RETARDANCE OF RAINWATER-LEACHED METALS FROM CCA-TREATED

(CHROMATED COPPER ARSENATE)

WOOD ASH IN SOIL

by

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ABSTRACT

The burning of wood treated with chromated copper arsenate (CCA) preservative produces an ash that contains high concentrations of copper, chromium, and arsenic. The subsequent leaching of these metals from burn sites can produce soil and water contamination. Soils have varying natural abilities to reduce leaching and impact metals speciation and toxicity, by sorption, conversion and sedimentation related mechanisms. Recent regulations have resulted in increased quantities of CCA-treated lumber entering the waste stream, making the study of metals leaching from ash, and the amendment of soils to more effectively immobilize metals, important areas of investigation.

The performance of various soil amendments to immobilize or retard Cu, Cr, and As species in soil/CCA-ash mixtures was studied. The amendments evaluated were agricultural lime ($CaCO_3$/$MgCO_3$), soil softener ($CaSO_4 \cdot 2H_2O$), and iron sulfate ($FeSO_4$). The evaluation was performed using batch and column leaching studies and pH studies. The control soil used in this study is from the Ultisol soil order, the dominant soil order in the Southeastern U.S. Ultisols form under humid, tropical conditions and are dominated by kaolinitic clay and lesser so by oxides of Fe and Al with a low percentage of organic carbon content. Results of this investigation show that native soil alone retards the mobility of As and Cr and amendments applied alone or in combinations further retard metal mobility compared to the control soil/CCA-ash mixture. The $CaSO_4$ soil amendment is most effective in reducing the rainwater leaching of high concentrations of Cr and As from CCA-ash in soil reducing the mobility by 72% and 77%, respectively, compared to the control soil-ash mixture. Cu mobility at low concentrations relative to Cr and As is increased in the presence of the native soil and by all amendments compared to the CCA-ash alone.

DEDICATION

To My Family And Friends, Past And Present.

LIST OF ABBREVIATIONS AND SYMBOLS

Al	Aluminum
As	Arsenic
ASTM	American Society of Testing and Materials
AWPI	American Wood Preservers Institute
˚C	Degrees of Celsius
C	Carbon
Ca	Calcium
CCA	Chromated copper arsenate
Cl	Chlorine
cm	Centimeter
Cr	Chromium
Cu	Copper
DC	Direct Current
EPA	Environmental Protection Agency
Fe	Iron
Ft	feet
g	Gram
H	Hydrogen
HP	Horsepower

ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
in	Inch
$inhr^{-1}$	Inch per hour
K	Potassium
m	Meter
mm	millimeter
m^2g^{-1}	Square meters per gram
m^3	Cubic meter
Mg	Magnesium
$mgkg^{-1}$	Milligram per kilogram
mg	Milligram
mgL^{-1}	Milligram per liter
mL	Milliliter
$mLhr^{-1}$	Milliliter per hour
Mn	Manganese
N	Nitrogen
Na	Sodium
NRC	National Research Council
O	Oxygen
P	Phosphorous
ppb	Parts per billion (μgL^{-1})
pH	Concentration of H_3O^+
RPM	Revolutions per minute

S	Sulfur
SDWA-MCL	Safe Drinking Water Act-Maximum Contaminant Level
Si	Silicon
SSSA	Soil Science Society of America
TCLP	Toxic Characteristic Leaching Procedure
$\mu g kg^{-1}$	Microgram per kilogram
$\mu g L^{-1}$	Microgram per liter
Zn	Zinc

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CHAPTER I

INTRODUCTION

1.1 Introduction

Chromium, arsenic, and copper metals enter into the soil and water environments from both anthropogenic sources (mining, agriculture, coal burning, wood preservation) and natural occurrences (weathering of metal-bearing minerals). Wood treated with chromated copper arsenate (CCA) preservative has been a major source for the introduction of these metals into the residential setting and potentially into the soil and water environments.

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 (Cooper, 1993; McQueen and Stevens, 1998; Clausen, 2000; Wu, 2000); a ban on CCA-treated wood use in domestic settings (Federal Register, 2003) and an associated increased public awareness of health concerns. The Southeastern region of the U.S. has been the largest producer and user of CCA-treated wood due to the climatic and parasitic pressures on untreated wood in this region. A common practice is to dispose of CCA-treated wood by onsite burning, producing an ash that poses a potential threat to humans and the environment (Solo-Gabriele et al., 1999).

Burning of CCA-treated wood waste to reduce the volume produces a leachable source of heavy metals, primarily Cu, Cr and As. At the μg/L 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 (Winner, 1984; Korte and Fernando, 1991; LaGrega et al., 1994; Palmer and Puls, 1994; Raven et al., 1998; Solo-Gabriele et al., 1999).

The oxidation states of arsenic and chromium species exhibit a significant influence on the mobility of the metals. In the burning of CCA-treated wood, combustion conditions can effect the Cr speciation in CCA-ash with a portion of the predominant Cr(III) converting to Cr(VI) (Helsen et al., 1997). The resulting ash, although still largely Cr(III), has varying Cr(VI) concentrations influenced by the degree of the wood treatment, with a range of 4-7% (Song et al., 2006). The Cr (VI) species is more toxic to humans and other animal receptors. It is also more soluble and therefore more mobile in the environment.

Arsenic species in CCA-treated wood ash are both the more toxic As(III) and the less toxic As(V), with As(III) being more soluble and mobile in the environment. The As(V) species is found in the CCA-treated wood and after pyrolysis the As(III) and As(V) species are found in the wood ash (Helsen et al., 1997).

