

## Aquatic Phytoremediation of CCA and Copper Contaminated Water

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### ABSTRACT

The removal of selected metals by duckweed (*Lemna minor*) and parrotfeather (*Myriophyllum aquaticum*) from a simulated aqueous environment contaminated with Chromated Copper Arsenate (CCA) and copper sulfate was studied in a controlled laboratory experiment. The duckweed and parrotfeather's tissues were analyzed to evaluate the removal of copper (Cu), chromium (Cr), and arsenic (As) from CCA contaminated water (125 mg/L Cu, 220 mg/L Cr, and 205 mg/L As) and from copper sulfate contaminated water (60 mg/L Cu) over a 7 day period. The vigor of the plants was also recorded during this period. The results showed that the duckweed and parrotfeather both removed the metals from the water in each experiment. For the CCA contaminated water study, duckweed removed approximately 60% of each metal from solution while parrotfeather removed approximately 45% of each metal. For the copper contaminated water study, duckweed removed approximately 85% of the copper concentration from solution while parrotfeather removed approximately 77% copper from solution. As for the vigor of the plants in the CCA study, duckweed remained rather healthy throughout most of this study. Parrotfeather sharply declined in vigor after two days into experiment. In the copper study, both plants remained fairly healthy through the duration of the experiment.

Keywords: Water Quality, Surface Water, Nonpoint Source Pollution

### Introduction

Chromated copper arsenate, also known as CCA, has been one of the most widely used and best known wood preservatives in the wood industry. Concerns regarding leaching of arsenic from playground equipment constructed of CCA treated wood and a greater public awareness of potential dangers from arsenic in drinking water resulted in various EPA rulings and the wood treating industry's decision in December 2003 to voluntarily halt the production of CCA treated wood for residential use (Hauserman, 2001, Pawlitz et al., 1997, Shalet et al., 2006, Smith et al., 1998, Saxe et al., 2006). Periodic application of copper sulfate  $\text{CuSO}_4$  to commercial channel catfish as parasitic control or algicide

have also resulted in copper accumulating four to five times higher in treated pond sediments than untreated pond sediments (Han et al. 2001). The high level of Cu in sediment could have long-term toxicological effects on pond phytoplankton hindering its critical role in maintaining suitable water quality for fish production (Han et al. 2001). Thus, cost-effective and environmentally friendly methods for the clean up of CCA and Cu contaminated sediments and water are needed (Shimp et al, 1993, Kakitani et al. 2006).

Presently there are several options for treating contaminated water (Kakitani et al. 2006). The most common technique is a coagulation/filtration method that involves removing pollutants by chemically conditioning particles to

agglomerate into larger particles that can be separated and settled. This scheme is followed by running the contaminated water through various filters that trap and hold the pollutants for disposal. This method for cleanup is usually disruptive to the environment that surrounds the contamination and not cost efficient.

Recently, a promising alternative remediation technique, called phytoremediation that can be utilized in certain situations to replace other costly methods has been explored (Shimp et al. 1993, Huang et al, 2004, Kakitani et al, 2006). Phytoremediation is the use of plants to absorb certain contaminants from soil or water through a plant's root system into the body of the plant where they are stored and ultimately disposed (Huang et al. 2004). The optimal results for successful phytoremediation would be the maximum removal of heavy metals from contaminated water with a minimal level of phytotoxicity to the plant tissues. The interaction between phytotoxicity, metal accumulation and plant species is highly complex and requires research.

The objectives of this study were to evaluate the removal of arsenic, chromium, and copper by aquatic plants during phytoremediation and to observe the effects of these metals on the health and vigor of the plants.

