

Environmental Monitoring of Heavy Metals and Arsenic in Soils Adjacent to CCA-Treated Wood Structures in Gangwon Province, South Korea

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Abstract: Chromated copper arsenate (CCA) is a chemical wood preservative that has been intensively used to protect wood from decay during the last few decades. CCA is widely used to build structures such as decks, fences, playgrounds and boardwalks. However, structures constructed of CCA-treated wood have caused adverse environmental effects due to leaching of Cr, Cu and As into surrounding soils. This research was conducted to monitor the vertical and horizontal distribution of Cr, Cu and As in soils adjacent to CCA-treated wood structures in Korea. Two structures constructed with CCA-treated wood were selected at Hongcheon and Chuncheon in Gangwon Province, South Korea. Eleven soil profile samples were collected at depths of 0 to 80 cm at each site, while 12 surface soil samples were collected at distances of 0 to 200 cm from each structure. The soil chemical properties, soil particle size distribution and total metal concentrations were then determined. The results revealed that soils near CCA-treated wood structures were generally contaminated with Cr, Cu and As when compared to the background concentration of each metal. In addition, the concentrations of Cr, Cu and As in soils decreased as the vertical and horizontal distance from the structure increased. Further studies should be conducted to evaluate the mobility and distribution of these metals in the environment as well as to develop novel technologies for remediation of CCA contaminated soils.

Key Words: Chromated copper arsenate, Wood preservative, Soil, pH, Heavy metals, Leaching

INTRODUCTION

Chromated copper arsenate (CCA) is a representative wood preservative that is used to prevent decay of wood by bacteria, fungi and termites¹⁾. During the last several decades, CCA has been used to treat wood structures such as utility poles and children's playgrounds in many countries²⁾. Indeed, it has been reported that CCA-treated wood accounts for more than 80% of the total treated wood in the United States³⁾.

In Korea, CCA-treated wood has been used extensively since the 1980s to build decks, picnic tables, fences, walkways, playground structures and sound barriers⁴⁾. The Korea Forest Research Institute (KFRI) has estimated that CCA-treated wood represents over 90% of the treated wood market (by volume) in Korea²⁾. Of the three types of CCA (A, B and C), type C is the most commonly used in Korea. This type of CCA is composed of 47.5% CrO₃, 18.5% CuO and 35% As₂O₅⁵⁾.

Several studies have shown that Cr, Cu and As leach from structures built using CCA-treated wood, resulting in contamination of the surrounding soils^{6,7)}. Additionally, it has been reported that As is the most mobile element of the components of CCA. However, the concentration

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gradients of Cr, Cu and As around CCA treated structures appear to be limited to 100-150 cm in both the horizontal and vertical distribution^{8,9)}.

Public concern regarding soil contamination and human health problems associated with the leaching of Cr, Cu and As from CCA-treated wood has increased in recent years^{10,11)}. Accordingly, the European Commission (EU) issued a directive restricting the use of wood preservatives that contain As in August of 2004¹²⁾. The USEPA also banned the use of CCA-treated wood for residential purposes such as children's playgrounds, decks, picnic tables, landscaping timbers, residential fencing and walkways in January of 2004¹³⁾. Additionally, the Korean government prohibited the use of CCA-treated wood on August 1, 2007. As a result, CCA-treated wood has been removed from the market in Korea¹⁴⁾; however, residential structures containing CCA-treated wood are still widespread throughout the country. Therefore, long-term monitoring of CCA-treated wood structures is necessary to evaluate their effects on the surrounding environment. This study was conducted to assess the horizontal and vertical distribution of Cr, Cu and As in soils surrounding CCA-treated wood structures in Gangwon Province, Korea.

