

# Changes of Distribution Coefficients of Cu, Cr, and As in Different Soil Matrix in a Laboratory Scale<sup>\*1</sup>

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## ABSTRACT

Chromated copper arsenate (CCA), a long history of successful preservative, have raised environmental concerns. Adsorption characteristics of domestic soils for chromium, copper, and arsenic were assessed by measuring distribution coefficient ( $K_d$ ) values of these metal components in a laboratory scale. The results revealed that  $K_d$  values were higher in chromium, followed by arsenic and copper in soil matrix. Different soil matrixes resulted in varying mobilities of CCA components. The values of  $K_d$  for all three metals increased with organic matter contents. The results suggest that the mobility of metal components may be very limited to the surface area adjacent to CCA-treated wood due to their fairly large distribution coefficient ( $K_d$ ). However, the metal components would be persistent and accumulated in the soil, resulting in high chemical concentration in service area of treated wood.

*Keywords* : CCA, distribution coefficient, mobility

## 1. INTRODUCTION

Chromated copper arsenate (CCA) has a long history of successful use as a wood preservative, but poisonous heavy metals such as chromium and arsenic in this preservative have raised environmental concerns. A number of studies have evaluated the movement of CCA component in soil environments (Morrell and Huffman, 2003; Shin, 2005; Solo-Gabriele *et al.*, 2003; Stefanovic and Cooper, 2003). Shin (2005) reported metal levels were elevated in soil immediately adjacent to the treated wood. Solo-

Gabriele *et al.* (2003) observed vertical migration of CCA components was limited to 10~30 cm in Florida. Beder (2003) showed that chromium, copper and arsenic level exceeded soil pollution standards and soil remediation criteria in Australia. Since a limitation of these studies is a lack of data on effect of soil on adsorption of leached CCA components, many scientists have tried to investigate the effects of soil characteristics on metal movement in soil (Bloomfield and Pruden, 1980; Chirenje, 2003; Griffin and Shimp, 1978). Affinity of metal adsorption to soil affects mobility properties for the metals.

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Table 1. Characteristics of tested soil

Physical characteristics	Sand (%)	Silt (%)	Clay (%)	Soil texture	Dulk density (g/ml)	Porosity	
	62.0	27.4	10.6	SL <sup>a</sup>	1.57	0.47	
Chemical characteristics	pH (H <sub>2</sub> O)	Organic Matter (%)		Total Nitrogen (%)	P <sub>2</sub> O <sub>5</sub> (mg/kg)		
	5.9	1.8		0.08	108		
CEC, exchangeable cations and base saturation	CEC <sup>b</sup> (cmol <sup>+</sup> /kg)	Exchangeable cations (cmol <sup>+</sup> /kg)					Base saturation (%)
		K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Sum of bases	
	8.14	0.41	0.09	0.60	0.45	1.55	19.04

<sup>a</sup> sandy loam<sup>b</sup> Cation exchange capacity

The affinity can be described as distribution coefficient ( $K_d$ ), and the values of  $K_d$  tend to vary with soil properties.

Because the use of CCA treated wood in Korea has increased continuously since 1983, total amount of CCA treated wood in service was assumed to be enormous. These huge amounts of CCA might result in soil contamination of the metals in near future. There has been, however, little available data for distribution coefficient ( $K_d$ ) of domestic soil, explaining chromium, copper and arsenic movement leached from CCA treated wood in soil.

The object of this study was to measure adsorption characteristics of domestic soils for chromium, copper, and arsenic.

## 2. MATERIALS and METHODS

Soil samples were collected from sandy loam area and organic matters (OM) such as leaves, plant debris were also harvested from the surface area of the soil collection sites. The test soil contained 1.8% of organic matter. Table 1 summarizes characteristics of tested soil including physical characteristics, chemical characteristics, Cation exchange capacity (CEC), exchangeable cations and base saturation. After samples had air dried, it was passed through 2

mm screen sieve. While large materials were ground using mills, soil aggregates were crushed using a clean mortar. Four different types of soil matrix [Soil, Soil : OM (8 : 2) Soil : OM (1 : 1) and OM] were prepared by mixing the samples homogeneously.

Sorption affinities for the test soil matrix were measured according to ASTM D4646-87. Standard solutions for chromium, copper and arsenic (Kanto chemical) were diluted to 100 ppm, and the solutions were added to 10 g soil to produce soil to solution ratio a 1 : 20. After 24 hour agitation, soil and solutions were separated using 0.45  $\mu$ m membrane filter. Metal concentrations for the solutions were measured using atomic absorption spectroscopy (AAS).

