).

Investigations have been made into incorporating waste CCA-treated wood into other products, such as wood-cement composites and particleboard.

Various processes which have been evaluated for extracting CCA components from waste wood. The latter include solvents, acid (sulphuric, oxalic, citric etc), chelating/sequestering agents, and electrical current. There have also been various investigations to identify fungi or bacteria which are tolerant to CCA to reduce the wood volume and solubilise CCA components, and some evaluation of these to process wood waste. In general the waste wood is first chipped or ground to sawdust to assist extraction.

The use of fungi in a biosorption process to remove CCA components from CCA-contaminated wastewater (ie from diluted CCA impregnation solution, but possibly the method could also be used for leachate) has been evaluated by Legay and Labat (1997).

Wood cement composites and particleboard possibilities for recycling CCA-treated wood

Huang and Cooper (1999)	Wood cement composites using spent CCA treated wood in Canada.
Qi and Cooper (2000)	Leaching of chromium and other CCA components from wood-cement composites made with spent CCA treated wood in Canada.
Clausen et al (2000):	Properties of particleboard made from recycled CCA-treated wood in the USA.
Kartal and Clausen (2001)	Effect of remediation on the release of copper, chromium, and arsenic from particleboard made from CCA treated wood in the USA.

Extraction of CCA components from waste wood

Clausen (1997)	Enhanced removal of CCA from treated wood by *Bacillus licheniformis* in continuous culture in the USA.
Clausen and Smith (1998)	CCA removal from treated wood by chemical, mechanical, and microbial processing in the USA.
Illman et al (2000)	Bioprocessing preservative-treated wood waste wood in the USA.
Kamdem (1999)	The recycling of CCA treated wood in the USA.
Kamdem et al (1998)	Recovery of copper, chromium and arsenic from old CCA treated communities in the USA.
Kartal (2002)	Effect of EDTA on removal of CCA from treated wood in Turkey.
Kazi and Cooper (1998)	Solvent extraction of CCA-C from out-of-service wood in Canada.
Leithoff and Peek (1997)	Experience with an industrial scale-up for the biological purification of CCA-treated wood waste in Germany.
Lin and Hse (2002)	Removal of CCA from spent CCA-treated wood in the UK.
Mateus et al (2002)	Electrodialytic remediation of creosote and CCA treated timber wastes in Denmark.
Pasek and McIntyre (1993)	Treatment and recycle of CCA hazardous waste.
Stephan and Peek (1992)	Biological detoxification of wood treated with salt preservatives in Germany.

Biosorption to process CCA wood waste effluent

Legay and Labat (1997):	Biosorption of metals for wood waste effluent clean-up in France

6.8.6. Summary and conclusions regarding disposal of CCA treated wood and wood waste

Investigators in Florida in particular have expressed concern at the large volume of CCA treated wood already in use and the potential implications of various disposal pathways for the environment, particularly due to the arsenic content. Some investigators have suggested disposal options that need to be avoided or controlled. Particular concerns centre on arsenic and the potential for it to leach from treated wood and reach soil or groundwater, or to reach the atmosphere during combustion of treated wood by volatilisation or in particulate form.

Studies indicate that the amount of arsenic released to air during burning depends on the combustion conditions, but can range from ~10-90% of the arsenic retained in the wood when it is burnt. Furthermore, the ash or char may contain high levels of arsenic, copper and chromium, and possibly also dioxins and furans formed through combustion. Hence uncontrolled burning of treated wood should not occur. Various studies have been conducted and are continuing in efforts to develop combustion or pyrolysis processes that would safely dispose of the wood, preferably while obtaining energy and recovering the arsenic, copper and chromium from the wood. Studies confirm the high leaching rate likely from wood that has been broken up into mulch or pulverised, hence depending on local conditions and legislative requirements there may be a need to direct such waste to lined, rather than unlined landfills. Leaching from mulch prepared from

CCA-treated wood has been confirmed to increase soil arsenic levels and potentially also arsenic levels in plants growing in the soil, hence this use too may be inappropriate, depending again on local conditions and legislation.

Many other disposal approaches for CCA-treated timber have been considered by researchers, including manufacture of products such as wood cement composites or particleboard, re-use of timber for the same or new purposes, and extraction of CCA components from pulverised wood by various solvent, biological or other processes. In addition to disposal of treated timber at the end of its service life, similar issues may arise regarding disposal of wood waste (off-cuts, sawdust etc) generated at the treatment plant or subsequently during wood preparation, construction and maintenance. To avoid environmental contamination with vapours, smoke or ash, at no stage should CCA-treated timber be burnt in uncontrolled facilities.

6.9. LIFE CYCLE ANALYSIS OF CCA USE

6.9.1. Life cycle analysis of choice of material for utility poles in Sweden

Erlandsson et al (1992) used a model for environmental life cycle analysis to compare the environmental impact from transmission poles made alternatively of concrete, steel, aluminium, and pine wood treated with CCA-B or creosote. This approach considers the main raw material and energy inputs required for manufacture, and the pollution sources and energy use/production during operation/service and disposal. Poles made from the different materials fell into two groups regarding pollution. Those made from concrete, steel and aluminium lead mainly to emission to air during manufacture and recycling, while treated wood leads to leaching of preservatives during the operation and service phase. Wooden poles could be used to produce energy during disposal, but with CCA there remained the issue of how to convert or deposit the copper, chromium and arsenic components.

6.9.2. OECD comments

Part 1 of the OECD emission scenario documents (ESD) for wood preservatives (OECD, 2003) comments on the use of life cycle evaluation in regulatory exposure assessment. This document indicates that the life cycle of a wood preservative involves the following stages:

- production of the active substance;
- formulation of the preservative product or preparation;
- product application –preventative and curative wood treatment;
- service life – ie wood-in-service;
- waste treatment (ie when unused wood preservative products or out-of-service treated wood is disposed of as waste);
- recovery – ie secondary uses of out-of-service wood;
- contaminated sites – ie operational and non-operational treating plants.

The OECD ESD for wood preservatives focuses on product application and wood-in-service and states that disposal of wastes from treatment plants or of treated wood after service fall outside the scope of the document.

6.10. Summary and conclusions regarding environmental fate

Heavy contamination of CCA treatment sites has clearly occurred from past practices. At the sites where data have been evaluated, the heaviest soil contamination was generally confined to areas near likely sources of CCA treatment solution, with leaching of CCA components deeper into the soil reflecting soil characteristics and the extent of contamination, potentially reaching groundwater in some situations. Mobilisation of CCA elements off-site through run-off and/or leaching has also been found, with arsenic accumulating in downstream sediments. No conclusive data are available regarding off-site movement of arsenic leached from wood in service, except for situations where treated wood is directly in contact, above or adjacent to a waterbody. However, it is likely that a proportion of arsenic or other heavy metals in run-off would accumulate in downstream sediments, particularly where affected waters do not reach the ocean.

It is clear from semi-field and field studies and *in situ* evaluations that arsenic, copper and chromium can be expected to leach from CCA-treated wood in service in all sorts of terrestrial use situations, with and without ground contact. Leachability may vary widely and is affected by a wide range of interacting factors associated with the treated wood itself, the nature of the structure and the environment in which it is located. Data regarding the form in which arsenic is leached are very limited, but suggest that a high proportion of the arsenic leached may be in insoluble or bound forms dislodged from the eroding wood surface, rather than dissolved from the wood. Regardless, various alteration and degradation processes may occur subsequently in the soil.

The rate of leaching declines greatly with the completion of fixation, though reactions of CCA in the wood are known to continue slowly for some months after that point. Accelerated laboratory leaching studies then indicate that over, for example, a five day test, the rate of leaching of each element declines to a very low level. However, leaching occurs much more gradually in wood in service and there are large differences in exposure conditions. Intermittent wetting and drying may “wick” components from the interior towards the surface and exposure to UV radiation may also significantly increase leaching from treated wood. The available data suggest that leaching continues indefinitely for the life of a structure, though it is likely that the initial leaching rate in the first weeks or months in service declines to a more or less steady state. This appears to be the case even in properly treated timber and in the absence of unfavourable conditions such as soil characteristics favouring leaching.

Field studies show that arsenic, copper and chromium leached from treated wood accumulates in soil adjacent to or underneath various types of structures. However, studies with stakes, posts and poles extending for decades show that even with long periods of service, there is very little lateral movement of CCA components from their immediate vicinity. Residues in soil with various types of structure were generally found to accumulate predominantly in the soil area reached by water running down the wood surface of support posts or poles to the ground, or dripping from horizontal surfaces. However, soil concentrations declined with lateral distance from posts and poles, generally to background levels within ~10-50 cm. Soil concentrations also generally declined with depth. Greater leaching within the soil may lead to lower peak concentrations near the surface in coarse textured, low organic matter content soils, as evident in a Florida study. Greater movement in the soil may occur with saturated soils, where the arsenic may be present in the more toxic As^{III} form.

Garden edges or structures containing CCA-treated timber may leach arsenic and other CCA components into soil. In general, leached arsenic is likely to remain in soil or compost close to the wood, but it may be taken up by plants growing predominantly in the affected soil, resulting in elevated plant levels. Similarly, soil amendments or mulches containing CCA-treated wood residues may leach arsenic and other components into soil, which may then be taken up by plants. Presumably, plants growing in soil close to decks or fences could also take up elevated levels of arsenic, copper or chromium in leachate from treated timber. However, as with garden borders, in most situations the affected zone of soil is likely to be very limited. Studies investigating plants growing near CCA-treated posts have failed to find elevated CCA-component concentrations in plant tissue, possibly because the plant roots grew largely in uncontaminated soil.

A study showed that surface area to volume effects lead to much more rapid leaching of CCA components from construction debris such as sawdust, wood shavings and small off-cuts, with the rate of leaching increasing with decreasing particle size. On a construction site the reservoir of CCA contained in such debris is relatively small compared to the wood in the structure, but debris can cause localised contamination of soil or water in the areas it has fallen. The author argued that contamination of a sensitive site by CCA-treated wood debris can be avoided by construction elsewhere or by collection and removal of debris at the time of construction.

A major potential means of disposal of treated timber and treated wood waste is combustion. Studies show that, depending on the combustion conditions, 10-90% of the arsenic present in CCA-treated wood may be lost to air, either as volatilised As_2O_3 or particulate matter. Furthermore, the ash produced contains all the copper, chromium and arsenic that were present in the treated wood before burning, less any loss of arsenic to the atmosphere. Studies confirm the high leaching rate likely from wood that has been broken up into mulch or pulverised, and leaching from mulch prepared from CCA-treated wood has been confirmed to increase soil arsenic levels and potentially also arsenic levels in plants growing in the soil. Hence consideration is necessary regarding the risks to the environment of burning, burial in landfills and use for mulch or soil amendment purposes as disposal options for CCA-treated wood waste or treated timber at the end of its service life.

7. ENVIRONMENTAL EFFECTS

7.1. INTRODUCTION

7.1.1. Overview

Data on the toxicity of various forms of arsenic to birds, fish, aquatic invertebrates, aquatic plants, terrestrial invertebrates, mammals and terrestrial plants were presented and included summaries of several studies on the toxicity of CCA-C leachate to the water flea and mysid shrimp. The latter are assessed in some detail below. Studies provided on arsenic, chromium and copper that did not relate directly to use of CCA were, in general not assessed in any detail for this review. However, the referenced results for arsenic are included in the Tables.

As already noted in this report, CCA-treated wood is used in marine and estuarine situations (e.g. piers), but this review concentrates on environmental exposure arising from the wood treatment/fixation process and use in terrestrial situations, with some examination of the disposal of treated material. Consequently, only impact on freshwater systems is considered at this time.

Environmental aspects of arsenic, chromium and copper have been reviewed in detail in the International Programme on Chemical Safety’s Environmental Health Criteria (EHC) series as Arsenic: EHC 18 (WHO, 1981), Arsenic and Arsenic Compounds: EHC 224 (WHO, 2001), Chromium: EHC 61 (WHO, 1988) and copper: EHC 200 (WHO, 1998). The reader is referred to these publications for additional specific information. Additionally, the Canadian Government (Canadian Environmental Protection Act, 1993) has released a report on arsenic and its compounds which addresses, *inter alia*, ecotoxicology of arsenic exposure and which provides summary information on the effects of inorganic arsenic on marine and freshwater environments, amphibians [noted as "quite sensitive" to arsenic], benthic organisms, terrestrial organisms, plants, birds and mammals.

7.1.2. Arsenic

ANZECC and ARMCANZ (2000) indicate many factors affect arsenic toxicity to aquatic organisms, such as the valency state. As^{III} is generally more toxic than As^{V}, but it is less common in seawater. Arsenic can bioconcentrate in marine organisms, but in the form of less toxic, easily excretable organo-arsenical compounds. Hence secondary poisoning is unlikely and arsenic tends not to biomagnify up the food chain. The toxicity of As^{V} increases with temperature but is independent of salinity. As^{III} is removed by sulphides but As^{V} is removed by clays. Chromium (Cr^{III}) reduces arsenic toxicity.

A 1996 report conducted for the US Department of Energy (US Department of Energy, 1996) for the purpose of presenting toxicological benchmarks for assessment of effects of certain chemicals on mammalian and avian wildlife species noted that the toxicity of inorganic compounds containing arsenic depends on the valence or oxidation state of the arsenic as well as on the physical and chemical properties of the compound in which it occurs. Trivalent arsenic (As^{III}) compounds are generally more toxic than pentavalent arsenic (As^{V}) compounds, and the relative toxicity of the trivalent and pentavalent forms are also possibly affected by factors such as water solubility, with the more toxic compounds generally more water soluble.

7.1.3. Chromium

As with arsenic, chromium toxicity is affected by valency with Cr^{III} generally less toxic than Cr^{VI}. While the toxicity of Cr^{VI} increases in fresh water at lower pH, that of Cr^{III} decreases with increasing hardness and pH, while both are generally more toxic at higher temperatures (ANZECC and ARMCANZ 2000).

7.1.4. Copper

Copper is an essential nutrient element and many aquatic organisms can regulate it to some degree. Toxicity can occur when uptake exceeds the rate of detoxification and excretion, which is more important than absolute body burden. Copper toxicity decreases with increasing hardness, pH and salinity. Copper is strongly adsorbed to suspended material with complexation increasing at higher pH, but the relationship to toxicity is complicated (ANZECC and ARMCANZ 2000).

7.2. BIRDS

Table 44. Summary of avian toxicity studies.

Species	Route	Duration	Parameter and Result	Formulation	Reference
Bobwhite quail (176-217 g body wt)	Oral	Single dose + 14 d obs	LD50 = 46 (25, 100), NOEL = 12.5, LOEL = 25 mg/kg	76.1% Arsenic acid (40.5% As)	Campbell et al. (1990)
Bobwhite quail chicks (10 d old)	Diet	8 d	LC50 = 432 (no 95% confidence limits specified) mg/kg food	76.1% Arsenic acid (40.5% As)	Long et al. (1990)

Arsenic acid is categorised as highly toxic (LC50 = 10 to 50 mg/kg body weight) via both acute oral and dietary exposure (LC50 = 51 to 500 ppm in the feed) routes to bobwhite quail. The LD50 and LC50 values found were of a similar magnitude to those reported in the IPCS report on arsenic (WHO, 2001) for mallard (LD50 of 323 mg As/kg body weight) and Californian quail (LD50 of 47.6 mg As/kg body weight) exposed to sodium arsenite.

7.3. FISH

Table 45. Summary of fish toxicity studies.