Copper, in the form of CuO, is dissolved in an acidic solution to produce the CCA treatment solution. The CCA-ash resulting from the burned CCA-treated wood has almost all copper present in the form of CuO which has been found by Palmer and Benezeth (2004) to be very sparsely water-soluble at 25˚ C.

The resulting interaction of CCA-treated wood ash with soil is a complex system. Factors such as soil chemical composition, organic content, pH, solution complex formation, climatic, and geologic conditions play a role in the movement of the metal species from the CCA-treated wood ash and soil mixture (US EPA, 1992; Evanko and Dzombak, 1997). The adverse effects of each metal species present are dependent, in part, upon the valence state of the metal (Helsen et al., 1997) and oxidation-reduction reactions of CCA-metals occurring naturally within the soil can change these metals to less toxic and less available metal species (NRC, 1994).

1.2 Dissertation Objective

In this study, soil contaminated with the ash of burned CCA-treated wood is under investigation. This soil was historically contaminated by the burning of scrap CCA-treated wood on a central burn site over a period of thirty years. The strong affinity for CCA-metals retention in the soil makes this investigation of importance for potential means of remediation of historical and recent contamination.

The effectiveness of various soil amendments to immobilize and retard CCA-metal species using agricultural lime ($CaCO_3/MgCO_3$), soil softener (gypsum) ($CaSO_4 \cdot 2H_2O$), and iron sulfate ($FeSO_4$) was studied. These soil amendments were chosen due to availability, current application as soil supplements, and potential to enhance chemical reactions that reduce the mobility of metal species within the soil (Brady, 1990). A CCA-treated wood burn site in Tuscaloosa County, Alabama was investigated to determine baseline conditions and obtain data for a laboratory study (Harden, 2005). Soil/CCA-treated wood ash burn site conditions were then replicated under laboratory conditions using batch and soil column leaching studies and pH studies.

1.3 Dissertation Arrangement

This dissertation consists of ten chapters that include a literature review (Chapter II), the hypotheses (Chapter III), experimental design (Chapter IV), five self-contained papers (Chapters V thru IX) that (1) characterized the extent of CCA-metals contamination at the burn site, (2) determined the CCA-metals concentrations in CCA-ash, (3) determined the relative natural attenuation of the soil for mobility of CCA-metals, (4) chronicled the experimental testing of various soil amendments for their effective retardance of CCA-metals mobility, (5) reported the efficiency of gypsum soil amendment to retard CCA-metals mobility and postulated immobilization mechanisms acting during the use of gypsum as a retardant of leaching CCA-metals, and (6) characterized the results of the liming effect of wood ash upon CCA-metals mobility and the conclusions (Chapter X).

The article in Chapter V examines chemical and physical characteristics of Ultisol soil, CCA-wood ash, and untreated wood ash. Major characteristics measured are as follows: particle size distribution of the study media, the CCA-metals content and the resulting CCA-metal oxide content of CCA-ash, the mobility of cations in Ultisol soil, the liming characteristics of untreated and CCA-treated wood ash, and the retardance to rainwater-leaching of CCA-metals resulting from mixing Ultisol soil with CCA-ash. The article was submitted for review on 1/18/2011 to *Soil and Sediment Contamination: An International Journal*. The journal specializes in scientific and technical information, data, and critical analysis in analytical chemistry, site assessment, risk assessment issues, environmental fate, risk management, environmental modeling, regulatory programs and policies, remediation technologies/corrective actions, and legal considerations.

The article in Chapter VI reports the search for effective soil amendments that will retard the rainwater-leaching of CCA-metals from CCA-ash/soil mixtures. CCA-metals composition of CCA-ash, potential contamination of water by CCA-metals, pH trends of soil amendments, and evaluation of retardance of CCA-metals by gypsum, agricultural lime, and iron sulfate are the major topics reported. The article was published by *Soil and Sediment Contamination: An International Journal*, (18) : 412-428, 2009 with Pauline D. Johnson listed as co-author. The journal specializes in scientific and technical information, data, and critical analysis in analytical chemistry, site assessment, risk assessment issues, environmental fate, risk management, environmental modeling, regulatory programs and policies, remediation technologies/corrective actions, and legal considerations.

The article in Chapter VII is a condensed version of the gypsum amendment results from the article in Chapter VI and was awarded First Place in the Graduate Student ASCE Technical Writing Competition and published in the *Proceedings of the World Environmental and Water Resources Congress, 2008* in May, 2008, Honolulu, Hawaii.

The article in Chapter VIII evaluates the effectiveness of gypsum soil amendment to retard the rainwater-leaching of CCA-metals from an Ultisol soil/CCA-ash mixture. The results reported are the batch rainwater-leaching of CCA-ash, the trend from the batch leaching of unamended and gypsum-amended soil/CCA-ash mixtures, and the column rainwater-leaching of unamended and gypsum-amended soil/CCA-ash mixtures. The article will be submitted to *Environmental Geology* (2011) for review. *Environmental Geology* is an international multidisciplinary journal concerned with all aspects of interactions between humans, ecosystems and the earth. Coverage includes water and soil contamination; environmental problems associated with transportation; geological processes affecting biosystems and people; remediation of man-made or geological hazards; environmental problems associated with mining and abstraction activities for industrial minerals, coal and ores as well as for oil and gas, water and energy; environmental impacts of exploration and recultivation; impacts of hazardous facilities and activities; land use management; management of environmental data and information in data banks and information systems.