A flame atomic absorption spectrometer (Shimadzu AA-6800) in an air-acetylene flame was used for determining the concentrations of chromium and copper in aqueous phases. Arsenic solution reacted with nascent hydrogen to generate gaseous hydride resulted from reactions with 5 M HCl and 0.4% NaBH<sub>4</sub>. The hydride was pyrolyzed in an atomizer to increase sensitivity. Arsenic analysis was also used air-acetylene flame method. The instrumental operating conditions are summarized in Table 2. Distribution coefficient ( $K_d$ ) was defined as the ratio of the concentration of solute sorbed on the soil

Table 2. Operating conditions for AAS

	Chromium	Copper	Arsenic
Lamp currents	8 mA	6 mA	12 mA
Wavelengths	357.9 nm	324.8 nm	193.7 nm
Slit widths	0.5 nm	0.5 nm	1.0 nm
Linear calibration ranges	0.5~10 ppm	0.5~10 ppm	5~20 ppb

Table 3. Values of distribution coefficient ( $K_d$ ) in 4 different soil matrix

Soil matrix	Distribution coefficient ( $K_d$ )		
	Chromium	Copper	Arsenic
Soil	420.5	138.9	357.7
8 : 2 (S : OM)	1808.5	310.2	313.9
1 : 1 (S : OM)	2216.0	539.9	596.3
OM	2315.0	784.9	818.0

divided by its concentration of solute.

### 3. RESULTS and DISCUSSION

In all 4 matrixes, values of the distribution coefficient  $K_d$  were higher in chromium, followed by arsenic and copper. Copper was about 3 times more mobile than chromium (Table 3 and Fig. 1). Griffin and Shimp (1978) also found similar results of distribution coefficient for three metals. Chromium tended to stick to soil matrix strongly, explaining limitation of chromium movement in soil surface (Morrell and Huffman, 2003; Shin, 2005).

Stefanovic and Cooper (2003) addressed that copper and chromium present in organic soils contaminated with CCA were less mobile and less bio-available than metals present in mineral soil. Chromium commonly exists in two anionic forms, the more mobile and toxic chromate ions from chromium (VI), and the less mobile and toxic from chromium (III) (Chirenje *et al.*, 2003). Therefore, the distribution coefficient of  $K_d$  for each ion should be investigated for further studies.

$K_d$  of all three metals in the soil matrixes exhibited a progression of decreasing pattern in the order pure organic matter (OM), Soil : OM (1 : 1), Soil : OM (8 : 2), and pure Soil matrix (Table 3 and Fig. 1). Compared to 100% soil matrix, pure OM matrix showed 5.5, 5.7, and 2.3 times higher distribution coefficient ( $K_d$ ) for chromium, copper, arsenic respectively (Fig. 1). Content of organic matter in soil is a very important factor, increasing the adsorption the metals. Soil organic matter is probably the principal reducing agent in surface soils. For example, Bloomfield and Pruden (1980) reported that soil organic matter was identified as the electron donor when hexavalent chromium was reduced to chromium (III) under normal soil pH and redox conditions. In Stefanovic and Cooper (2003)'s sequential extraction procedures, mobilities of those elements decreased in highly organic soils.

### 4. CONCLUSIONS

Values of the distribution coefficient ( $K_d$ ) were

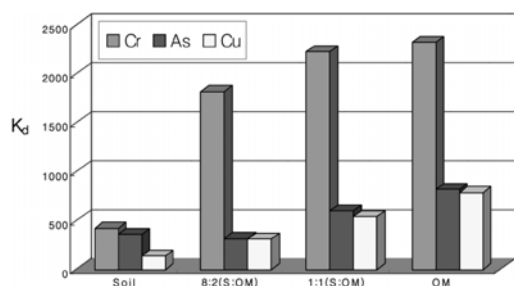


Fig. 1. Values of  $K_d$  for three metals in different soil matrix.

higher in Chromium, followed by Arsenic and Copper in all 4 matrix. Different soil matrixes resulted in varying mobilities of CCA components. The values of  $K_d$  for all three metals were lower in the soil without organic matter, but increased with organic matter contents.

While further studies will be necessary to explain leaching behavior at different soil characteristics such as soil texture, pH, and porosity, density and exchangeable cation, the results suggest that the mobility of metal components may be very limited to the surface area adjacent to CCA-treated wood due to their fairly large distribution coefficient ( $K_d$ ). However, the metal components would be persistent and accumulated in the soil, resulting in high chemical concentration in service area of treated wood.

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