Organism	Life Stage	Test Type	Time	LC50 and 95% confidence limits (mg/L)*	Formulation (% a.i.)	Reference
Rainbow trout	4.1 cm, 0.82 g	Static	96 h	72 (51, 110)	76.1% Arsenic acid (40.5% As)	LeLievre (1990b)
Sheepshead minnow	2.4 cm, 0.27 g	Static	96 h	28 (22, 35)	76.1% Arsenic acid (40.5% As)	LeLievre (1990c)
Bully (*Gobiomorphus cotidianus*)	Juvenile	Static	96 h	LC50 = 133 (116, 154)	As^V	Hickey et al. (2000)**
Bully (*Gobiomorphus cotidianus*)	Juvenile	Static renewal	18 d	NOEC = 32, LOEC = 56, LC50 = 66.9 (95% limits not reported)	As^V	Hickey et al. (2000)**
Jollytail (*Galaxias maculatus*)	Juvenile	Static	96 h	LC50 = 56.8 (48.9, 64.5)	As^V	Hickey et al. (2000)**
Jollytail (*Galaxias maculatus*)	Juvenile	Static renewal	21 d	NOEC = 18, LOEC = 32, LC50 = 28.9 (23.5, 33.4)	As^V	Hickey et al. (2000)**
Fathead minnow	Embryos and fry	Flow through	35 d	NOEC = 0.97, LOEC = 1.9, MATC = 1.4 mg/L. [Values based on larval survival, identified as the most sensitive biological parameter].	Arsenic acid	Machado (1991) reviewed by US EPA

*LC50 unless stated otherwise. **As cited in Markich et al. (2002).

The LC50 values for arsenic acid [AsH_3O_4] indicate it is slightly ($10 \leq LC50 \leq 100$ mg/L) toxic to the fish species tested.

The bully and jollytail LC50 and NOEC values cited in Markich et al. indicate slight to practically no toxicity to acute exposure and slight to very slight toxicity through chronic exposure, with the observation made that the fathead minnow NOEC for arsenic acid exposure is approximately one order of magnitude less than the NOECs reported for the bully and the jollytail.

7.4. AQUATIC INVERTEBRATES

Table 46. Summary of toxicity studies on aquatic invertebrates.

Organism	Test Type	Time	EC50 and 95% confidence limits of Cu/Cr/As (µg a.i./L, unless stated otherwise)	Formulation (% a.i.)	Reference
Water flea (*D. magna*)	Static	48 h	15 (12, 19) mg/L	76.1% Arsenic acid (40.5% As)	LeLievre (1990d)

Organism	Test Type	Time	EC50 and 95% confidence limits of Cu/Cr/As (µg a.i./L, unless stated otherwise)	Formulation (% a.i.)	Reference
Quahog clam	Static	48 h	EC50 = 16 mg/L (no 95% confidence limits), NOEC = 12, LOEC = 17 mg/L	76.1% Arsenic acid (40.5% As)	Dionne (1991)
Mysid shrimp	Static	96 h	LC50 = 2.0 (0.85, 4.8) mg/L	76.1% Arsenic acid (40.5% As)	LeLievre (1990a)
Mysid shrimp	Static renewal	7 d	LC50 = Cu 174 (80, 320), Cr 10.3 (4.7, 19), As 250 (115, 460), 10‰ salinity – see assessment.	CCA-C leachate	Putt (1997a)
Mysid shrimp	Static renewal	7 d	NOEC = Cu <22, Cr <3.1, As <4.2, LOEC = Cu 22, Cr 3.1, As 4.2, 32‰ salinity – see assessment.	CCA-C leachate	Putt (1997b)
Water flea	Static renewal	21 d	NOEC = Cu 5.9, Cr 2.2, As 22, LOEC = Cu 11, Cr 3.6, As 4.5 – see assessment.	CCA-C leachate	Putt (1997c)
Water flea	Flow through	21 d	NOEC = 20, LOEC = 38	Arsenic acid	McNamara (1991)
Water flea (*Daphnia magna*)	Static	96 h	LC50 = 3.0 (2.7, 3.3) mg/L	As^{III}	Hickey et al. (unpublished) **
Amphipod (*Paracalliope fluviatilis*)	Static	96 h	LC50 = 3.0 (2.1, 3.4) mg/L	As^{III}	Hickey et al. (unpublished) **
Amphipod (*Chaetocorophium lucasi*)	Static	96 h	LC50 = 1.1 (0.9, 1.4) mg/L	As^{III}	Hickey et al. (unpublished) **
Midge (*Chironomus* sp)	Static	96 h	LC50 = 9.8 (8.8, 10.8) mg/L	As^{III}	Jeyasingham and Ling (2000) **
Midge (*Chironomus zealandicus*)	Static	96 h	LC50 = 16.2 (13.8, 18.6) mg/L	As^{III}	Jeyasingham and Ling (2000) **
Midge (*Polypedilum pavidis*)	Static	72 h	LC50 = 6.2 (5.2, 7.2) mg/L	As^{III}	Jeyasingham and Ling (2000) **
Mollusc (*Sphaerium novaezelandiae*)	Static	96 h	EC50 = 12.2 (10.5, 14.2) mg/L for reburial	As^{III}	Hickey et al. (unpublished) **
Worm (*Lumbriculus variegatus*)	Static	96 h	LC50 = 18.9 (16.6, 21.4) mg/L	As^{III}	Hickey et al. (unpublished)
Water flea (*Daphnia magna*)	Static	96 h	LC50 = 6.4 (5.8, 7.0) mg/L	As^{V}	Hickey et al. (unpublished) **
Water flea (*Ceriodaphnia dubia*)	Static renewal	7 d	EC50 = 0.491 mg/L (95% confidence limits not reported), NOEC = 0.32 mg/L	As^{V}	Hickey et al. (2000) **
Amphipod (*Chaetocorophium lucasi*)	Static	96 h	LC50 = 9.4 (7.4, 16.5) mg/L	As^{V}	Hickey et al. (unpublished) **
Amphipod (*Paracalliope fluviatilis*)	Static renewal	32 d	LC50 =0.232 (0, 0.724) mg/L	As^{V}	Hickey et al. (2000) **
Amphipod (*Paracalliope fluviatilis*)	Static	48 h	LC50 =8.9 (7.6, 10.7) mg/L	As^{V}	Hickey et al. (2000) **

Organism	Test Type	Time	EC50 and 95% confidence limits of Cu/Cr/As (µg a.i./L, unless stated otherwise)	Formulation (% a.i.)	Reference
Midge (*Chironomus* sp)	Static	96 h	LC50 = 104 (98, 110) mg/L	As^V	Jeyasingham and Ling (2000) **
Midge (*Chironomus zealandicus*)	Static	72 h	LC50 = 184 (150, 218) mg/L	As^V	Jeyasingham and Ling (2000) **
Midge (*Polypedilum pavidis*)	Static	48 h	LC50 = 21.4 (12.2, 30.6) mg/L	As^V	Jeyasingham and Ling (2000) **
Mollusc (*Sphaerium novaezelandiae*)	Static	96 h	EC50 = 88.5 (76.3, 103)	As^V	Hickey et al. (unpublished)**
Worm (*Lumbriculus variegatus*)	Static	96 h	LC50 = 54.1 mg/L (41.8, 62.4)	As^V	Hickey et al. (unpublished) **
Water flea	Static renewal	21 d	NOEC = Cu 9.1, Cr 22, As 26 mg/L, LOEC = Cu 15, Cr 36, As 42 mg/L – see assessment.	CCA Type C	Sims (1993)

**As cited in Markich et al. (2002).

7.4.1. Acute toxicity

Arsenic acid showed moderate toxicity to the mysid [1 < LC50 ≤ 10 mg/L] and slight toxicity to the water flea [10 = LC50 ≤ 100 mg/L] while the water flea NOEC indicates moderate chronic toxicity [NOEC in the range 10 to 100 mg/L]. The As^{III} results indicated slight to moderate toxicity to the organisms tested. *Ceriodaphnia dubia* and the amphipod, *Paracalliope fluviatilis*, were the most sensitive aquatic invertebrates tested with respect to As^V toxicity with the respective EC50s of 0.491 and 0.232 mg/L indicating this valence state of arsenic was highly toxic to these organisms [EC50 of 0.1 to 1 mg/L].

7.4.2. Chronic toxicity

7.4.2.1. Water flea, static renewal 1

Putt (1997c) exposed daphnids to mean measured concentrations of copper, chromium and arsenic up to 11, 3.6 and 45 µg/L (speciation not specified) for 21 d in a static renewal study. Concentrations in the water control were 1.4, 1.0 and 0.56 µg/L while those in the untreated wood control were 5.6, 0.39 and 2.1 µg/L, respectively. Only a partial report was submitted so full methods and results were not available for assessment. The only water quality parameter reported was the water temperature of 20-23°C.

After 21 d, survival was >90% in all treatments giving an LC50 greater than the highest treatment. Reproduction and mean total length were not significantly different to the water controls and no neonates were observed to be immobilised. However, the mean dry weight of daphnids in the highest treatment was significantly different to the water control, but not the untreated wood control, giving a NOEC of 5.9, 2.2 and 22 µg/L and LOEC of 11, 3.6 and 45 µg/L of copper, Chromium and arsenic, respectively. As the full report was not submitted for assessment, these results must be treated with some caution.

7.4.2.2. Water flea, static renewal 2

Sims (1993) exposed neonate *Daphnia magna* to CCA Type C at mean measured concentrations up to 15.5, 37.9 and 44.6 mg/L of copper, chromium and arsenic, respectively. The methodology followed OECD Test Guideline 202b with renewal of treatment solutions three times per week. The control solutions contained a slightly higher concentration of CCA than the lowest tested concentration, presumably due to some contamination. Ten daphnids were housed in each beaker with four replicates per treatment for a total of 40 animals per treatment. Water quality parameters during the test were temperature of 18.7-20.5°C, pH 7.6-8.4, hardness 228-292 mg/L as $CaCO_3$ and dissolved oxygen 87-107% saturation under a 14 h light photoperiod.

Based on adverse effects on fecundity, the NOEC was 9.06, 22.1 and 26.1 mg/L of copper, chromium and arsenic, respectively, with a LOEC of 14.6, 35.6 and 41.8 mg/L. Mortality of the parents was observed at 45% in the highest treatment after 21 d.

7.4.2.3. Mysid shrimp, low salinity

A partial report (Putt 1997a) examined mysid shrimp (*Mysidopsis bahia*) exposed to serial dilutions of CCA-C leachate at 24-26°C and 10‰ salinity for 7 d. There was no indication of any recognised protocol or test guideline being followed. The highest mean measured concentrations of copper, chromium and arsenic in the treatments (speciation not reported) were 320, 19 and 460 µg/L, respectively, while that in the water control (3.2, 0.85 and 1.9 µg/L) and untreated wood leachate control (15, 1.3 and 4.7 µg/L) were much lower but still measurable. The highest treatment corresponded to leachate diluted to 16% of the original strength which leached 209, 15.3 and 255 mg of copper, chromium and arsenic per m^2 of treated wood.

After 7 d, 90 and 88% survival were observed in the water control and wood control, respectively, while fecundity was 88 and 100%. Growth of mysids in the water control was below standard guidelines, presumably because the salinity was 10‰ and at the lower end of the recommended range. Slow growth was also shown by only 22% of the water control mysids being identified as females after 7 d compared to the expected 50%. Given these indications and the lack of full methodology and results, the outcomes of this study must be treated with caution.

The reported LC50 was given as 174, 10.3 and 250 µg/L of copper, chromium and arsenic, respectively (8.7% of the original leachate) while the 95% confidence limits of 80, 4.7 and 115 and 320, 19 and 460 µg/L of copper, chromium and arsenic were calculated by the imprecise binomial method. The NOEC and LOEC based on survival were 80, 4.7 and 115 and 160, 9.5 and 230 µg/L of copper, chromium and arsenic, respectively.

7.4.2.4. Mysid shrimp, high salinity

Putt (1997b) apparently followed the same methodology as Putt (1997a) except used a salinity of 32‰ and temperature of 25-27°C. The highest concentrations of copper, chromium and arsenic tested were 22, 3.1 and 4.2 µg/L, respectively, in the 1% leachate. Mean measured concentrations of the three elements in the untreated wood control were 22, 1.6 and nondetectable (<1.9) µg/L, respectively.

After 7 d exposure, ≥95% survival was observed in all treatments while the untreated wood control and water control had 85 and 92%, respectively, which were not significantly different. Therefore the 7-d LC50 was >22, >3.1 and >4.2 µg/L of copper, chromium and arsenic, respectively. However, fecundity in the two highest treatments was only 22-23% and presumed to be statistically significantly different from controls (46-60%) although insufficient results were presented to allow confirmation. Therefore a worst case scenario of a 7-d LOEC of 22, 3.1 and 4.2 µg/L of copper, chromium and arsenic, respectively, and NOEC of less than these concentrations will be assumed.

7.4.2.5. Freshwater sediment invertebrates

MacDonald et al (2000 – cited by Ingersoll et al, 2000 – original not seen) listed a range of freshwater sediment quality guidelines for copper, chromium and arsenic based on 10-14 day or 28-42 day toxicity tests with the amphipod *Hyalella azteca* and chironomids *Chironomus tentans* or *C. riparius*. These were used to calculate a "consensus-Based Probable Effect Concentration" (PEC, above which harmful effects are likely to be observed) for sediment toxicity for each of a range of substances, including copper, chromium and arsenic (Table 47). The species of metal present in sediment (eg As^{III} or As^{V}) was not specified. The values for these three heavy metals were considered reliable as they were each based on >20 samples and a >75% correct identification as toxic.

Table 47. Consensus-based Probable Effect Concentrations (PECs) for copper, chromium and arsenic from previously published sediment quality guidelines (McDonald et al, 2000 – cited by Ingersoll et al, 2000).

Substance	Individual guideline values from which the calculated value was obtained	Consensus-Based PEC
Copper	197, 110, 86, 390, 100	149
Chromium	90, 110, 100, 145, 120	111
Arsenic	17, 33, 17, 85, 48	33.0

7.5. AQUATIC PLANTS

Table 48 and Table 49 present summaries of, respectively, the freshwater and marine aquatic plant toxicity results compiled by the Department of the Environment and Heritage.

Table 48 Summary of toxicity studies on freshwater aquatic plants cited in Markich et al. (2002) or, for two green algae, Levy (2002).

