

Review

Leaching of chromated copper arsenate wood preservatives: a review

J.A. Hingston^a, C.D. Collins^a, R.J. Murphy^b, J.N. Lester^{a,*}

^a*Environmental Processes and Water Technology Research Group, T.H. Huxley School of the Environment, Earth Sciences and Engineering, Imperial College of Science, Technology and Medicine, Royal School of Marines Building, London SW7 2BP, UK*

^b*Department of Biology, Imperial College of Science, Technology and Medicine, London SW7 2AZ, UK*

Received 2 July 1999; accepted 18 December 1999

“Capsule”: *A review of the existing literature about the wood preservative chromated copper arsenate (CCA) indicates not enough is known about leaching of CCA from treated wood.*

Abstract

Recent studies have generated conflicting data regarding the bioaccumulation and toxicity of leachates from preservative-treated wood. Due to the scale of the wood preserving industry, timber treated with the most common preservative, chromated copper arsenate (CCA), may form a significant source of metals in the aquatic environment. The existing literature on leaching of CCA is reviewed, and the numerous factors affecting leaching rates, including pH, salinity, treatment and leaching test protocols are discussed. It is concluded from the literature that insufficient data exists regarding these effects to allow accurate quantification of leaching rates, and also highlights the need for standardised leaching protocols. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copper; Chromium; Arsenic; Wood preservation; Biocides

Contents

1. Introduction.....	54
2. Wood preservative treatment.....	56
2.1. Fixation.....	56
2.2. Formulation.....	57
2.3. Wood anatomy.....	57
2.4. Preservative treatment.....	57
2.5. Loading.....	58
3. Leaching.....	58
3.1. Standard leaching protocols.....	58
3.2. Block size.....	59
3.3. Leaching media.....	59
3.3.1. Salinity.....	59
3.3.2. pH.....	60
3.3.3. Temperature.....	60
3.4. Field trials.....	60
3.5. Results of laboratory and field trials.....	61
4. Component redistribution.....	62

* Corresponding author. Tel.: +44-020-7594-6015; fax: +44-020-7594-6464.

E-mail address: j.lester@ic.ac.uk (J.N. Lester).

5. Speciation	62
6. Leaching mechanism.....	63
7. Conclusions.....	63
Acknowledgements.....	63
References	63

1. Introduction

During the development of freshwater, estuarine and marine coastlines, considerable quantities of wood are used in the construction of docks, pilings and bulkheads. Environmental pressures are increasingly inhibiting the continued use of naturally durable hardwood timbers in these structures (Eaton and Hale, 1993). However, many features of wood make it a particularly attractive building material; wood is a renewable resource, has excellent strength-to-weight properties, has a relatively low price and is easily produced (Desch and Dinwoodie, 1996). Timbers that are not naturally durable are treated with preservatives to prevent decay by wood-boring crustaceans, molluscs and fungi.

Currently, the most widely used wood preservative for timbers exposed in aquatic environments is chromated copper arsenate (CCA). CCA belongs to a group of inorganic, waterborne preservatives including chromated copper boron, ammoniacal copper arsenate, acid copper chromate, ammoniacal copper zinc arsenate and ammoniacal copper quaternary. This group has largely replaced alternative organic preservative types such as creosote, coal tars and pentachlorophenol for aquatic use, due to the environmental and human health concerns of these chemical types, as well as rising costs and declining availability of those treatments.

The metal elements in CCA are usually present in the form of oxides, and wood is industrially treated using a vacuum-pressure impregnation process according to British Standard guidelines (BSI, 1987a, b, 1989). The treatment and use of preservative-treated timber is also subject to industry and international guidelines (Environment Canada, 1988; UNEP, 1994; BWPDA, 1995; WWPA, 1996). Three CCA formulations, referred to as types A, B and C, have been developed, although type C is now the most commercially popular (Table 1). Minimum lifespans in fresh and marine water are considered to be 30 and 15 years, respectively (BSI, 1989).

Out of the 591 million cubic feet (16.7 million m³) of wood preserved in the USA in 1996, 467 million cubic feet (13.2 million m³) (79.1%) were treated with waterborne preservative types. Approximately 144 million lbs (65.3 million kg) of CCA solution was used, while other waterborne preservatives amounted to 4.3 million lbs

Table 1
Chromated copper arsenate (CCA) formulations (oxides basis) (Cooper, 1994)

Type	CuO	CrO ₃ (%)	As ₂ O ₅
CCA-A	18.1	65.5	16.4
CCA-B	19.6	35.3	45.1
CCA-C	18.5	47.5	34.0

(1.9 million kg). Nearly 19 million board feet (5.8 million board m) of preserved timber were prepared for marine construction, of which 95% was treated with CCA (AWPI, 1997).

CCA-treated wood has been used extensively for over 60 years and its success as a building material suggests that leaching may not be a problem in terms of long-term efficacy. Wood preservation is an important industry in Europe and North America, with annual gross sales in the USA of around $\$3.91 \times 10^9$ (3.61×10^9 Euros) in 1996 (AWPI, 1997). However, recent toxicity testing studies have suggested that leaching of preservative components from wood used in aquatic situations may be harmful to the environment, particularly with the proliferation of residential docks around North American coastal waterways.

The toxicity of copper (Cu), chromium (Cr) and arsenic (As) to aquatic organisms is well recorded (Bodek et al., 1988a, b; Fleming and Trevors, 1989; Wong and Chang, 1991; Havens, 1994; Nriagu, 1994a, b; Walley et al., 1996a, b), and all are listed as priority pollutants by the United States Environmental Protection Agency (Weis et al., 1992; Weis and Weis, 1995). The reactions that take place in the wood during the fixation of CCA have a great influence on the metal species that are emitted from the wood, and the subsequent toxicity of these leachates. The toxicity of Cu, Cr and As is highly dependent on the specific form present. Cr in the +6 oxidation state is known to be carcinogenic and mutagenic, but if reduced to Cr (III), as during the CCA fixation process, it may be significantly less harmful (Sanders and Reidel, 1987). As may also be carcinogenic and mutagenic as well as teratogenic and, of the predominant oxidation states, As (V) is thought to be the more prevalent and less toxic form than As (III). Due to its chemical similarity to phosphate,

arsenate may have an elevated rate of uptake by phytoplankton (Sanders and Windom, 1980), and it has been suggested that in low phosphate marine environments, arsenate may actually be more toxic than arsenite (W.S. Atkins Environment, 1998). Although Cu is an important micronutrient, it is toxic in the free ionic state above trace levels, though it may be largely partitioned to organic material in the aquatic environment, particularly humic acids (Newell and Sanders, 1986; Fleming and Trevors, 1989; Livens, 1991; Hung et al., 1993).

Studies have been conducted exposing marine organisms to CCA-treated wood or leachate waters and deleterious effects have been shown against a range of aquatic organisms (Weis et al., 1991, 1992). Criticism of this work focused on the unrealistically high ratio between wood and water volume, which allowed the metal concentrations to build up to toxic levels (Albuquerque and Cragg, 1995a; Breslin and Adler-Ivanbrook, 1998). Further work has suggested a decrease in biodiversity close to CCA-treated marine structures, and elevated levels of metal elements in benthic organisms (Weis and Weis, 1994a, b, 1995, 1996; Albuquerque and Cragg, 1995a; Wendt et al., 1996; Cragg and Eaton, 1997; Weis et al., 1998). Although Cu concentrations were found to be significantly elevated in algae growing on CCA-treated wood panels, no increase was found in fish species associated with the same panels (Weis and Weis, 1999). This suggests that trophic transfer to consumers did not occur, although it was possible that the duration of the studies was insufficient to allow accumulation in higher consumers. Similarly, Adler-Ivanbrook and Breslin (1999) found little metal accumulation in blue mussels exposed to treated wood panels in laboratory and field exposures. Again, experimental design may have influenced results, where continuous flushing of the laboratory system may have prevented bioaccumulation.

In contrast, leachates from untreated wood were shown to have a greater toxicity towards fish and invertebrates than leachates from CCA-treated wood. The adverse effects noted were thought to be due to naturally occurring extractives including aldehydes, phenols, terpinene, camphene and pinene (Baldwin et al., 1996; Taylor et al., 1996). These naturally occurring extractives may be leached out somewhat during the treatment process, or may be more strongly bound to wood as a result of complex formation during treatment.

