

Retardance of Rainwater-Leached Metals in Amended Soil Systems: A Case Study, Agricultural Amendments Effect on a CCA-wood Ash/Soil System

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Abstract

This ongoing research study evaluates the performance of various soil amendments to immobilize or retard the leaching of Cu, Cr, and As species from a soil/CCA-treated wood ash mixture. The amendments evaluated were agricultural lime ($\text{CaCO}_3/\text{MgCO}_3$), gypsum soil softener ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and iron sulfate (FeSO_4). Results of this investigation show that native soil alone retards the leaching of As and Cr species, while amendments applied alone or in combinations further retard As and Cr species leaching compared to the unamended soil/CCA-treated wood ash mixture. The gypsum soil amendment is most effective in reducing the rainwater leaching of Cr and As species by 72% and 77%, respectively, compared to the unamended soil/CCA-treated wood ash mixture. Cu leaching is increased in the presence of the native soil and by all amendments. This research further evaluates the influence upon metals leaching by the soil/CCA-ash system components, pH conditions, the composition of wood ash, and also the potential for water contamination by the leached CCA-metals.

1. Introduction

1.1 Background

Increasing quantities of used CCA-treated wood are entering the waste stream in the Southeastern United States due to a combination of factors that include; normal end of the service life; design changes (Clausen, 2000); a ban on future use in domestic settings (Federal Register, 2003) and an associated increased public awareness of health concerns related to CCA-treated wood use. The Southeastern region of the U.S. has been the largest producer and user of CCA-treated soft pine wood due to the adverse effects of the hot and humid climate and the increased presence of parasitic insects on untreated wood in this region. A common practice is to dispose of waste CCA-treated wood by onsite burning, producing an ash that poses a threat to humans and the environment (Solo-Gabriele et al, 1999).

CCA-treated wood ash is a source of heavy metals, primarily copper, chromium and arsenic. At the μgL^{-1} level in water, copper species are toxic to marine algae and macro-invertebrates (Harrison et al., 1984), chromium species exhibit teratogenic and carcinogenic effects, and arsenic species exhibit toxic and carcinogenic effects in humans and other animal receptors (Solo-Gabriele et al., 1999; LaGrega et al., 1994).

The interaction of CCA-treated wood ash with soil is complex. Factors such as soil chemical composition, organic matter content, pH, solution complex formation, climatic and geologic conditions, all play a role in the changes of the metal species found in the

CCA-wood ash and soil mixture (Evanko and Dzombak, 1997). Since the adverse effects of each CCA-metal species present are dependent, in part, upon the valence state of the metal (Helsen et al., 2003) the oxidation-reduction reactions of CCA- metals occurring naturally with a soil system can change these metals to more or less toxic and available metal species (NRC, 1994). Concentrations of metal species leaching from disposal sites tend to overwhelm the natural ability of the soil to change the valence state of these metal species; therefore, a chemical soil amendment may increase the rate and extent of this remediation process (Evanko and Dzombak, 1997).

The overall goal of this research has been to determine the effectiveness of various soil amendments to immobilize or retard the leaching of CCA-metal species. A CCA-treated wood burn site was investigated to determine baseline conditions and obtain data for the lab study. The CCA-metals concentrations in the soil/CCA-treated wood ash at the burn site were replicated in the laboratory to conduct batch and soil column leaching studies and pH studies. Figure 1 presents the comparative effectiveness of the amendments and combination of amendments toward the reduction in leaching of CCA-metals. Gypsum soil softener (CaSO_4 in legend and filled black squares in Figure 1) was determined overall to be the most effective amendment in retarding the leaching of the CCA-metals and therefore is the focus of this paper.

