

# Leaching of Chromium, Copper and Arsenic in Soils and Rapid Identification of CCA-Treated Woods Using Modified PAN Stain

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Although several studies have reported that Cr, Cu and As can leach from CCA-treated woods, few studies have been conducted on this topic in Korea. Therefore, this study was conducted to monitor Cr, Cu and As leaching from CCA-treated wood products and to develop a rapid identification method for CCA-treated wood products by using indicators such as PAN stain. Soil samples were collected at depths of 0-70 cm and wood samples were collected by thickness of wood layer. The soil and wood samples were then digested and analyzed for Cr, Cu and As concentrations using an atomic absorption spectrometer. The As and Cu concentrations decreased sharply with depth from 34.38 and 33.65 mg kg<sup>-1</sup> at 0-1 cm to 1.72 and 7.84 mg kg<sup>-1</sup> at 70 cm, respectively. In general, As was more mobile than Cr and Cu in the soil. For wood samples, the Cr, Cu and As concentrations were higher in the outer layer (0-0.5cm) than the inner layers (0.6-4.5cm). Evaluation of rapid identification methods revealed that 100% acetone with 0.1% PAN indicator was the best combination for detection of CCA-treated wood in the field.

**Key words:** Chromated copper arsenate (CCA), Leaching, PAN stain, Soil, Wood preservative

## Introduction

Wood is treated with chemical preservatives to prevent biological degradation. Chromated copper arsenate (CCA) treated wood contains copper and arsenic, which serve as a fungicide and an insecticide, respectively, as well as chromium to fix the copper and arsenic into the wood fibers (Warner and Solomon, 1990; Chirenje, 2003). Wood preservatives are divided into two groups oil borne and water borne preservatives (Ibach, 1999). Wood products treated with oil-borne preservatives are usually used for outdoor industrial applications because they are oily to the touch and in many cases have odors associated with them (Ibach, 1999). Conversely, wood products treated with waterborne preservatives are preferred for residential applications because they can be painted, do not have an odor and are dry to the touch (Freeman and McIntyre, 2008). Water borne wood preservatives are typically composed of metal oxides and in some cases an

added organic co-biocide (Freeman and McIntyre, 2008).

There are three types of CCA-treated wood: Type A, Type B and Type C. The most common CCA-treated wood used in Korea is Type C, which is composed of 35.0% As<sub>2</sub>O<sub>5</sub>, 47.5% CrO<sub>3</sub> and 18.5% CuO, by weight (Lebow and Foster, 2004). CCA-treated wood has recently attracted a great deal of attention due to its adverse impacts on the surrounding environment (Gezer et al., 2005; Green III and Clausen, 2005). Indeed, several studies have reported elevated levels of toxic metals in the vicinity of CCA-treated wood structures (Hingston et al., 2001; Townsend et al., 2003), and leaching of CCA from treated wood into surrounding soil has been well-documented (Chirenje et al., 2003; Morrell et al., 2004; Robinson et al., 2006; Dagan et al., 2006). Arsenic and chromium (VI) have been found to leach in substantial quantities from CCA treated wood. Additionally, carcinogenic hexavalent chromium, which is known to account for up to 50% of the total chromium in CCA (Nygren et al., 1999), has been shown to leach out of CCA treated wood. Stilwell and Gorny (1997) found that the soil around CCA-treated wood structures that had been in place for four months to 15 years contained an overall

average chromium concentration of  $43 \text{ mg kg}^{-1}$ , while control soils only contained  $20 \text{ mg kg}^{-1}$ . They also reported that the overall average arsenic concentration underneath the treated decks was  $76 \text{ mg kg}^{-1}$ , while the concentration of the control samples was only  $3.7 \text{ mg kg}^{-1}$ . The copper in CCA-treated wood can also be toxic to aquatic life. Specifically, the  $LC_{50}$  for aquatic invertebrates and fish ranges from 5 to  $100,000 \text{ } \mu\text{g l}^{-1}$  (Cox, 1991). The potential toxicity of Cu, Cr and As from CCA-treated wood to humans, animals and plants has been well documented in recent years (Clausen, 2004; Kartal et al., 2005; Green III and Clausen, 2005). Moreover, workers exposed to massive quantities of arsenic, chromium and copper have reported skin irritation and found to have an increased risk of chronic health effects. Such exposure may occur via direct contact with the wood surface (Stilwell and Graetz, 2001) or indirectly through leaching of the chemicals from the CCA-treated samples to surrounding soils (Hingston et al., 2001).