One of the major problems is that due to inadequate understanding of long-term leaching rates, recommended preservative loading is presently set at very high levels. For example, common treated timbers such as Scots pine and Douglas fir have densities between 500 and 550 kg m⁻³ (Desch and Dinwoodie, 1996). Therefore, with a salt loading of up to 50 kg m⁻³ recommended (BSI, 1989; Eaton and Hale, 1993), the preservative may represent around 10% of the final timber weight. It is

unclear from the current literature if these levels are based on toxicity thresholds of common decay organisms, or are merely intended to account for losses expected throughout the service period. Preservatives must be persistent enough to allow protection throughout the predicted lifespan of the structure, which may be up to 30 years in fresh water conditions. The active components must be of low solubility to resist leaching, yet soluble enough to continue to be effective against organisms responsible for decay (Hegarty and Curran, 1986).

In addition to the possible environmental problems of losses of preservative components during the life of timber, disposal of timbers still retaining high levels of preservative is also of concern. In Germany and France, around 2.1–2.4 million tons of wood waste is considered dangerous (according to the European Council directive 91/689/EEC on hazardous waste). In France alone, out of 25 million CCA-treated poles, 500,000 (or 50,000 tons) are removed from service annually and must be disposed of (Helsen and Van den Bulck, 1998). Better understanding of losses in service may facilitate a reduction in initial loading, and thus alleviate the problems of disposal.

The wood preserving industry is also engaged in a considerable research and development programme to generate improved biocides. A number of these are based on Cu, with the Cr and As replaced by a triazole biocide in copper azole, or a quaternary ammonium biocide in ammoniacal copper quaternary. The novel biocides, in addition to containing Cu, will bind to wood along the same ion exchange mechanisms, so better understanding of the factors that affect CCA leaching will be of benefit in their further development.

Wood preservatives are also subject to increasingly stringent environmental legislation, particularly within the European Union where they will fall under the control of the new Biocidal Products Directive, which will come into force in the year 2000. As-containing wood preservatives have also recently been scrutinised under the Marketing and Use Directive (W.S. Atkins Environment, 1998).

Wood preservatives must be considered as part of a much wider suite of biocides. Of these, the adverse environmental effects of antifouling paint biocides containing organotin have been widely reported (Gibbs et al., 1987, 1988; Clark et al., 1988). Cu remains an important active ingredient in the antifouling paint industry following legislation against the use of organotin compounds, and is also likely to remain a mainstay of the wood preserving industry in the future. Closer examination of the wood preservatives as an additional source of Cu to the aquatic environment is therefore relevant.

To enable a more realistic assessment of the possible environmental effects of CCA-treated timber accurate quantification of component leaching rates is required.

Leaching involves a number of different processes, including initial loss of surface deposits and unfixed components, penetration of water into wood and hydrolysis or dissolution of the fixed or complexed components and migration of preservative to the surface of the wood (Cooper, 1994). Aspects of the preservative treatment of wood may affect its leachability, in addition to the environment the wood is exposed to in its period of service.

A comprehensive literature review conducted for the United States Department of Agriculture provides a summary of pertinent data available up to 1995 on leaching of a number of preservative types in terrestrial and aquatic environments (Lebow, 1996). This earlier review concluded that despite the numerous laboratory studies that had been conducted, the data generated often had little applicability to in-service leaching rates. It also highlighted the need for further research to address the effects of different environmental exposures, such as fresh water, seawater and highly organic environments, and the need to monitor the overall environmental fate of leached wood preservative components.

The aims of this review are to evaluate the existing data on leaching of CCA, and the principal factors that affect leaching rates in order that releases to different aquatic environments can be predicted and risks assessed. While much of the literature reviewed concerns research conducted with CCA applications in terrestrial as well as aquatic environments, the authors have made every effort to rely upon work which has a specific aquatic focus.

2. Wood preservative treatment

2.1. Fixation

Although the fixation of CCA is still not completely understood, the process is generally defined by the reduction of hexavalent chromium. The reduction of the reactive and mobile Cr (VI) to Cr (III) is crucial in the formation of insoluble complexes in CCA-treated wood. As can be seen in Table 2, there is a direct correlation

Table 2
Effect of chromium (Cr) fixation on chromated copper arsenate (CCA) leaching losses from red pine pole sections following 2 h simulated rainfall (Cooper et al., 1995)

% Cr fixation	Cr (VI)	Leaching ($\mu\text{g cm}^{-2}$)		
		total Cr	Cu	As
68.2	799	1499	755	120
84.1	200	376	162	96
92.6	53	71	34	4
98.2	0.1	2	4	3

between the level of unreacted Cr (VI) in treated wood and the leaching concentration of CCA components and complete fixation is essential to minimise leaching (Cooper et al. 1995; Walley et al., 1996b). Fixation of wood at 15°C takes around 14 days (Eaton and Hale, 1993).

The fixation of multi-component preservative types such as CCA is a complex and active process, and the components are not simply taken up through the conducting tracheid cells and deposited in the lumens of these cells (Hayes et al., 1994). Chou et al. (1973) used analytical electron microscopy techniques to demonstrate component penetration of the primary and secondary cell wall and the presence of coarse deposits of mainly Cu on cellulose microfibrils. Merkle et al. (1993) demonstrated that the highest metal concentrations were found in the porous ring tissues, and granular precipitates were observed in the tracheids. Hager (1969) demonstrated that Cu could fix to wood in the absence of a fixing agent, such as Cr.

Pizzi worked extensively on the chemistry and kinetic behaviour of CCA wood preservatives. Studies of the reactions of mixtures of metal salts with the various constituents of wood, lignin and cellulose and simple model components such as guaiacol and D (+)-glucose were conducted (Pizzi, 1981, 1982a, b, c). 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 type C was considered to have only $\pm 10\%$ of the total Cr 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 As. Later work highlighted the presence of chrome arsenates that may be weakly adsorbed or simply precipitated on wood carbohydrates or lignin (Pizzi, 1990a, b). Wood extractives have also been suggested as a potential site for CCA fixation (Pizzi et al., 1986; Ryan and Plackett, 1987; Forsyth and Morrell, 1990; Kennedy and Palmer, 1994).

Developments in the use of techniques such as electron paramagnetic resonance spectroscopy (EPR) and X-ray photoelectron spectroscopy (XPS) have allowed further identification of chemical species and complexes bound to specific sites in the wood anatomy. XPS analysis, for example, has indicated increased carbon–hydrogen bonding and decreased carbon–oxygen bonding, suggesting oxidation of hydroxyl groups on cellulose or lignin and decarboxylation of carbonyl and carboxyl groups during fixation (Ruddick et al., 1993; Kaldas et al., 1998). Evolution of CO_2 resulting from this oxidation and decarboxylation as Cr is reduced has also been monitored as fixation proceeds (Porandowski et al., 1998). EPR techniques have suggested the

presence of CuN_2O_2 complexes in amine copper-treated wood, and Cu bound to four oxygen atoms in nitrogen-free formulations, such as CCA (Hughes et al., 1994).

Although these initial reaction steps are generally well characterised, the continuing longer-term reactions, and the effects these have on the distribution of metal species is not so well understood. A general scheme for the different stages of fixation has been proposed (Table 3). The available literature pertaining to CCA fixation suggests that many wood constituents may play a role in the overall reactions. This is to be expected considering the number of potential reactive sites in wood, the tendency of Cu to adsorb strongly to organic matter in general, and the strong reducing capacity of hexavalent Cr (Lebow, 1996).

2.2. Formulation

The ratio of preservative components in CCA formulations is crucial to allow rapid and 'complete' fixation. Fahlstrom et al. (1967) found a clear relationship between the Cr:As ratio and total metal leachability, and proposed a ratio of Cr:As of 1–1.30 as optimum. Smith and Williams (1973a, b) studied a range of CCA formulations and suggested a Cr:As ratio of 1.9 or greater for maximum As fixation. As a consequence of this variation in fixation of different formulations, early leaching studies generated variable results, with As often proving to be the most leached element, presumably due to insufficient Cr available for complexation (Fahlstrom et al., 1967; Henshaw, 1979).

2.3. Wood anatomy

Since lignin is thought to be a primary site for binding of Cr complexes, an increased lignin content may result in improved treatment. Softwood species, high in lignin, are therefore often found to perform better than hardwoods

in terms of preservative treatment, and the anatomy of softwoods, with a high proportion of xylem tracheids also results in improved performance (Hayes et al., 1994).

Earlywood tracheid cells of softwood species function primarily as a means of conduction, and consequently have a higher proportion of bordered pits in the cell walls (Desch and Dinwoodie, 1996), and larger volume of lumen (Nicholas et al., 1991). Hayes et al. (1994) suggest that although earlywood is thought to be higher in lignin than latewood, which allows improved fixation, the anatomy of cells may be more important in determining fixation, and allow more rapid preservative movement and increase subsequent losses due to leaching. The distance that solutes such as CCA must diffuse will influence preservative treatment. Hardwoods are penetrated mainly via vessels, and estimated diffusion paths in these species is much longer than softwoods (Cooper and Churma, 1990). It is suspected that long diffusion times may prevent the saturation of the cell wall before the fixation reactions are completed, leading to an altered microdistribution of elements.

