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Children's Exposure to Arsenic from CCA-Treated Wooden Decks and Playground Structures

Harold F. Hemond[1] and Helena M. Solo-Gabriele[2]

CCA-treated wood is widely used in the fabrication of outdoor decks and playground equipment. Because arsenic can be removed from the surface of CCA-treated wood both by physical contact and by leaching, it is important to determine whether children who play on such structures may ingest arsenic in quantities sufficient to be of public health concern. Based on a review of existing studies, it is estimated that arsenic doses in amounts of tens of micrograms per day may be incurred by children having realistic levels of exposure to CCA-treated decks and playground structures. The most important exposure pathway appears to be oral ingestion of arsenic that is first dislodged from the wood by direct hand contact, then transferred to the mouth by children's hand-to-mouth activity. The next most important pathway appears to be dermal absorption of arsenic, while ingestion of soil that has become contaminated by leaching from CCA-treated structures appears to be of lesser importance, except possibly in the case of children with pica. Considerable uncertainty, however, is associated with quantitative estimates of children's arsenic exposure from CCA-treated wood. Priorities for refining estimates of arsenic dose include detailed studies of the hand-to-mouth transfer of arsenic, studies of the dermal and gastrointestinal absorption of dislodgeable arsenic, and studies in which doses of arsenic to children playing in contact with CCA-treated wood are directly determined by measurement of arsenic in their urine, hair, and nails.

KEY WORDS: Arsenic; CCA; decks; playgrounds

1. INTRODUCTION

Children who contact CCA (chromated copper arsenate)-treated wood acquire arsenic on their skin. This arsenic may be ingested via hand-to-mouth activity, or absorbed by the skin. In addition, because arsenic leaches from CCA-treated wood, soil beneath CCA-treated structures can become arsenic-contaminated, and children who ingest the soil will also ingest this arsenic. To estimate the magnitude of the arsenic dose a child may receive from playing on or under a CCA-treated structure it is therefore necessary to estimate (1) the extent of transfer of arsenic from CCA-treated wood surfaces to the skin, (2) the extent to which arsenic acquired on the skin is either ingested or absorbed by the body, (3) the amount of arsenic that may be ingested from contaminated soil, and (4) the relative bioavailability of each form of absorbed or ingested arsenic. It is the purpose of this article to review the state of knowledge of these processes, estimate the general magnitude of arsenic dose that may be ingested by children who play on CCA-treated structures, and identify key research needs.

[1]R. M. Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA.
[2]Department of Civil, Architectural, and Environmental Engineering, University of Miami, Coral Gables, FL, USA.

2. CHEMISTRY AND TRANSPORT OF CCA IN WOOD

Treatment with CCA protects wood from fungal and insect attack, greatly increasing its service life in applications such as outdoor structures, where high moisture levels would result in rapid decay of untreated wood. The preservative action is a result of both the copper and the arsenic components of CCA. The amount of CCA added to wood, or retention level, typically varies from 4 kg/m^3 to 40 kg/m^3. Lower retention levels are used for above-ground applications and in freshwater contact, whereas higher retention levels are used for wood that is in contact with the ground or saltwater. Three different formulations for CCA have been standardized by the American Wood Preservers' Association.[1] The formulation currently used by the majority of the wood treaters is type C, composed of 47.5% Cr as CrO_3, 18.5% Cu as CuO, and 34.0% As as As_2O_5.

The general features of CCA chemistry in wood are well known.[2] The preservative is forced into wood as an aqueous solution of salts that includes arsenate (As(+V)), chromate (Cr(+VI)), and cupric (Cu^{2+}) ions. Over a period of hours to weeks, the chromium is reduced to Cr(+III) by chemical reaction with the wood. The resulting Cr^{3+} ions play the major role in immobilizing arsenic. Copper is immobilized by direct complexation with solid wood components, although some studies have indicated that chromium also plays a role in the fixation of copper.

Microanalytical studies confirm that arsenic in CCA-treated wood is largely fixed as inorganic precipitates. Greaves[3] demonstrated the presence of soluble cellular inclusions containing arsenic (plus chromium and copper) in the form of both crystalline and amorphous deposits in all wood species tested. Although Dahlgren and Hartford[4] considered that a variety of copper arsenate complexes could contribute to the immobilization of arsenic, these were not found in model experiments,[2] and results of more recent studies[5] using EXAFS (X-ray absorption fine structure spectroscopy) showed arsenic fixed only as chromium (III) arsenate ($CrAsO_4$).

The effectiveness of CCA derives from the fact that the solubility of arsenic in CCA-treated wood, though low compared to the arsenic salts used in the treating solution, is high enough to maintain pesticidal levels. As a result, arsenic can be slowly leached from the wood by water, as has been shown both in the laboratory and from wood in service.[6–11] Leaching by rainwater also leads to accumulation of arsenic in soil underneath CCA structures.[12] The rate of As leaching does vary among samples of wood, an observation that is not unexpected given the inherent heterogeneity of wood as well as variations in total retention (the amount of preservative that becomes incorporated into a given amount of wood), in the ratio of chromium to arsenic in the original preservative formulation (a modest excess of chromium should favor As retention), and in the species of wood. It is known that leaching solutions of higher acidity favor higher leaching rates, as do solutions containing compounds that can form complexes with CCA components (e.g., citrate, humic substances, silage juice).[7] The time-temperature history of the fixation process also affects the rate of conversion of chromate to chromium (III) and hence the effectiveness of arsenic fixation in newly treated wood.[13]

Both leaching and the presence of dislodgeable arsenic (arsenic that is removable by physical contact) on the surface of in-service CCA-treated wood continue for years to decades, demonstrating that surface arsenic is renewed over time. Given the very slow kinetics of diffusion through solids, this arsenic must be transported via diffusion through water present in the wood or advection of water through the wood. The advection of water through wood is well known[14] and predictable from its hydraulic properties. The renewal of arsenic at the surface is thus consistent with its solubilization from the interior of the wood, followed by transport to the surface as drying occurs.