Organism	Test Type	Time	Parameter and 95% confidence limits (mg/L)	Formulation (% a.i.)	Reference
Green alga (*Chlorella* sp)	Static	72 h	E_bC50 = 33 (27, 35) E_rC50 = 47 (44, 48)	As^{III}	Stauber (unpublished)
Green alga (*Monoraphidium arcuatum*)	Static	72 h	E_bC50 = 16 (9.6, 20)	As^{III}	Stauber (unpublished)
Green alga (*Pseudokirchneriella subcapitata*)	Static	72 h	E_bC50 = 24 (17, 31)	As^{III})	Stauber (unpublished)
Green alga (*Chlorella* sp isolate 12)	Static	72 h	E_rC50 = 25.2 (23.3-29.2)	As^{III}	Levy (2002)
Green alga (*Monoraphidium arcuatum*)	Static	72 h	E_rC50 = 14.6 (11.7, 17.7)	As^{III}	Levy (2002)
Green alga (*Pseudokirchneriella subcapitata*)	Static	72 h	E_bC50 = 18 (0, 23)	As^{III}	Stauber et al (unpublished)
Green alga (*Chlorella* sp)	Static	72 h	E_bC50 = 5.2 (3.7, 6.3) E_rC50 = 13 (11, 18)	As^V	Stauber (unpublished)
Green alga (*Monoraphidium arcuatum*)	Static	72 h	E_bC50 = 128 (100, 153)	As^V	Stauber (unpublished)
Green alga (*Pseudokirchneriella subcapitata*)	Static	72 h	E_bC50 = 132 (110, 152)	As^V	Stauber (unpublished)
Duckweed (*Lemna disperma*)	Static	28 d	EC50 = 150 (95% confidence limits not reported)	As^V	Brown and Rattigan (1979)
Elodea (*Elodea canadensis*)	Static	28 d	EC50 = 850 (95% confidence limits not reported)	As^V	Brown and Rattigan (1979)
Green alga (*Chlorella* sp)	Static	72 h	E_rC50 = 13 (11, 18) E_bC50 = 5.2 (3.7, 6.2)	As^V	Stauber et al (unpublished)
Green alga (*Monoraphidium arcuatum*)	Static	72 h	E_rC50 = 0.275 (0.166, 0.383) E_bC50 = 0.128 (0.100, 0.153)	As^V	Levy (2002) Stauber et al (unpublished)
Green alga (*Pseudokirchneriella subcapitata*)	Static	72 h	E_bC50 = 0.127 (0.105, 0.147), 0.15 mg/L PO_4^{-3} E_bC50 = 0.181 (0.127, 0.262), 1 mg/L PO_4^{-3}	As^V	Stauber et al (unpublished)

Exposure to trivalent arsenic gave EC50 values between 14 and 47 mg/L while As^V exposures resulted in EC50s of 0.127 to 850 mg/L. The freshwater plant table shows there is varying sensitivity to arsenic exposure with the green algae *Monoraphidium arcuatum* and *Pseudokirchneriella subcapitata* being the most sensitive algae with respect to As^V exposure.

Table 49 Summary of toxicity studies on marine aquatic plants cited in Markich et al. (2002).

Organism	Test Type	Time	Parameter and 95% confidence limits (mg/L)	Formulation (% a.i.)	Reference
Diatom (*Nitzschia closterium*)	Static	72 h	E_bC50 = 0.355 (0.271, 0.442)	As^{III}	Stauber et al (unpublished)
Alga (*Phaeodactylum tricornutum*)	Static	72 h	E_bC50 = 7.9 (7.6, 8.2), range finding test only	As^{III}	Stauber et al (unpublished)
Alga (*Minutocellus polymorphus*)	Static	72 h	E_bC50 = 3.94 (3.93, 3.95), range finding test only	As^{III}	Stauber et al (unpublished)
Alga (*Dunaliella tertiolecta*)	Static	72 h	E_bC50 > 50, range finding test only	As^{III}	Stauber et al (unpublished)
Diatom (*Nitzschia closterium*)	Static	72 h	E_bC50 = 78 (68, 87)	As^{V}	Stauber et al (unpublished)
Diatom (*Nitzschia closterium*)	Static	72 h	E_bC50 > 50	As^{V}	Stauber (unpublished)
Alga (*Phaeodactylum tricornutum*)	Static	72 h	E_bC50 = 2.9 (2.4, 3.4), range finding test only	As^{V}	Stauber et al (unpublished)
Alga (*Minutocellus polymorphus*)	Static	72 h	E_bC50 > 50, range finding test only	As^{V}	Stauber et al (unpublished)
Alga (*Dunaliella tertiolecta*)	Static	72 h	E_bC50 = 2.98 (2.89, 3.06), range finding test only	As^{V}	Stauber et al (unpublished)
Alga (*Tetraselmis* sp)	Static	72 h	E_bC50 = 49.0, range finding test only	As^{V}	Stauber et al (unpublished)

The EC50 values for As^{III} ranged from 0.355 to >50 mg/L and for As^{V}, 2.9 to >50 mg/L, indicative of similar toxicity to arsenic of both valencies. The most sensitive marine organism was the diatom, *Nitzschia closterium*, with greater toxicity to As^{III} reported compared to that seen following As^{V} exposure.

No studies were presented on the toxicity of CCA leachate to aquatic plants.

7.6. TERRESTRIAL INVERTEBRATES

Table 50 Summary of toxicity studies to terrestrial invertebrates

Organism	Test Type	Time	Parameter and 95% confidence limits (mg/kg soil)	Formulation	Reference*
Minute grey commoner (*Proisotoma minuta*)	Synthetic soil	28 d	EC50 = 4.4 (2.2, 8.4) for reproduction	As^{III}	Vaughan and Greenslade (1998)
Sandy jumper (*Sinella communis*)	Synthetic soil	28 d	NOEC = 0.38, EC50 = 9.9 (7.0, 14) for reproduction	As^{III}	Vaughan and Greenslade (1998)
White springtail (*Folsomia candida*)	Synthetic soil	28 d	EC50 = 3.0 (2.2, 4.0) for reproduction	As^{III}	Vaughan and Greenslade (1998)
Pasture worm (*Aporrectodea caliginosa*)	Static	28 d	NOEC = 40, LOEC = 60 for growth of juveniles	As^{V}	O'Halloran and Booth (2000)
Pasture worm (*Aporrectodea caliginosa*)	Static	28 d	NOEC = 50, LOEC = 100, EC50 = 45 (20, 102) for growth of adults	As^{V}	O'Halloran and Booth (2000)
Red wriggler worm (*Eisenia andrei*)	Static	14 d	LC50 = 472 (440, 510)	As^{V}	Vaughan and Greenslade (1998)
White springtail (*Folsomia candida*)	Static	28 d	NOEC = 10, EC50 = 119 (95, 149) for reproduction	As^{V}	Vaughan and Greenslade (1998)
Woodlouse (*Porcellio scaber*)	Static	14 d	NOEC = 200, LOEC = 300, LC50 = 207 (152, 285)	As^{V}	O'Halloran and Booth (2000)
Earthworm (*Lumbricus terrestris*)	Forest soil	Various	2 to 10 d LC50 values 400 to 100 µg/g soil dry weight. See assessment.	Arsenate (As^{V})	Meharg et al. (1998)

*As cited in Markich et al. (2002) except Meharg et al. (1998).

7.6.1. Toxicity of CCA leachate

Crumière et al. (2002) treated radiata pine decking boards with CCA type C (86, 148 and 133 g/kg copper, chromium and arsenic, respectively) to the H3 above ground retention standard before exposing them to natural rainfall in urban Brisbane. The boards (surface area not specified) were exposed 14 months after reaching equilibrium moisture content. Runoff rainfall was collected, analysed and stored prior to application to soil. An area (0.23 m^2 replicated twice) of mown lawn on a clay loam (pH 5.2, 10.9% OC) was treated with leachate water on 15 June (29.5 mm) and 1 July 2001 (10 mm). The leachate contained 0.73-0.85, 0.47-0.58 and 1.05-1.37 mg/L of copper, chromium and arsenic, respectively, but resulting soil concentrations were not given. Soil samples were taken at various times up to 12 d after the second watering. Invertebrates were extracted from the soils and identified.

Of the >13,000 invertebrates collected, mites (84%) and springtails (8%) were predominant. Analyses of the community data and similarity indices found no significant effect of CCA leachate on the density of mites, although the community structure and diversity was altered. It was not determined if this was a permanent change or indeed an adverse effect given the identification of mites was only at the family level.

7.6.2. Toxicity of CCA sawdust to soil invertebrates

Comfort (1993) investigated, *inter alia*, the effect of sawdust from CCA treated timber on soil invertebrates. Sawdust from CCA treated timber was placed in piles of ~300 g directly on foot-trampled vegetation in a wilderness area. The piles were approximately one metre apart with sawdust from untreated wood similarly distributed to act as a control. Soil samples from beneath the sawdust piles were taken 103 and 195 days later and soil invertebrates counted and identified to at least the family level. Of the eight orders of invertebrates present, three had higher numbers for the untreated sawdust – these were Arthopleona [a sub-order of the Collembola, primitive invertebrates, sometimes known as "springtails"], Hemiptera [the "true" bugs] and Hymenoptera ["membrane-winged" insects such as bees, ants, and wasps.]. Overall, there were a total of 89 individual invertebrates [from six Orders] from the CCA treated sawdust areas and 126 [from eight Orders] from the untreated sawdust areas. The report also noted that there was no difference in the germination rate of *Leptospermum scoparium* placed beneath CCA treated sawdust or untreated sawdust in a glass house experiment. The report concluded, *inter alia*, that efforts should be made to minimise the amount of sawdust generated in the field and that such sawdust should be disposed of in the same way as CCA treated off-cuts [at that time at least, disposed of at local municipal tips] – in the field, sawdust was not always collected.

7.7. MAMMALS

Hullinger et al. (1998) investigated the poisoning of seven cows (four of which died) in the USA due to ingestion of ash from the burning of CCA-treated fence posts on a farm. Pathologic examinations of the dead cows found evidence consistent with arsenic toxicosis such as renal and hepatic disease, hemorrhagic gastroenteritis and arsenic in the liver (4.2 mg/kg) and rumen contents (105 mg/kg) along with symptoms of weakness and diarrhea. Normal concentrations in tissue should be <0.5 mg/kg. A sample of unburnt wood from the ash site contained 1,850 mg/kg arsenic while five samples of ash contained "much higher" levels (not quantified). Arsenic was not detectable in feed, plants, pond water and lagoon sediment in the pasture area. The authors suggest that arsenic provided a salty taste to which the cows were likely attracted.

The IPCS report on arsenic poisoning noted:

- cases of arsenic toxicosis in seven of a herd of 75 cattle – possibly through accidental poisoning;
- five horses dying after being fed grass cuttings that had been given an arsenic treatment; and
- two cases of deaths of white-tailed deer through exposure to arsenic by a now replaced arsenical debarking of trees and a misuse situation where arsenic was sprayed to control a weed and the deer grazed the treated areas.

7.8. SOIL MICROORGANISM PROCESSES

Yeates et al. (1994) reported that at a site that had been moderately to heavily contaminated with copper [0-5 cm soil layer 109-835 mg/kg; control soil 19 mg/kg], chromium [0-5 cm soil layer 109-739 mg/kg; control soil 47 mg/kg] and arsenic [0-5 cm soil layer, 161-790 mg/kg; control soil 27 mg/kg], all biological parameters measured, e.g. respiration, nitrification, enzymatic activity and nematode, enchytraeids and earthworm activity, showed correlations with levels of copper, chromium and arsenic present. Contamination of pasture soil at 100 mg/kg of copper, chromium and arsenic were reported not to cause significant depression of biological activity, whereas at 400 mg/kg, there was some depression reported while at 800 mg/kg, normal processes were said to be inhibited. The contamination was caused by a timber preservative containing the metals.

Speir et al (1992b) investigated the effects of CCA residues in soil following amendment with 10% v/v CCA-treated sawdust on soil biochemical and biological properties (see corresponding plant uptake study, Section 6.6.6). With the levels of soil contamination present (increased total soil concentrations by 45, 136 and 63 mg/kg for copper, chromium and arsenic, respectively), there were few negative effects attributable to the CCA amendment on soil respiration, microbial biomass C, enzyme activities, indices of N mineralisation and nitrification, numbers of nematodes, total microbial numbers and numbers of selected actinomycetes. Any negative effects that did occur were generally non-significant. The authors concluded that the results warrant a cautious acceptability of CCA-treated sawdust as a mulch or garden amendment. However, Speir et al (1992a) also noted that the amount of arsenic added at this amendment rate would lead to additions of arsenic above maximum permissible additions to uncontaminated soil in the form of sewage sludge, though the sewage sludge criteria may not be appropriate because of differences in bioavailability of the elements in treated sawdust.

7.9. TERRESTRIAL PLANTS

7.9.1. Vegetables in contaminated soil

Grant and Dobbs (1977) grew dwarf French bean (*Phaseolus vulgaris*), carrots (*Daucas carota sativa*) and tomatoes (*Lycopersicon esculentum*) in potting compost (pH 7.3, no other characteristics specified) spiked with CCA (containing 8.9, 15.9 and 11.4% copper, chromium and arsenic, respectively). The control (treatment A) contained total copper, chromium and arsenic at 37, 25 and 14 ppm, respectively. Treatments B, C, D and E contained total copper, chromium and arsenic concentrations of 37, 28 and 10 ppm, 52, 53 and 24 ppm, 250, 380 and 200 ppm, and 1900, 3100 and 1700 ppm, respectively. Seeds were planted in pots in a greenhouse and kept moist with rainwater but no growing conditions or rainwater analyses were provided. Unspecified amounts of liquid fertiliser were added 45 d after sowing and at weekly intervals thereafter. After germination counts were made, pots were thinned to one plant with measurements of plant growth made at various times where practical. After 27 d (for beans), 91 d (carrots) or 105 d (tomatoes), crop weights were recorded before sampling for elemental analysis (Section 6.6.10).

No germination occurred in any of the crops at the highest treatment level (treatment E). Maximum germination of each crop occurred in the control. Germination % did not follow a consistent pattern with soil CCA levels below the highest level, but in some cases was substantially reduced at intermediate treatment levels (most notably, carrots in treatment C). However, treatment D increased the number of days to maximum germination of beans to 20 d compared to 15 d in controls, with an increasing trend for the intermediate treatment levels.

After 27 d, bean stem height and leaf length statistically decreased with higher concentrations of metals but the NOEC and LOEC were not specified. However, it is likely from the data that treatment C did significantly reduce these parameters while also causing leaf chlorosis and necrotic lesions on the stems. Crop weight of the beans appeared significantly affected by treatment C, and there was no crop with treatment D. Growth of carrots (number of fully expanded leaves) was adversely affected by the same treatment at 69 d after treatment (DAT), but had recovered to control levels by 91 DAT. However, the yield of carrots appeared significantly affected by treatments C and D. Tomato stem height showed the same trend of adverse effects at 34 DAT that dissipated by 62 DAT and were still absent at 105 days, with no effect on yield of tomatoes. An increased tendency to early wilting was noted among tomato plants with treatments C and D. This was noted to be consistent with previously reported symptoms of arsenic toxicity (thought to be due to plasmolysis or rotting of the roots), but that it may also have been a consequence of increased salt concentration in the soil.

Perennial ryegrasses (*Lolium perenne*) and bent grass (*Agrostis tenuis*) tested under the same conditions failed to germinate at the highest treatment level. Insufficient replication was available for inferences to be drawn regarding germination at lower treatment levels, but visual observations indicated that their growth was similar in those treatments.

7.9.2. Carrots in contaminated soil

Carrots were grown in soils contaminated with CCA at levels giving 6.5-917 µg arsenic/g dry soil and 11.0-811 µg Cu/g for an arsenic bioavailability and speciation study (Helgesen and Larsen, 1998 – see Section 6.6.9). There was a pronounced depression in growth evident in the height of the tops at concentrations from 6.5-338 µg arsenic/g (11.0-251 µg Cu/g), and no growth at higher concentrations (406-917 µg arsenic µg/g). The carrot tops were wilted and yellow in soils with 93.3 and 338 µg arsenic/g (125-251 µg Cu/g). Root length also decreased, from approximately 12 cm in uncontaminated soil (6.5 µg arsenic and 11 µg Cu/g) to 10, 8 and 5 cm as arsenic content in the soil increased from 30.0 to 93.3 to 338 µg/g (Cu 39.9, 125 and 251 µg/g). The authors concluded that the observed failure of the crops may have been caused by phytotoxic effects of arsenic or copper. A further possible influence is that the texture/structure of the soil was affected by increasing levels of contaminated soil from the former timber preservation plant, which was added to uncontaminated soil in various ratios to produce the differing levels of contamination evaluated (see Section 6.6.9).

7.9.3. Seedlings in treated plant boxes

Arsenault (1975) cited results by Christensen (1967 – not seen) of the effect of CCA treated plant boxes on a variety of plants. There was a slight effect on root development which was minimised if the boxes were washed after treatment. There was no effect on the roots of tomatoes and no evidence of any effect of residues from this source on plant top development.

7.9.4. Ryegrass in contaminated soil

Bergholm (1990) grew ryegrass in sandy clay loam (pH 5.8, 5.5% OC) and loamy sand (pH 4.6, 6.9% OC) soils with various amounts of copper, chromium and arsenic made by mixing clean and contaminated soil from two Swedish timber treatment plants. No details were given on incubation conditions during growth or other analytical methods. Growth decreased when the soil water concentration of arsenic exceeded about 0.25 mg/L in both soils with complete inhibition at about 1 mg/L. The uptake rate was found to be dependent on the soil type with about three times the uptake from the loamy sand than from the sandy clay loam; this was suggested to be due to the different "releasing intensity" of arsenic.

Table 51 Summary of toxicity studies on terrestrial plants

Organism	Test Type	Time	Parameter and 95% confidence limits (mg/kg soil)	Formulation	Reference*
Lettuce (*Lactuca sativa*)	Static	120 h	EC50 = 6.2 (5.4, 7.0) for seed germination	As^{III}	Vaughan and Greenslade (1998)
Lettuce (*Lactuca sativa*)	Static	120 h	NOEC = 12, EC50 = 26 (24, 28) for seed germination	As^{V}	Vaughan and Greenslade (1998)
Lettuce (*Lactuca sativa*)	Static	14 d	NOEC = 25, LOEC = 50 for shoot weight	As^{V}	O'Halloran and Booth (2000)
Millet (*Panicum milliaceum*)	Static	14 d	LOEC = 100, EC50 = 29 (13, 61) for shoot weight	As^{V}	O'Halloran and Booth (2000)
Vetiver grass (*Vetiveria zizanioides*)	Static	84 d	EC50 = 237 (143, 349), MDEC = 125 for shoot weight	As^{V}	Truong (2000)

*As cited in Markich et al. (2002).

7.10. Conclusions regarding environmental effects

Limited data are available for CCA, so results for arsenic have also been considered.

Arsenic acid consumption, either by acute exposure or through the feed is highly toxic to bobwhite quail.

Based on two fish LC50 values, slight toxicity to fish exposed to acute arsenic acid [AsH_30_4] exposure is indicated. The bully and jollytail LC50 and NOEC values cited in Markich et al (2002) indicate slight to practically no toxicity to acute exposure and slight to very slight toxicity through chronic exposure.

Arsenic acid showed moderate toxicity to the mysid [$1 < LC50 \leq 10$ mg/L] and slight toxicity to the water flea [$10 = LC50 \leq 100$ mg/L] while the water flea NOEC indicates moderate chronic toxicity [NOEC in the range10 to 100 mg/L]. The As^{III} results indicated slight to moderate toxicity to the organisms tested. *Ceriodaphnia dubia* and the amphipod, *Paracalliope fluviatilis*, were the most sensitive aquatic invertebrates tested with respect to As^{V} toxicity with the EC50s respectively, 0.491 and 0.232 mg/L indicating this valence state of arsenic was highly toxic to these organisms [EC50 of 0.1 to 1 mg/L].

Based on 21 day chronic daphnid toxicity results, a CCA leachate study indicated moderate toxicity with respect to arsenic and high toxicity with respect to chromium and copper [NOECs of 10 to 100 and < 10 µg/L, respectively] to the water flea after 21 days exposure. An earlier 21 day study, however, indicated very slight chronic toxicity with NOECs in the order of 10 to 30 mg/L for the three metals. For the mysid, the seven day NOECs after exposure to CCA-C leachate under low salinity conditions were arsenic 115, chromium 4.7 and copper 80 mg/L, while under conditions of high salinity, the NOECs were arsenic <4.2, chromium <3.2 and copper < 22 mg/L.

Incidences of reported mammalian toxicity appear limited, apart from a report on the poisoning of seven cows after ingestion of ash from burnt CCA treated posts. The IPCS report on arsenic poisoning noted cases of arsenic toxicosis in cattle, horses and white-tailed deer.

Soil biological processes were inhibited in pasture soil following contamination with a CCA timber preservative. At 100 mg/kg of copper, chromium and arsenic the processes were reported not to be significantly depressed, whereas at 400 mg/kg, some depression took place while at 800 mg/kg, normal processes were inhibited.

Based on the EC50 values seen, the effects of arsenic may relate more to the species or the test environment rather than solely the valence state [e.g. EC50s of 6.2 for As^{III} and of 26 and 237 mg/kg soil for As^{V} were reported]. NOEC and LOEC values point to effects in the hundred mg/kg soil range. The IPCS report notes that phytotoxicity is dependent on the environment and that arsenic phytotoxicity was recorded in the 1930s.

8. ENVIRONMENTAL RISK ASSESSMENT

8.1. NATURAL BACKGROUND CONCENTRATIONS AND CONTAMINATED SITES

Peters et al (1996) described arsenic as the 52nd most common element in the Earth's crust, with an average abundance of approximately 1.5-3 mg/kg. They indicate it is ubiquitous in the environment, occurring from both natural cycling and anthropogenic input. Igneous rocks contain an average content of about 2-3 mg/kg, varying up to 100 mg/kg, and it occurs naturally in many mineral ores (eg FeAsS). It is present at 0.02-0.5% in a large number of mineral species, and up to 5% in pyrite minerals. Nozaki (2001) indicates that the oceanic mean concentration of arsenic is 1200 ng/kg as $HAsO_4^{2-}$ [As^{V}] and 5.2 ng/kg as $As(OH)_3$ [As^{III}], ranking it as 24th in order of the elements in seawater.

8.1.1. Aquatic environment

Copper, chromium and arsenic are present in soils and aquatic ecosystems at natural background concentrations. ANZECC and ARMCANZ (2000) list these concentrations for copper, chromium and arsenic in Australian waters (Table 52).

Table 52. Natural background concentrations of arsenic, chromium and copper in Australian waters (ANZECC and ARMCANZ 2000, Smith et al. 2003).

Element	Marine water (µg/L)	Estuarine water (µg/L)	Fresh water (µg/L)
As	1.0-1.6	1.0-3.3	<10
Cr	0.062-0.1	0.01-0.1	No information
Cu	0.025-0.38	0.06-1.3	0.11

Smith et al. (2003) report general arsenic concentrations in natural Australian waters to be <10 µg/L. Maximum concentrations in rural Victorian surface waters were <1-283 µg/L with 47 of 74 sites sampled having maximum concentrations >7 µg/L. Surface water in the greater Melbourne area had maximum concentrations of <1-52 µg/L.

The groundwater used for drinking in the coastal community of Stuarts Point, NSW contained up to 300 µg/L of arsenic derived naturally from weathering of geological formations (Smith et al. 2003). Similar natural processes resulted in concentrations up to 70 µg/L in groundwater in the lower Namoi River catchment. However, the majority of groundwater arsenic contamination is caused by anthropogenic activities such as mining (eg. gold and titanium). For example, titanium extraction from sand beds near Newcastle, NSW allowed the oxidation of arsenopyrite material causing arsenic concentrations up to 30,000 µg/L in the unconfined aquifer. Industrial accidents such as a spill of arsenic solution in the production of ammonia at Kwinana, WA caused groundwater pollution of 5-220,000 µg/L.

Coastal marine sediments contained arsenic at 2-180 mg/kg sediment and 50 mg/kg sediment has been suggested as the upper limit of natural background with >50 mg/kg sediment indicative of anthropogenic contamination (Smith et al, 2003). Sediments from a mangrove in Jervis Bay, NSW only had a mean of 1.4 mg/kg sediment whereas those from Victorian rivers near historical mining areas contained up to 1159 mg/kg sediment.

8.1.2. Terrestrial environment

Natural background concentrations of arsenic, chromium and copper have been studied in Australian soils and are summarised in Table 53 (Smith et al, 2003). The study authors state that As soil concentrations in the natural environment are generally <50 mg/kg soil with a mean of about 5-6 mg/kg soil. Smedley and Kinniburgh (2002) report the background concentration in world soils is generally 5-10 mg/kg soil with a mean of about 7.2 mg/kg soil (mean of 7.4 mg/kg soil in American soils, n = 901). As expected, there are localised wide variations to this as soils from naturally weathered quartzite in Queensland contained 70-100 mg/kg soil.

Table 53. Natural background concentrations of arsenic, chromium and copper in Australian and New Zealand agricultural (mainly horticultural) soils (McLaughlin et al. 2000), unspecified Australian soils (NEPC 1999) and Queensland rural and urban soils (Smith et al. 2003) in mg/kg soil.

Element	Australian and NZ agricultural soils	Australian soils (unspecified locations)	Queensland rural soils	Queensland urban soils
arsenic	1-20	1-50	<5-40	3-31
chromium	2-700	5-1000	Not measured	
copper	0.4-200	2-100		

In terms of anthropogenic contamination, a site in Watson, Canberra near a former cattle dip had 32-1,597 mg/kg soil (Smith et al. 2003). Ng et al (1998) noted that arsenic in the soil in the Watson area was likely to be naturally occurring because of the presence of a gossan which is a geological formation formed by weathering zones of sulphide mineralisations and known sources of arsenic and base metals, although there was the likelihood of arsenic in the soil in some sections of the Watson area could be the result of earlier use as a sheep dip. In the nine composite soils and one rock sample analysed (atomic absorption spectroscopy), arsenite, As^{III} made up 0.33% to 56% of the total arsenic in the soil samples and 48% in the rock sample, with eight of the ten soils and rock tested containing ~99% of the arsenic as arsenate (As^{V}). Using a rat bioavailability model, the absolute bioavailabilities of the soils, relative to As^{III} or As^{V}, were respectively, 1.02 to 9.87 or 0.26 to 2.98%. The report concluded that speciation was highly significant for interpretation of bioavailability and risk assessment data and that, because the bioavailability of arsenic in the soil was relatively low, there would be very limited health impact on the environment in the study area.

Surveys of former railway corridors in South Australia where arsenic-based herbicides were used found contamination up to 1,400 mg/kg soil with ≤1.27 mg/kg dry weight in plant foliage in these areas. Old mine waste disposal sites in Victoria have high concentrations of 280-15,000 mg/kg soil.

Bhattacharya et al. (2002) cited Eckel and Langley (1988) and Yan Chu (1994) in stating that arsenic is widely distributed in soils, with average concentrations in the range 1-40 mg/kg, with a mean value of approximately 5 mg/kg. They stated that the background arsenic concentration in soils is controlled by the lithology of the parent rocks. They instanced the arsenic content in Swedish till soils, which ranges between <5 and 175 mg/kg, with a median value of 8 mg/kg (presumably the high values reflect material of volcanic origin).

8.1.3. Biota

Smith et al. (2003) summarised Australian data on measured concentrations of arsenic in biota. Fish (sole, carp, flathead, perch, mullet, tailor and trevally) and mussels (common mussel and Little Black Horse mussel) contained 0.1-13.6 mg/kg dry weight indicating possible accumulation, but the conditions of their growth were not specified. It was presumed that arsenic was predominantly present as organo-arsenic species.

Green et al. (2001) reported cutworm larvae of Bogong moths bioaccumulated sublethal levels of arsenic from the inland plains of eastern Australia and transported them to their adult winter aestivation cave sites in the Snowy Mountains, NSW where grass receiving the washout of accumulated cave debris was killed. Adult moths and affected grass contained means of 2.3 and 5-7 µg/kg, respectively, compared to moths and grass from control and other areas of 0.1-0.3 and 0.0 µg/kg where no adverse effects on vegetation were seen. Mean soil arsenic concentrations in the caves, washout areas and adjacent unaffected areas were 6,029, 504 and 0.5 µg/kg soil, respectively. These soil levels are much lower than those reported with respect to other contaminated soils e.g. the studies of Grant and Dobbs (1977) and Bergholm (1990) discussed under “Vegetables in contaminated soils”, page 131 of this report and the work of Smith et al (2003), discussed below. Analyses of faeces of bogong predators and control herbivore show exposure of predators (<200-600 µg/kg faeces) is higher than the herbivore (<100 µg/kg faeces) indicating that arsenic may biomagnify in the food web, although it is hoped to resume research into what food source the cutworm larvae are presumably ingesting arsenic and at what initial concentration (see also Green, 2003).

Uptake of arsenic by plants has been generally assumed to be low. However, some plants such as the brake fern (*Pteris vittate*) can hyper-accumulate arsenic in their above ground biomass and may have the potential to remediate contaminated sites. In a mangrove ecosystem in Jervis Bay with a natural background concentration of 1.4 mg/kg sediment, leaves and bark had low levels of 1.2 mg/kg while the fine root system (including epiphytic algae/fungi) contained 12-14 mg/kg and detritivorous crabs had the highest tissue concentrations of 56 mg/kg (Kirby et al. 2002). Radiata pine needles from trees grown in Ballarat East goldfields in Victoria contained 4.4 mg/kg which was higher than background (not specified).

Contaminated waste materials from the Mole River mine, NSW supported some plant growth (e.g. couch grass, *Cynodon dactylon*) containing arsenic up to 3,530 mg/kg dry weight (Smith et al. 2003). Other surveys of old railway corridors with concentrations up to 500 mg/kg soil supported plants containing <0.5-6.2 mg/kg. Both silver-beet leaves and peeled radishes grown in contaminated soils (concentration unspecified) under favourable conditions concentrated arsenic up to 2.9 and 1.4 mg/kg fresh weight, respectively. Yields of tomatoes and silver-beet were dramatically reduced to <10% when grown in soils of >100 mg arsenic/kg soil.

8.2. AUSTRALIAN WATER QUALITY GUIDELINES

ANZECC and ARMCANZ (2000) derived water quality guidelines (or trigger values) for the protection of aquatic ecosystems in Australia. These were based on various methods, including a statistical distribution which protects a percentage of species in that particular habitat (see Table 54).

Table 54. Australian Water Quality Guidelines for As^{III} and As^{V}, Cr^{III} and Cr^{VI} and Cu.

	Fresh water trigger values (µg/L)			**Marine water trigger values (µg/L)**		
	Level of protection (% of species)					
Element	99%	95%	90%	99%	95%	90%
As^{III}	1	24	94	Insufficient data		
As^{V}	0.8	13	42	Insufficient data		
Cr^{III}	Insufficient data			7.7	27.4	48.6
Cr^{VI}	0.01	1.0	6	0.14	4.4	20
Cu	1.0	1.4	1.8	0.3	1.3	3

High reliability trigger values are indicated by light shading, while moderate reliability trigger values have dark shading.

From these values, chromium and copper appear more toxic to aquatic organisms than arsenic.

Trigger value is defined as “the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of impact if exceeded and should ‘trigger’ some action, either further ecosystem specific investigations or implementation of management/remedial actions” (ANZECC and ARMCANZ 2000).

High reliability trigger values have a higher degree of confidence because they are derived from an adequate set of **chronic** toxicity data and hence require less extrapolation from the data to protect ecosystems.