Variation in the preservative penetration and retention in sapwood and heartwood of identical species grown in separate areas has been observed, despite the lack of differences in size and number of growth rings, or a consistent relationship between specific gravity and retention (Taylor, 1991).

2.4. Preservative treatment

Physical parameters of the preservative process such as magnitude and duration of vacuum and pressure cycles may influence penetration and retention of preservatives. Increasing the pressure treatment period may reduce the proportion of elements on the surface of the wood, and may thus reduce leaching. Conversely, increasing the length of the vacuum stage may affect the proportion of more readily leached surface components (Cooper, 1994).

The temperature at which the treatment cycle is conducted, and post-treatment drying conditions have been shown to exert a considerable influence on fixation and leaching. Early work in the field of accelerated fixation was pioneered by Peek and Willeitner (1981, 1988). Fixation times are known to be greatly reduced when timbers are exposed to increased temperatures both during and following treatment, with fixation complete within 1 h at temperatures in excess of 85°C (Cooper and Ung, 1992; Eaton and Hale, 1993). However, Dahlgren (1975b) first observed increased leaching of Cu at elevated drying temperatures. Post-treatment drying of wood in kilns at temperatures of 60–80°C resulted in increased leaching of CCA elements compared with wood left to dry at ambient temperature (Dahlgren, 1975a; Lee et al., 1993). Initial leaching rates of Cu were approximately double from steam-fixed wood compared

Table 3
General scheme for chromated copper arsenate (CCA) fixation reactions (Murphy, 1998)

Reaction	Description	Products
Initial (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	?

with naturally fixed pine, while Cr losses were substantially reduced by steam fixation (Van Eetvelde et al., 1995a, b). Rapid drying may cause redistribution of chemicals between lignin and cellulose, leading to higher proportions of leach-susceptible components, or deposition of CCA products in the cell lumens, where again they may be more accessible to leaching (Lee et al., 1993; Cooper et al., 1997). Pizzi (1983a) observed that the ratio of CCA components reacting between carbohydrates and lignin increased at increasing temperatures of the preservative solution. Hardwoods subject to accelerated fixation have been shown to be more susceptible to biological decay and the possible causes were postulated to be due to altered Cu complexation that made it less available as a toxicant. Alternatively the diffusion of components to the susceptible cell wall areas may not be able to occur when reaction rates are increased by accelerated fixation, and therefore the microdistribution of CCA may be affected (Preston and McKaig, 1983).

2.5. Loading

Increasing the concentration of the treatment solution has been suggested to increase the rate of fixation and to affect the binding of Cr complexes in favour of lignin, possibly due to the lower pH (Pizzi, 1983b). Conversely, increasing treatment concentrations was observed to lengthen the time period for initial fixation reactions to occur (Dahlgren, 1975a, b). However, in the conditions typically used commercially, solution concentration and retention does not seem to have a major influence on fixation rate (Pizzi, 1983b; Cooper and Ung, 1992).

Preservative loading will affect the absolute concentration of elements leached and the percentage of total leached, although the exact relationship between preservative loading or retention and leaching is not clear (Cooper, 1994; Albuquerque and Cragg, 1995a, b; Albuquerque et al., 1996). Fahlstrom et al. (1967) suggested the effect of retention on leaching was dependent on preservative composition, with percentage leaching decreasing with increasing retention in As-rich formulations. In Cr-rich formulations, leaching increased with retention. Proportional losses have been found to decrease at increased loadings (Archer and Preston, 1994; Hayes et al., 1994). Following 85 months exposure in the marine environment, percentage losses were 52 and 44% from pine-treated to retentions of 24 and 48 mg kg⁻³, respectively. The reduced leaching was suggested to be due to increased total Cr concentrations in the system available to fix the remaining metal elements (Archer and Preston, 1994). However, other workers have shown increased leaching with increasing retentions (Hager, 1969; Irvine et al., 1972; Albuquerque et al., 1996). Breslin and Adler-Ivanbrook (1998) observed that long-term Cu and Cr leaching rates were highest in

CCA-treated wood with retention levels > 35 kg m⁻³, whereas long-term As leaching rates were increased in wood with retention levels < 35 kg m⁻³. These observations may possibly be explained due to competition for binding sites between Cu and Cr, and the role of Cr in the fixation of As.

3. Leaching

There has been a considerable amount of literature published concerning leaching of CCA wood preservatives in aquatic environments. However, the focus of much of the early work has been on monitoring leaching in terms of the durability of wood and the ability of treated timbers to withstand biological decay, rather than quantify releases to, and effects on, the marine environment (Fahlstrom et al., 1967; Hager, 1969; Cherian et al., 1979; Johnson, 1982; Eaton, 1989; Green et al., 1989). Although it is clear that large amounts of preservative do remain in properly fixed wood after prolonged exposure, due to the high loading even small percentage losses may be environmentally significant due to the high toxicity of the components.

3.1. Standard leaching protocols

A number of standard protocols exist for conducting laboratory leaching studies (AWPA, 1983; ANS, 1986; BSI, 1994, 1997). For example, ENV. 1250:2 (BSI, 1994) recommends immersing five end-sealed test blocks (50×25×15 mm) in 500 ml of water or synthetic seawater, and stirring at 20°C, for six leaching periods of increasing duration up to 48 h. Researchers have either followed one of these standard protocols or designed original leaching trials using a range of different parameters, but few studies have been conducted using identical parameters and protocols, making direct comparison of results difficult. Willeitner and Peek (1998) briefly reviewed standard test methods for measuring environmental inputs of waste and other material by leaching and propose general requirements necessary for leaching studies with wood preservatives. Recommendations for the harmonisation toward a single protocol have been made, with modification of the biological efficacy testing protocol B.S. EN. 84 (BSI, 1997) suggested as being the most appropriate (Van Eetvelde et al., 1998; Wegen et al., 1998). The principal advantage of B.S. EN. 84 appears to be the incorporation of a water impregnation stage, where test blocks are immersed in water and maintained in a vacuum desiccator for 2 h prior to leaching. This may therefore represent the most severe leaching test of all available protocols. Potential drawbacks of this approach are the inability to end-seal test blocks, the use of static water conditions, and the lack of a rigid sampling regime.

ENV. 1250:2 (BSI, 1994) recommends an intermediate drying period of 16 h during the test to simulate natural drying of wood exposed to tidal regimes.

Although these protocols may be regarded to be relatively simple, and therefore easily repeatable, results do not necessarily give an accurate estimation of losses from commercial size timber. This is due to differences in size, physical stresses and environmental conditions. A number of researchers highlight the important point that laboratory results should not be used to interpret losses from commercial size timber, but should only be used as a comparison between preservative types (Cooper, 1994; Albuquerque et al., 1996). However, there is continued reliance on laboratory-based data to make judgements on the acceptability of wood preservatives. Agreement to adopt a single recognised protocol for all leaching studies would certainly aid comparison of laboratory-based data in the future. For the purposes of reducing inter-laboratory variation the methodology of such a single protocol should be kept as simple as possible. One important facet of any leaching protocol is that sampling should be conducted at sufficiently regular intervals to allow quantification of the decline in leaching rates during the early period of exposure. It is also important that the tests are of sufficient duration in order that the longer-term leaching rates be accurately quantified. End-sealing of test blocks will help minimise the effects of high leaching rates from timber end-grains, which may form a significant proportion of standard test blocks. Simulation of water motion and tidal movements, by incorporation of stirring devices and daily drying periods may also be important parameters in any leaching protocol.

Despite a considerable amount of literature available, the leaching rates of common preservative types, such as CCA, from commercial size timber remain poorly defined. The existing literature has indicated that a number of factors may influence the leaching rate of wood preservatives, including pH, salinity, block size and wood surface exposed. These are reviewed below.

3.2. Block size

The size of wooden block used during laboratory leaching trials appears to have a major influence on the leaching rates obtained. The relatively large surface area-to-volume ratio of the typical small sample blocks used in most laboratory studies allows proportionately more wood available for leaching, and distances components must diffuse decreases (Cooper, 1994).

Significant reductions in leaching rates of all CCA elements were observed with a decrease in surface area-to-volume ratio (Hayes et al., 1994), although the exact relationship has not been fully characterised. Attempts have been made to model the three-dimensional transport of organic wood preservatives, taking into account

the differential diffusivities of the wood surfaces (Haloui and Vergnaud, 1995, 1997). One trial has attempted to conduct a laboratory study with more realistic timber dimensions, with a pile 250 mm in diameter and 1200 mm long, although sampling did not allow full characterisation of leaching rates (Baldwin et al., 1996).