Recently, the USEPA announced a voluntary decision by industry to phase out the consumer use of CCA-treated wood products by 31 Dec. 2003. Thus, as of the year 2004, CCA treated-products were no longer allowed for residential use. Residential purposes include dimensional lumber and wood used in play structures, decks, picnic tables, landscaping timbers, residential fencing, patios and walkways/boardwalks (Rahman et al., 2004). The European Commission has also issued a rule restricting the use of As-containing wood preservatives (European Commission, 2003). Furthermore, the Korean government has prohibited the use of CCA-treated wood in wood structures since August 1<sup>st</sup>, 2007. As a result, CCA-treated wood has been removed from the Korean market (Kim et al., 2006). Although the production of CCA-treated wood for residential applications has been prohibited, there are still large structures constructed of CCA-treated wood present worldwide (Kim et al., 2008). Thus, identification of CCA contamination is very important for the protection of human health.

Several stains are used to identify CCA-treated wood. Specifically, PAN and/or Chrome Azurol S can be used to determine the presence of copper in the -treated wood (Blassino et al., 2002), while a Diphenyl carbazide/isopropyl alcohol stain can be used to detect Cr in CCA treated wood (Jacobi et al., 2007). The primary objective of this study was to develop a rapid and accurate stain that could identify CCA-treated wood in the field. In addition,

metal leaching from CCA-treated wood into surrounding soils was also investigated.

## Materials and Methods

**Experimental design** Wood blocks that had been treated with chemical preservatives were obtained from a local market in Chuncheon City, Korea. PAN (1-(2-pyridylazo)-2-naphthol) stain was used to confirm the presence of chromium, copper and arsenic-based preservatives in these wood blocks (Blassino et al., 2002), after which they were embedded in test soil located in Chuncheon at random (Fig. 1). To monitor the environmental impact of metals that leached from CCA-treated wood into the adjacent soils, the wood blocks were left in the soil for five years. The average annual rainfall in Chuncheon during the study period was approximately 1266.8 mm, the majority of which was concentrated in the summer (Chuncheon Weather Station, 2009).



**Fig. 1. View of the CCA-treated wood structures used in the experiment.**

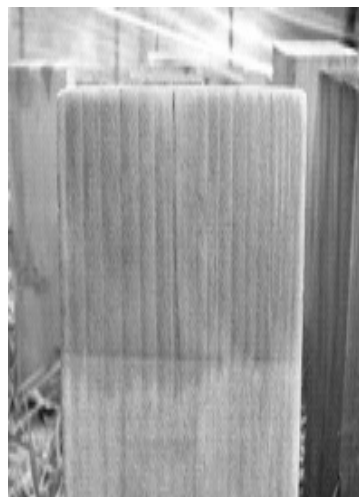
**Soil and wood samples** To evaluate the vertical distribution of the tested trace elements, 11 soil samples were collected from locations around the abandoned CCA-treated wood blocks. Specifically, profile soil samples (0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm, 25-30 cm, 30-35 cm, 35-40 cm, 40-60 cm and 60-80 cm) were collected at various vertical distances from soil surface using a soil tube auger. The soil samples were then passed through a screen to remove the stones, roots and debris, after which they were air-dried, crushed and passed through a 2-mm sieve.

Wood samples were collected from structures constructed of CCA-treated wood. Specifically, three wood samples were collected based on the thickness of the wood layer. Inner and outer layers (0-0.5 cm and 0.6-4.5 cm from wood surface, respectively) were collected as were composite samples from 0-5 cm. The wood samples were collected according to the differences in wood color due to the application of CCA-chemical preservative. The samples were air dried, crushed and passed through a 2-mm sieve for further chemical analysis (Abdelhafez et al., 2009).