MATERIALS AND METHODS

On-site identification of CCA treated wood structures

On-site identification of CCA-treated wood structures was conducted using two types of indicators, Chrome Azurol and PAN stains¹⁵⁾. Chrome Azurol stain was prepared by adding 0.6 g of Chrome Azurol S and 5 g of sodium acetate to 500 mL of ethanol. PAN was prepared at 0.065% by weight by dissolving the compound in methanol to create a reagent that could be sprayed over wood. To determine if the samples contained CCA, the surface of the test material was sanded, after which each stain was sprayed onto the surface. As shown in Fig. 1, development of a deep blue color following application of the Chrome Azurol stain or a red color following application of the PAN stain within one minute indicated the presence of copper.

Sampling

Two locations were selected to evaluate CCA-treated wood structures (Fig. 2). Specifically, a site that has been in use for five years in Chuncheon, which is the capital of Gangwon Province, and a site that has been

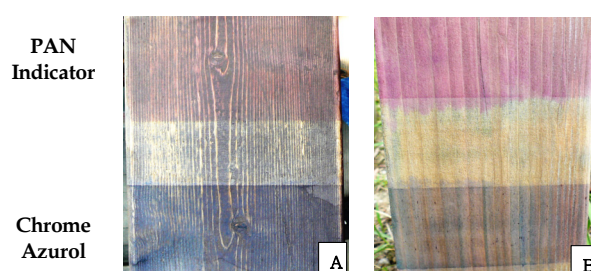


Fig. 1. Stained samples of CCA-treated wood structures at Hongcheon (A) and Chuncheon (B) in Gangwon Province, Korea. The formation of a pink and blue color in response to application of PAN indicator and Chrome Azurol, respectively, indicate that the wood was treated with CCA.

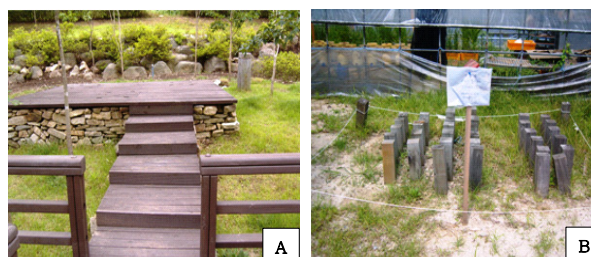


Fig. 2. View of CCA-treated wood structures at Hongcheon (A) and Chuncheon (B) in Gangwon Province, Korea.

in use for six years in a national park in Hongcheon were evaluated. The metrological data indicates that the sites are characterized by heavy annual rainfall, with averages of 1291.3 and 1266.8 mm for Hongcheon and Chuncheon, respectively. Eleven soil samples were collected adjacent to each structure at depths of 0-1, 1-5, 5-10, 10-15, 15-20, 20-25, 25-30, 30-35, 35-40, 40-60 and 60-80 cm using a tube auger to determine the vertical distributions of Cr, Cu and As at each location. In addition, 12 surface soil samples were collected from a 0-30 cm depth at distances of 0-2, 2-4, 4-6, 6-8, 8-10, 10-20, 20-30, 30-40, 40-50, 50-100, 100-150 and 150-200 cm from the structures constructed of CCA treated wood. Soil samples were air-dried and then passed through a 2-mm sieve after removing the coarse fragments, roots and debris, after which they were subjected to the analyses described below. In addition, wood samples were collected from the structures constructed of CCA treated wood at Chuncheon and Hongcheon. The wood samples were air-dried, ground and passed through a 2-mm sieve, after which they were subjected to further chemical analysis.

Analyses

The particle size distribution was determined using the pipette method as described by Akoto, et al.¹⁶. The soil pH and electrical conductivity (EC) were measured in 1:5 deionized water/soil extracts at room temperature¹⁷. Soil and wood samples were digested using a microwave (Mars-X, HP-500 plus, CEM Corporation) according to the USEPA methods 3051 and 3052, respectively^{18,19}. For microwave digestion, the power setting was held at 1600 watts to digest all 40 samples. Overall, 0.5g of each soil sample was digested using 10 mL of concentrated nitric acid (60%) in a microwave by ramping the temperature to 175°C over 5.5 minutes, where it was held for 4.5 minutes. Additionally, 0.2 g of each wood sample was digested using a mixture of 10 mL 60% nitric acid and 2 mL 30% hydrogen peroxide, after which it was heated to 180 ±5°C and held at that temperature for 9.5 min. The extract was then centrifuged, after which the supernatant was diluted to 50 mL using deionized water. The total contents of Cr, Cu and As in the soil and wood extracts were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

RESULTS AND DISCUSSIONS

Soil properties and Cr, Cu and As contents of CCA treated wood

Table 1 shows the particle size distribution of surface

soil samples collected from the sites at Hongcheon and Chuncheon. Soils at both locations were classified as sandy loam, but soil at Hongcheon contained a higher amount of clay (10%) than soil at Chuncheon (4.7%). The average pH of the soil profile samples at Chuncheon and Hongcheon ranged from 6.36 to 7.81 and 5.38 to 5.96, respectively (Fig. 3). These findings indicate that the surface soil pH at Chuncheon was within the neutral range (with an average of 6.5), whereas that of Hongcheon was slightly acidic (with an average of 5.42). Table 2 shows the EC values of the soil samples collected from each location. The highest EC values, which were 0.056 and 0.033 dS m⁻¹ for Chuncheon

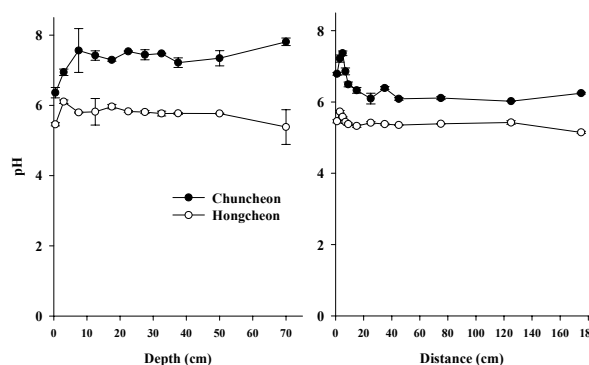


Fig. 3. pH of profile soil samples collected at depths of 0-1 to 60-80 cm and surface soils collected at distances of 0-2 to 150-200 cm from the structures at the study locations.

Table 1. Particle size distribution of surface soils collected from Gangwon Province, Korea

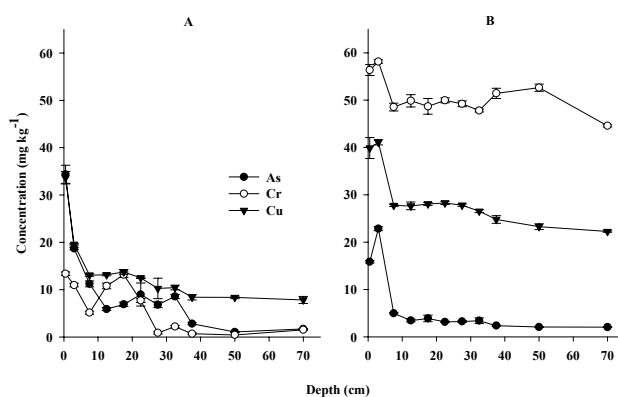
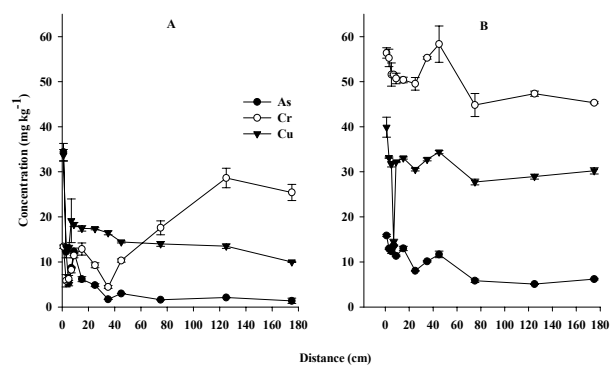
Location	Particle size distribution %			Texture
	Sand	Silt	Clay	
Chuncheon	73.60	21.73	4.67	Sandy loam
Hongcheon	62.05	27.61	10.33	Sandy loam

Table 2. EC of surface soils collected from Gangwon Province, Korea

Depth/Distance (cm)	Direction	EC dS m ⁻¹	
		Chuncheon	Hongcheon
0-1	Vertical	0.050±0.013	0.033±0.00
1-5		0.044±0.006	0.043±0.004
40-60		0.027±0.007	0.031±0.00
60-80		0.063±0.028	0.025±0.00
0-2	Horizontal	0.056±0.001	0.033±0.00
2-4		0.043±0.001	0.027±0.00
100-150 (Background)		0.030±0.00	0.033±0.00
150-200 (Background)		0.017±0.002	0.046±0.00

Table 3. Cr, Cu and As contents in CCA treated wood from Gangwon Province, Korea

CCA-treated wood site	Concentration (mg kg ⁻¹)		
	Cr	Cu	As
Hongcheon	3320.74±19.93	1342.94±2.09	825.05±6.184
Chuncheon	2636.34±15.59	1305.97±35.42	1198.67±234.20

**Fig. 4.** Vertical distribution of Cr, Cu and As (mg kg⁻¹) in profile soil samples collected from (A) Chuncheon and (B) Hongcheon in Gangwon Province, Korea.**Fig. 5.** Horizontal distribution of Cr, Cu and As concentrations (mg kg⁻¹) in surface soil samples collected from (A) Chuncheon and (B) Hongcheon in Gangwon Province, Korea.

and Hongcheon, respectively, were observed in surface soil samples. Generally, the EC values decreased as the distance from the structures constructed using CCA-treated wood increased.

Table 3 shows the total Cr, Cu and As content of CCA treated wood collected from the structures at Hongcheon and Chuncheon. The results showed that the mean concentrations of Cr, Cu and As in the CCA-treated wood at Hongcheon were 3320.74, 1342.94 and 825.05 mg kg⁻¹, respectively, while they were 2636.34, 1305.97 and 1198.67 mg kg⁻¹, respectively, at Chuncheon. Similar findings were observed by Aceto et al.²⁰⁾ and Dawson et al.²¹⁾, who found that the concentrations of Cr, Cu and As in wood samples ranged from 1000 to 5000 mg kg⁻¹. Overall, the highest concentrations of As were observed in CCA-treated wood collected from Chuncheon, while the highest concentrations of Cr and Cu were detected in CCA-treated wood collected from Hongcheon.

Vertical and horizontal distributions of Cr, Cu and As in soil

Figure 4 shows the distribution of leached CCA elements in soil samples collected at Chuncheon and Hongcheon. At Chuncheon, the highest total concentrations of Cr, Cu and As in soil at a depth of 0-1 cm were

13.38, 33.65 and 34.38 mg kg⁻¹, respectively. The highest concentrations of Cr, Cu and As at Hongcheon were found to be 58.15, 41.11 and 22.86 mg kg⁻¹, respectively, and these values were observed at soil depths of 1-5 cm. These findings are similar to the results of a previous study conducted at the same location by Kim et al.²²⁾, who found that the average concentrations of Cr, Cu, and As in surface soil samples collected from underneath the structures constructed from CCA-treated wood were 50.10, 28.7 and 7.52 mg kg⁻¹, respectively, indicating that As and Cu can easily be leached over time from structures constructed of CCA-treated wood. Overall, the concentrations of the metals in the soil at Chuncheon and Hongcheon were Cu > As > Cr and Cr > Cu > As, respectively.

Figure 5 shows the horizontal distribution of metals in surface soil samples collected from each location at depths of 0-30 cm. The concentrations of leached CCA elements clearly decreased as the distance from the structure constructed of CCA-treated wood increased, except for Cr at the Chuncheon location. The highest concentration of As (34.38 mg kg⁻¹) was found at 0-2 cm from the structure constructed of CCA-treated wood, while the As concentration of the background soil was 1.37 mg kg⁻¹ at the Chuncheon location. The highest concentration of Cu was found at a distance of 0-2

cm from the CCA-treated structure, after which it decreased as the distance increased. The highest concentrations of Cr, Cu and As (56.37, 39.89 and 15.87 mg kg⁻¹, respectively) were found in surface soil samples collected at 0-2 cm from the CCA-treated structures at Hongcheon. These values were higher than the background values of 45.32, 30.22 and 6.19 mg kg⁻¹ for Cr, Cu and As, respectively.

The concentrations of Cr, Cu and As in soil near the structures constructed of CCA-treated wood were varied with both soil depth and the distance from the wood structure at both studied locations. The concentrations were generally found to follow the order of Cu > As > Cr and Cu > Cr > As for the profile and surface soil samples collected at Chuncheon, respectively, while they were in the order of Cr > Cu > As for both the profile and surface soil samples collected at Hongcheon. The concentrations of Cr, Cu and As typically decreased as the depth of soil and the distance from the CCA-treated structure increased, which is in agreement with the results of previous studies^{4,22,23,24}. There were also high increases in the concentrations of metals in soils collected from the two studied locations when compared with the concentrations of background soils. Taken together, these findings indicate that Cr, Cu and As can easily leach and become mobile in surrounding soils, which is similar to the results of studies conducted by Stilwell and Graetz²⁵ and Jang et al.²⁶.

Several factors may have contributed to the differences in concentrations of Cr, Cu and As among soil samples collected at Chuncheon and Hongcheon. Specifically, the concentrations of Cr and Cu in the CCA-treated wood collected from Hongcheon were higher than those of the wood that was collected from Chuncheon, which corresponded to the concentrations observed in the soils surrounding the structures at both sites. In addition, the period of service use may have played a role in the concentrations of Cr, Cu and As in the soil surrounding the CCA-treated structures. Furthermore, higher concentrations were observed in the soil surrounding the structure at Hongcheon, which had a longer service time (6 years) than the structure at Chuncheon (5 years). Moreover, the lower soil pH may have led to increased leaching of the metals from the constructed CCA-wood into the surrounding soils in conjunction with intensive rainfall^{10,11,27}. The average pH of the surface soil and soil profile samples at Hongcheon (5.77 and 5.42, respectively) led to increased leaching of the metals from the constructed

CCA-wood when compared to the pH of surface and profile soil samples collected from Chuncheon (7.31 and 6.5, respectively). Finally, the clay fraction percentage (10%) was higher at Hongcheon than (4.7%) at Chuncheon, which may have resulted in decreased leaching at Hongcheon due to the metals sorbing to the clay particles²⁶. Overall, the following factors likely impacted the leaching of elements from the CCA-treated wood structures: 1) the direct contact of CCA-treated wood with the soil, 2) the period of service use, and 3) the retention level of the treated wood.

CONCLUSIONS

This study demonstrated that Cr, Cu and As are released from CCA-treated wood, after which they migrate vertically and horizontally into the surrounding soils. The distribution of Cr, Cu and As in surface and profile soils collected from adjacent to structures constructed from CCA-treated wood at Hongcheon and Chuncheon varied in response to the period of service use, the soil particle size distribution and the soil pH. In addition, the Cr concentration gradient was the highest, followed by Cu for the horizontal distribution at both locations. The USEPA has listed Cr, Cu and As as high risk pollutants based on the results of several studies of the impacts of long-term use of CCA-treated wood during the last few decades. Additionally, the use of CCA-treated wood in the construction of parks, fences, ground planks and houses is considered to be a major source for the release of Cr, Cu and As into the environment. In the present study, high levels of Cr, Cu and As were found in the soils surrounding two structures constructed of CCA-treated wood. These findings indicate that long-term monitoring is required to assess the impacts of CCA-treated wood structures on the environment. Furthermore, development of novel technologies is required for the remediation of CCA contaminated soils.

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