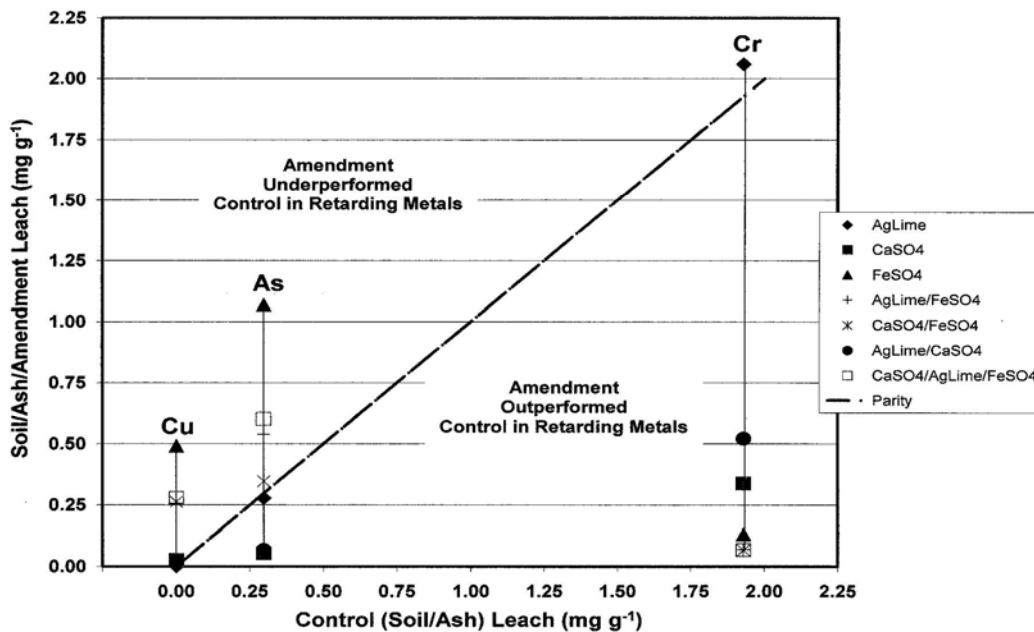


Figure 1 – Evaluation of Metals Leached from Amended Soil/CCA-ash (mg g^{-1}) vs Control (Soil/CCA-ash) (From Harden and Johnson, 2009)

1.2 Site Description

The site investigated for baseline studies is located on the shoreline of Lake Tuscaloosa, a 5,900 acre municipal water reservoir located in Tuscaloosa County, Alabama. Lake Tuscaloosa reservoir serves as the main source of water for a population

of approximately 125,000 and is a local recreation area. With over 3,000 permitted residential lots along the reservoir, the use of treated wood for decks, boathouses, piers, and retaining walls is extensive. The study site is a residential lot with a 30-year history of scrap CCA-treated wood burning at a single burn site during the construction of two boathouses, a pier, and a deck. This burn site of 2.5 meter diameter is located 6 meters from Lake Tuscaloosa on a 15 degree slope. Potential paths of metal movement into the lake are by direct runoff and infiltration.

2. Methods and Materials

2.1 Analytical Methods

The metals content of the CCA-treated wood ash and the CCA-treated wood ash/soil mixtures were determined by acid microwave digestion (HNO_3) analyses in a MARS-X microwave using EPA SW-846 Methods 3015 and 3051 and the Toxic Characteristic Leaching Procedure (TCLP) (EPA SW-846 Method 1311) was used to provide regulatory context to the waste ash (US EPA, 1996). Leachates and TCLP extracts were analyzed with inductively coupled plasma atomic emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 3000DV) to determine the concentrations of As, Cr, and Cu. The ICP limits of detection (LOD) were as follows: Cu, 0.025 mg L^{-1} ; Cr, 0.026 mg L^{-1} ; As, 0.034 mg L^{-1} and results were converted to mg g^{-1} for soil/ash and ash as necessary. The total carbon and organic carbon content of the test soil was determined by the loss on ignition method (LOI) and the soil pH values were determined by standard methods from SSSA Book 5, Methods of Soil Analysis, Part 3 Chemical Methods (Soil Science Society of America, 1996). The pH values for soil and column leachates were determined with a ThermoOrion pH Meter, Model 520. The pH 4.6 natural rainwater used in the experimentation was collected under the controlled conditions of rainwater flowing from plastic sheets into a plastic container and had no detectable levels of Cu, Cr, or As. All metals results are stated on a mass basis unless otherwise noted.