**Methods and Materials**

Hydroponic Study

Survival and Selection Test

Four sets of aquatic plants were screened in a preliminary trial, duckweed (*Lemna minor*), water lily (*Nymphaea* spp.), parrotfeather (*Myriophyllum aquaticum*), and an azolla (*Azolla filiculoides*)/duckweed (*Lemna minor*) mixture. Each plant was divided into two groups with three jars in each group. One group served as a control, and the other as the treatment group. In the treatment groups, 100 ml of CCA solution (adjusted to 5 mg/L arsenic, 7 mg/L chromium, and 2.5 mg/L copper concentrations) was added to each jar. The plants were placed into each respective jar and allowed to sit for 5 days. All plant samples were collected, dried, digested, and a chemical analysis performed to see which plants were better accumulators of selected metals. Duckweed and parrotfeather were selected for further studies

based on these results (Table 1) .

Table 1. Screening results from preliminary trail.				
Plant Selection Test				
Plant Species	Metal Analysis (mg/kg)			Tolerance
	Arsenic	Chromium	Copper	
<i>Duckweed</i>				
control	14	19	86	good
treatment	9199	30952	18020	good
<i>Parrotfeather</i>				
control	6	4	226	good
treatment	5381	14489	5239	fair
<i>Water lily</i>				
control	1	0	26	good
treatment	729	3354	4275	fair
<i>Azolla/Duckweed</i>				
control	15	0	272	good
treatment	4509	21403	15211	fair

**Selected Species Study**

Duckweed: CCA Phytoremediation Experimental Design

The CCA solution was adjusted to a 205 mg/L arsenic concentration, 220 mg/L chromium concentration, and 125 mg/L copper concentration. Duckweed was obtained from the Department of Plant and Soil Sciences at Mississippi State University. Sixteen 500 ml glass jars were obtained and labeled. Eight jars were the control group and eight were to serve as the treatment group. In each group, approximately 5-6 grams of duckweed plants were added to four jars and the other four contained no plants for comparative purposes. In the treatment group, 100 ml of the CCA solution (consisting of CCA, de-ionized water, and Miracle-Gro) was added to each jar. In the control group, the jars were filled with 100 ml of the de-ionized water/Miracle-Gro solution. The plants were allowed to sit for 7 days under the fume hood with monitored light conditions and a consistent temperature approximately 24 °C.

## Parrotfeather: CCA Phytoremediation Experimental Design

The same CCA solution prepared for the duckweed hydroponic study was used for the parrotfeather hydroponic study. Parrotfeather (*Myriophyllum aquaticum*) was obtained from the Department of Plant and Soil Sciences at Mississippi State University. Sixteen 500 ml glass jars were obtained and labeled. Eight jars served as the control group and eight jars served as the treatment group. In each group, parrotfeather plants were added to four jars and four jars were left without plants for comparative purposes. In the treatment jars, 100 ml of the CCA solution (consisting of CCA, de-ionized water, and Miracle-Gro) was added to each jar. In the control group, the jars were filled with 100 ml of the de-ionized water/Miracle-Gro solution. Parrotfeather plants were allowed to sit for 7 days under the fume hood with monitored light conditions and a consistent temperature approximately 24°C.

## Duckweed: Cu Phytoremediation Experimental Design

Sixteen 500 ml glass jars were obtained and labeled. Eight jars served as controls and were filled with 100 ml of de-ionized water/Miracle-gro. Four jars received three teaspoons (5-6 grams) of duckweed per jar and four jars were left without plants for comparative purposes. The second eight jars were to act as the treatment group. Each of these jars were filled with 100 ml of a water/Miracle-gro mix that had been amended with Cu SO<sub>4</sub> (adjusted to 60 mg/L copper concentration). Four jars were given three teaspoons (5-6 grams) of duckweed and four jars were left without plants for comparative purposes. The plants were allowed to sit for 7 days under the fume hood with monitored light conditions and a consistent temperature of around 24°C.