The proportion of the three wood surfaces exposed may also affect leaching rates. Losses within 24 h have been shown to be greatest from the radial and tangential surface, although long-term leaching was greatest from the end-grain (Orsler and Holland, 1993). End-grain penetration has been shown to be 40 times greater than lateral penetration and may greatly influence leaching rate (Morgan and Purslow, 1973). In commodity size timber, end-grain may represent only a small percentage of exposed surfaces, but may form a significant proportion of standard test blocks. This may lead to laboratory studies grossly overestimating leaching rates (Archer and Preston, 1994; Cooper, 1994; Albuquerque and Cragg, 1995a). However, the advantage of using relatively small blocks, apart from ease of manipulation and relatively high percentage losses, includes the homogeneity of the sample and consistent preservative loading throughout the sample. With increasing size of timber, the heterogeneity of the sample increases, increasing variation in preservative loading. Variations in heartwood and sapwood can significantly alter loading. For example, in wood treated to a specified level of 40.7 kg m⁻³, outer 1.3 cm sample retention levels ranged from 4.5 to 64 kg m⁻³ (Breslin and Adler-Ivanbrook, 1998). Clearly this magnitude of variation may obscure losses due to leaching. The use of end-matched sections in leaching trials has been recommended to reduce such variability (Rak and Clarke, 1974; Albuquerque et al., 1996).

3.3. Leaching media

A number of features of the leaching media are important in determining leaching rates, particularly salinity and pH. Attention has also been drawn to the importance of the volume of leaching water used, particularly in toxicity studies, where a high wood:water volume ratio allowed toxic concentrations of metals to build up (Weis et al., 1991; Albuquerque and Cragg, 1995a). It is possible that a high wood:water volume ratio, or insufficient replacement of leaching waters may inhibit diffusion of elements into water (Brooks, 1997; Breslin and Adler-Ivanbrook, 1998). Van Eetvelde et al. (1995a, b) quote a wood:water volume ratio of 1–5, as recommended in a Dutch government standard for simulating releases from building materials.

3.3.1. Salinity

Scots pine and beech sapwood blocks treated with CCA were exposed in cooling towers receiving water

from fresh water, sewage effluent and marine sources with results indicating increased loss of Cu and Cr with increasing conductivity of the surrounding waters (Irvine et al., 1972). Solutions of higher ionic strength have been shown to leach greater concentrations of CCA, although in the salinity range from 0 to 24‰ no increase in Cu loss was observed. It has been suggested that at low salinities, NaCl has a coagulating effect on the crystallite Cu fixation complexes increasing surface area and decreasing solubility, whilst at salinities above 24‰ the increased formation of complexes between chloride and Cu may explain the increased leaching (Irvine and Dahlgren, 1976). Pine sapwood treated with CCA and leached with varying strengths of salt solutions (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ or $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ at 0.03–1.00 M) resulted in increased Cu leaching compared with deionised water controls, and leaching rates increased with salt solution concentration (Plackett, 1984).

3.3.2. pH

Studies investigating the effects of solution pH on preservative loss were conducted using water buffered with sodium hydroxide and citric acid. This study indicated very high leaching rates at low pHs, with losses of Cu of up to 100% at pH 4.5 (Warner and Solomon, 1990). Leaching in dilute sulphuric acid solutions was reduced by up to a factor of 5, and Cooper (1991) later demonstrated that the high losses were due to the use of the citric acid buffer. The carboxylate group of the citric acid acted as a bidentate ligand that bonded with metal ions, forming water-soluble complexes. When pH of solutions was adjusted using a mineral acid with no such chelating properties, no consistent effect on leaching was observed at pH 3.5–5.5. Publication of the initial work resulted in considerable media interest, amid raised concerns over the environmental effects of wood preservative leachates (Cooper, 1990). Van Eetvelde et al. (1995a, b) observed maximum leaching of Cr and As under neutral conditions, with initial losses of Cu increasing with higher acidity. The influence of increased acidity is explained due to the role of the additional hydrogen ions acting in the acid-ion-exchange reactions at the acid adsorption points on wood cell walls (Van Eetvelde et al., 1998). Results of typical leaching trials investigating effects of pH are shown in Table 4.

3.3.3. Temperature

Effects of temperature have also been investigated. Leaching of Cu, Cr and As has been shown to be reduced at lower temperatures, with leaching of Cr at 20°C reported to be $0.119 \mu\text{g m}^{-2} \text{s}^{-1}$ compared with $0.079 \mu\text{g m}^{-2} \text{s}^{-1}$ at 8°C (Van Eetvelde et al., 1995a), although one study has indicated decreased flux of As at 20°C compared with leaching at 4°C (Breslin and Adler-Ivanbrook, 1998).

Table 4
Effects of pH on leaching of copper from chromated copper arsenate (CCA)-treated wood

pH	Percentage leached	Duration	Reference
3.5	3.4	13 days	Cooper (1991)
4.5	2.8		
5.5	2.6		
4.0	4.1	79 hours	Van Eetvelde et al. (1995b)
5.5	3.4		
7.0	2.3		
8.5	1.9		
2.5	145 ^a	40 days	Warner and Solomon (1990)
3.5	75		
4.5	21		

^a Values represent a single replicate, and the percentage loss reported is thought to be an artefact of block-to-block variation and underestimation of initial loading.

3.4. Field trials

A number of field trials have been instigated to better quantify the losses of wood preservatives under more realistic environmental conditions. In long-term marine field trials, CCA-treated pine leached as much as 25% of total active ingredients within 6 months, with total losses only rising to 52% after 85 months (Archer and Preston, 1994). Hayes et al. (1994) also observed losses of Cu from pine submerged in coastal waters occurred most within the first 12 weeks of a 72-week leaching trial. Work on toxicity of leachates indicated a reduction in toxicity of wood used in subsequent trials, suggesting reduced leaching with time (Weis et al., 1991, 1992). Field trials testing the durability of different CCA-treated timbers indicated that the average leaching rates of CCA were 1.8–17.3%, and that those with the highest leaching rates had the minimum lifespan (Cherian et al., 1979).

One of the problems with field trials is that monitoring of leaching is conducted by measuring preservative concentrations remaining in wood after a set period of submergence rather than measuring element concentrations in leaching solutions. Even small variations in the high loading concentrations can obscure trends in losses of preservatives and this has led to apparent negative leaching rates in some studies (Hayes et al., 1994; Albuquerque et al., 1996). Calculation of variation in the As:Cr and Cu:Cr ratio has been used to assess changes in wood recovered from a bulkhead after 13 years exposure (Breslin and Adler-Ivanbrook, 1998). This is based on the assumption that Cr is leached the least. A 53% decrease in both ratios was observed in sections of timber removed from an area that was constantly submerged. Only a 5–7% decrease was seen in samples from wood submerged in sediment. This suggests that even though the sediment may be saturated,

the wood was not subject to the constant flushing required to elicit leaching.

Test blocks in the field may be exposed to a more severe leaching environment than in the laboratory due to increased physical stresses leading to abrasion and cracking, and borer attack may increase the surface area available for leaching (Merkle et al., 1993). Due to the effect of pH on leaching rates, it has been postulated that high concentrations of humic acids in surface waters may increase leaching (Cooper, 1994). The growth of fouling organisms on the surface of wood in the field has been considered a possible cause of reduced leaching rates (Hayes et al., 1994). Periodic wetting and drying of CCA-treated wood in seawater, as in tidal flux, has been shown to result in surface separation of tracheids, possibly due to the formation of salt crystals as water evaporates (Johnson et al., 1992) and may result in increased losses of preservative.

3.5. Results of laboratory and field trials

Although direct comparison of results from laboratory and fieldwork is difficult, due to the varying effects of numerous parameters, particularly wood species, loading and environmental conditions, two clear points emerge from the available literature.

Firstly, it is clear that leaching of individual metal elements is not proportional to concentrations in the original formulation. Although Cr losses with some formulations exceed losses of Cu and As (Fahlstrom et al., 1967; Irvine et al., 1972; Hegarty and Curran, 1986), studies with more modern formulations, such as CCA type C, tend to show that Cu and As are lost to the greatest degree, despite being present in the smallest proportions. Total losses released following 28 days exposure in seawater were 530 mg m⁻² for Cu, 56.2 mg

m⁻² for As, and total Cr loss was equivalent to background concentrations (Baldwin et al., 1996). Following 21 days exposure in seawater, leaching rates for Cu and As were approximately 1 µg cm⁻² day⁻¹ and only 0.01 µg cm⁻² day⁻¹ for Cr (Merkle et al., 1993). In tests with 0.5 g of wood shavings, the increased surface area led to losses of 2060 µg l⁻¹ Cu, 720 µg l⁻¹ As and 870 µg l⁻¹ Cr following submergence for 8 weeks in 50 ml of artificial seawater (Weis et al., 1991).

Studies have also indicated that leaching rates of all metal components are highest initially, and decrease significantly over time. Leaching rates of a variety of CCA formulations were observed to decrease to around one-fifth to one-tenth of initial values within 18 h, and down to one-hundredth within 48 h (Fahlstrom et al., 1967). Breslin and Adler-Ivanbrook (1998) calculated 90-day fluxes for a number of previous studies, and Table 5 shows that though these were consistent for Cu, more variability was seen with As and Cr.

Rates of Cu loss were similarly seen to decrease from 3.6 µg cm⁻² day⁻¹ down to 1.4 µg cm⁻² day⁻¹ after 6 months, with As rates lower, and Cr leaching to the smallest degree (Albuquerque et al., 1996). Of potentially environmental significance was the reported slower decline in flux of As compared to Cu and Cr (Hayes et al., 1994; Breslin and Adler-Ivanbrook, 1998).

In a spreadsheet-based computer model developed to predict Cu concentrations leached from CCA-treated marine structures, based on the results of Putt (1993), non-linear regression techniques were used to produce an equation to describe the decrease in Cu leaching with time:

$$\text{Cu loss } (\mu\text{g cm}^{-2} \text{ day}^{-1}) = 3.566e^{-0.048 \times \text{time}(\text{day})}, \quad (1)$$

under Eq. (1), Cu leaching rates are reduced to 24% of initial rates within 30 days, and to 1% after 90 days

Table 5
Leaching flux of copper, chromium and arsenic (after Breslin and Adler-Ivanbrook, 1998)

Element	Calculated 12-h flux (µg cm ⁻² day ⁻¹)	Calculated 90-day flux (µg cm ⁻² day ⁻¹)
<i>Copper</i>		
(Breslin and Adler-Ivanbrook, 1998)	5.7–17.8	0.08–1.4
(Putt, 1993)	7.6	0.8
(Weis et al., 1991)	41.3	0.3
(Merkle et al., 1993)	4.3–5.6	0.5–0.6
<i>Chromium</i>		
(Breslin and Adler-Ivanbrook, 1998)	0.2–1.0	0.004–0.04
(Putt, 1993)	1.5	0.01
(Weis et al., 1991)	0.08	0.0003
(Merkle et al., 1993)	0.03–0.1	0.003–0.006
<i>Arsenic</i>		
(Breslin and Adler-Ivanbrook, 1998)	0.1–3.9	0.04–0.2
(Putt, 1993)	6.9	0.2
(Weis et al., 1991)	0.4	0.001
(Merkle et al., 1993)	3.3–8.2	0.4–0.5

(Brooks, 1996, 1997). It is interesting to note that even though this work takes a relatively conservative approach, Cu concentrations are predicted to exceed marine water quality standards only in very poorly flushed aquatic environments, or where the surface area of the surrounding water body is less than 259 times the surface area of exposed wood.

4. Component redistribution

Work has also been done to try to quantify movement of individual components within the wood during leaching trials. Cu concentrations were observed to increase significantly in the peripheral zones, with large-scale depletion from the inner sections, in long-term trials with marine piles in New Zealand (McQuire, 1976). Similarly, although loss of Cu was greater from the outer zone after just 6 months marine exposure, between 12 and 85 months exposure losses were much greater from the inner zone compared with peripheral zones (outer 8 mm) (Archer and Preston, 1994). Further evidence of redistribution of Cu at the surfaces of CCA-treated wood has been observed, and it has been proposed that treated stakes in seawater may behave as chemical cells and that redistribution be caused electrolytically (Shelver et al., 1992). The phenomenon of transverse movement of Cu ions through wood cell walls has implications for leaching mechanisms, as well as efficacy of treated timber, where redistribution may leave sections of wood vulnerable to decay.

5. Speciation

Although considerable information exists on speciation of the individual elements in CCA, there is little

research specific to CCA leachates (Albuquerque and Cragg, 1995a). It is not clear if metals are leached as individual elements, as Cu or Cr arsenates, as inorganic complexes or possibly even as organometallic complexes bound to water-soluble wood extractives (Lebow, 1996).

Baldwin et al. (1996) studied partitioning of metals to sediment during laboratory leaching trials with marine piles, and found that Cu bound to both low and high organic carbon sediment to the same degree, and did not desorb to the overlying waters. Cr exhibited minimal adsorption to a high organic carbon sediment only, and As was found in all cases in the interstitial or overlying waters. Speciation into oxidation states was not possible due to low concentrations.

Some workers have speculated as to the possible mobile species that may be subject to leaching from treated wood. These may include soluble Cu hydroxide ions, CrO_3 , HCrO_4^- or CrAsO_4 , although little data was provided to support this (Hayes et al., 1994). Pizzi (1982c) suggested that of the forms of Cu present in CCA-treated wood, CuSO_4 physically adsorbed by the various wood constituents was the likely leachable component.

Analysis of the valence state of As on treated wood has been more widely conducted due to human health concerns. Water-soluble arsenite on the surface of wood was measured and found to be relatively constant at 3–4 $\mu\text{g } 100 \text{ cm}^{-2}$, or about 3% of total As in treated wood. Arsenite is inversely proportional to Cr (VI) concentration, indicating that Cr (VI) may oxidise any arsenite in the CCA mixture (Woolson and Gjovik, 1981). Further speciation analysis of preserved wood from commercial supplies indicated no trivalent As to be present, but that up to 20% of the Cr was present in the hexavalent form, suggesting that fixation may not be complete in impregnated timber available on the market (Nygren and Nilsson, 1993).

Table 6
General scheme for leaching of chromated copper arsenate (CCA) from treated timber in aquatic environments

Reaction	Description	Reference	Principal factors affecting rate
Initial (hours)	Loss of surface deposits	Cooper (1994)	Surface area
Mid term (days/weeks)	Capillary absorption and diffusion of H_2O into wood and loss of unfixed components	Cooper (1994)	Timber type
	Solvation of crystallite CCA fixation products (particularly copper)	Chou et al. (1973)	Degree of fixation
	Formation of soluble complexes of copper and chromium with chloride and hydroxide ions	Merkle et al. (1993)	Post-treatment handling
	Disassociation of complexes merely precipitated in lumen of tracheid cells rather than chemically bound to wood carbohydrate or lignin	Hegarty and Curran (1986)	Volume of wood
Long term (months/years)	Reversible disassociation of ion-exchanged metals, redistribution to surface and loss	Irvine and Dahlgren (1976)	Salinity
	Physical or biological decay of timber	Breslin and Adler-Ivanbrook (1998)	pH

6. Leaching mechanism

Just as a general scheme for the fixation of CCA has been developed (Table 3) it is possible to propose a similar scheme to describe the possible leaching mechanism, based on the published literature (Table 6). The principal factors likely to affect each reaction stage are also included.

The mid-term solvation of crystallite forms of Cu may explain the relatively high leaching rate for this element compared with the other metals. The longer-term reactions and redistribution of elements may take place according to the electrolytic cell hypothesis proposed by Shelver et al. (1992).

7. Conclusions

Aspects of both the preservative treatment of wood and the environmental conditions the wood is exposed to may affect its leachability. Factors such as preservative formulation, fixation temperature, post-treatment handling, timber dimensions and leaching media pH, salinity and temperature have been shown to affect leaching rates. However, more rigorous examination of these factors is required if accurate prediction of in-service leaching rates is to be made based solely on results of laboratory studies. Although the fixation reactions greatly reduce leaching, measurable quantities of Cu, As and Cr can be found in leaching solutions from properly treated wood. The toxicity of these leachates will be largely dependent on the speciation of the individual metal elements. In addition, removal of metals from the aqueous phase through partitioning to sediments and dilution by water movements may moderate toxicity.