**Chemical analyses** The dried soil and wood samples were prepared for analysis by microwave digestion (Mars-X, HP-500 plus, CEM Corporation) according to USEPA methods 3051 and 3052 (Chirenje et al., 2003 and Baba et al., 2008). Three 0.5 g replicates from each soil sample were weighed ( $\pm 0.1$  mg) into microwave teflon vessels containing 10 mL of concentrated nitric acid (60%) and then sealed. The microwave power program was set at 1600 watts and  $175^{\circ}\text{C}$  for 10 minutes. The digests were then transferred to 50 mL volumetric flasks, brought up to volume with distilled deionized water and stored until analysis. For wood sample digestion, 0.2 g of each sample was digested in 10 mL nitric acid (60%) and 2 mL hydrogen peroxide (30%). The microwave temperature was set at  $180 \pm 5^{\circ}\text{C}$  for 9.5 min. The digests were then centrifuged and transferred to 50 mL volumetric flasks and then brought up to volume with distilled deionized water. The soil and wood digests were analyzed for Cr, Cu and As using an atomic absorption spectrometer.

**Wood staining** PAN (1-(2-pyridylazo)-2-naphthol), which is an orange-red solid with a molecular formula of  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}$  (Blassino et al., 2002), was used to identify trace elements in the CCA-treated wood (Fig. 2). PAN staining was conducted in the laboratory and under field conditions. To prepare the indicator solution, PAN was added to methanol in solid form at 0.05% (weight basis) to create a reagent that could be sprayed over wood. To deepen the magenta color formed on the wood, it is recommended that the PAN concentration be increased to 0.065% (weight basis) (Blassino et al., 2002). In this study, the PAN indicator was used at different concentrations and solubilized in different solvents. Specifically, 0.1 or 0.15% PAN was dissolved in 100%

(weight basis) methanol (Blassino et al., 2002). In addition, 0.1 or 0.15% PAN was dissolved in a 50: 50 mixture of methanol and acetone and in 100% acetone (weight basis). The differences between the CCA-treated and untreated wood color are shown for different concentrations and solvents.



**Fig. 2.** PAN stains of CCA-treated wood samples located in Chuncheon, Korea. The formation of magenta to red color indicates that the wood was treated with CCA.

## Results

**Concentrations of target elements in CCA-treated wood** Figure 3 shows the average concentrations ( $\text{mg kg}^{-1}$ ) of chromium, copper and arsenic in different CCA-treated wood samples. The results showed that the concentrations of tested trace elements were significantly higher in the outer layer than the inner layer. The concentrations of Cr, Cu and As in the outer layer (0.0-0.5 cm) were 4759.47, 2528.34 and 3672.43  $\text{mg kg}^{-1}$ , respectively. These values were 17.64, 14.32 and 96.27 times greater than those collected from 0.6-4.5 cm, which were 269.80, 256.52, and 26.26  $\text{mg kg}^{-1}$ , respectively. Overall, the concentrations increased in the following order:  $\text{Cr} > \text{As} > \text{Cu}$ , which was similar to the trends observed in the other samples (Fig. 3). Conversely, the concentration of target contaminants was very low in the inner layer (0.6-4.5 cm) when compared to the outer layer and the composite sample. Overall, the concentrations of Cr, Cu and As in the composite sample were 2636.34, 1305.97 and 1198  $\text{mg kg}^{-1}$ , respectively, and occurred in the following order:  $\text{Cr} > \text{Cu} > \text{As}$  as shown in Fig. 3.

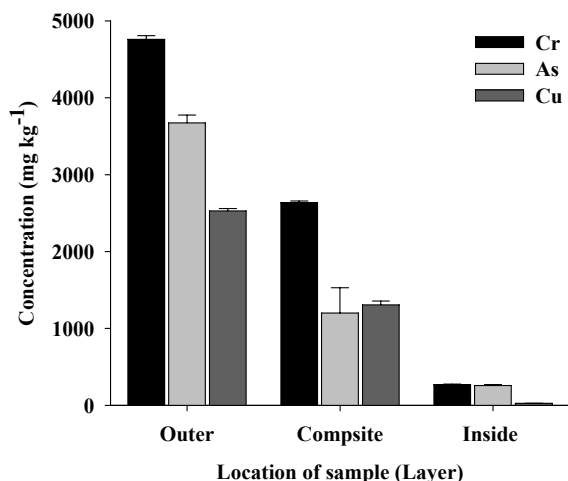


Fig. 3. Cr, Cu, and As concentrations in the inner, outer and composite CCA-treated wood samples.