The article in Chapter IX evaluates CCA-metals concentration data from the characterization of a CCA-wood ash burn site to postulate the retardance mechanisms of gypsum amendment reducing the rainwater-leaching of a mixture of Ultisol soil and CCA-ash. The article was submitted to *Water, Air, & Soil Pollution* on 1/27/2011 for review. *Water, Air, & Soil Pollution* is an international, interdisciplinary journal on all aspects of pollution and solutions to pollution in the biosphere. This includes chemical, physical and biological processes affecting flora, fauna, water, air and soil in relation to environmental pollution. Because of its scope, the subject areas are diverse and include all aspects of pollution sources, transport, deposition, accumulation, acid precipitation, atmospheric pollution, metals, aquatic pollution including marine pollution and ground water, waste water, pesticides, soil pollution, sewage, sediment pollution, forestry pollution, effects of pollutants on humans, vegetation, fish, aquatic species, micro-organisms, and animals, environmental and molecular toxicology applied to pollution research, biosensors, global and climate change, ecological implications of pollution and pollution models.

The conclusions of the research, Chapter X, presents a summary of research findings and a comparison between the results of Table of Contrasts and ANOVA analysis of the experimental data.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction to CCA-Treated Wood

The use of chromated copper arsenate (CCA) preservative has been of major significance in the wood treatment industry. This water-born preservative is composed of oxides of arsenic, copper, and chromium and the most common treatment solution is composed of 47.5% As_2O_5, 18.5% CuO & 34.0% CrO_3. In the treated wood, copper serves as a fungicide, arsenic as an insecticide, and chromium as a fixing agent for bonding the Cu and As to the wood fiber (Solo-Gabriele et al., 1999).

The treatment process usually involves immersing wood in a 2 to 3% solution of CCA and subjecting it to high pressure, which encourages deep penetration of CCA into the wood. The treated wood has concentrations each of Cr, Cu, and As that range from 1000 to 5000 mg kg^{-1} (Stehouwer, 2001).

CCA-treated wood has comprised roughly 75% of the treated wood market by volume until 2003 regulations mandated treatment processes that avoid the use of Cr and As compounds (Federal Register, 2003). According to the American Wood Preservers Institute, during 1997, 144 million pounds of CCA were used in the United States to produce 450 million cubic feet of wood product (AWPI, 1997). The State of Florida has produced from 6 to 15% of the U.S. production of CCA-treated wood (Solo-Gabriele et al., 1998). The American Wood Preservers

Institute estimates that there is 75 billion board feet of CCA-treated wood currently in service (Federal Register, 2003).

In the future, a very large quantity of CCA-treated wood will be removed from service. Using a conservative estimate of service life of 20 to 50 years, Cooper (1993) estimates 1.6 x 10^7 m^3 will be removed annually by 2020. In a survey, McQueen et al. (1998) found that the actual service life of CCA-treated lumber of 9 years is much shorter than the expected service life. Another survey revealed that 43% of the time, removal from service was due to aesthetics, either of the wood or a change in design of the structure (Clausen, 2000). Wu (2000) estimated that CCA-treated wood waste in Florida alone will increase from 5 million cubic feet per year to 35 million cubic feet in 2015. Clausen (2000) reported the amount to be 32 million cubic feet at its peak in 2012 with 31,000 metric tons of arsenic having been introduced into Florida over the past 30 years.

The CCA-treatment of wood involves several toxic chemicals. Copper is known to be toxic to marine macroinvertebrates. The cupric ion, Cu^{+2}, is the most toxic species of copper and copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{+2}$ (LaGrega et al., 1994). Arsenic and chromium are known carcinogens and chromium is a mutagenic teratogen. In the environment, Cr(VI) is acutely toxic and more mobile than Cr(III) (Palmer and Puls, 1994). Arsenite, As(III), is 25-60 times more toxic than arsenate, As(V), and has been reported to be more mobile in the environment (Korte and Fernando, 1991; Raven et al.,1998).

During the 1990's notable research on disposal of CCA-treated wood was conducted by Dr. Helena Solo-Gabriele, University of Miami and Dr. Timothy Townsend, University of Florida (Solo-Gabriele et al., 1999). A portion of their work was conducted in conjunction with the Florida Center for Solid and Hazardous Waste Management, Gainesville, Florida. The emphasis of their research was primarily the environmental effects of burning of construction and demolition waste that contains some CCA-treated wood and the introduction of CCA-treated wood into unlined landfills. Additional investigations were conducted to determine the amounts of CCA compounds that leach from wood into adjacent soil and potential methods for reduction of arsenic emissions from waste incinerators that burn construction and demolition waste containing CCA-treated wood.

2.2 Burning of CCA-Treated Wood

The burning of CCA-treated wood waste is restricted and it is common to see warnings about the hazards of inhalation of the resulting smoke but there is little notice to the public or information provided on the toxicity of the resulting CCA-treated wood ash (CCA-ash) (Solo-Gabriele et al., 1999).

At the low temperatures of burning, Cu and Cr do not pose any significant problems in the air because they are not released in significant amounts into the air, only concentrated in the ash. McMahon et al., (1986) found the percentages of the mass of copper and chromium compounds in the preserved wood that are volatized during combustion to be 11 and 15, respectively. On the other hand, a large portion of the arsenic is released to the air at temperatures between 300˚C and 400˚C. They found that arsenic release to the air ranged from 22 to 77 % as temperatures ranged from low to very high. The mechanism responsible for arsenic release is identified as the reduction of As(V) to As(III), which occurs sharply at 327˚C. Arsenic is released as arsenious oxide (As_4O_6), which is very difficult to capture and is toxic (Helsen et al., 1997).