3. ARSENIC EXPOSURE

3.1. Transfer of Arsenic from Wood Surface to Children's Skin

Two approaches have been used to estimate the amount of arsenic that may accumulate on skin by contact with CCA-treated wood. One approach is to rub wood samples with a wiping device (typically a piece of cloth or paper, although in at least one study a brush was used), then explicitly or implicitly invoke a relationship to relate the amount of arsenic measured on the wiping device to loadings that would have resulted on human skin as a result of contact with the wood. The second approach is to measure directly the arsenic that accumulates on skin during contact with CCA-treated wood.

Many researchers have measured the amount of arsenic that can be wiped from CCA-treated wood using a wiping device.[15–18] Numerous protocols have been followed, differing, for example, in type of wiping device used, whether the device was moist or dry, the area of wood wiped, the area of the wiping device, and whether new or used wood was tested. Different chemical measurement protocols are also followed (e.g., colorimetric or instrumental analysis, removal of arsenic from wiping device by total digestion or by one of a variety of acid leaches). Further, existing studies differ in the way in which measured total arsenic is normalized to give a real concentration; some report arsenic normalized by the area of the wiping device, while in others arsenic mass is normalized by the area of wood that is contacted.[15,19–21] Reported values are typically in the range of tens of micrograms per 100 cm^2 of wiping device area, though values as high as hundreds of micrograms per 100 cm^2 may be observed, especially in the case of moist contact and when new wood is used.[18]

In a few instances, investigators have compared arsenic collected on a wiping device with arsenic collected on persons' hands by contact with similar pieces of wood. SCS and Ecosense[22] compared arsenic loading on volunteers' hands with arsenic accumulated on paper laboratory wipes (Kimwipes™) and found a strong correlation ($r = 0.825$), the wipe data being higher than the hand loadings. Wipe tests on CCA-treated structures in Cedar-Rose Park in Berkeley, CA, yielded from 31 to 314 μg/100 cm^2 arsenic, compared with 130 and 280 μg total arsenic collected on the hands of a volunteer in a "quick grab" and after 3 minutes of "vigorous contact," respectively.[23] The Consumer Products Safety Commission (CPSC 2003)[18] evaluated the relationship between arsenic accumulated on dry hands and arsenic collected on both wet (2% saline) and dry polyester wiping cloths. As an example, the amount of arsenic collected on dry hands (141 cm^2 average hand area, 700 cm^2 of wood rubbed 20 times) was 7.3 μg/100 cm^2, whereas with polyester cloth wiping devices (area of 50 cm^2 rubbed over 400 cm^2 of wood) 181 μg/100 cm^2 and 85 μg/100 cm^2 was dislodged onto moist and dry cloth, respectively. The highest correlation between hand loading and a cloth-wiping device loading in this study was observed with dry wipe data ($r = 0.91$). Unfortunately, because of the large variety of protocols in use, quantitative relationships between hand loadings of arsenic and the corresponding results of wipe tests appear to be usable only within individual studies where both were measured.

3.1.1. Direct Measurements of Arsenic Loading on Hands

Arsenic accumulation on skin has been directly measured in only a few studies. Of these, some have used only dry hands, while some have used wet or moist hands, simulating skin that is either mouthed by a young child or is moist with perspiration from a child at play. Loadings of arsenic on hands resulting from contact with CCA-treated wood are summarized in Table I. As in the case of studies using wiping devices, experimental protocol differs among these studies. For this reason, as well as their high relevance to exposure assessment, they warrant individual discussion.

In the protocol of Arsenault,[24] individual hands were rubbed over "two ft. square sections" of CCA-C-treated plywood, washed three times vigorously with detergent and a brush, and the wash water analyzed for arsenic by the silver diethyldithiocarabamate

Table I. Dislodgeable Arsenic Loadings (μg/100 cm^2 ± 1 s.d.) for Studies that Utilized Human Hands

References	Moist Hands	Dry Hands	Notes
Arsenault (1975)[24]	196 ± 76 ($N = 4$)	6.7 ± 6.6 ($N = 4$)	New and used wood
	73 ± 35 ($N = 4$)	3.6 ± 4.4 ($N = 4$)	Washed wood
CalDHS (1987)[23]	78 ± 39 ($N = 5$)		New pine log
	68 ± 35 ($N = 2$)		Public playground
	477		Playground pole
	425		Wood sample
Williams *et al.* (1985)[25]		86.6 ± 67.3	Wood slats with varying residue level
SCS/Ecosense (1998)[22]		7.5 ± 3.4 ($N = 30$)	Residue-free yellow pine and hemlock
CPSC (2003)[18]	30 ± 7.3 ($N = 4$)		10 rubbing cycles
		6.1 ± 6.6 ($N = 32$)	10 rubbing cycles
		7.7 ± 9.2 ($N = 32$)	20 rubbing cycles
Carlson-Lynch and Smith (1998)[26]	48 ± 15 ($N = 10$)	27 ± 18 ($N = 10$)	2-year old deck
	42 ±18 ($N = 3$)		Child's hands

method. Extensive details of the analytical chemistry are not provided, but the existence of low values within the data set argues against the existence of large positive interferences in the analysis. Trials were conducted with both wet and dry hands, with both new and two-year-old wood, and with or without first washing the wood by hosing with water.

Areal hand loadings reported by Arsenault,(24) and shown in Table I, are calculated using the assumption of a hand area of 150 cm^2. Arsenic loadings were lower in the case of wood that had been washed ("hosed") prior to hand contact experiments. However, the transfer of arsenic to the hands from CCA-treated wood was enhanced when the hands were moist.