Moderate reliability trigger values have a lower degree of confidence because they are derived from an adequate set of **acute** toxicity data and hence require more extrapolation than high reliability trigger values, including an acute-to-chronic conversion.

8.3. NEPC SOIL INVESTIGATION LEVELS

The National Environment Protection Council (NEPC 1999) derived Ecologically-based Investigation Levels (EILs) for arsenic, chromium and copper in soils. These are defined as “the concentration of a contaminant above which further appropriate investigation and evaluation will be required”. They are not cleanup/response levels or indicate a desired soil quality but are to assess existing contamination to prompt an appropriate site-specific assessment when exceeded. The EILs presented in Table 55 may be used as generic values at a national level but should be reviewed to protect relevant ecological values at a specific site.

Table 55. Ecologically-based Investigation Levels (EILs) for arsenic, copper and chromium (NEPC 1999).

Element	**Interim urban Ecological Soil Investigation Level (mg/kg soil)**	**Background range (mg/kg soil)**
As (total)	20	1-50
Cr^{III}	400	5-1000 (Cr total)
Cr^{VI}	1	
Cu	100	2-100

Dudka and Miller (1999) used levels of arsenic (and lead) in soils treated with fly ash from various US power plants or sewage sludge to conduct a risk assessment to children. High application rates [100-120 ton/ha, dry weight] were used. Arsenic level in the soils [determined by mass spectroscopy] after crop harvest were 3.8-6.1 mg/kg, compared to a value of 2 mg/kg in control soil. Based on calculated intake of arsenic from the contaminated soils, the authors concluded arsenic concentrations in the soil could reach 40 mg/kg without appreciable toxicological or environmental concern, based on child ingestion of contaminated soil as the most likely path of environmental exposure.

8.4. NEPC GROUNDWATER INVESTIGATION LEVELS

Table 56 lists investigation levels for the protection of marine and fresh water ecosystems. These values have been derived from Australian Water Quality Guidelines for the assessment of contaminated sites (NEPC 1999). When these concentrations are exceeded, further investigation should determine the extent and source of contamination.

Table 56. Groundwater investigation levels (NEPC 1999).

Element	Marine water (µg/L)	Fresh water (µg/L)
As (total)	50	50
Cr (total)	50	10
Cu	5.0	2.0-5.0

8.5. RISK ASSESSMENT – APPLICATION OF CCA TO TIMBER

8.5.1. Nature of the risks to the environment during CCA treatment of timber

The general treatment process for application of CCA to timber involves the timber being placed under vacuum to remove air and water from the wood cells (Section 5.1). The timber is then pressure treated with the CCA mixture to refill the wood cells with CCA. During these processes, environmental contamination with CCA may occur through spillage, leakage or other emissions. Waste material such as treated wood waste, sludge or used solutions from the treatment process could also be a source of environmental contamination with CCA. While the freshly treated wood is still wet, CCA solution may drip from it. Various reactions occur between the treatment solution and wood during contact and these reactions continue for a period following release of the pressure, 99% fixation taking of the order of 9-21 days (Section 6.3.2). During this time, CCA in the treated wood is more subject to leaching if wetted by rain etc. Furthermore, until fixation is complete, chromium in the more toxic and mobile Cr^{VI} form may leach. It is not necessarily just the processing site where contamination could occur as a result of such excessive leaching - if treated wood leaves the site before fixation is satisfactorily complete, contamination of the environment could occur during transport, at lumber yards or even at construction sites.

8.5.2. Risk assessment of timber preservation plants in the United Kingdom

The United Kingdom Health and Safety Executive (HSE) has conducted an environmental risk assessment of industrial pre-treatment of timber using vacuum/pressure impregnation of CCA using the European Risk Assessment Technical Guidance Document (EURATGD – presumably now updated by the OECD 2003 documents), with some adjustments (HSE, 2001). It is noted that the total scale of the UK industry appears similar to that in Australia, but there are more plants in the UK (~6000 t/annum by 300 plants, compared to 6500 t/annum by ~100 plants in Australia – Section 5.2.1). This suggests that plants in Australia are on average significantly larger. There may also be significant other differences between the location and operation of the industries in the UK and Australia. However, this assessment provides some indications of the potential impact of environmental contamination of aquatic environments from the CCA application process.

The model assumed a scenario where 1% loss of CCA occurred, all of it going to a stream. Based on the scenarios used, HSE calculated PEC/PNEC ratios (Predicted Environmental Concentration/Predicted No Effect Concentration) of 82-4120 for copper, 3.4-172 for chromium, 129-6417 for arsenic, and 300-15,444 for CCA, depending on the flow rate in the receiving watercourse. The PNECs were based on values of 0.05 µg/L for copper (100 X safety factor to an EC50 of 0.005 mg/L for a 48 h *Daphnia* study), 2.0 µg/L for chromium (1000 X safety factor to an EC50 of 2.0 mg/L from a 48 h *Daphnia* study), 0.048 µg/L for arsenic (1000 X safety factor to an EC50 of 0.048 mg/L for a 14 d algae study), and 0.09 µg/L for CCA (1000 X safety factor to an EC50 of 0.09 mg/L for a 48 h *Daphnia* study). The safety factors were based on the numbers of studies available. These PEC values were acknowledged to be very conservative.

While these results all indicate a potential environment concern from release of CCA during application, HSE was very cautious in considering these results. They had concerns regarding the use of the model for metals and the assumption of a 1% loss all going to a receiving watercourse. While loss may occur to drains and culverts, some loss may be attenuated by infiltration through soil (it is noted that greater amounts of paving, while reducing the extent of soil contamination, may reduce the opportunity for soil to intercept contaminants that may otherwise flow to watercourses). The PEC/PNEC ratios also failed to consider the behaviour of the active substances in water/sediment situations. The report suggested that only a small percentage of the metals may be present as the toxic free metal ions - most copper and chromium and to a lesser extent arsenic may be adsorbed to colloidal particles or combined in complexes, which are generally considered less toxic than the free ion. For example, only 0.01-0.1% of total copper may be present in the free hydrated cationic form. Partitioning to sediment of the metals adsorbed to particulate matter may then occur and other reactions may follow in the different redox and pH conditions of sediment. However, arsenic is more likely to be present in fresh water or sediment in a toxic, available form. HSE therefore considered that greater bioavailability may make arsenic the most toxic element in CCA in freshwater situations, though at first sight copper appears to be the most toxic component. To clarify these issues, HSE asked for a study to be conducted to establish the mobility and partitioning of copper, chromium and arsenic from CCA in natural fresh and marine waters.

Thus the HSE (2001) risk assessment indicates that in a worst case analysis of a 1% loss situation there may be risks to aquatic organisms from CCA application, depending on the fate of the toxic elements in the natural water/sediment situations. While more information is needed to fully interpret predicted total environmental concentrations in terms of bioavailability and toxicity, it is clear that release of CCA to aquatic environments should be minimised.

8.5.3. Evaluations of CCA treatment sites

Several published reports of wood preservation plants overseas where past or present CCA treatment has resulted in contaminated sites have been reviewed for this assessment (Section 6.2). In some cases, off-site movement into streams or lakes was demonstrated. The available studies show that soil levels of arsenic, copper and chromium may accumulate to high levels in the area of CCA treatment plant facilities, with the most susceptible areas being near the impregnation cylinder or its concrete pad, and in areas where wood piles had stood for fixation and drying.

Maximum measured concentrations of arsenic, copper and chromium in the surface soil at different sites ranged from 513-73,000 ppm, 74-82,000 ppm and 153-37,000 ppm, respectively. Very high levels of contamination have also been found in surface soil in natural drainage areas downstream of CCA application sites (up to 66,000 ppm arsenic, 58,000 ppm copper and 45,000 ppm chromium). These concentrations are far above natural background concentrations of arsenic (1-20 or 1-50 ppm for arsenic in Australia – Section 8.1.2), and also above natural background levels of copper (0.4-200 ppm) and chromium (2-700 or 5-1000 ppm). In several cases, concentrations of arsenic were higher than those at arsenic-contaminated cattle dip sites, or gossan areas where naturally high levels of arsenic may occur (Section 8.1.2). It was evident by the depth of penetration of chromium in some soils that much of it had been added directly from CCA treatment solution in the Cr^{VI} form.

The HSE (2001) review of CCA evaluated plants operating in the UK. Their evaluation indicated that local soil contamination was greater at the older plants of poor design and poor working practices. Contamination was much less at the most modern plant, but even so was found in the top 2 cm of some sampling points, which was traced to careless drum cleaning and storage.

These and other studies (Section 6.1) show that, in some soils (eg coarse texture, low organic matter content, acid pH and anoxic/reducing conditions) and sites (eg where there is a shallow watertable), there is a risk of contaminating shallow groundwater with CCA components - in particular chromium in the Cr^{VI} form, and arsenic as As^{III}. However, in the majority of the cases reviewed, concentrations of these elements fell with increasing soil depth, leaving areas of severely contaminated soil down to 20-60 cm, but without contaminating groundwater (Section 6.2.1). Drainage of water containing CCA residues could potentially contaminate soil downhill, and evidence from a UK study indicates that this may occur to very high levels. Sites where aquatic or sediment contamination was detected in the above reports were located adjacent to rivers, drained to nearby streams, or even had a stream flowing straight through them. Drainage water may also reach more distant aquatic areas, though flow over and through soil is likely to reduce heavy metal content by adsorption and other processes. Contamination of surface streams or groundwater from run-off or seepage could continue gradually long after the site has ceased to be used for wood treatment purposes, as exemplified by the case studies which have been reviewed.

A study using soil from an old wood preservation facility (Section 7.8) showed directly that contamination with CCA at the high levels found at such sites (ie in the 100s of mg of copper, chromium and arsenic) reduces respiration, nitrification and enzymatic activity of soil microorganisms and reduced the activity of nematodes, enchytraeids and earthworms. Comparison with EC50 values for arsenic (As^{III} or As^{V}) to various terrestrial invertebrate species (Section 7.6) also suggests that in many cases the soil concentrations may have exceeded toxic levels, depending on the extent to which arsenic was bioavailable in the soil. Studies also show that the growth of plants was affected by heavily contaminated soil from various old CCA facilities (Section 7.9). With lower levels of contamination where plants could grow, concentrations of arsenic in plants were elevated, with differences between species and plant tissue. On the other hand, microbes, plants and other organisms differ in their susceptibility to arsenic in soil and highly tolerant strains may develop.

Measured data for water concentrations were only available for a brook within an old plant area. At 50 µg/L for copper, the concentration in the brook exceeded the Australian Water Quality Guidelines fresh water trigger value for copper by >25 X at the 90% level of protection (Section 8.2). The trigger value for 90-95% level of protection was also exceeded by arsenic, at 59 µg/L.

Thus, depending on the forms of copper and arsenic present, aquatic organisms in the brook may have been impacted by the metals present, particularly by copper. Possibly dilution and loss to sediment would have been sufficient to minimise impacts from dissolved copper and arsenic once the brook flowed into the river.

Surface sediment concentrations of 66-70 ppm were found in a stream and a river reached by CCA, with 18 ppm in surface sediment in a downstream lake. A "Consensus-Based Probable Effects Concentration" (CBPEC) for arsenic in freshwater sediment based on toxicity tests with amphipods and chironomids was 33 mg/kg (Section 7.4.2.5). The higher sediment concentrations found are above this level, while the lowest value just exceeds the Environment Canada Probable Effect Level guideline (one of those considered in calculating the CBPEC). Thus arsenic concentrations in surface sediment in stream and river samples close to the CCA source were above a level likely to cause harmful effects to sediment dwelling organisms, while that in the lake just exceeded a more conservative guideline level. Sediment concentrations were much higher in a pool and brook within an old plant area.

Thus, available data for existing contamination in and around CCA treatment facilities indicate that soil concentrations of arsenic, copper and chromium may reach very high concentrations as a result of poor design and poor working practices. There is evidence that off-site contamination of soil downhill can reach very high levels. In many cases where data have been obtained, soil concentrations were sufficiently high that significant effects on vegetation and soil invertebrates would be expected. Contamination of downstream aquatic environments has also been found, at sufficiently high levels near the source of contamination that aquatic or sediment dwelling organisms might be affected, depending on the bioavailability and form of the metals present. However, except where conditions were unfavourable, soil contamination was limited in depth and while areas of soil may have been severely contaminated, the contaminants did not reach groundwater. This indicates the importance of avoiding sites with shallow groundwater or where soil conditions favour mobility of the contaminants, rather than retaining them.

8.5.4. Australian sites

Many of the above reports referred to plants which were old and had been abandoned or decommissioned. Hence they were likely to have been in use before modern environmental standards were adopted. However, they do indicate the extent to which environmental contamination can occur if suitable facilities and management practices are not in place. There are presumably many more published and unpublished assessments from around the world, including Australia, that address this issue. For example, the 1996 State of the Environment Report (DEH, 1996) listed as an example of point source environmental contamination "localised contamination of the shallowest aquifer leading to long term resource degradation, environmental effects and some potential public health impacts" from arsenic and chromium (as well as tin compounds, phenols, cresols and pesticides) as a consequence of timber treatment in the Mt Gambier region of South Australia.No detailed reports were provided for CCA treatment plants in Australia, but there are unsubstantiated indications that there have been contamination problems at some sites in the past.

8.5.5. Conclusions

8.5.5.1. Overall conclusions regarding risks to the environment from the CCA application process

There is ample evidence from evaluations of sites where CCA has been used that poor design and operation of CCA application facilities can lead to significant contamination of the environment, both at the treatment site itself and off-site through run-off into soil and water. Consideration of these data together with a risk assessment conducted in the UK indicates that off-site aquatic contamination could potentially reach harmful levels, though assessment of the aquatic toxicity of arsenic, copper and chromium is difficult because of the complex behaviour of these elements in natural waters and sediment. Suitable procedures should therefore be in place to minimise on-site and off-site contamination with CCA as a direct consequence of the application process.

Furthermore, until fixation of the CCA is achieved, the potential rate of leaching is much greater than after fixation has occurred, including the specific risk of leaching of chromium in the more mobile and toxic Cr^{VI} form. Thus in order to minimise environmental contamination associated with the CCA application/fixation process, protective measures need to extend beyond the actual vacuum-pressure process, through drying of the wood until it is drip dry and until fixation can be considered complete. To ensure adequate protective measures are maintained, treated wood should not leave the application site until fixation is satisfactorily complete. It will therefore be necessary to have appropriate means of identifying when this point has been reached.

Various factors may influence the leachability of CCA components from treated timber in service. Hence inappropriate management of the treatment process may also compromise leachability of CCA components from the final product (ie after fixation is complete). It is also important that the whole application/fixation process is correctly managed to achieve the desired retention rate and penetration depth. Hence appropriately designed and maintained equipment and thorough training of operators are essential to avoid inadequacies in the treatment process causing excessive leaching of the product in service. In addition, a possible consequence of treated timber not reaching the minimum retention and penetration requirements for the specified hazard class is that it could fail prematurely in service. This would add unnecessarily to end-of-use disposal volumes.

8.5.5.2. Available guidance

Guidance on appropriate plant design and operation to protect the environment is provided in the relevant Australian Standards (Section 5.1.1.2). It is considered that strong adherence to these guidelines is necessary for the risk to the environment from the CCA application process to be acceptable.

As evident from the above contaminated site data, appropriate site selection is a first step to minimising the likelihood of potential offsite effects through groundwater or surface water contamination, as in the absence of other control measures the toxic elements are then retained on the site by adsorption in the soil profile. As indicated in Section 5.1.1.2, steps may be available to improve a problem site.

Various recommendations are made for treatment plant layout that are important in minimising contamination of the soil at the site, and in capturing and controlling contaminated water so that it does not leave the site. The most salient features of plant design recommendations include:

- appropriate stormwater management for different parts of the plant to keep water that is likely to be contaminated separate from uncontaminated water and direct contaminated water to appropriate storage/processing facilities;
- impervious concrete paving of the treatment plant site (including vessels, pumps, tanks and other chemical storage vessels, chemical unloading areas and freshly treated timber drip pads);
- bunding of the plant site/individual vessels located and designed so as to collect leakage and contain a safety margin above the maximum total volume of timber preservative solution in use and/or in storage;
- installation of leak detection systems;
- all stored concentrates to be held in a bunded, roofed and secure compound;
- provision of drip pads in the treatment plant site with sufficient capacity to hold freshly treated timber until the surface is dry (and no sooner than 48 h after treatment with CCA), with facilities to collect and recycle solution which has dripped;
- provision for subsequently holding treated wood in the plant yard until the CCA preservative is well fixed, with stormwater leaving the treatment plant yard not to exceed relevant environment authority limits – it would appear that this area should be sealed or the wood covered to assist control of stormwater and minimise soil contamination on the site, but the Standards are not very clear on this.

Aspects of plant operation are also important, eg so as to minimise the generation of waste containing CCA by re-use or recycling of process solutions and run-off water. Salient recommendations include:

- operational training, controlled access etc;
- appropriate design and maintenance of pressure vessels, vacuum pumps etc;
- procedures established to contain spills and prevent them flowing into drains and watercourses or blowing away, eg placement of soil levee banks and the use of absorbent material (sand, sawdust etc[1]) and/or stabilising agents (90% lime and 10% sodium metabisulphite mixture for large spills of CCA which cannot be recycled);
- wherever practicable, spilt material, washings etc should be collected and returned to the treatment process;
- chemical sludge can be formed from CCA components under some conditions and cannot be re-used directly, but should be processed by recycling where possible;
- waste which cannot be used should be drummed, labelled and disposed of at a site approved for acceptance of such waste, or after appropriate treatment according to relevant regulatory authority requirements;
- wastes should not be disposed of on site.

The guidelines generally provide satisfactory steps to minimise soil contamination in the potentially most contaminated areas and to contain and manage run-off. In the treatment plant site (ie where the application process occurs, through to the end of drip drying of the treated wood) contamination should be confined to equipment, sealed surfaces, sumps, drains and tanks etc. In the plant yard area where treated wood is stored during fixation, it is indicated that groundwater contamination must be minimised and unacceptably contaminated surface water must not leave the yard area, but how this should be achieved is unclear. It seems that soil contamination on site

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[1] However, the Timtech C Oxide product label specifically states NOT sawdust, possibly to avoid the risk that contaminated sawdust may be disposed of inappropriately, such as by burning.

in this area may be considered tolerable by the industry because of the cost of sealing large storage areas. If such contamination did occur, the guidance provided would ensure that it is limited to the plant yard.

If a requirement is made that timber must remain on site until fixation is complete, it will be necessary to indicate how “complete” fixation can be determined. The time required for fixation varies widely, particularly in relation to temperature, and users may wish to use processes to accelerate fixation. Hence it is inappropriate to base requirements to ensure fixation is complete solely on a time basis. Assessment of fixation should also be based on the amount of Cr^{VI} remaining in the timber, rather than the percentage of CCA applied which has been fixed, as otherwise the large difference in retention rates between hazard classes has a large impact on the level of protection offered (Section 6.3.1.3.3). An appropriate means of doing this is the water leachate/diphenylcarbazide method. This method is already indicated in Australian Standard “Methods for sampling and analysing timber preservatives and preservative-treated timber” (AS/NZS 1605-2000) (Sections 5.1.1.2, 6.3.1.3.2). An alternative method may be the chromotropic acid spot test on wood borings, a qualitative rather than quantitative method, but which is considered sufficiently sensitive for the purpose and may suit some operators better.

8.6. RISK ASSESSMENT – CCA TREATED TIMBER IN USE

8.6.1. Rate and extent of leaching of CCA components from treated timber

It is clear from semi-field and field studies and *in situ* evaluations that arsenic, copper and chromium can be expected to leach from CCA-treated wood in service in all sorts of terrestrial use situations, with and without ground contact (Sections 6.4.1, 6.4.2, 6.5, 6.6, 6.7). Leachability may vary widely and is affected by a wide range of interacting factors associated with the treated wood itself, the nature of the structure and the environment in which it is located – factors such as the CCA formulation type and-treatment process used, CCA retention rate in the wood, additional wood treatments, surface area to volume ratio of the wood, soil contact, soil physical and chemical characteristics, exposure to weather, climatic conditions (eg the quantity of rainfall, intensity and duration of rainfall events, temperature, UV radiation exposure), soil drainage, and presence of extreme factors such as very acid rain or the use of alkalis or oxidising agents during cleaning.

Data regarding the form in which arsenic is leached are very limited, as in almost all cases only total arsenic has been determined in actual leachate or surface residue tests. Even if the form of arsenic or chromium in soil were determined, it would not necessarily reflect that leaving the wood in leachate. Data for surface dislodgeable arsenic on treated wood indicate soluble arsenic on the wood surface may range between 0.9-23.5% of total arsenic removed in the test (Section 6.5.4), thus a high proportion of the arsenic leached may be in insoluble or bound forms dislodged from the eroding wood surface, rather than dissolved from the wood. Regardless, various alteration and degradation processes may occur subsequently in the soil.

The rate of leaching declines greatly with the completion of fixation, though reactions of CCA in the wood are known to continue slowly for some months after that point (Section 5.1.1.1.2). Accelerated laboratory leaching studies then indicate that over, for example, a five day test, the rate of leaching of each element declines to a very low level. However, leaching occurs much more gradually in wood in service, and there are large differences in exposure conditions. For example, intermittent wetting and drying may “wick” components from the interior towards the surface (Section 6.3.1.3.10). A recent paper (Lebow et al, 2003) indicates that exposure to UV radiation significantly increase leaching from treated wood, possibly as a result of increased surface area during weathering as well as loss of fibres caused by UV-induced surface erosion.

It is difficult to conduct field studies in a fashion that enables the effects of age in service on cumulative leaching to be judged - eg even where structures of different ages were available, there was significant variability between individual sites and between and within poles, plus uncertainties as to the original retention rate. Mobility in soil may also prevent the concentration in soil rising continuously in association with the amount leached from wood. Thus there are examples where age in service has not apparently affected levels in soil or loss from the wood (eg soil water concentrations in Section 6.4.1.9). Results with utility poles also show that CCA treatment may remain effective for decades, hence the long term rate of loss can be very slow. However, the available data suggest that leaching continues indefinitely for the life of a structure, though it is likely that the initial leaching rate in the first weeks or months in service declines to a more or less steady state. This appears to be the case even in properly treated timber and in the absence of unfavourable conditions such as soil characteristics favouring leaching.

For example, evaluations of CCA component concentrations in water running off poles in a Canadian study did not drop off with increasing age of the poles (Section 6.4.1.5). Leaching of copper, chromium and arsenic showed initially more rapid loss which then declined to a lower level (Section 6.4.2.1). Wipe tests on CCA-treated pine boards showed arsenic concentrations tended to follow a similar pattern over time during the 2 year study, which led the authors of the study to suggest an approximate steady state in surface concentration resulted from a balance between the amount on the surface washed off by rain, countered by an increase in surface levels caused by diffusional and erosion effects. An 18 month leaching study with chips of CCA-treated wood in lysimeters indicated an initial steady decline in leaching of copper, arsenic and chromium, but leaching of chromium and arsenic subsequently increased (Section 6.1.3.5). While in most soils copper, chromium and arsenic leached from a structure are likely to gradually rise in concentration in the soil over time, this clearly did not occur in a very sandy soil in Florida, where mobility of the leached elements evidently limited cumulative effects (Section 6.4.1.11).

However, field studies with stakes, posts and poles (Section 6.4.1) show that even with periods of service of several decades, there is very little lateral movement of CCA components from their immediate vicinity, with residues evidently accumulating predominantly in the soil area reached by water running down the wood surface to the ground. Measured concentrations of arsenic, copper and chromium near posts and poles at this point ranged from ~7-325 ppm, ~9-995 ppm and ~0.5-280 ppm, respectively (note that the highest levels of arsenic were from CCA-B formulations, known to leach arsenic to a relatively greater extent in terrestrial situations, and not currently in use in Australia). However, all the studies where soil concentrations were examined laterally from stakes, posts or poles showed a sharp decline with lateral distance from the treated surface, generally to background levels within ~10-50 cm. Studies where the effect of depth in the soil has been examined generally show a decline in concentration of each element in soil adjacent to or below the stake, post or pole, with differences reflecting the mobility of the elements in the different soils (eg greater downward movement in very sandy soils). The authors of one study (Section 6.4.1.5) calculated a “mixing radius” for each pole, ie the distance around the pole that the soil would have to be uniformly tilled to acceptably reduce the arsenic levels in the soil for agricultural use: they estimated an annulus 0.90 m thick around the pole would need to be mixed (depth not specified) in the worst case, and 0.3-0.7 m in the other cases. In studies where poles located in continually saturated soil were examined, there were water concentrations ranging from 40-970 μg/L for copper, 10-280 μg/L for chromium, and 20-1400 μg/L for arsenic

(Sections 6.4.1.5, 6.4.1.9) in samples taken close to the poles. Sampling did not indicate how far from the poles elevated concentrations extended in such wet situations.

Studies with structures such as decks, walkways, fences and playgrounds (Section 6.4.2) also generally show that maximum concentrations of arsenic, copper and chromium arising from CCA-treated wood occur in the soil immediately below or adjacent to the structure, with little lateral movement beyond the soil reached readily by leachate water. Mean arsenic concentrations in soil beneath or adjacent to a range of structures were increased to ~12-79 ppm, though individual sample points ranged as high as 350 ppm. Extrapolation of mathematical models fitted to data for a Queensland model deck leaching study (Section 6.4.2.1) gives estimates of cumulative losses of arsenic, copper and chromium of 6947, 451 and 1258 mg/m^2 deck, respectively, over a ten year period (an average of 1.9, 0.12 and 0.34 $mg/m^2/day$, respectively). If distributed into the surface 15 cm of soil below a treated deck, this could increase soil arsenic concentration by ~33 ppm - a comparable level to that found in field measurement studies adjacent to or under decks (possibly an overestimate - a longer study period would be necessary to avoid large extrapolation).

8.6.2. Risk to the environment from elevated arsenic concentrations near treated structures or in run-off water

The use of CCA-treated timber clearly does lead to increased levels of arsenic, copper and chromium in the soil environment. However, except possibly in continuously saturated soils, this contamination is generally limited to the immediate vicinity of treated structures, eg near support posts, adjacent to and under fences, decks and walkways. Soil concentrations of arsenic in these limited areas may rise substantially above the background level in local soils near the structure. They may also rise above the general range in natural background levels in Australian soils. Two different published sources (McLaughlin et al, 2000 and NEPC, 1999) indicate ranges of 1-20 ppm or 1-50 ppm for arsenic, 0.4-200 or 2-100 for copper and 2-700 or 5-1000 for chromium (Section 8.1.2). They may also exceed the National Environment Protection Council (NEPC) Ecologically-based Investigation Levels (EILs) for arsenic (20 ppm), copper (100 ppm) and chromium (400 ppm for Cr^{III}, 1 ppm for Cr^{VI})..

The available data summarised in this assessment give an indication of typical and peak concentrations which might arise. Whether or not the soil concentrations reached (at worst up to a few hundred ppm for arsenic) could affect soil organisms and plant growth would depend on the bioavailability of the element. Regardless, any harmful effects would be greatly restricted by the limited volume of soil affected. There is evidence that plant uptake from contaminated soil areas could increase concentrations of arsenic in the tissues of some plants, but again the extent to which this can occur is restricted to a limited area of soil.

Various studies indicate that leachate from treated wood may carry arsenic concentrations of the order of up to 1-2 mg/L or even ~8 mg/L (Sections 6.4.1.5, 6.4.2.1, 6.4.2.5). Depending on the form and bioavailability of the arsenic present, such leachate could be toxic to a range of aquatic organisms. Similarly, toxic levels of copper and chromium may be present. However, the elements contained are likely to be removed by adsorption and other processes as the water passes over or through soil in the immediate vicinity of the structure (Sections 6.1.1, 6.1.3), and/or to be adsorbed to organic matter dissolved or suspended in the water. In any case, leachate from CCA-treated structures would be greatly diluted by other run-off before reaching aquatic situations, where it would be further diluted and undergo complex interactions with other components in the water and sediment, as discussed earlier (Sections 6.1 and 8.5.2). Hence concentrations of arsenic, copper or chromium in aquatic situations reached by leachate from treated wood in service are unlikely to reach toxic levels. However, arsenic, copper and chromium from all sources (anthropogenic and natural) may gradually accumulate in sediments downstream of urban areas where CCA-treated timber may be used, particularly where outflows are poor.

Thus, most contamination is likely to be restricted to soil in the immediate vicinity of the structure, but some arsenic, copper and chromium may ultimately reach aquatic areas, eg via leachate reaching drains without passing through soil. However, toxicity to aquatic organisms is not expected from this due to great dilution and complex interactions with other components in the water and sediment. Nonetheless, action should be taken to ensure that as far as possible, the CCA-treatment is applied properly and fixation is completed before the treated timber is used, so that leaching in service is minimised.

8.6.3. Possible means of minimising leaching from wood in service

An essential factor to minimise the potential extent of leaching during the service life of the treated timber is that the CCA fixation process is complete before the timber is used. Prior to this point, leaching of all three elements may occur at an elevated rate, and chromium may leach in the more mobile and toxic Cr^{VI} form (Section 6.4.1.2). Correct treatment is also necessary to ensure that fixation is not interrupted (eg by excessive drying before the reactions are complete, a possible concern in Australia’s dry climate). There are various choices in the treatment process that can influence leachability once fixation is complete (Sections 6.3.2.2, 6.3.2.3, 6.3.2.4, 6.3.2.6, 6.3.2.7).

Timber with a low retention rate (eg hazard Classes H1 and H2) should not be used in environments subject to leaching, not just because of efficacy reasons, but also because low retention is a factor leading to elevated leachability of arsenic, though the potential store of CCA in the wood is relatively low (Section 6.3.2.5). Hence it would not be appropriate to seek to minimise environmental exposure by using a lower hazard class than that specified for outdoor situations. Timber species, wood quality, seasoning and sapwood/heartwood differences can also affect the end result (Sections 6.3.2.8, 6.3.2.9). , and appropriate handling of the process is necessary to achieve the required penetration depth in sapwood (Section 6.3.2.8, 6.3.2.9).

Factors affecting leachability in service may be difficult to control, but there may be situations warranting avoidance of CCA-treated wood as a construction material. For example, leachability is very high in the presence of high levels of simple organic acids, as occur in silage (Section 6.3.4.1).

