



UNITED STATES  
CONSUMER PRODUCT SAFETY COMMISSION  
WASHINGTON, DC 20207

**Memorandum**

Date: 1/13/2003

TO : Patricia Bittner M.S., Project Manager for CCA-Treated Wood in Playground Equipment  
Directorate for Health Sciences

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SUBJECT : Toxicity Review for Copper

**Introduction**

The U.S. Consumer Product Safety Commission (CPSC) was petitioned to ban the use of chromated copper arsenate (CCA) pressure treated wood for use on playground structures. Therefore, as a component of CCA, copper and its potential toxicity is reviewed in this document.

Copper (Cu) is required for normal physiologic function, as it is essential for the activity of many different proteins. It is a component of the enzyme cytochrome C oxidase, a member of the electron-transport chain that is the energy source for all cells in the body. Superoxide dismutase is a protein requiring copper for its activity in protecting cells from free radicals. Copper also plays a role in connective tissue biosynthesis, neurotransmitter biosynthesis, blood clotting, and gene expression through many important proteins (Uauy et al. 1998).

Copper has many commercial uses due to its versatile properties. It is used in the manufacture of bronzes, brass, and other copper alloys. As a good conductor, copper is commonly used in electrical wiring and in thermal cookware. Copper salts are beneficial agriculturally as they have fungicidal as well as algacidal properties, and are also widely used in wood preservatives (WHO 1998; ATSDR 1990). Female intrauterine devices utilize copper metal due to its contraceptive qualities, and at one time copper sulfate was prescribed medically as an emetic. Copper metal and copper salts are also used in pigments and dyes, fabrics, textiles, glass, ceramics, cement, nylon, paper products, flame-proofing products, and fuel additives (Poisindex® 2001).

**Physical/Chemical Properties**

Copper is classified as a transition metal and can be found in nature in its elemental form; it occurs at 70 ppm in the earth's crust and is present in seawater at 0.001-0.02 ppm. Copper is

also present in combined form in minerals such as chalcopyrite, chalcocite, bornite and tetrahedrite. It can be present in four oxidation states: Cu (0), Cu (I), Cu (II), and Cu (III) (ATSDR 1990; Budavari 1989). Most copper compounds contain the Cu(I) or Cu (II) oxidation states. Cu (II) is the most soluble form of copper in aqueous solutions [Cu(I) quickly disproportionates to Cu(0) and Cu(II), and Cu(0) is virtually insoluble in water], and may therefore be most responsible for the toxicity of copper (ATSDR 1990). However, many factors affect the bioavailability of copper such as pH, particulate matter, and complexing ligands (ATSDR 1990; WHO 1998). Therefore, speciation of possible copper contamination is required to determine copper bioavailability.

### 1. Cu (0): Elemental Copper

CASRN: 7440-50-8

Atomic Weight: 63.54 atomic mass units

Description: Reddish, lustrous, ductile, malleable metal with a face centered cubic structure.

Solubility: Insoluble in water

Density: 8.94

Melting point: 1083 °C

Boiling point: 2595 °C

Resistivity: 1.673 microhm-cm

Uses: Manufacture of bronzes, brass and other alloys, electrical conductor, ammunition, copper salts and works of art.

### 2. Cu (I): Cuprous ion

Cuprous ion quickly disproportionates to yield Cu(0) and Cu(II) when dissolved in aqueous solutions. The only Cu (I) compounds that are stable in water are those which are insoluble.

Copper (I) Oxide (red copper oxide)

CASRN: 1317-39-1

Molecular Formula: Cu<sub>2</sub>O

Molecular Weight: 143.08 g/mol

Water Solubility: Practically insoluble

Density: 6.0 g/cm<sup>3</sup>

Uses: Fungicide, antiseptic for fishnets, antifouling marine paints, red pigment for glass, ceramic glazes and in photoelectric cells.

### 3. Cu (II): Cupric ion

Cupric ion is the most common oxidation state in aqueous solution. Cupric compounds are generally blue or green in color and most are readily soluble in water. Cu(II) oxide is the form of copper used in CCA pressure treated wood.

Copper (II) Oxide (black copper oxide)

CASRN: 1317-38-0

Molecular Formula: CuO

Molecular Weight: 79.55 g/mol

Water Solubility: Practically insoluble

Density: 6.32 g/cm<sup>3</sup>

Uses: Wood preservative (including CCA), fungicide, insecticide, miticide, molluscicide, pigment for glass and ceramics, batteries and electrodes, welding flux, feed additive, antifouling paints.

Copper (II) Sulfate

CASRN: 7758-98-7

Molecular Formula: CuSO<sub>4</sub>

Molecular Weight: 159.60 g/mol

Water Solubility: Soluble

Density: 2.284 g/cm<sup>3</sup>

Uses: fungicide, algaeicide, bactericide, herbicide, nutritional animal feed additive, insecticide mixtures, mordant in textile dyeing, tanning leather, preserving wood, electroplating, battery electrolyte, laundry and metal-marking inks, petroleum refining, flotation agent, pigment in paints and varnishes, photography, pyrotechnics, water resistant adhesive for wood, metal coloring, anti-rusting for radiator and heating systems. Also used as antidote to phosphorus, as a topical antifungal, and emetic.

Copper (II) Chloride

CASRN: 7447-39-4

Molecular Formula: CuCl<sub>2</sub>

Molecular Weight: 134.45 g/mol

Water Solubility: soluble

Density: 3.39 g/cm<sup>3</sup>

Uses: Catalyst for organic and inorganic reactions, petroleum deodorant, mordant for dyeing and printing textiles, in indelible invisible and laundry marking inks, metallurgy and refining, photography fixer, pyrotechnics, feed additive, wood preservative, disinfectant.

Copper (II) Carbonate

CASRN: 12069-69-1

Molecular Formula: CH<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>

Molecular Weight: 221.11 g/mol

Water solubility: Practically insoluble

Uses: seed treatment fungicide, pyrotechnics, paint and varnish pigment, animal and poultry feeds copper deficiency nutritional factor.

#### 4. Cu (III): Trivalent Copper ion

The trivalent copper ion is strongly oxidative, however, it only occurs in a few compounds (ATSDR 1990).

## **Death and Systemic Effects**

### **1. ACUTE**

a) Human: Acute human ingestion of large amounts of copper salts can lead to severe gastrointestinal distress (irritation, vomiting, nausea, abdominal pain, epigastric burning, gastric bleeding, hemorrhagic gastritis, and bloody vomit and stool) as well as other systemic effects including hepatic and renal failure, anemia, hypotension, jaundice, seizure, coma, shock and potentially death (Poisindex<sup>®</sup> 2001; ATSDR 1990). A case report described an 18-month old child that developed hemolytic anemia and renal tubular damage after drinking an older siblings chemistry solution containing 3 g of copper sulfate (1.2 g Cu) (Walsh et al. 1977; ATSDR 1990). Gastrointestinal effects occur primarily through copper contamination of drinking water or beverages, and are also seen at lower doses than the more serious hepatic and renal effects. Case reports have described mild gastrointestinal effects in humans after acute ingestion of water containing a copper level of 30 mg/L or higher from copper-lined or scaled café water heaters (Nicholas and Brist 1968; Semple et al. 1960; ATSDR 1990). Chemical food poisoning also resulted from the ingestion of 5.3-32 mg Cu from copper tainted cocktails producing vomiting, diarrhea, and abdominal pain (Wyllie 1957).

Human no-observable-adverse-effect levels (NOAEL) and lowest-observable-adverse-effect levels (LOAEL) are presented in Table 1. NOAEL values for acute copper consumption in adults were reported to be 4 and 6 mg Cu/L for gastrointestinal effects (nausea, vomiting and abdominal pain) in two combined populations (equivalent to 0.8 mg and 1.2 mg total Cu as determined in the study) (Araya et al. 2001). The same group measured the NOAEL for gastrointestinal effects after a single exposure to copper, and found that subjects were more sensitive to nausea than vomiting (Olivares et al. 2001).

**Table 1. Acute Human LOAEL and NOAEL Values for Gastrointestinal Symptoms (in adults unless otherwise noted)**

<b>NOAEL/LOAEL</b>	<b>Cu Concentration</b>	<b>Total Cu</b>	<b>Study</b>
LOAEL		5.3 mg Cu <sup>a</sup>	Wyllie 1957
NOAEL (Infant)	2 mg/L	0.4-0.6 mg Cu/day <sup>b</sup>	Olivares et al. 1998
NOAEL	4 or 6 mg/L <sup>c</sup>	0.8 or 1.2 mg Cu <sup>d</sup>	Araya et al. 2001
NOAEL nausea	2 mg/L purified water	0.4 mg Cu <sup>d</sup>	Olivares et al. 2001
NOAEL vomiting	4 mg/L purified water	0.8 mg Cu <sup>d</sup>	Olivares et al. 2001
NOAEL	2 mg/L orange drink	0.4 mg Cu <sup>d</sup>	Olivares et al. 2001
LOAEL	4 mg/L orange drink	0.8 mg Cu <sup>d</sup>	Olivares et al. 2001
LOAEL	3 mg/L	Average 5 mg Cu/day <sup>e</sup>	Pizarro et al. 1999

- a. Based on reproduction of copper-tainted cocktail consumption as calculated in this study
- b. Based on average infant water consumption of 0.2-0.3 L/day (EPA Exposure Factors Handbook 1997)
- c. Study completed in 2 populations
- d. Based on 200 mL consumption volume used in study
- e. Based on average measured consumption of 1.64 L/day in study

Copper sulfate has historically been used as an emetic in the management of poisoning, although this method of decontamination has been replaced by safer alternatives. The clinical dose of copper sulfate utilized for induction of emesis has been reported between 250-500 mg CuSO<sub>4</sub>, which is equivalent to 100-200 mg Cu (Stein et al. 1976; Karlsson and Noren 1965). A

poisoning case was treated with approximately 2 grams  $\text{CuSO}_4$ , or 800 mg Cu, for induction of emesis and ultimately resulted in death of the patient due to a toxic reaction to copper (Stein et al. 1976). Death was also reported in 13 of 53 cases of suicide by method of copper sulfate ingestion. The highest level of intake in this study was one gram of copper sulfate, indicating a lethal dose of copper to be as low as 400 mg elemental copper (40% of 1 gram  $\text{CuSO}_4$ ) (Chuttani et al. 1965). An eleven-year-old child died after accidentally swallowing a mouthful of a copper sulfate solution from a chemistry set. She ingested greater than 200 mg Cu (as the stomach contents contained 226 mg total Cu) leading to postmortem blood copper levels 66 times greater than normal (Gulliver 1991; Mucklow 1997).

b) Animal: Acute intratracheal instillation studies in rats indicate that exposure to copper sulfate and copper (II) oxide at 0.018 mg Cu/kg and 0.073 mg Cu/kg respectively, led to acute lung inflammation (Drummond et al. 1986).  $\text{LD}_{50}/\text{LC}_{50}$  values (lethal dose/concentration causing lethality in 50% of subjects) estimated from animal studies are presented in Table 2. The  $\text{LC}_{50}$  of inhaled copper (II) hydroxide (for an unreported length of time) was greater than 1303 mg  $\text{Cu}/\text{m}^3$  in rabbits. Acute pulmonary exposure to copper aerosol (1.3 or 1.6 mg  $\text{Cu}/\text{m}^3$  for 1 hour) in the guinea-pig led to inflammation of the lungs, significant reduction in tidal volume and reduced lung compliance with increased respiratory frequency (Chen et al. 1991; Hirano et al. 1990; Hirano et al. 1993). Copper (II) oxide administered by intratracheal instillation to the rat displayed a lethal dose of 222 mg Cu/kg (WHO 1998).

**Table 2.  $\text{LD}_{50}/\text{LC}_{50}$  Values for Copper Compounds in Various Species (WHO 1998).**

Compound	Species/Route	$\text{LD}_{50}$	Reference
Copper(I) oxide	Rat	470 mg/kg	Smyth et al. 1969
	Oral	414 mg Cu/kg	
Copper(II) acetate	Rat	595 mg/kg	NIOSH 1993
	Oral	208 mg Cu/kg	
Copper(II) acetate monohydrate	Rat	710 mg/kg	Smyth et al. 1969
	Oral	226 mg Cu/kg	
Copper(II) acetate monohydrate	Mouse Oral	1600 mg/kg (lethal dose) 509 mg Cu/kg	Schafer and Bowles 1985
Copper(II) carbonate	Rat Oral	159 mg /kg 82 mg Cu/kg	Lehman 1951
Copper(II) carbonate	Mouse Oral	320 mg /kg (lethal dose) 165 mg Cu/kg	Shafer and Bowles 1985
Copper(II) carbonate hydroxide	Rat (male) Oral	1350 mg/kg 388 mg Cu/kg	Hasegawa et al. 1989
Copper(II) carbonate hydroxide	Rat (female) Oral	1495 mg/kg 430 mg Cu/kg	Hasegawa et al. 1989
Copper(II) carbonate hydroxide	Rabbit Oral	317 mg/kg 91 mg Cu/kg	NIPHEP 1989
Copper(II) chloride	Rat	140 mg/kg	Lehman 1951
	Oral	66 mg Cu/kg	

Table 2. (Continued)

Compound	Species/Route	LD <sub>50</sub>	Reference
Copper(II) chloride	Mouse Oral	190 mg/kg 90 mg Cu/kg	NIPHEP 1989
Copper(II) chloride	Guinea-pig Oral	32 mg/kg 15 mg Cu/kg	NIPHEP 1989
Copper(II) hydroxide	Rat Oral	1000 mg/kg 651 mg Cu/kg	Pesticide Manual 1991 as in WHO 1998
Copper (II) hydroxide	Rabbit Inhalation	>1303 mg Cu/m <sup>3</sup> duration unspecified	Tomlin 1994
Copper (II) hydroxide	Rat Dermal	>2058 mg Cu/kg/day	Tomlin 1994
Copper(II) nitrate trihydrate	Rat Oral	940 mg/kg 247 mg Cu/kg	Smyth et al. 1969
Copper(II) oxychloride	Rat Oral	700-800 mg/kg 417-476 mg Cu/kg	Tomlin 1994
Copper(II) oxychloride	Rat Oral	1440 mg/kg 857 mg Cu/kg	NIPHEP 1989
Copper (II) oxide	Rat Intratracheal instillation	Lethal dose 222 mg Cu/kg	NIOSH 1993
Copper (II) oxysulfate	Rat Dermal	>1124 mg Cu/kg/day	NIOSH 1993
Copper(II) sulfate	Rat Oral	300 mg/kg 120 mg Cu/kg	Lehman 1951
Copper(II) sulfate pentahydrate	Rat Oral	960 mg/kg 244 mg Cu/kg	Smyth et al. 1969
Copper(II) sulfate	Mouse Oral	LD <sub>100</sub> 50 mg/kg (lethal dose) 20 mg Cu/kg	Venugopal and Luckey 1978
Copper(II) sulfate	Rabbit Oral	125 mg/kg 50 mg Cu/kg	Eden and Green 1939

Depending on the solubility of the copper salt, the oral LD<sub>50</sub> values vary (Table 2). The trend indicates that more soluble salts have lower LD<sub>50</sub> values than less soluble salts. Copper (I) oxide, a virtually insoluble copper salt, has an LD<sub>50</sub> value of 414 mg Cu/kg in the rat whereas highly soluble salts copper (II) chloride and copper (II) sulfate show lower LD<sub>50</sub> values of 66 mg Cu/kg and 120 mg Cu/kg. LD<sub>50</sub> values are also conditional on the species of animal used in the acute toxicity studies, as some species seem more susceptible to copper sulfate (mouse 100% lethal dose-20 mg Cu/kg and rabbit LD<sub>50</sub>-50 mg Cu/kg) than the rat (LD<sub>50</sub>-120 mg Cu/kg) (WHO 1998). Symptoms of large doses of copper include gastrointestinal effects (vomiting, diarrhea, and gastric hemorrhage), cardiovascular changes (hypotension, tachycardia, and

hemolytic crisis), and centrally mediated convulsions and paralysis leading to death (WHO 1998).

## 2. CHRONIC

a) Human: Inhalation exposure to copper fumes, dust or mist has caused metal fume fever in factory workers. Symptoms include a sweet metallic taste in the mouth, labored breathing, nausea, headache, chills and fever. The onset and duration of symptoms are short, often dissipating the next day. Supportive treatment including bed rest and nasal oxygen are recommended, although intravenous steroids have also been used. Tolerance to the metal fumes may develop over successive days of exposure (Armstrong et al. 1983). In factory workers exposed to airborne copper ( $111-434 \text{ mg Cu/m}^3$ ), gastrointestinal symptoms (nausea and diarrhea), decreased hemoglobin and erythrocyte levels, and hepatomegaly were observed. However, it was shown that these workers were also exposed to cadmium, iron and lead (Suciu et al. 1981; Finelli et al. 1981). The guidelines for copper fume exposure set by the American Conference of Governmental and Industrial Hygienists recommends a threshold limit value-time-weighted average (TLV-TWA) of  $0.2 \text{ mg Cu/m}^3$  for copper fumes and  $1 \text{ mg Cu/m}^3$  for copper dust or mist. The Occupational Safety and Health Association recommends a permissible exposure limit-time-weighted average (PEL-TWA) of  $0.1 \text{ mg Cu/m}^3$  as copper fumes and  $1 \text{ mg Cu/m}^3$  for copper dust and mist (Poisindex® 2001).