The study by California Department of Health Services (CalDHS 1987)(23) is supplemented by an unpublished draft report that contains additional experimental details. Adult volunteers rubbed both hands on either new CCA-treated wood, or on wood in service on CCA-treated wooden playground structures. Arsenic was collected from hands for analysis by rubbing the hands together while spraying with 50–75 ml of distilled water. Although the analytical method for arsenic is not given, other details that are provided, such as experiments conducted to test the efficiency of the rinsing procedure and solubility of the rinsate, suggest that the researchers were aware of suitable analytical practices. Following collection of arsenic from volunteers' hands, from 2 to 18 μg of additional As were found to be removable by a second hand rinse, indicating that the reported total arsenic loadings underestimate the true values by at least a few percent. Filtration experiments indicated that the dislodged arsenic was soluble in HCl solutions but only about 10% soluble in distilled water. Hand loadings calculated from (Reference 23) (Table I) are based on a total (both hands) grasping area of 300 cm^2.

Williams *et al.*(25) (as cited in Reference (23)) carried out tests with dry hands. CCA-treated wooden slats ranging in condition from "clean" to "visibly dirty" were rubbed, resulting in hand loadings ranging from 5 to 182 μg/100 cm^2, with higher levels observed at higher levels of visible residue on the wood. The study found that hand contact removed much less arsenic from wood surfaces than could be removed using a brush with a vacuum collection system. Information on the chemical analysis method employed was not available.

In Reference 22, adults grasped samples of CCA-treated wood "firmly but not tightly" 10 times with dry hands, after which each hand was rinsed with three 15-ml aliquots of water, evidently without rubbing or other means of facilitating arsenic transfer from the hands to the rinsate. Because this method is less rigorous than the protocol used by CalDHS (1987),(23) which in turn was demonstrated to remove less than 100% of the dislodgeable arsenic from hands, it may underestimate hand loadings of arsenic. The rinsate was analyzed by graphite furnace atomic absorption spectrophotometry (GF/AAS). Mean hand area of the volunteers was estimated by tracing to be 146 cm^2. New yellow pine, old yellow pine, hemlock/fir wood, and various treated wood samples were tested. In general, the various treatments (e.g., stains, water repellents) had little discernable effect on hand loadings.

Carlson-Lynch and Smith(26) report a study carried out by the Maine Department of Health Services, in which CCA-treated wood on a two-year-old deck was rubbed with wet or dry hands, for periods varying from three seconds to one minute. Arsenic was removed from subjects' hands using wipes from a lead test kit, then measured by acid extraction and analyzed using EPA Method 200.7. The efficiency of this method of removing arsenic from hands was not reported. Thirteen trials (12 from Fig. 2 of the study, one from Fig. 1 of the study) were conducted with moist hands. Three measurements were also made of arsenic accumulated on a child's hands during play on a CCA-treated structure; the total arsenic accumulation on the child's hands was not very different on an areal basis from the amounts accumulated on adult hands. Results summarized in Table I were calculated using hand areas of 100 cm^2 and 150 cm^2 for the child's hands and the adults' hands, respectively.

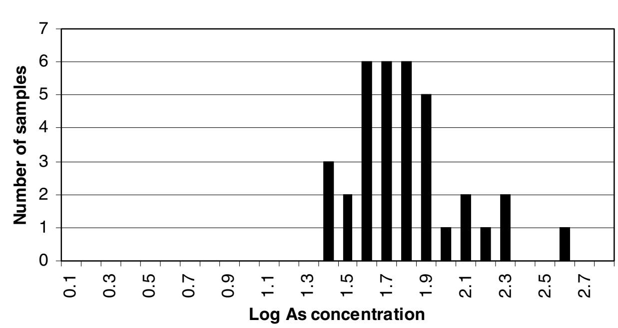

Fig. 1. Distribution of log of areal loading of dislodgeable arsenic on volunteers' hands after contact with CCA-treated wood under moist conditions. Data from four studies.(18,23,24,26) Areal loading expressed in micrograms/100 cm^2.

Comparison with data obtained with dry hands (Figures 1, 3, and 4 of Reference 26) further confirmed that moist hands acquire more arsenic from CCA-treated wood than do dry hands. The experiments also showed that the arsenic on the wood surfaces was not readily depleted, as repeated rubbings continued to produce similar hand loadings. Short (seconds) periods of contact with CCA-wood produced nearly as much hand loading of arsenic as did longer (minute) contact periods.

CPSC (2003)[18] evaluated arsenic accumulated on hands from eight decks that were in service in the Washington, D.C. area. Four boards were selected randomly per deck and four different volunteers (chosen at random among eight) were asked to rub a dry hand over 700 cm^2 sections of each board either 10 or 20 times, the applied pressure being controlled by placing a 1.1 kg weight on the back of the hand. CPSC (2003) also conducted four experiments in which a volunteer's wet hand was rubbed over new (but in some cases washed and dried) CCA-treated boards. Arsenic accumulated on hands was removed for analysis by using a relatively rigorous procedure that included a rinse with 100 ml of 5% acetic acid, followed by a wipe with a polyester cloth wetted with 5% acetic acid, and a second rinse with 5% acetic acid. Preliminary studies had shown that an acetic acid rinse alone failed to remove much of the arsenic—often only half or less—from the hands. The average surface area of the volunteer's hands was measured as 141 cm^2, the value used in converting total dislodged arsenic values to the areal values reported in Table I.

Assuming that moist, rather than dry, hand loadings more accurately represent the arsenic that would be accumulated on the hands of a child who engages in frequent hand-to-mouth activity, we calculated the mean of all individual moist-hands measurements that we could locate in the literature.[18,23,24,26] We judged each of these four studies containing moist hand data to be useful, with no evident methodological flaws except perhaps for insufficiently rigorous removal of arsenic from hands prior to chemical analysis. Each datum (total of 37) was weighted equally.

The mean loading on wet or moist hands, for the entire data set, is 91 μg/100 cm^2, with a standard deviation of 106 μg/100 cm^2. The distribution appears to be upwardly skewed. When two values, 477 and 420 μg/100 cm^2 (the "playground pole" and the "wood sample"),[23] are removed on the grounds that they were observed during an experiment whose purpose was to gather dislodgeable arsenic for solubility and bioavailability testing rather than to simulate playtime contact by children, the mean was reduced to 70 μg/100 cm^2 with a standard deviation of 63 μg/100 cm^2. There seems to be no justification for the removal of additional high loadings, however, and even removal of the two previously discussed values may be questioned, given that some actual arsenic loadings on children's hands at playgrounds may be accumulated as a result of high levels of contact effort. Furthermore, several of the moist hand values in Table I are the result of deliberately low (e.g., only several seconds) contact efforts, and would tend to counter concern about upward bias of the mean. Possible underrecovery of arsenic from hands prior to chemical analysis in some of the studies also mitigates concern about upward bias in the data set.