2.2 Sampling Methods

Surface and core soil samples were taken from the burn site and also at contaminated and uncontaminated sites up-gradient and down-gradient of the burn site to the lake shore. These samples were used to determine CCA-metals concentrations in the soil columns and establish the ratio of soil:CCA-ash used in preparation of the laboratory soil:CCA-ash mixture.

Surface samples were taken at the burn site by collecting several samples down to a depth of 5 centimeters. These samples were then combined to obtain one composite sample. The samples were dark gray in color indicating the presence of ash in the topsoil. Core samples were taken by driving a 5 centimeter diameter conduit pipe into the sample point. The soil cores were cut at 7.5 and 15 centimeter depths. Depth samples were taken from the interior of the core to eliminate potential wall effects. All samples were taken under dry conditions.

2.3 Characterization of the Soil and Soil/Ash Mixture at the Burn Site

Up-gradient Soil

The test soil used in lab experiments was uncontaminated up-gradient topsoil taken from the vicinity of the burn site. The soil was analyzed for As, Cr, and Cu to establish baseline metals concentrations in the test soil. No detectable concentrations of the CCA metals were found. The soil was classified as Paleudult Ultisol with a 10-15 centimeter layer of sandy clay loam of 2-33% clay and 0.5-2% organic matter (USDA Soil Survey, 1981) underlain by impermeable kaolinitic clay over fractured rock. The soil was sieved (STS #30, 0.6 mm) to increase particle uniformity and remove large particles that could cause column channeling.

CCA-treated Wood Ash

The test ash was prepared under controlled burn conditions and sieved (STS #10, 2.00 mm) to remove large unburned cinders. This ash was used in the preparation of the soil/CCA-ash control and amended soil mixtures

Soil/CCA-treated Wood Ash Mixture

The test soil/CCA-ash mixture (control) was produced by mixing up-gradient soil with CCA-ash in the ratio of 5.28:1 to replicate soil/CCA-ash metal concentrations in the topsoil layer at the burn site. The resulting approximate CCA-metal concentrations in the mixture were (metal mg g⁻¹ control mixture ± 95% confidence interval): As (11.1±0.3); Cr (12.2±2.6); Cu (13.7±1.8) and were found to closely approximate the field conditions at the burn site of Cu (14.5±0.2), Cr (17.4±0.6), and As (12.2±0.5). The gypsum soil amendment was added to produce the gypsum-amended soil/CCA-ash mixture.

2.4 Column Experiment Design and Stoichiometry

Redox-stoichiometric data for potential metal-amendment reactions (Buerge and Hug, 1988) were used to establish minimum soil amendment/CCA-metal ratios. These ranged from 3:1 for single amendments up to 9:1 for all three amendments (Harden, 2005) which was in excess of minimum soil amendment/CCA-metal ratios.

Accelerated leach experiments with pH 4.6 rainwater, to determine the effects of controlled rainwater leaching events on duplicate sets of test soil/CCA-ash columns, were designed to closely replicate the As, Cr, and Cu concentrations in the soil at the site. Data was generated on the mass of each metal leached from individual and cumulative results of the nineteen leachings. Leach event volumes ranged from 45-100mL for a total of 1845 mL which is equivalent to the typical annual rainfall for the site (130 cm yr⁻¹) (Pitt and Durrans, 1995). The metals concentrations and the pH of the leachates were measured in order to determine the mass of metal leached per unit mass of ash and to compare the mass leaching and pH changes of the amended and unamended soil/CCA-ash mixtures.