Copper is an essential mineral, therefore, daily consumption is required for normal biologic activity. The Food and Nutrition Board recently reported allowances of dietary copper for infants, children and adults; these values are presented in Table 3 (IOM 2001). Infant Adequate Intake (AI) levels ( $200-220 \text{ } \mu\text{g Cu/day}$ ) were estimated from studies reporting copper concentration in mother's breast milk and in complementary foods. Infant levels are based on Adequate Intake because there are no defined criteria to demonstrate effects due to dietary copper in children this age (IOM 2001). The adult Recommended Dietary Allowance (RDA) level of  $900 \text{ } \mu\text{g Cu/day}$ , proposed by the Food and Nutrition board, was estimated from copper levels causing changes in sensitive biochemical markers in depletion/repletion studies (IOM 2001). The RDA values for children, extrapolated from these adult values, ranged from  $340-890 \text{ } \mu\text{g Cu/day}$  (IOM 2001).

**Table 3. Recommended Daily Allowances of Copper in Children and Adults (IOM 2001).**

Age	Measure	Level
0-6 months	Adequate Intake <sup>a</sup>	$200 \text{ } \mu\text{g/day}$
7-12 months	Adequate Intake <sup>b</sup>	$220 \text{ } \mu\text{g/day}$
1-3 years	RDA <sup>c</sup>	$340 \text{ } \mu\text{g/day}$
4-8 years	RDA <sup>c</sup>	$440 \text{ } \mu\text{g/day}$
9-13 years	RDA <sup>c</sup>	$700 \text{ } \mu\text{g/day}$
14-18 years	RDA <sup>c</sup>	$890 \text{ } \mu\text{g/day}$
Adult	RDA <sup>d</sup>	$900 \text{ } \mu\text{g/day}$

a. Based on copper concentration in mother's breast milk

b. Based on copper concentration in breast milk plus complementary foods

c. Extrapolated from estimated average adult requirement values

d. Based on studies of depletion/repletion and biochemical markers

The Institute of Food Research of the United Kingdom utilized animal models and human volunteers to determine acceptable human intake of copper based on copper metabolism (Aggett and Fairweather-Tait 1998; Aggett 1999). Adequate daily intake of copper ranged from 8.5 to 34  $\mu\text{g}/\text{kg}$  based on conservation of endogenous copper, hepatic turnover and homeostasis, as well as normal biliary excretion and gastrointestinal uptake. At a daily intake of 100  $\mu\text{g}/\text{kg}$  the homeostatic regulation of copper absorption was appropriately maintained via a plateau level of copper absorption from the gastrointestinal tract. Consumption of 5.0 mg Cu/kg or greater per day led to changes in copper metabolism indicating the inability of homeostatic mechanisms to control copper absorption, leading to the potential for copper toxicosis (Aggett and Fairweather-Tait 1998; Aggett 1999). Symptoms of chronic exposure to excess copper include Kayser-Fleischer rings in the eye (blue rings around outer border of the cornea), green discoloration of hair and/or skin, gastroenteritis, anemia, as well as liver and kidney toxicity (Poisindex<sup>®</sup> 2001).

The majority of reported cases of chronic copper exposure in children occurred due to contamination of tap water from copper piping (data summarized in Table 4). A German epidemiological study found that infants consuming formula made from tap water containing greater than 0.8 mg Cu/L with consumption of at least 200 mL/day for 12 months did not show any signs of liver malfunction (Dassel de Vergara et al. 1999). The World Health Organization (WHO) determined that infants consuming water containing 2 mg Cu/L or less for the first year of life also did not display acute or chronic adverse events. It was hypothesized that adaptive responses of copper intake, storage and excretion were protective against the water copper levels (Olivares et al. 1998). However, a case study of two infant siblings consuming tap water containing 2.2-3.4 mg Cu/L for more than 9 months via infant formula, suffered from severe liver damage (micronodular cirrhosis) (Mueller-Hoecker et al. 1988). It is of note that the older siblings in the family did not suffer deleterious effects from consumption of the tap water. Another German study (1984-1994) of children suffering from early childhood cirrhosis, found that copper was a probable etiologic factor in up to 8 cases. It was determined that five of these children consumed tap water with levels between 9-26 mg Cu/L used in the preparation of infant formula (Dieter et al. 1999). An older child of 3.8-years-old was exposed to copper levels up to 8.6 mg/L in tap water for 1.8 years, and developed sub-acute liver failure (micronodular cirrhosis) due to chronic copper intoxication (Trollmann et al. 1999). A family (father aged 32 and children aged 5 and 7) reported abdominal pain and vomiting after consumption of tap water in the morning with a Cu concentration up to 7.8 mg Cu/L for a period of 1.5 years. Symptoms resolved after cessation of water consumption (Spitalny et al. 1984).

Adult epidemiological studies have not shown clear associations between gastrointestinal illness or liver disease and the copper content of tap water (Olivares and Uauy 1996; Fewtrell et al. 1996; Scheinberg and Sternlieb 1994; Low et al. 1996; Buchanan et al. 1998; NRC 2000). An adult clinical study examining diet supplementation with 10 mg Cu/day as copper gluconate did not show increased gastrointestinal side effects above control levels. Also, the additional copper did not lead to hematologic (hematocrit level or mean corpuscular volume) or hepatic changes (serum aspartate aminotransferase, alkaline phosphatase, serum gamma glutamyl transferase, or acetate dehydrogenase activity)(Pratt et al. 1985). However, a case report of liver failure was described in a 26-year-old man after diet supplementation with 30-60 mg Cu/day for 3 years. At presentation, the patient was in acute renal failure and his liver function quickly deteriorated; an



emergency liver transplant was required for recovery (O'Donohue et al. 1999). Although most cases of copper toxicity from ingestion occur from copper salts, there are two cases of copper metal poisoning in mentally-ill patients from ingestion of 275 and 700 coins containing copper. The gastric corrosion and absorption of the copper coins led to severe chronic copper poisoning and death (Yelin et al. 1987; Hasan et al.1995).

**Table 4. Chronic Human Copper Exposure Effects and Dose.**

Copper Exposure	Subject	Duration of Exposure/ Type of Study	Effect	Dose (mg Cu/kg/day)	Reference
≥ 0.8 mg Cu/L in tap water ≥200 mL/day	Infants <1 year of age	12 months Epidemiological Study	No signs of liver malformations	0.02 <sup>a</sup>	Dassel de Vergara et al. 1999
<2mg Cu/L in tap water	Infants < 1 year	3-12 months Epidemiological Study	No acute or chronic adverse effects	0.04-0.07 <sup>b</sup>	Olivares et al. 1998
2.2-3.4 mg Cu/L in tap water	Infant siblings < 1 year	> 9 months Case Study	Micronodular cirrhosis	0.04-0.11 <sup>b</sup>	Mueller-Hoecker et al. 1988
9-26 mg Cu/L in tap water	Infants: 5 cases	Epidemiological Study	Early childhood cirrhosis	0.2-0.86 <sup>b</sup>	Dieter et al. 1999
Up to 8.6 mg Cu/L in tap water	3.8 year old	1.8 years Case Study	Micronodular cirrhosis	0.29 <sup>c</sup>	Trollmann et al. 1999
Up to 7.8 mg Cu/L in tap water	Children 5 & 7 years old	1.5 years Case Study	Abdominal pain and vomiting	0.23 <sup>d</sup>	Spitalny 1984
	Adult			0.15 <sup>e</sup>	
10 mg Cu/ day as copper gluconate supplement	Adult	12 week Clinical Study	No increase in gastrointestinal effects. No hematological or hepatic effects	0.14 <sup>f</sup>	Pratt et al. 1985
30-60 mg Cu/ day as dietary supplement	Adult 26 years old	3 years Case Study	Liver cirrhosis necessitating liver transplantation	0.42-0.84 <sup>f</sup>	O'Donohue et al. 1999

- a. Daily volume based on minimum 200 mL consumption volume as stated in this study. Weight based on mean body weight of 9.1 kg for a 6-11 month old child as expressed in the EPA Exposure Factors Handbook (EPA 1997).
- b. Daily volume based on mean consumption of 0.2-0.3 L for children less than 1 year of age. Weight based on mean body weight of 9.1 kg for a 6-11 month old child (EPA 1997).
- c. Daily volume based on mean consumption of 0.58 L/day for children 1-4 years of age. Weight based on mean body weight of 17.4kg for a 4 year old (EPA 1997).
- d. Daily volume based on mean water intake of 0.67 L/day for children 5-9 years of age. Weight based on average body weight of 5 and 7 year old calculated as 22.3 kg (EPA 1997).
- e. Daily volume based on mean water consumption of 1.4 L/day in an adult. Weight based on mean body weight of 71.5 kg for a 25-35 year old adult (EPA 1997).
- f. Weight based on mean body weight of 71.5 kg for a 25-35 year old adult (EPA 1997).

b) Animal: Inhalation exposure of copper (II) chloride aerosol for 4-6 weeks at 0.6 mg Cu/m<sup>3</sup> in the rabbit did not lead to macroscopic changes in the lung. The NOAEL of inhaled copper sulfate exposure for a duration of 1-2 weeks was 3.3 mg Cu/m<sup>3</sup> and 1.2 mg Cu/m<sup>3</sup> in the mouse and hamster respectively (ATSDR 1990).

NOAEL and LOAEL values for oral copper exposure in various species after subchronic or chronic exposure are listed in Table 5. Gastrointestinal, hepatic, renal, and hematopoietic effects, as well as changes in body weight were recorded in these studies. The lowest LOAEL recorded was 7.9 mg Cu/kg/day for activation of a liver enzyme indicating hepatic injury (serum aspartate transaminase) after treatment of rats with copper acetate for 90 days. (Epstein 1982; ATSDR 1990). In general, copper supplied in water led to symptoms at lower exposure levels than if copper was added to solid food, possibly due to the increased bioavailability of copper ions in water.

**Table 5. Oral Systemic no-observable-adverse-effect-levels (NOAEL) and lowest-observable-adverse-effect-level (LOAEL) for copper compounds in various species (ATSDR 1990; WHO 1998).**

Species/ Exposure	Compound/ Route	NOAEL (mg Cu/kg/day)	LOAEL (mg Cu/kg/day)	Reference
<b>Sub-chronic</b>				
Rat 7-14 days	Copper sulfate Diet	100 renal	100 hepatic	Haywood 1980
Rat 7-14 days	Copper sulfate Diet		100 hepatic	Haywood and Comerford 1980
Rat (F 344) 15 days	Copper sulfate Diet	Male: 46 renal 92 hepatic Female: 23 gastrointestinal 93 hematopoietic, body weight	Male: 92 renal 198 hepatic Female: 44 gastrointestinal 196 hematopoietic, body weight	NTP 1993
Rat (F 344) 15 days	Copper sulfate Water	Male: 29 respiratory, cardiac, gastrointestinal, hepatic Female: 26 body weight	Male: 10 renal Female: 31 mortality (100%)	NTP 1993
Mouse 15 days	Copper sulfate Diet	Male: 92 gastrointestinal 717 respiratory, cardiac, hepatic, renal, body weight	197 gastrointestinal	NTP 1993
Mouse 15 days	Copper sulfate Water	Male: 24 respiratory, cardiac, gastrointestinal, hepatic, renal, body weight	62 increased mortality	NTP 1993
Rat 20 days	Copper sulfate Gavage		100 hematopoietic, muscular and skeletal, hepatic, renal, body weight	Rana and Kumar 1980
Rat 28 days	Copper sulfate Diet	89 body weight	144 body weight	Boyden et al. 1938
Rat 30 days	Copper sulfate Gavage		40 hematopoietic, hepatic, other biochemical	Kumar and Kumar 1980
Pig 49 days	Copper carbonate, Copper hydroxide Diet		36 hematopoietic, hepatic	Suttle and Mills 1966

Table 5. Continued

Species/ Exposure	Compound/ Route	NOAEL (mg Cu/kg/day)	LOAEL (mg Cu/kg/day)	Reference
Pig 54 days	Copper sulfate Diet	8.8 hematopoietic, body weight	14.6 hematopoietic, body weight	Kline et al. 1971
<b>Chronic</b>				
Rat 7-105 days	Copper sulfate Diet		100 hepatic	Haywood and Comerford 1980
Rat 7-105 days	Copper form not reported Diet		150 hepatic, renal	Haywood et al. 1985a; Haywood et al. 1985b
Rat 21-105 days	Copper sulfate Diet		100 hepatic, renal	Haywood 1980
Rat (F 344) 90 days	Copper sulfate Diet	43 hepatic, body weight *	53 hepatic, body weight *	Aburto et al. 2001
Rat 90 days	Copper acetate Water	7.9 body weight	7.9 hepatic	Epstein et al. 1982
Rat 91 days	Copper sulfate Diet	Male: 66 Female: 68		NTP 1993
Mouse 91 days	Copper sulfate Diet	Male: 398 Female: 536		NTP 1993
Rat 91 days	Copper sulfate Diet	Male: 8 hepatic 16 gastrointestinal 33 hematopoietic 66 body weight Female: 134 respiratory, cardiac 9 renal	Male: 17 renal 33 gastrointestinal 66 hepatic 140 body weight	NTP 1993
Mouse 91 days	Copper sulfate Diet	Male: 187 body weight 814 respiratory, cardiac, hepatic, renal female: 126 gastrointestinal	Male: 398 body weight Female: 267 gastrointestinal	NTP 1993
Rat 105 days	Copper sulfate Diet		150 less serious hepatic, renal, body weight 300 serious hepatic, body weight	Haywood and Loughran 1985
Rat 126 days	Copper acetate Diet	130 musculo-skeletal	130 decreased growth and testes weight	Llewellyn et al. 1985
Rat 140 days	Copper carbonate Diet		10 cardiovascular, hematology	Liu and Medeiros 1986
Rat 280-308 days	Copper sulfate Diet		Male: 27 non-neoplastic effects Female: 40 non-neoplastic effects	Harrisson et al. 1954

\* Food consumption based on reported value of 14.9 g/day in Fischer 344 rats (Morrissey and Norred 1984)

### **Dermal and Ocular Effects**

Rare cases of allergic reactions can occur due to copper metal in copper-containing jewelry or intrauterine devices (IUD) leading to local contact allergic dermatitis or hives respectively (Barkoff 1976; Saltzer and Wilson 1968; Sterry and Schmoll 1985; Gaul 1958). Copper metal is utilized in IUD devices as a method of contraception with a mean dose of approximately 26-74  $\mu\text{g}$  Cu/day absorbed from these devices (Timonen 1976). Patch testing has shown that a dermal allergic reaction requires 24-48 hours of contact with 0.5-5% copper sulfate in water or petrolatum (WHO 1998).

Acute copper toxicosis (hemolytic anemia, jaundice, renal insufficiency) resulted from use of copper sulfate as a topical anti-fungal during skin graft procedures to repair third-degree burns in a 2-year old child. The amount of copper applied was not reported, although the serum level of copper was approximately 4-fold greater than normal. The treatment, occurring during 7 procedures over a course of 9 weeks, may have augmented copper absorption, as the dermal surface was open and bleeding at the time of copper application (Holtzman et al. 1966). In another case, subcutaneous absorption of Cu occurred in an adult as a result of a copper azide explosion and subsequent implantation of copper-contaminated glass shards into the skin. The reported level of 7.7 mg Cu absorbed did not lead to symptoms of copper toxicity (Bentur et al. 1988).

In animals, copper compounds appear to be poorly absorbed through dermal contact. The LD<sub>50</sub> values for dermal exposure of copper compounds are >1124 mg Cu/kg/day for copper oxysulfate and >2058 mg Cu/kg/day for copper hydroxide in the rat and rabbit respectively, as presented in Table 2 (WHO 1998; NIOSH 1993; Tomlin 1994).

A patient case report described retinal toxicity in response to the presence of a copper-containing foreign body. Removal of the object led to reversal of the copper-associated damage (Dayan et al. 1999). Ocular mucosal irritation was also described in a case report of sheet metal workers exposed to copper dust (Askregren and Mellgren 1975).

### **Mutagenicity, Genotoxicity and Carcinogenicity**

Human prospective epidemiological studies observed an association with serum copper levels greater than 1.25 mg Cu/L with cancer (Coates et al. 1989; Overvad et al. 1993; Kok et al. 1988). However, copper levels may be increased in the serum as a result of cancer and other disease states (NRC 2000). Studies quantifying the copper ingested from the diet did not show a correlation between levels of copper intake and cancer (WHO 1998). There is, therefore, insufficient evidence available to determine whether copper plays a role in cancer development. The EPA assigned copper Classification D (not classifiable as to human carcinogenicity) (EPA 1987).

Results of mutagenic *in vitro* assays in eukaryotic and prokaryotic systems were equivocal (WHO 1998). In a mammalian *in vitro* system, copper nitrate led to chromosomal damage thought to occur by the binding of copper to DNA (Sideris et al. 1988). *In vivo* mouse studies with a single injection of 1.7 mg Cu/kg as copper sulfate led to bone marrow chromosomal aberrations, and an increase in micronuclei in one of the two studies, suggesting potential

clastogenicity of copper (Agarwal et al. 1990; Bhunya and Pati 1987). In mice, a subcutaneous injection of 1000 mg/kg copper hydroxyquinoline (181 mg Cu/kg) led to an increased incidence of reticulum cell sarcomas, however, increases in tumor incidence were not seen following 77 weeks of oral ingestion of 1000-2800 mg/kg copper hydroxyquinoline (181-505 mg Cu/kg) (Bionetics 1968). Rats exposed to 130 mg Cu/kg/day as oral copper acetate, did not display liver tumors (Kamamoto et al. 1973). In several other animal studies, copper compounds decreased the formation of tumors produced by recognized carcinogens (Howell 1958; Burki and Okita 1969; Carlton and Price 1973). These data support the determination that copper is not classifiable as to human carcinogenicity (EPA 1987).

### **Neurological Effects**

In a clinical observation of factory workers exposed to copper dust, central nervous system symptoms such as headache, vertigo, and drowsiness were reported (Suciu et al. 1981). However, this study did not include a control group of workers, a defined dose-response, statistics, or a description of the study design. There is inadequate human data to indicate that copper exposure leads to neurologic effects.

*In vitro* assays in neuronal cells treated with copper showed that copper is taken into, but not stored, in neurons. Copper did not inhibit neuronal cell growth, however, oxidative damage did occur (Watt and Hooper 2001; White et al. 1999; White et al. 2002). Copper treatment of human neuronal cultures (NT2-N) also led to toxicity via apoptotic cell death, with a correlating increase in p53 nuclear protein levels (VanLandingham et al. 2002). Copper metal fragments implanted into rabbit spinal cord led to localized neuronal toxicity (Tindel et al. 2001). Rats exposed to dietary copper sulfate (~12.5 mg Cu/kg/day) did not show changes in learning and memory with increased brain copper levels. However, brain biochemistry was altered by an increase in dopamine and norepinephrine content (Murthy et al. 1981). Rats challenged with 21 daily intraperitoneal injections of 2 mg Cu/kg/day as copper chloride also displayed increases in dopamine as well as norepinephrine in the brain (Malhotra et al. 1982). After rats were exposed for 11 months to 46 mg Cu/kg/day as copper sulfate in drinking water, brain dopamine levels were unaffected. However, there was an increase in dopamine metabolism, and a small increase in dopamine receptor affinity with a decrease in dopamine receptor levels (De Vries et al. 1986; WHO 1998; NRC 2000). Neurologic changes in response to copper were shown experimentally in the rat species by 2 routes of administration, however behavioral changes were not shown. Therefore, there is limited evidence of copper neurotoxicity based on animal data, and Cu meets the definition of a possible neurotoxic substance under the FHSA.

### **Reproductive/Developmental Effects**

Few data are available on the reproductive or developmental effects of copper in humans. In an occupational study, sexual impotence was reported in 16% of factory workers exposed to copper dust, but no data on control workers were reported (Suciu et al. 1981). Copper wire is currently utilized in female intra-uterine devices; it acts as a contraceptive by rendering sperm immobile within the uterus and/or by deterring egg implantation (Holland and White 1982).

Environmental exposure to copper from a copper smelter (quantified with liver copper concentrations) was correlated with increased sperm abnormalities (neck vacuoles) in impalas

(Ackerman et al. 1999). Reproductive effects of copper administration have also been studied experimentally in animal models. When adult male rats were exposed to copper chloride aerosol (2.5 or 19.6 mg Cu/m<sup>3</sup> for 4 months) a decreased incidence of sperm, decreased sperm motility, lower testes weight, and decreased levels of testosterone were observed. In the same experiment, females displayed a decrease in levels of estradiol, LH, FSH and prolactin (Gabuchyan 1987). Administration of copper chloride (2 or 3 mg/kg bw/day, i.p.) to male albino rats led to reduction in testes weight, and testosterone levels (no effect after 1 mg/kg bw/day) (Chattopadhyaya et al. 1999). When exposure occurred through dietary consumption, there were no effects on male or female sex organs or on the estrous cycle with exposure up to 67 mg Cu/kg/day in the rat and 537 mg Cu/kg/day in the mouse (Hebert et al. 1993). In response to 82-120 mg Cu/kg/day as copper gluconate in the diet for 44 weeks, female rats showed hypertrophy of the uterus and ovaries and male rats showed hypertrophy of the seminal vesicles (Harrisson et al. 1954; WHO 1998). Llewellyn et al. reported an increase in rat testes weight after administration of 30-45 mg Cu/kg/day as copper acetate to male rats in the diet (Llewellyn et al. 1985; WHO 1998). In reviewing the previously described Harrison and Llewellyn studies, the World Health Organization expressed doubt on the data supporting changes in seminal vesicles and testes weight (WHO 1998). Copper meets the definition of a possible reproductive toxicant under the FHSA, as the experimental evidence of reproductive toxicity in animals is limited.

Abnormal fetal development including fetal resorption, kinked-tail, thoracic and ventral hernias, microphthalmia, cleft lip, and ectopic cordis were observed after injection (i.p.) of copper (10 mg Cu/kg) to pregnant hamsters on day 8 of gestation (Ferm and Hanlon 1974; NRC 2000). Administration of copper sulfate at 1.6 mg Cu/kg/day (from gestational day 13 until delivery) to mice in drinking water did not lead to changes in fetal body or organ weight (abnormalities or litter size were not reported in this study). However, if maternal copper administration was continued during lactation (1.3 mg Cu/kg/day as copper sulfate for 13 days post-partum), observations of decreased neonate body weight and lower weight and protein content of organs were reported (Kasama and Tanaka 1988). Copper sulfate administration to mice (C57BL and DBA) in the diet led to reduced litter size, fewer live fetuses, and lower fetal weight (NOAEL 53 mg Cu/kg/day, LOAEL 80 mg Cu/kg/day). Fetal developmental abnormalities occurred in both strains of mice above 155 mg Cu/kg/day and included hydrocephalus, encephalocoeles, and abnormalities of ribs and vertebrae (however, statistics were not reported) (Lecyk 1980; WHO 1998; ATSDR 1990). Administration of up to 65 mg Cu/kg/day to rats as copper acetate in the drinking water for 7 weeks prior to mating led to delayed ossification, decreased yolk sac diameter, reduced crown-rump length, and decreased somite number (Haddad et al. 1991; WHO 1998). Mink displayed a decrease in kit weight and increased kit mortality with maternal administration of copper sulfate pentahydrate in the diet from 9 months prior to mating to 3 months post-mating (information on developmental malformations were not reported) (NOAEL 6 mg Cu/kg/day, LOAEL 12 mg Cu/kg/day) (Aulerich et al. 1982; WHO 1998). Developmental effects were seen in several animal species in response to different routes of administration and doses of copper. However, the quality of data and lack of statistics in the experimental studies limits the evidence. Therefore, copper meets the definition of a possible developmental toxicant under the FHSA.

### **Pharmacokinetics**

There are biologic mechanisms that control the oral absorption, distribution and excretion of copper in humans. These homeostatic mechanisms regulate copper levels in the body, and protect against potential disease resulting from poisoning.

a) **Absorption**: Human exposure due to industrial inhalation of copper from dust and fumes has led to absorption and increased copper levels in the body (WHO 1998). Inhalation of copper oxide was also observed in rat lung capillaries after several hours of exposure to welding dust emitted from copper wires (Batsura 1969).

In humans, copper is absorbed from the stomach and to a greater extent from the upper small intestine (Bearn and Kunkel 1955). An inverse relationship between the fraction of copper absorbed and copper available in the intestinal tract has been observed in children and adults. A smaller percentage of copper is absorbed with high levels of copper intake, and a larger percentage is absorbed when low levels of copper are ingested. (Turnlund et al. 1989; Ehrenkranz et al. 1989). Although copper retention in the body does increase with high copper intake, it seems that copper absorption is saturable at high concentrations, protecting the body's copper balance. It is of note that in infants, this homeostatic mechanism is not as efficient, therefore making them more susceptible to copper toxicity. Infants are also at increased risk because of greater inherent liver copper levels at birth, and a potential increased exposure due to higher liquid intake than adults based on body-weight ratios (NRC 2000).

The ionic forms of copper (unbound or free) or copper bound to amino acids are absorbed from the gastrointestinal tract. Compounds that decrease the absorbability of copper include hemicellulose, fructose and divalent cations such as zinc, cadmium, iron, tin and molybdenum. Copper absorption is increased with a high protein diet and natural polybasic amino acids (Wapnir 1998). Absorption of copper depends on the amount of copper intake in the diet. Overall copper absorption ranges from greater than 50% with intake of copper less than 1 mg/day, to less than 20% absorption when copper intake exceeds 5 mg/day (IOM 2001).

Dermal absorption of copper is low, however it can occur when an agent is utilized to increase absorption through the epidermis or through damaged skin (ATSDR 1990).

b) **Distribution and Metabolism**: After copper is absorbed from the stomach and intestine, it is bound by the plasma proteins albumin and transcuprein and transported to the liver via the portal circulation. These proteins readily release the copper that is then taken up by hepatocytes. Once taken up by hepatocytes, copper is either retained for storage, bound by bile salts to be excreted, or released back into the plasma for transport to non-liver cells. Copper retained in the adult liver normally constitutes approximately 8-20% of total body copper content. Ionic copper is taken up by hepatocytes and is bound by proteins such as metallothionein and glutathione. These copper complexes serve as storage forms of copper, and also as carriers to plasma proteins if the metabolic need for copper increases (Luza and Speisky 1996; WHO 1998). Plasma proteins, such as ceruloplasmin, bind copper and are responsible for the transport and distribution of copper to non-hepatic cells throughout the body (Luza and Speisky 1996).

c) **Excretion:** Copper can be excreted via kidney blood filtration and released in the urine, or bound by bile salts in the liver and eliminated in the feces. Urinary excretion constitutes only 3% of copper excretion while 50-80% of copper from the liver is bound by bile salts and released into the intestine. Reabsorption of this copper is negligible, as it is tightly bound to bile and virtually nonabsorbable in the gastrointestinal tract. Therefore it passes through the intestine and is ultimately excreted in the feces. Biliary excretion, as the major route for copper release, is an important mechanism in the maintenance of copper levels in the body. This is demonstrated in animal studies in which rats were given an 18-fold increase in oral copper concentration, and showed a 16-fold increase in biliary copper excretion. Therefore, a majority of excess copper taken into the liver was bound by bile salts and excreted, rather than being stored in the liver or absorbed into systemic circulation (Gross et al. 1989 in Luza and Speisky 1996). In humans, a deficiency in this biliary copper transport leads to an accumulation of copper in the liver, resulting in hepatotoxicity as seen in Wilson's disease.

### **Discussion**

Copper is absorbed through respiratory and oral routes of exposure. Inhalation exposure has been reported in factory workers exposed to metal fumes or dust, leading to symptoms of metal fume fever at high exposure levels. As a result, OSHA has recommended a PEL-TWA of 0.1 mg Cu/m<sup>3</sup> as copper fumes and 1 mg Cu/m<sup>3</sup> for copper dust and mist (Poisindex® 2001). However, the duration of symptoms is short, often dissipating in a day. Also, systemic effects such as lung inflammation have been reported in animals exposed to copper by inhalation (1.3-1.6 Cu/m<sup>3</sup>/1hr) (Chen et al. 1991; Hirano et al. 1990; Hirano et al. 1993).

Acute and chronic exposures to copper compounds have caused systemic effects in humans. Acute exposure to relatively low levels of copper led to gastrointestinal effects. For example, a 1957 recreated case of acute ingestion of copper-tainted cocktails resulted in gastrointestinal symptoms at a single dose of 5.3-32 mg Cu (Wyllie 1957). Also, studies have shown that consumption of less than 1 mg Cu has led to nausea and vomiting (Olivares et al. 2001). Acute ingestion of greater amounts of copper (225-800 mg Cu) has led to severe hepatic and renal toxicity and also death (Karlsson and Noren 1965; Stein et al. 1976). Chronic exposure to copper in contaminated tap water has led to hepatotoxicity in infants and young children (2.2-26 mg Cu/L) (Mueller-Hoecker et al. 1988; Dieter et al. 1999; Trollmann et al. 1999). An adult also suffered from liver failure after supplementing his diet with 30-60 mg Cu/day for 2 years (O'Donohue et al. 1999). Therefore, copper compounds may be considered 'known to be toxic in humans' by the oral route as defined in the FHSA, based on sufficient evidence of systemic effects in humans as seen in case studies.

Individuals may suffer from excessive retention of copper due to a genetic disorder of transport and/or excretion of copper, although normal levels of copper are ingested. This disorder, called Wilson's disease, can lead to hepatic and renal lesions as well as hemolytic anemia if not treated (Barceloux 1999). Other manifestations of disorders in copper metabolism are Indian Childhood Cirrhosis (ICC) and Idiopathic Copper Toxicosis (ICT). These genetic diseases are defined by a deficiency in copper transport and/or excretion and lead to a predisposition to massive accumulation of copper in the liver in response to increased ingestion of copper (for example from food prepared/stored in copper vessels or from contaminated tap water) (Barceloux 1999).



Therefore ICC and ICT, unlike Wilson's disease, require ingestion of higher levels of copper to be expressed. Infants are also more susceptible to copper toxicity, due to a greater inherent copper liver concentration at birth and undeveloped homeostatic mechanisms protecting against excess copper absorption from the gastrointestinal tract (NRC 2000). Therefore, there are population subsets that are genetically or developmentally predisposed to copper toxicity.

In order to calculate an acceptable daily intake (ADI) value for copper, NOAEL and/or LOAEL levels need to be determined. A 12 week clinical study observed an NOAEL of 0.14 mg Cu/kg/day for gastrointestinal, hematologic and hepatic effects (chronic studies summarized in Table 4) (Pratt et al. 1985). The maximum acceptable daily intake value (ADI) based on this NOAEL would be 14  $\mu$ g Cu/kg/day, as calculated by dividing the NOAEL of 0.14 mg Cu/kg/day by a safety factor of 10 for interindividual variation. This ADI value represents the consumption of 1000  $\mu$ g Cu/day in an adult (multiplying the ADI by the mean body weight of an adult, 71.5 kg) (EPA 1997). This value is equivalent to the Food and Nutrition board's Recommended Daily Allowance (RDA) level for copper in an adult of 900  $\mu$ g Cu/day (Table 3) (IMO 2001). Also, the actual average intake of copper in the adult US diet has been reported to be greater than 1000  $\mu$ g Cu/day (Turnlund 1988). Therefore, total copper exposures (dietary and environment) that do not surpass the age-specific RDA are not expected to present a hazard.

Copper is poorly absorbed through the intact dermal layers. Effects of dermal copper exposure are limited to potential localized allergic reactions.

The Federal Hazardous Substances Act (FHSA) defines a "hazardous substance" as a substance that satisfies both parts of a two-part test. To meet the statutory definition of a hazardous substance, a product must first present one or more of the hazards enumerated in the statute, that is, it must be toxic, corrosive, flammable, an irritant, a strong sensitizer, or generate pressure through decomposition, heat, or other means. Second, the product must have the potential to cause substantial personal injury or substantial illness during or as a result of any customary or reasonable foreseeable handling or use, including reasonably foreseeable ingestion by children. Consumer exposures to copper from playground equipment are most likely to occur through oral and dermal routes.

In evaluating the potential hazards presented by copper chemicals, the Commission staff has followed the definitions for toxicity (both acute and chronic), irritation, and sensitization in the FHSA and its implementing regulations, 16 C.F.R. §1500.

In the rabbit and rat, the lowest LD<sub>50</sub> values were 50 and 66 mg Cu/kg respectively, although the guinea pig showed a value of 15 mg Cu/kg and a lethal dose in the mouse was 20 mg/kg (Table 2) (Eden and Green 1939; Lehman 1951; NIPHEP 1989; Venugopal and Luckey 1978). The LD<sub>50</sub> values for copper compounds were widely variable due to differences in species sensitivity to copper. It is determined by the Commission staff that copper compounds meet the definition of acutely toxic by the oral route as defined in the FHSA, based on these animal studies.

Inhalation studies determined an LC<sub>50</sub> value >1303 mg Cu/m<sup>3</sup> was calculated after inhalation exposure in the rabbit, although the time of exposure was not indicated (Tomlin 1994).

Exposure of the guinea pig to 1.3-1.6 mg/m<sup>3</sup> of copper aerosol for 1 hour led to respiratory symptoms, but did not result in death (Chen et al. 1991, Hirano et al. 1990, Hirano et al. 1993). The LD<sub>50</sub> values for dermal exposure of copper in the rat and rabbit are greater than 1-2 g Cu/kg/day (NIOSH 1993, Tomlin 1994). It is concluded that copper is not acutely toxic by the inhalation and dermal routes of exposure as defined under the FHSA.

It has been shown that copper is a mild skin irritant, and may cause allergic dermatitis with extended contact.

It is the staff's opinion that there is not sufficient evidence based on human and animal studies to show that copper meets the definition of a mutagen or carcinogen under the FHSA. The US EPA has determined that copper is not classifiable as to human carcinogenicity (EPA Classification D, EPA 1987).

Changes in rat brain biochemistry involving dopamine and norepinephrine levels were seen in response to copper administered by injection and in the diet (2 mg Cu/kg/day and 12-46 mg Cu/kg/day respectively)(WHO 1998; NRC 2000). However, behavioral changes were not shown. These observations suggest that copper meets the definition of a possible neurotoxic substance under FHSA based on limited animal data.

Case reports in the literature of copper exposure to humans do not give evidence of developmental or reproductive effects. In rats, reproductive effects such as depressed hormone levels, decreased sperm incidence and hypertrophy of the ovaries and uterus have been seen in rats in response to copper administration (2.5 -19.6 mg Cu/m<sup>3</sup> aerosol, 2 - 3 mg/kg/day i.p., 82-120 mg Cu/kg/day oral) (Gabuchyan 1987; Chattopadhyaya et al. 1999; Harrisson et al. 1954; WHO 1998). These data suggest the copper meets the definition of a possible reproductive toxicant under FHSA based on limited animal data.

Oral administration of copper (65-155 mg/kg/day) and i.p. injection of copper (10 mg Cu/kg) have led to developmental abnormalities in several species. Decreased neonate body weight and increased neonate mortality was seen when copper (1.3-12 mg/Cu/kg/day) was orally administered to lactating females (Aulerich et al. 1982; Kasama and Tanaka 1988; WHO 1998). Copper meets the definition of a possible developmental toxicant under FHSA due to limited available animal data based on quality of experimental designs.

Copper may meet the statutory definition of 'toxic' by oral route of exposure under the FHSA, however a quantitative assessment of exposure and risk must be performed to determine whether a household substance would appear to satisfy the second element of the statutory definition when present in playground equipment as a result of the use of wood treated with CCA in its construction.

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**TAB G**



UNITED STATES  
CONSUMER PRODUCT SAFETY COMMISSION  
WASHINGTON, DC 20207

**Memorandum**

Date: January 13, 2003

TO : Patricia Bittner, M.S., Project Manager  
CCA-Treated Wood in Playground Equipment  
Directorate for Health Sciences

THROUGH: Hugh McLaurin, Associate Executive Director *Hmm*  
Directorate for Engineering Sciences  
Robert Ochsman, Ph.D. *RO*  
Director, Division of Human Factors (ESHF)

FROM : Jonathan D. Midgett, Ph.D. *JDM*  
Engineering Psychologist, ESHF

SUBJECT : Children's Contact with Playground Structures

In June 2001, the CPSC docketed a petition by the Environmental Working Group and the Healthy Building Network to ban the use of chromated copper arsenate (CCA) treated wood in playground equipment. In response to this petition, CPSC staff began to assess the health risks associated with exposure to CCA pressure-treated lumber used in playground equipment. The CPSC staff has undertaken several studies to assess the transfer of arsenic to the hand as a result of rubbing pressure-treated lumber. These data will be used to estimate risks to children of arsenic exposure from playing on playground equipment made with CCA-treated wood.

The risk assessment requires information about certain variables of child behavior related to playground use. Specifically, the CPSC staff conducting hand-wipe studies of CCA-wood need to know a broad-spectrum estimate of the amount of surface area a child might contact during a typical play episode on a playground. Another memo addresses the annual frequency of visiting a playground (Midgett, 2003). The estimate in this memo will provide the rationale to support the size of the surface area rubbed during the hand-wipe studies. The CPSC's Division of Human Factors (ESHF) has been asked to address the rate of children's hand contact with playground structures during normal use. Less common avenues of exposure to CCA residues are also possible, such as contact with soil under a structure, contact with decks, direct mouthing of handrails or other surfaces, eating directly from picnic tables, or other activities. Although these other avenues of exposure are not included in this particular risk calculation, they could contribute to the total exposure of a child to arsenic.

Consistent with common developmental milestones in children's play, we assume that playgrounds are of key interest for children aged 2 to 12 years. Younger children have not achieved the gross-motor skills necessary for full enjoyment of most play structures without

significant caregiver supervision, and by age 12, most children choose group activities and team sports over play structures. Since the children most likely to ingest CCA-wood residues from hand-to-mouth contact are younger than 7 years (Freeman, et al., 2001), this discussion defines the critical playground users to be children aged 2 to 6 years.

### **Extent of Playground Visits:**

To determine how long children play on playground structures, several sources were examined. The U. S. Environmental Protection Agency (EPA) Exposure Handbook (EPA, 1997) cites a study by Tsang and Klepeis (1996) using the National Human Activity Pattern Survey's (NHAPS)<sup>1</sup> responses made about the behaviors of thousands of children aged 3-11 years. The factor "Time spent on a schoolground/playground" showed an average of 88 minutes per day for 5-11 year olds (n=64). The 95th percentile spent 220 minutes per day. It is not clear that participants in this study differentiated the time spent playing from time just spent 'physically on' school grounds. The maximum time reported was over 10 hours. Because this mean seems skewed by such extremes, it seems reasonable to avoid the mean for this group and to use, instead, the 50<sup>th</sup> percentile report, i.e. 60 minutes, as an estimate of the average time of a playground visit. This was the EPA's approach in a preliminary risk assessment (EPA, 2001) of children's exposure to arsenic from CCA-treated playground structures.

A different approach used by Gradient Corporation's (2001) risk assessment prepared for Arch Wood Protection and Osmose Corp. includes a 1-hour estimate and the 90<sup>th</sup> percentile (2.9 hours/day) for the risk assessment inputs, however, they calculated day-equivalents based on playground exposure for every day of the year. It is unlikely that children will visit a playground every day of the year. Although it is possible, this is likely an overestimate of exposure. In a report prepared for the American Chemistry Council, Exponent (2001), a consulting firm, acknowledges the difficulties of finding a central tendency measure for such a variable activity and avoids describing a frequency average by suggesting that a *daily risk* estimate be created for later tailoring to various geographic regions with different climates. Of these disparate approaches to estimating the extent of a playground visit, HF staff favors the EPA's use of an hour estimate for the average playground visit's length, per day.

### **Hand Contact with Play Equipment:**

HF staff members are not aware of any research that has focused on the ways that children contact play equipment. Therefore, HF staff estimated the amount of wood that might be touched during a play episode by viewing several hours of CPSC video footage, filmed for a different project, of children playing on playground equipment. Since these videos were made for a different purpose, no information was gathered from participants. The children ranged in age from toddlers to adolescents. The following qualitative observations were made while observing playing children.

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<sup>1</sup> The National Human Activity Pattern Survey (NHAPS) was conducted for the EPA from 1992 to 1994. The NHAPS database describes activity patterns for 9,386 subjects over a 24-hour day and has been extensively used for exposure studies. More information is available at <http://www.epa.gov/headsweb/edrb/hap.htm>.

Children contact the play equipment in various ways while playing. They grasp, wipe, and push off of the equipment, giving certain key parts of the structure repeated contacts. These key contact points, on ladders, the tops of cross-members, railings, and supports, may receive significant touching during a play episode. Children's grasping capabilities aid locomotion and provide balance and support. Sometimes children wipe surfaces in an exploratory way, to clean off a spot before sitting down, or to improve their grip or balance. Some significantly forceful wipes occur as children launch their bodies off one part of the equipment to another or jump to the ground. Some very light contacts occur as children casually lean against a post, beat out a tune while waiting in line, or steady themselves while balancing. These various kinds of hand contact occur in all sorts of combinations with varying degrees of forcefulness and proportions of the palm surface used. Sometimes just fingertips graze the structure. Other times, the entire palm is pressed forcefully against the equipment. A more detailed task analysis of play would be beyond the scope of the current discussion and would require controlled observation of different categories of playground equipment.

After several hours of observing these anonymous subjects, few definitive conclusions can be made due to the dearth of information about the subjects viewed. The videos were made to observe the use of play equipment, so a single child was seldom followed for longer than it took him/her to traverse a bridge or climb an incline. However, counting hand contacts for ten-second periods gives a general idea of the rate of contact and the pace of play. Naturally, these rates vary a great deal from child to child, but the children on these videos touch the play equipment from 2 or 3 times to 50 times per minute, depending on their activity. The most active children generally explore all ways of mounting the equipment until they find a sequence of activity that they like and then often repeat that sequence over and over, sometimes with a long line of comrades. The youngest children's pace of play is slow, cautious and plodding. Most hand grips and foot placements are carefully weighed. Many are just gentle balancing motions. Watching the various rates of contact, one can derive only an *extremely tentative* estimate that children may contact the play equipment an average of about 15-30 contacts a minute. These contacts are mostly light pushes or grasps, and a few forceful wipes. At this rate however, children might touch some part of a play structure, any part, with their hands about 900-1800 times an hour. Most of these touches would involve light contact with part, but not all, of the hand. Most touches will occur in key contact points on the equipment that are repeatedly touched by children many times over. Contacts vary from very forceful to very light. Not all contacts scrape or slide across the wood's surface.

An estimate of how often children contact wooden portions of play equipment will need to account for the fact that few play structures are totally wooden. Most include metal, rubber, and plastic supports and surfaces as well as wood. Many common supports on play structures are made from round metal bars and this is probably where the most forceful contacts occur. Forceful contact with wood is less common than with metal because of the risk of splinters.

A final estimate of the extent of exposure to dislodgeable wood residues must account for variation within the pace of play of children at various ages, the type of equipment, the forcefulness of the contact events, the amount of the hand used, and the percentage of wooden playground parts. Due to the lack of empirical data on these factors, any estimate will be

extremely tentative. The following educated guess of the amount of wood contacted/hour by 2- to 6-year-old children on some unknown "average wooden play structure" divides the types of contact, the types of materials comprising the key contact points, and the amount of the hand's surface area into thirds. Under this assumption with this model, a third of the contacts may be on metal, a third on wood, and a third on rubber/plastic. A third of the contacts may be with the whole hand, a third with 2/3 of a hand, and a third with 1/3 of the hand or less. A third of the contacts may be very forceful and include the average child's entire weight, a third may be 2/3 of their weight, and a third may be 1/3 of their weight or less. This yields 300 contacts an hour with a wood surface, if we choose the lower end estimate of 900 contacts/hour. Choosing the lower number is a reasonable starting point because the children most likely to have the highest rates of hand-to-mouth activity are the youngest children in the relevant age range (2-6 years). Younger children also play with the slowest pace on equipment because they have the most immature physical skills. Of these 300 contacts, a hundred contacts may use the whole-hand, a hundred may include contact with most of the hand, and the last hundred may involve just a small portion of the hand. As mentioned above, many, possibly most, of these contacts will be on key contact points that are repeatedly touched by equipment users. A third of the whole-hand contacts may be heavy, a third moderate, and a third light, etc. The average 2-6 year-old's hand is 64 cm<sup>2</sup> (Snyder et al, 1977). This means that the visits to a playground will *average* 300 touches with 2/3 of the palm area (43 cm<sup>2</sup>) or about 12,900 cm<sup>2</sup> contacted/hour (300 X 43 cm<sup>2</sup> = 12,900 cm<sup>2</sup>) with a moderate force.

Calculating the number of whole-hand contacts/hour using the average area touched per hour, one would expect an average of about 200 *whole-hand* contacts/hour ( $12,900/64 \text{ cm}^2 = 201.6$  contacts) with moderate force. These "average hand contacts" are a middle-point of activities, representing an aggregate of several light touches using partial palm contact and one or two forceful ones. The activities of the playground, which we will call "play events", generally involve a sequence of actions. For instance, the child climbs up a ladder, sits at the top of a slide and then slides down. Or, they climb an inclined chain mesh, mount a platform, cross a bridge, and then slide down a pole. This sort of "play event" makes up a basic activity common to the playground and includes several hand contacts with play equipment. If the average pace of activity includes about 200 average hand contacts/hour and is spread equally over the hour, we might reason that this equals about 100 two-handed "play events"/hour, or about 1.6 play events/minute, or one "play event" every 38 seconds. Given the pace of play observed in the videos, an empirical study of playing 2- to 6-year-old children, with operationalized and quantified "play events," would likely find a rate of play very near this estimate, with the exception of swings, which tend to engage children for longer periods. While no such formal study has been done, the numbers in this discussion can be treated as reasonable estimates.

### **Extent of Exposures:**

Although children may not be getting residue on their hands the instant they arrive at the playground, they will be carrying the residues from their playground exposure for some time after they leave the playground, thus stretching their exposure beyond the 60 minutes of playtime. Playing children should also be expected to occasionally wipe their hands on their clothes, easily transferring some amount of residue from their hands to their clothing. This

residue might then be transferred back to the hands, thereby extending exposure to that residue beyond the time of their visit to the playground. Studies of wood residue availability have shown that sometimes cloth wipes can pick up more residues from lumber than bare skin (Levenson, 2003). Use of play equipment will involve hands and other body parts, like knees, thighs, forearms, and elbows, which are often covered with clothing that may pick up CCA residue as well as, or possibly *better than*, bare skin, depending on the fabric. For instance, children preparing to leap from a platform often sit down first and then slide off the edge. This maneuver will forcefully scrape the backside of their pants across the surface edge of the platform, possibly picking up wood residues. Climbing children lift themselves on play structures by using their forearms, knees and elbows as fulcrums of action, giving these body parts and the clothing covering them rough use during some play events. The fabric covering knees and elbows, especially on outerwear that is worn repeatedly between washings may dislodge some amount of residue from wooden structures. Since some patterns of play and rest are anticipated throughout a child's day, we may expect certain areas of homes, schools, or family vehicles to get repeated exposures to dirty hands and clothes, and to accumulate higher concentrations of residue than other areas of the home. For instance, storage places for coats and jackets might be particularly susceptible to accumulations of residue because these types of clothes are frequently worn many times between washings and are most likely to be soiled while playing. Since outdoor play frequently precedes television viewing, we may expect that the leisure areas in family rooms, like sofas, recliners and the rug in front of the television, to dislodge outdoor residue from children's clothing. Such areas with repeated accumulations of wood residues may contribute to non-play related exposures to arsenic during other parts of children's daily schedules.

Additionally, playground use can also include some play activities in the soil, gravel, sand, or other protective surfacing beneath play structures. The soil around a play structure may also contain residues from the wood above it.

Also, in extreme, but possible, cases, pre-schoolers, especially the 2 to 3 year olds, may occasionally directly mouth portions of a play structure, such as a railing, stair, or cross-beam. This behavior is not likely to be frequent for most playground users, however, if observed by a caregiver it would be unsurprising behavior. Children under 3 constantly explore their world with their mouths.

Splinters are also possible wherever lumber is used. Children may occasionally get a splinter during their playground visits.

Finally, many common playsets include a platform area, or "fort," often covered with a roof, which offers a resting/seating spot on the playground. These platforms can be used for picnics, snacks, tea parties, or other such play activities. It is likely that many playground users will occasionally bring food and drinks to a play structure. During a picnic, food may sometimes be placed directly on wood structures.

Staff members are not aware of any studies of these additional routes of possible exposure.



## Summary:

While only limited data are available to support conclusions regarding the nature of children's contacts with playground structures, HF staff recommends conservative estimates of playground contact behavior for the proposed risk assessment and hand-loading study. Two to 6 year old children may be likely to visit a playground for about an hour per day. During this hour it is reasonable to estimate that they may contact the structure 900 times or more, touching wooden parts 300 times or more, touching about 12,900 cm<sup>2</sup> of wood at mostly key contact points that are repeatedly touched by playground users. Their clothes may dislodge and carry wood residues for some time after their playground visits end, surfaces beneath play structures may engage them during play, direct mouthing of structures may sometimes occur, splinters are possible, and food consumption may occur on play structures. All these estimates could be empirically verified.

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UNITED STATES  
CONSUMER PRODUCT SAFETY COMMISSION  
WASHINGTON, DC 20207

Memorandum

Date: January 13, 2003

TO : Patricia Bittner, M.S., Project Manager  
CCA-Treated Wood in Playground Equipment  
Directorate for Health Sciences

THROUGH: Hugh McLaurin, Associate Executive Director *Hmm*  
Directorate for Engineering Sciences  
Robert B. Ochsman, Ph.D. *RBO*  
Director, Division of Human Factors (ESHF)

FROM : Jonathan D. Midgett, Ph.D. *JDM*  
Engineering Psychologist, ESHF

SUBJECT : Playground Usage Estimate for CCA-Wood Risk Assessment

In June, 2001, the CPSC docketed a petition made by the Environmental Working Group and the Healthy Building Network to ban the use of chromated copper arsenate (CCA) treated wood in playground equipment. In response to this petition, CPSC staff began to assess the health risks associated with exposure to CCA pressure-treated lumber in playground equipment and has undertaken a risk assessment to estimate risks to children from playing on equipment made with CCA-treated wood.

This assessment requires information about certain variables of child behavior related to playground use. Specifically, the CPSC's Division of Human Factors (ESHF) has been asked to address the rates of playground use during early and middle childhood. Another memo (Midgett, 2003) addresses the length of the average visit and the amount of surface area contacted during the visit.

Consistent with common developmental milestones in children's play, we assume that playgrounds are of key interest for children aged 2 to 12 years. Younger children have not achieved the gross-motor skills necessary for full enjoyment of most play structures without significant caregiver supervision, and by age 12, most children choose group activities and team sports over play structures. Since the children most likely to ingest CCA-wood residues from hand-to-mouth contact are younger than 7 (Freeman, et al., 2001), this discussion defines the critical playground users to children ages 2 to 6 years.

**Playground Visits:**

Few studies exist about playground usage. The following discussion describes several ranges of

likely central tendency estimates for yearly playground visits. Note, however, that the actual range is quite restricted (0 to 365 days/year). Arriving at a reasonable estimate for a risk analysis is relatively straightforward.

A study in Canada by Butcher (1993) of 64 active 7-9 year olds attending a summer sports camp offers some relevant data on the subject. This study explored the effects of parental socialization, such as providing practice opportunities and direct playground involvement, on children's gross motor skill development. To do this, the researcher needed to ascertain the frequency of the children's playground visits. Frequencies were reported as a parental estimate of monthly and weekly visiting rates for three types of playgrounds. Butcher found that parents reported a *composite average of 3.5 visits per week to playgrounds outside of school, ranging from once/month to more than 4 times/week, depending on the type of playground*. About 20% of the respondents reported *seven or more visits per week* outside of school hours, but a definition of what constituted 'a visit' was not given. These reports included visits to playgrounds at home, public parks in walking distance, and parks within driving distance. A "playground" was broadly defined as an outdoor space with play equipment. The most common equipment mentioned by participants was a swing. All but one home with equipment had a swing. Very few homes had other types of equipment. Because a "playground" was so broadly defined, the estimated rate of visits from this study likely overestimates the rate of visits to playgrounds constructed with CCA-treated lumber. This study included any playground, such as those constructed of metal, plastic, concrete or other composite materials, as well as those made of CCA-treated lumber. Although this study can be used to estimate the rates of visits to playgrounds, it should not be construed to predict exposures to playgrounds specifically with CCA-treated lumber. It includes all playgrounds, even those with just a swing.

The average rate of playground visiting outside of school found in Butcher's study was about 0.5 visits per day (3.5 visits/week) for this sample of 7- to 9-year-old children. We assume that this average is a conservatively high estimate because the participants were attending a sports camp during this study. Sports camp participants would probably be leading an active lifestyle. These participants would also likely represent an upper middle class group judging from the distribution of single family dwellings in the sample compared to apartments. Attending a sports camp may also indicate upper middle class income levels. Also, since parents were answering the questions in this study during the summertime, we can assume that they answered with their then-current summer activities in mind and would have likely assumed that the question did not refer to winter rates of playground visiting. Winter estimates would likely have produced lower rates in their geographic location (Manitoba). For at least the summer months, participants reported this average rate of 0.5 visits per day. These reports are also subject to inflation by social desirability because the study was exploring socialization and parents may have wanted to appear to the researcher as if they were active, involved parents (apt to support their child's socialization skills and physical development). Since this analysis is based on estimates that so broadly define what constitutes a playground, originate with active families attending a sports camp, and rely on parental self-reports possibly affected by social desirability, the chosen risk assessment input should probably be closer to the lower side of the reported range of 1 to 7 times/week. Accounting for these limitations, the average North American child probably visits some sort of playground 2.5 to 3 times per week.

At a rate of 3 times a week, children may visit playgrounds, including at-home and public playgrounds, about 156 days a year in warm climates (52 weeks/year X 3 visits/week = 156 visits) and 120 days a year in colder regions (40 weeks/year X 3 visit/week = 120 visits).

Children in school and in daycare have more scheduled access to playgrounds, usually at least once a day. Given that most children aged 2 to 6 years are not in school (school attendance typically begins around 5 years of age), as a population they have less regularly scheduled access to playgrounds than children in school, unless they are in full-time daycare. In 1997, 35% of preschoolers were in a non-relative's care, 20% in an organized child care facility, for an overall average of 37 hours/week (Smith, 2002).

Scheduled access to playgrounds is affected by weather. The National Weather Service has posted average precipitation rates in hundreds of U. S. cities (1993). The average rate of days with precipitation for these cities is 32% of the year. Preschool children in full-time daycare in warm climates could have up to 230 days a year with scheduled access to a playground (5 days/week = 260 days in daycare minus the 32% rained-out days, or about 177 days). Then, to account for weekend visits, they may have about 53 more (105 weekend days at a rate of 0.5 visits/day = 52.5 visits), reaching about 230 visits a year for children in full-time daycare in temperate climates.

Since school-age children have access to school playgrounds for about 180 days per year minus an average 32% rained-out days (National Weather Service, 1993), we assume that these children have 122 days per year of clear-weather access to school playgrounds plus their extra-curricular access on weekends and vacations. The total number of weekend days and vacations, excluding school days, is about 185 days. Using the average number of visits per week leaves a possible 78 visits for weekends and vacations (26 weeks X 3 visits/week = 78 visits) throughout the year. These 78 visits, plus the 122 clear days for school playground access, equal 200 visits to a playground. This would be the conservatively high estimate for school-age children living in very temperate climates with year-round play and includes visits to home playgrounds, some with just a swing, and other public playgrounds.

For a central estimate, HF staff favors 156 days, which is an average of 3 visits a week, for the most active children in temperate climates. Less active children will likely visit playgrounds less, perhaps an average of twice per week. This would yield a lower-range rate of 104 visits per year. A large amount of variability across children is expected in an activity like playground visitation. Rendered graphically, such a variable activity would appear as a low and flat curve (see Figure 1). This means that a significant portion of the population will fall within the higher visitation rates.

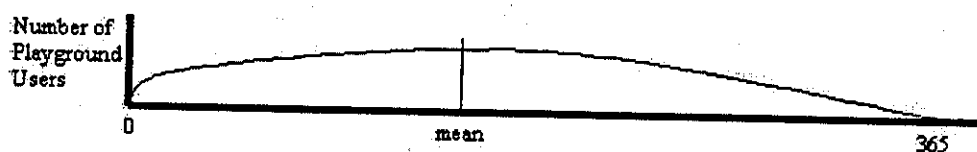


Figure 1: Expected Curve Shape of Playground Visitation Rates (Days/Year)

Other relevant discussions of playground usage agree with this hypothesized range, although arriving at it via different approaches. The EPA's (2001a) discussion suggests that 130 days per year seems appropriate as an estimate of an "intermediate term exposure" (p. 6). The EPA's Scientific Advisory Panel (SAP) (2001b) disagreed and cited the National Human Activity Pattern Survey (NHAPS)<sup>1</sup> which found that on any given day, only 40% of half of 1-4 year olds play outside on the kinds of substrates (gravel, sand) found under play equipment. This finding may or may not apply to playground usage because the types of substrates under playgrounds vary so much. Respondents in that study would be reflecting on a wide range of experiences. Since they were not asked specifically about 'playground visiting' in that item, it is questionable to apply their responses to the issue of playground exposure.

In their comments on the EPA's draft risk assessment of children's exposure to arsenic from CCA-treated play sets, Exponent (a consulting firm)(2001), suggested that children visit playgrounds an average of 100 days/year. This was based on an assumption that children spend 10% of their playtime on playground equipment. This 10% assumption has no supporting rationale. Since EPA (2001a) was attempting to frame a "worst-case child residential exposure to CCA-treated wood" (p. 6) it is more valid to use a higher percentage, or all, of children's estimated outdoor playtime. This approach was taken in the Gradient risk assessment (2001), which estimated exposures for the average playtime (1 hour/day) and the 90<sup>th</sup> percentile (2.9 hours/day) for 2- to 6-year-olds for 365 days a year. This is probably an overestimate of playground visitation rates.

## Conclusion

The lowest central tendency estimate for playground visitation rates given by any stakeholder in the CCA-wood debate was 100 days/year. The preceding HF analysis suggests that EPA's use of an average playground visitation rate of 130 days/year is a reasonable estimate. While HF staff prefers a central estimate of 156 visits/year, staff acknowledges a large variation in average visitation rates across geographical regions, from as little as 104 visits/year to as many as 230 visits/year in the most temperate climates. These estimates could be empirically verified.

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<sup>1</sup>The National Human Activity Pattern Survey (NHAPS) was conducted for the EPA from 1992 to 1994. The NHAPS database describes activity patterns for 9,386 subjects over a 24-hour day and has been extensively used for exposure studies. More information is available at <http://www.epa.gov/headsweb/edrb/hap.htm>.

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**TAB H**





UNITED STATES  
CONSUMER PRODUCT SAFETY COMMISSION  
WASHINGTON, DC 20207

**Memorandum**

Date: January 23, 2003

**TO :** Patricia M. Bittner, M.S.  
Project Manager, CCA-Treated Wood in Playground Equipment Petition  
Directorate for Health Sciences

**THROUGH:** Mary Ann Danello, Ph.D., Associate Executive Director,  
Directorate for Health Sciences *md*  
Lori E. Saltzman, M.S., Division Director, Directorate for Health Sciences *ls*

**FROM :** Treye A. Thomas, Ph.D., Toxicologist *TT*  
Directorate for Health Sciences

**SUBJECT:** Determination of Dislodgeable Arsenic Transfer to Human Hands and  
Surrogates From CCA-Treated Wood

**Executive Summary**

**Background**

CPSC staff has completed a series of investigations that estimated the potential exposure of young children to arsenic (As), while playing on playground equipment composed of CCA- (chromated copper arsenate) treated wood. In June 2001, CPSC docketed a petition from the Environmental Working Group (EWG) and the Healthy Building Network (HBN) to ban the use of CCA-treated wood in playground equipment. In response to this petition, CPSC staff conducted a risk assessment that quantified the potential increase in lifetime risks of lung or bladder cancer to children exposed to CCA-treated wood in playground equipment. A major factor in the determination of the potential risk was the quantification of the intake of arsenic (As) for children who contact CCA-treated playground structures<sup>1</sup>. By estimating the exposure to As resulting from hand contact with treated structures, the lifetime risk of lung and bladder cancer for exposed children was estimated.

The primary objective of the investigation was to estimate the amount of As that might be transferred to a child's hands during normal play activities on CCA-treated playground structures. A secondary objective was to create a standard protocol that could be used to quantify As transfer from pressure-treated wood.

<sup>1</sup> While CCA also contains chromium and copper, CPSC staff believe that As carcinogenicity is the most sensitive endpoint for human health effects.

## Hand Sampling of Decks

CPSC conducted field studies to estimate the amount of As that can transfer to hands in contact with CCA-treated decks and playsets. In the first portion of the field study, CPSC staff used bare adult human hands to sample decks made from CCA-treated boards. Eight decks at homes in the Washington, DC metropolitan area were tested, which allowed staff to estimate As migration with boards of a variety of ages, use patterns and surface treatments, as well as exposure to the elements typical of conditions CCA-treated wood would likely experience during consumer use.

A total of eight volunteers were involved in the investigation. A board selection and randomization scheme was established by CPSC's Hazard Analysis (HA) staff, and was used to locate boards on each deck for sampling and randomly determine the order of sampling for 5 sections of each board (Levenson, 2003b). Upon arrival at a deck site, boards were selected at varying locations on the deck that would reflect different traffic and use patterns. The boards were labeled 1, 2, 3, and 4 with a numbered placard placed on each board designating the number. A photograph was taken of each board with the numbered placard in order to assist in locating the board if any further sampling was needed. The photographs were useful to recall the condition of the boards. The selected boards were divided into five sections labeled a, b, c, d, and e.

The randomization scheme outlined which sampling operation would occur on a specific board in a particular sequence (Levenson, 2003b). Hand rubbing was performed on two of the five sections, one section for a 10-rub sequence, and another for a 20-rub sequence. The 10- and 20-rub sequences were later compared to determine if there were significant differences in As transfer between them. The other sections were used to sample boards with wet polyester cloth, dry polyester cloth and high-density polyethylene (HDPE) surrogate materials.

Prior to rubbing each board, the hands of volunteers were washed thoroughly with soap and water and rinsed with deionized water, which was collected and analyzed for As contamination. After rubbing a CCA-treated board on a deck, the rigorous rinse-wipe-rinse (RWR) procedure was utilized to remove the As from the hands for analysis. This procedure was performed twice. A detailed description of the methods used in sampling, and the methodology for board selection and assigning volunteers to decks can be found in other CPSC staff memos (Cobb and Davis, 2003; Levenson, 2003b).

Volunteers rubbed two boards at two different locations on each deck. The selected boards were rubbed 10 and 20 times in two 700 cm<sup>2</sup> sections. The sum of the rubs comprising the sampling scheme resulted in 64 samples on 32 deck boards from eight decks. The decks were also wiped with wet and dry polyester cloths and HDPE material for 10 back-and-forth rub sequences (800 cm<sup>2</sup> X 10 rubs).

The rinsates from the hands and the surrogate materials were prepared for analysis by digestion with nitric acid (Cobb, 2003). Following preparation, the samples were analyzed simultaneously for As by Inductively Coupled Plasma Spectroscopy (ICP). Quality control measures were utilized in the laboratory analysis. A detailed description of the laboratory and sampling methods can be found in another CPSC staff memo (Cobb, 2003).

The amount of As transferred to hands varied significantly among decks ( $p < 0.001$ ), and was not due to the volunteer effect. The estimated (geometric mean) concentration on the hands ranged from a high of 20.9  $\mu\text{g}$  to a low value of 1.0  $\mu\text{g}$  total As per hand, with a mean value of 7.7  $\mu\text{g}$  and a median of 4.8  $\mu\text{g}$  (Levenson, 2003b). Measureable amounts of As were transferred to bare hands on all of the eight decks sampled, regardless of age and surface treatment. Potential effects of the age and maintenance of the deck on As migration cannot be determined from these experiments.

The relationship between the transfer of dislodgeable As to bare hands and that to a polyester cloth was investigated. The polyester cloth was tested in two forms, dry and wetted with a 2% saline solution. The relationships (correlation coefficients ( $r$ )) between the bare hands and wet polyester ( $r = 0.79$ ,  $p < 0.01$ ) and dry polyester ( $r = 0.91$ ,  $p < 0.01$ ) were statistically significant. The conversion factors (CF) for translating surrogate measurements to hands are 0.08 for wet polyester and 0.20 for dry polyester. Translating these values to hands suggests that a bare human hand will extract approximately 20% of what the dry polyester will remove from rubbing an equivalent area of wood. For example, if the dry polyester extracts 100  $\mu\text{g}$  from a wood surface, a hand is expected to remove 20  $\mu\text{g}$  from the same wood surface.

These results suggest that the dry polyester cloth can be used to estimate the As transfer from wood surfaces that would occur with bare hands with a reasonable degree of confidence. The polyester cloth also has the advantage of being durable, relatively inexpensive, and is not difficult to analyze. The dry form of the polyester cloth was used in deck and playset sampling because it had the closest association with bare hand values. Along with the surrogates, the sampling template proved to be an effective device when sampling both horizontal and vertical board surfaces (Cobb, 2003).

### **Surrogate Sampling of Playsets**

The second portion of the field investigation involved sampling 15 residential playsets, including 3 non-CCA-treated control playsets, with the dry and wet polyester materials for dislodgeable As from boards. The playgrounds represented a variety of ages and surface treatments in homes in the Washington, DC metropolitan area. Some of these structures were in use by their owners while others had not been used for several years. Some of the wood used to construct the playsets was provided by playset manufacturers, while other playsets were made of wood purchased by the consumer.

The surrogate materials were attached to the sampling template that was designed and tested by the Laboratory Sciences Chemistry (LSC) and Laboratory Sciences Mechanical (LSM) staff (Cobb and Davis, 2003). The materials were wiped across the wood surface for 10 strokes of approximately 400  $\text{cm}^2$  to estimate the amount of As that would be removed from 14,000  $\text{cm}^2$  (10 back-and-forth strokes of 400  $\text{cm}^2$ ) of wood surface that is subjected to repeated hand contact.

The results of the playset sampling are similar to the deck sampling. The polyester wipe data from the playsets was converted to bare hand values by multiplying the values by 0.2 (conversion factor) and compared with the actual bare hand values from the deck sampling. The

overall converted "bare hand" mean dislodgeable As of 7.6 µg (median = 3.5 µg) for the 12 play sets composed of CCA-treated wood was comparable to the overall mean dislodgeable As from the 8 decks sampled with bare hands which was approximately 7.7 µg (median = 4.8 µg). When the dry polyester values for dislodgeable As from decks (n=8) and playgrounds (n=12) were combined and converted to "bare hand" estimates, the overall mean of the 20 structures is 7.9 µg.

Although there was wide variation among the individual playsets and decks, the results of these studies suggest that when hand or surrogate samples are taken from a variety of wood ages and treatments, the average As levels on the hands and surrogates may be comparable for the various sampling sets.

Table 1. Removal of Arsenic by Hands and Surrogates

CCA-Treated Wood Source	Mean (µg)	Median (µg)	Converted "hand" value (µg)	N
Decks – Bare Hands	7.7	4.8	NA	8
Decks – Dry Polyester	41.7	38.1	8.3	8
All Playsets – Dry Polyester	37.9	17.4	7.6	12
Playgrounds and Decks – Dry Polyester	39.4	26.9	7.9	20
DP – Dry Polyester				

### Sampling Method

The results of this experiment also validated the use of a polyester cloth surrogate for the bare hand. This method involves using either a wet or dry polyester cloth, and attaching the cloth to a circular disk (8 cm in diameter) that is attached to a sampling template. The cloth is rubbed a total area of approximately 400 cm<sup>2</sup> back-and-forth in the template 10 times. A conversion factor (0.20) is applied to the results of the sampling to estimate the amount of As that would be transferred to a bare hand rubbing 700 cm<sup>2</sup> back-and-forth 10 times.

### Conclusions

- Rubbing existing CCA-treated wood structures resulted in detectable levels of As on the hands of volunteers
- Surrogate materials were highly correlated with hand values
  - Hands extract approximately 20% of the dislodgeable As removed by dry polyester cloths using the CPSC staff methodology.
- The average amount of dislodgeable As removed by both hands and surrogates from a sample of playsets representing a variety of ages and surface treatments was comparable to the amount removed from a similar variety of decks.
- Reasonable estimates of dislodgeable As transferred to a child's hand during a "typical" play episode can be made from the data obtained from the rubs of 12 playsets and 8 decks. When the dry polyester for all play and deck structures are combined and converted to bare hand values, the mean is approximately 7.9 µg (n=20).

## **Determination of Arsenic Migration to Human Hands and Surrogates From CCA-treated Wood**

### **Purpose and Objectives**

A series of experiments were completed with the primary objective of estimating the amount of As that may be transferred to a child's hands during normal play activities on playground structures. The potential impact of behavioral factors, such as the amount of contact with treated structures, was considered in this investigation. A secondary objective was to create a standard protocol that can be used to quantify As migration from CCA-treated wood. In creating a protocol for wood sampling, several factors were examined, including the use of surrogate materials, creation of sampling devices to minimize variability, and the extraction efficiency of removing As from hands exposed to CCA-treated wood.

The CPSC Human Factors (HF) and Health Sciences (HS) staff believe that the exposure route that leads to the greatest intake of As by young children is hand-to-mouth contact where young children place their contaminated hands into their mouths and ingest available As. Experimental procedures were designed to estimate the amount of As that may be transferred to children's hands. Estimating the potential exposure to As from playgrounds through hand contact is best determined by measuring the amount of As on human hands that have been in contact with CCA-treated wood. Since it is not always feasible to use human volunteers to rub wood surfaces in exposure assessment studies, surrogate materials such as polyester or nylon cloths have been utilized in exposure assessment studies to estimate the amount of As that transfers to human hands during contact with CCA-treated wood. An acceptable correlation between the As transfer to hands and As transfer to the surrogate materials must be established before the surrogate materials can be used with confidence in exposure assessment.

The overall objectives of the investigation were to:

- 1) Quantify the amount of As that transfers to human hands during contact with CCA-treated wood;
- 2) Examine the impact of factors such as the amount of hand contact on As transfer to human hands;
- 3) Examine wood characteristics that affect As migration to human hands;
- 4) Identify surrogate materials that can be used in sampling to estimate As transfer to the hand; and
- 5) Create a wood sampling protocol that includes: a) development of a template for consistent board rubbing using the surrogate materials; b) procedure for rubbing the wood with adult hands and; c) procedure to extract As from the hands used to rub the wood.

The exposure assessment study was divided into four phases. Phase I, Exploratory Studies, consisted of a series of tests to determine the critical factors, such as surface area, pressure, and number of strokes, that may influence As transfer to bare human hands and surrogate materials. Based on the observations in Phase I, testing of individual new and weathered CCA-treated boards for dislodgeable As was conducted in the CPSC laboratory. In the Phase II studies, many of the results from Phase I were re-examined in addition to testing additional factors that affect

As transfer to hands. Based on the data and conclusions in Phase II, a protocol to measure dislodgeable As was finalized. This protocol was utilized in the Phase III Field Study to conduct measurements of As migration to hands and surrogate materials from existing decks composed of CCA-treated wood. The results of Phase III studies suggest that surrogate materials can be used to predict the amount of As that can be picked up by the bare hand rubs of CCA-treated wood. The surrogate materials were then used in a Phase IV Field Study to estimate the amount of As that may be removed from CCA-treated wood play structures by human hands.

### **Phase I - Exploratory Studies**

Prior to initiating a field investigation, a number of tests were performed in the CPSC's laboratory facilities to create a protocol to be used in field sampling. Factors that may affect As migration to hands and surrogates from CCA-treated wood were examined. The following is a description of the factors that had the greatest impact on As removed from the surfaces of CCA-treated wood. The details regarding the methodology used in these exploratory studies can be found in a memo by CPSC staff (Cobb, 2003).

#### Hand Contact

The CPSC staff used a rubbing action on CCA-treated boards as the standard hand sampling method for all phases of the investigation. While playing on wood playsets, the manner in which young children make manual contact with the structures varies considerably. Some of the hand contacts are firm grasps while others are light touches (Midgett, 2003). CPSC staff determined that firm rubbing of wood, as used in the previous CPSC investigation and other studies, is an action that serves as a reasonable aggregation of the various manual contacts young children have with the playground wood (Midgett, 2003). The staff believes that the amount of As that is transferred to the hand when rubbing samples of CCA-treated wood can be used as a reasonable estimate of the migration of As to the hand that will occur during children's play on structures composed of CCA-treated wood.

#### Weight/Pressure Applied

During normal child contact with treated playground structures, there will be a variety of contacts with wood. Some will be full weight, such as hanging from the structure, to very light touches that exert minimal pressure on the wood (Midgett, 2003). CPSC staff found that the transfer of dislodgeable As to polyester cloths from the wood surface increased with increasing rubbing pressure (weight) on the wood (Cobb, 2003).

As part of the sampling protocol, a 1.1 kg circular disk, 8 cm in diameter, was used for surrogate sampling. The 1.1 kg weight provides a firm pressure that allows the materials to be rubbed across boards with a reasonable amount of friction, but does not interfere with the movement of the material along the board surface. The disk was also placed on top of human hands in an attempt to increase the consistency of the pressure applied by each volunteer. In balancing the disk on the hand, the disk was beneficial in maintaining a steady rate of wood rubbing across the board by the study participants. The 1.1 kg disk provided a firm weight but was not too heavy to cause discomfort or to simulate an unlikely amount of pressure for volunteers during sampling.

### Rinsing Procedure

CPSC staff conducted studies to determine the most efficient procedure for the removal of As from adult hands for subsequent analysis (Cobb, 2003). After each volunteer rubbed CCA-treated boards with a bare hand, the As was removed by rinsing the hand with a mildly acidic solution. In initial studies, the rinse procedure included rinsing with 100 ml of a 5% acetic acid/deionized (DI) water solution. The solution was sprayed from a squeeze bottle directly onto the volunteer's hand with moderate pressure. The hand was rinsed over a large glass funnel that was placed over a screw-top flask for collection.

In subsequent sample collections, the 100 ml acetic acid rinse was followed by a wiping of the hands with a polyester cloth that was saturated with 5% acetic acid. The polyester cloth and acetic acid rinse were analyzed separately. Analysis of the total amount of As collected in the two extraction steps showed that approximately 43% of the total amount of As collected, was collected in the initial rinse. These results suggested that on average, the rinse procedure was less than 50% efficient in removing As from hands. Subsequently, a more rigorous collection procedure was implemented by LSC staff that included an initial rinse with 100 ml of the 5% acetic acid solution followed by a wiping of the hand with a polyester cloth saturated with 5% acetic acid solution, followed by a final rinse of the hand with 100 ml of 5% acetic acid solution. This procedure is repeated, and the wipe and rinses are collected in a separated flask. This new series of extractions is referred to as the rinse-wipe-rinse (RWR) procedure and was used in the laboratory hand study and field investigation for each hand sample.

### Surrogate Materials

Surrogate materials are a useful tool in exposure assessment to predict the amount of As that transfers to a human hand from CCA-treated wood. Obtaining an accurate measure of As that can be dislodged from the wood surface is a critical factor because of the difficulties that are associated with using human volunteers in conducting field measurements. In order to be useful as a surrogate, the amount of As removed from wood by the material must be highly correlated with the amount removed by the hand, so that results from surrogate sampling can be extrapolated to human hands. Correlation refers to the relative amounts of As picked up by these materials. For example, a good correlation suggests that if the hand picks up higher concentrations on board 1, the surrogate material will also extract a higher amount. Conversely, if hand values were lower on board 2, the surrogate values will also be proportionately lower. A mathematical relationship can be established that describes this correlation and permits one to estimate the amount of As that would be transferred to the hand by knowing the amount of As transferred to the surrogate. This relationship allows investigators to use a surrogate for sampling boards, and then estimate the amount of As that would be picked up by a hand contacting the same board. The strength of the relationship is measured statistically by the correlation coefficient ( $r$ ), which ranges from 0 to 1.

In addition to establishing an acceptable correlation with hand values, identifying the most appropriate surrogate material involves a comparison of other factors including: durability, ease of analytical preparation, hand/surrogate ratio, cost, and availability. CPSC staff compared the utility of a number of potential surrogate materials in dislodgable As experiments. Table 2 lists the surrogate materials reviewed by LSC staff and their correlation with human hands. The

suitability of these materials, based on each of the factors presented, are subjectively categorized as excellent, good, fair, or poor.

Table 2. Comparison of Surrogate Materials

Surrogate	Correlation Coefficient	Conversion Factor <sup>1</sup>	Analysis <sup>2</sup>	Availability	Durability	Consistency <sup>3</sup>	Comments
Polyester Cloth (Texwipe TX 1099)	Dry: 0.91 Wet: 0.79	Dry: 0.20 Wet: 0.076	Excellent	Good	Excellent	Excellent	
High density polyethylene fiber material (HDPE)	0.88	0.96	Excellent	Excellent	Excellent	Fair	
Kimwipe™ (laboratory tissue wipes)	0.825		Excellent	Good	Fair-Poor <sup>4</sup>	Good	
Latex	ND	ND	Good	Good	Poor	ND	
Instrumental Pipe Organ Membranes	ND	ND	Good	Poor	Poor	ND	
Instrumental Pipe Organ Leathers	ND	ND	High Cr <sup>5</sup>	ND	ND	ND	High costs
Chamois Leathers	ND	ND	Poor	Good	Excellent	Poor	High costs

<sup>1</sup>Is specific to the areas rubbed and other parameters in this investigation

<sup>2</sup>Includes ease of digestion and background interference during analysis

<sup>3</sup>The properties of the material must be the same regardless of source

<sup>4</sup>Fair on new boards

<sup>5</sup>Contains chromium

ND - not determined

In addition to the materials listed in Table 2, a number of cloths were compared to determine if they would have a better correlation with the bare hand values than the Texwipe TX 1099 polyester cloths. These materials included cotton, polyester-cotton blends, and other materials. Natural materials such as the instrumental pipe organ membrane were not considered useful for sampling wood. Although natural materials may remove As from wood in concentrations that are more comparable to bare human hands, other factors such as durability, consistency, and analytical difficulties diminished their suitability as surrogate materials. Staff decided that given the durability, availability, and consistency of the polyester cloth, this material was the best material for use as a surrogate.

Initial experiments compared the transfer of As to a polyester cloth attached to an 8 cm metal disk, bare human hands, and hands covered with mittens made of the polyester cloth. The correlation coefficient between As migration to the cloth-covered disk and the cloth covered hand (mittens) was excellent ( $r=0.96$   $p<0.001$ ; Levenson, 2003a). These data demonstrated that a correlation between two sampling methods, cloth covered hand and disk, could be established. Later experiments in Phase III showed that the polyester wetted with 2% saline consistently removed approximately 13 times more As when rubbed across CCA-treated wood samples than bare adult human hands rubbing the same sample on average. These laboratory and field studies also demonstrated a roughly 5:1 ratio for dry polyester versus human hands (Levenson, 2003a).



### Sampling Template

CPSC staff developed a mechanical device (sampling template) specifically for using surrogate materials in measuring dislodgeable As from CCA-treated wood structures. The "template" is a metallic frame with a lever for attaching the 8cm diameter, 1.1 kg disk to the apparatus. The disk slides 50 cm within the interior track of the template, for a total of approximately 400 cm<sup>2</sup> per each swipe of the disk through the template. The template can be held in a vertical position by clamps for sampling vertical posts on playgrounds and other structures. CPSC staff compared the migration of As to polyester cloths on a board in horizontal and vertical positions. The results of this test demonstrated comparable levels of migration from both positions (Cobb, 2003). There were no statistically significant differences in transfer of As from boards in horizontal and vertical positions to polyester cloths ( $p=0.996$ ; Levenson, 2003a). Photographs of the sampling in the horizontal and vertical positions are available in CPSC staff reports (Cobb, 2003).

The advantages of using the template are numerous. The use of the template eliminates much of the variability associated with the application of pressure by human hands when rubbing surrogate materials on treated wood especially from person to person. It allows for a consistent comparison of wood classes and materials at various locations without having to involve human subjects. Finally, the size and morphology of the disks used in the template were consistent, unlike human hands.

### Conclusions

The data collected in the exploratory phase of the investigation provided useful information in the development of a protocol for sampling CCA-treated boards with human hands and surrogate materials. The selection of a rubbing motion, back and forth across the board, was determined to be a reasonable measure of child hand contact with playground structures. The rubbing action on CCA-treated boards with bare hands and surrogate materials resulted in measurable concentrations of As on these materials. The polyester cloth was found to be a useful surrogate for hand contact, and could be placed on the metal disk that is inserted into the template for board sampling. A rigorous rinsing procedure was established that ensured a high extraction efficiency of As from hands. Hand measurements obtained in subsequent phases of the study were regarded with greater confidence because of the improved sampling methods developed by CPSC staff.

## **Phase II - Laboratory Hand/Surrogate Study**

### Overview

The procedural details of Phase II (Laboratory Experiments) of the exposure assessment, have been presented in other staff memos (Cobb, 2003; Levenson, 2003a). The objectives of the laboratory investigation were to quantify the amount of As that migrates to hands when rubbing new CCA-treated boards and CCA-treated boards that had been subjected to outdoor weathering. A comparison was made between the amount of dislodgeable As removed by bare hands versus the polyester cloth or a high density polyethylene fiber material (HDPE) which was also being considered as a surrogate. These data were used to calculate the correlation of the amount of As transferred to human hands with As levels transferred to selected surrogate materials. The high

correlation coefficient derived from the data demonstrated that it is possible to extrapolate As measurements collected with the use of wet and dry polyester surrogates, to estimate As migration to a child's hand.

Another critical exposure factor examined in this investigation involved increasing the amount of wood area rubbed and the number of rubs on a given area of wood to reach a potential maximum As load on the hand (i.e., the point at which increasing contact with the wood does not result in increasing transfer of As from the wood to the hand). Staff also investigated the impact of re-rubbing the same area on a board with respect to the depletion of available As.

The following are the hypotheses tested by Staff in Phase II of their studies.

#### Hypotheses:

H<sub>01</sub>:  $T_{\text{hand(bare)}} = 0$  : There is no detectable level of As transfer from new and non-new CCA-treated wood to hands

H<sub>02</sub>:  $\rho = 0$ : There is a correlation between the transfer of arsenic to a bare hand and to a cloth-covered disk

H<sub>03</sub>:  $T_2 = T_5 = T_{10} = T_{20}$  : There is no difference in As transfer when an area is rubbed 2, 5, 10, or 20 times

H<sub>04</sub>:  $T_a = T_b = T_c \dots$  : Re-rubbing an area several times will not result in significant decreases in As on hands

T= Transfer of arsenic from wood to hand or disk

$\rho$ = Correlation Coefficient

#### Methods

The staff compared concentrations of As on adult hands and surrogate materials after rubbing new CCA-treated boards purchased from local retailers, and "non-new" (including laboratory-aged boards) and "old" boards obtained from individual deck owners. Many of the "non-new" (under deck) boards were extraneous boards that had been purchased to build decks, and were stored in piles when they were not used in deck construction. Because these boards were stored in piles, their weathering was not consistent compared to weathering experienced by boards that comprised decks. The laboratory-aged boards were purchased new from a local commercial lumber supplier by staff and placed outdoors for approximately 5 months. The "old" wood was a part of a deck that was constructed approximately 22 year ago. The deck had been dismantled, and the free boards were placed in a stack. CPSC staff believes that the boards used in the study were support structures under the deck planks, and were not subject to full weathering compared to boards used for planking.

Volunteers rubbed boards with bare hands and surrogate materials. A "rub" consisted of one back-and-forth motion and is referred to as the "rub cycle", hence, the "rub" area was twice the area of the section. For example, a section of a board designated for 1 hand rub cycle contained 700 cm<sup>2</sup>, and the total area encompassed in a back-and-forth motion was 1400 cm<sup>2</sup>. Study volunteers rubbed a 700 cm<sup>2</sup> (50 cm x 14 cm) section of different boards 2, 5, 10, and 20 times (Figure 4; Levenson, 2002a). The boards were divided into sections to allow for hand and surrogate material rubbings of the boards. The surrogate materials: wet poly cloth, dry poly cloth and HDPE were placed on the disk (diameter = 8 cm) and rubbed 50 cm along the board for a total of approximately 400 cm<sup>2</sup>. The amount of area rubbed by a child on wood structures may vary considerably (Midgett, 2003). However, the area rubbed by volunteers in this investigation was well within the range that a child is expected to rub during a "typical" play

episode on playground equipment (Midgett, 2003). CPSC staff also designed experiments to quantify the effects of rubbing the same area of a piece of wood an increasing number of times.

### Data Review

CPSC staff performed statistical analyses of the data from the Phase II Studies (Levenson, 2003a). The analyses focused on determining whether certain factors significantly affected As transfer to hands and surrogates including: 1) The effect of the age of the wood sampled on the amount of As dislodged by rubbing, and 2) whether repeated rubs on a section of wood results in reaching a "maximum" hand load. Listed below are the specific hypotheses that were tested.

### Effect of Board Age

The statistical analysis is described in other CPSC staff memos (Levenson, 2003a). The results of Phase II experiments demonstrated that detectable amounts of As were extracted from the hands of volunteers for new and weathered wood (non-new and old). The average bare hand and polyester As levels dislodged from old wood were (Hand: 52.9 µg (range=41.6 µg - 64.2 µg); polyester 196.5 µg (175.5 µg - 217.5 µg) and new wood values were (Hand: 44.6 µg (range=21.6 µg - 115.6 µg); polyester 157.8 µg (range=63.6 µg - 256.5 µg). Green particulate material, which is believed to be CCA residue, was clearly visible on many of the new boards, and boards appearing to have higher residue levels also had elevated As transfer to hands and surrogate materials. The lab-aged wood [(Hand: 14.7 µg (range=10.2 µg - 19.2 µg); Polyester 35.9 µg (range=12.0 µg - 59.8 µg)] and the "non-new" under deck wood [(Hand: 13.5 µg (range=5.8 µg - 19.8 µg); Polyester 64.4 µg (range=32.6 µg - 98.6 µg)] had average As values considerably lower than the new and "old" wood.

Table 3. Comparison of Arsenic Transfer by Wood Class

Wood Class	Number of Boards	Bare Hand		Polyester	
		Mean(µg)	Range (µg)	Mean (µg)	Range (µg)
New	6	44.6	21.6-115.6	157.8	63.6-256.5
Old Deck	2	52.9	41.6-64.2	196.5	175.5-217.5
Under Deck	4	13.5	5.8-19.8	64.4	32.6-98.6
Lab Aged	2	14.7	10.2-19.2	35.9	12.0-59.8

### Maximum Hand Load

CPSC staff included an experiment in Phase II that determined whether the hand collects a "maximum" amount of As after a certain number of rubs on treated wood. That is, the staff was interested in knowing whether it was possible to obtain a maximum hand load of dislodgeable arsenic, where increasing contact with the wood does not result in appreciable increases in the amount of As transferred to the hand. Several boards were connected to provide a larger area of new wood surface. Volunteers rubbed 700 cm<sup>2</sup> and 2100 cm<sup>2</sup> of wood surface. The total amount of As transferred to the hand was 22.2 µg for 700 cm<sup>2</sup> and 33.6 for 2100 cm<sup>2</sup>. However, when the total amount of As is normalized per 100 cm<sup>2</sup> of wood surface, the amount of As transferred to the hand when rubbing 700 cm<sup>2</sup> (3.2 µg/100cm<sup>2</sup>) was higher than the amount transferred to the hand when volunteers rubbed 2100 cm<sup>2</sup> (1.6 µg/ 100cm<sup>2</sup>) (Cobb, 2003a). These results suggest

that when the amount of wood rubbed is increased, the amount of As transferred does not increase proportionally and a "maximum" hand load is being approached. It also suggests that the amount of As picked up by the hand should be reported in total amounts of As on hands, rather than standardized to a specific area (i.e.,  $\mu\text{g}/100\text{cm}^2$ ).

Another segment of the study examined changes in dislodgeable As with increasing number of rubs on the same section of a new board. Statistical analysis of the data revealed that the estimated slope of the line from 2 to 20 rub cycles is not significantly different from zero ( $p=0.58$ ,  $\alpha=0.05$ ; Levenson, 2003a). These results suggest that there were no significant increases in As transfers to the hand with increasing number of rubs on new wood. An important supposition derived from these data is that a point exists after a sufficient amount of wood contact where an equilibrium between the amount of As transferred to the hand and the amount removed from the hands is approached. This observation has particular relevance to long term child play because it suggests that following a sufficient amount of contact with a playground, young children may not pick up additional As on their hands until the As is removed, for example, by mouthing or other means. The results also suggest that the maximum loading occurs after a relatively limited amount of contact with the treated wood (i.e., as few as two rubs).

CPSC staff also investigated the effects of re-rubbing the same area on a board. Volunteers rubbed a  $700\text{ cm}^2$  portion of a CCA-treated board five times, and repeated the 5 rub sequence 3 times for a total of 4 sets of rubs in the same section on the new boards. The As was removed from the hands following each 5 rub cycle using the RWR procedure. A similar procedure was conducted on non-new boards where each rub sequence consisted of 10 rub cycles. Statistical analysis of the rubbing data suggested that there was a significant decrease in As values (approximately 20%) with each rubbing set on new boards ( $p=0.001$ , Levenson, 2003a). The results observed in non-new boards were inconclusive.

Taken together, these results suggest that as a defined section of a new board is repeatedly rubbed, the amount of As transferred to the hand will reach a "maximum" level. The results also suggest that as an increasing number of rubs are applied to a given area of new wood, the amount of available As will decline, although measureable amounts of As remain on the wood. This limit on the amount of As transferred to the hand may be the result of a saturation point, and the depletion of easily dislodgeable As from the wood surface, or a combination of both factors. Even though surface As levels are reduced, measureable amounts were removed from the surface following several rubbings. Although the easily dislodgeable As on the wood surface may be depleted, dislodgeable residue is expected to return to the surface. The pressure treatment process results in As penetration deep into the boards. Through weathering, release of As compounds, or other mechanisms, the subsurface As may eventually become available for migration from the wood to the hands of young children. Once the available As is removed from the surface, the amount of time it takes for the "recovery" of dislodgeable As residues on wood surfaces is unknown.

### Conclusions

The results of Phase II of the study provided CPSC staff with data to create a protocol for the Phase III field investigation, and to make inferences about the As exposure potential of different

types of wood. The rubbing of new wood by hands and surrogates generally resulted in higher levels of As compared to rubbing of boards exposed to outdoor conditions. When the same area on new boards was rubbed repeatedly, the amount of dislodgeable As declined. When the CCA-treated boards rubbed with the hand was increased so that greater areas of "virgin" CCA-treated wood was contacted, the amount of As found on bare hands tended to approach a "maximum" level. This observation was based on measurements on new boards. Staff assumed that 10 rub cycles were sufficient to approach a maximum hand load on both new and weathered boards. The polyester cloth and HDPE surrogate materials were significantly correlated with hand As concentrations, but for reasons stated previously, polyester cloths were selected as the surrogate material of choice for the field studies. These materials withstood the pressure of multiple board rubbings on the metal disk, and appeared to be suitable surrogates for field sampling. Some data on the effects of wood aging on dislodgeable levels of As were obtained, but these are insufficient to make inferences about the As exposure potential of new and weathered wood.

### Phase III – Field Study

#### Background

Obtaining data on the amount of As found on the hand after rubbing wood on structures composed of CCA-treated wood was a critical component in assessing potential As exposure to young children. The field investigation involved sampling boards on decks with bare adult hands and surrogate materials. Staff determined that using decks allowed for more controlled sampling and method development. Further, since playground structures may be constructed from the same lumber used to build decks, and since outdoor decks and play structures in a given geographic area will be exposed to the same weather conditions, wood from decks was used in this study of wood playsets. Structures tested included eight decks in homes in the Washington, DC metropolitan area. These structures were in use by their owners, which allowed staff to estimate dislodgeable As on boards of a variety of ages, use patterns, surface treatments, and exposure to the elements typical of conditions CCA-treated wood would likely experience during consumer use.

The following are the hypotheses tested by Staff in Phase III of their studies.

#### Hypotheses:

H<sub>01</sub>:  $\mu_{\text{hand(bare)}} = 0$  : There is no detectable As transfer from CCA-treated wood on decks and playgrounds to hands

H<sub>02</sub>:  $\mu_{\text{board1}} = \mu_{\text{board2}} = \mu_{\text{board3}}$  : The As transfer to hands does not vary between boards

H<sub>03</sub>:  $\mu_{>10\text{years}} = \mu_{<1\text{year}}$  : The age of the wood has no effect on As transfer to hands on non-coated boards

H<sub>04</sub>:  $\mu_{10} = \mu_{20}$ : There is no difference in mean As transfer when a 700 cm<sup>2</sup> area is rubbed 10 or 20 times

H<sub>05</sub>:  $\rho_{\text{correlation coefficient}} = 0$ : There is no significant correlation between the transfer of As from a bare hand and a cloth-covered disk

The overall objectives of the field investigation were to:

- 1) Quantify the total amount of dislodgeable As that is transferred to hands from rubbing finished and unfinished boards on existing decks,
- 2) Determine the board variability within and between decks,
- 3) Estimate the effects of board age and surface treatments on As migration,

- 4) Determine if dislodgeable As concentrations from wood samples vary with degree of hand contact resulting in a maximum hand load reached, and
- 5) Study the correlation between dislodgeable As transfer to hands and surrogate materials

### Methods

A detailed description of the methods and results of the field study are presented in other CPSC staff memos (Cobb and Davis, 2003; Levenson, 2003b). The eight decks sampled represented a variety of ages and surface treatments. The deck samples consisted of six decks that were not coated with any surface treatment (unfinished), and two decks that had been coated with surface treatments (finished) within the past five years. Non-coated decks are those that have not been subject to application of any surface treatment by the deck owner. Decks treated with a water-repellant by the wood manufacturer (during pressure treatment), were also classified as non-coated decks. On one of the six unfinished decks, the owner was uncertain whether the previous owner(s) had applied any form of surface coating. Based on a visual analysis of the boards, staff determined that there was little, if any, topical treatment on the boards at the time of sampling.

A total of eight adult volunteers were involved in the investigation. A board selection and randomization scheme was established by CPSC's staff to locate boards for sampling on the decks, and determine the order of sampling on the deck (Levenson, 2003b). Upon arrival at a deck site, boards were selected at varying locations on the deck that would reflect different traffic and use patterns. The boards were labeled 1, 2, 3, and 4, with a numbered placard placed on each board designating the number. A photograph was taken of each board with the numbered placard in order to assist in locating the board if any further sampling was needed. The selected boards were divided into five sections labeled a, b, c, d, and e. The randomization scheme outlined which sampling operation would occur on a specific board in a particular sequence (Levenson, 2003b). By closely following the sampling scheme, the total number of hand samples collected was 64 on 32 deck boards.

For the deck sampling, two volunteers were assigned to a deck. Volunteers rubbed two boards on two different segments of each deck. The selected boards were rubbed in two separate 700 cm<sup>2</sup> sections, one section was rubbed ten times, and the other was rubbed twenty times. Prior to rubbing each board, the hands of volunteers were washed thoroughly with soap and water and rinsed with deionized water, which was collected and analyzed for As contamination. The rigorous RWR procedure was utilized following each rub sequence. A detailed description of the methods used in sampling, and the methodology for board selection and assigning volunteers to decks can be found in other CPSC staff memos (Cobb and Davis, 2003; Levenson, 2003b).

### Data Analysis

A detailed description of the statistical procedures used in the data analysis is described elsewhere (Levenson, 2003b). The amount of As migrating to hands varied significantly among the decks tested ( $p < 0.001$ ). The adjusted average concentration of total As per hand transferred from deck wood ranged from a high of 20.9  $\mu\text{g}$  to a low value of 1.0  $\mu\text{g}$ , with a mean of 7.7  $\mu\text{g}$  (median=4.8  $\mu\text{g}$ ; Levenson, 2003b). Measureable amounts of As were transferred to bare hands on all of the eight decks sampled, regardless of age and surface treatment. The mean

dislodgeable As transferred to dry polyester fabric from decks was 41.7  $\mu\text{g}$  (median=38.1; range=2.25-114.1) which was converted to a "bare hand" value using the conversion factor of 0.2 to a mean of 8.3  $\mu\text{g}$  (median=7.6; range=0.45-22.8).

#### Variability Within and Between Decks

A comparison was made between the As migration on hands that were rubbed on boards on the same deck, and the average values between the decks themselves. Based on the 10-rub samples, the differences between boards on the same deck were marginally non-significant ( $p=0.094$ ,  $\alpha=0.05$ ). This result is an interesting contrast to the results for brand new wood where the amounts of As removed from these boards by bare hands were significantly different ( $p=0.001$ ) from each other (Levenson, 2003b). The estimated value of each board was combined to determine the overall mean hand As level for a deck. The differences in the average As hand concentration for each deck were statistically significant ( $p<0.001$ ).

#### Age and Surface Finish

The CPSC study of CCA-treated wood decks and playsets represented a variety of ages and surface treatments. CPSC staff tested eight decks that ranged in age from a few days to approximately 15-18 years. In general, the average amount of arsenic on hands rubbing unfinished decks less than 1 year old was higher than the amounts from decks older than 10 years. Regardless of age or surface finish, As was removed from the wood.

#### Hand Contact/Maximum Hand Load

CPSC staff developed tests to estimate whether a maximum hand load can be reached when an increasing number of hand rubs are applied to the same location on a board. The volunteers rubbed one section of the board 10 strokes and another section of the same board 20 times. The 20-cycle rubs produced 18% more As on bare hands than the 10-cycle rubs. The differences in As transfer to the hands when these sections were rubbed were not statistically significant ( $p=0.129$ , 95% CI: -5%-45%). These results suggest that if an individual rubs 1.4  $\text{m}^2$  of wood, re-rubbing that area until the total area rubbed is doubled will not result in significant increases in As load on the hand.

#### Volunteer Effect and Hand Size

A special effort was made in Phase III to minimize the effects that individual volunteer variability may have on the amount of dislodgeable As transferred to hands rubbing CCA-treated boards. Volunteers were given an orientation session and trained on the method for rubbing boards at a relatively constant pace with the 1.1 kg weight placed on top of their hands. Statistical analysis was conducted to determine if there was a volunteer effect on As levels found on the hands. A volunteer effect is an aggregation of factors that may impact As removal from boards, such as pressure applied and hand size. The overall volunteer effect was marginally non-significant ( $p=0.073$ ,  $\alpha=0.05$ ).

CPSC staff investigated the impact of variation in the size of the volunteers' hands on the transfer of As to their hands. The volunteers' hands were photocopied, then traced on a piece of plain paper. The hand area was determined by weighing the plain paper tracing of the volunteer

hand, and comparing the weight of the hand cutout to a standard size cutout. The hand areas ranged from 113 cm<sup>2</sup> to 182.6 cm<sup>2</sup> (mean = 141.3, sd=19.6). However, the volunteers' hands only varied in size by about 1.6-fold, which may not be sufficient to distinguish an effect from among the other variables. The differences in the area of the hand did not account for all of the volunteer variation in As transfer to hands. However, when the contribution of hand size is removed from the overall volunteer effect, the impact of the volunteer effect on As removal decreases (p=0.135). These results suggest that hand size is a factor in the overall volunteer effect.

### Hands and Surrogates

The relationship between the migration of As to bare hands and polyester wipes was investigated. The polyester cloth was tested in two forms, dry, and wetted with a 2% saline solution. The relationships [(correlation coefficients (r) between the bare hands and wet polyester (r=0.79, p<0.01) and dry polyester (r=0.91, p<0.01)] were statistically significant. In addition to the numerical evaluation of the relationship, a review of the data plots was completed (Levenson, 2003b). Quantitative analysis and visual inspection of the data suggested that dry polyester wipes had the closest association with bare hand values. The conversion factors (CF) for translating surrogate measurements to hands are 0.08 for wet polyester, and 0.20 for dry polyester. Translating these values to hands suggests that a bare human hand rubbing 700 cm<sup>2</sup> 10 times will remove approximately 20% of what the dry polyester will remove from rubbing 400cm<sup>2</sup> of wood 10 times using the CPSC methodology.