Most of the chemical components of burned CCA-treated wood complete their degradation under conditions of pyrolysis. Initially the wood fibers and wood gases burn under high oxygen conditions and volatile metals are released. Burning is completed under lower oxygen conditions of smoldering wood embers and ash. The As and Cu compounds in the pyrolysis residues are highly leachable, about 30% being relatively easily leached in a neutral environment. The chromium, on the other hand, undergoes major leaching only in a strongly oxidizing or strongly reducing environment and will pose fewer problems upon disposal (Helsen et al., 1997). Combustion conditions can effect the Cr speciation in CCA-ash with a portion of the predominant Cr(III) converting to Cr(VI) (Helsen et al., 1997). The resulting ash, although still largely Cr(III), will have varying Cr(VI) concentrations influenced by the degree of the wood treatment, with a range of 4-7% (Song et al., 2006).

The presence of As(III) in the pyrolysis residues indicates that the As, present as the As(V) compound chromium arsenate ($CrAsO_4$) in the treated wood, is partly reduced to As(III) during the pyrolysis process. If the pyrolysis residues were to be landfilled, As(III) would be liberated into the environment. The As content in the pyrolysis residue decreases as the temperature or duration of the burning process increases. The arsenic compounds are thus more volatile than the copper and chromium compounds (Helsen et al., 1997).

To prepare the CCA solution, wood preservers mix As, Cr and Cu in the form of arsenic pentoxide (As_2O_5), chromic acid (CrO_3) and cupric oxide (CuO). As and Cr are thus both in the high oxidation state, being As(V) and the toxic hexavalent chromium (Cr(VI)). During the fixation process Cr(VI) is partly reduced to Cr(III) in order to fix the As as $CrAsO_4$. The decomposition of $CrAsO_4$ results in the compounds chromium oxide (Cr_2O_3) and arsenic pentoxide (As_2O_5), that further dissociate into arsenic trioxide (As_2O_3) and O_2. Both metals appear in the lower oxidation state, being As(III) and Cr(III), after pyrolysis. The resulting Cr (III) compound Cr_2O_3 is insoluble in water, acids, alkali and alcohols, which could be the explanation for the fact that Cr is more strongly bound in the pyrolysis residue compared to the CCA-treated wood and for the lower mobility (Helsen et al., 1997).

Characteristics of the metals Cu, Cr, and As and their common species found in CCA-ash are summarized below in Table 2.1, CCA-metals Species Characteristics.

Table 2.1 – CCA-metals Species Characteristics

Name Symbol	Oxidation State	Cation/ Anion	Species	Characteristics
Copper Cu	Cu(II)	Cation	Cu^{+2} $CuOH^+$ $Cu_2(OH)_4^-$	varying toxicity varying solubility varying mobility
Chromium Cr	Cr(III)	Anion	Cr Hydroxides $Cr(OH)_4^-$	less toxic less soluble less mobile
	Cr(VI)	Anion	chromate CrO_4^{-2} dichromate $Cr_2O_7^{-2}$	more toxic more soluble more mobile
Arsenic As	As(III)	Anion	arsenite AsO_3^{-3}	more toxic (25-60 times) more soluble more mobile
	As(V)	Anion	arsenate AsO_4^{-3}	less toxic less soluble less mobile

2.3 Nature and Properties of Soils

Soils have both physical and chemical properties that influence or control the toxicity and mobility of metal contaminants.

2.3.1 Physical Properties of Soils

Soils have varying size particles ranging from gravel to sand to silt to clay. Most reactions occur within the clay-size portion of the soil, which ranges from 31.25 to 0.97 microns for clay size and 0.97 microns to infinity for colloidal clay. The surface area per unit mass of clay is very high, as shown in Figure 2.1, because of the small size of the individual particles. Fine colloidal clay has about 10,000 times as much surface area as the same weight of medium-size sand. The specific surface of colloidal clay ranges from about 10 to 1000 square meters per gram (m^2/g) compared to 1 and 0.1 m^2g^{-1} for the smallest silt particle and fine sand. Since the adsorption of water, nutrients, and gas and the attraction of particles for each other are all surface phenomena, the very high specific surface of clay is significant in determining soil properties (Brady, 1990).