Each polycarbonate column, 4.2 cm in diameter and 61 cm in length, contained 231 g test soil, 49 g CCA-ash, and 68 g of each soil amendment when applied alone or in combinations. These proportions of soil amendment to CCA-ash were established from calculations described previously to provide for potential stoichiometric conversion by oxidation-reduction reactions. The columns flowed by gravity infiltration from the top with samples collected as the leachate exited the bottom.

3. Results and Discussion

Results presented include baseline characterization of the burn site soil, CCA-metals analysis of the ash and soil-ash (control) mixture and both batchwise and column rainwater leaching studies of CCA-metals from the gypsum-amended and unamended soil/CCA-ash mixtures.

3.1 CCA-ash Metals Characterization and CCA-metals Concentration at the CCA-treated Wood Burn Site

Laboratory ash samples, analyzed in triplicate by microwave digestion and ICP-OES, revealed that metals concentrations in the ash ($\text{mg metal g}^{-1} \text{ ash} \pm 95\%$ confidence interval) were: As (69.6 ± 2.1); Cr (76.7 ± 16.0); Cu (86.3 ± 11.3) for a total ash CCA-metals mass of $232.6 \text{ mg metals g}^{-1} \text{ ash}$. Although the ash samples were sieved for uniform size, the variation in the range of metals concentrations across replicate samples is an indication of the heterogeneous nature of the ash material.

Spatially variable surface and depth samples were taken in a straight line extending from the lakeshore sediment located 6 meters down-gradient from the burn site, through the burn site (0 meters data point) and to the up-gradient area located 4 meters from the burn site. The metals concentrations were highest at the burn site (As, $12.2 \pm 0.5 \text{ mg g}^{-1}$; Cr, $17.4 \pm 0.6 \text{ mg g}^{-1}$; Cu $14.5 \pm 0.2 \text{ mg g}^{-1}$) with lower concentrations appearing down-gradient toward the lakeshore. This is a result of the movement of leached metals and with downgrade re-adsorption of metals to soil and/or physical transport of ash toward the lakeshore. Furthermore, leached metals penetrated the topsoil to a depth of 15 centimeters at the burn site and 3 meters down-gradient from the burn site, whereas in all other areas sampled the metals were confined to the upper 5 centimeters of topsoil. Up-gradient metals concentrations near the burn site were all low ($<0.025 \text{ mg g}^{-1}$).

3.2 Regulatory Classification of the CCA-Ash by TCLP

The Toxic Characteristic Leaching Procedure (TCLP) test was performed on triplicate ash samples to establish the potential Resource Conservation and Recovery Act (RCRA) status of waste ash. The RCRA TCLP regulation limit is 5.0 mg L^{-1} for both Cr and As while Cu is not regulated. The results of the TCLP test on the ash ($\text{mg L}^{-1} \pm 95\%$ confidence intervals) yielded: As (578 ± 44.7); Cr (0.719 ± 0.057); Cu (6.72 ± 0.713). The data shows that As TCLP is two orders of magnitude above the RCRA limit of 5.0 mg L^{-1} while Cr TCLP is 0.719 mg L^{-1} which is below the 5.0 mg L^{-1} RCRA limit. The TCLP result for Cu is 6.72 mg L^{-1} but Cu is not a RCRA regulated TCLP metal. The TCLP data for As classifies the CCA-ash as a RCRA D004 hazardous waste exhibiting the

characteristic of toxicity. Generators of CCA-ash are therefore subject to RCRA regulations although household generators are exempt. Although TCLP analyses yield data that is useful for regulatory context, the TCLP leach conditions are unlikely to accurately model the expected results from rainwater leaching of metals from CCA-ash.