#### Vertical distribution of target metal concentrations in soil

Figure 4 shows the vertical distribution of Cr, As and Cu in soils collected from CCA-treated wood structures. The target contaminants appeared to show increased concentrations for the 0–1 cm soil sample when compared to the levels in the underlying soil layers. Arsenic, copper and chromium were present in the highest concentrations (34.38, 33.65 and 13.38 mg kg<sup>-1</sup>, respectively) at 0-1 cm, being present in concentrations 20, 4.30 and 9.00 times greater, respectively, than at 70 cm (1.72, 7.84 and 1.53 mg kg<sup>-1</sup>, respectively). Overall, the target contaminants gradually declined with increasing soil depths.

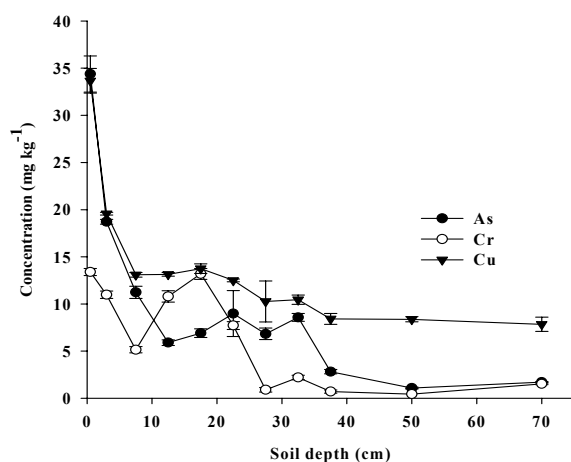


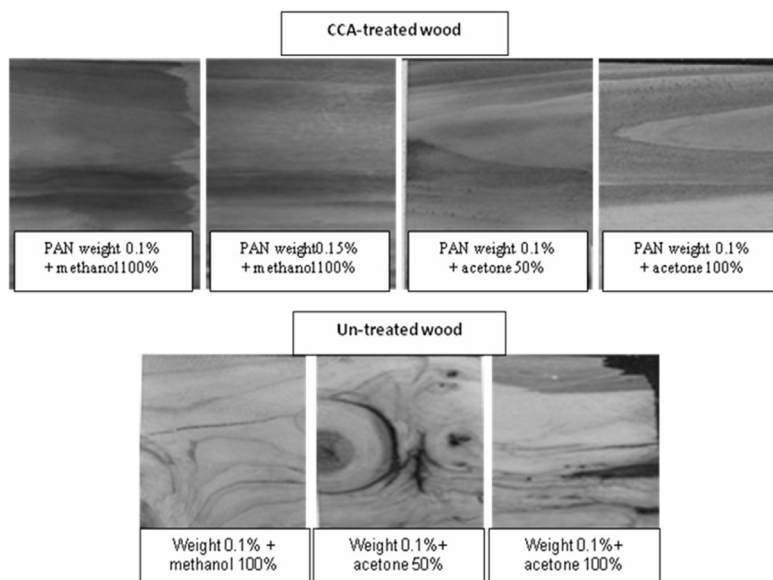
Fig. 4. Vertical distribution of Cr, Cu and As in soils collected from CCA-treated wood structures (adapted from Abdelhafez et al., 2009).