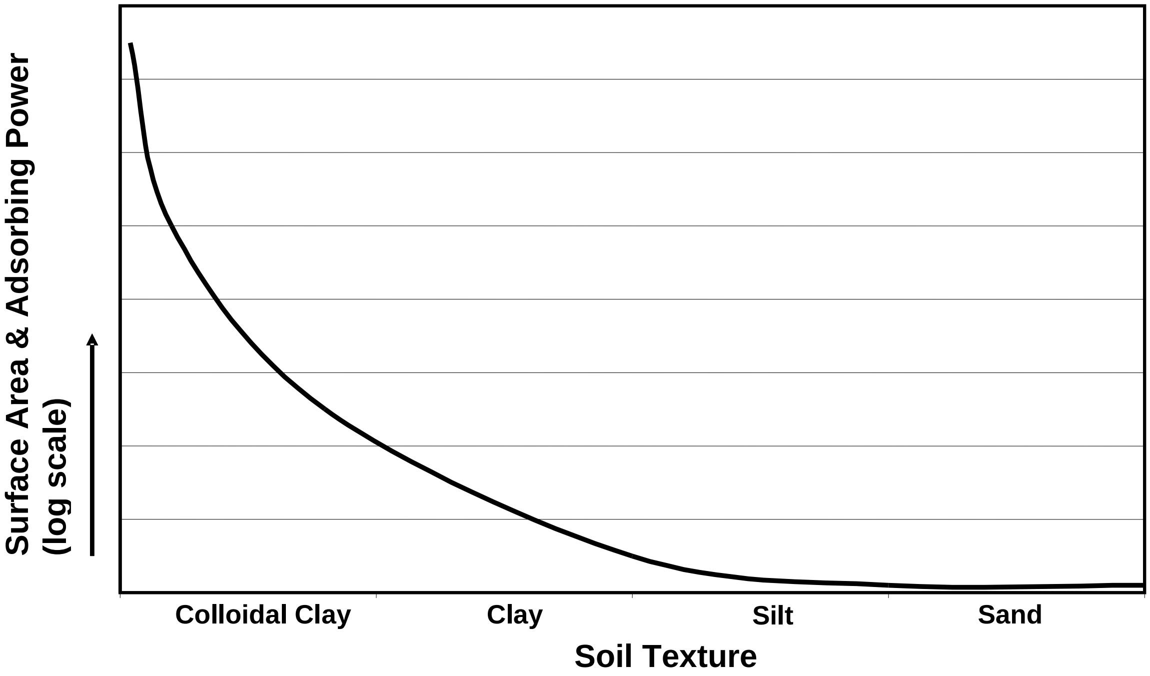


Figure 2.1 – Surface Area and Adsorbing Power vs. Soil Texture
(Adapted from Brady, 1990)

Particle size distribution can influence the level of metal contamination in a soil. Since fine particles are more reactive and have a higher surface area than coarser material, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies (Dzombak et al., 1994).

2.3.2 Chemical Properties of Soils

The movement of heavy metals in soils is strongly influenced by many retention processes. The soil system pH, charges on soil components, and oxidation-reduction reactions in the soil system greatly influence adsorption, co-precipitation, and precipitation reactions that affect the capture and release of Cu, Cr, and As cations and anions. Cation Exchange Capacity (CEC) is the sum total of exchangeable cations that a soil may absorb and is expressed as the number of moles of positive charge adsorbed per unit mass with units of centimoles of charger per kilogram (cmol kg^{-1}). Increasing the pH of most soils will increase the CEC, influence by complementary cations and the type of colloid will affect the CEC (Brady, 1990; Brady and Weil, 2002).

Chemically, the silicate clays in soils vary widely. Some are relatively simple alumino-silicates while others contain in their crystal structures varying quantities of iron, magnesium, potassium, and other elements. The surfaces of all the silicate clays hold small but significant quantities of cations such as Ca^{+2}, Mg^{+2}, K^{+}, H^{+}, Na^{+}, NH_4^{+} and Al^{+3} (Brady, 1990).

In highly weathered soils, such as those found in the Southeastern United States, oxides of iron and aluminum are prominent if not dominant, even in the clay-size fraction. Thus, weathering can have a profound effect on the chemical and mineralogical composition of soil (Brady, 1990; Brady and Weil, 2002).

Soil solutions contain varying amounts of colloidal material that may be charged. An important consequence of the charges on soil colloids is the attraction of ions of an opposite charge to the colloidal surfaces. Such attraction is of particular significance for negatively charged colloids. The colloidal particles, micelles, attract hundreds of thousands of positively charged ions, cations, such as H^+, Al^{+3}, Ca^{+2}, and Mg^{+2}. This gives rise to an ionic double layer. The colloidal particle constitutes the inner ionic layer, essentially a huge anion, with both external and internal layers that are negative in charge. The outer layer is made up of a swarm of adsorbed cations attracted to the negatively charged surfaces. Thus, a colloidal particle is accompanied by a swarm of cations that are adsorbed or held on the particle surfaces (Brady, 1990; Brady and Weil, 2002).

In the case of Fe and Al oxides, the negative charge associated with humus is dependent on the soil pH. Under very acidic conditions, the negative charge is not very high, lower than that of some of the silicate clays. With a rise in pH, however, the hydrogen ions dissociate from first the carboxyl groups and then the enolic and phenolic groups. This leaves a greatly increased negative charge on the colloid. Under neutral to alkaline conditions, the electronegativity of humus per unit weight greatly exceeds that of the silicate clays. In these higher pH soils, the adsorbed hydrogen is replaced by calcium, magnesium, and other cations (Brady, 1990; Wu et al., 2001; Brady and Weil, 2002).

Two major factors will determine the relative proportion of the different cations adsorbed by clays. First, these ions are not all held with equal tightness by the soil colloids. The order of strength of adsorption of major cations, when the ions are present in equivalent quantities, is $Al^{+3} > Ca^{+2} > Mg^{+2} > (K^+ = NH_4^+) > Na^+$ (Brady, 1990). Second, the relative concentration of the cations in the soil solution will help determine the degree to which adsorption occurs. Thus, in the soil solution of very acid soils, the concentrations of both H^+ and Al^{+3} are high, and these ions dominate the adsorbed cations. At neutral pH and above, however, the concentrations in the soil solution of both H^+ and Al^{+3} are very low, and consequently, the adsorption of these ions is minimal. In neutral to moderately alkaline soils, Ca^{+2} and Mg^{+2} dominate (Brady and Weil, 2002).

Table 2.2 provides data on the averaged adsorbed cation compositions for soil orders in the United States. The test soil used in this research is classified as an Ultisol and is relatively high in H^{+}, Al^{+3}, and Ca^{+2} adsorbed ions. Ultisols are soils with an argillic (clay) horizon and a low-base status (less than 35% of the exchange capacity satisfied with base-forming metallic cations). A udult is a moist, well-drained ultisol that is the most extensive of soils in the humid southeast and comprises 12.9% of the total U.S. soils. This soil extends from the east coast (Maryland to Florida) to and beyond the Mississippi River Valley (Brady, 1990; Brady and Weil, 2002).

Table 2.2 – Typical Proportions of Major Adsorbed Cations on Surface Layers of Different Soil Orders (Brady and Weil, 2002)

Soil Order	Typical location	H^{+} and Al^{+3}	Ca^{+2}	Mg^{+2}	K^{+}	Na^{+}
Oxisols	Hawaii	85	10	3	2	tr
Spodosols	New England	80	15	3	2	tr
Ultisols	**Southeast U.S.**	**65**	**25**	**6**	**3**	**1**
Alfisols	PA to WI	45	35	13	5	2
Vertisols	AL to TX	40	38	15	5	2
Mollisols	Midwest U.S.	30	43	18	6	3
Aridisols	Southwest U.S.	□	65	20	10	5

The percentage figures are based on the sum of the cation equivalents taken as 100
Al^{+3} adsorption includes that of complex aluminum hydroxy ions
Adapted from Brady & Weil, 2002

There are numerous chemical properties and processes active within the matrix of a soil or the soil in contact with soil solution. Those processes include the effects of negative charges, positive charges, cation and anion adsorption, dispersion and flocculation, organic matter and the humic group, sulfur oxidation and reduction, oxidation states and pH, and chelates.

Negative Charges: Hydroxy (OH^{-}) groups exist on the edges and surfaces of inorganic and organic colloids. The hydroxyl groups are attached to iron and/or aluminum in the inorganic colloids and to carboxyl (CO^{-}) groups in humus. Under moderately acid conditions, there is little or no charge on these particles, but as the pH increases, the hydrogen dissociates from the colloid OH^- group, and negative charges result (Brady, 1990; Wu et al., 2001; Brady and Weil, 2002).

Positive Charges: Under moderate to extreme acid soil conditions, some silicate clays and iron and aluminum hydrous oxides may exhibit positive charges. As the soil becomes more acid, protonation occurs (Brady, 1990; Brady and Weil, 2002) resulting in positively charged iron and aluminum hydroxides which sorb humic substances as reported by Wu et al. 2001.

Cation and Anion Adsorption: The charges associated with soil particles attract simple and complex ions of opposite charge. A given colloidal mixture may exhibit not only a maze of positive and negative surface charges but an equally complex complement of simple cations and anions such as Ca^{+2} and SO_4^{-2} that are attracted by the base charge on soil surfaces (Brady, 1990; Brady and Weil, 2002).

Dispersion and Flocculation: Dispersion of clays results from the repulsion of negatively charged particles for each other. Dispersion is encouraged by the large number of water molecules and the adsorbed cations. Highly hydrated cations, such as Na^+ enhance clay dispersion. Tightly held cations, such as Ca^{+2} and Al^{+3}, inhibit dispersion. The ability of common cations to flocculate soil colloids is in the general order of $Al^{+3}>H^+>Ca^{+2}$, $Mg^{+2}>K^+>Na^+$ (Brady, 1990).

Organic Matter and the Humic Group: Organic material makes up less than 10% of most soils and has a tremendous amount of surface area that can react with various soil constituents, and it may impart a large influence on soil chemical properties (Walworth, 1998).

Humic substances are important components of organic matter for many reasons including that they play a major role in the transport mechanisms of metal ions (Carter and Suffet, 1982; Winner, 1984; Magee et al., 1991; Chakrabarti et al., 1994; Otto et al., 2001). They are also known to affect the bioavailability and toxicity of metal ions (Winner, 1984). Humic substances are characterized by aromatic, ring-type structures that are very complex. They are amorphous, dark in color, and have high to very high molecular weights, varying from a few hundred to several thousand (Brady, 1990).

Humic acid is a complex aromatic macromolecule with various linkages between the aromatic groups. It is medium in molecular weight and color, soluble in alkali but insoluble in acid (Brady, 1990). The linkages between groups include amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. Humic acid associations of molecules form aggregates of elongated bundles of fibers at low pH and open flexible structures perforated by voids at high pH. The voids can physically trap and/or adsorb both organic and inorganic particles if the charges are complimentary (Sanjay et al., 1996).

In a soil solution, the surface area of humus colloids per unit mass is very high, generally exceeding that of silicate clays. The colloidal surfaces of humus are negatively charged, the extent of the negative charge is pH dependent, i.e. high at high pH values. At high pH values the cation exchange capacity of humus far exceeds that of most silicate clays. Cation exchange reactions with humus are qualitatively similar to those occurring with silicate clays. Soil organic matter may produce 2 to 30 times greater cation exchange capacity in a mineral soil and account for 20 to 90 per cent of the adsorbing power of a typical soil. For example, the CEC of soil humus may range from 150-250 cmol kg^{-1} compared to Ultisol soils at 3.5 cmol kg^{-1} (Brady, 1990).

Sulfur Oxidation and Reduction: Most sulfur oxidation in soil environments results from biochemical reactions between organic sulfur compounds and bacteria. Sulfate ion reacts with organic soil compounds and bacteria to produce sulfide. The sulfate ion is soluble and would be readily leached were it not for its adsorption by soil colloids. Soils in the Southeastern United States tend to be higher in sulfate adsorption because of the high content of iron and aluminum oxides and silicate clays (Brady, 1990). Porter et al., 2004 reported that in anaerobic conditions with sulfur-containing materials and iron, arsenic forms insoluble sulfides of arsenopyrite (AsFeS) or without iron, orpiment (As_2S_3).

<u>Oxidation State and pH</u>: At pH values common in soils, the oxidized states of iron, manganese, and copper are generally much less soluble than are the reduced states. The hydroxides (or hydrous oxides) of these high-valence forms precipitate even at low pH values and are extremely insoluble (Brady, 1990; Brady and Weil, 2002).

<u>Chelates</u>: Arsenic, being present in the anionic form (H_2AsO_4), is absorbed (as are phosphates) by hydrous iron and aluminum oxides. Arsenic toxicity can be reduced by applications of sulfates of zinc, iron, and aluminum that tie up the arsenic in insoluble forms (Brady, 1990; Brady and Weil, 2002; Williams et al., 2003).

2.4 Fate of Metals in the Soil Environment

The fate and transport of a metal in soil and ground water depend significantly on the chemical form and speciation of the metal (Allen and Torres 1991). The mobility of metals in ground water systems is hindered by reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevent them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants (US EPA, 1992; NRC, 1994).

Metals added to soil will normally be retained at the soil surface. Movement of metals through ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The movement of a metal in the soil system is closely related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix. Therefore, increasing the effectiveness of the soil retention capacity is the primary goal of any remediation strategy.

Shuman (1991) describes metals in soils as being found in several "pools" of the soil. In situations where metals have been introduced into the environment through human activities, metals are associated with five pools. These pools are:

1. dissolved in the soil solution,
2. precipitated as pure or mixed solids in the solid phase,
3. occupying exchange sites on inorganic soil constituents during surface reactions,
4. specifically adsorbed on inorganic soil constituents during surface reactions, and
5. associated with insoluble soil organic matter during surface reactions.

Soils not only have the capacity to be a source of contaminants, but also a sink for contaminants. For example, at low levels of contamination, arsenic may strongly be adsorbed by soil and not be bio-available; however, solubility and bio-availability may increase as the capacity of soil to adsorb arsenic is exceeded or if soil conditions change (Basta et al., 1999). While the various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions vary under particular conditions (Evanko and Dzombak, 1997).

The mobility and bio-availability, and hence potential toxicity, of a metal in the soil depend on its concentration in soil solution, the nature of its association with other soluble ionic species, and the ability of the soil to release the metal from the solid phase to replenish that removed from the soil solution (Krishnamurti and Naidu, 2002). Therefore, rainfall episodes may drive the equilibrium conditions of the soil solution to increase mobility of the metal.

2.4.1 Soil Solution Chemistry

Metals exist in the soil solution as either free metal ions, in various soluble complexes with inorganic or organic ligands, or associated with mobile inorganic and organic colloidal material.

2.4.2 Solid Phase Formation

Metals may precipitate to form three-dimensional solid phases in soils. These precipitates may be pure solids or mixed solids formed when various elements co-precipitate. There are several types of co-precipitation, inclusion, adsorption and solid solution formation, distinguished by the type of association between the trace element and the host mineral (Sposito, 1989).

The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems (Lindsay, 1979). Precipitation reactions may be of much greater importance in waste systems where the concentration of metals may be exceedingly high (McBride, 1980). Such conditions are likely to be found in residential burn piles containing CCA-ash residues and high concentrations of As, Cr, and Cu.

Solid forms of chromium will be either a chromium hydroxide or associated with the soil organic matter, with chromium hydroxide becoming more dominant at higher total concentrations of chromium in the soils (Icopini, 2002). Chromium mobility in soil depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present (Smith et al., 1995). Grain size fraction analyses show that chromium is preferentially accumulated in the clay-size fraction and more specifically with alumino-silicate clay particles (Loyaux-Lawniczak et al., 2001).

2.4.3 Surface Reactions

Adsorption is the accumulation of ions at the interface between a solid phase and an aqueous phase and differs from precipitation in that the metal does not form a new three-dimensional solid phase but is instead associated with the surfaces of existing soil particles. The pH-dependent charged surfaces of soil particles are associated with the edges of clay minerals, with the surfaces of oxides, hydroxides and carbonates, and with organic matter and are major factors in the degree of adsorption reactions in a soil system.

Exchange Sites: A surface-complexation model is often used to describe adsorption behavior (Sposito, 1989). Several types of surface complexes can form between a metal and soil surface functional groups and are defined by the extent of bonding between the metal ion and the surface. From Figure 2.2 it can be seen that metals in a diffuse-ion association or in an outer-sphere complex are surrounded by waters of hydration and are not directly bonded to the soil surface. These ions accumulate at the interface of the charged surfaces in response to electrostatic forces. The resulting reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. These metal-surface interactions have also been termed exchange reactions because the introduction of other cations into the system, in sufficient concentration, causes the replacement or exchange of the original cations. Metals associated with exchange sites may, depending on the environment, be relatively mobile. Exchangeable metals may be the most significant reserve of potentially mobile metals in soil (Silveira and Sommers, 1977; Latterell et al., 1978).

Specific Adsorption Sites: As seen in Figure 2.2, with inner-sphere complexation, the metal is bound directly to the soil surface, no waters of hydration are involved. It is distinguished from the exchangeable state by having ionic and/or covalent character to the binding between the metal and the surface. A much higher bonding energy is involved than in exchange reactions, and the bonding depends on the electron configuration of both the surface group and the metal. This adsorption mechanism is often termed specific adsorption. The term specific implies that there are differences in the energy of adsorption among cations, such that other ions, including major cations, Na^+, Ca^{+2}, Mg^{+2}, do not effectively compete for specific surface sites. Specifically-adsorbed metal cations are relatively immobile and unaffected by high concentrations of the major cations due to large differences in their energies of adsorption (Sposito, 1984; Manning et al., 1998).

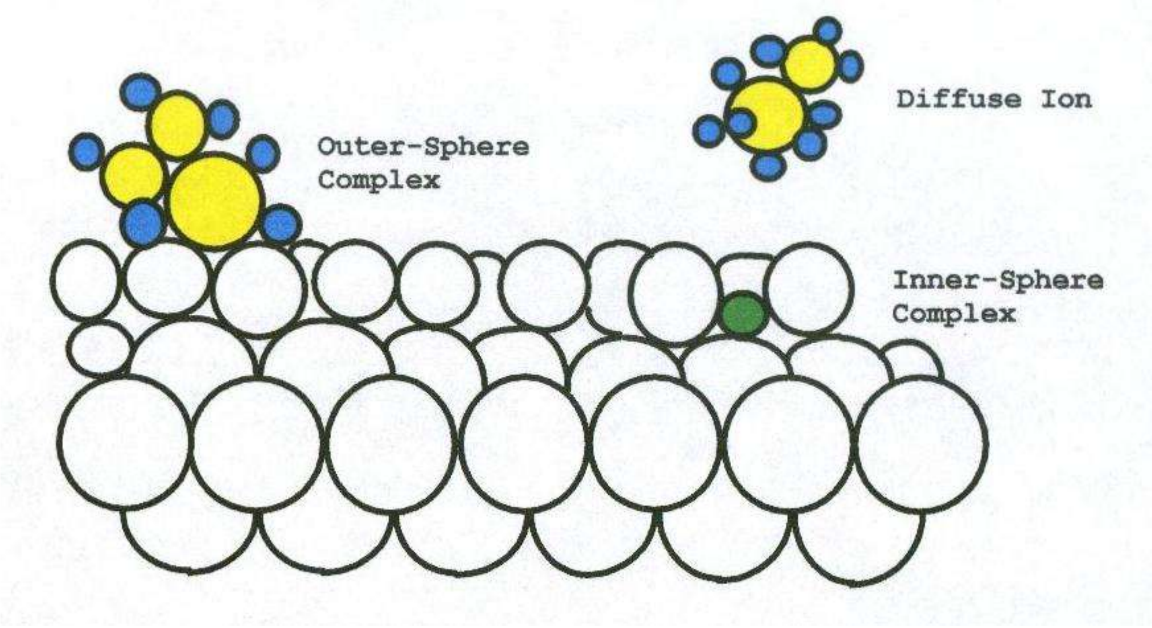


Figure 2.2 – Diffuse Ion, Outer-Sphere Complex and Inner-Sphere Complex Mechanisms of Cation Adsorption (Adapted from Sposito, 1989)

2.4.4 Surface Adsorption Mechanisms

Insoluble Organic Matter: The presence of natural organic matter has been shown to influence the adsorption of metal ions to mineral surfaces. Organic matter has been observed to enhance adsorption of Cu^{+2} at low pH, and suppress Cu^{+2} adsorption on mineral surfaces at high pH

(Tipping et al., 1983; Davis, 1984), thus copper species may form strong solution complexes with humic acids. The affinity of Cu for humic acid increases as pH increases and ionic strength decreases (Evanko and Dzombak, 1997). Arsenic is also bound to soil particles, but in general it is not held as tightly as Cr or Cu. Consequently, As tends to be somewhat more mobile in soil (Stehouwer, 2001).

Copper Mechanisms: Lehmann and Harter (1984) used kinetics of desorption to study the strength of Cu bonding to a soil. A plot of concentration of Cu in solution versus time indicated an initial rapid release of the Cu followed by a slow reaction. They interpreted these results to indicate that Cu was held at two sites: the rapidly released Cu being loosely held on the soil surfaces and the slowly released Cu by tightly bound sites.

Chromium Mechanisms: Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides (Evanko and Dzombak, 1997). The iron and aluminum oxide surfaces will adsorb CrO_4^{-2} at acidic and neutral pH (Davis and Leckie, 1980; Zachara et al., 1987; Ainsworth et al., 1989), and because of the anionic nature of Cr(VI), its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Stollenwerk and Grove (1985) also concluded that the adsorption of Cr(VI) by groundwater alluvium was due to the iron oxides and hydroxides coating the alluvial particles. The adsorbed Cr(VI) was, however, easily desorbed with the input of uncontaminated groundwater, indicating nonspecific adsorption of Cr(VI).

Arsenic Mechanisms: Adsorption reactions on mineral surfaces, especially iron and aluminum oxides, can retain dissolved As and are well-studied phenomena (Anderson et al., 1976; Manning et al., 1998; Williams *et al*., 2003; Goldberg *et al*., 2005; Zhang and Selim, 2005). As(III) has a relatively weak affinity for aluminum oxides compared with iron(III) oxides (Manning and

Goldberg, 1997). The iron(III) oxide surface has a high affinity for As(V) capable of forming inner-sphere bidentate, binuclear As(V)-Fe(III) complexes and there is a similar mechanism for As(III) in inner-sphere adsorption (Lumsdon and Evans, 1994; Fendorf *et al.*, 1997; Manning, