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Leaching of Wood Preservative Components and Their Mobility in the Environment

Summary of Pertinent Literature

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Abstract

Preservative-treated wood is an economical, durable, and aesthetically pleasing building material; therefore, it is a natural choice for construction projects in our National Forests, National Parks, and other public lands. However, we need to ensure that the chemicals used in treated wood do not pose a threat to people or the environment. The purpose of this report is to provide a summary of the pertinent literature on leaching of wood preservative components and their mobility in the environment.

The waterborne wood preservatives chromated copper arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), ammoniacal copper quat (ACQ), copper dimethyldithiocarbamate (CDDC), and ammoniacal copper citrate (CC) resist leaching during service because of complex chemical reactions that take place within the treated wood. The effectiveness of these reactions in preventing leaching is dependent on treating factors, such as preservative formulation, preservative retention, and processing techniques, as well as post-treatment conditioning factors, such as temperature, humidity, and air flow. Copper naphthenate, an oilborne wood preservative, resists leaching because it is relatively insoluble in water. Little information is available on the in-service leaching rates of any of these wood preservatives, although CCA has been studied more extensively than the other preservatives.

Past studies report widely varying leaching rates, but generally agree that the most rapid leaching occurs within the first months of service and is greatest in products with high retention levels and high proportions of exposed surface area, especially end-grain. Leaching is also increased by exposing the wood to high water flow, low pH, and water-soluble organic acids. Movement of leached chromium and copper appears quite limited in soil, because the metals are tightly bound to organic soil constituents. Arsenic is slightly more mobile in soil, but binds to iron, aluminum, and manganese. Generally, the preservative components are least mobile in organic soils, slightly more mobile in clay soils, and most mobile in sandy soils. In aquatic applications, the leached preservative components form complexes with the organic sediment fines, and accordingly are either deposited or moved downstream with the sediments. Additional research is needed to characterize typical in-service leaching rates of these preservatives and to determine how processing parameters affect long-term leaching rates.

Keywords: wood preservatives, leaching, in service, CCA, ACZA, ACQ, CDDC, CC, copper naphthenate

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Executive Summary

Preservative components resist leaching during service because of fixation reactions that take place after the preservative contacts the wood. With chromated copper arsenate (CCA), some of these reactions, such as the adsorption of copper and chromium onto wood components, occur within minutes or hours, while others are completed during the ensuing days, weeks, or even months. The final reaction products of CCA fixation have been theorized to include precipitates of basic copper arsenate, chromium hydroxide, chromium arsenate, and chromium chromate. In addition, the copper cation has been reported to be adsorbed or to form complexes with lignin or cellulose, and copper chromates and chromium arsenates have been reported to form complexes with lignin or extractives. Much of the evidence indicates that phenolic hydroxyls of lignin and extractives are reacting with copper and chromium, although it is probable that hexavalent chromium, because of its high reduction potential, is also reacting with other wood components.

Ammoniacal copper zinc arsenate (ACZA) fixation appears to involve cation exchange reactions of copper with wood components, especially lignin, as well as precipitation of insoluble copper carbonate, copper oxide, and copper arsenate. Much of the arsenic in this preservative appears to be fixed in the form of insoluble zinc arsenate precipitates. Similar methods of copper fixation are likely with ammoniacal copper citrate (CC), ammoniacal copper quat (ACQ), and ammoniacal copper azole (CuAz), although reports of these mechanisms have only been published for ACQ-B. In contrast to the ammoniacal systems, copper dimethyldithiocarbamate (CDDC) fixation is achieved through the reaction of copper ethanolamine with sodium dimethyl dithiocarbamate to form insoluble copper dimethyldithiocarbamate. With copper naphthenate, resistance to leaching is provided by the hydrophobic properties of the carrier oil, although there are indications that a portion of the copper also binds to the wood.

After treatment, the most important consideration in leach prevention is to ensure that adequate time is allowed for fixation before placing the wood in service. For CCA, the time required for fixation varies with wood species, specimen size, and retention, but the most important parameter is temperature. Because temperature is so important in obtaining adequate and timely fixation, much work has been done to develop methods of high-temperature fixation, such as kiln drying, steam baths, or water baths. Although some studies have reported that these accelerated fixation techniques can increase leach susceptibility if they employ extreme temperatures or low humidities, accelerated fixation appears to be a potentially important tool to aid CCA fixation in colder climates. The degree of chromium reduction in treated wood is used as an indicator of the completeness of the CCA fixation process.

With the amine and ammoniacal systems, fixation is achieved by drying the wood to the point that the majority of the ammonia or amine has left the wood. However,

established tests are not available to quickly determine the degree of fixation in these systems, and little data exist to correlate ammonia content in the wood to preservative leachability. The CDDC system appears to achieve fixation rapidly enough that storage time after treatment is not a major concern. Similarly, copper-naphthenate-treated wood may be shipped when oil no longer drips from the wood, and this stage can often be achieved within the treating process.

Relatively little research has been done to quantify or evaluate leaching of preservatives from treated wood after it has been placed in service. Although numerous laboratory studies have been conducted to evaluate the effect of various parameters on CCA fixation and leaching, these studies often have had little applicability to actual exposure conditions. The studies that have monitored leaching in field or service exposures have reported results ranging from no leaching to losses of 50 percent or more for CCA components. Little or no data exist for in-service or product-size leaching rates from ACZA, copper naphthenate, and the newer waterborne systems. The studies that have been conducted report copper losses ranging from 0 to more than 70 percent. For each type of preservative, including CCA, the higher leaching rates noted have generally resulted from the use of small-sized samples with a high proportion of exposed end-grain.

The variability of these findings is not surprising, because these types of studies are difficult to conduct and many factors can affect the amount of leaching that occurs from treated wood. Such factors include time exposed, preservative retention, orientation and exposed surface area of the product, wood species, and site factors, such as water movement, pH, and the presence of solubilized organics or inorganics. As expected, greater leaching rates were reported from products or specimens that had a high proportion of exposed surface and were placed in an area of high flow rate of water. The presence of organic acids in soil or freshwater exposures and inorganic ions in seawater also appear to increase the rate of CCA leaching.

The significance of the relatively small amounts of copper, chromium, arsenic, and zinc that leach from wood is unclear, but it is a function of their mobility and speciation in the surrounding environment. Mobility and speciation are, in turn, dependent on factors such as water volume and flow rate, pH, reduction and oxidation potential, ion adsorption sites, and presence of soluble ligands. The potential for rapid movement of preservative components is much greater if leached into moving water than if leached into an impermeable soil with fine particles that provide a large reactive surface.

Studies on the effect of soil and water composition on movement and speciation of preservative components reveal several key points. Chromium appears to be the least mobile of the elements; boron is the most mobile. In soil and freshwater, the type and amounts of stationary, dissolved, or suspended organics are important in controlling the movement of chromium and copper, and inorganics play a greater role in

seawater and the mobility of arsenic and zinc. Although the interactive effects of soil constituents are complex, preservative components generally appear to be least mobile in highly organic soils, slightly more mobile in clay soils, and most mobile in sandy soils. The exception for copper and chromium may be high organic soils of low pH that are rich in soluble organic acids. Of the inorganic components, iron, aluminum, and manganese appear most effective in stabilizing the preservative components. Manganese may also have the opposite effect on chromium, because manganese can oxidize chromium to its more soluble hexavalent state. Arsenic and zinc, in particular, are dependent on the presence of inorganics for complexation. Conversely, high levels of sulfates and phosphates can increase movement of copper and arsenic. Movement is generally decreased at high pH levels that increase adsorption and precipitation of the metals, although the effect of pH on arsenic movement is less clear.

The valence state of arsenic and chromium influences both their mobility and toxicity. Moist, high pH soils or alkaline-oxygenated streams may stimulate the oxidation of trivalent chromium to the more toxic hexavalent form. Similarly, reducing environments such as saturated, anaerobic soils, or poorly oxygenated waters may favor the formation of more toxic trivalent arsenic species. However, the speciation of arsenic appears to be significantly affected by the presence of microorganisms that may convert the arsenic to volatile methylated forms of arsine gas.

It is evident that more research is needed to quantify preservative leaching rates from product-size specimens in various exposure environments. In addition, more research is needed to determine the speciation and mobility of the leached components in the environment. Such studies will allow an assessment of the risk: benefit ratio of using treated wood as a construction material.

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Summary of Pertinent Literature

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Introduction

Because preservative-treated wood is an economical, durable, and aesthetically pleasing building material, it is a natural choice for construction projects in our National Forests, National Parks, and other public lands. However, we need to ensure that the chemicals used in treated wood do not pose a threat to people or the environment. The most widely used waterborne wood preservative is chromated copper arsenate (CCA), favored for lumber treatment because it is inexpensive, leaves a dry, paintable surface, and binds to the wood to become relatively leach resistant. CCA-treated wood is used extensively by the Forest Service and other government agencies in the construction of structures, such as walkways, piers, restraining walls, and bridges. Many of these applications place the wood in pristine or sensitive ecosystems where contamination by significant amounts of chromium, copper, or arsenic compounds could negatively affect the environment. In addition, other types of wood preservative formulations are proposed as possible alternatives to CCA for many of the same applications. Undoubtedly, the same concerns will be raised when these alternative preservatives are recommended for construction projects on public lands.

Preservatives that are widely used for pressure treatment of wood in the United States can be grouped into two broad categories: oilborne and waterborne. Commonly used oilborne preservatives are creosote, pentachlorophenol, and copper naphthenate. Creosote and pentachlorophenol have been widely used for many years to protect poles, piling, laminated beams, and timbers, but their use in lumber has been less extensive; this is especially true in areas where human contact with the treated wood is likely. Creosote and pentachlorophenol are less likely to be used than other preservatives for applications, such as boardwalks, that place large amounts of material into sensitive environments; therefore, these preservatives are not addressed in this report. Although the wood preservative properties of oilborne copper

naphthenate have been recognized for decades, this preservative has only gained commercial importance for pressure treatment in recent years, largely because it is perceived to cause fewer safety and environmental concerns than do other oilborne preservatives. Because of this perception, copper naphthenate is considered a viable preservative for uses such as boardwalks and is addressed in this report. American Wood Preservers' Association (AWPA) standards list the use of copper naphthenate for treatment of Southern Pine and Douglas Fir lumber, timbers and poles, for above-ground, soil, and freshwater applications. Such uses are not listed for western hemlock or the Hem-Fir group of species, but copper naphthenate is approved for use in treatment of Sitka Spruce lumber and timbers (AWPA 1994).

The waterborne formulations, which have characteristically been used by the Forest Service for treatment of boardwalks and other trail and recreational use construction, have primarily been limited to CCA, ammoniacal copper arsenate (ACA), and ammoniacal copper zinc arsenate (ACZA). ACA was used until the early 1980s for treatment of Douglas Fir in the Pacific Northwest, but was replaced for this use by ACZA. However, in the past few years, a new generation of waterborne preservatives, based on amine or ammoniacal copper, has been either under consideration or specified by the AWPA. Those that have been accepted by the AWPA for treatment of Douglas Fir, Southern Pine, and Hem-Fir in above ground, soil and freshwater uses include ammoniacal copper quat (ACQ Type B), alkaline copper quat (ACQ Type D), copper dimethyldithiocarbamate (CDDC), and ammoniacal copper citrate (CC). A formulation under consideration by AWPA for approval in the near future is ammoniacal copper azole (CuAz). All these new formulations have the potential for future use within the Forest Service trails and recreation system, although only ACQ-B and ACQ-D were commercially available at the time this article was printed.

Chromated copper arsenate is currently the predominant preservative for many applications; CCA accounted for more than 98 percent of the approximately 437,675,000 ft³ (12,390,600 m³) of wood that was treated in 1990 (Micklewright 1992). Because of its widespread use, CCA-treated wood has generated the most concern from environmental and safety standpoints and has been the most heavily studied of preservatives considered in this report. Accordingly, much of the information presented in this report will be most applicable to CCA leaching and mobility in the environment. The AWWA currently specifies three CCA formulations, types A, B and C, that differ in the relative proportions (oxide basis) of chromium, copper, and arsenic (AWPA 1994) (Table 1). However, the use of CCA-B is currently confined to field and remedial treatments, and relatively few treaters use CCA-A for pressure treatments. Thus, the vast majority of CCA treated wood produced in the United States is treated with CCA-C, the formulation that appears to offer the best combination of performance and leach resistance. Note that much of the data generated in the past for CCA leaching in service has been from formulations other than CCA-C and does not necessarily reflect the rate of leaching that might be expected from CCA-treated wood that has been produced in recent years.

The components of CCA, chromium, copper, and arsenic all play important roles in preservative efficacy. The primary

role of chromium in CCA fixation is part of a complex series of reactions driven by reduction of chromium from the hexavalent to trivalent valence state. These reactions result in the insolubilization of CCA components in the wood so that they resist leaching and provide lengthy service, even when the wood is placed in ground contact. Copper and arsenic are vital to the preservative efficacy of CCA because of their toxicity to fungi and insects. Copper is an excellent fungicide, and arsenic is especially effective against insects and helps to provide protection against some copper-tolerant fungi.

Because of its excellent fungicidal properties and low mammalian toxicity, other waterborne formulations also include copper (Table 2). ACZA combines copper with zinc and arsenic. Zinc provides some protection against fungi and assists in the insolubilization of arsenic, and as with CCA, arsenic helps provide protection against copper-tolerant fungi and insects. In addition to copper, ACQ contains the quaternary ammonium compound didecylmethylammonium chloride (DDAC), which improves the fungicidal properties of the preservative. Similarly, CuAz incorporates the fungicide tebuconazole, as well as boron, to improve both fungicidal and insecticidal properties. CDDC is a somewhat different type of system in that the preservative is applied in two stages. The wood is first treated with copper ethanalamine, and subsequently treated with sodium

Table 1—Composition of three CCA formulations as specified by AWWA Standards^a

Component	Type A (percent)		Type B (percent)		Type C (percent)	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cr as CrO ₃	59.4	69.3	33.0	38.0	44.5	50.5
Cu as CuO	16.0	20.9	18.0	22.0	17.0	21.0
As as As ₂ O ₅	14.7	19.7	42.0	48.0	30.0	38.0

^aFrom AWWA 1994.

Table 2—Composition of various waterborne formulations as specified or proposed for AWWA standards

Formulation	Composition (percent)							
	CuO	ZnO	As ₂ O ₅	DDAC ^a	Boric acid	AZOLE ^b	SDDC ^c	Citric acid
ACZA	50.0	25.0	25.0					
ACQ-B,D	66.7			33.3				
CuAz	49 ^d				49	2		
CDDC	17-29 ^e						71-83 ^e	
CC	62.3							37.7

^aDidecylmethylammonium chloride.

^bAs tebuconazole.

^cSodium dimethyldithiocarbamate.

^dPercentage is as elemental copper.

^eCDDC is produced by dual treatment; proposed standard calls for a weight ratio of between 5:1 and 2.5:1 SDDC: copper in the treated wood.

dimethyldithiocarbamate, which reacts with the copper to form an insoluble 1:2 (copper:dimethyldithiocarbamate) complex. Although it is not possible to adequately test this system without both copper and dithiocarbamate present, the dithiocarbamate is thought to increase the resistance of the wood to both fungal and insect attack. Ammoniacal copper citrate relies principally on copper to prevent decay and insect attack; the citric acid appears to benefit the system by improving the distribution or form of copper in the wood.

An important aspect of wood preservative treatments is the amount of preservative that is added to the wood. The amount of preservative needed, or retention level, varies with the intended use of the product, because varying exposure environments greatly affect the susceptibility of wood to degradation. For example, AWPAs standards list seven retention levels of CCA active ingredients: 0.25 lb/ft³ (4 kg/m³) for above-ground exposures, 0.4 lb/ft³ (6.4 kg/m³) for ground contact exposures, 0.6 lb/ft³ (9.6 kg/m³) for poles and foundations, 0.8 and 1.0 lb/ft³ (12.8 and 16 kg/m³) for land and freshwater piling, and 1.5 and 2.5 lb/ft³ (24 and 40 kg/m³) for seawater applications (AWPA 1994). ACZA, ACQ, and CC are recommended at similar loadings for listed applications, and the required retention levels for CuAz and CDDC have not been established. Oilborne copper naphthenate requires a retention (as elemental copper) of only 0.04 lb/ft³ (0.64 kg/m³) above ground and 0.06 lb/ft³ (0.96 kg/m³) for lumber in soil or water contact, but the actual retention is much greater due to the weight of the solvent and naphthenic acid. The retention specified is the minimum amount of preservative required in a prescribed assay zone, not the average for the entire piece. For example, AWPAs standards require that a Southern Pine nominal 2 by 4 in. (standard 38 by 89 mm) have at least 0.4 lb/ft³ (6.4 kg/m³) of CCA in the outer 0.60 in. (15 mm), if the piece is to be used in ground contact. As a result, most treated wood, and especially the larger dimension pieces, contain less preservative than implied by the pounds per cubic foot retention.

Theory Review

Although the term fixation is routinely used, the actual meaning of this term in the context of preservative treatments has not been precisely defined. In general terms, fixation refers to the series of chemical reactions that render the preservative nonleachable during service. However, this definition must be qualified, because even fully-fixed CCA will leach to some degree, depending on the exposure conditions (Ruddick 1993b). Therefore, fixation might be more appropriately defined as the process that minimizes the leaching of preservative components, or according to Cooper and others (1993) in reference to CCA: "the state of the chemical components of the preservative and wood or other substrate when all chemical reactions are complete." Some debate whether fixation is an appropriate term to use when describing the mechanisms that minimize the leaching of components of ammoniacal systems, but based on the definitions in this report and for convenience of discussion, the term is applied to all waterborne systems described in this paper. With oilborne systems, such as copper naphthenate, leach

resistance is supplied by the hydrophobic properties of the solvent, and the term fixation may not be as appropriate. However, Engdahl and Baileys (1992) indicate that a portion of the copper in copper naphthenate does react with the wood.

CCA Fixation

The interactions of CCA preservatives with wood during and after the treating process are complex and poorly understood, although aspects of these reactions have been studied by many researchers. Interest in the effect of composition on CCA effectiveness and permanence has led to research in this area (Dahlgren and Hartford 1972; Dahlgren 1974, 1975; Fahlstrom and others 1967; Hagar 1969; Henshaw 1979; Pizzi 1983; Pizzi and others 1984) and on the health hazards of unfixed components (Coggins and Hiscocks 1979; McNamara 1989). Additional concerns are the effect of CCA fixation on wood components (Ostmeyer and others 1988, 1989) and the distribution of CCA within the cell wall (Chou and others 1973a; Daniel and Nilsson 1987; Greaves 1972, 1974; Petty and Preston 1968). Research has also been conducted on the effect of fixation on sludging and preservative properties during treatment (Hartford 1986, Pizzi and others 1984).

Initial Reactions

Although completion of fixation may take days, weeks, or even months, some reactions do occur during the first few hours, corresponding to the time during and immediately after treatment (Cooper and Ung 1989; McNamara 1989). Dahlgren (1972) and Dahlgren and Hartford (1972) conducted extensive tests on wood flour from the sapwood of pine and spruce and reported that the course of fixation had three periods: momentary initial reactions, primary fixation reactions, and conversion reactions. They observed that within 3 min the H⁺ activity of CCA decreased to less than 20 percent of that in the original solution and attributed this to ion exchange and adsorption reactions between copper and chromium and the wood components. Portions of copper and chromium appeared to react with the wood almost instantaneously (Cooper 1991a; Dahlgren and Hartford 1972; Eadie and Wallace 1962; Gray and Dickinson 1988; Forsyth and Morrell 1990; Levi 1969; Pizzi 1982; Rennie and others 1987; Wilson 1971). Pizzi, who conducted extensive research on the reactions of CCA with cellulose, glucose, guaiacol, and finely ground pine sapwood, also noted an initial fixation of copper, but postulated that it was only physical absorption and not as extensive as suggested by others (Pizzi 1982).

Following the initial ion exchange and adsorption reactions, precipitation reactions continue the course of fixation in what Dahlgren calls the "primary precipitation fixation period." Reactions in this period are driven by the reduction of chromic acid to trivalent chromium and cause a steady increase in the pH of the solution (Dahlgren 1972, 1975). Pizzi (1981, 1982) also describes a main precipitation and fixation period following the initial ion exchange and adsorption reactions and divides this period into three reaction zones that occur

within the first 2 h. However, note that because both Pizzi and Dahlgren conducted their tests on wood flour where wood constituents are easily available, the reaction times may be underestimated. This is especially true for Pizzi's work, much of which was conducted at elevated temperatures.

Reactions During Storage

Following treatment, fixation reactions can continue within the wood for weeks or even months (Dahlgren 1972). Dahlgren theorizes that the primary precipitation fixation period concludes when the pH of the wood-CCA system reaches a maximum, because at this point, there is complete precipitation of chromium. Following the precipitation of chromium, slow reactions may continue for several months as acid and tertiary copper arsenates are converted into basic copper arsenate. The pH of the wood-CCA system increases and decreases during this period, as liberated protons are consumed in the reduction of chromates and chromate-wood complexes to trivalent chrome in the form of $\text{Cr}(\text{OH})_3$. Some of this trivalent chrome arsenate then forms tertiary chrome arsenate with AsO_4 liberated from other reactions. Dahlgren lists the final equilibrium fixation products as copper fixed to the wood by ion exchange reactions: CrAsO_4 , $\text{Cu}(\text{OH})\text{CuAsO}_4$, and $\text{Cr}(\text{OH})_3$.

Pizzi (1981, 1982) postulates that the majority of the CCA becomes copper chromates or chromium arsenate that either complexes with lignin or physically precipitates into the cellulose as inorganic salts. The remaining copper reacts with cellulose or lignin as Cu^{2+} , the majority binding to lignin, and a small amount of chromium chromate precipitates onto cellulose. In Pizzi's description, the reduction of chromium occurs with cellulose, but insolubilization also results from the reaction of hexavalent chromium with lignin (Hartford 1986). These reactions proceed more rapidly than was suggested by Dahlgren and Hartford (1972; Pizzi 1981, 1982). In addition, copper arsenates, reported by Dahlgren and Hartford, were not detected by Pizzi, possibly because the Tanalith C formulation used by Pizzi contains less arsenic than the Boliden K33 used by Dahlgren and Hartford.

Interaction With Wood Components and Structure

Properties of wood, such as pH, lignin structure and content, and extractive content, can also influence fixation. The natural pH of the wood may influence fixation by altering the amount of hexavalent chrome fixed to the wood (Dahlgren 1975) and shifting the distribution of preservative components between cellulose and lignin (Pizzi 1983). Dahlgren, in his work with several species of softwoods and hardwoods, found that species with a high pH level, such as beech (pH 5.6), took much longer to complete fixation than did more acidic species, such as ponderosa pine (pH 3.7), possibly because species with low pH levels tend to precipitate more hexavalent chrome early in fixation. The amount and type of lignin present can also be a factor, as chromium and copper compounds form more stable complexes with guaiacyl units of lignin, such as found in softwoods, than with the syringyl units common in hardwood fibers (Pizzi 1983; Ostmeier 1989).

Researchers have also attempted to directly determine the microdistribution of chromium, copper, and arsenic within CCA-treated wood. In some of the initial work, using a scanning electron microscope (SEM) combined with an electron microprobe microanalyzer (EMMA), Petty and Preston (1968) reported that the CCA components were fairly evenly distributed through the cell wall layers of Sitka Spruce. A similar instrument was used in the analysis of CCA-treated Scots pine (Chou and others 1973a). Researchers found that although the ratio of Cu:Cr was fairly constant throughout the cell wall, the Cu:As ratio was more variable, with a generally higher ratio in the middle lamella than the S2 layer. They also noted coarse deposits of almost pure copper within the cell wall and a thin film of deposition on the microfibrils. In addition, the lumen surfaces were coated with a layer of granules that contained a greater overall CCA concentration but lower proportional arsenic concentration than did either the S2 layer or middle lamella (Chou and others 1973a). Other researchers have found that the proportion of arsenic in the S2 layer is less than that in the solution, and the proportions of Cu and Cr are greater (Ryan and Plackett 1987).

In a similar study of CCA distribution in Scots pine and birch, investigators reported a relatively even distribution of preservative across and within the cell wall layers of pine tracheids, but noted that in birch the preservative was concentrated in the rays and vessels and somewhat lacking in the fibers (Dickinson and others 1976). Similarly, in SEM-EDAX analysis of Scots pine, *Radiata* pine, and several hardwoods, Greaves (1974) noted that CCA distribution was relatively even in pine, but variable within hardwood species. In addition, high levels of CCA were associated with the pit membranes in pine, and the inner surfaces of the cell walls were coated with amorphous and crystalline deposits of CCA with different elemental ratios of components than those in the treating solution.

Other researchers have used spectroscopic analysis to study the effect of fixation reactions on wood (Kaldas and Cooper 1993; Ostmeier and others 1988, 1989; Ruddick and others 1992; Williams and Feist 1984; Yamamoto and Inoue 1990; Yamamoto and Ruddick 1992). In a two-part study, x-ray photoelectron spectroscopy (XPS) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) were used to evaluate CCA-treated Southern Pine (Ostmeier and others 1988, 1989). They concluded that the carbon-hydrogen bonds of the aromatic rings were being oxidized, with possible formation of hexavalent chromium chromate esters. The authors further suggest that preservative components undergo substitution reactions with the aromatic portion of guaiacyl-type lignin only, because the second methoxyl group on syringyl units would limit formation of stable wood-metal complexes. In conflict with other studies (Kaldas and Cooper 1993; Ruddick and others 1992; Yamamoto and Inoue 1990), Ostmeier and others (1988, 1989) did not find evidence of the oxidation of hydroxyl groups to carbonyls.

In a subsequent XPS study of CCA-treated wood, Yamamoto and Inoue (1990) detected an increase in the proportion of carbon-carbon or carbon-hydrogen bonds, and

a decrease in hydroxyl concentration. Ruddick and others (1992) also noted a decrease in hydroxyl concentration, although a corresponding increase in carbonyl compounds that might be expected to result from oxidation of hydroxyls was not detected. In both studies, the absence of excess carbonyls was attributed to their further oxidation to carboxylic groups and subsequent decarboxylation. A similar mechanism was suggested in a previous XPS evaluation on the effects of aqueous chromium trioxide treatments on wood and cellulose surfaces (Williams and Feist 1984). In that study, carbon dioxide production after chromium trioxide treatment of filter paper was noted as possible evidence of decarboxylation. A more recent study used trapping techniques to show that carbonyl groups are formed by oxidation of hydroxyls and noted carbon dioxide production during fixation (Kaldas and Cooper 1993). The conflicting results of the study by Ostmeier and others (1988) could have been caused by the presence of extractives that migrated to the surface and interfered with XPS spectra (Kaldas and Cooper 1993; Yamamoto and Inoue 1990).

Studies using other techniques suggest that carbonyl groups and phenolic hydroxyl groups are affected by CCA treatment. Infrared, nuclear magnetic resonance spectroscopy (NMR), and ultraviolet spectroscopic analysis of guaiacol and catechol (lignin model compounds) demonstrated that the phenolic hydroxyls of both compounds were altered by reaction with chromium trioxide (Hon and Chang 1985). Similarly, previous work reported that methylation of phenolic hydroxyls greatly decreased the reactivity of lignin model compounds with bichromate solutions (Sanderman and others 1954).

The role of extractives as reactive sites in CCA fixation has also been studied. Polyflavanoid tannins, a common type of extractive, readily form complexes with metal ions such as copper, chromium, and arsenic (Ryan and Plackett 1987). The catechol and pyrogallol beta-rings can coordinate with copper in 1:1, 1:2, and 1:3 copper:flavanoid ratios, and precipitate after a 1:1 complex is formed (Pizzi and others 1986). These metal-flavanoid complexes apparently form more readily than those with other wood constituents; flavanoid-CCA mixtures precipitate almost instantly at room temperature, while it may take a few hours for a lignin-CCA mixture to precipitate completely. In work with pine and eucalyptus blocks, CCA components were depleted from the treating solution in increasing amounts as the tannin content increased. Even the slight increase from 0 to 2 percent tannins produced a dramatic increase in CCA depletion from the treating solution. The complexes formed appeared to be similar to those formed by copper and chrome with the guaiacyl units of lignin, but were more stable because they were formed with two hydroxyl groups instead of one hydroxyl and one methoxyl group. Of all the CCA components, trivalent chromium forms the most stable complexes with flavanoids, bivalent copper is nearly as stable, and hexavalent chromium is much less stable. Arsenic is also capable of complexing with flavanoids, but does so at a much slower rate than chromium or copper.

The presence of extractives may also help explain why fixation proceeds much more quickly in Douglas-fir heartwood

than sapwood (Forsyth and Morrell 1990), and why it proceeds rapidly in eucalyptus despite the high pH level of that species (Dahlgren 1975). One recent study also reported that arsenic leaching from CCA-C-treated pine heartwood was approximately twice that from sapwood, suggesting that the presence of extractives in the heartwood interfered with the fixation process (Kennedy and Palmer 1994).

In general, studies on the interaction of CCA with wood have provided evidence for involvement of many wood constituents. This is not surprising considering the high reduction potential of hexavalent chromium, the rapid adsorption of copper by many organic substrates, and the wide array of reactive sites available in wood. Anderson (1990) proposed a composite theory of fixation to encompass the wide range of fixation reactions. He divides fixation into two modes, termed macro- and microfixation. In macrofixation, the CCA components react rapidly in easily accessed fluid pathways, forming mainly inorganic precipitates but also reacting with extractives and readily available cell wall components. Subsequently, during microfixation, the preservative diffuses through the cell wall, giving rise to a variety of inorganic and organic reaction products, depending on wood structure and species.

Fixation in Ammoniacal and Amine Systems

Fixation of the ACZA, ACQ, and CC ammoniacal systems has been studied much less than the CCA fixation mechanisms. The general premise of fixation in these systems is that the cupriammonium ion is fixed through cation adsorption reactions with the wood substrate and through precipitation as the ammonia evaporates from the wood (Cooper 1991a; Hulme 1979; Jin and Archer 1991; Lebow 1992).

Research on ACZA fixation suggests that ammoniacal copper is readily adsorbed to phenolic hydroxyls, such as found in lignin or extractives, although the majority of copper is probably precipitated in the wood as copper carbonates, copper oxides, or copper arsenate complexes (Lebow 1992). The zinc in ACZA is adsorbed to wood components to a lesser degree than is copper, and the majority of the zinc appears to precipitate in the form of zinc arsenate as the ammonia evaporates from the treated wood. Both copper and zinc are relatively leach resistant, regardless of the presence of arsenic in the solution, because the precipitates they form upon ammonia evaporation have low water solubility. The primary method of arsenic fixation appears to be as insoluble zinc arsenate precipitates, although a minor portion of the arsenic may precipitate with copper (Lebow 1992). The ratio of the metals (copper and zinc) to arsenic appears to be very important in achieving maximum arsenic fixation, because arsenic leaching increases substantially when the metal oxide:arsenic pentoxide ratio is less than 2.0. The fixation, or leach resistance, of the arsenic is further improved when the ratio of zinc to copper in the solution is increased (Best and Coleman 1981; Lebow 1992; Rak 1976).

Similar mechanisms of fixation have been postulated to explain the leach resistance of copper in ACQ-treated wood,

although it has been observed that copper adsorption is slowed in the amine formulation (Anon. 1990; Jin and Archer 1991). It also appears that the didicyldimethylammonium chloride in the treating solution competes with the copper for the ion exchange sites in the wood and may reduce the proportion of copper fixed in this manner (Jin and Archer 1991; Preston and others 1987). DDAC was shown to rapidly react with both lignin and cellulosic model compounds, although reaction with lignin is preferred (Jin and Archer 1991). Others have noted that alkylammonium compounds appear to react with the wood through both cation exchange and ion pair mechanisms (Loubinoux and others 1992; Preston and others 1987). These ion pair mechanisms may be a process related to micelle formation and probably result in weaker bonds that are more easily water leachable (Loubinoux and others 1992). Unreacted DDAC is highly water soluble (Henderson 1992).

Little information is available on the fixation mechanisms on the components of ammoniacal CC and the amine-based CuAz preservatives, although it is probable that the process of copper fixation is very similar to that of ACZA. Laboratory and field tests have indicated that the citrate portion of the preservative is relatively leachable (Anderson and others 1993) and may not undergo fixation reactions in the wood. Similarly, high leaching rates have been noted for the boron component of CuAz (Fox 1994). Little information has been published on the fixation mechanism of tebuconazole, although tests have indicated that it is leach resistant (Fox and others 1994; Anon. 1993).

Fixation of CDDC

The fixation of copper in the CDDC systems is somewhat different than that in the preservative systems previously described, because the desired fixation product is known and the treating conditions are adjusted to achieve that product. Reaction of the copper ethanolamine and sodium dimethyldithiocarbamate (SDDC) produces an insoluble copper dimethyl-dithiocarbamate chelate that appears to form in a 1:2 molar ratio of copper to dithiocarbamate (Cooper and Stokes 1993; Freeman and others 1994). Researchers noted an increase in copper leaching when the molar ratio of Cu:SDDC was 1:1 or greater, indicating that excess copper is not as well fixed in the wood, although it is possible that a portion of the copper may react with the cell wall by ion exchange (Cooper and Stokes 1993). In treatments with excess SDDC, it is thought to decompose with time as the wood buffers the solution pH down to near neutral (Cooper and Stokes 1993).

Assessing the Degree of Fixation

Perhaps of most practical consequence to treaters is determining when fixation is complete, because the preservative then becomes least leachable and most effective against decay organisms. Several methods have been used to assess the progress of fixation. The most obvious method is to perform leaching tests, but this approach is time consuming and requires relatively sophisticated equipment to measure the low levels of wood components removed from the wood.

In addition, it is difficult to standardize laboratory leaching tests for all products and extrapolate the results to service conditions. However, leaching tests are a fundamental tool in the research of preservative fixation and in verifying the validity of other methods of assessing the degree of fixation.

The most common techniques of assessing the degree of CCA fixation are based on the reduction of hexavalent to trivalent chromium that takes place during fixation. Fixation is often considered complete when hexavalent chromium can no longer be detected in leachate or expressate from the treated wood. This approach has been found to be a fairly conservative measure of fixation when compared with the levels of copper, arsenic, and chromium actually leached from CCA-treated wood (Cooper and Ung 1992a). Foster (1989) developed a rapid field method of detecting hexavalent chromium levels as low as 15 parts per million (ppm). A core is removed from the wood, placed on white absorbent paper, and washed with a few drops of 0.5-percent chromotropic acid in sulfuric acid. Available hexavalent chromium is washed out of the wood and develops a purple color upon reacting with the chromotropic acid. Other approaches are less adaptable to field use but provide better quantitative estimates of hexavalent chromium levels. Cores removed from treated wood may be agitated in a 0.5-N sulfuric acid solution that is then reacted with diphenylcarbazide reagent (Cooper and Ung 1993). The intensity of the resulting purple color is measured using a visible light spectrophotometer (Cooper and Ung 1993). A more sensitive but less convenient method is to squeeze or press borings removed from treated wood, then assess the extent of the reaction of the expressed solution with diphenylcarbazide reagent (Cooper and Ung 1993). One problem with these types of tests is that they show only if the chromium is reduced, not if the fixation process has proceeded correctly (Ruddick 1993b).

Other tests more closely approach short-term leaching trials. Wood borings may be removed, extracted in water, and the water analyzed for the concentration of each preservative component (Homan 1994). Alternatively, stacks of lumber may be showered with artificial rainfall and the runoff collected and analyzed for levels of preservative components (Homan and Militz 1993; Homan and others 1993). These methods provide quantitative information about the degree of fixation of each preservative component, but are time consuming and require more sophisticated analytical equipment than the colorimetric indicator methods just described.

Standardized procedures are not available to assess the degree of fixation in ammoniacal or amine systems. If not actual leaching tests, such tests would presumably either directly or indirectly measure the ammonia or moisture content of the wood and relate that value to leachability. However, not much data are available that relate wood ammonia content to preservative leachability for most ammoniacal systems. Adequate fixation can be achieved by either air or kiln drying the wood after treatment, but this process can be time consuming and expensive, depending on the plant facilities and type of product produced. Because ammonia is more volatile than water, it may not be necessary to completely dry the wood to remove sufficient ammonia to prevent leaching.

Assessing fixation in CDDC-treated wood is an additional challenge, but research indicates that fixation with this system is much more rapid than with other waterborne wood preservatives (Cooper and Stokes 1993).

In the case of oilborne preservatives, such as copper naphthenate, the treated product is assumed to be acceptable for use when the carrier oil is no longer dripping from the wood and the surface is relatively free of oily residues. This stage can often be achieved during the treating process with the use of techniques, such as expansion baths, steaming, and final vacuum.

Treating and Conditioning Parameters

Many factors affect the rate and degree of fixation of waterborne preservatives, including wood properties, treating schedule, and dimensions of the treated product. However, the overriding factors appear to be the solution formulation, preservative retention, and temperature, humidity, and rate of air flow around the wood after treatment.

Solution Formulation

Preservative composition can affect fixation, and differing commercial formulations have been produced that meet AWWA standards for CCA types A, B, or C (AWWA 1994). These include Tanalith C and Celcure AP formulations that are similar to CCA-Type C, Boliden K33 that resembles CCA-Type B, and Greensalt that meets specifications for CCA-Type A. The major difference between the CCA types A, B, and C is the amount of chrome and arsenic; the percentage of copper varies only slightly (Table 1). Dahlgren (1972) compared fixation rates of commercial formulations and found that Boliden K33 fixed the fastest, followed by Celcure AP and then Tanalith C. He suggests that Tanalith C solubilizes tertiary chrome arsenates at higher pH levels than Boliden K33 because of the greater chrome:arsenic ratio and that the increased chromium emphasizes the final stage in chromium precipitation). These findings conflict with those of Pizzi (1982), who reports that CCA-Type A has the highest fixation rate, followed by Tanalith C, Celcure AP, and then Boliden K33. Pizzi postulates that it is the As:Cu ratio that determines fixation rate, with increased arsenic slowing the reactions and increased copper stimulating them. In accordance, CCA-Type A has the lowest As:Cu ratio and Boliden K33 has the highest proportion of arsenic. With increased arsenic, more chromium arsenates are formed and less hexavalent chromium is available as HCrO_4 for rapid complexation with lignin, while with increased copper more hexavalent chromium is available as CuCrO_4 . Other researchers have noted that increased arsenic levels can slow or decrease the proportion of copper fixed to the wood by ion exchange reactions, apparently by lowering the solution pH (Gray 1993; Gray and Dickinson 1988).