3.3 Batch Rainwater Leaching of Unamended CCA-Ash and the Soil/CCA-Ash Mixture

The main objective of this experiment was to determine the potential of unamended test soil/CCA-ash mixture to inhibit or promote the rainwater leaching of metals compared to CCA-ash alone. The total carbon content of the test soil was analyzed to be 2 percent which is consistent with the carbon content reported by the USDA Soil Survey. Triplicate CCA-ash samples were leached and triplicate soil/CCA-ash samples were leached then re-leached to simulate wet weather events as described earlier. Data generated from this experiment indicates that the leachability of Cr and As is significantly lowered in the presence of the test soil while Cu leachability is increased. During the first leach the soil/CCA-ash mixture retarded the leaching of Cr and As by 75% and 74% respectively, but enhanced Cu leaching by 280% compared to CCA-ash alone. Subsequent re-leaching of the test soil/CCA-ash resulted in a cumulative decrease of 250% in the leached mass of As and 1150% in the leached mass of Cr compared to CCA-ash alone. Conversely, an increase of 1550% was recorded in the leached mass of Cu.

Mass Transfer Mechanisms

The retardance of Cr and As by mixing with test soil is likely due to adsorption of Cr and As to the mineral and organic components of the kaolinitic clay and the presence of the oxides Al and Fe which may lower the metals mobility during the first leach of test soil/CCA-ash compared to the leach of CCA-ash alone (Evanko and Dzombak, 1997). As supported by Stollenwerk and Grove (1985), describing nonspecific adsorption, Cr had its largest leached mass during the first leach of test soil/CCA-ash compared to the release of As, indicative of mobile soil particles and clays, through colloidal mobility, contributing to the initial higher leached mass of Cr.

The mobility of Cu significantly increases as Cu becomes bound to mobile organic material. Through depletion of Cu-binding organic matter from the soil, an increased mass of Cu leaches from the test soil/CCA-ash combination. During this depletion, release of Cu from surface adsorption sites in the soil decreases and release from inner-sphere adsorption sites becomes dominant as supported by Lehmann and Harter (1984).

Metals Composition of CCA-Ash and Rainwater Leach of CCA-metals from the Soil/CCA-ash Mixture

The CCA-ash sample is composed of a total of 23% (232.6 mg g^{-1}), by mass, of the metals Cu, Cr, and As, determined by microwave digestion and ICAP-OES analysis. During a rainwater first leach of the CCA-ash sample mixed with test soil, the total mass of those metals leached was 6.9 mg g^{-1} ash with individual leachings of As 2.6 mg g^{-1} , Cr

4.2 mg g⁻¹, and Cu 0.03 mg g⁻¹. In summary, the data reveals that the first rainwater leach results in only a 3.0% leached mass of the combined mass of Cu, Cr, and As and that the mass of each metal represents approximately one-third of the total mass of As, Cr, Cu in the ash. Of the three metals, the leached mass during the first leach follows the order: Cr > As > Cu.

Evaluation of Potential Contamination of Water by Leached CCA-metals

A batchwise study of the potential contamination of water by CCA-metals and the regulatory contamination levels of those metals in water shows that As, Cr, and Cu metals in an unamended test soil/CCA-ash mixture, have the potential to contaminate large volumes of water to beyond Safe Drinking Water Act - Maximum Contaminant Level (SDWA MCL) standards (Cr, 100 µg L⁻¹; As, 10 µg L⁻¹) and standards for toxicity to freshwater clams (Cu, 10 µg L⁻¹) (Harrison et al., 1983). That contamination potential in L of water contaminated per gram of CCA-ash is: As, 469 Lg⁻¹; Cr, 29 Lg⁻¹; Cu, 113 Lg⁻¹.

3.4 Column Rainwater-leaching of Amended and Unamended Soil/CCA-ash

Effect of Gypsum Amendment on pH and CCA-metals Mobility During Rainwater-Leaching

System pH conditions and amendment combinations have varying effects on the leaching of As, Cr, and Cu. The Control (unamended) and Gypsum (gypsum-amended) combinations are weakly basic systems (7.3-8.0 pH) that become more neutral as the columns reach equilibrium and exhibit relatively low leachability of CCA-metals.