Lebow and Tippie (2001) provided a number of suggestions for strategies to minimise the effect of preservative-treated wood on sensitive environments (eg for wetland boardwalk construction – see also Section 6.7). These include the following pertaining to CCA-treated wood:

- prefabrication – whenever possible, cut wooden members to length and perform boring and other machining processes prior to pressure treatment (increases durability by minimising exposure of untreated wood during fabrication and minimises the production and discharge of treated sawdust, drill shavings and other construction debris);
- avoid over-treatment – use wood treated to the retention specified for the appropriate hazard class for the purpose it is required;

- avoid if possible using batches of wood which have been re-treated, eg because they initially failed to meet penetration or retention requirements, as there is an increased risk of increased leaching of preservative;
- reject treated wood which has obvious surface residues;
- customers should not demand treated product on very short notice - the treatment/fixation process should not be rushed;
- evaluate treated wood for fixation before it is used (details of the chromotropic acid method are given, a suitable technique for sampling poles is indicated and minimum re-sampling intervals in the event of failure are specified);
- possible techniques to hasten fixation include kiln drying, hot water baths and steaming;
- store treated material that is shipped to a job site in an area free from standing water or wet soil, preferably on skids or support timbers and covered until used (desirably on untreated lumber if stored along the intended path of a wetland walkway);
- reasonable care to minimise release of debris produced during construction by using tarpaulins to collect sawdust and tubs to collect shavings etc;
- use factory- or field-applied water-repellents and stains, but application in the filed requires care to avoid dripping or spillage into sensitive environments;
- only use mild cleaning techniques in sensitive aquatic environments to avoid inducing excessive leaching.

8.6.4. Conclusions regarding risks to the environment from treated wood in service

Thus use of CCA timber treatments will be likely to result in increased levels of copper, chromium and arsenic in the environment beyond local background levels in soil in close proximity to treated wood as a result of leaching during service. Any impact on soil dwelling organisms or plants is likely to be greatly restricted by the limited surface area and volume of soil affected. In terrestrial areas, most contamination is likely to be restricted to soil in the immediate vicinity of the structure, but some arsenic, copper and chromium may ultimately reach aquatic areas, eg via leachate reaching drains without passing through soil. However, toxicity to aquatic organisms is not expected from this due to great dilution and complex interactions with other components in the water and sediment. Nonetheless, action should be taken to ensure that as far as possible, the CCA-treatment is applied properly and fixation is completed before the treated timber is used, so that leaching in service is minimised.

8.7. RISK ASSESSMENT – DISPOSAL OF CCA-TREATED TIMBER

8.7.1. Overview

The need to dispose of CCA-treated timber may arise throughout its life cycle. Timber facilities treating timber with CCA may need to dispose of off-cuts, sawdust, damaged timber or other timber waste containing CCA residues. Sawdust, shavings and off-cuts etc or damaged or excess timber is also produced at lumber yards, carpentry workshops and construction sites. However, much greater quantities of treated timber material ultimately need to be disposed of when the service life of the timber structure or product comes to an end. Investigators in Florida in particular have expressed concern at the large volume of CCA treated wood already in use and the potential implications of various disposal pathways for the environment, particularly due to the arsenic content. This issue is also concerning state environmental agencies in Australia (Section 1). Particular concerns centre on arsenic and the potential for it to leach from treated wood waste in situations such as landfill and reach soil or groundwater, or to reach the atmosphere during combustion of treated wood by volatilisation or in particulate form.

Similar issues arise in the disposal of timber treated with arsenic trioxide for termite control. However, the potential extent of environmental exposure is far smaller, and treatment occurs *in situ* and not in devoted application facilities.

8.7.2. Combustion

A major potential means of disposal of treated wood and treated wood waste is combustion. This could occur on a scale and frequency ranging from an *ad hoc*, casual basis (eg burning scrap timber in a domestic fireplace) through to routine industrial or domestic waste incineration, or even to use of the wood as fuel to recover the energy contained in it. Combustion may also arise accidentally through bush- or house fires. Studies show that, depending on the combustion conditions, 10-90% of the arsenic present in CCA-treated wood may be lost to air, either as volatilised As_2O_3 or particulate matter (Section 6.8.2). Even with well designed and managed industrial incinerators, it may be difficult to capture all the arsenic released, as evident in some of the research conducted into combustion of CCA-treated wood (Section 6.8.2.3). Furthermore, the ash produced contains all the copper, chromium and arsenic that were present in the treated wood before burning, less any loss of arsenic to the atmosphere. The metals present are likely to be susceptible to leaching, though this may depend on the nature of the residue – eg in a pyrolysis study the chromium was bound to the pyrolysis residue and difficult to leach, whereas the copper and arsenic were likely to leach (Section 6.8.2.6). A proportion of the arsenic and chromium may be in more toxic forms (As^{III} and Cr^{VI}) than were generally present in the wood (eg see Section 6.8.2.6).

For example, 1 tonne of timber treated to the retention rate of Australian Hazard Class H4 (as used for fence posts, vineyard trellis posts etc) originally contains approximately 7 kg total CCA elements, ie approximately 1.7 kg copper, 3.2 kg chromium and 2.2 kg arsenic. However, these elements will be far more concentrated in the ash, eg van Alkemade et al (1999) indicated that the ash produced from combustion of reject timber is ~1.5-3% by weight of the combusted material. Thus, if only 70% of the applied CCA remained in the wood at the time it was burnt, and 20% of the arsenic were lost to air, 1 tonne of wood would produce ~20 kg of ash containing 1.2 kg copper, 2.2 kg chromium and 1.2 kg arsenic (respectively, approximately 6%, 11% and 6% by weight in the ash, or ~23% total metals). Possibly a tendency for the treated wood to char may produce a greater quantity of ash and charcoal residues, but actual analyses of ash from combustion of treated wood has shown total copper + chromium + arsenic residues as high as 36% of the ash by weight for treated wood samples containing high residues of CCA, and the ash produced failed the standard TCLP and SPLP leachability tests (Section 6.8.2.5). Thus, combustion of treated wood leads to the production of ash containing toxic heavy metal residues. Recent Australian research also indicates that dioxins and furans may also be formed in the smouldering material after flaming combustion.

Hence, from an environmental point of view deliberate burning of CCA-treated wood or wood waste should be avoided because there is a risk of contamination of the atmosphere with arsenic during combustion, and of soil and water by contaminated ash. Incineration should only occur in very controlled facilities where release of arsenic to the atmosphere is minimised and the potentially highly toxic ash is processed and disposed of appropriately. As discussed in Section 6.8.2, research is continuing into developing suitable incineration or pyrolysis techniques that would achieve this and hopefully recover energy as well as a high proportion of the heavy metals in the ash.

In the context of regulatory action available to the APVMA, it is recommended that suitable label instructions be provided to prevent wood waste or other waste containing CCA produced at CCA treatment facilities from being disposed of by incineration.

8.7.3. Leaching

While residues of CCA components in soil as a consequence of leaching from individual posts *in situ* are likely to be confined to a relatively small volume of soil surrounding the post, more significant soil contamination could ultimately occur below material such as damaged or used posts if they were stored for long periods in large quantities either on the soil surface or buried in soil. Disposal in quantity to land should therefore be undertaken with care, particularly if there is a risk of heavy metals contaminating groundwater (a particular concern in Florida).

Studies confirm a much higher leaching rate if such material is broken up into mulch or pulverised. Leaching from mulch prepared from CCA-treated wood has been confirmed to increase soil arsenic levels, as has amendment of soil with sawdust from CCA-treated wood. Increased soil arsenic levels may then lead to increased levels in plants growing in the soil, though heavy cumulative application rates would be needed to raise soil concentrations of available arsenic to levels generally harmful to the growth of plants or soil organisms. Thus caution is also necessary in disposal of waste CCA-treated wood as mulch or as soil amendments.

In the context of regulatory action available to the APVMA, it is recommended that suitable label instructions be provided to prevent wood waste or other waste containing CCA produced at CCA treatment facilities from being disposed of on site and indicate that disposal must meet local or state regulatory requirements.

8.7.4. Other options

Many other disposal approaches for CCA-treated wood have been considered, including manufacture of products such as wood cement composites or particleboard, re-use of timber for the same or new purposes, and extraction of CCA components from pulverised wood by various solvent, biological or other processes (Sections 6.8.1 and 6.8.5). These are beyond the scope of this review and have not been reviewed in detail, but are noted for interest in the wider context of disposal of waste from CCA-treated wood.

8.8. RISK ASSESSMENT - ARSENIC TRIOXIDE TIMBER TREATMENTS

Unlike CCA treatment, arsenic trioxide blown into termite workings is not chemically fixed to the wood and is intended to be mobile in the short term via adherence to the bodies of termites moving through their workings. Much of the applied dust is likely to stay unchanged while it remains relatively dry in the treated wood, though initial adherence to the wood may be assisted by damp conditions likely to prevail in active termite workings. Hence arsenic, largely in the form of the trioxide, is expected to be available for release to the environment if the treated surfaces are exposed.

A proportion of applied dust may be relatively mobile, eg in surface residues or dust applied to trees or exposed timber. However, the majority of use is likely to be in sheltered or enclosed situations such as under a house or in a roof cavity, which should minimise release during the lifetime of the treated timber. Ultimately, though, the applied dust will be released to the surrounding environment, as the structure is dismantled, and as the treated timber is damaged or decays, exposing the treated cavities. Dust may then be washed, fall or be blown back out of the areas it has reached through mechanical action, rain or other sources of water (eg garden watering), or wind.

Hence it can be assumed that eventually release may occur in the vicinity of the treated timber, at the final disposal destination and/or during transport of treated timber waste to a disposal site. However, the scale of contamination is likely to be very low (1-2 g per infestation) and the contaminated area limited in extent. If it is assumed that in a worst case 2 g of arsenic trioxide were distributed on a 1 m^2 area, the resulting increase in arsenic concentration if mixed into the surface 15 cm of soil with a bulk density of 1.5 g/cm^3 would be 8.9 ppm (mg arsenic/kg soil). This is within the range in natural background levels in Australian soils and below levels shown to be toxic to soil organisms, but in any case is a very limited area of contamination. Greater dispersal would result in lower soil concentrations.

Arsenic trioxide in plywood glueline treatments would be expected to remain in the plywood product through its service life, with little release to the environment (possibly less than that with CCA, if the arsenic is in fact trapped within the matrix of the glue). However, there may be similar disposal issues to low hazard classes of CCA treated timber, given that the arsenic concentration is 0.13% on a mass/mass basis, similar to CCA hazard classes H1 and H2 (Table 13).

As with CCA treated timber, burning of timber treated with arsenic trioxide termite treatments or plywood with arsenic trioxide glueline treatment could volatilise arsenic trioxide and leave some residues in the ash. However, the scale of use of arsenic trioxide for these purposes is small compared to the overall use of CCA-treated timber.

9. CONTROLS/LABELLING

9.1. CCA TIMBER TREATMENT PRODUCTS

9.1.1. Australian Guidelines and Standards

In recent decades, various action has been taken in Australia to improve the design and operation of wood preservation plants, as evidenced by documents such as “Environmental Guidelines for Timber Preservation Plants” (EPA Victoria, 1981), earlier versions of the Australian Standards (including AS 2843-1985, AS 1604-1980 and AS 1605 – 1974), and the “Draft Environmental Guidelines for Copper Chrome Arsenate Timber Preservation Plants” (ANZECC/TPAA, 1995). The latter were finalised in 1996 (ANZECC/TPAA, 1996) and have been followed by the development of the Australian/New Zealand Standard™ “Timber preservation plant safety code“ (AS/NZS 2843-2000), Australian Standard™ “Specification for preservative treatment” (AS 1604-2000) and Australian/New Zealand Standard™ “Methods for sampling and analysing timber preservatives and preservative-treated timber” (AS/NZS 1605-2000) (Section 5.1.1.2).

Evidently these guidelines and standards have been developed in close consultation with industry and represent agreed desirable/good practice to “ensure that the environment and public health are protected from contamination." By definition, these guidelines and standards are not compulsory, though ANZECC/TPAA (1996) indicated that "compliance" with these guidelines was expected immediately for new plants and within two years (ie presumably by September 1998) for existing plants (where presumably there may in some cases be contaminated areas from inadequate plant design and operation in the past). An audit of wood preservation plants in NSW by the NSW EPA has found that in various respects of design or operation, NSW plants are not meeting the Australian Standards (and hence ANZECC Guidelines). A survey by the Timber Preservers Association of Australia (see Section 5.2.1) indicated that they generally treated wood in accordance with the requirements of AS1604 series of Standards, but 3 out of 29 respondents indicated that their plant did not conform to AS2843 or similar specifications.

The NSW EPA submission also notes that the Standards contain most, but not all of the best environmental management practices used within the industry worldwide. They indicate that they have asked the industry to consider a review of the Standards to address the gaps. Three areas that a review of the Standards could usefully address are:

- Incineration of wood, sawdust and shavings treated with CCA - the current recommendation is:

  "Treated wood, sawdust and shavings shall be disposed of in a landfill area approved for the purpose by the relevant authority (and) the incineration of treated wood, sawdust and shavings shall not be carried out except in plants specifically designed for that purpose."

  However the advice regarding incineration is not sufficiently prescriptive, as facilities handling any significant amount of CCA treated wood would need to have adequate provisions to prevent release of volatilised arsenic to the atmosphere, and for managing ash containing toxic metal residues;

- The Standards do not seem very clear as to the extent to which soil in the treatment plant yard used for holding CCA-treated timber should be protected from contamination, or how the yard should be constructed so as to ensure that groundwater contamination is minimised and that unacceptably contaminated water does not leave the yard area - the ANZECC Guidelines indicate that impervious treated timber storage areas may need to be provided in cooler areas where fixation times may be extended in winter, but the Standards do not refer to any need for sealing;

- The use of the chromotropic acid test (Section 6.3.1.3.2) as an alternative means of assessing fixation to that indicated under AS/NZS 1605-2000.

9.1.2. Use manuals

There may also be other material, such as manuals to guide use, available from different sources, such as product suppliers, treatment companies, timber industry groups and state environmental agencies – eg some product labels refer to state timber preservation industry guidelines and to the QTITC-Preservation Operators Manual in Queensland.

9.1.3. Product labels

9.1.3.1. Current label inconsistencies and inadequacies

Labels for CCA products generally provide very limited information on application of the product to wood. Some general comments on each label are listed in Table 57, in particular those pertaining to use.

Most labels indicate that the product should only be used in pressure (or vacuum pressure) timber impregnation plants, and two labels seek to limit use to “authorised persons for industrial and manufacturing purposes only.” Several labels refer in some way to Australian Standard AS 1604-2000 or its predecessor. However, in all cases, they refer only to AS 1604 for sawn and round timber, and not to the related standards (all AS 1604 – see Section 5.1.1.2) for other timber products (plywood etc), though presumably such products are treated with CCA (specific advice for CCA treatment is given in those other standards). Some labels also refer to state timber preservation industry guidelines, particularly those for Queensland, and to the Queensland QTITC or FITEC – Preservation Operators Manual. Only the Timtech C Oxide label specifically describes the different Hazard Classes and presents the retention rates required for each class. The Timtech C Oxide label is also the only label that provides advice regarding spillages. Several labels refer to the need for timber to be weathered for 4-6 weeks after treatment or else kiln dried before use, evidently towards ensuring that fixation is complete before the timber is used, but no mention of this is made on other labels.

Hence it is immediately clear that most product labels fall very short of the standard already provided by the Timtech C Oxide label and in the first place need to be brought to a similar standard to that label, in particular to include:

- a table listing and describing the Hazard Classes for treated timber and required retention rates for each class;
- advice to prevent use before fixation is complete - however, more specific measures are required than simply the advice that timber be weathered or kiln dried before use, and measures taken should be on site, as they would be beyond the control of the applicator once the timber leaves the treatment facility;
- appropriate advice regarding spillage.