## Parrotfeather: Cu Phytoremediation Experimental Design

Sixteen 500 ml glass jars were obtained and labeled. Eight jars served as controls and were filled with 100 ml of de-ionized water/Miracle-gro only. Four jars received one healthy parrot feather per jar and four jars were left without plants for comparative purposes. The treatment group had eight jars. Each jar was filled with 100 ml of water/Miracle-gro that had been amended with Cu SO<sub>4</sub> (adjusted to 60 ppm copper concentration). Four jars were given a parrot-

feather per jar and the other four were left without plants for comparative purposes. The plants were allowed to sit for 7 days under the fume hood with monitored light conditions and a consistent temperature approximately 24°C.

## Chemical Analysis

Water samples were taken before and after the experiment from each jar. All plant samples were collected from containers, washed in 3% HNO<sub>3</sub> and de-ionized water, and weighed. The plant tissues were then dried, ground, and weighed. Plant samples (approximately 0.2 g) were digested in HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (Han and Banin, 1997). The digested plant and water samples were then filtered and analyzed for As, Cr, and Cu using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

## Results and Discussion

### CCA Hydroponic Study

The average total concentrations of arsenic, chromium, and copper in water samples before planting and after the harvest of duckweed and parrotfeather are shown in figures 1 and 2. Duckweed and parrotfeather both showed significant removal of all three metals from the water samples. Duckweed, however, showed the greatest metal removal from the water with approximately 60% of each metal removed from solution. Parrotfeather removed approximately 45% of the metals from the water samples.

The average total metal concentrations in the plant tissues of duckweed and parrotfeather are presented in Table 2. Duckweed accumulated more metals into the plant tissues than did parrotfeather. Duckweed accumulated about twice the chromium than arsenic and about four times more chromium than copper. One reason that the aquatic plants were able to remove more of the heavy metals from the water than terrestrial plants could from soil is the soluble form of the metals in water. Metals must be in a soluble form in soils before plants can absorb them. In an aqueous solution, metals are already in soluble form so accumulation by the plants can be achieved much easier. Also, water is homogeneous and metal concentrations are uniform throughout the water sample.

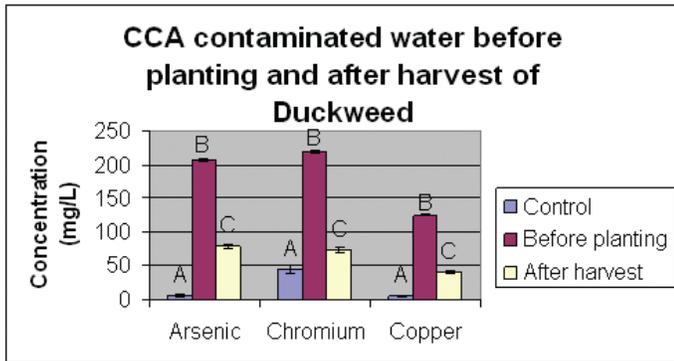


Figure 1. Average metal concentration of arsenic, chromium, and copper in CCA contaminated water before planting and after the harvest of duckweed. Columns with the same letter indicate no significant difference in concentration values at the  $\alpha = .05$  probability level. Error bars represent standard deviations.

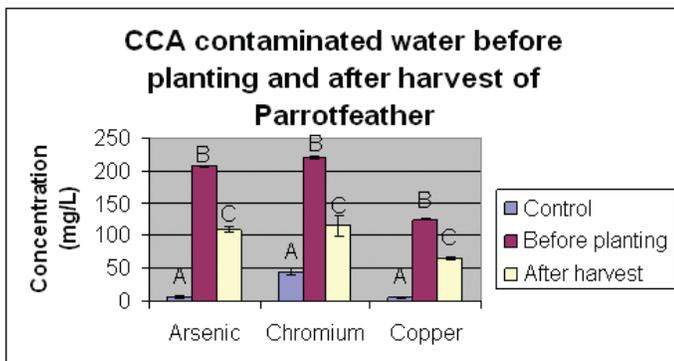


Figure 2. Average metal concentration of arsenic, chromium, and copper in CCA contaminated water before planting and after the harvest of parrotfeather. Columns with the same letter indicate no significant difference in concentration values at the  $\alpha = .05$  probability level. Error bars represent standard deviations.