The Control and Gypsum columns exhibited similar impacts on Cu increased mobility with leached masses from the Gypsum column nearly two orders of magnitude greater than for the Control column. This relationship is evidence of the binding mechanism of Cu to organic material in the soil and the adsorption to CaCO₃ in the ash, while CaSO₄ supplies Ca⁺² ions that displace Cu⁺² ions from organic material and surface adsorption sites of soil (Lehmann and Harter, 1984). Chromium in this pH range of 7.3-8.0 hydrolyzes to sparsely soluble chromium hydroxides, adsorbs strongly to mineral and organic surfaces, and coprecipitates with other minerals (Hug et al., 1997) and Su and Puls (2001) which explains the adsorption of As in terms of both ionization of adsorbates and adsorbents which reaches its maximum adsorption at pH 7.

Evaluation of Gypsum Amendment Performance

A projection of the effect of the gypsum amendment on the leaching of CCA-metals over a one-year period of rainfall was performed using CCA-metals leaching data and data generated by interpolating between analyses leach data points. The results are presented in Figures 2a (Cr), 2b (As), and 2c (Cu), the graphic presentations of the simulated one-year leach of Cr, As, and Cu – Control vs Gypsum Amendment. These plots extend to 1845 mL of rainwater, the equivalent of 19 rainfall events or one year of rainfall (130cm) at the burn site.

The simulated one-year cumulative mass leach of metals (mg g^{-1}) from the soil/CCA-ash without amendment is as follows: As, 2.53; Cr, 4.31; Cu, 0.012. The resulting simulated one-year cumulative mass leach of metals (mg g^{-1}) from the soil/CCA-ash with gypsum amendment is as follows: As, 0.578; Cr, 1.20; Cu, 0.048. It is noted that the mass leaching data percentages project a 400% increase of Cu leaching, but this represents a small relative mass of Cu compared to Cr and As masses. The data also reflects a 72% and 77% reduction in the leaching of Cr and As and therefore significant reductions in the mass of the leached metal. The figures indicate that Cr has the largest remaining initial leaching after amendment with gypsum, while As is the most retarded.

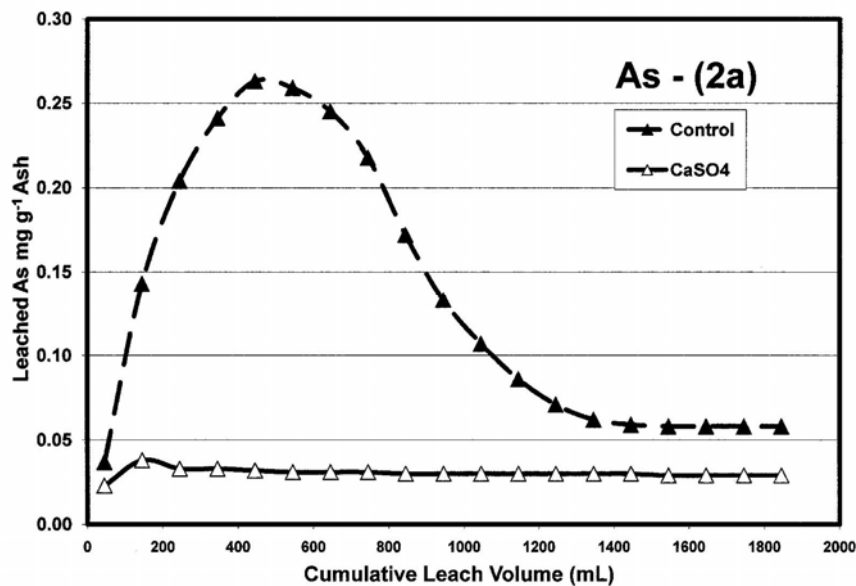


Figure 2a – Simulated One-Year Mass Leach of As – Control vs CaSO_4 Amendment (Harden, 2005)