**Wood staining** Figure 5 shows the effect of different concentrations of PAN stain and solvents on the CCA-treated wood and untreated wood color. Application of PAN stain to CCA treated wood results in magenta to red color, while the sample is stained orange if CCA is not present. As shown in Fig. 5, different concentrations (0.1 and 0.15%) and solvents (methanol and acetone) of PAN had no effect on the untreated wood color. Conversely, the addition of PAN and solvents always resulted in the formation of magenta to red color on CCA-treated wood. The formation of the magenta to red color had no effect when the concentration of PAN increased from 0.1% to 0.15% in 100% methanol. Similar results were obtained for PAN stain at concentrations of 0.1% and 0.15% in 50% acetone with 50% methanol and in 100% acetone (Data not shown). In contrast to methanol, 100% acetone gave an increased magenta to red color formation and clearance, especially in combination with 0.1% PAN indicator, whereas 50% acetone had only a slight effect. The results showed that the reaction time for the PAN stain and the magenta to red color formation was 60 and 45 s for 100% methanol and 50% acetone combined with 50% methanol, respectively. Similarly, the reaction time for color formation was about 25 s for 100% acetone, and samples treated with this reagent dried quickly (Data not shown). Based on these findings and the previous results, 100% acetone in combination with 0.1% PAN indicator is the best solvent for the identification of CCA-treated wood.

## Discussion

#### Concentration of target elements in CCA-treated wood

The results of the present study indicated that the concentrations of Cr, Cu and As in the CCA treated wood ranged from 1000 to 5000 mg kg<sup>-1</sup>. Similar findings were observed by Dawson et al., (1991) and Aceto et al., (1994). Additionally, the results showed that the concentrations of target trace elements were significantly higher in the outer 0.0-0.5 cm than the inner 0.6-4.5 cm of the constructed CCA-treated wood. These findings were likely due to the heavy rainfall in the study area. The effect of weathering and water repellents on the amount of Cr, Cu and As released from the CCA-treated wood through leaching was studied by several investigators. In this regard, the amount of Cr, Cu and As leached can be influenced by a number of factors, including the dimensions and wood



**Fig. 5.** Effect of PAN stain concentrations and solvents (methanol and acetone) on the red color of treated and untreated wood.

species of the treated product, the concentration of preservative in the wood and the exposure environment (Lebow et al., 2004). However, the size and dimension of the wood products determine the surface area/volume ratio and the wood-grain angle that is exposed. Because the leaching rate is a function of the rate of movement of water into and out of the wood, leaching is more rapid when water is able to move along the wood grain rather than across it. In addition, the pH of rain water plays an important role in the release of metals from the constructed CCA-treated wood (Cooper et al., 1991 and Temiz, et al., 2006).

#### **Vertical distribution of target metal concentrations in soil**

As shown in Fig. 4, the As, Cu and Cr concentrations sharply decreased to 34.38, 33.65 and 13.38 mg kg<sup>-1</sup>, respectively, at 0-1 cm and these values were 20, 4.30 and 9.0 times greater, respectively, than the values observed at 70 cm, which were 1.72, 7.84, and 1.53 mg kg<sup>-1</sup>, respectively. These results may be attributed to heavy rainfall during the summer (1266.8 mm) (Chuncheon Weather Station, 2009) in the Chuncheon region, which might have contributed to the release of the metals. The amount of metal leaching can be impacted by a number of factors such as the type of wood species, the retention values of the treated wood and the exposure environment. For example, rainwater may penetrate the inner portions of the wood and dissolve the Cr, Cu and As, thereby leading to their release into the surrounding soil

(Warner and Solomon, 1999; Kartal et al., 2007; Kim et al, 2007). Arsenic was the most mobile of the three target metals in the soil samples, which is in good agreement with the results of previous studies that have reported that the arsenic concentration tended to persist to a depth of 15 cm, after which it decreased rapidly (Stilwell et al., 1997). Conversely, the amount of chromium released from the CCA-treated wood was the lowest. This likely occurred because chromium serves as a binding agent that fixes arsenic and copper into the wood fibers (Lebow et al., 2005). The results of the current investigation indicated that the concentration of chromium and copper increased in the surface soil when compared with the subsurface samples. These findings agree with the results of previous studies in which chromium and copper concentrations were found to rapidly decrease with depth (Kartal et al., 2005; Rahman et al., 2004; Janget al., 2002).

**Wood staining** The results indicate that PAN indicator had no effect on the untreated wood color (Fig. 5). Furthermore, the use of 100% acetone in combination with 0.1% PAN indicator was found to be the best solvent for the detection of CCA-treated wood. These findings suggest that acetone facilitated the penetration into wood and enhanced the reaction between the metals and the PAN indicator. The reaction occurs when metal is bound to the oxygen of an OH- group by replacing the hydrogen atom and concurrent binding to pyridine and the azo nitrogen atoms, producing magenta to red color. These

findings are similar to the results of a study conducted by Blassino et al. (2002) who recommended increasing the PAN indicator concentration up to 0.065% by weight to deepen the magenta color formed on the wood.