Examination of the existing information suggests that a number of other areas are worthy of further research in order to gain a more realistic assessment of the risks posed by the use of preservative-treated timber in aquatic environments:

1. establishment of a single laboratory leaching protocol to enable meaningful comparison of all laboratory work conducted in the future; the need for standardisation is increasingly pertinent in light of the forthcoming Biocidal Products Directive;
2. better quantification of effects of surface area: volume ratio and total sample size on leaching rates in order that models may be developed to allow extrapolation of leaching rate data generated from standard laboratory protocols to wood with commercial use dimensions;
3. field trials in both saline and freshwater environments to evaluate losses in-service to allow further

refinement of laboratory-based data to losses expected from real environmental exposures;

4. speciation analysis of leached components to determine if metals are lost as individual elements, metal complexes, or bound to inorganic or organic ligands; this will allow further refinement of risk assessments since the toxicities of CCA components, particularly Cr and As, are greatly influenced by valence state;
5. examination of other environmental factors likely to influence leaching rates, including Redox conditions, presence of organic acids in natural waters and growth of fouling communities on timber surfaces; and
6. examination of the long-term fixation reactions, particularly the equilibrium dynamics between Cr (VI) and Cr (III) which may strongly influence leaching over the lifetime of preserved timbers.

In addition, equally rigorous examination of the potential alternative biocides should be made before any further regulatory action against CCA can be recommended.

Acknowledgements

One of the authors (J.A.H.) is grateful to the Natural Environment Research Council for partial funding of a CASE studentship in association with Laporte Industries.

References

- Adler-Ivanbrook, L., Breslin, V.T., 1999. Accumulation of copper, chromium, and arsenic in blue mussels (*Mytilus edulis*) from laboratory and field exposures to wood treated with chromated copper arsenic type C. *Environmental Toxicology and Chemistry* 18, 213–221.
- Albuquerque, R.M., Cragg, S.M., 1995a. Evaluation of Impact of CCA-Treated Wood on the Marine Environment (IRG/WP 95-50040). The International Research Group on Wood Preservation, Stockholm.
- Albuquerque, R.M., Cragg, S.M., 1995b. Fouling Organisms as Indicators of the Environmental Impact of Marine Preservative Treated Wood (IRG/WP 95-50063). The International Research Group on Wood Preservation, Stockholm.
- Albuquerque, R.M., Cragg, S.M., Icely, J.D., 1996. Leaching of CCA Treated Wood Submerged in Seawater: Effects of High Loadings, and a Comparison Between Laboratory and Marine Conditions (IRG/WP 96-50080). The International Research Group on Wood Preservation, Stockholm.
- ANS, 1986. Measurement of the Leachability of Solidified Low-level Radioactive Waste by a Short Term Test Procedure (ANSI/ANS 16.1). American Nuclear Society, La Grange Park, IL, USA.
- Archer, K., Preston, A., 1994. Depletion of Wood Preservatives After Four Years' Marine Exposure in Mt. Maunganui Harbour, NZ (IRG/WP94-50036). The International Research Group on Wood Preservation, Stockholm.

- AWPA, 1983. Standard M-10. Testing wood preservatives by laboratory soil block cultures. In: Book of Standards. American Wood Preservers Association, Washington, DC.
- AWPI, 1997. The 1996 Wood Preserving Industry Production Statistical Report. American Wood Preservers Institute, Virginia.
- Baldwin, W.J., Pasek, E.A., Osborne, P.D., 1996. Sediment toxicity study of CCA-C treated marine piles. *Forest Products Journal* 46, 42–50.
- Bodek, I., Lyman, W.J., Reehl, W.F., Rosenblatt, D.H. (Eds) 1988a. Arsenic, Chapter 7.2, Environmental Inorganic Chemistry Properties, Processes, and Estimation Methods (SETAC special publications service). Pergamon Press, New York pp. 7.2-1–7.2-10.
- Bodek, I., Lyman, W.J., Reehl, W.F., Rosenblatt, D.H. (Eds.) 1988b. Chromium, Chapter 7.6, Environmental Inorganic Chemistry. Properties, Processes, and Estimation Methods (SETAC special publications service). Pergamon Press, New York pp. 7.6-1–7.6-12.
- Breslin, V.T., Adler-Ivanbrook, L., 1998. Release of copper, chromium and arsenic from CCA-C treated lumber in estuaries. *Estuarine Coastal and Shelf Science* 46, 111–125.
- Brooks, K.M., 1996. Evaluating the environmental risks associated with the use of chromated copper arsenate-treated wood products in aquatic environments. *Estuaries* 19, 296–305.
- Brooks, K.M., 1997. Literature Review and Assessment of the Environmental Risks Associated with the Use of CCA Treated Wood Products in Aquatic Environments. Prepared for Western Wood Preservers Institute, Vancouver, WA.
- BSI, 1987a. B.S. 4072. Wood Preservation by Means of Copper/Chromium/Arsenic Compositions. Part 1: Specifications for Preservatives. British Standards Institution, London.
- BSI, 1987b. B.S. 4072. Wood Preservation by Means of Copper/Chromium/Arsenic Compositions. Part 2: Methods for Timber Treatment. British Standards Institution, London.
- BSI, 1989. B.S. 5589. British Standard Code of Practice for Preservation of Timber. British Standards Institution, London.
- BSI, 1994. ENV. 1250:2. Wood Preservatives — Methods of Measuring Losses of Active Ingredients and Other Preservative Ingredients From Treated Timber — Part 2: Laboratory Method for Obtaining Samples for Analysis to Measure Losses by Leaching into Water or Synthetic Seawater. British Standards Institution, London.
- BSI, 1997. B.S. EN. 84. Wood Preservative Accelerated Ageing of Treated Wood Prior to Biological Testing. Part 2: Leaching Procedure. British Standards Institution, London.
- BWPDA, 1995. Code of Practice for the Safe Design and Operation of Timber Treatment Plants. British Wood Preserving and Damp-proofing Association, London.
- Cherian, P.V., Sharma, M.N., Cherian, C.J., 1979. A study on the leaching of copper–chrome–arsenic (CCA) from some common Indian timbers tested in Cochin harbour waters. *Journal of the Indian Academy of Wood Science* 10, 31–34.
- Chou, C.K., Chandler, J.A., Preston, R.D., 1973. Microdistribution of metal elements in wood impregnated with a copper–chrome–arsenic preservative as determined by analytical electron microscopy. *Wood Science and Technology* 7, 151–160.
- Clark, E.A., Sterritt, M.R., Lester, J.N., 1988. The fate of tributyltin in the aquatic environment. *Environmental Science and Technology* 22, 600–604.
- Cooper, P.A., 1990. An Example of Media Response to Perceived Environmental Problems with CCA-treated Wood (IRG/WP/3564). The International Research Group on Wood Preservation, Stockholm.
- Cooper, P.A., 1991. Leaching of CCA from treated wood: pH effects. *Forest Products Journal* 41, 30–32.
- Cooper, P.A., 1994. Leaching of CCA: is it a problem? In: Environmental Considerations in the Manufacture, Use and Disposal of Pressure-Treated Wood. Forest Products Society, Madison, WI, USA.
- Cooper, P.A., Churma, R., 1990. Estimating diffusion path length in treated wood. *Forest Products Journal* 40, 61–63.
- Cooper, P.A., Ung, Y.T., 1992. Accelerated fixation of CCA-treated poles. *Forest Products Journal* 42, 27–32.
- Cooper, P.A., ManVicar, R., Ung, Y.T., 1995. Relating CCA Fixation to Leaching of CCA Components from Treated Products (IRG/WP/50045). The International Research Group on Wood Preservation, Stockholm.
- Cooper, P.A., Ung, Y.T., Kamden, P.D., 1997. Fixation and leaching of red maple (*Acer rubrum* L.) treated with CCA-C. *Forest Products Journal* 47, 70–74.
- Cragg, S.M., Eaton, R.A., 1997. Evaluation of creosote fortified with synthetic pyrethroids as wood preservatives for use in the sea. II. Effects on wood-degrading micro-organisms and fouling invertebrates. *Material und Organismen* 31, 197.
- Dahlgren, S.-E., 1975a. Kinetics and mechanism of fixation of Cu–Cr–As wood preservatives. Part V. Effect of wood species and preservative composition on the leaching during storage. *Holzforchung* 29, 84–89.
- Dahlgren, S.-E., 1975b. Kinetics and mechanism of fixation of Cu–Cr–As wood preservatives. Part VI. The length of the primary fixation period. *Holzforchung* 29, 130–134.
- Desch, H.E., Dinwoodie, J.M., 1996. Timber Structure, Properties, Conversion and Use. Macmillan Press, London.
- Eaton, R., 1989. An international collaborative marine trial to investigate the effect of timber substrate on the efficacy of CCA and CCB wood preservatives. *Material und Organismen* 24, 51.
- Eaton, R.A., Hale, M.D.C., 1993. Wood: Decay, Pests, and Protection. Chapman and Hall, London.
- Environment Canada, 1988. Chromated Copper Arsenate (CCA) Wood Preservation Facilities: Recommendations for Design and Operation. Environment Canada, Ottawa, Ontario.
- Fahlstrom, G.B., Gunning, P.E., Carlson, J.A., 1967. Copper–chrome–arsenate wood preservatives: a study of the influence of composition on teachability. *Forest Products Journal* 17, 17–22.
- Fleming, C.A., Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. *Water, Air, and Soil Pollution* 44, 143–158.
- Forsyth, P.G., Morrell, J.J., 1990. Hexavalent chromium reduction on CCA treated sawdust. *Forest Products Laboratory* 40, 48–50.
- Gibbs, P.E., Pascoe, P.L., Burt, G.R., 1988. Sex change in the female dogwhelk, *Nucella lapillus*, induced by tributyltin from antifouling paints. *Journal of the Marine Biology Association of the United Kingdom* 68, 715–731.
- Gibbs, P.E., Bryan, G.W., Pascoe, P.L., Burt, G.R., 1987. The use of the dogwhelk, *Nucella lapillus*, as an indicator of tributyltin (TBT) contamination. *Journal of the Marine Association of the United Kingdom* 67, 507–523.
- Green, C.A., Smith, G.M., King, B., 1989. The effects of aqueous leaching on the moisture uptake and decay of CCA-treated wood exposed to soil burial. *Material und Organismen* 24, 193–205.
- Hager, B., 1969. Leaching tests on copper–chromium–arsenic preservatives. *Forest Products Journal* 19, 21–26.
- Haloui, A., Vergnaud, J.M., 1995. Modelling the process of release of a chemical from wood in finite volumes of water in succession. *Wood Science and Technology* 29, 77–85.
- Haloui, A., Vergnaud, J.M., 1997. Study of the release in water of chemicals used for wood preservation. Effect of wood dimensions. *Wood Science and Technology* 31, 51–62.
- Havens, K.E., 1994. Structural and functional-responses of a freshwater plankton community to acute copper stress. *Environmental Pollution* 86, 259–266.
- Hayes, C., Curran, P.M.T., Hynes, M.J., 1994. Preservative leaching from softwoods submerged in Irish Coastal waters as measured by atomic-absorption spectrophotometry. *Holzforchung* 48, 463–473.
- Hegarty, B.M., Curran, P.M.T., 1986. Biodeterioration and micro-distribution of copper–chrome–arsenic (CCA) in wood submerged in Irish coastal waters. *Journal of the Institute of Wood Science* 10, 245–253.