Although some disagree about which CCA formulation fixes at the highest rate and how formulation affects fixation, there appears to be general agreement that arsenic leaching is

greatest from the CCA-B formulation (Arsenault 1975; Cserjesi 1976; Johnson 1977; Kim and Kim 1993; Murphy and Dickinson 1990; Ruddick 1993b; Sheard 1991). This finding agrees with much of the initial work in developing CCA formulations, where researchers noted that significant arsenic leaching can occur in formulations with a low proportion of chromium (Hagar 1969; Henry and Jeroski 1967; Fahlstrom and others 1967; Smith and Williams 1973). The effect of chromium content on copper fixation is less clear, although copper leaching does increase in formulations with very low chromium contents (Hagar 1969; Henry and Jeroski 1967). Note, however, that CCA-B is no longer used in pressure treating; the vast majority of treaters in North America use the CCA-C formulation.

Solution Concentration and Retention Level

Studies on the effect of CCA concentration on fixation have produced conflicting results. In an early study with bichromate solutions, Jonas (1956) noted that increasing the solution concentration increased the rate of chromium reduction. In other work, increasing solution concentration was reported to cause slower fixation of copper and chromium and faster fixation of arsenic (Wilson 1971) or to accelerate overall fixation while shifting the distribution of chromium-linked compounds in favor of lignin (Pizzi 1983). Dahlgren (1975) found that increasing the concentration tended to lengthen the primary precipitation period, although not with all species and preservative formulations. He notes that in spruce, where poor permeability limits preservative access to reducing agents, a large increase in fixation period resulted from increased concentration. Dahlgren also suggests that although higher solution concentrations result in more overall chromium to reduce and precipitate, they may also increase the proportion of hexavalent chromium fixed initially, thus shortening the fixation period. The effect of changes in solution concentration may also depend on the range of concentrations tested. In laboratory tests with dilute solutions, increases in chromium concentration can be expected to greatly increase the rate of fixation, but at the relatively high concentrations used commercially, this effect may be less important (Anderson 1990; Pizzi 1983). This observation was supported by the work of Osborne and Pasek (1991) who treated Southern Pine blocks with a range of solution concentrations to produce weight gains from 1 to 12 percent. They found that although the rate of fixation increased at higher concentration levels, the percentage of chromium fixed at any one period was fairly uniform across all concentrations.

The role of solution concentration is also intertwined with pH effects. Increases in solution concentration lower the pH of the wood preservative system and can subsequently accelerate the rate of fixation (Anderson 1990; Jonas 1956; Pizzi 1983). In practical use, however, solution concentration and retention do not appear to correlate well or have a large effect on the rate of fixation (Anderson 1990; Cooper and Ung 1992a; Pizzi 1983).

The effect of retention on leaching of CCA components appears to be of more practical importance. Several researchers have noted that the percentage of leachable arsenic decreases with increased retention (Archer and Preston 1994; Arsenault 1975; Coetze 1980; Hagar 1969; Irvine and others 1972; Lee and others 1993; Wood and others 1980). The effect appears to be similar to increasing the proportion of chromium in the original treating solution. At high retention levels, increased amounts of chromium are available to react with arsenic because a lower proportion of the total chromium is adsorbed to wood components (Arsenault 1975). It has also been suggested that higher retention levels provide more water repellency to the wood, thus limiting leaching (Coetze 1980). The effect of retention on leaching of copper and chromium is less clear. Increased retention has been reported to both increase (Irvine and others 1972) and decrease (Lee and others 1993; Wood and others 1980) the percentage of these leached elements.

Temperature and Humidity

The use of elevated temperatures to speed CCA fixation has drawn much interest, especially in areas where cold winter temperatures cause inconveniently lengthy fixation periods. Several techniques have been used or proposed to elevate the temperature of treated wood, including various forms of kiln drying, hot water baths, and steaming (Alexander and others 1993; Boone and others 1995; Christensen 1990; Connell and others 1995; Edlund 1987; Conradie and Pizzi 1987; Cooper and Ung 1992a; Peek and Willeitner 1981, 1988; Willeitner and others 1986; Wood and others 1980; Zahora and others 1993). All these techniques are capable of greatly reducing the time needed for reduction of hexavalent chromium, although they also increase costs and pose processing difficulties.

In addition, care must be taken with accelerated CCA fixation to ensure that fixation proceeds in a manner that minimizes leaching. Some studies indicate that steam fixation may actually increase initial copper leaching in pine, perhaps by the mobilization of resin containing copper to the wood surface (Peek and Willeitner 1988; Van Eetvelde and others 1994). Several researchers also note that the use of elevated temperatures can interfere with fixation or result in increased leaching, especially if the moisture content of the wood is lowered too quickly (Alexander and others 1993; Avramidis and Ruddick 1989; Boone and others 1995; Henshaw 1979; Conradie and Pizzi 1987). Sufficient water must remain in the wood for the chemical reactions of fixation to occur (Anderson 1990). Conradie and Pizzi (1987) found that leaching of CCA elements increased by four times when the fixation temperature was increased from room temperature to 248°F (120°C), although fixation at 176°F (80°C) did not appear to have negative effects. Similarly, air drying small blocks, even at room temperature, increased leaching of copper and arsenic compared with that of blocks dried in moist air (Henshaw 1979). Lee and others (1993) also reported increased leaching when air drying was conducted at temperatures as low as 140°F to 180°F (60°C to 82°C). This problem does not seem to occur or is minimized if the

wood remains moist during heating, such as with steam or water baths (Avramidis and Ruddick 1989; Boone and others 1995; Peek and Willeitner 1981). A recent study suggests that kiln drying at moderate temperatures (140°F (60°C)), with an initial period of high humidity may provide better fixation than does air drying or kiln drying at 165°F (74°C) (Boone and others 1995).

Recently Developed Waterborne Preservatives

Little research has been done to determine the effects of various treatments and conditioning parameters on the fixation of the recently developed waterborne systems. Proper fixation in the ammoniacal and amine systems appears to be less sensitive to humidity conditions, because it is a drying process. Consequently, the same factors that speed drying of wood, such as elevated temperatures, air flow, and low humidity, will also increase the rate of fixation with ammoniacal systems. However, the effect of drying conditions on leachability has not been well studied for ammoniacal systems, and it may be that certain processes, such as drying too rapidly after treatment, will affect the distribution of copper in the wood and the manner in which cobiocides are precipitated (Lebow 1992). In addition, care must be taken with drying cycles to avoid damaging the mechanical properties of the wood (Barnes and others 1993).

Summary of Leaching Studies

The majority of past research on preservative leaching has been laboratory studies designed to compare the effects of various factors on leaching or the leaching rates of various preservatives. Although these studies are useful as comparative tools, they are not intended to demonstrate the amount of leaching that may occur in service conditions. Many factors that can influence leaching in-service are difficult to simulate in a laboratory; exposure environment, product size, and surface area are examples. Although experimental conditions are more difficult to control in field or service leaching studies, the results tend to be more useful indicators of actual leaching amounts. However, information about leaching gained from these studies must be evaluated with respect to exposure conditions and product type. In this report, an effort is made to present leaching data that are most applicable or closely simulate leaching in-service.

Because other waterborne preservatives have not been as widely used as CCA, leaching studies are primarily limited to small-block laboratory tests and soil-bed or field small-sized stake tests. Although the applicability of these data to field leaching rates is difficult to determine, some of this type of data will be presented for lack of better information. Many of these studies compare leaching rates to those of CCA, which provides a reference for comparison as well as strengthens the CCA leaching database.

CCA

Belowground Contact

Tasmanian Boardwalk Study

Perhaps the most pertinent study of leaching from CCA-treated wood used for applications similar to those of the Forest Service was conducted by the Tasmanian Parks and Wildlife Service (Comfort 1993). In this study, which was conducted to address many of the same concerns faced by the Forest Service, chromium, copper, and arsenic levels were measured adjacent to CCA-treated boardwalks at several sites in southern Tasmania. At each site, three soil samples were taken within 150 mm (5.9 in.) of the boardwalk, and three reference samples were removed several meters from the boardwalk. The boardwalks at the sites varied from 1 to 14 years in age; the preservative retention and treating solution formulation were not reported. Levels of copper and chromium adjacent to the track were significantly elevated in comparison with the control samples, but not to extreme levels. Arsenic levels were not found to be significantly elevated above that of the controls. The highest copper level detected was 49 ppm; the control level was between 1 to 3 ppm for that site; the highest chromium level detected was 88 ppm, approximately 60 ppm more than the reference sample. There did not appear to be any relationship between the age of the boardwalk and the CCA levels detected. The highest copper levels were detected around a 1-year-old structure, and the highest chromium levels were detected around the 14-year-old structure.

The elevation of chromium levels in the soil is surprising relative to the copper and arsenic levels detected. Most other studies have indicated that copper and arsenic are leached in much greater quantities than chromium. It is possible that the copper and arsenic were more mobile in the soil and that levels had dissipated over time. However, not one site was sampled immediately after installation or repeatedly sampled over time, so it is difficult to ascertain if copper and arsenic levels were initially greater. In addition, copper or arsenic analyses were not done at the sites that contained the highest chromium levels; the levels of these two components may have also been more elevated at these two sites (Comfort 1993).

Poles

Leaching of CCA from utility poles has been a source of concern because of their widespread distribution and large volume of preservative. Unfortunately, studies to determine the amount of leaching from poles are difficult because the original CCA content is rarely known. To avoid this problem, researchers have compared the CCA content above and belowground (on the assumption that leaching is much slower above ground) or assayed the surrounding soil in an effort to detect CCA leaching.

In an Australian study, spotted gum poles treated with an unspecified CCA preservative were analyzed for CCA content 300 mm above and 150 mm belowground after 6 years of service (Nicholson and Levi 1971). Arsenic content in the

belowground portion of the poles was significantly less (11 to 21 percent) than that in the above-ground samples, although no statistically significant difference was found in copper or chromium levels. It appeared that arsenic levels had declined throughout the treated zone, not just near the pole surface. Both sandy clay and light-textured clay soils were present at the sites (Nicholson and Levi 1971). Arsenault (1975) reported on work in which the above- and belowground preservative content of CCA-A (low arsenic formulation) treated Southern Pine poles was compared after 15, 16, 17, 27, or 32 years of exposure. No overall difference in any component concentration was noted when comparing levels at 36 in. (914 mm) above ground to those 6 in. (152 mm) belowground. The poles were exposed in soil types that included sandy loam, loam with clay, and wet clay. Soil samples removed adjacent to selected poles placed in clay soils revealed that arsenic levels were four times background levels 2 in. (51 mm) away from the poles, but were not significantly elevated 12 in. (305 mm) from the poles.

In a recent study, researchers found elevated levels of copper and arsenic in soil around CCA-B and CCA-C treated poles that had been in service for 11 years (Nurmi 1993). Levels of arsenic were 760 times greater than that in the natural background adjacent to the CCA-B treated poles, and 92 times greater than that in the background around CCA-C treated poles. Copper levels in the soil were between 10 and 50 times greater than background levels for both types of treatments.

Posts and Timbers

Evaluation of leaching from CCA-treated posts and timbers presents much the same problem as found in pole leaching studies, in that the original CCA content is rarely known. Arsenault (1975) compared CCA content in above- and belowground portions of Southern Pine posts that had been treated with CCA-A and exposed for 17 years in a sandy Florida site. Belowground copper levels were significantly less than above-ground levels in the outer 0.5-in. (13-mm) zone, and belowground arsenic levels were depleted in the second 0.5-in. (13-mm) zone. The author suggests that the original CCA retention was too low to allow proper fixation to occur. Surprisingly, soil samples removed adjacent to the posts did not contain elevated levels of any CCA component. In related work, CCA-B treated Southern Pine posts were sampled 6 in. (152 mm) belowground immediately prior to installation and after 7 years of exposure in Florida (Arsenault 1975). High arsenic leaching (22 to 57 percent) was detected, in agreement with laboratory leaching studies of CCA-B formulations (Fahlstrom 1967; Henry and Jeroski 1967; Smith and Williams 1973). In addition, arsenic content in soils removed 2 in. (51 mm) from the posts was more than ten times greater than background levels, but decreased to near background levels only 4 to 6 in. (102 to 152) from the posts.

In a study of CCA-B leaching, *Radiata pine* vineyard posts, in service for up to 15 years in New Zealand, contained slightly less copper and arsenic belowground than above ground (Hedley 1984). However, the original treatment

appeared suspect in both formulation ratio and overall retention (Hedley 1984). Other researchers examined CCA-B treated playground timbers and the surrounding sand after 2 to 4 years in service (Henningsson and Carlsson 1984). They noted that the proportion of arsenic in the treated wood was 20 to 25 percent less than it should have been if the wood was treated according to Swedish standards, but the initial retention was not known. Arsenic levels in sand adjacent to the timbers was more than five times that found 20 in. (0.5 m) from the timbers; copper and chromium levels in the sand were not significantly elevated (Henningsson and Carlsson 1984).

Stakes

Although proportional rate of CCA leaching from small stakes is probably greater than that from larger, dimensional material, studies of this type do provide information about leaching in "real world" exposure conditions.

In one study, above- and belowground CCA-A retention levels in Southern Pine stakes (0.75 in. (19 mm) square) were compared after 9 to 12 years of exposure in a New Jersey test plot, and no significant difference in component ratios was detected (Arsenault 1975). Similarly, soil samples removed 1 in. (25 mm) away from three 6-year-old CCA-C treated stakes exposed in South Carolina did not contain elevated levels of any CCA components. Subsequently, De Groot and others (1979) conducted a thorough study of the soil adjacent to nominal 2- by 4-in. (standard 38- by 89-mm) Southern Pine stakes that had been treated with CCA-A or CCA-B and exposed for 30 years in acidic fine sandy loam in Mississippi. Soil was collected at 3, 6, and 9 in. (76, 152, and 229 mm) laterally from the stakes and at depths of 6 and 12 in. (152 and 305 mm) below the stakes. The concentration of CCA components was at background levels 12 in. (305 mm) beneath the stakes or 6 in. (152 mm) laterally from the stakes, but elevated levels of all three components were detected 6 in. (152 mm) beneath the stakes. Maximum levels (average) in the soil were 73 and 183 ppm for arsenic, 76 and 50 ppm for copper, and 46 and 24 ppm for chromium for CCA types A and B, respectively. Average background levels were 1 ppm for arsenic, 4 ppm for copper, and 4 to 9 ppm for chromium.

In a 1993 study, Evans and Edlund (1993) analyzed 0.8- by 2- by 20-in. (20- by 50- by 500-mm) Scots pine stakes that had been treated with CCA-B and exposed for 20 to 43 years at a Swedish test site. Based on original gross retention data, they noted that the stakes had lost an average of 23 percent copper, 19 percent chromium, and 25 percent arsenic. Similarly, 0.75- by 0.75- by 18-in. (19- by 19- by 450-mm) CCA-C treated Southern Pine stakes lost 20.5 percent copper, 8.9 percent chromium, and 21.5 percent arsenic after 44 months of exposure in Hawaii (Jin and others 1992).

Plywood

Although CCA-treated plywood is used extensively in many ground-contact exposures, little research has been done to evaluate the leaching potential of plywood in service. This is unfortunate, because structural differences make it difficult to

relate leaching data from studies of whole-wood products to plywood. However, the little work that has been done suggests that leaching of CCA components from plywood is minimal.

Arsenault (1975) reported on a study in which CCA component levels in ground water were monitored before and after construction of a building with treated plywood in the foundation. Ground water removed from the basement reached maximum levels of copper (0.13 ppm) and arsenic (0.11 ppm) during and immediately after construction, but 6 months after construction copper levels had decreased to less than 0.01 ppm and arsenic levels had decreased to 0.02 ppm. It is difficult to determine, however, if the copper and arsenic initially detected were leached from the plywood or released during construction activities. In a controlled study of Southern Pine plywood treated with CCA-A, B, and C, little arsenic leaching was detected from any formulation except CCA-C (salt formulation), in which 30 percent of the arsenic was lost (Chen and Walters 1979). This finding conflicts with other laboratory and field leaching studies that have generally concluded that arsenic is most leachable from CCA-B treatments (Arsenault 1975; De Groot and others 1979; Fahlstrom 1967; Henry and Jeroski 1967; Smith and Williams 1973).

Seawater

Piling and Timber

Piling and other CCA-treated wood exposed in seawater have a greater leaching potential than many other products because of their high preservative retention. Despite this, studies of CCA leaching from piling in service are rare. Arsenault (1975) reported that a single CCA-A treated piling, after 18 years of exposure in North Carolina waters, had no significant difference in CCA levels or component ratios between the above-water zone, tidal zone, below-water zone, or below-mudline zone. In a detailed study, Southern Pine posts were treated with CCA-C and exposed for 8 years in Key West, Florida (Gjovik 1977). Little change in overall CCA retention was noted, although a migration of copper did appear on the outside of the posts over time. These reports conflict with previous work that reported substantial losses of CCA components from *Radiata pine* piling after 4 to 5 years exposure in New Zealand waters (Hutchinson and McQuire 1970). Within the 0.5- to 1.5-in. (13- to 38-mm) penetration zone, samples removed from the intertidal zone and below-water zone had 45 to 55 percent and 80 to 85 percent less copper, respectively, than samples removed above the water line. In some piling, there was a corresponding increase in copper levels in the outer 0.5-in. (13-mm) zone below the water line; losses of arsenic and chromium were also noted (Hutchinson and McQuire 1970). A recent laboratory test of CCA-C leaching from full-sized piling exposed in seawater appears to confirm that copper is the most leachable component. Researchers found that approximately 529 mg of copper, 60 mg of arsenic, and little or no chromium were released from each square meter of pile surface after 28 days (Baldwin and others 1994).

Timbers and large dimensional lumber also represent a substantial portion of CCA-treated wood used in seawater exposures. Leightley (1987) reported on work in which timbers of *Pinus sylvestris* and four hardwood species were treated with CCA and exposed in coastal waters of Italy, Sweden, and Australia for 72 months. Some loss of all elements was detected, with copper leaching generally the greatest, followed by arsenic, then chromium. In most species, and especially pine, an apparent movement of copper from the inner part of the timber to the outside was also noted.

Small-Sized Samples

Although studies using small-sized samples are easier to conduct and replicate than those using full-sized piling or timbers, long-term leaching studies may be difficult to interpret because erosion and attack by marine organisms often removes substantial portions of treated wood (Baechler and others 1970; Cooper 1990). As with other leaching exposures, the greater surface area to volume ratios and larger proportions of exposed end grain in small-sized test samples may be expected to increase leaching.