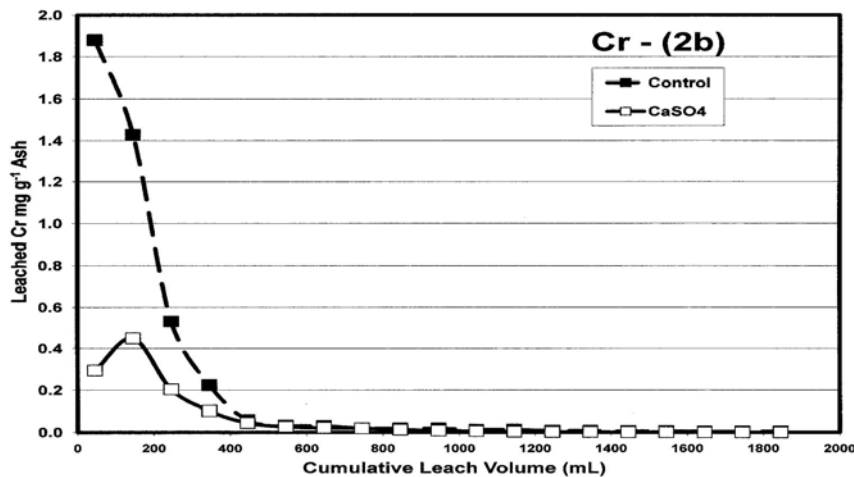


Figure 2b – Simulated One-Year Mass Leach of Cr – Control vs CaSO_4 Amendment (Harden, 2005)

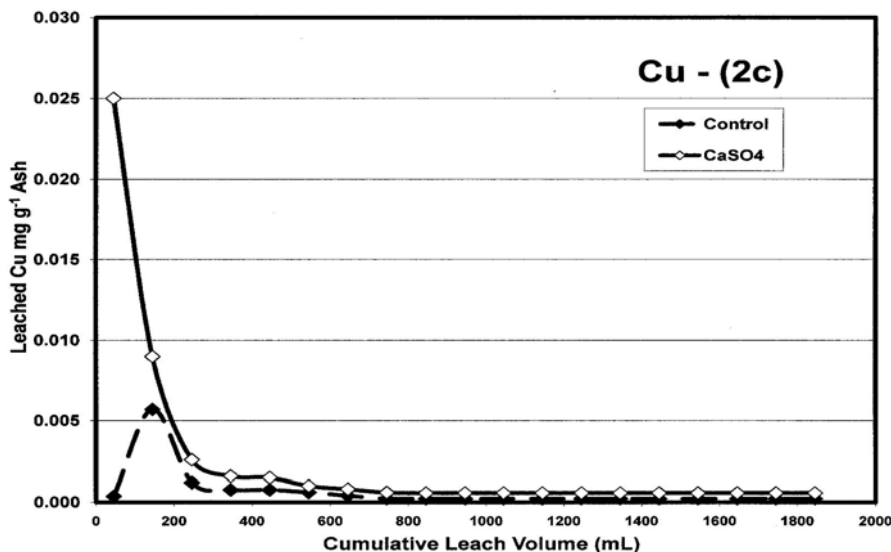


Figure 2c – Simulated One-Year Mass Leach of Cu – Control vs CaSO₄ Amendment (Harden, 2005)

4. Conclusions

The use of gypsum soil-softener (CaSO₄ · 2H₂O) acting as a stabilizing agent within the pH 7.3-8.0 range may be a feasible soil amendment for the stabilization of Cr and As from CCA-treated wood burn sites while also reducing the potential contamination of water resulting from leached CCA-metals.

The unamended soil/CCA-ash mixture exhibits the potential for retardance of CCA-ash metals during rainwater leaching through natural attenuation by the soil compared to the leaching of CCA-ash alone. Amendment of the soil/CCA-ash mixture with gypsum increased the Cu leaching compared to the Cu leaching from CCA-ash alone.

The gypsum as a reactive soil amendment for the treatment of soils contaminated by Cr and As metals results in significant rates of reduction of metals leaching, nearly 80% compared to unamended CCA-metals contaminated soil, over a simulated one-year leaching period, and in a case study where high CCA-metals concentrations in the soil leach at high concentrations.

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