- Helsen, L., Van den Bulck, F., 1998. The microdistribution of copper, chromium and arsenic in CCA treated wood and its pyrolysis residue using energy dispersive x-ray analysis in scanning electron microscopy. *Holzforschung* 52, 607–614.
- Henshaw, B., 1979. Fixation of copper, chromium and arsenic in softwoods and hardwoods. *International Biodeterioration Bulletin* 15, 66–73.
- Hughes, A.S., Murphy, R.J., Gibson, J.F., Cornfield, J.A., 1994. Electron-paramagnetic-resonance (EPR) spectroscopic analysis of copper-based preservatives in *Pinus-Sylvestris*. *Holzforschung* 48, 91–98.
- Hung, T.-C., Meng, P.-J., Wu, S.-J., 1993. Species of copper and zinc in sediments collected from the Antarctic Ocean and the Taiwan Erhjin Chi coastal area. *Environmental Pollution* 80, 223–230.
- Irvine, J., Dahlgren, S.-E., 1976. The mechanism of leaching of copper–chrome–arsenic preservatives in saline waters. *Holz-forschung* 30, 44–50.
- Irvine, J., Eaton, R.A., Jones, E.B.G., 1972. The effect of water of different ionic composition on the leaching of a water borne preservative from timber placed in cooling towers and in the sea. *Material und Organismen* 7, 45–71.
- Johnson, B.R., 1982. A look at creosote versus chromated copper arsenate salts as wood preservatives for the marine environment. *Industrial and Engineering Chemistry Product Research and Development* 21, 704–705.
- Johnson, B.R., Ibach, R.E., Baker, A.J., 1992. Effect of salt water evaporation on tracheid separation from wood surfaces. *Forest Products Journal* 42, 57–59.
- Kaldas, M.L., Cooper, P.A., Sodhi, R., 1998. Oxidation of wood components during chromated copper arsenate (CCA-C) fixation. *Journal of Wood Chemistry and Technology* 18, 53–67.
- Kennedy, M.J., Palmer, G., 1994. Leaching of Copper, Chromium, and Arsenic from CCA-treated Slash Pine Heartwood (IRG/WP94-50020). The International Research Group on Wood Preservation.
- Lebow, S., 1996. Leaching of Wood Preservative Components and their Mobility in the Environment. Summary of Pertinent Literature. United States Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI.
- Lee, A.W.C., Grafton, J.C., Tainter, F.H., 1993. Effect of rapid redrying shortly after treatment on leachability of CCA-treated southern pine. *Forest Products Journal* 43, 37–40.
- Livens, F.R., 1991. Chemical reactions of metals with humic material. *Environmental Pollution* 70, 183–208.
- McQuire, A.J., 1976. The Performance of Preservative Treated Marine Piles in New Zealand. Sixth Conference of Harbour Engineers, Auckland, New Zealand.
- Merkle, P., Gallagher, D.L., Soldberg, T.N., 1993. Leaching rates, metals distribution and chemistry of CCA treated lumber: implications for water quality monitoring. In: Forest Product Society's Symposium, Environmental Considerations in the Use of Pressure Treated Wood. Forest Products Society, Madison, WI, pp. 69–78.
- Morgan, J.W.W., Pursiow, D.F., 1973. Physical and chemical aspects of preservative treatment by non-pressure methods. *Holzforschung* 27, 153–159.
- Murphy, R., 1998. Chromium in Timber Preservation. The Chromium File, from the International Chromium Development Association.
- Newell, A.D., Sanders, J.G., 1986. Relative copper binding capacities of dissolved organic compounds in a coastal-plain estuary. *Environmental Science and Technology* 20, 817–821.
- Nicholas, D.D., Williams, A.D., Preston, A.F., Zhang, S., 1991. Distribution and permanency of DDAC in southern pine sapwood treated by the full cell process. *Forest Products Journal* 41, 41–45.
- Nriagu, J.O., 1994a. Arsenic in the Environment. Part I. Cycling and Characterization. John Wiley, New York.
- Nriagu, J.O., 1994b. Arsenic in the Environment. Part II. Human Health and Ecosystem Effects. John Wiley, New York.
- Nygren, O., Nilsson, C.A., 1993. Determination and speciation of chromium, copper and arsenic in wood and dust from CCA-impregnated timber. *Analisis* 21, 83–89.
- Orsler, R.J., Holland, G.E., 1993. Assessment of Losses of Wood Preservatives from Treated Wood by Leaching into the Environment. 2nd International Symposium on Wood Preservation, Cannes-Mandelieu, France.
- Peek, R.-D., Willeitner, H., 1981. Accelerated fixation of chromate-containing wood-preservatives by superheated steam. I. Effect of different heat-treatment on the leaching of preservatives. *Holz Als Roh-Und Werkstoff* 39, 495–502.
- Peek, R.-D., Willeitner, H., 1988. Fundamentals of Steam Fixation of Chromated Wood Preservatives (IRG/WP 3483). The International Research Group on Wood Preservation, Stockholm.
- Pizzi, A., 1981. The chemistry and kinetic behaviour of Cu–Cr–As/B wood preservatives. I. Fixation of chromium on wood. *Journal of Polymer Science: Polymer Chemistry Edition* 19, 3093–3121.
- Pizzi, A., 1982a. The chemistry and kinetic behaviour of Cu–Cr–As/B wood preservatives. II. Fixation of the Cu/Cr system on wood. *Journal of Polymer Science: Polymer Chemistry Edition* 20, 707–724.
- Pizzi, A., 1982b. The chemistry and kinetic behaviour of Cu–Cr–As/B wood preservatives. III. Fixation of a Cr/As system on wood. *Journal of Polymer Science: Polymer Chemistry Edition* 20, 725–738.
- Pizzi, A., 1982c. The chemistry and kinetic behaviour of Cu–Cr–As/B wood preservatives. IV. Fixation of CCA to wood. *Journal of Polymer Science: Polymer Chemistry Edition* 20, 739–764.
- Pizzi, A., 1983a. A new approach to the formulation and application of CCA preservatives. *Wood Science and Technology* 17, 303–319.
- Pizzi, A., 1983b. Practical Consequences of the Clarification of the Chemical Mechanism of CCA Fixation to Wood (IRG/WP/3220). The International Research Group on Wood Preservation, Stockholm.
- Pizzi, A., 1990a. Chromium interactions in CCA/CCB wood preservatives. Part I. Interactions with wood carbohydrates. *Holz-forschung* 44, 373–380.
- Pizzi, A., 1990b. Chromium interactions in CCA/CCB wood preservatives. Part II. Interactions with lignin. *Holzforschung* 44, 419–424.
- Pizzi, A., Conradie, W.E., Bariska, M., 1986. Polyflavanoid Tannins — From Cause of CCA Soft-rot Failure to the “Missing Link” Lignin and Microdistribution Theories (IRG/WP/3359). The International Research Group on Wood Preservation, Stockholm.
- Plackett, D.V., 1984. Leaching Tests on CCA-treated Wood Using Inorganic Salt Solutions (IRG/WP 3310). The International Research Group on Wood Preservation, Stockholm.
- Porandowski, J., Cooper, P.A., Kaldas, M., Ung, Y.T., 1998. Evolution of CO₂ during the fixation of chromium containing wood preservatives on wood. *Wood Science and Technology* 32, 15–24.
- Preston, A.F., McKaig, P.A., 1983. Effect of accelerated fixation on decay of CCA-treated wood. *Forest Products Journal* 33, 41–44.
- Putt, A.F., 1993. Sediment Bound CCA-C Leachate 10 Day Repeated Exposure Toxicity to *Amplisca abdita* Under Static Conditions. Springborn Laboratories Inc, Wareham, MA, USA.
- Rak, J.R., Clarke, M.R., 1974. Leachability of new water-borne preservative systems for difficult-to-treat wood products. Proceedings of the American Wood Preservation Association 70, 27–32.
- Ruddick, J.N.R., Yamamoto, K., Wong, P.C., Mitchell, K.A.R., 1993. X-ray photoelectron spectroscopic analysis of CCA-treated wood. *Holzforschung* 47, 458–464.
- Ryan, K.G., Plackett, D.V., 1987. The Interaction of Polyflavanoid Tannins with CCA in *Pinus radiata* (IRG/WP/3422). The International Research Group on Wood Preservation, Stockholm.
- Sanders, J.G., Windom, H.L., 1980. The uptake and reduction of arsenic species by marine algae. *Estuarine and Coastal Marine Science* 10, 555–567.
- Sanders, J.G., Reidel, G.F., 1987. Control of trace element toxicity by phytoplankton. In: Saunders, J.A., Kosak-Channing, L., Conn, E.E. (Eds.), *Phytochemical Effects of Environmental Compounds*. Plenum Press, New York, pp. 131–149.