#### Copper Hydroponic Study

The average total concentrations of copper in water samples before and after the harvest of duckweed and parrotfeather are shown in figures 3 and 4. Duckweed and parrotfeather both showed significant removal of copper from the water samples. Duckweed removed the greatest

Table 2. Metal concentrations in duckweed and parrotfeather tissues.

Plant species	Metal Analysis (mg/kg)		
	Arsenic	Chromium	Copper
Duckweed			
control	0	33	80
treatment	11,828	2,728	5,322
Parrotfeather			
control	0	0	31
treatment	2,766	6,152	1,809

Table 3. Copper concentrations in duckweed and parrotfeather tissues.

Plant Species	Metal Analysis
	(mg/kg)
Copper	
Duckweed	
control	76
treatment	19,037
Parrotfeather	
control	251
treatment	8,414

amount of copper with around 85% being removed from solution. Parrotfeather removed around 77% of the copper from the water samples.

The average total copper concentrations in the plant tissues of duckweed and parrotfeather controls and treatment plants are given in Table 3. Duckweed accumulated over twice the amount of copper into its plant tissues as did parrotfeather. This could be due to an increased surface area of the duckweed compared to parrotfeather or because duckweed is a better accumulator of copper than parrotfeather.

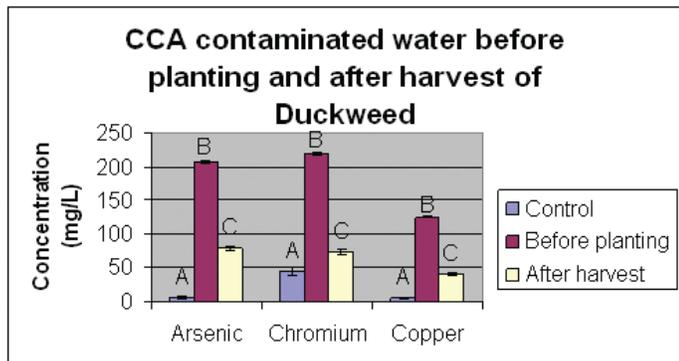


Figure 3. Average concentration of copper in Copper contaminated water before planting and after the harvest of duckweed. Columns with the same letter indicate no significant difference in concentration values at  $\alpha = .05$  probability level. Error bars represent standard deviations

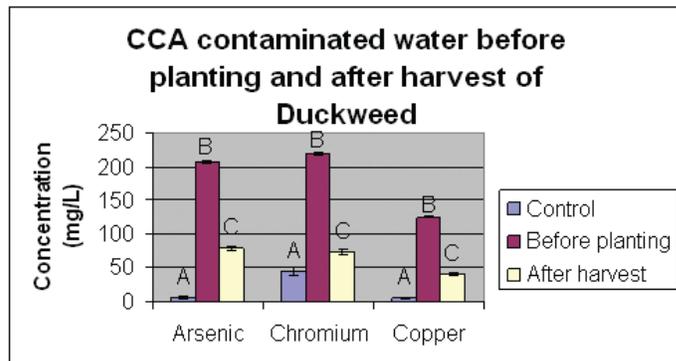


Figure 4. Average concentration of copper in Copper contaminated water before planting and after the harvest of parrotfeather. Columns with the same letter indicate no significant difference in concentration values at  $\alpha = .05$  probability level. Error bars represent standard deviations.

## Conclusion

Duckweed and parrotfeather were both found to be effective accumulators of the metals present in CCA and copper contaminated water. Duckweed could be considered a superior accumulator because of its ability to remove large concentrations of metals and remain vigorous and healthy. These studies have shown that certain plants can have remedial effects on metals in aqueous environments. More research is needed to better understand the symbiotic or antagonistic relationship between plants and metals. Also, the results obtained from the hydroponic experiment described in this paper could provide good preliminary data for using aquatic plants in remediating contaminated lakes or lagoons.

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# POSTER SESSION

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