However, all labels also need to be revised to improve advice and requirements regarding environmental protection. The current labels carry some general environmental protection instructions, such as to avoid contamination of streams, rivers or waterways with the chemical or used containers. However, they do not provide any instructions regarding the need for sealed, bunded areas for mixing, application, drip drying and fixation stages and for run-off capture and control facilities to minimise the risk of soil and water contamination. Relevant key measures recommended in the Australian Standards for Plant Design and Plant Operation (AS/NZS 2843-2000) should therefore be included on the product label, to ensure they are followed. Instructions regarding the disposal of wood waste should also be explicit. Labels should also be revised to update instructions regarding storage and disposal where necessary.

There is much detail regarding application methods and according to the equipment used, a wide range of treatment conditions may be used. Hence it would be difficult to elaborate on these in the product label. Similarly, the depth of penetration required, as set out in the various parts of Australian Standard 1604-2000, is relatively complex, varying with hazard class and the type of timber product – this too would be difficult to specify on the label, unless in an accompanying booklet. It is consider unnecessary to provide this detail on the product label, but the relevant Australian Standards should be referred to, and this should be done comprehensively for any form of timber for which the product may be used (ie not simply that for sawn and round timber, unless this is the only timber product where treatment may occur).

More detailed, specific recommendations regarding label revision are provided below.

Table 57. Comments regarding Copper Chrome Arsenate (CCA) formulations currently registered in Australia.

Product Number	Product Name	Label advice regarding use, plus other general comments
30691	Tanalith CP Wood Preservative Paste	Simply states "to be used in pressure impregnation plants only"
39884	Tanalith O Type C Oxide Wood Preservative	Specifies "to be used in timber treatment pressure impregnation plants only in accordance with state timber preservation industry guidelines and in Queensland with QTITC-Preservation Operators Manual". Also specifies that treated timber should be weathered for 4-6 weeks after treatment or kiln dried before use.
40092	Impretect CS	Refers to the need to dilute the concentrate to a concentration calculated to achieve a retention of CCA in pressure treated hardwood or softwood for the Hazard class defined by the end-use of the treated timber, as "defined in Australian Standard (AS1604-1997) titled Timber – Preservative-treated – Sawn & round."
41482	Impretect CO Timber Preservative	As for Impretect CS.
41680	Sarmix 3 CCA Salts	Simply states "for use in pressure impregnation plants only" and "to be used in vacuum pressure impregnation plants only" and gives directions for preparing a 10% solution using from the two different packages for the copper and the chromium + arsenic components.
41681	Sarmix Oxcell C-680 for Timber Treatment	States "to be used in pressure impregnation plants for timber treatment only" and refers to "Australian Standard 1604-1997 'Timber – Preservative-treated – Sawn & round' or where applicable other local or state regulations."
51821	A & C CCA Salt Wood Preservative	Stipulates "available to authorised persons for industrial and manufacturing purposes only." Specifies "to be used in timber treatment pressure impregnation plants only in accordance with state timber preservation industry guidelines and in Queensland with QTITC-Preservation Operators Manual." Also specifies that treated timber should be weathered for 4-6 weeks after treatment or kiln dried before use.
51822	A & C CCA Oxide Wood Preservative	As for A & C CCA Salt Wood Preservative, except that reference is to "Queensland with FITEC - Preservation Operators Manual" rather than QTITC.
55939	Timtech C Oxide Wood Preservative	Directions for use include Hazard Class descriptions and required retention rates, and state "apply only using vacuum-pressure treatment in approved industrial facilities according to Australian Standard AS1604-2000 "Timber-Preservative treated – Sawn and round"; or as described under the Timber Utilisation & Marketing Act (Queensland) or the Timber Marketing Act (NSW)." Also specifies that treated timber should be weathered for 4-6 weeks after treatment or kiln dried before use.

9.1.3.2. Recommendations for revision of CCA product labels

Specific recommendations for label statements pertaining to environmental protection in the revision and updating of CCA product labels follow. These recommended label changes apply to all CCA product labels. While outside the scope of the environmental assessment, it is noted that all labels would benefit from being updated to accord with the *Ag Labelling Code*.

APPLICATION INSTRUCTIONS

Labels for all products must specify application rates (retention levels in treated timber) according to relevant hazard classes described by AS 1604.1—2000. [*Note: the label for product 55939 mostly meets this recommendation and serves as a useful guide. Rates would need to be adjusted according to the level of the active constituents present in each product.*]

MIXING AND VACUUM/PRESSURE OPERATIONS

Mixing and vacuum/pressure treatment operations must be conducted on impervious, sealed and bunded areas with facilities to contain and collect leakage, spills, excess treatment solution, drips and waste materials. Avoid spilling product while mixing. If product is spilled, follow instructions for management of liquids, sludge or waste material containing CCA residues.

MANAGEMENT OF FRESHLY TREATED TIMBER (DURING DRIP DRYING AND THE FIXATION PROCESS)

Freshly treated timber must be placed on drip pads that ensure treatment solution is contained and can be collected for recycling. Treated timber must not be moved from the drip pads for at least 48 h, and not until the timber surface is dry. Treated timber must then be held on site until chromium has become fixed to the wood (an appropriate indication of adequate fixation is that described in AS/NZS 1605:2000 “Methods for sampling and analysing timber preservatives and preservative-treated timber”). Leachate water contaminated by product must not enter natural watercourses or waterbodies or reach groundwater. This could be achieved by storing timber in a sealed, bunded area with provision for storing and processing drainage water. [*Note: the chromotropic acid test may provide a practicable alternative means of determining fixation is satisfactorily complete, but is not yet referred to in the Australian Standards – it is listed as a standard method for the US and Canadian industries].*

MANAGEMENT OF LIQUIDS, SLUDGE OR WASTE MATERIAL CONTAINING CCA RESIDUES

Do NOT allow spilled product or mixed solution to enter drains, streams, rivers or waterways. Cover spilled product or mixed solution with sand (NOT sawdust) and/or a suitable stabilising agent (such as a 90% lime and 10% sodium metabisulfite mixture).

Where practicable, spilt material, washings or other materials containing CCA residues from all stages of the mixing, vacuum/pressure treatment, fixation and drying processes or from other sources on the site should be collected and returned to the treatment process. If not used or re-used directly in the treatment process, all liquids, sludge or other waste containing CCA residues must be recycled to recover the active ingredients, or disposed of off site according to local State Government regulations.

WARNING

Timber waste or sawdust treated with this product should not be burnt as this could produce gases and ash toxic to animals and plants.

PROTECTION OF WILDLIFE, FISH, CRUSTACEANS AND THE ENVIRONMENT

Do NOT contaminate streams, rivers or other waterways with product or mixed solution.

STORAGE AND DISPOSAL

Store the product in a locked, cool, well-ventilated, bunded and roofed room.

Triple or preferably pressure rinse containers before disposal. Add rinsings to the treatment process. Do not dispose of undiluted chemicals on site. If recycling, replace cap and return clean containers to recycler or designated collection point. If not recycling, break, crush, or puncture and bury empty containers in a local authority landfill. Empty containers and product must not be burnt. [*Note the absence of the usual on site burial option as these are industrial sites, not farms*].

9.1.4. Related action – recommendation that CCA be made a Restricted Chemical Product

In addition to the foregoing recommendations regarding label changes, it is noted that from an environmental perspective there is a critical issue in ensuring the competence of persons using the products and the nature of the facilities in which treatment occurs. Both these factors influence the potential for harm to the environment generally by significantly influencing the extent to which release to the environment may occur as a consequence of the application process or subsequently from leaching from treated timber over time, both at treatment facilities during the drip drying and fixation processes, and subsequently during storage and use of treated timber in various structures. At this point in time, CCA products can be supplied to any person (under the Agvet Codes).

Appropriate advice for plant design and operation is provided in the Australian Standards, though as discussed above, the need to update the current Standards to address some issues has been identified (despite the fact that they were only revised recently). Several product labels already refer to these Standards and/or to state guidelines or manuals, and in some states there may be action available to environmental agencies or local government to address plant design and operation issues pertaining to the environment. However, these Standards and the ANZECC guidelines on which they are based are not compulsory, and it appears that they are not well followed by all users of CCA. It is noted that the quality of treated timber is tested in NSW and Queensland, to ensure that it meets the minimum retention and penetration standards for the stated hazard class. However, there is no national timber quality testing system in place.

Therefore, it is considered that the nature of the treatment facilities required to treat timber with CCA and the training and experience required by operators to use that equipment and manage freshly treated timber properly together warrant declaration of CCA products to be Restricted Chemical Products under the Agvet Code Regulations. This would enable state and territory agencies to ensure, on an ongoing basis, that plant design and operation and use of the products occur in a fashion which will protect the environment.

9.2. ARSENIC TRIOXIDE TERMITE TREATMENTS

All three labels provide label guidance as to the rate (1-2 g per infestation) and means by which the product should be applied, and some indication as to the strategies to be used and follow-up required. If the label advice regarding the method and rate of use is followed, the risk to the environment should be acceptable (Section 8.8).

All three labels refer to Australian Standard AS 3660-2000 – “Termite management” (Section 5.1.2), though more consistency is required in the detail provided (one label refers to AS 3660.2-2000, one to AS 3660-1993, and one does not specifically elaborate on the relevant standard).

The One Bite and Garrard's labels carry prominently located statements indicating that the product should only be used by (or in one case, sold to) licensed pest control operators. The Aldi label is more specific as to the nature of this competency (licensed pest manager assessed as competent to National Pest Management Industry Competency Standards, Certificate II), but the message is less prominently located and is not stated clearly. The statements referring to the Australian Standards and to use by licensed pest control operators on each of the three labels should therefore be made consistent and placed in similar prominent position on each label.

All three registered products carry the following standard statement under "Protection of wildlife, fish, crustacean and the environment"

> Do not contaminate streams, rivers or waterways with the chemical or used containers.

The One Bite label adds "Do not use as a soil treatment" under this heading, whereas the other labels carry this advice prominently under "General instructions." Either location should adequately convey the message, although standardisation may be appropriate.

10.RECOMMENDATIONS REGARDING RECONSIDERATION OF REGISTRATION AND LABEL APPROVAL

The following recommendations (Sections 10.1 and 10.2) deal with the risk assessments and conclusions described in Sections 8.5, 8.6, 8.7 and 8.8) of this environmental assessment.

10.1. CCA TIMBER TREATMENT PRODUCTS

1. That the APVMA not be satisfied that use of the products listed in Table A (below) in accordance with their respective recommendations for their use (label instructions) would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

Table A

Product Number	Product Name
30691	Tanalith CP Wood Preservative Paste
39884	Tanalith O Type C Oxide Wood Preservative
40092	Impretect CS
41482	Impretect CO Timber Preservative
41680	Sarmix 3 CCA Salts
41681	Sarmix Oxcell C-680 For Timber Treatment
51821	A&C CCA Salt Wood Preservative
51822	A&C CCA Oxide Wood Preservative
55939	Timtech C Oxide Wood Preservative

2. That the APVMA not be satisfied that labels for each of the products listed in Table A (above) contain adequate instructions to ensure that the use of the product in accordance with their respective instructions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment, in respect of:

   i) how the products should be used;
   ii) management (containment and re-use, recycling or disposal) of liquids and sludge containing CCA residues produced during treatment, fixation and drying processes,

including excess treatment solution, spillage, condensation, drips from freshly treated wood and leaching from stored wood or other surfaces containing CCA residues;

iii) the storage and disposal of containers of the products; and

iv) the safe handling of the product in the event of an accident caused by handling of the products (spillage).

3. Consideration has been given as to whether the concerns discussed in this environmental assessment could be dealt with by varying label instructions. It is recommended that the following label variations be made. However, these variations are not of themselves sufficient to recommend that labels would then contain adequate instructions to ensure that the use of the product in accordance with their respective instructions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment. Other such instructions could not be identified, based on the information provided initially and other information identified subsequently. These recommended label changes apply to all CCA product labels.

APPLICATION INSTRUCTIONS

Labels for all products must specify application rates (retention levels in treated timber) according to relevant hazard classes described by AS 1604.1—2000. [*Note: the label for product 55939 mostly meets this recommendation and serves as a useful guide. Rates would need to be adjusted according to the level of the active constituents present in each product.*]

MIXING AND VACUUM/PRESSURE OPERATIONS

Mixing and vacuum/pressure treatment operations must be conducted on impervious, sealed and bunded areas with facilities to contain and collect leakage, spills, excess treatment solution, drips and waste materials. Avoid spilling product while mixing. If product is spilled, follow instructions for management of liquids, sludge or waste material containing CCA residues.

MANAGEMENT OF FRESHLY TREATED TIMBER (DURING DRIP DRYING AND THE FIXATION PROCESS)

Freshly treated timber must be placed on drip pads that ensure treatment solution is contained and can be collected for recycling. Treated timber must not be moved from the drip pads for at least 48 h, and not until the timber surface is dry. Treated timber must then be held on site until chromium has become fixed to the wood (an appropriate indication of adequate fixation is that described in AS/NZS 1605:2000 “Methods for sampling and analysing timber preservatives and preservative-treated timber”). Leachate water contaminated by product must not enter natural watercourses or waterbodies or reach groundwater. This could be achieved by storing timber in a sealed, bunded area with provision for storing and processing drainage water. [*Note: the chromotropic acid test may provide a practicable alternative means of determining fixation is satisfactorily complete, but is not yet referred to in the Australian Standards – it is listed as a standard method for the US and Canadian industries].*

MANAGEMENT OF LIQUIDS, SLUDGE OR WASTE MATERIAL CONTAINING CCA RESIDUES

Do NOT allow spilled product or mixed solution to enter drains, streams, rivers or waterways. Cover spilled product or mixed solution with sand (NOT sawdust) and/or a suitable stabilising agent (such as a 90% lime and 10% sodium metabisulfite mixture).

Where practicable, spilt material, washings or other materials containing CCA residues from all stages of the mixing, vacuum/pressure treatment, fixation and drying processes or from other sources on the site should be collected and returned to the treatment process. If not used or re-used directly in the treatment process, all liquids, sludge or other waste containing CCA residues must be recycled to recover the active ingredients, or disposed of off site according to local State Government regulations.

WARNING
Timber waste or sawdust treated with this product should not be burnt as this could produce gases toxic to animals and plants.

PROTECTION OF WILDLIFE, FISH, CRUSTACEANS AND THE ENVIRONMENT
Do NOT contaminate streams, rivers or other waterways with product or mixed solution.

STORAGE AND DISPOSAL
Store the product in a locked, cool, well-ventilated, bunded and roofed room.

Triple or preferably pressure rinse containers before disposal. Add rinsings to the treatment process. Do not dispose of undiluted chemicals on site. If recycling, replace cap and return clean containers to recycler or designated collection point. If not recycling, break, crush, or puncture and bury empty containers in a local authority landfill. Empty containers and product must not be burnt.

10.2. ARSENIC TRIOXIDE TERMITE TREATMENTS

1. It is recommended that the APVMA be satisfied that use of the products listed in Table B (below) in accordance with their respective recommendations for their use (label instructions) would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

Table B

Product Number	Product Name
48410	Aldi Arsenic Trioxide Termite Dust
48909	Garrard's Termite Powder Insecticide
51234	One Bite Arsenic Trioxide Termite Treatment

2. It is recommended that the APVMA be satisfied that labels for each of the products listed in Table B (above) contain adequate instructions to ensure that the use of the product in accordance with their respective instructions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

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