- Shelver, G.D., McQuaid, C.D., Tarin, M., Baecker, A.A.W., 1992. Surface Accumulation of Copper on CCA-impregnated *Pinus patula* Stakes During Marine Preservative Trials in the Southern Hemisphere (IRG/WP 4181-92). The International Research Group on Wood Preservation, Stockholm.
- Smith, D.N.R., Williams, A.I., 1973a. The effect of composition on the effectiveness and fixation of copper/chrome/arsenic and copper/chrome preservatives part II: selective absorption and fixation. *Wood Science and Technology* 7, 142–150.
- Smith, D.N.R., Williams, A.I., 1973b. The effect of composition on the effectiveness and fixation of copper–chrome–arsenic and copper–chrome preservatives part I: effectiveness. *Wood Science and Technology* 7, 60–76.
- Taylor, F.W., 1991. Variations in CCA penetration and retention in loblolly and shortleaf pine. *Forest Products Journal* 41, 25–28.
- Taylor, B.R., Goudey, J.S., Carmichael, N.B., 1996. Toxicity of aspen wood leachate to aquatic life: laboratory studies. *Environmental Toxicology and Chemistry* 15, 150–159.
- UNEP, 1994. Environmental Aspects of Industrial Wood Preservation: A Technical Guide. United Nations Environment Programme, Paris.
- Van Eetvelde, G., Homan, W.J., Militz, H., Stevens, M., 1995a. Effect of Leaching Temperature and Water Acidity on the Loss of Metal Elements from CCA Treated Timber in Aquatic Conditions. Part 2: Semi-industrial Investigation (IRG/WP 95-50040). The International Research Group on Wood Preservation, Stockholm.
- Van Eetvelde, G., Orsler, R., Holland, G., Stevens, M., 1995b. Effect of Leaching Temperature and Water Acidity on the Loss of Metal Elements from CCA Treated Timber in Aquatic Applications. Part 1. Laboratory Scale Investigation (IRG/WP/95-50046). The International Research Group on Wood Preservation, Stockholm.
- Van Eetvelde, G., Stevens, M., Mahieu, F., Wegen, H.-W., Platen, A., 1998. An Appraisal of Methods for Environmental Testing of Leachates from Salt-treated Wood; Part 1 (IRG/WP 98-50115). The International Research Group on Wood Preservation, Stockholm.
- Walley, S., Cobham, P., Vinden, P., 1996a. Leaching of Copper–Chrome–Arsenic Treated Timber: Simulated Rainfall Testing (IRG/WP 96-50074). The International Research Group on Wood Preservation, Stockholm.
- Walley, S., Cobham, P., Vinden, P., 1996b. Preservative Leaching from Copper–Chrome–Arsenate Treated Timber: Towards an International Standard for Environmental Monitoring (IRG/WP 96-50076). The International Research Group on Wood Preservation, Stockholm.
- Warner, J.E., Solomon, K.R., 1990. Acidity as a factor in leaching of copper, chromium and arsenic from CCA-treated dimension lumber. *Environmental Toxicology and Chemistry* 9, 1331–1337.
- Wegen, H.-W., Platen, A., Van Eetvelde, G., Stevens, M., 1998. An Appraisal of Methods for Environmental Testing of Leachates from Salt-treated Wood (IRG/WP 98-50110). The International Research Group on Wood Preservation, Stockholm.
- Weis, J.S., Weis, P., 1994a. Effects of contaminants from chromated copper arsenate-treated lumber on benthos. *Archives of Environmental Contamination and Toxicology* 26, 103–109.
- Weis, J.S., Weis, P., 1994b. Studies on biological effects of CCA treated wood structures in estuaries. In: *Environmental Considerations in the Manufacture, Use and Disposal of Pressure-Treated Wood*. Forest Products Society, Madison, WI, USA.
- Weis, J.S., Weis, P., 1995. Effects of chromated copper arsenate (CCA) pressure treated wood in the aquatic environment. *Ambio* 24, 269–274.
- Weis, J.S., Weis, P., 1996. The effects of using wood treated with chromated copper arsenate in shallow-water environments: a review. *Estuaries* 19, 306–310.
- Weis, J.S., Weis, P., Proctor, T., 1998. The extent of benthic impacts of CCA-treated wood structures in Atlantic coast estuaries. *Archives of Environmental Contamination and Toxicology* 34, 313–322.
- Weis, P., Weis, J.S., 1999. Accumulation of metals in consumers associated with chromated copper arsenate-treated wood panels. *Marine Environmental Research* 48, 73–81.
- Weis, P., Weis, J.S., Coohill, L.M., 1991. Toxicity to estuarine organisms of leachates from chromated copper arsenate treated wood. *Archives of Environmental Contamination and Toxicology* 20, 118–124.
- Weis, P., Weis, J.S., Greenberg, A., Nosker, T.J., 1992. Toxicity of construction materials in the marine environment: a comparison of chromated-copper-arsenate-treated wood and recycled plastic. *Archives of Environmental Contamination and Toxicology* 22, 99–106.
- Wendt, P.H., Van Dolah, R.F., Bobo, M.Y., Mathews, T.D., Levisen, M.V., 1996. Wood preservative leachates from docks in an estuarine environment. *Archives of Environmental Contamination and Toxicology* 31, 24–37.
- Willeitner, H., Peek, R.-D., 1998. How to Determine What is a Realistic Emission from Treated Wood (IRG/WP 98-50 105). The International Research Group on Wood Preservation, Stockholm.
- Wong, P., Chang, L., 1991. Effects of copper, chromium and nickel on growth, photosynthesis and chlorophyll-A synthesis of *Chlorella pyrenoidosa*-251. *Environmental Pollution* 72, 127–139.
- Woolson, E.A., Gjovik, L.R., 1981. The valence state of arsenic on treated wood. *Proceedings of the American Wood-Preservers Association* 77, 15–22.
- W.S. Atkins Environment, 1998. Assessment of the Risks to Health and to the Environment of Tin Organic Compounds and of Arsenic in Certain Biocidal Products and of the Effects of Further Restrictions on their Marketing and Use. European Commission Directorate General III, Epsom, Surrey.
- WWPA, 1996. Best Management Practices for the Use of Treated Wood in Aquatic Environments. Western Wood Preservers Institute, Vancouver, WA.