Exposure of CCA (48.2 percent $\text{Na}_2\text{Cr}_2\text{O}_7$, 27.4 percent $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, 24.4 percent $\text{As}_2\text{O}_5\cdot 2\text{H}_2\text{O}$) treated 0.2- by 1- by 2-in. (5- by 25- by 51-mm) samples at two sites in English coastal waters resulted in significant losses of all three CCA components within 36 weeks (Irvine and others 1972). At lower preservative concentrations (1.1 and 2.5 lb/ft^3 (17.6 and 40 kg/m^3)), arsenic was the most leachable component, with losses ranging from 26 to 49 percent. However, at higher retention levels (3.8 and 5.2 lb/ft^3 (61 and 83 kg/m^3)), chromium was the most leachable component, with losses ranging from 45 to 55 percent. Arsenic leaching appeared to peak at the 2.5- lb/ft^3 (40- kg/m^3) retention, and copper and chromium leaching increased with each retention increase. Both the high rate of chromium leaching and the increased leaching of copper and chromium with greater retention noted in this study are interesting, as these results conflict with much of the laboratory work done on leaching in distilled water.

In a subsequent study, extensive leaching of all three components was noted when 0.25- by 1.5- by 6-in. (6- by 38- by 152-mm) Southern Pine panels were treated with CCA type B or C and exposed for 78 months in Key West, Florida (Johnson 1977). The CCA-B treated panels lost approximately 80 percent copper, 50 percent chromium, and 50 percent arsenic from the original retention. Similar losses of copper and chromium were noted from the CCA-C treatments, but arsenic leaching was decreased, especially at the highest retention level. The results of a similar study, which evaluated leaching from panels that had been treated with CCA-A or a salt formulation with component ratios similar to CCA-B, have been reported (Archer and Preston 1994). In that study, 1- by 2- by 12-in. (25- by 51- by 300-mm) *Radiata* pine panels were exposed for up to 85 months in New Zealand waters, then analyzed for CCA components by x-ray fluorescence. The CCA-A panels, which had been treated to a retention of 1.5 lb/ft^3 (24 kg/m^3), lost ap-

proximately 48 and 77 percent copper, 44 and 42 percent chromium, and 37 and 35 percent arsenic from the outer and inner zones, respectively, after 85 months. The outer zone consisted of an 8-mm- (0.3-in.-) deep strip cut from around all four edges of each panel. The panels treated to a similar retention with the salt formulation of CCA-B lost approximately 49 and 79 percent copper, 38 and 40 percent chromium, and 55 and 62 percent arsenic from the outer and inner zones, respectively, and those treated to 3 lb/ft^3 (48 kg/m^3) lost 41 and 77 percent copper, 36 and 35 percent chromium, and 42 and 35 percent arsenic, respectively, from inner and outer zones. These results demonstrate the importance of the role in chromium in reducing arsenic leaching and agree with other work that noted an apparent migration of copper from the inner portion of samples toward the wood surface (Gjovik 1977, Hegarty and Curran 1986; Shelver and others 1991).

In their work, Hegarty and Curran (1986) treated 0.2- by 1- by 20-in. or 0.8- by 0.8- by 6-in. (5- by 25- by 500-mm or 20- by 20- by 150-mm) pine and beech sapwood blocks with CCA-C and exposed them in Irish coastal waters. The smaller blocks appeared to lose at least 50 percent of CCA components after only 1 year, with losses of copper less than those of chromium or arsenic. An apparent redistribution or slower loss of preservative from the tracheids, rays, and crossfield pits of pine was noted, and a portion of the copper appeared to migrate to the surface of the larger blocks. Significant CCA leaching and copper movement was also noted in 6- by 6- by 20-in. (50- by 50- by 500-mm) CCA-treated *Pinus patula* stakes exposed off the coast of South Africa for 2 years (Shelver and others 1991). Overall losses of both copper (25 to 40 percent) and arsenic (70 percent) were detected, but copper content in the outer 0.24 in. (6 mm) of the blocks increased almost 40 percent over pre-exposure retentions. Treated hardwood samples have also been reported to suffer substantial losses of CCA components (17 to 100 percent) after 6 to 9 years of exposure in the coastal waters of India (Cherian and others 1979).

The apparent increase in leaching in seawater exposures, as well as the higher CCA retention levels used, led to studies to evaluate the fate of CCA components leached from the wood (Weis and Weis 1992; Weis and others 1993). One study reported that green algae collected from CCA-treated bulkheads had elevated levels of all three CCA components, suggesting that these organisms either take up leachate as it leaves the wood or remove nonleached components (Weis and Weis 1992). Similarly, oysters and crabs collected from CCA-treated wood at several sites had elevated levels of copper, and crabs at another site had elevated levels of all three elements. Unlike the algae and oysters, the crabs were not in direct contact with the treated wood, and the authors attributed high levels in that species to contamination of sediments near the treated wood. Further investigation revealed that levels of CCA components in sediments were elevated, and that these levels were a function of both proximity to the treated wood and sediment particle size (Weis and others 1993). Levels of copper in the sediments were consistently greater than those of chromium or arsenic, but it

is not clear if this was because of higher leaching rates of copper or stronger adsorption of copper by sediments. Similar concerns were the subject of a recent study that assessed the potential harm of CCA- and ACZA-treated wood to aquatic organisms (Brooks 1993). This review concluded that copper was the preservative component of greatest concern, but that most applications of properly treated products were unlikely to have any effect on marine flora or fauna. However, the author did note the potential for environmental harm with improperly treated products or when excessive amounts of treated wood are used in or above small volumes of still water.

Above-Ground Contact

Leaching of CCA components is generally assumed to be less severe in above-ground exposures, because the wood is not in constant contact with water or soil. Because of this, relatively few field or in-service product studies have been conducted to monitor leaching from CCA-treated wood in above-ground exposures. However, above-ground uses of CCA-treated wood are numerous, and many applications, such as decks, fencing, and shakes, expose large areas of treated wood to precipitation.

Because of their large surface area and direct exposure to the elements, CCA-treated cedar shakes were evaluated as an above-ground leaching hazard (Cserjesi 1976). Rainwater runoff CCA-B and CCA-C shakes treated to 0.29 and 0.69 lb/ft³ (4.7 and 11.1 kg/m³), respectively, was monitored for 2 years. Copper and arsenic levels from the CCA-C treated shakes never exceeded 10 ppm; they peaked during the fifth month and were not detectable by the second year. However, leaching of copper and arsenic from the CCA-B treated shakes was more than double that from the CCA-C treated shakes and still detectable the second year. Levels of chromium were uniformly less than 1 ppm, regardless of formulation. In a study by Evans (1987), rainwater was collected from a plank roof made of boards treated with CCA-B to a retention of approximately 0.75 lb/ft³ (12 kg/m³). Copper, arsenic, and chromium levels in the runoff during the first year were initially 4–5, 7, and 0.1 ppm, respectively. Chromium levels remained fairly constant during the 2-year study; copper levels decreased to 0.8 ppm; arsenic levels decreased to 1.2 ppm.

The above-ground portion of utility poles also provides a large exposed surface area for leaching. Ruddick and others (1991) compared CCA-C content in the above-ground portion of 10-year-old red pine and jack pine poles to the content in similarly treated new poles. They concluded that relatively little leaching had occurred above ground, although it appeared that about 0.03 lb/ft³ (0.48 kg/m³) arsenic and 0.13 lb/ft³ (2.1 kg/m³) copper had been lost from the outer 0.4 in. (10 mm) of the poles.

Freshwater and Silos

Few reports have been published on CCA leaching from in-service structures exposed to freshwater application. However, one study did assess waterway contamination from lock gates constructed from lumber treated with CCA (Cooper

1991c). Water samples were collected above and at varying distances beneath a newly constructed lock gate and a gate that had been in service for 5 years. Elevated CCA component levels were not found in water around the older gate, but significantly elevated levels of all three CCA components were detected in water downstream from the newly installed gate. Copper levels in the water were elevated by approximately 200 ppb (parts per billion) adjacent to the gate and 400 ppb 131 ft (40 m) downstream. Chromium levels were elevated by approximately 100 ppb in both locations, and arsenic levels were elevated by approximately 90 ppb near the gate and 60 ppb 131 ft (40 m) downstream. Estimates of percentage losses from the wood or volume of treated wood were not reported (Cooper 1991b).

Several researchers have conducted studies on leaching from CCA-treated wood in cooling towers. The applicability of these findings to other conditions is unclear, because waters within cooling towers may differ tremendously in temperature and chemical composition. A 1962 study on leaching of a CCA-C salt formulation from redwood sapwood cooling-tower timbers reported that minimal, if any, leaching occurred during 11 years in service (Dunbar 1962). However, the original sampling was conducted after the boards had been in service for 1,000 h, so leaching prior to that time would not have been detected. In a 1972 study, redwood, Douglas-fir, hemlock, and ponderosa pine cooling-tower slats were treated with CCA and exposed for 10 years (Gjovik and others 1972). Total CCA losses from the slats were 36 percent for redwood, 18 percent for ponderosa pine, 14 percent for western hemlock, 25 percent for flat-grain Douglas-fir, and 33 percent for edge-grain Douglas-fir, with most losses occurring during the first 18 months. Unfortunately, interpretation of these results was made difficult by the high chromium content of the cooling-tower water, which caused the chromium content in the boards to increase 44 to 120 percent during the test.

A study of CCA leaching from small (0.2- by 1.0- by 2-in.) (5- by 25- by 51-mm) Scots pine coupons exposed in seven cooling towers reported extremely variable leaching rates. In blocks treated to 1.1 lb/ft³ (17.6 kg/m³), 30 to 67 percent arsenic, 0 to 29 percent copper, and 12 to 86 percent chromium leached out after 40 weeks exposure, with average losses of 44.1, 18.6, and 31.8 percent for arsenic, copper, and chromium, respectively. At 2.5-lb/ft³ (40-kg/m³) retention, arsenic leaching varied from 2 to 44 percent, copper leaching from 0 to 22 percent, and chromium leaching from 8 to 41 percent, with average losses of 27.7, 13.7, and 25.4 percent for arsenic, copper, and chromium, respectively. The highly variable leaching rates were attributed to the differences in temperature, ionic activity, and biological activity between the cooling towers, although none of these factors clearly explained the results (Irvine and others 1972).

Another type of severe exposure for CCA-treated wood is in a highly acidic environment, such as a silo where grass is mixed with formic acid, forming lactic and acetic acids (Evans 1987). Evans evaluated leaching from pine boards that were treated with CCA-B (oxide) or CCA-C (salt) to 0.75 to 0.93 lb/ft³ (12 to 15 kg/m³) and placed inside a silo

for 2 years. Leaching losses from the boards averaged 75 to 80 percent for arsenic, 20 to 50 percent for copper, and 50 to 60 percent for chromium. Greater losses of copper and chromium occurred from boards treated with the CCA-C salt formulation than from the corresponding CCA-B oxide formulation. Applications with leaching conditions this severe are likely to rare.

Surface Deposits

Users of CCA-treated wood are often concerned with the amount of CCA components that may be removed by touching or wiping the wood surface. This is particularly true in the case of playground equipment, decks, and handrails. Several investigators have evaluated this problem, each under different conditions. Johanson and Dale (1973) treated *Radiata pine* round stock with CCA, allowed it to fix, and then gently scrubbed various surfaces in distilled water. A maximum of 8.1×10^{-5} lb/ft² (40 µg/cm²) arsenic was dislodged from the round surface of the wood, but as much as 3.3×10^{-4} lb/ft² (160 µg/cm²) was recovered from the end grain of one specimen. A maximum of 2.9×10^{-4} lb/ft² (140 µg/cm²) copper was also removed from the end grain of one section, although levels were generally much lower. However, in a later study, CCA-treated nominal 2- by 4-in. (standard 38- by 89-mm) lumber that was gently scrubbed with distilled water released arsenic levels that varied only from 1.6 to 4.3×10^{-7} lb/ft² (0.08 to 0.21 µg/cm²) (Woolson and Gjovik 1981). Generally, about 97 percent of the arsenic was in the pentavalent form, although in one area tested, all the arsenic released was arsenite. Lower levels of arsenic were also dislodged from CCA-treated plywood when wiped with a damp sponge (5.3×10^{-7} lb/ft² (0.26 µg/cm²)) or with a bare wet hand (6.5×10^{-7} lb/ft² (0.32 µg/cm²)) (Arsenault 1975). These lower levels of arsenic appear to be in general agreement with a larger study that reported mean dislodgeable arsenic as 3.4×10^{-7} lb/ft² (0.168 µg/cm²) (Williams and McNamara 1991).

The presence of available chromium on the wood surface has drawn less concern. Coggins and Hiscock (1979) found that when allowed to properly fix, little detectable chromium was removed from CCA-treated wood swabbed with glass wool. However, in all these studies, note that the amount of surface deposits on CCA-treated wood can vary between producers and individual charges.

ACZA

Little research has been done on leaching rates from ACZA, other than that done in the laboratory. However, an interesting comparison of arsenic leaching from ACA- and ACZA-treated wood was conducted in two watering trough leaching studies (Anon. 1985). In 1982 and subsequently in 1985, watering troughs with inside dimensions of 24.5 by 10.9 by 80.75 in. (622 by 277 by 2,051 mm) were constructed with Douglas Fir lumber that had been treated with either ACA (1982) or ACZA (1985). The troughs were filled with tap water, allowed to stand for 4 h, and a water sample was then removed from the center of the trough at half the water depth. This process was repeated two more times. The

samples removed from the ACA-treated trough contained 1,630, 760, and 330 ppb arsenic for the first, second, and third water additions, respectively. The samples removed from the ACZA-treated watering trough contained 19, 17, and 2 ppb arsenic after the same series of water changes. Analysis of the tap water revealed that it also contained 2 ppb arsenic. Although the lack of replication does not allow estimation of variation within sampling points, this study demonstrated the vast improvement in arsenic leach resistance achieved by adding zinc to the ACA formulation, as well as the tendency for the majority of leaching to occur early after exposure. Another ACZA-leaching test was conducted on 24-in.- (610-mm-) long Douglas Fir pole stubs that had been treated to add 0.97 lb/ft³ (15.5 kg/m³). Morgan (1989) reported an overall leaching rate of 0.14 ppm after 2 months of exposure.

Some field leaching data are available for ACA, but the study noted previously and small-block laboratory comparisons indicate that leaching, at least of arsenic, is substantially reduced in the ACZA formulation (Best and Coleman 1981; Lebow 1992; Rak 1976). In addition, the fixation of copper might be expected to be substantially different in the ACA and ACZA formulations, because much of the copper in ACA is thought to precipitate as copper arsenate complex and copper precipitation in ACZA is more likely to occur in the form of copper carbonate. It is probably reasonable to assume that the rate of copper loss from ACZA treated wood is similar to that from ACQ-B and CC treated material. However, one soil-bed study (Jin and others 1992) reported that copper leached at a slightly higher rate from ACZA treated stakes than from ACQ-B treated stakes.

ACQ and DDAC

Copper leaching from ACQ-B, CCA, and ACZA was compared in a soil-bed test with 0.75- by 0.30- by 7.9-in. (19- by 8- by 200-mm) stakes (Jin and others 1992). After 9 months, copper loss from stakes treated to 0.6 lb/ft³ (9.6 kg/m³) averaged 19 percent from ACQ-B, 30 percent from ACZA, and 17.9 percent from CCA. The ACQ treated stakes lost 30 percent of their DDAC, and ACZA lost 30 percent zinc oxide and 35 percent arsenic pentoxide. CCA lost 11 percent chromium trioxide and 16 percent arsenic pentoxide during the test. In a subsequent soil-bed test, leaching of ACQ-B and ACQ-D was compared in Southern Pine stakes (0.25 by 0.75 by 8 in. (6 by 19 by 203 mm)) that had been treated to 0.4 lb/ft³ (6.4 kg/m³) retention (Anon. 1994). After 3 months, the ACQ-D stakes had lost 15.4 percent CuO and 12.9 percent DDAC, and ACQ-B stakes had lost 17.4 percent CuO and 32.7 percent DDAC (Anon. 1994). It is evident that these tests presented severe leaching conditions because of the small stake size and the soil-bed conditions.

ACQ-B and CCA leaching data were also collected from 44 month ground contact depletion tests conducted in Hilo, Hawaii, using 0.75- by 0.75- by 39-in. (19- by 19- by 1,000-mm) stakes treated to 0.4 lb/ft³ (6.4 kg/m³) retention (Jin and others 1992). Averaging losses from the top, bottom, and middle of the stakes revealed that 21 percent

copper oxide, 9 percent chromium trioxide, and 22 percent arsenic pentoxide were lost from CCA-treated stakes, and 19 percent copper oxide and 42 percent DDAC were lost from the ACQ-B treated stakes.

Three-year leaching data were also collected on 0.75- by 0.75- by 26-in. (19- by 19- by 650-mm) red pine stakes that were treated with ACQ-B 1:1 (copper to quat ratio) and exposed in Ottawa, Ontario. At the highest retention (0.8 percent CuO and DDAC or about 0.25 lb/ft³ (0.4 kg/m³) CuO), 1.2 to 8.8 percent copper was lost from the groundline area, and 32 to 34 percent DDAC was depleted. Greater percentages of quat appeared to leach from the lower retention levels, and the percentage of copper leached did not appear to be strongly correlated to retention (Anon. 1990).

Above-ground depletion tests were conducted in Hawaii on 2.0- by 0.75- by 14.0-in. (51- by 19- by 356-mm) CCA and ACQ-B-treated Southern Pine samples (Jin and others 1992). After 12 months, copper oxide losses from stakes treated to 0.25 lb/ft³ (4 kg/m³) were 14 percent from ACQ-B and 8 percent from CCA. Twenty-seven percent of the DDAC was lost from the ACQ treated stakes, and 14 percent chromium trioxide and 19 percent arsenic pentoxide were lost from the CCA-treated stakes. A similar test was conducted with ACQ-D and CCA-C treated samples. After 6 months, the ACQ-D samples treated to 0.25 lb/ft³ (4 kg/m³) had lost approximately 10 percent copper oxide and 32 percent DDAC, and the CCA-C treated samples had lost 9 percent copper oxide (Anon. 1994). In an earlier test, little, if any, DDAC loss was detected when 1.5 by 1.5- by 9.0-in. (38-by 38- by 229-mm) samples were treated and exposed above ground for 6 months in Hawaii (Preston and others 1987).

The leaching of DDAC, in the absence of copper, was also evaluated in larger dimension material in an earlier study (Preston and others 1987). Southern Pine posts, 6 to 8 in. (152 to 203 mm) in diameter, were treated with didecyl-dimethylammonium chloride to a retention of approximately 2 percent (w/w basis), air dried, and placed in a Florida test site for 18 months. In the above-ground portion of the posts, approximately 12 percent DDAC was leached from the outer 0.5 in. (13 mm) and 6 percent from the 0.5 to 1 in. (13 to 25 mm) zone; no loss was detected from the inner portion of the posts. In the belowground region, 25 percent was leached from the outer 0.5 in. (13 mm), and the 0.5 to 1 in. (13 to 25 mm) and 1 to 2 in. (25 to 51 mm) assay zones actually appeared to gain DDAC retention, suggesting downward migration within the posts.

CC

A 5-year study of copper loss from 7- to 9-in.- (178- to 229-mm-) diameter Southern Pine pole stubs that had been treated to a target retention of 0.6 lb/ft³ (9.6 kg/m³) was conducted in Gainesville, Florida (Anderson and others 1993). The researchers removed increment cores from 6 in. (152 mm) belowground, at groundline, and 24 in. (610 mm) above ground before exposure and 12, 24, 36, 48, and 60 months after exposure. Leaching data were variable

between sampling periods, but copper losses of approximately 50, 10, and 39 percent were noted for the 0 to 0.5, 0.5 to 1, and 1 to 2 in. (0 to 13, 13 to 25, and 25 to 52 mm) assay zones, respectively, in the belowground zone after 5 years. Losses from the region were 19, 5, and 22 percent for these same assay zones. The authors estimate a total copper loss of approximately 28 percent from the below-ground zone during the first year, with minimal losses in subsequent years.

A 5-year depletion study using 0.75- by 0.75- by 39-in. (19- by 19- by 1,000-mm) Southern Pine stakes, which were treated with CC to target retentions of 0.4, 0.6, and 0.8 lb/ft³ (6.4, 9.6, and 12.8 kg/m³), was also conducted at the Gainesville site (Anderson and others 1993). After 3 years, copper losses varied from 34 to 43 percent for the below-ground portion of the stakes, 26 to 39 percent for the groundline portion of the stakes, and 15 to 18 percent for the above-ground portion of the stakes. After 5 years, losses from belowground varied from 43 to 50 percent, groundline from 39 to 56 percent, and above ground from 30 to 40 percent. Percentage leaching rates did not appear to be directly related to retention level. Greater losses were reported from similarly treated stakes exposed at a Mississippi test plot (Anderson and others 1993). After 5 years in Mississippi, losses of 60 to 65 percent were reported belowground, 49 to 57 percent at groundline, and 28 to 40 percent from the above-ground portion of the stakes. In addition, it was noted that all or nearly all the citric acid was leached from the ground-contact portion of the stakes.

CuAz

In a study that supplies insight into leaching rates of treated wood exposed above ground under in-service conditions, depletion tests were conducted on decks built with 1.5- by 5.5-in. (38- by 140-mm) lumber that had been treated with CCA-C, ACQ-B, or copper boron (Cu:BAE = 25:25) with formulation characteristics similar to those of CuAz (Fox and others 1994). The boards were treated with either full cell or empty cell processes to a retention of 0.25 lb/ft³ (4 kg/m³) copper for the copper boron or to 0.4 lb/ft³ (6.4 kg/m³) (total retention) with either ACQ-B or CCA-C. During 20 months in Conley, Georgia, the decks were exposed to more than 80 in. (2 m) of rainfall that was periodically collected and analyzed for copper and boron. The copper-boron decks leached 8 to 12 percent copper and 55 to 65 percent boric acid, and the ACQ-B decks lost 8 to 10 percent copper and the CCA-treated decks lost 5 percent copper. This loss corresponded to leaching rates of approximately 0.0035 and 0.0024 lb/ft² (1,722 and 1,184 µg/cm²) for copper from the copper-boron treated material, 0.0026 and 0.0020 lb/ft² (1,292 and 969 µg/cm²) for the ACQ-B treated material, and 0.0004 and 0.0003 lb/ft² (215 and 161 g/m²) for the CCA-treated material for modified full cell and full cell treatments, respectively. With both types of treating schedules, copper loss from the copper-boron treated wood was greatest during the first 20 in. (508 mm) of rainfall and minimal during the last 10 in. (254 mm) of rainfall.

The same authors also reported on small-block laboratory leaching tests (AWPA E10-87), in which blocks were treated with two retention levels of CuAz in the ratio of 25:25:1 Cu:BAE:tebuconazole (Fox and others 1994). At the 0.15-lb/ft³ (2.40-kg/m³) retention (as copper), approximately 8 percent copper, 100 percent boron, and 9 percent tebuconazole were leached from the blocks. At the 0.22 lb/ft³ (3.52 kg/m³) retention, approximately 13 percent copper, 100 percent boron, and 6 percent tebuconazole were lost. The rate of copper loss was very comparable to that found in the deck study, but the percentage of boron loss was much greater in the laboratory tests. This demonstrates the difficulty of extrapolating data from small-block laboratory tests to in-service conditions.

Also pertinent to the leaching of boron and copper from ammoniacal formulations is a study evaluating leaching from 1.5- by 3.5-in. (38- by 89-mm) stakes treated with ammoniacal copper borate and exposed for 11 years at a test site in Mississippi (Johnson and Foster 1991). The original copper oxide retention in the stakes varied from 0.29 to 1.98 percent, and the boric acid content varied from 0.10 to 0.71 percent. During exposure, 95 percent to more than 99 percent of the boron leached from the groundline portion of the stakes, and 78 to 93 percent of the boron was lost from the above-ground portion of the stakes. Copper losses varied from 3 to 33 percent in the groundline portion of the stakes and 0 to 28 percent in the above-ground portion of the stakes. With both copper and boron, the greatest percentage loss occurred at the lower retention levels. Because of the relatively large dimensions of the stakes used in this study, the leaching rates noted for ammoniacal copper may be more representative of losses in service than stake test data reported previously for other ammoniacal formulations.

CDDC and SDDC

Long-term (23 years) leaching data were reported on 0.75- by 0.75- by 18-in. (19- by 19- by 457-mm) Southern Pine stakes exposed in Bainbridge, Georgia (Freeman and others 1994). The stakes were treated to either 0.6 lb/ft³ (9.6 kg/m³) with CCA or to 0.22 lb/ft³ (3.5 kg/m³) (as copper) with a CDDC formulation in which copper sulfate was the copper source. Copper retention levels in the above- and below-ground portions of the stakes were compared to estimate preservative leaching. The CDDC-treated stakes had 77 percent less copper below than above ground, and the CCA-C treated stakes had 72 percent less copper below than above ground. Actual copper losses were undoubtedly greater because some leaching does occur above ground. These leaching rates may sound extreme, but it is important to remember the length of the test and that small-sized stakes lose a much greater percentage of their preservative than does product-sized material.

Subsequently, fungal cellar leaching tests were conducted on 0.12- by 0.75- by 6-in. (3- by 19- by 152-mm) Southern Pine stakes that were treated to copper retention levels of 0.04, 0.07, 0.11, and 0.17 lb/ft³ (0.64, 1.12, 1.76, and 2.72 kg/m³) (copper ethanolamine formulation) or to 0.03, 0.05, 0.09, and 0.14 lb/ft³ (0.48, 0.80, 1.76, and

2.24 kg/m³) (copper sulfate formulation) (Arsenault and others 1993). Copper loss decreased with increasing retention and appeared to be greater for copper sulfate formulations than for copper ethanolamine formulation. Losses varied from 14 percent (low retention CuSO₄) to 0 percent at all of the higher retention levels of the copper ethanolamine formulations. SDDC losses were much greater, ranging from 99 percent at the lowest retention to 40 percent at the highest retention. Losses of copper from stakes treated to proportional retentions with CCA-C (but generally lower copper retentions) varied from no loss at the lowest copper retention (0.006 lb/ft³ or 0.096 kg/m³ copper) to 42 percent loss at the highest retention (0.031 lb/ft³ or 0.50 kg/m³ copper).

Copper Naphthenate

Little published data are available on the rate of loss of naphthenic acid from copper naphthenate treated wood in-service, but studies have evaluated the movement of carrier oil and copper. As with other oilborne preservatives, the leach resistance of copper naphthenate is affected by the type of solvent used to carry the preservative into the wood. In a laboratory study of leaching from small pine sapwood wafers, it was reported that copper naphthenate dissolved in mineral spirits was less leachable than that dissolved in diesel oil, and an oil conforming to AWPA Standard P-9 (AWPA 1994) was the solvent that resulted in the most copper leaching (McAfferty 1989). In contrast, a soil leaching test with the same solvents found that copper naphthenate was most leachable when delivered with mineral spirits. It also appears that the rate of copper naphthenate leaching may be affected by the leaching medium. In one study, 0.09- by 0.75- by 6 in. (1.5- by 19- by 152-mm) copper naphthenate treated stakes, buried for 12 weeks in wet soil, lost more than 15 times as much copper as similar stakes soaked for 12 weeks in distilled water (Nicholas 1988).

Copper naphthenate movement and leaching in poles were investigated in two large, in-service studies. One study evaluated levels of copper and oil at various depths within Southern Pine poles that had been treated with copper naphthenate in P9-A oil to approximately 0.08 lb/ft³ (1.28 kg/m³) as copper (Engdahl and Baileys 1992). During 3 years, the researchers detected what appeared to be a slight loss of copper from the outer zones near the groundline and some downward movement of the carrier oil. However, the increase in copper levels at the groundline was not as apparent as the increase in oil concentration, suggesting that at least a portion of the copper was bound to the wood and not moving with the oil.

As part of a large, ongoing study, Harp and Grove (1993) reported on copper naphthenate migration within and out of treated poles in service. In an attempt to track movement of preservative within the poles, core samples were removed at two heights and various depths from within the poles and were analyzed for copper. At the time of the report, variability of the results from year to year and within sampling zones made it difficult to draw conclusions about migration within the pole or to quantify leaching out of the poles. However, soil samples removed from around the poles did contain

elevated levels of copper. Samples taken 4 in. (102 mm) away from Douglas Fir poles that had been treated with copper naphthenate in P9-A type solvent had copper levels that were elevated by 10 to 310 ppm after 1 year, 20 to 1,950 ppm after 2 years, and 190 to 1,850 ppm after 4 years. Copper levels were much lower 12 in. (305 mm) from the poles, although increases of as much as 160 ppm were detected. These poles had been treated to a retention of 0.075 lb/ft³ (1.2 kg/m³) copper and placed in-service in Northern California. Also in Northern California, much lower levels of copper were detected in the soil adjacent to poles that had been treated with copper naphthenate in butane. At a distance of 4 in. (102 mm) from the poles, copper levels were elevated by 40 to 450 ppm after 1 year, 30 to 550 ppm after 2 years, and 20 to 520 ppm after 4 years. Copper levels 12 in. (305 mm) from the pole were typically lower, although in one case, levels of 1,270 ppm greater than background were detected. These poles, also Douglas Fir, contained greater copper retention levels (0.17 lb/ft³ (2.7 kg/m³) target) than those treated with copper naphthenate in P9-A solvent. It is noteworthy that as a result of excessive bleeding, the poles had to be shipped back to the treater for steaming several times prior to installation.

Elevated copper levels were also detected in the soil adjacent to the Douglas Fir poles that were treated to a retention of approximately 0.15 lb/ft³ (2.4 kg/m³) (as copper, 0.25 to 1 in. (6 to 25 mm) assay zone) with copper naphthenate in P9-A solvent. Copper levels 4 in. (102 mm) from the poles were elevated 10 to 1810 ppm after 1 year, 0 to 2,630 ppm after 2 years, 40 to 1,850 ppm after 3 years, and 0 to 2,180 ppm after 4 years. Copper levels were generally within the range of background levels 12 in. (305 mm) from the poles.

Copper levels in soil adjacent to Southern Pine poles treated with copper naphthenate in P9-A oil were less than those for the Douglas Fir poles. Southern Pine poles treated to 0.06 lb/ft³ (0.96 kg/m³) (as copper) and placed in service in Alabama appeared to cause no elevation in adjacent soil copper levels after 1 year and between 0 to 360 ppm elevation after 2 years. Slightly greater levels were detected around poles treated to 0.08 lb/ft³ (1.28 kg/m³) and exposed near Cleveland, Ohio. After 1 year, copper levels 4 in. (102 mm) from the poles were elevated by 0 to 830 ppm, but the maximum elevation after 2 years was only 290 ppm.

In each case, copper levels were compared at depths of 0 to 3 in. (0 to 76 mm) and 3 to 6 in. (76 to 152 mm) from the soil surface, but no consistent correlation between depth and copper content was observed. The variability in copper levels measured in the wood and the surrounding soil makes it difficult to reach conclusions about copper naphthenate leaching rates, but it is evident that the treated poles, and especially Douglas Fir poles, may increase soil copper levels in the immediate area. The subsequent mobility of the copper in the soil is also a concern. In some cases, it does appear that the soil copper levels decreased over time, suggesting that a portion of the copper did migrate out of the sampling area. However, the relatively low levels detected 12 in.

(305 mm) from the poles indicate that copper mobility is limited.

Two internal laboratory studies conducted by a copper naphthenate producer also indicate that this form of copper has limited mobility in soil (Hein 1987, 1990). In an initial study, 5 g of 2-percent copper naphthenate in fuel oil was placed on top of a 15-in.- (381-mm-) long column of sandy loam soil. Tap water was then passed through the soil column at a rate of about 0.3 to 1.2 in³/h (5 to 20 mL/h) for 30 days. No copper was detected by periodic analysis of the eluant (Hein 1987). In a subsequent study, two 4-in.- (102 mm-) long soil columns were prepared from a mixture of sand and topsoil, and 0.11 oz (3 g) of 8-percent copper naphthenate was placed on top of each column (Hein 1990). The soil was then leached for 1 year with either tap water (pH 7) or tap water that had been modified to pH 5 with sulfuric acid. However, the pH of the water exiting the soil was generally between 6 and 7 for both columns, as a result of the buffering capacity of the soil. The flow rate used in the test was initially between 5.5 and 7.3 in³/h (90 and 120 mL/h), and it then decreased over time to a minimum of 0.1 in³/h (1.8 mL/h). The eluant was collected in 200-ml samples, but only every fourth sample was analyzed. No copper was detected at any time in the eluant in the column leached with tap water, and copper was not detected in the pH 5 column until approximately 18.5 gallons (70 L) of water had passed through the soil. Levels detected in eluant in that second column varied from 0.01 to 0.05 ppm, and it then decreased below detection limits after 23.8 gallons (90 L) had passed through the soil. The author attributed the temporary appearance of copper in the leachate to the development of channels through soil. In both these soil-column studies, copper analyses were performed by atomic absorption, with a lower detection limit of approximately 0.01 ppm copper.

Background Levels

When considering the amount of preservative components that may leach from treated wood, it is helpful to consider the levels of these elements that occur naturally in the environment. Chromium is a relatively common element, the seventh most abundant on earth (McGrath and Smith 1990). Chromium levels ranging from undetectable to as high as 10,000 ppm have been reported in soils, with average levels ranging from 6 to 200 ppm (Brown 1986; McGrath and Smith 1990). Naturally occurring chromium levels in water are much less than those in soil, although levels as high as 84 ppb have been reported; freshwater levels are generally less than 5 ppb and seawater levels less than 1 ppb (Brown 1986; Florence and Batley 1980; Spotte 1979). Copper levels in soil are also variable, with levels ranging from 8 to 300 ppm and average levels ranging from 15 to 30 ppm (Baker 1990; Brown 1986). Copper levels in water tend to be slightly greater than chromium, with levels ranging from 0.8 to 105 ppb and average levels between 1 and 10 ppb (Brown 1986; Spotte 1979). Natural levels of arsenic in soils typically range between 1 and 40 ppm, with most levels falling in the lower half of this range (O'Neill 1990). In

agricultural areas, arsenic levels in soil are often much greater because of the widespread use of arsenical insecticides in the past. Arsenic levels in water vary tremendously, with naturally occurring levels of more than 2 ppm in some hot springs, thermal waters, and even some well-water (USDA 1980). In general, however, most freshwater in the United States has less than 50 ppb arsenic, and arsenic levels in seawater typically range from 1 to 6 ppb (USDA 1980).

Zinc constitutes 0.004 percent of the earth's crust and is the twenty-fifth most abundant element (Eisler 1993). The average concentration of zinc in U.S. soil is 40 ppm, with a range of 25 to 300 ppm reported. Zinc levels in freshwater in the United States range from 0.5 to 10 ppb, and levels in seawater (worldwide) ranging from 0.002 to 40 ppb have been reported. Sediments contain high but variable levels of zinc, with reported levels up to 11,000 ppm in the United States. Much greater levels of zinc are found in soil, water, and sediments in polluted areas (Eisler 1993).

As an element, boron is somewhat less abundant than zinc, comprising about 0.001 percent of the earth's crust (Kleinberg and others 1960). The average naturally occurring boron concentration in U.S. soil is 30 ppm, although values ranging from 10 to 300 ppm have been reported (Eisler 1990). Because boron is readily water-soluble, it occurs naturally in both freshwater and seawater at relatively high levels compared with the other inorganic preservative components. Within freshwaters of the United States, boron levels are generally less than 0.1 ppm, although levels may reach 15 ppm or greater in some areas of the southwestern United States (Eisler 1990). Compared with freshwaters, boron levels in seawater are somewhat greater, with levels from 0.2 to 4.7 ppm reported (Eisler 1990).

Factors that Affect Leaching and Movement

Product Factors

Exposure Time

In general, the majority of leaching from treated wood, whether in-service or laboratory tests, occurs upon initial exposure to the leaching medium. Although the overall amount of leached components is relatively small, an initial wave of readily available and unfixed or poorly fixed components moves out of the wood, followed by a rapid decline to a more stable leaching rate (Bergholm 1992; Evans 1987; Fahlstrom and others 1967; Fowlie and others 1990; Merkle and others 1993; Teichman and Monkan 1966). This trend is most obvious for the very tightly bound chromium in CCA, which leaches little after initial releases upon exposure (Bergholm 1992; Sheppard and Thibault 1991). However, this time-dependent leaching pattern depends on the size of the treated product, the amount and type of surface area exposed, and the degree to which the preservative components are fixed. Because the highest rate of preservative leaching occurs initially, products that have not made a significant environmental impact within the first few years are not likely to do so in the future.

Surface Area and Wood Properties

The rate and overall amount of leaching from a given product are affected by penetration, retention, and surface area. A deeply penetrated utility pole, with a reservoir of chemical at some distance from the pole surface, is expected to show a much more gradual decrease in leaching than does a small-sized stake. Arsenault (1975) noted that CCA levels in soil were greater around poles than around posts, because the poles had a much larger exposed above-ground surface area. It is partly this factor that makes it so difficult to use data from small laboratory specimens to predict leaching in service.

The type of grain exposed can also influence leaching characteristics. The AWP standard 0.75-in. (19-mm) cubes (AWPA 1994) used for leaching trials, in addition to their small dimensions, greatly accelerate leaching, because the proportion of exposed end grain is many times greater than that of most products in service. CCA leaching has been shown to be greatest from exposed end-grain in seawater exposures (Shelver and others 1991) and from flat-grain than edge-grain Douglas Fir exposed in cooling towers (Gjovik 1977). A recent laboratory study also reported that CCA-C leaching from round post sections is greater than that from sawn lumber with a similar surface area (Van Eetvelde and others 1995). The authors theorized that the post dimensions may have caused slower fixation or that the posts may have had a greater proportion of permeable sapwood. A similar effect has been noted with wood species; those that are more permeable tend to leach at a higher rate because of more rapid movement of leachate (Cockroft and Laidlow 1978; Wilson 1971). However, Kennedy and Palmer (1994) also noted that leaching of CCA may be greater from heartwood than sapwood, possibly because the heartwood extractives interfere with the fixation process.

Although wood properties may affect leaching in different ways, comparative studies generally agree that CCA components are more leachable from hardwoods than softwoods (Becker and Buchmann 1966; Cooper 1990; Nicholson and Levi 1971; Yamamoto and Rokova 1991) and CCA-treated hardwoods are more susceptible to soft-rot attack (Butcher and Nilsson 1982; Gray 1993). This phenomenon has been attributed to the lower content and type of lignin in hardwoods (Butcher and Nilsson 1982; Cooper 1990; Gray 1993). However, this trend is not always consistent and softwood species also differ in leach susceptibility. Slow fixation and high leaching rates have been noted for Japanese cedar (Yamamoto and Rokova 1991), and Cooper (1990) reported that CCA leaching rates from small, red pine specimens were approximately double those from lodgepole pine, Douglas Fir, and red cedar.

Preservative Components

An important factor in determining both the mobility and toxicity of leached preservative components is the form in which they leave the wood. Chromium and arsenic, in particular, may exist in either of two relatively stable valence states, the properties of which are very different. Copper and zinc are much less likely to remain stable in the environment

in any form other than +2, and so the valence state leached is of much less concern. Generally, trivalent arsenic is many times more toxic than pentavalent arsenic, and hexavalent chromium is many times more toxic than trivalent chromium, to most organisms (Ferguson and Gavis 1972; Stackhouse and Benson 1989). In addition, the different valence states of chromium and arsenic have very different solubilities and mobilities in the environment, as discussed in later sections of this report.

It is generally assumed that arsenic within CCA and ACZA treated wood is in the pentavalent and chromium in the trivalent valence state. However, little research is available to verify this assumption. Woolson and Gjovik (1981) determined that 3 percent of the arsenic washed from the surface of freshly CCA-treated wood was in the trivalent form, as was 3 to 7 percent of arsenic extracted from sawdust. They also noted that some arsenate in a mixture of CCA and sawdust is converted to arsenite over several weeks (Woolson and Gjovik 1981).

Conversion of chromium from the hexavalent state in the treating solution to the trivalent state in the wood is assumed as the basic premise of CCA fixation. Considerable effort has been made to monitor the proportion of hexavalent chromium in extracted treating solution as a means of assessing degree of fixation (Cooper and Ung 1993, 1992a; Foster 1989; McNamara 1989), and the results generally show that the conversion to the trivalent state proceeds to completion under proper conditions. In addition, one researcher concludes that all the chromium present within fixed, treated wood is in the trivalent state (Wright 1989). However, a 1992 study reported that chromium reduced only to the pentavalent state, a form previously not considered significant, is present in wood up to 6 months after treatment (Yamamoto and Ruddick 1992). Although the proportion of hexavalent chromium in the wood appears to be quite small, this form is more water-soluble and less reactive with the wood than the trivalent form, and so may be expected to leach more readily. In addition, if fixation is not allowed to proceed to completion before exposure, the rates of total and hexavalent chromium leached will be much greater. Unfortunately, little work has reported the valence state of chromium leached from wood placed in service. However, as discussed in the following sections, environmental factors, not simply the valence state of the leached components, influence the valence state of preservative components in the environment.

In addition to valence state, chemical species effects influence the toxicity and mobility of copper, zinc, and arsenic. Studies on leaching of these components have not revealed whether they are leached as individual elements, as copper or chrome arsenates, or as complexes with inorganic or organic ligands. It is probable that portions of copper, zinc, and chromium leached from treated wood are bonded to cobio-cides or water-soluble wood extractives. In the case of copper naphthenate, the majority of copper leached might be expected to be bonded to organic compounds. Copper, zinc, and chromium leached in complexes with organic ligands are less likely to be adsorbed to humic matter, thus having greater mobility or behaving differently in the environment.

Although such studies are complex, additional work is needed to determine the species of preservative components that are leached from treated wood.

Exposure Factors

Water Conditions

Regardless of whether the treated wood is exposed to air, freshwater, salt water, sediments, or soil, water is the key to the leaching of preservative components from the wood and their subsequent movement through the surrounding substrate. Water acts as a medium for leaching of fixed preservative components in several ways. Even fixation products with low water solubility can be gradually solubilized if enough water moves through the wood. In addition, the water can carry organic or inorganic components into the wood that either react with fixation products directly or alter the pH sufficiently to make the fixation products soluble. Alternatively, water may solubilize or erode portions of the wood that contain CCA components.

A study of runoff from CCA-treated pine roof boards revealed that concentrations of copper, arsenic, and chromium were greater when exposed to a drizzling rain than to heavy showers, but this trend could be a result of dilution rather than leaching (Evans 1987). Other work also suggests that for an equivalent amount of rainfall, more leaching is caused by a slow, steady rain than by intermittent heavy showers (Cockroft and Laidlaw 1978). Although little research has been done in this area, the volume of water flow around treated wood in ground contact might be expected to have conflicting effects on leaching. Although wet soils may allow for maximum solubility and transport of compounds into and out of the wood, high rates of water flow may also dilute the concentration of soil constituents that solubilize CCA fixation products. In a laboratory study, water temperature was also found to significantly affect leaching from wood treated with a CCA-C salt solution (Van Eetvelde and others 1995). In that study, copper, chromium, and arsenic leaching were approximately 1.4, 1.6, and 1.5 times greater, respectively, from wood leached at 20°C than from wood leached at 8°C.

The rate of volume of water flow greatly affects the mobility of preservative components when they have been leached into the environment. Generally, arsenic and the metals can either diffuse through soils as free ions or in complexes, be carried by the mass flow of a water front, or percolate through soil pores in particulate form. Of these transport mechanisms, mass flow with a water front is probably most responsible for moving metals appreciable distances in soil. This is especially true in highly permeable, porous sites where water moves through the soil quickly and is less affected by the chemical composition of the soil. For movement over long distances, the preservative components must either be in soluble form or attached to soluble soil constituents (Dowdy and Volk 1983). Solubility is affected by many factors, including pH, ion adsorption sites, the presence of soluble ligands, and ionic strength. Consequently, significant interaction takes place between the water and the soil.

The movement mechanisms of preservative components leached in water exposures are similar to that in soil, but with variations because of the much greater ratio of water to solids. It is also apparent that elements leached into water have the potential for faster migration over much greater distances than those leached into soil. Factors that increase the solubility of the leached preservative components lead to rapid dispersion in the water; factors that decrease solubility cause accumulation in the sediments. Although decreased solubility and mobility of pollutants are usually considered desirable, this is not as clearly the case in aquatic exposures where bottom sediments are rich in biologic activity. When considering the fate of the low levels of components leached from treated wood, accumulation in sediments may be the primary concern, because the soluble components released are likely to quickly disperse to below background levels in large bodies of water.

Previous studies have shown that river and ocean currents have a great effect on the movement of CCA components released into water. Neary and others (1989) tracked CCA that had been carried from a treating plant into a nearby stream by storm runoff. Elevated levels of all three CCA components were found up to 3.1 mi (5 km) away from the source, with highest levels occurring during rainstorms and high water levels. (This appeared to be caused mostly by overflow of the wood-treatment holding ponds.) Highest concentrations of all three components were found in the sediments of beaver ponds, which appeared to act as sinks or traps; levels in stream bottom sediments were less than those in the ponds. A separate study of river water contaminated by runoff from a wood-treatment plant also found that levels of all three CCA components remained elevated more than 2.5 mi (4 km) downstream from the source (Ndiokwere 1984). Although amounts of CCA components introduced into the streams were far in excess of those that might occur with leaching, these studies do demonstrate that all three components can be transported considerable distances. The primary mechanism of this type of movement in rivers is probably as suspended sediment, not as water-soluble species (Neary and others 1989).

Another effect of current flow was noted in research examining CCA levels in sediments near CCA-treated bulkheads exposed in seawater (Weis and others 1993). Sediments immediately adjacent to treated bulkheads that were composed primarily of sand had lower levels than those 39 in. (1 m) away where sediments were composed of finer particles. The authors noted that current flow near the bulkheads had scoured away fine particles and that sediment fines, not sand, were primarily responsible for adsorbing CCA components. Thus currents, by determining the placement of metal-adsorbing sediment fines, may greatly influence the location of the highest concentration of leached preservative components.

Substrate Composition

A wide range of exposure conditions exist within the soils and waters of North America. Leaching and mobility of preservative components are potentially affected by the

composition of soil, soil water, freshwater, or seawater. The exposure site pH may vary from less than 4 in acid bogs to more than 8 in hard water lakes, and the types of minerals solubilized vary accordingly. Suspended or solubilized compounds from soil or sediment may solubilize or precipitate preservative components and alter the pH. In addition, stationary soil or sediment constituents can serve as adsorption sites for preservative components. All these factors influence chromium, copper, arsenic, and zinc solubility to various degrees, although sorption to organic and inorganic ligands may be the most important process in determining the environmental fate of metals in the aquatic environment (Stackhouse and Benson 1989). Movement and speciation of preservative components in seawater are influenced by many of the same factors, although the relative role that these factors play is somewhat altered. The inorganic components play a larger role, while the role of organics is decreased. In addition, seawater pH is generally greater and less variable than that of freshwater, and the potential for dilution can also be greater.

Studies illustrate that soil composition may affect both leaching and subsequent mobility of CCA components. Bergholm (1992) covered CCA-treated wood chips with three different types of soil and analyzed losses caused by precipitation. Leaching of copper from chips covered with marsh peat soil (high organic content) was greater than from chips covered with sand or clay soil. Arsenic and chromium were found to be more mobile in the fine sand soil than in clay or marsh peat soils, and copper movement was greatest through marsh peat soil. The increased copper leaching and mobility from chips exposed in the marsh peat soil were attributed to copper complexation with soluble organics. In general, all three soils retained CCA components quite well, because less than 1 percent of the elements lost from the wood chips moved out of the soil columns after 11 years.

Other studies of movement of CCA constituents in soils with varying compositions generally agree that, although the constituents are not highly mobile, significant movement of arsenic may occur in sandy soils (Bergholm 1990; Bergholm and Dryler 1989; Bergman 1983; Brown 1986; Chen and Walters 1979; De Groot and others 1979; Holland and Orsler 1995; Lund and Fobian 1991; Murphy and Dickinson 1990). Holland and Orsler (1995) evaluated the ability of various soil types to adsorb CCA components from a 3-percent solution. They found that a sandy, free-draining soil adsorbed little, if any, of the CCA components, and sphagnum peat, containing 98-percent organic material, readily adsorbed all three CCA components. Two loam/clay soils evaluated adsorbed copper and arsenic, but little chromium, and a third of the loam/clay soil adsorbed only arsenic and to a lesser degree. The authors concluded that although a high organic content was generally associated with the capability to adsorb all three CCA components, other factors such as pH or inorganic constituents must also play a role. The relatively poor adsorption of chromium found in the study is somewhat surprising, and it should be noted that although the concentration of CCA components exposed to the soil in this test may simulate the conditions of a spill at a treating plant,

results were many times greater than would result from CCA leaching in service.

Holland and Orsler's arsenic adsorption results generally agree with studies of contaminated soils around treating plants, in which the highest levels of arsenic were retained in the soils with high levels of clay or organic matter (Bergholm 1990, Bergholm and Dryler 1989; Bergman 1983). One other study of CCA-contaminated soils in Denmark also reported that virtually all the chromium and the majority of copper and arsenic were deposited within the first 250 mm (9.9 in.) of soil, the area high in organic carbon (Lund and Fobian 1991). A similar Swedish study reported that elevated chromium, copper, and arsenic levels were found only in the top 3.9 to 15.7 in. (100 to 400 mm) of contaminated soil and levels were greatest in soils with a high proportion of organics (Bergman 1983). A Swedish study reported that the retention capacity of arsenic in fine sand was approximately 100 ppm; in clay soil, about 500 ppm; in marsh peat soil, about 5,000 ppm (Bergholm and Dryler 1989).

In a study of leachate adsorption, Murphy and Dickinson (1990) analyzed soils exposed to CCA-treated pine stakes and reported that clay (pH 6.5) and peat (pH 5.7) soils retained much greater amounts of arsenic than did sandy soil (pH 3.7). Copper movement was minimal in all three soil types, and little chromium was found in the soil or leachate. A conflicting study reported that neither sand nor loam soil retained significant amounts of arsenic leached from CCA-treated plywood, although increased levels were detected in both surface runoff and soil leachate (Chen and Walters 1979). In addition, this study found that arsenic levels in surface runoff were greater from loam than sandy soil. The reason for the difference in findings is unclear, but it may be a factor of the very low rate of arsenic loss from the treated plywood in the latter study.

The presence of organic material, such as organic acids, appears to play a dual role in leaching and movement of CCA components. As noted, although several researchers credit the organic component of soils with binding of CCA components, Bergholm (1992) attributed increased leaching to soluble organic acids. Other scientists have noted that soluble organic acids can increase the leaching of CCA from treated wood. Warner and Solomon (1990) demonstrated that adding citric acid to leaching water greatly increased leaching in laboratory tests. Although it is doubtful that high levels of citric acid will be a problem in service, surface waters containing high levels of humic or fulvic acid from peaty organic soils can have the potential for increasing CCA leaching (Cooper 1990, 1991b,c). Cooper and Ung (1992b) compared CCA-C losses from jack pine blocks exposed in garden soil and organic-rich compost and found that leaching more than doubled by compost exposure. Copper appeared to be the most affected, although arsenic and slight amounts of chromium were also lost. In addition, humic acid solutions have been shown to extract copper from copper metal and solubilize copper sulfide and copper carbonate precipitates (Weber 1988).

Other evidence of the importance of organics in chromium, copper, and zinc mobility is that metal concentrations in sediments with humic material may be as much as a thousand times greater than those that do not contain humic matter (Weber 1988). Typical total organic carbon values are about 5.8×10^{-5} lb/gal (7 $\mu\text{g/mL}$) in rivers, 2.1×10^{-4} lb/gal (25 $\mu\text{g/mL}$) in bogs and marshes, and 4.2×10^{-6} lb/gal (0.5 $\mu\text{g/mL}$) in seawater. Of this, humic matter is about 60 percent in rivers, 70 percent in wetlands, and 20 percent in seawater. However, seawater organic levels may be much greater in less saline coastal estuaries, where many preservative-treated structures are located. Dissolved organic carbon contents in one estuary varied from 5.0×10^{-5} lb/gal (6 $\mu\text{g/mL}$) on the upstream end to 3.0×10^{-5} lb/gal (3.6 $\mu\text{g/mL}$) in areas with higher salinity. Copper binding capacities varied accordingly, from 2.5×10^{-4} lb/gal (30 $\mu\text{g/mL}$) at the upstream site to 7.1×10^{-5} lb/gal (8.5 $\mu\text{g/mL}$) in more saline waters. Conditions for precipitation of humic materials and their associated metals are apparently very favorable where freshwater and saltwater meet, such as in estuaries (Newell and Sanders 1986).

It has also been reported that inorganic ions can increase leaching from CCA-treated wood (Irvine and others 1972; Plackett 1984; Ruddick 1993a). Plackett (1984) measured copper losses from CCA-treated sawdust leached in solutions that contained either calcium chloride, calcium nitrate, magnesium nitrate, or a 1:1 mixture of di-potassium hydrogen orthophosphate and potassium di-hydrogen ortho-phosphate. All solutions caused increasing copper leaching with increasing ionic strength, and even at low concentrations (0.06 M), losses were several times those caused by deionized water. Among the solutions tested, the phosphate ions caused the most copper leaching at high concentrations, and calcium chloride appeared to have the most effect at low to moderate levels. The effects of these inorganic ions on leaching of arsenic and chromium were not evaluated. Evidence also shows that inorganic ions such as sodium, potassium, calcium, and manganese contribute to CCA leaching from wood exposed in cooling towers (Irvine and others 1972). Samples in the study lost an average of 19 percent copper, 44 percent arsenic, and 32 percent chromium after only 40 weeks. Iron content of soil may also play a role in leaching of CCA from treated wood. Mistakes exposed in iron orthic gleysol-type soil absorbed more than 0.08 lb/ft³ (1.3 kg/m³) of iron after 12 weeks (Ruddick 1993a). After only 4 weeks of exposure, 65 percent copper and 35 percent arsenic were leached from the wood, much more than was lost in distilled water leaching of matched stakes. The cause of the rapid copper depletion was not verified, although the author suggested that bacteria reacting to the high iron content of the soil secreted enzymes that solubilized copper compounds in the wood. Alternatively, it may be that copper was sequestered by humic acid from the soil, and neither iron content nor bacterial action was responsible for the high leaching rate. Iron, like copper, is actively adsorbed by organic acids, and its high mobility in the soil suggests the presence of solubilizing agents, such as low molecular weight organic acids. Conversely, one study suggested that the presence of high levels of iron and aluminum in soil surrounding CCA-treated

wood can retard arsenic leaching, because these metals may migrate into the wood and irreversibly precipitate the arsenic (Evans and others 1994)

Inorganic ions may also be a factor in the relatively high rate of leaching of wood exposed in seawater (Gjovik 1977, Hegarty and Curran 1986, Hutchinson and McQuire 1970; Johnson 1977; Leightley 1987; Merkle and others 1993; Shelver 1991; Weis and others 1991). Salinity, perhaps the most obvious difference between freshwater and seawater, does appear to have an effect on leaching of CCA components. (Salinity is defined as all dissolved solids.) Leaching of chromium and arsenic from pine sapwood blocks was increased when sodium chloride was added to distilled water to create salinities from 0 to 70 parts per thousand (ppt), although losses leveled off at about 50 ppt (Irvine and Dahlgren 1976). After 40 weeks at a salinity of 34 ppt, typical for seawater, arsenic leaching was increased by 25 percent and chromium leaching by 45 percent more than that in deionized water. The trend of copper leaching was less clear, because leaching was inhibited at low salinities and increased when salt levels reached 35 ppt. Because sodium chloride levels in seawater are typically less than 30 ppt, this finding suggests that seawater will have minimal effect on copper leaching. However, other studies (Hutchinson and McQuire 1970; Johnson 1977; Leightley 1987) have reported that copper appeared to be the CCA constituent most affected by exposure in marine environments. It is possible that other seawater ions, such as evaluated by Plackett (1984), also contribute to CCA leaching.

The pH level is also a factor in preservative leaching and mobility, although in practice the effects of pH are difficult to separate from those of organic and inorganic constituents. In one study, sulfuric acid/nitric acid buffers were used to investigate the effect of pH on CCA leaching from western hemlock blocks. The study showed that leaching of copper was between 16 and 25 percent at pH 3, but decreased to about 1 percent at pH 4. Leaching of arsenic was less affected by pH, but was generally around 2 to 3 percent at pH 4 and above (Kim and Kim 1993). In a similar study, leaching of CCA from pine blocks was generally less than 5 percent for any element, even at pH levels as low as 3.5 (Cooper 1991b). A study on the effect of acid rain on leaching of CCA-C from pine stakes yielded somewhat similar results (Murphy and Dickinson 1990). Although 40 percent of the copper was lost at pH 3, there was no significant loss of copper at pH 5.6, and no significant loss of chromium or arsenic at either pH. Rainfall in parts of Northern Europe does reach pH values as low as 3.0 for short-term occurrences (Murphy and Dickinson 1990). However, the pH of the water in the environment is not necessarily the same as that which contacts CCA components within the wood, as both soil and the wood act as buffers. Murphy and Dickinson (1990) reported that when clay, peat, and sandy soils were exposed to acid rain, the pH of the resulting leachate remained constant, regardless of the pH of the rain. However, the authors warn that this natural buffering capacity might be lost with prolonged exposures. Cooper (1990) also points out that in acid rain situations or cases where the volume of water is

relatively low, wood has the capacity to buffer the acidity. He notes field observations where water dripping from treated wood is consistently 0.8 to 1.2 pH units greater than that of the rain. Although the extremely low pH of acid rain may be a concern for above-ground exposures in some areas, these studies generally suggest that the pH ranges encountered in service are not acidic enough to cause excessive leaching of CCA-C treated wood.

However, 1994 and 1995 laboratory studies of wood treated with a salt formulation of CCA-C found that pH does significantly affect leaching. In a small-block study (0.6 by 1 by 2 in. (15 by 25 by 50 mm)) of pine sapwood, copper leaching was greater in water that had been lowered to pH 4 with nitric acid than in demineralized water with pH 5.5 (Van Eetvelde and others 1994). A subsequent study with larger dimension material noted that copper leaching was about 1.3 times greater in water of pH 5.5 to 7.0 than in water with pH ranging from 7 to 8.5 (Van Eetvelde and others 1995). In contrast, arsenic and chromium leaching was significantly greater in the higher pH range. These studies suggest that the pH ranges that occur in the environment may significantly affect CCA leaching rates. The mobility of CCA components in soil has been found to be a function of pH, with the lowest releases around pH 6 to 7 and increased mobility at higher or lower pHs (Bergholm 1990). The effects of rain, soil, and water pH on the leaching of copper from the ammoniacal CDDC and copper naphthenate systems have received little study.

The noted studies tend to support the review by Brown (1986), who reported that greatest mobility of CCA components, thus presumably copper from other preservatives, would be expected in soils with high permeability, low clay content, low pH, and low organic matter content. However, it appears from Bergholm's work (1992) that organic matter with a high proportion of soluble components may also increase copper mobility. The effects of specific soil, water, and sediment components on the mobility of individual preservative components are discussed in detail in the following sections.

Chromium

Chromium appears to be the least mobile of the CCA elements, although its mobility is highly dependent on its valence state. Trivalent chromium is highly reactive with organics and quickly fixes to soil or sediments, and hexavalent chromium is more soluble, less likely to be adsorbed, and has been reported to move through soil at the same rate as groundwater (Rouse and Pyrih 1990). Unfortunately, little work has been done to determine the valence state of chromium in compounds that leach from treated wood in service. When introduced into soil or water, the valence state of chromium is a function of the oxygen content and redox potential, pH, the presence and type of suspended inorganics, and the presence of dissolved or particulate organic matter (Florence and Batley 1980).

In the absence of organic compounds, hexavalent chromium (Cr) is the most stable form in equilibrium with atmospheric oxygen (McGrath and Smith 1990). In many exposures,

especially those where organics are present, Cr (VI) may be reduced to the trivalent form (Cox and Richardson 1979), much like the reactions that take place within treated wood. Laboratory tests have shown that humic acids can reduce hexavalent chromium (Weber 1988), although this reaction apparently does not proceed rapidly under a wide range of conditions. Studies have also shown that iron will reduce chromium, but the reaction is highly dependent on the presence of excess iron (Schroeder and Lee 1975). Sulfides are also capable of reducing chromium, suggesting that this may be an important process near sediments or in marshes where sulfides are produced by decomposition of organic matter. However, when hexavalent chromium was added to natural lake or marsh water, no significant reduction occurred after 2 weeks (Schroeder and Lee 1975). In soil, where electron donating components are relatively plentiful, hexavalent chromium is usually reduced to the trivalent state. This reaction is especially rapid in acid soils (McGrath and Smith 1990). However, one study reported that 135 of 150 moist field soils in the United States and Canada had measurable levels of hexavalent chromium (Bartlett and James 1979).

Trivalent chromium may also be oxidized to the hexavalent form under some conditions. Oxidation is most likely to occur in oxygenated water, such as in a rapidly moving stream, especially if the water is alkaline or "hard" (Florence and Batley 1980). One study reported that at pH levels ranging from 5.9 to 9.9, only 1 percent of Cr (III) solution was oxidized to Cr (VI) after 2 weeks of oxygenation (Schroeder and Lee 1975). However, addition of 100 ppm manganese oxide to the solution caused 100 percent of the chromium to be oxidized after only 7 days. The rapid oxidizing effects of manganese oxide noted in pure solutions were largely eliminated when unfiltered lake water was used, suggesting that other cations reacted with manganese oxides or the chromium was sorbed by suspended solids (Schroeder and Lee 1975). Trivalent chromium was also reported to undergo significant oxidation in moist soils that have relatively high pH (<5–6) and are rich in electron acceptors, such as oxidized manganese (Bartlett and James 1979; McGrath and Smith 1990).

The ratio of valence states of chromium in seawater has been the subject of much study, but with conflicting results. Thermodynamic calculations indicate that within the normal pH range of seawater, the ratio of Cr (VI):Cr (III) should be 100 or more (Florence and Batley 1980; Fukai 1967; Pettine and Millero 1990). However, studies of chromium valence in seawater have reported much higher proportions of Cr (III), with Cr (VI):Cr (III) ratios ranging from 70 to less than 1 (Fukai 1967; Pettine and Millero 1990). The high variability of the ratio of Cr (VI):Cr (III) and the relatively high proportion of Cr (III) present suggest that several factors are influencing chromium oxidation/reduction reactions. In addition to the effects of inorganic and organic constituents, these factors include the slow rate of oxidation of Cr (III) to Cr (VI) and the presence of varying hydrogen peroxide levels in seawater (Pettine and Millero 1990). The half-life of Cr (III) in water has been reported to range from 1 to 20 months (Pettine and Millero 1990; Schroeder and Lee 1975), but the

oxidation rate can be increased by up to 20 times by naturally occurring levels of hydrogen peroxide (Pettine and Millero 1990).

The resistance of trivalent chromium to leaching and immobility in the environment is a result of its ability to form stable, inert complexes with a wide range of organic and inorganic ligands. These reactions include octahedral coordination with oxygen- or nitrogen-containing ligands, such as found in soil organics (Bartlett and Kimble 1976). Stackhouse and Benson (1989) found that 4.1×10^{-5} and 4.1×10^{-4} lb/gal (5 and 50 mg/L) additions of humic acid decreased the percentage of free chromium in a CrCl₃ solution (8.1×10^{-4} lb/gal (98 mg/L)) by about 70 and 80 percent, respectively, after 24 h. Interestingly, the humic acid additions to trivalent chromium solutions also decreased the toxicity of chromium to water fleas (*Daphnia* sp.), suggesting that it is the free ion form, not the soluble organic form of chromium, that is toxic. Similar tests with hexavalent chromium found that humic acid additions had little effect on the percentage or toxicity of free chromium (Stackhouse and Benson 1989). Bonds formed to soluble organic acids, such as humic, citric, or fulvic acid, can increase the solubility and mobility of Cr (III) at higher pH levels (Bartlett and Kimble 1976; McGrath and Smith 1990).

A significant proportion of trivalent chromium also appears to form insoluble inorganic oxides and hydroxides with iron, phosphorous, and calcium (Bartlett and Kimble 1976, McGrath and Smith 1990; Selim and others 1989). In one study, sand, bentonite, and iron oxide sorbed more than 90 percent of Cr (III) from a solution in 7 days, while only 1 to 2 percent was oxidized (Schroeder and Lee 1975). Other work has noted that chromium is associated with suspended solids; suspended solids in streams across the United States had chromium contents ranging from 37 to 460 ppm. Chromium content in the streams did not correlate well with the total suspended sediment content, but did correlate closely with levels of iron and manganese oxides contained in the sediments (Turekian and Scott 1967).

Chromium complexes with sediment material appear to be fairly stable in seawater. Giblin and Valiela (1983) found that only 20 percent of the chromium collected from salt marsh sediment was acid-labile (extractable with 0.1 N HCl). Another study reported that levels of chromium released from seawater sediments were unaffected by a wide range of oxidation/reduction conditions (Lu and Chen 1976). However, the chromium can still be transported by currents that move sediments, and organisms that live in polluted sediments, such as oysters, may accumulate above normal chromium levels (Giblin and Valiela 1983).

Although trivalent chromium bonds strongly to soil and sediments, there are limits to the amounts of chromium that these substrates can retain. Schmitt and Sticher (1986) reported that significant chromium movement can occur when high levels of metals are applied to soils annually, suggesting that it is possible to saturate reactive sites within the soil. Similarly, when 0.09 oz (2.5 g) chromium nitrate (Cr(NO₃)₃·9H₂O, a trivalent form) was injected just below

the litter layer into a soil column, 32 percent of the chromium leached out within the first year. In three subsequent years, however, no significant chromium leaching was detected (Sheppard and Thibault 1991), suggesting that the initial dose overwhelmed the reactive sites. However, note that leaching from CCA-treated wood is unlikely to produce large doses of chromium.

Although hexavalent chromium is more soluble and mobile than the trivalent form, it does interact with some soil types and can be significantly retained if the rate of water flow through the soil is slow (Alesii and others 1980; McGrath and Smith 1990; Selim and others 1989). Physical adsorption, anionic adsorption, formation of surface complexes, and precipitation are mechanisms that can slow the movement of hexavalent chromium (Selim and others 1989).

These noted studies indicate that both hexavalent and trivalent chromium are somewhat stable in the environment. If chromium leached from treated wood is in the trivalent form, it might form inert complexes with organic or inorganic ligands. Chromium mobility under these conditions would then be attributed to the formation of water-soluble complexes or events that suspend and move soil or sediments. Conversely, if chromium leaches in the hexavalent form, it has the potential to remain in this more soluble, mobile, and biologically available form for extended periods, especially in alkaline waters.

Copper

Unlike chromium, copper (Cu) solubility and movement is not highly dependent on interchangeable oxidation states. The toxicity and solubility of Cu (I) and Cu (II) are not as widely different as the trivalent and hexavalent forms of chromium, and Cu (II) tends to be much more stable than Cu (I) in most aerated conditions. Although significant proportions of Cu (I) can exist if copper is present in low concentrations in saturated soils (Baker 1990; Parker 1981), emphasis in this report is placed on the prevalent Cu (II) form.

If organic and inorganic adsorption agents are not present, water-soluble copper is primarily in the forms $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, $\text{Cu}(\text{H}_2\text{O})_5^{2+}$, and CuOH^+ below pH 7, with species such as $\text{Cu}(\text{OH})_2$ and CuCO_3 becoming more stable at pH levels greater than 7 (Baker 1990; McBride 1981; Parker 1981). Within the pH range of most exposure environments, copper solubility is greatest at the acid and alkaline extremes and reaches a minimum at around pH 7 (McBride 1981; Baker 1990; Parker 1981). However, reactions with inorganic and organic compounds greatly affect the solubility and form of copper. For example, the amount of solubilized copper in seawater is less than might be expected because of its complexation with various ligands (Florence and Batley 1980). Accordingly, copper deposited in sediments from pollution sources is usually complexed with organics or precipitated with inorganic oxides (Messure and others 1991). Both these forms are relatively acid-labile or more capable of being disassociated than are naturally occurring copper minerals (Messure and others 1991). Similarly, copper binding capacity and organic content of the sediment and water, not sim-

ply total copper, determine the toxicity of copper in the freshwater environment (Newell and Sanders 1986).

Inorganic and organic adsorption of copper are extremely important in determining its mobility; therefore, these processes are discussed in detail. Adsorption of copper is influenced by the amount and type of adsorbents as well as pH. Copper, unlike many other metallic elements, undergoes "specific" adsorption in addition to adsorption caused by simple ion exchange reactions (Baker 1990; Elliot and others 1986; McBride 1981; McLaren and Crawford 1973b). Specific adsorption refers to adsorption that occurs in the presence of excess quantities of a competing cation that would prevent chromium adsorption by simple ion exchange (McBride 1981). Although simple ion exchange phenomena are governed by valence and ionic radius, specific ion exchange is a function of the specific electrochemical and structural properties of the adsorbent and metal ion (Elliott and others 1986). Although the total simple cation exchange capacity of a substrate can be greater than that of the specific adsorption capacity, specific adsorption is thought to control the concentration of copper in solution because of the greater stability of the complexes (Baker 1990; McLaren and Crawford 1973b).

The copper specific adsorption capacity of major soil constituents has been rated in the order Mn oxides > organic matter > iron oxides > clay minerals, yielding a maximum soil specific adsorption capacity of 340 to 580 ppm copper at pH 5.5 (McLaren and Crawford 1973b). However, when abundance in soil and simple ion exchange capacities is considered, the importance of soil constituents in retaining copper has been rated in the order organics > Fe/Mn >>> clay minerals (Baker 1990), with general agreement that the vast majority of introduced copper is associated with organics (Baker 1990; Dowdy and others 1991; Elliott and others 1986; Levy and others 1992; McLaren and Crawford 1973; Payne and others 1988; Tiller and Merry 1981; Stevenson and Fitch 1981; Williams and others 1984). Soil pH affects both the species of copper (as discussed) and the charge on the adsorbents. At low pH, the charge of the adsorbents tends to be positive because of adsorption of protons, and at high pH, the adsorbents become more negatively charged (James and Barrow 1981). Consequently, adsorption generally increases with increasing pH (Baker 1990; James and Barrow 1983; McBride 1981), although this effect is not easily separated from the increased precipitation of copper oxides, hydroxides, and carbonates that occurs at neutral and alkaline pHs.

The distribution of copper between water, soil, and sediments is largely determined by factors that influence the solubility or suspension of copper-organic complexes (Weber 1988). Adsorption of copper by organic components of soils, sediments, and water has drawn substantial research interest, but it is still poorly understood because of the tremendous variability and complexity of the organic components. It is notable, however, that because much of the organic content is derived from degraded lignocellulosic material (Gieseking 1975; Tan 1993), there are many similarities to the chemistry of wood.

The two primary classes of organics responsible for copper adsorption appear to be the humic and fulvic acids (Gieseking 1975; Stevenson and Fitch 1981; Tan 1993). No exact structure or repeating unit has been determined for either humic or fulvic acid; they are distinguished by the solubility of fulvic acid and insolubility of humic acid in acid solutions (Gieseking 1975; Tan 1993). Humic and fulvic acids form both soluble and insoluble complexes with copper, depending on the degree of copper saturation (Stevenson and Fitch 1981). Complexation with copper lowers organic acid solubility, and high levels of copper causes linking of the complexes to form, making them larger and less soluble (Stevenson and Fitch 1981). Fulvic acids form the most soluble complexes with copper because of their higher acidity and relatively low molecular weights (Stevenson and Fitch 1981). Metal complexes with humic acids are decreasingly soluble at lower pH, or in the presence of strong electrolytes (Gieseking 1975). The strong complexing ability of humic and fulvic acids is largely a result of their oxygen-containing functional groups, such as carboxyl groups, phenolic hydroxyls, and ketones (Gieseking 1975; Giusquiani and others 1992; Stevenson and Fitch 1981; Tan 1993). Both acids are capable of undergoing electrostatic bonding, coadsorption, complex formation, and chelation reactions with metals (Tan 1993). Amino and imino groups may also play a role, because chelating centers containing both oxygen and nitrogen are strong copper bases (Parker 1981; Stevenson and Fitch 1981).

Organic acids may also solubilize copper that has previously precipitated into soil or sediments; a strong correlation exists between copper binding capacity and dissolved organic content in estuaries (Newell and Sanders 1986). A humic acid solution (1,000 ppm) was shown to at least partially solubilize all sulfides and carbonates of copper, and a more concentrated solution prevented precipitation of copper sulfides and carbonates at several times above normal soluble levels. However, the ability of humic acids to solubilize common copper precipitates of iron, manganese, and aluminum is less clear. Other types of organic acids, such as formic, acetic, and oxalic acid, exist in soil in smaller quantities and tend to have less complexing capacity than the humic and fulvic acids (Tan 1993).

Although adsorption by inorganics may be less prevalent than organic adsorption, inorganic/copper complexation products are generally less soluble, thus playing an important role in immobilizing copper (Dowdy and Volk 1983; Stevenson and Fitch 1981). Inorganic adsorption of copper is most important when soils or sediments contain high levels of silicon, iron, aluminum, and manganese oxides, because all these compounds specifically adsorb copper (Baker 1990; Dowdy and Volk 1983; McLaren and Crawford 1973a,b). The complexing capacity of these oxides varies with pH; manganese is strongly copper-adsorbing at all soil pH levels, and adsorption by iron is not maximized until pH 5 to 6 (McBride 1981; James and Barrow 1981). Clay soils are formed from tiny particles that have eroded from igneous rocks and have large exposed surface areas of aluminum oxides and silicates that may specifically adsorb copper.

In seawater, precipitation with sulfides or metal oxides, such as manganese and iron, becomes prevalent over reactions with organic compounds (Florence and Batley 1980). Ferric oxide, in particular, has been suggested to be an important contributor to copper precipitation in seawater. Swallow and Morel (1980) found that in distilled water a 0.001-M Fe solution adsorbed 10 percent of the Cu from a 0.00001-M Cu solution at pH 4.5, and nearly 100 percent at pH 7 and 8. The presence of NaCl in solution decreased Cu adsorption at lower pH levels and lower Fe concentrations, but as the pH and iron concentration increased, the effect of NaCl was negligible. Similar high adsorption rates were noted when tests were performed in synthetic seawater (Swallow and Morel 1980). Although much copper is removed from seawater by such reactions, substantial fluxes of copper through estuaries have been reported (Giblin and Valiela 1983).

As noted in previous studies (Weis and Weis 1992; Weis and others 1993), the accumulation of copper in fine sediments may be a concern when using CCA-treated wood in seawater. Although it is generally believed that metals bound to sediments pose less of a hazard than do metals suspended or solubilized in sediment pore waters (Weis and others 1993), copper in sediments does not appear to be as strongly bound as chromium (Giblin and Valiela 1983). Portions of copper deposited in sediments may be solubilized under oxidizing conditions, possibly because of the formation of soluble hydroxides and carbonates (Lu and Chen 1976). Conversely, a reducing environment lowers the solubility of copper in sediments, possibly through the formation of sulfidated solids (Lu and Chen 1976).

Arsenic

The mobility of arsenic in the environment has been of some concern because it is relatively more water-soluble than copper or chromium and less likely to be adsorbed. Like chromium, it exists in significant quantities in at least two valence states (+III and +V), but unlike chromium, arsenic is almost always associated with oxygen to form oxyanions. Arsenic is also similar to chromium in that valence state and speciation are important in determining toxicity. Trivalent arsenic is much more toxic than pentavalent arsenic, and the methyl arsenic forms are generally less toxic than the inorganic forms (O'Neill 1990).

Many types of microorganisms are known to convert inorganic arsenic to other, more soluble species, although their ability to do this in the presence of high retention levels of copper, chromium, and zinc has not been established. Microorganisms can methylate the oxyanions to form monomethylarsonic acid, dimethylarsinic acid, trimethylarsonic oxide, trimethylarsine, and dimethylarsine (O'Neill 1990), but the methyl-arsines are generally volatilized as gases (Braman 1975). Although the significance of these microbial activities in preservative leaching is unknown, evidence shows that microorganisms affect the mobility and fate of arsenic when it enters the environment. Many common soil fungi and bacteria are capable of reducing arsenate to arsenite (Bautista and Alexander 1972; Osborne and Erlich 1976) or methylate oxyanions (Braman 1975; Cheng and

Focht 1979; Cox 1974; Cullen and others 1984; O'Neill 1990; Sandberg and Allen 1975; Stranks 1976). Researchers have postulated that biomethylation plays a vital role in the global arsenic cycle by volatilizing and redistributing the element (Sandberg and Allen 1975; Wood 1974). In water, arsenic that is introduced as arsenic acid (As V) is precipitated by iron, aluminum, or clay minerals into the sediment, where it is methylated by microorganisms or reduced to trivalent form and then methylated. The soluble methylated forms then move up to the water surface where they can react with oxygen to form oxyanions that are again precipitated by reactions with inorganic constituents (Ferguson and Gavis 1972; Wood 1974). The biomethylation reactions that occur are influenced by not only the microorganisms present, but also the species of arsenic involved (Cheng and Focht; O'Neill 1990). Some organisms appear able to fully methylate arsenic compounds over a wide range of pH values, and others can methylate only certain species and to a lesser degree (O'Neill 1990). For inorganic species, the equilibria between arsenic acid (H_3AsO_4 , As (V)) and arsenous acid (H_3AsO_3 , As (III)) are a function of pH and redox potential (Eh). Between pH values of 4 and 8, H_3AsO_3 will be most thermodynamically stable only if the Eh is below about +300 mV at pH 4 and below 100 mV at pH 8. At higher Eh values, arsenic acid forms will be more stable: H_2AsO_4^- up to pH 7, and HAsO_4^{2-} at higher pH values (O'Neill 1990; Stewart and others 1975). In practical terms, this means that in very wet or reduced soils, As (III) may be the more stable form, although complexing species and methylating organisms in soil will alter the As (V)/As (III) equilibria (Deuel and Swoboda 1972; Frost and Griffin 1977; O'Neill 1990; Stewart and others 1975; Walsch and Keeney 1975). A study of soils in England found that As (V) made up 90 percent of the soluble arsenic in aerobic soils, but only 15 to 40 percent of the soluble arsenic in anaerobic, waterlogged soils. In mineralized areas, small quantities of monomethylarsonic acid were also detected (O'Neill 1990). Relatively few studies of this type have been done in soil because of the difficulty of isolating, preserving, and determining arsenic species.

In oxygenated water, inorganic arsenates are the most common species, but arsenites are commonly formed in sediments or deep waters (Andreae 1978; Ferguson and Gavis 1972; Florence and Batley 1980). Andreae (1978) sampled freshwater lakes and rivers in California and found that As (V) composed the vast majority of arsenic, although significant levels of organic arsenicals were found in waters high in algae and microorganisms.

The speciation of arsenic in seawater is also variable, although inorganic arsenate is the dominant form (Andreae 1978; Florence and Batley 1980; Fowler 1977). A study of water off the coast of Southern California detected arsenate, arsenite, monomethylarsonic acid, and dimethylarsonic acid in the upper photic zone, with arsenate in the highest concentration, followed by the organic forms and then inorganic arsenite (Andreae 1978). However, in deeper waters, below the photic zone, little organic arsenic was found, and the author suggests that the organic form was produced by plankton in

the photic zone. Subsequent laboratory studies noted that phytoplankton were capable of reducing and methylating up to 50 percent of pentavalent arsenic added to culture media (Sanders and Windom 1980). Although relatively inert, organic forms of arsenic may be more toxic than inorganic forms to certain organisms (Riedel and others 1989). Because treated wood is usually placed in relatively shallow water, the arsenic that leaches will be susceptible to conversion reactions by marine organisms in the photic zone.

Within seawater sediments, anaerobic conditions exist that are favorable for reducing arsenic from the pentavalent to trivalent form (Riedel and others 1989). Brannon and Patrick (1987) studied sediments collected from several harbors and found that arsenite was generally the predominant form, although organic forms of trivalent arsenic were also present. Arsenate added to the sediment was also converted to the trivalent state (Brannon and Patrick 1987). The solubility or release of arsenic from the sediments appeared to be closely related to the oxygen content of the water. When oxygen was allowed to reach the sediment, only 17 percent of added arsenic was soluble, but in an anaerobic system, 70 percent of added arsenic was released. This was attributed to the higher proportion of more soluble trivalent arsenic formed under anaerobic conditions and agrees with another study that reported that arsenic levels in a contaminated lake were negatively correlated with oxygen levels (Lis and Hopka 1973). It has also been reported that when sediments were mixed or stirred, arsenite was the primary form initially released, with subsequent release of arsenate as the sediments became oxygenated by the mixing (Brannon and Patrick 1987). The importance of sediment mixing in the release of arsenic was also noted by Riedel and others (1989). They noted that several types of marine organisms that burrow in arsenic-contaminated estuarine sediments cause a measurable flux of sediment into the surrounding water, stirring the sediment and exposing more surface area. Arsenic released by this activity was initially trivalent, but after 15 days, pentavalent arsenic was most prevalent, with additional trace amounts of organic species.

Although not as strongly adsorbed as copper and chromium, arsenic can be removed from solution by both inorganic and organic compounds. Unlike copper, arsenic retention in soil appears to be most related to inorganic constituents (Walsch and Keeney 1975). Of the inorganic compounds, iron, aluminum, calcium, and clay are the most important in preventing arsenic leaching (Fordham and Norrish 1974; Frost and Griffin 1977; Stewart and others 1975; Walsch and Keeney 1975; Woolson and others 1971; Woolson 1973). In sediments, arsenite can also form complexes with the sulfur that is produced by the decomposition of organic materials (Ferguson and Gavis 1972; O'Neill 1990; Riedel and others 1989). Iron oxide appears to be a particularly effective arsenic adsorber, although the reaction is strongly pH dependent (O'Neill 1990). As (V) is reported to be adsorbed most strongly by iron at pH 4; As (III) adsorption peaks at pH 7 and is not as complete as that of As (V) (O'Neill 1990). In soils with a high content of iron, nearly all the arsenic present is associated with this metal (Fordham and Norrish

1974; O'Neill 1990; Walsch and Keeney 1975). Aluminum is slightly less effective at fixing arsenic, but it does form relatively insoluble arsenates, and calcium forms more soluble complexes (Woolson and others 1971). The adsorption of arsenate by clay is reported to be maximized at pH 5, although there is a general increase in arsenite adsorption as soil pH increases from 3 to 9 (Frost and Griffin 1977). The authors speculated that at under alkaline conditions, arsenic would be quite mobile through pure clay minerals.

Although their role is relatively minor, organics, such as humic acids, do complex arsenic, apparently through anion exchange reactions. Maximum arsenate adsorption is reported to occur at pH 5.5, with arsenite adsorption peaking at higher pH levels (O'Neill 1990). Arsenate adsorption appears to be about 20 percent greater than arsenite adsorption (O'Neill 1990). Phosphates can decrease arsenate and arsenite adsorption by competing for reactive sites and desorbing complexed arsenic (O'Neill 1990; Walsch and Keeney 1975; Woolson 1973). Arsenic solubility may also be increased at higher pH levels as the humic materials become more soluble (O'Neill 1990). Monomethylarsonates appear to be sorbed in a manner similar to arsenates, but dimethylarsinates are less reactive, perhaps because of their higher pK values and larger size (O'Neill 1990).

These noted studies suggest that arsenic released into the environment, although concentrated in soil and sediments, can remain somewhat mobile because of the conversion by microorganisms, the relative solubility of arsenite species, and the movement of the sediments themselves during times of high water flow.

Zinc

Like copper, the only oxidation state of importance for zinc under most conditions found in the environment is +2. In freshwater, in the pH range of 4 to 7, zinc exists primarily as the Zn^{2+} ion $[Zn(H_2O)_6]^{2+}$, and in seawater, the predominant species are Zn^{2+} and $ZnCl^+$. At higher pH levels, $Zn(OH)_2$ is the most stable species in both seawater and freshwater. The presence of organic ligands in water does not greatly affect the speciation of zinc unless the proportion of organics becomes high, such as in polluted areas (Bodek and others 1988).

The solubility of zinc in natural waters is strongly affected by pH, redox potential, temperature, and the presence of complexing ligands, competing ions, and precipitating reagents. Zinc is one of the most mobile of heavy metals, because it commonly forms complexes with ligands that are soluble in both neutral and acid waters. At higher pH levels, the formation of $Zn(OH)_2$ greatly increases the solubility of zinc (up to approximately 160 ppm), even without considering the effect of water-soluble ligands. However, other factors work to lower the concentration of zinc in water. In reducing conditions, zinc sulfide precipitates can form, and in oxidizing conditions, precipitation as $ZnCO_3$ or $Zn(OH)_6(SO)_4$ can occur. In addition, sorption to insoluble ligands, such as iron and manganese oxides and organic matter, can lower the zinc concentration in natural waters (Bodek and others 1988).

Most zinc introduced into aquatic environments is eventually partitioned into the sediments through the precipitation and sorption reactions just mentioned (Bodek and others 1988; Eisler 1993). As with copper, higher levels of zinc are found in sediments with smaller grain size. However, much less of zinc in sediments is bound to organic matter than is the case with copper. Less than 5 percent of the zinc in sediments is estimated to be bound to organic matter (Bodek and others 1988). Zinc bioavailability from sediments is increased under conditions of high dissolved oxygen, low salinity, and low pH, and when high levels of inorganic oxides and humic substances are present (Eisler 1993).

In soils, the mobility of zinc is limited by precipitation and sorption processes (Bodek and others 1988). In acid soils, zinc is most stable as the Zn^{2+} or $ZnSO_4$ species, and at higher pH levels, compounds such as $ZnHCO_3^+$, $ZnCO_3$, and $ZnB(OH)_4^+$ can be formed (Alloway 1990). Variations in the oxidation–reduction condition of soils has less effect on the mobility of zinc than on many other metals, although zinc may be indirectly affected by reactions with other soil constituents. For examples, iron and manganese oxides are sensitive to redox conditions and will coprecipitate other ions, including zinc. Similarly, under reducing conditions, sulphate ions are converted to sulphide, leading to the precipitation of zinc sulphide (Alloway 1990). One study reported that zinc in soils is 30 to 60 percent associated with manganese and iron oxides and 20 to 45 percent with the clay fraction (Bodek and others 1988).

Zinc also reacts with soil constituents through cation exchange reactions, with ligands in humic matter and clay providing reactive sites. Zinc also forms chelates with organic acids, although these complexes have much less stability than those formed by copper (Alloway 1990). Some of these complexes may be soluble, preventing the adsorption or precipitation of zinc as it moves through soil or water.

Although not as strongly adsorbed as copper, zinc also undergoes specific adsorption reactions with soil components beyond those that would result from simple cation exchange reactions. One study showed that the zinc sorption capacities of iron and aluminum oxides were 7 and 26 times greater, respectively, than would be expected from cation exchange capacity alone. Such specific adsorption is highly pH dependent (Alloway 1990).

Boron

The leaching and mobility of boron in the environment may be of much less concern than that of chromium, copper, and arsenic, because most organisms tolerate relatively high aqueous concentrations of boron compounds (EPA 1986). However, reports of boron leaching from treated wood indicate that nearly all the boron is lost from the wood during the first few years (Fox and others 1994; Johnson and Foster 1991), thus a potential for introducing significant quantities of boron into the water or soil surrounding the treated wood. It is probable that this same leachability and solubility will prevent the accumulation of boron to levels that will have significant environmental impacts, because this element

exists in forms that are highly water-soluble and less tightly bound to the soil (Eisler 1990).

The chemistry of boron compounds is quite complex, although it appears that in soil solution, freshwater, and salt-water, it occurs primarily as boric acid, H_3BO_3 or as borate ions, such as $B(OH)_4^-$ (Eisler 1990; Kleinberg and others 1960). Although boron is relatively mobile in soil, it is assumed to adsorb to some degree to organic matter and aluminum and iron oxides (Eisler 1990; Goldberg and Glaubig 1986). Adsorption is greatest in heavy textured soils with a high pH, with the greatest leaching occurring in fine-textured soils with low pH (Eisler 1990). Boron is notably leachable in sandy soils (Gupta 1993).

Organic Preservative Components

Like boron, the organic co-biocides used in the newly developed preservative formulations are considered to be relatively environmentally friendly, thus having received less scrutiny than the copper component. It is known that DDAC, used in the ACQ system, is highly water-soluble if no complexing ligands are present (Henderson 1992). However, in the environment, DDAC mobility can be limited by its ready adsorption onto both organic and inorganic substrates. An adsorption/desorption study with concentrations of 0.7, 3.5, 5.25, and 7 ppm DDAC in sand, sandy loam, silty clay loam, and silt loam soil found that DDAC is essentially immobile in soil (Henderson 1992).

Unlike many organic compounds, DDAC appears to strongly resist degradation in the environment (Henderson 1992). DDAC photolysis tests found no degradation after 30 days exposure to a xenon light source. In addition, DDAC was also stable to hydrolysis in solutions buffered to pH 5, 7, and 9. It also appears that DDAC is not rapidly degraded by soil, water, or sediment microorganisms. A microbially active sandy loam was treated with 10 ppm of carbon-14 labeled DDAC and incubated in the dark for 1 year. After this time, approximately 73 percent of the radioactive carbon remained in the form of parent compound. Similar tests in pond water and sediment revealed that 89 percent of the DDAC remained as the parent compound after 1 year. Similar results were also found in tests with anaerobic sediment (Henderson 1992).

In contrast, tebuconazole has been reported to break down rapidly in the environment (Anon. 1993). Investigations in water and sediment systems with light excluded indicated that the active ingredient is rapidly degraded to CO_2 . However, when taken up by fish, tebuconazole was metabolized only to a small extent, with two-thirds of radioactivity still attributable to the parent compound after 28 days (Anon. 1993).

Conclusions

Relatively little research has been done to quantify or evaluate leaching of preservatives from treated wood after it has been placed in service. Although numerous laboratory studies and small-sized stake field studies have been conducted to

evaluate the effect of various parameters on preservative fixation and leaching, these studies often have little applicability to in-service leaching rates. Studies of in-service leaching rates of CCA have typically been plagued by a lack of information about the original preservative content in the wood, and little opportunity has been provided for such studies with the newly developed systems. Studies that have monitored leaching in field or service exposures report results ranging from no leaching to losses of 50 percent or more for CCA-C components. With this wide discrepancy in reported leaching rates, it is difficult to develop realistic predictions of the significance or effect of leaching. Of the studies available, an applicable one appears to be a study of leaching in an above-ground exposure, in which Southern Pine decking lost approximately 5 percent of CCA components and 8 to 10 percent of copper from ACQ-B treated wood during exposure to 80 in. (2,032 mm) of rain during 20 months (Fox and others 1994). The majority of leaching occurred during the first 20 in. (508 mm) of rainfall. Although it is difficult to relate these data to other types of exposures, these values probably provide a realistic estimate of above-ground in-service leaching rates of CCA and the ammoniacal copper systems (ACQ-B, ACZA, CC). It is often assumed that belowground leaching rates are greater, because several studies have noted that the above-ground portion of wood removed from service contained more preservative than the belowground portion. In most applications, however, the proportion of treated wood exposed above ground is much greater than that in ground contact, so above-ground leaching rates may be the most relevant.

Studies of preservative leaching in seawater have produced some of the most conflicting results and some of the highest leaching rates. However, in a controlled study of piling contained in seawater tanks, CCA-C leaching rates were relatively low (Baldwin and others 1994). Little attempt has been made to determine leaching rates from wood exposed in freshwater, although one study detected elevated levels of CCA components in water below newly installed lock gates (Cooper 1991c). Little or no data is available for in-service or product-size leaching rates from ACZA, copper naphthenate, and the newly developed waterborne systems. The studies that have been conducted report copper losses ranging from 0 to more than 70 percent. The higher leaching rates noted have generally resulted from the use of small-sized samples with a high proportion of exposed end-grain.

The variability of these findings is not surprising, because these types of studies are difficult to conduct and many factors can affect the amount of leaching that occurs from treated wood. Such factors include treatment and conditioning parameters, preservative retention, time exposed, orientation and exposed surface area of the product, wood species, and site factors, such as water movement, pH, and the presence of solubilized organics or inorganics. As might be expected, greater leaching rates were reported from products or specimens that had a high proportion of exposed surface and had been placed in an area of high water flow. The presence of organic acids in soil or freshwater exposures and inorganic

ions in seawater also appears to increase the rate of CCA leaching.

The significance of the relatively small amounts of copper, chromium, arsenic, and zinc leached from the wood is unclear, but it is a function of their mobility and speciation in the surrounding environment. Mobility and speciation are, in turn, dependent on factors such as water volume and flow rate, pH, reduction/oxidation potential, ion adsorption sites, and presence of soluble ligands. The potential for rapid movement of preservative components is much greater if leached into moving water than if leached into an impermeable soil with fine particles that provide a large reactive surface.

Studies on the effect of soil and water composition on movement and speciation of preservative components reveal several key points. Chromium appears to be the least mobile of the elements, and boron is the most mobile. In soil and freshwater, the type and amounts of stationary, dissolved, or suspended organics are important in controlling the movement of chromium and copper, and inorganics play a greater role in seawater and in the mobility of arsenic and zinc. Although the interactive effects of soil constituents are complex, preservative components generally appear to be least mobile in highly organic soils, slightly more mobile in clay soils, and most mobile in sandy soils. Of the inorganic components, iron, aluminum, and manganese appear most effective in stabilizing the preservative components. Manganese may also have the opposite effect on chromium, because manganese can oxidize chromium to its more soluble hexavalent state. Arsenic and zinc, in particular, are dependent on the presence of inorganics for complexation. Conversely, high levels of sulfates and phosphates can increase movement of copper and arsenic. Movement is generally decreased at high pH levels that increase adsorption and precipitation of the metals, although the effect of pH on arsenic movement is less clear.

The valence state of arsenic and chromium influences both their mobility and toxicity. Moist, high pH soils or alkaline-oxygenated streams can stimulate the oxidation of trivalent chromium to the more toxic hexavalent form. Similarly, reducing environments, such as saturated, anaerobic soils, or poorly oxygenated waters, may favor the formation of more toxic trivalent arsenic species. However, the speciation of arsenic appears to be significantly affected by the presence of microorganisms that may convert the arsenic to volatile methylated forms of arsine gas.

Further research is needed in several areas to allow realistic estimation of the leaching rates of treated products in service and the resulting effect on the environment. One area that has been neglected is the effect of processing parameters on leaching rates. For example, it is clear that exposure of CCA-C-treated wood before fixation is completed will lead to higher initial leaching rates. However, it is unclear how initial incomplete fixation will affect the total amount of CCA components leached in the long term. The effect of post-treatment conditioning on the leaching of the other waterborne systems has received little study, although the loss of

copper from poorly conditioned ammoniacal systems is visibly evident. It is possible that fixation techniques, such as kiln drying, water baths, or steaming, could be used to substantially reduce leaching in service, but more research into the benefits of these techniques is needed before the industry can be expected to adopt these practices. It will also be necessary to develop better methods of assessing the degree of fixation for the various preservative systems.

Additional data on in-service leaching rates for all the waterborne preservative systems are greatly needed. Research should address the effects of various types of exposure environments, such as freshwater, seawater, or highly organic soils, on leaching rates. It is not possible to evaluate leaching rates in all types of exposures, but studies can and should be conducted in environments that are suspected to produce high leaching rates. If leaching rates in these environments are not significant, less severe types of exposures should be evaluated.

Finally, the movement and environmental fate of wood preservative components that have leached from treated wood need to be addressed. Research to this point indicates that leached copper, chromium, and arsenic have little mobility in soil. However, concerns still need to be addressed about the environmental fate of these elements when leached into a water or wetland environment.

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