These results confirm that the dry polyester cloth can be used to estimate, with a reasonable degree of confidence, the As transfer that would occur with bare hands. The polyester cloth also has the advantage of being durable, relatively inexpensive, and is not difficult to analyze. Along with the surrogates, the sampling template proved to be an effective device when sampling horizontal board surfaces.

### **Phase IV – Playset Sampling**

The results of Phase III testing demonstrated that the amount of As removed from CCA-treated wood by rubbing with dry polyester, is highly correlated with hand values. This surrogate material was used to estimate the potential exposure to As on existing playsets. This phase of the investigation involved sampling 15 play sets, including 3 non CCA-treated control playsets, with the dry and wet polyester materials for dislodgeable As from boards. The playsets represented a variety of ages and surface treatments at homes in the Washington, DC metropolitan area, including home structures in the District of Columbia, Maryland, and Virginia. Some of these structures were in use by their owners while others had been used sporadically for several years. Some of the wood used to construct the playsets was provided by playset manufacturers, while others were made of wood purchased by the consumer. For example, one playset, composed of wood supplied by the manufacturer, was ten years old and was finished only once following one year of use, while another playset was composed of lumber purchased by the consumer from a local supplier. This structure was approximately five months old at the time of testing, and no other finishes had been applied to this structure.



The surrogate materials were attached to the sampling template that was used in Phase II and Phase III and the methodology was identical to that used in Phase III (Cobb and Davis, 2002). The materials were wiped across the wood surface area of 400 cm<sup>2</sup> for 10 strokes. The results of the play set sampling were very similar to those of the deck sampling.

On the first two playset samples, two volunteers were used to collect hand measurements along with the dry polyester. An adult volunteer was used to rub each playset with their bare hands. The first playset was composed of wood provided by a playset manufacturer, and was approximately 10 years old. The average amount of As transferred to hands was 16.9 µg. The other playset was approximately six months old and had As hand levels of 11.5 µg. These results are comparable to hand measurements on decks.

With these experiments, staff again confirmed the utility of dry polyester as a surrogate material and its ability to reasonably estimate the amount of dislodgeable As that would be transferred to a human hand. The mean amount of arsenic picked by dry polyester cloth on the 12 playsets was 37.9 µg (sd = 13.8 µg; median = 17.35 µg; range = 1.6-168.5) compared to 41.7 µg (sd = 13.2 µg; median = 38.1 µg; range=2.25-114.1) for the eight decks. The individual results of the wipe sampling can be found in the CPSC staff memo by Cobb and Davis (2003).

The amount of arsenic removed from the wood by the polyester cloth was multiplied by the correction factor (0.2) to estimate the amount of As that would be removed by a bare human hand (Levenson, 2003c). The mean (average) amount of As picked up by the dry polyester cloths from playsets was 37.9 µg (median=17.4 µg; range=1.6-168.5) or approximately 7.6 µg (median=3.5 µg; range=0.32-33.7) for converted "hand" values. The three control playgrounds composed of non-CCA-treated wood had average arsenic values of 0.3 µg on the dry polyester cloth, or 0.06 µg for the converted "hand" values. These results suggest that negligible amounts of As are picked up by the dry polyester cloth on non-CCA wood structures.

The results of the playset sampling in Phase IV are similar to the deck sampling in Phase III (Levenson, 2003c). The overall mean dislodgeable As from the 8 decks sampled in Phase III for the bare hands was approximately 7.7 µg (median = 4.8 µg; range=1.0-20.9 µg), which is comparable to the overall converted the estimated "bare" hand mean dislodgeable As of 8.3 µg (median=7.6 µg; range=0.45-22.8). The converted dry polyester estimate for bare hand values is 7.6 µg (median = 3.5 µg; range=0.32-33.7) for the 12 play sets composed of CCA-treated wood. The mean for all deck and playset structures sampled in phases III and IV of the study was 7.63 µg, which is calculated by combining the bare hand values for the decks and the surrogate estimate of hand values from the playsets. The median, 3.5 µg, is identical to the median for the estimated hand mean for the playset structures alone. When the converted dry polyester values for dislodgeable As from decks and playsets were combined, the overall mean is 7.9 µg (median =5.4 µg; range=0.32-33.7).

Although there was wide variation among the individual playsets and decks, the results of these studies suggest that when hand or surrogate samples are taken from a variety of wood ages and treatments, the average As levels on the hands and surrogates may be comparable for the various sampling sets. The sampling template proved to be an effective device when sampling both horizontal and vertical board surfaces. The template was used on both decks and play sets. The

playset boards were sampled in both horizontal and vertical positions. The template was secured to the boards by two plastic clamps. The rubbing of the boards by the template apparatus is believed to decrease variation in pressure that may occur when human volunteers are used in sampling.

### **Comparison to other Investigations**

Several investigations have attempted to quantify the amount of As transferred to human hands and surrogate materials resulting from contact with CCA-treated wood. The methodologies employed in these studies vary considerably in terms of the sampling device used (hands or surrogates), wood contact (rubbing, grasping), area contacted, and reporting units (As per hand area, As per board area rubbed).

#### CPSC 1990 Study

In 1990, CPSC staff completed an investigation of the migration of As from treated playset wood to a nylon cloth (Lee, 1990). The 1990 study used a method similar to the one employed in the current CPSC investigation, which involved rubbing a nylon cloth attached to a weight (wood block) along CCA-treated boards. The amount of As transferred to nylon cloths ranged from non-detect (ND) (method detection limit (MDL) =  $6.3 \mu\text{g} / 100 \text{cm}^2$ ) to  $68.84 \mu\text{g} / 100 \text{cm}^2$ . Because hand measurements of As migration were not quantified in the 1990 CPSC study, it is not known how the amounts of As removed by the nylon are correlated with what would be removed by the hand.

#### Canadian Playset Study

A Canadian investigation sampled 10 playground structures in eastern Ontario, Canada (Reidel et al., 1991). The structures were composed primarily of CCA-treated wood of various dimensions. The CCA-treated surface of the wood was wiped with a folded 10cm x 10cm 8-ply gauze pad that was moistened with 3 ml of distilled water. Long surfaces (1 meter) were wiped twice and shorter surfaces (50 cm) were wiped 4 times. The mean As values for wipe samples from 10 playgrounds ranged from  $4.8 \mu\text{g}$  to  $149.3 \mu\text{g}$  total As per gauze wipe. The values reported in the Canadian study are similar to the dry polyester measurement in the current CPSC study, where average playset values ranged from 1.6-168  $\mu\text{g}$  total As per polyester wipe.

#### California State Playground Study

The California Department of Health Services (CDHS) conducted a study to assess the degree of hazard associated with the use of CCA-treated wood in playground structures (CDHS, 1987). The study consisted of a series of tests that used various sampling techniques on a variety of structures including wiping tissue or gauze pads, and vacuuming while brushing. Wipe sampling included 32 samples from a park playground in Berkeley, California. The playground structures were sampled with  $100 \text{cm}^2$  cotton pads with concentrations of As ranging from  $3.4 \mu\text{g} / 100 \text{cm}^2$  to  $250 \mu\text{g} / 100 \text{cm}^2$  with a mean of  $95.1 \mu\text{g} / 100 \text{cm}^2$  (CDHS, 1987). This structure was retested one month after being coated with an oil-based stain. The amount of As removed by the gauze was reduced considerably compared to the initial phase with values ranging from  $6\text{-}11 \mu\text{g} / 100 \text{cm}^2$ . A second phase of the study involved five volunteers vigorously rubbing their hands over  $300 \text{cm}^2$  of unused CCA-treated pine for 3 minutes. The amount of As found on these hands ranged from  $59.2 \mu\text{g}$  to  $193.3 \mu\text{g}$  As. These values are comparable to those found in

brand new wood in phase II of the 2003 CPSC study where As migration to hands that rubbed new wood ranged from 21.6  $\mu\text{g}$  - 115.6  $\mu\text{g}$  As (Levenson, 2003a).

#### Osmose Corporation Study

In 1998 Scientific Certification Systems completed a report to the Osmose Corporation on the removal of As from CCA-treated lumber (SCS, 1998). New lumber samples did not have any visible surface residue, and all of the aged lumber samples had been weathered for at least five years. The investigation consisted of adult volunteers firmly grasping and releasing a variety of treated lumber samples ten times in succession. Their hands were rinsed with a total of 45 ml of deionized (DI) water. Kimwipes™ (laboratory wiping tissues) were used as surrogate materials, and were rubbed firmly over approximately 100  $\text{cm}^2$  of wood surface. The mean dislodgeable As transferred to hands in contact with CCA-treated yellow pine was 3.94  $\mu\text{g}/100\text{cm}^2$  and 9.9  $\mu\text{g}/100\text{cm}^2$  for CCA yellow pine with Osmose water repellent. The results for the Kimwipes™ were higher than hand values with a mean As level of 15.4  $\mu\text{g}/\text{wipe}$  for yellow pine and 27.4  $\mu\text{g}/\text{wipe}$  for yellow pine with Osmose brightener. A correlation coefficient ( $r$ ) of 0.825 was calculated for the Kimwipe™ versus hand As measurements.

The results of the SCS study suggest that some surrogate materials might be used to reasonably estimate As migration to hands. The concentrations of As on the hands of volunteers was lower than those found in the current CPSC study. A potential explanation for this observation is that the rinsing procedure used in this investigation did not efficiently remove the As from the hands of the volunteers. CPSC staff discovered in Phase I of its study (Cobb, 2003) that rinsing the hand with 100 ml of an acidic solution resulted in an extraction efficiency less than 50%. Given these findings, the lower amounts of As found on the hands of volunteers in the SCS study must be questioned because of a potentially inefficient extraction method. In addition, the volunteers in this study grasped the wood and released 10 times. This action may be less accurate and efficient in removing dislodgeable As from wood surfaces than the rubbing action used in the CPSC investigation.

#### State of Connecticut Study

A study by the State of Connecticut used wetted polyester cloth material attached to a wood block to test wood surfaces (Stillwell, 1998). The cloths were dragged across 28-30 cm of wood surfaces five times, which was similar to methods used in the 1990 and current CPSC investigation. New boards purchased from lumberyards were sampled in addition to play sets in municipal parks. The average amount of As migrating from wood surfaces was 35  $\mu\text{g}/100\text{cm}^2$  for new lumber and 8.8  $\mu\text{g}/100\text{cm}^2$  for existing playgrounds. These results are consistent with the current CPSC study where the average As migration from newly purchased wood was considerably higher than on existing playground and deck structures (Levenson, 2003b).

#### EWG/HBN Nationwide Study

The Environmental Working Group (EWG) and the Healthy Building Network completed a study of new wood purchased in the stores of two major home improvement companies (EWG, 2001). Wood was purchased in stores across the United States including; Washington, DC; Philadelphia, PA; San Francisco, CA; Omaha, NE; Detroit MI; Houston, TX, and other cities across the US. The investigators purchased new wood ranging in size from 2'x4', 2'x6' to decking, and rubbed 100  $\text{cm}^2$  of these boards in undulating patterns with a wetted cloth. The

average concentration of As on the cloths collected from all the samples (for all cities and all woods) was 247  $\mu\text{g}$  (range=18  $\mu\text{g}$  -1020  $\mu\text{g}$ ). These values were, on average, higher, but comparable to, As concentrations for the current CPSC study, where the mean As value on the polyester cloth was 158  $\mu\text{g}$  (range=63.6  $\mu\text{g}$  -256.5  $\mu\text{g}$ ) for new wood. The area rubbed for the CPSC study was 0.8  $\text{m}^2$  (10 strokes in a 400  $\text{cm}^2$  template). The EWG performed an unspecified number of strokes in a 100  $\text{cm}^2$  template that could have resulted in a considerably larger area of board that is wiped, which may explain the relatively minor differences in results. However, given the wide range of values that are present on new boards, the results of the EWG and CPSC investigations are relatively consistent.

A review of the available data suggests that when using similar methods to test As migration from wood, the average results are relatively consistent. The investigations reviewed were conducted in various regions of the United States with variability in weather conditions. The differences in hand migration values are believed to be due, in part, by inadequate removal of As from hands. The data suggest that a relatively narrow range of average values, are representative of a variety of CCA-treated wood types in various regions of the country. The studies also demonstrate that surrogate materials are widely used as a practical means of estimating As exposure to children.

### Summary

The results of these investigations have given CPSC staff a greater understanding of the complexities and factors that impact As migration to hands and surrogates, and the ability to use these measurements as estimates for human exposure to As from contact with CCA-treated wood. The Phase I and Phase II studies demonstrated the effects of factors such as the area rubbed and pressure on hand and surrogate removal of As from CCA-treated wood. CPSC staff also found that a rigorous hand rinsing procedure is needed to more completely remove As from the hand, which increases the accuracy of the results. The utility of surrogate materials to estimate As migration to hands was confirmed. The template designed by CPSC staff provided consistency for surrogate sampling of CCA-treated structures.

The properties of the wood and the contact with wood are key determinants in As migration to hands and surrogates. In Phase II and Phase III, the data suggest that the hand will remove a maximum amount of As, and repeatedly rubbing the same portion of new wood results in diminishing migration of As to hands per  $\text{cm}^2$ . When the area of rubbing was increased from 10 rub cycles to 20 rub cycles, there were no significant increases in As migration to hands. These experiments also suggested that newly purchased CCA-treated wood has higher amounts of As transfer to hands than does non-new wood.

Based on the migration of dislodgeable As from a variety of wood sources sampled in this investigation, estimates for As removal in a "typical" playground scenario can be derived to determine the risk of health effects resulting from CCA-treated wood contact. Measures of central tendency (mean and median) obtained from the bare adult hand sampling of CCA-treated decks in this investigation can be used to estimate the average amount of As that may be removed from CCA-treated play structures by a bare human hand (Levenson, 2003b). For a typical playset, a reasonable estimation of the amount of As removed by a human hand is 7.6  $\mu\text{g}$  of As after rubbing 1.4  $\text{m}^2$  (10 rub cycles, 700  $\text{cm}^2$ ) of the same section of a board. These

estimates are based on the area a child is expected to rub during a "typical" play episode on a CCA-treated wooden playground (Midgett, 2003). The rubbing action is used to estimate the exposure from a variety of contacts with CCA-treated wood that vary in pressure and action (e.g. grasping, light touching; Midgett, 2003). These estimates are critical components in calculating the potential risk of health effects to children who play on CCA-treated wood structures.

The average amount of As removed from the 8 deck samples using bare hands (mean=7.7 µg) or using surrogate material extrapolated to bare hands using the 0.2 correction factor (mean= 8.3 µg) was comparable to the amount removed from playsets when the surrogate results are extrapolated to bare hands (mean=7.6 µg). When the dry polyester data for all playsets (n=12) and deck (n=8) structures are combined and converted to "bare hand" values, the mean is approximately 7.9 µg (n=20).

The staff recognizes that its investigation is relatively small and was conducted in one region of the U.S. However, the current set of studies represents one of the most comprehensive studies to date. The effects different weathering conditions might have on the amount of dislodgeable arsenic is not clear, but it likely involves several factors and complex mechanisms. While CPSC studies are not representative of all climatic conditions across the U.S., they do provide a reasonable characterization of decks and playsets and possible As exposures in the Washington, D.C. metro area. These results are not expected to differ greatly from other major metropolitan areas within several hundred miles of the Washington, D.C. area (AWPA, 2001).

If hand measurements of wood are not feasible, surrogate materials can be used to estimate As transfer to hands. This is especially useful in larger studies. The polyester wipes proved to be useful surrogates for wood sampling. The polyester cloths were also durable, and could be easily analyzed for As content. CPSC staff studies demonstrated a consistent correlation between the As transferred from wood to bare hand and to a polyester cloth surrogate. The conversion factors (CF) for translating surrogate As measurements to bare hands is 0.20 for dry polyester. The dry polyester cloth was successfully used to estimate the amount of As that would be removed from playground structures composed of CCA-treated wood by bare human hands.

In addition to hand-to-mouth activity, there are other routes of exposure not explored in these exposure assessment studies that could increase the exposure to As from CCA-treated wood playsets. Some children may directly mouth wood and ingest wood particles that contain As. Dermal exposure to CCA-treated wood was not estimated. Clothing may also absorb particles that may be subsequently transferred to the hands or bare skin. This investigation did not account for As exposure that may result from contact with contaminated soil under, and adjacent to, CCA-treated wood playsets. Additional risks of chronic health effects may also result from exposure to chromium, which is also present in CCA-treated wood.

## Conclusions

- Rubbing existing CCA-treated wood structures resulted in detectable levels of As on the hands of volunteers.
- Certain surrogate materials were highly correlated with hand values.

- Hands extract approximately 20% of the dislodgeable As removed by dry polyester cloths using the CPSC methodology.
- The average amount of dislodgeable As removed by both hands and surrogates from a sample of play sets representing a variety of ages and surface treatments was comparable to the amount removed from a similar variety of decks.
- Reasonable estimates of dislodgeable As transferred to a child's hand during a "typical" play episode can be made from the data obtained from the rubs of 12 playsets and 8 decks. When the dry polyester data from all play and deck structures (n=20) are combined and converted to bare hand values, the mean is approximately 7.9  $\mu\text{g}$  As.

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