The distribution of the remaining 35 loadings still appears to be skewed upward. However, the histogram of the logarithms of loadings appears, by eye, to be close to normal (Fig. 1), as would be expected if the loading measured in each experiment were a *product* of several factors, such as CCA retention level, amount of recent transport of arsenic to the surface, and degree of wiping effort, each by itself approximated by a normal distribution.

3.2. Ingestion of Arsenic via Hand-to-Mouth Activity

The ingestion rate from hand-to-mouth arsenic transfer may be taken as the product of the hand area that is mouthed (units of area), the frequency with which mouthing takes place (units of $time^{-1}$), and the efficiency with which arsenic on the mouthed area is taken into the body. These quantities are discussed below:

Area. A child's entire hand is usually not placed in the mouth. U.S. EPA 2000 Draft SOPs for Residential Exposure Assessments recommends using a median area of 20 cm^2, comprising the middle three fingers, for a child age 1 to 6 years. This area changes with age, and the 20 cm^2 area appears to represent the surface area of the fingers of a 3-year-old, who would have a typical mass of 14.7 or 13.9 kg in the case of a male or female child, respectively.[27] There is justification for the use of a constant hand area value if the corresponding average body mass is also used in subsequent calculation of arsenic dosage per unit body mass to a child.

Frequency of hand-to-mouth activity. The frequency of hand-to-mouth activity depends highly upon the age of the child, with a higher frequency among younger children.[28–30] In general, studies conducted either by an observer or indirectly using videotapes of play sessions report hand-to-mouth frequencies of several per hour for children younger than six years of age. Zartarian *et al.*[28] quantified mouthing frequencies for four children between the ages of two and four years old at three and ten events per hour for the children's left hand and five to nine per hour for their right. This observation is consistent with those of Reed *et al.*,[31] who found that the average hand-to-mouth frequency was 9.5 contacts per hour for 30 children between the ages of two and six years old. Freeman *et al.*[32] recommend a value of 8.5 events per hour, which is the median of the data reported by Reed *et al.*[31] Tulve *et al.*[30] found higher mouthing frequencies. For children between the age of ten months and two years the average frequency of mouthing was 81 events per hour. For children between the ages of two and five years, mouthing events were observed at 42 per hour. Freeman *et al.*[32] found much lower hand-to-mouth frequencies for children between the ages of 3 and 12 years. For the three children of age 3 years that were evaluated, hand-to-mouth frequencies of six events per hour were noted. The mouthing frequency decreased significantly among older children. Among the older children, hygiene and eating habits are thought to play an important role in the amount of chemicals ingested by children through hand-to-mouth activity.[33]

Frequency and duration of surface contact. The duration and number of contacts with a surface is dependent upon the type of activity. Although not quantified, it is noted that in active play children's contacts with playground surfaces are very frequent, with hundreds occurring per hour.[32] The duration of contact is typically shorter for children engaged in active play (3–5 seconds per contact) versus children who were watching television or resting (29 seconds). Given this observation, there appears to be ample opportunity for a child's hand to be re-loaded with contaminants between mouthing events, where several contacts with playground surfaces occur between each mouthing episode. The observations of arsenic loading on hands (Table I) are based on hand-to-wood contact times ranging from a few seconds to a maximum of five minutes, which is shorter than the mean time between mouthing (7 minutes) that is implied by an event frequency of 8.5 per hour.

Efficiency of transfer. For purposes of dose calculation, the efficiency of transfer of dislodgeable arsenic from hands to the oral cavity is the ratio of percentage of arsenic transferred by mouthing, divided by the percentage of arsenic transferred in the experiments in which hand loadings are measured. Transfer efficiency is by definition 100% if the protocol for removing dislodgeable arsenic from hands for purposes of measurement is equally as effective as mouthing.

Hand loading data reported by CalDHS,[23] which include some of the higher values in Table I, were measured by spraying distilled water over the hands as they were rubbed together; no brush or detergent was used. By comparison, mouthing is also a wet process augmented by rubbing between the mouthed parts and the lips and tongue. Given these similarities, it is difficult to argue that the experimental protocol was either more or less effective at removing arsenic from the hands than a child's mouthing would have been. In the absence of measurements, the implied value for transfer efficiency is thus 100%.

While we are aware of no direct measurements of the absolute or relative transfer efficiency of dislodgeable arsenic from the hands to the oral cavity, Kissel *et al.*[34] made measurements of hand-to-oral-cavity transfer of a loamy sand soil. Volunteers who loaded their hands by a hand press onto soil were found to transfer an average of 10%, 16%, and 22% of *total* hand loading to the oral cavity by an event of thumb sucking, finger mouthing, or palm licking, respectively. Because these values are reported relative to total hand loading, they include a factor that accounts for the percentage of hand actually mouthed. For example, a child having a hand area of 100 cm^2 and mouthing 20 cm^2 with a transfer efficiency of 100% would remove 20% of the hand load. Thus, given the caveat that dislodgeable arsenic may have different hand-to-mouth characteristics than soil, these data are consistent with the hypothesis that transfer efficiency of arsenic from hands to the oral cavity by mouthing is high.

A transfer efficiency of 50% is recommended by the U.S. EPA[35] for evaluating pesticide exposures. This recommendation is based upon Reference 36, which reports the efficiency of human saliva in extracting chlorpyrifos, piperonyl butoxide, and pyrethrin from hands. We consider the 50% value to be too low to represent dislodgeable arsenic, given that the skin exhibits higher permeability to oil-soluble materials such as the pesticides listed above than to more polar, inorganic chemicals; saliva, being water-based, is expected to be an indifferent solvent for these hydrophobic chemicals.

We argue that a transfer efficiency of 100% for dislodgeable arsenic is the most appropriate to use, being consistent with the results from Reference 34, and with the implications of the relatively mild procedures used to remove arsenic from hands for analysis in the existing measurements of hand loading. Nevertheless, improving the accuracy of transfer efficiency estimates for dislodgeable arsenic should be a priority for additional research.

Calculations based on analogy with soil ingestion. Another approach to estimating ingestion of dislodgeable arsenic is based on analogy with the ingestion of soil by children at play. The mass of soil ingested per day can be estimated by measuring the daily fecal excretion of a soil tracer element (e.g., silicon), and dividing this value by the percentage of the tracer element in soil where the child plays. Soil adherent to the hands is removed and measured to obtain a value of hand loading. The mass of soil ingested daily, divided by hand loading of soil, is a measure of ingestion expressed in hand loadings per day. This quotient may alternatively be thought of as an efficiency of soil transfer from hand to mouth. If multiplied by total hand area, it can also be thought of as the effective area of hand surface from which soil is ingested daily. If dislodgeable arsenic is assumed to be ingested in the same proportion as adherent soil, then daily arsenic ingestion can be estimated as the product of hand loadings per day times arsenic loading on the hands.

Estimates of ingestion based on this approach bypass the need to estimate either the mouthed hand area or the efficiency of transfer during mouthing. However, in addition to the uncertainties associated with estimating daily soil ingestion, additional uncertainties are introduced by the need to assume that dislodgeable arsenic behaves similarly to soil particles, and that children mouth hands containing grossly observable soil to the same degree as hands loaded with dislodgeable CCA but containing no tangible deposits. Finally, because many studies of soil ingestion calculate only daily ingestion, this method does not provide estimates that are sensitive to hours of daily exposure to CCA-treated wood.

As a result, we have not used this approach to formulate estimates of arsenic ingestion from CCA-treated wood, but instead use hand loadings together with estimates of frequency of hand-to-mouth activity and of transfer efficiency per mouthing event. This latter approach is the more mechanistically satisfying, and is also more readily amenable to step-by-step testing and refinement.

3.3. Bioavailability of Ingested Dislodgeable Arsenic

For purposes of exposure assessment, it is necessary to determine the fraction of ingested arsenic that is bioavailable. Because toxicological data for arsenic have typically been developed on the basis of dosages of soluble salts, the most relevant measure of bioavailability of the arsenic ingested from CCA-treated wood is its bioavailability relative to the bioavailability of a soluble arsenic salt such as sodium arsenate.

It is common to use urinary arsenic measurements to estimate the relative bioavailablity of arsenic in mammals. Thus, the relative bioavailability of an ingested arsenic dose is calculated as the fraction of the dose that appears in urine, divided by the percentage of a dose of a soluble arsenic salt (e.g., sodium arsenate) that appears in urine. Zheng *et al.*[37] found that about 38% of the oral dosage of arsenic from drinking water was excreted in the urine of human volunteers; others typically find that about half of a soluble oral arsenic dose appears in the urine of humans.[38] We are aware of only one experiment[23] in which arsenic rubbed from CCA-treated wood was ingested by a human and subsequently measured in urine. In this experiment about 12% of the arsenic appeared in the urine by four days, at which time measurements were discontinued even though arsenic excretion was still occurring. A lower bound on relative bioavailability was thus about 25%, with the actual value being higher to an unknown degree, depending on how much additional arsenic was eventually excreted in urine.

Given this near-absence of direct measurements of relative bioavailability of arsenic dislodged from CCA-treated wood, estimates must be made on the basis of (1) solubility, or (2) animal studies. The former approach is based on the assumption that the fraction of arsenic that dissolves as it enters the stomach is equally as bioavailable as a soluble arsenic salt, and hence has a relative bioavailability of unity. In Reference 20, the U.S. Consumer Products Safety Commission assumes that the absorption of acid-soluble dislodgeable arsenic is 100%. Tallis[39] argues that extensive arsenic absorption can occur from ingestion of the minimally soluble (at neutral pH) pesticide, lead arsenate, due to its greatly enhanced solubity at the low pH of the stomach. Mann *et al.*[40] implicitly invoke soluble arsenic in their pharmacokinetic model for human arsenic exposure. Weston and Mayer[41] found that solubility in digestive fluid was a strong predictor of absorption efficiency in the case of PAH absorption by polychaetes.

Chromium arsenate, the compound into which arsenic is fixed within the wood, has a log-solubility product (log K_{SO}) of −20.11. Neglecting ionic strength effects and possible complexation of chromium by other ions (each of which would increase its solubility), the calculated solubility of chromium arsenate is approximately 0.1 mg/L at pH 5, in excess of 100 mg/L at pH 2, and as high as 1.5 g/L at pH 1. Measurements of the arsenic content of solutions used to leach CCA-treated wood, and measurements of the solubility of dislodgeable arsenic, demonstrate increased solubility at low pH.[23,42–45] The pH of the human stomach is typically 2 or lower; during fasting the adult stomach contains approximately 100 ml of gastric fluid at a pH of 1.[46] At pH 2, a hand loading of arsenic in the range of tens of micrograms would be expected to be soluble in a very few milliliters of gastric fluid.

One uncertainty concerns the kinetics of dissolution, though this might be expected to be rapid given the small size of chromium arsenate particles in wood. A second uncertainty arises from the possibility that a significant amount of arsenic absorption occurs beyond the stomach, where the pH is higher. Gonzalez *et al.*,[47] for example, demonstrate that arsenic (V) can be absorbed from the small intestine of the rat. In this region, the possibility of re-precipitation of Cr(III) arsenate should be considered. Whether or not re-precipitation is important would depend on the kinetics of precipitation versus the kinetics of absorption, as well as factors such as competition for Cr(III) by other ligands or by absorption, either of which could prevent precipitation of chromium arsenate.

Another approach is to study the bioavailability of arsenic dislodged from CCA-treated wood in animal models. Thus, Aposhian[48] made direct measurements of *absolute* bioavailability to the hamster, finding a mean value of 11.4% ± 1.8% (the corresponding relative bioavailability would be about 23% if a soluble arsenic salt were to have an absolute bioavailability of 50% in these animals). In this study, however, the arsenic was administered as a slurry in which some of the arsenic may have been occluded by wood particles. Moreover, the total administration was 16.5 μg per 75 g hamster. Scaled to a 75 kg adult human having 100 ml of gastric fluid, this corresponds to a concentration of 165,000 μg/L, which exceeds the calculated solubility at pH 2. Thus the findings of this study should be interpreted as lower limits on bioavailability.

Marafante and Vahter[49] administered ^{74}As to hamsters in several forms including lead arsenate, which has a log K_{SO} of –35.39 and thus, like chromium arsenate, has low water solubility at circumneutral pH. The amount of As administered was 2 mg/kg, a dosage somewhat higher than that used by Aposhian,[48] and thus subject to similar concerns about solubility. The cumulative elimination of ^{74}As in urine by the end of three days was 22.2 ± 3.4% of the total amount administered, contrasting with 74.4 ± 4.7% for sodium arsenate and 35.6 ± 8.3% for sodium arsenite. The minimum inferred relative bioavailability is thus about 30%, though Marafante and Vahter[49] conclude that "There was a good correlation between the solubility of the ^{74}As particles in dilute hydrochloric acid and the apparent gastrointestinal absorption in the hamster."

Therefore, although there is considerable uncertainty about the relative bioavailability of dislodgeable arsenic to humans, most existing evidence argues that it lies in a range from 25% to 100%. We have thus chosen a mid-range value of 50% for use in exposure calculations. Further research on the absorption of dislodgeable arsenic by humans, however, is a high priority.

3.4. Dermal Absorption

Arsenic is known to be absorbed through the skin.[50–53] The importance of this pathway to the total dose of arsenic absorbed by a child playing in contact with CCA-treated wood depends on skin loading of arsenic, on the area of skin that becomes loaded with arsenic, and on the efficiency with which the arsenic is percutaneously absorbed.

Skin loading is discussed above in the context of loadings on hands. The authors are aware of no direct measurements of dislodgeable arsenic on non-hand skin surfaces, and caution should be used in extrapolating hand data to other body surfaces. The issue may be partially informed, however, by literature describing the adherence of soil to skin, in which case there is evidence that areal loadings on most body parts tend to be lower than on hands. Kissel[34] measured soil mass and percent of soil coverage accumulated on exposed skin during 30 minutes of play by children aged 8 to 12 years on a prepared, wetted, fluorescent-labeled soil surface. The mean percentage of surface that fluoresced after play was 75%, 20%, 7%, and near-zero for hands, lower legs, forearms, and faces, respectively. An average, calculated using the mid-points of measured ranges of body part areas and normalized by percentage of fluorescing hand area, is 27%. We multiply this value (27%) by the average value for moist-hand loading of dislodgeable arsenic (70 μg/100 cm^2) to estimate a skin loading of 19 μg/100 cm^2 for exposed body parts, and we use this latter value in our exposure estimates. There are considerable uncertainties in this estimate; one uncertainty arises from the unknown time course of arsenic accumulation on skin of the legs, arms, and face. There is a suggestion that the cumulative area of skin to which soil adheres continues to increase throughout a play session; Kissel[34] reports experiments in which the percentage of adults' lower leg area that fluoresced averaged 18% after 15 minutes of work activity in soil, but had increased to 40% after 45 minutes.

Nonhand skin contact with CCA-treated wood may occur during numerous play activities such as sitting, crawling, or rolling on decks or play structures. Arsenic could also be first accumulated on the hands, and then transferred to other body parts. Although arsenic loadings on nonhand body parts may be lower than on the hands, absorption may be higher than from hands because skin on most of the body is thinner than on the palms, and is also subject to abrasion (e.g., on the knees) during play, which increases the efficiency of percutaneous absorption.[54]

Area of skin available for arsenic loading during play. Average body surface area of a two-to-three-year-old male or female child is approximately 0.6 m^2 (50th percentile), increasing to 0.9 m^2 for a child aged six to seven years.[27] This surface area is well correlated ($r = 0.986$) with children's masses,[55] thus simplifying the estimation of doses expressed in terms of mass arsenic per unit mass body weight. U.S. EPA[27] recommends a mean ratio of surface area to body mass (m^2/kg) of 0.0423 for humans in the age range of 2.1 to 17.9 years. However, clothing prevents all of this skin from directly contacting the play surface; thus it is further indicated in Reference 27 that from 10% to 25% of skin may be exposed to contact with soil during play, with the larger values corresponding to summertime exposures. U.S. EPA[27] gives an area of 1,600 cm^2 for the exposed skin (hands, legs, arms) of a three-year-old child. The duration of effective skin contact with dislodged arsenic can exceed play time if loadings acquired during play are not removed by washing immediately following play.

Efficiency of percutaneous absorption. Dermal absorption is typically greatest for small, lipid-soluble (typically uncharged and nonpolar) molecules.[54] On this basis, absorption of arsenate ions (which, complexed with chromium, comprise the bulk of the dislodgeable arsenic) through the skin surface would not be expected to be very efficient. Wester *et al.*[51] studied percutaneous absorption of ^{73}As in the form of arsenate from both water and soil. Absorption into the skin of the rhesus monkey from an aqueous dose was 6.4 ± 3.9% for a trace level dose and 2.0 ± 1.2% for a dose of 2.1 μg/cm^2. Total absorption into samples of human cadaver skin averaged 1.9% over 24 hours, including arsenic that permeated into a receptor fluid (0.93 ± 1.1%) plus residual that could not be washed from the skin afterward. Similar absorption was observed for arsenic from soil.[51] Larger values were observed by Rahman *et al.*,[52] who measured arsenate sorption into mouse skin and found 60% to be absorbed in 24 hours. Because mouse skin is generally considered to be more permeable than human skin, this value may be unrealistically large when applied to humans. On the other hand, Bernstam *et al.*[56] report arsenate permeabilities in laboratory-grown human skin that are consistent with Rahman *et al.*,[52] and high enough that dermal absorption of arsenic could be a significant route of exposure to humans who bathe in water that exceeds drinking water standards for arsenic. To the authors' knowledge, no studies have directly investigated arsenic absorption through living humans' skin, nor have differences between different areas of the body (e.g., through the thicker skin of the palms as compared with the thinner skin of a leg or arm) been studied. We use an absorption value of 2% of dermal loading, based on Reference 52, in order-of-magnitude exposure calculations that appear later in this article. Like the loading values discussed earlier, this value carries significant and unquantifiable uncertainty, and further research is required to better predict percutaneous absorption of arsenic from CCA-treated wood.

3.5. Ingestion from Soil

Arsenic concentrations in soil under CCA-treated wooden equipment. It has been suggested that an additional arsenic exposure pathway for children playing on or around CCA-treated wood structures is via ingestion of soil beneath the structures, which becomes contaminated with arsenic that leaches from the structure. Stilwell and Gorny[12] found average arsenic concentrations in 85 soil samples from under seven different decks to be 76 mg/kg. Larger concentrations in soil were generally found under the older decks. SCS[57] collected 84 samples from under 10 decks in northeast Virginia and found an average of 22 mg/kg and a maximum of 85 mg/kg arsenic. The latter authors argue that Stilwell and Gorny[12] did not control for construction debris (e.g., sawdust) and that therefore their results cannot be conclusively attributed to leaching; however, from the standpoint of exposure of children to CCA-derived arsenic the distinction may be moot. In other studies, Riedel *et al.*[58] found arsenic levels averaging 6 mg/kg under a variety of CCA-treated playground structures. These measurements were to an unrecorded depth, and were in sand, which is generally less sorptive of metals than finer-textured soil, due to its lesser amount of surface area per unit mass. Doyle *et al.*[59] found levels averaging 17 mg/kg in soil and 13 mg/kg in sand beneath CCA-treated wooden fences, while Townsend *et al.*[60] report concentrations in the vicinity of 28 mg/kg beneath CCA-treated wooden structures.

A simple mean of the values reported above is 27 mg/kg, but the data are widely variable and represent a large number of structure types and ages, soil conditions, and climate. This uncertainty is only important to exposure assessment, however, if soil ingestion represents a significant fraction of a child's exposure to arsenic from CCA-treated wood. We have therefore selected the highest reported average, 76 mg/kg, to use in exposure calculations. If use of this value results in relatively low exposures, it can be concluded that obtaining improved estimates of soil contamination beneath CCA-treated structures is not a task of high priority.

There is a possibility for the surface under a playground set to comprise a wood chip buffer material. Because waste wood, from which wood chips are often prepared, has been found to contain a significant amount of CCA-treated wood,[60] this could present an additional pathway for arsenic exposure to children.

Ingestion of soil by children. Calabrese *et al.*[61] used soil tracer methods to estimate daily ingestion of soil by a group of 64 children aged one to four years. They found median estimates of soil ingestion ranging from 9 to 40 mg/day (possibly up to 96 mg/day when corrections for food ingestion were considered), but also observed one child who ingested an estimated 5–8 g/day. Such values differ somewhat depending on the tracer elements used, for which reason Van Wijnen *et al.*[62] use minimum values obtained from among several tracers; they find geometric means of children's daily soil intake values to range from 0 to 90 mg/day under "normal living conditions." Higher values were found, for example, among children at campgrounds, and occasional values in excess of 1 g/day were observed. Thompson and Burmaster,[63] who re-evaluated the results of Binder *et al.*,[64] found an average soil ingestion rate of 91 mg/day, based on Al and Si tracers. Sedman and Mahmood[65] reviewed results of References 61 and 66 with respect to the reliability of the various tracers, and recommend 250 mg/day as a conservative estimate of soil ingestion by young children. Kissel *et al.*[34] consider 100 mg/day hand-to-mouth ingestion of soil by children to be reasonable, and attribute this to a result of many small transfers. U.S. EPA[27] recommends, for assessment purposes, an average daily soil ingestion of 50 mg/day for a $2^1/_2$-year-old child; the corresponding recommended rate of soil ingestion in outdoor play is 20 mg/hr. We use the latter estimate for purposes of estimating exposure, while acknowledging the considerable uncertainty with which it is associated. However, this uncertainty has only a minor effect on the total exposure estimates, due to the dominance of ingestion and absorption of dislodgeable arsenic.

Soil ingestion can be much larger, in the vicinity of several grams per day, in the case of children with pica. Although several percent to over a quarter of children exhibit some degree of pica, the types of nonfood items that they eat vary widely.[67] Thus only a small fraction of pica children seem likely to eat several-gram quantities of soil from beneath CCA-treated decks, or large quantities of playground buffer material. Nevertheless, estimates of arsenic ingestion from CCA-treated wood should be tempered by recognition that surprisingly large amounts of soil can be ingested by children in unusual cases.

Bioavailability of arsenic in soil. Because of the natural variability among soils, bioavailability of arsenic ingested in soil varies with site. This expectation is verified in the literature. Both Roberts *et al.*[38] (Table I) and Ruby *et al.*[68] review reports of relative arsenic bioavailability in soil, which range from 0% to 78% in a variety of test animals including swine, rabbits, and monkeys. Freeman *et al.*[69] found absolute arsenic absorption of about 14% (based on urinary excretion over five days) from soil arsenic administered by gavage to female Cynomolgus monkeys. This would correspond to a relative bioavailability of about 28%. Roberts *et al.*[38] found relative bioavailability (based on urinary excretion data) of arsenic to Cebus monkeys that ranged from 11% to 25% among soils from five different sites. Given these findings, we have chosen 18%, the middle of the range found by Reference 38, to represent relative arsenic bioavailability from soil. Despite the uncertainty in relative bioavailability of arsenic in soil, it has only a minor effect on estimated total arsenic exposure due to the dominance of dislodgeable arsenic.

4. DISCUSSION

The literature relevant to estimating children's exposure to CCA-treated wood contains considerable uncertainty. The calculations that follow are intended to show the probable relative importance of the several exposure pathways, and provide an order-of-magnitude estimate of a daily average arsenic dose to a three-year-old child playing on CCA-treated wood structures. The fraction of days per year a child plays on a CCA-treated structure (f), and where applicable the number of hours per day of such play (HD), are set at arbitrary but reasonable values of 0.5 and 1 hour/day, respectively. The choice of other parameters is as discussed earlier in the text.

Dose from oral ingestion (micrograms per day) = EPC × SA × MF × HD × TE × B × f

EPC = Exposure point concentration (hand loading in micrograms/100 cm^2) = 70 micrograms/100 cm^2
SA = Surface area of skin mouthed (cm^2) = 20 cm^2
MF = Mouthing frequency (events/hour) = 8.5/hr
HD = Time per day exposed to CCA-treated wood (hour) = 1 hour
TE = Transfer efficiency per mouthing (unitless) = 100%
B = Relative bioavailability (unitless) = 50%
f = Fraction of days per year a child plays on a CCA-treated structure (unitless) = 0.5.

The calculated dose is about 30 μg per day.

Dose from dermal absorption = EPC × SA × EFF × B × f

EPC = Exposure point concentration (hand loading in micrograms/100 cm^2 multiplied by percentage of exposed skin loaded with As) = 70 μg/100 cm^2 × 27% = 19 μg/100 cm^2
SA = Area of skin that is uncovered and exposed to the CCA-treated wood (unitless) = 1600 cm^2
EFF = Percent of skin loading that is absorbed (unitless) = 2%
B = Relative bioavailability (unitless) = 1
f = Fraction of days per year a child plays on a CCA-treated structure (unitless) = 0.5 (unitless).

The calculated arsenic dose is about 3 μg/day. Note that EPC is the hand loading value used in the oral ingestion calculation, multiplied by a value that accounts for the expected lesser coverage of dislodgeable arsenic on surfaces other than the hands. B is the quotient of an approximate 50% transmission of absorbed arsenic through the skin, divided by the approximate 50% absorption expected from oral ingestion of soluble arsenic. This estimate does not explicitly incorporate information on hours per day that a child plays on CCA-treated structures, as some of the data on which the above quantities are based either do not contain explicit time course information, or are obtained over different time periods (order of a half hour for skin coverage, order of many hours for skin absorption).

Dose from ingestion of soil = EPC × SI × B × HD × f

EPC = Arsenic content of soil = 76 μg/g
SI = Soil ingestion rate = 20 mg/h
HD = Time per day exposed to CCA-treated wood (hour) = 1 hour
B = Bioavailability (unitless) = 18%
f = Fraction of days per year a child plays on a CCA-treated structure (unitless) = 0.5.

The calculated dose is 0.3 μg/day, which can be neglected relative to dosages from dislodgeable arsenic. It is still less than a microgram per day if the daily or yearly soil ingestion recommendations of U.S. EPA[27] are invoked, and its low magnitude, despite use of a relatively large EPC, suggests that refinement of the parameters is not a task of high priority. It should be noted, however, that the dose could be much larger, of the order of tens of micrograms per day, for a pica child ingesting 1 g of soil per hour, the value suggested for assessment purposes by U.S. EPA.[27]

The sum of the estimates of all three pathways is 33 μg/day. Although this is very approximate, it is also eight times larger than a child's permissible inorganic arsenic intake via drinking water in the United States. Daily water intake of a child, aged 1 to 10 years, averages approximately 0.4 L/day,[27] giving a dose of 4 μg/day for a child whose water intake is from a source containing the current arsenic limit of 10 μg/L.

5. CONCLUSIONS

Existing data suggest that arsenic dosages for children who play in contact with CCA-treated wood can be in the range of tens of micrograms per day, a value high enough that it warrants further study. Oral ingestion of dislodgeable arsenic appears to be the dominant exposure pathway. Dermal absorption may also be important, although data on this pathway are few and incomplete, and even the appropriate form of an exposure model is not certain. Except in exceptional cases (e.g., a pica child, or a situation where CCA-contaminated wood chip buffer material occurs beneath a structure), ingestion of arsenic from soil under a structure ranks lower in importance. It is emphasized, however, that actual exposures remain quite uncertain, due not only to variability among the CCA-treated wood materials and exposure scenarios from location to location, but to severe limitations of the data sets on which these calculations are based. We emphasize, also, that this large (and unquantified) uncertainty means that individual children could ingest significantly more or less arsenic than the above calculations would indicate.

Exposure can be expected to range from near zero for children who rarely contact CCA-treated wood with bare skin, to significantly higher than the above estimates for children who exhibit high hand-to-mouth activity, play much more than an hour per day on CCA-treated wood, live in warm or humid climates that promote extensive and moist contact between wood and skin, or have a deck or playground structure whose wood yields particularly high levels of dislodgeable arsenic. We propose that climates with frequent wetting and drying episodes also promote exposure of children by increasing the rate of arsenic migration to the wood surface, and that structures associated with standing water or abundant ground water may yield especially high dislodgeable arsenic levels both due to enhanced wicking of arsenic from the wood and due to the fact that higher arsenic retention levels are typically used for wood intended for application in wet locations.

Because of the uncertainties associated with exposure, additional research is urgently needed. Direct measurement of urinary arsenic would provide a practical method for directly estimating total arsenic exposure, while concomitant measurements of arsenic excreted in hair, nails, and feces could improve the accuracy of exposure estimates by closing the mass balance of arsenic and yielding insight into mechanisms of arsenic transfer. To more fully understand the dominant mechanisms of exposure, concomitant measurements of skin loadings of arsenic on children at play on CCA-treated wooden structures are essential, as are studies of the uptake processes of both ingested and dermal arsenic.

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