## Conclusions

Our study showed that the concentrations of tested trace elements were significantly higher in the outer layers than the inner layers of CCA treated wood. Because the leaching rate is a function of the rate of movement of water into and out of the wood, leaching occurs more rapidly when water is able to move along the wood grain rather than across it. In addition, the pH of rain water plays an important role in the release of metals from CCA-treated wood. The results of the present study indicated that the use of acetone at a rate of 100% in combination with 0.1% PAN indicator produced the best results for the identification of CCA-treated wood. These findings may have been due, at least in part, to increased penetration of the wood in response to acetone and promotion of the reaction between metal and PAN indicator. CCA-treated wood structures that were five years of age released large amounts of chromium, copper and arsenic into the soil, and the levels were especially higher in the surface soil. The high levels of metals observed in the surface soil could be attributed to the high level of annual rainfall in the study area. Furthermore, the results of this study revealed that arsenic was more mobile than chromium and copper. Taken together, the results presented here indicate that CCA-treated wood does impact the environment by increasing the metal concentrations (Cr, Cu and As) of soil. However, the potential impacts of these releases on soil contamination, human health risk and ecological hazards are open to interpretation.

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## CCA 목재방부제 설치지역 토양의 크롬·구리·비소 분포와 PAN 지시약을 이용한 CCA 방부목의 현장 검출방법 개발

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목재방부제는 목재의 수명 연장을 위해 오랜 기간 사용되어 왔으나 이중 상당수는 환경에 유해한 금속을 다량 함유하고 있다. 특히 전세계적으로 목재방부시장을 점유하고 있는 크롬·구리·비소계열의 목재방부제 CCA (Chromated Copper Arsenate)는 환경에 유해한 독성 금속류로 구성되어 인체에 대한 피해와 환경오염에 대한 우려가 지적되고 있다. 미국의 경우 플로리다 주를 비롯하여 CCA 오염지역에 대한 복원사업을 추진하였으며 주별 CCA 오염도를 조사한 바 있다. 그러나 국내의 경우 목재방부제의 사용으로 인한 토양오염에 대한 연구는 극히 미비한 실정이므로 CCA에 대한 환경적 측면에서의 평가가 절실하다. 본 연구는 국내에서 가장 널리 사용된 목재방부제인 CCA를 선정하여 목재방부제 설치지역 토양의 깊이별 크롬·구리·비소 농도를 측정하였으며 국내에 널리 산재된 CCA 방부목 설치지역을 현장에서 효율적으로 검출할 수 있는 간이 PAN 지시약을 개발하고자 수행하였다. 토양 시료는 0~70cm 깊이에서 채취하였고 방부목은 목재 깊이별로 구분하여 채취한 후 산분해하였고 AAS를 이용하여 각 원소의 전함량을 측정하였다. 토양 중 비소와 구리는 0~1 cm에서 각각 34.38 mg/kg, 33.65 mg/kg 였으나 70 cm에서는 1.72 mg/kg, 7.84 mg/kg로 토양 깊이에 따라 급격히 감소하였다. 원소별 이동성의 경우 비소가 타 원소(크롬, 구리)에 비해 상대적으로 이동성이 높은 것으로 평가되었다. 목재 시료의 경우 내부보다는 표면(외부)의 농도가 높게 나타났으며 각 원소별로 1,000~5,000 mg/kg의 수준으로 검출되었다. 현장에서 CCA 방부목을 효율적으로 판단하기 위한 지시약의 조성을 개발하고자 다양한 종류 및 농도의 용매와 PAN의 농도를 조절하며 발색 시간과 정도를 측정한 결과 100% 아세톤을 용매로 0.1% 수준의 PAN을 조제하는 경우 가장 짧은 시간에 발색하여 현장에서 방부목을 효율적으로 검출할 수 있을 것으로 평가되었다.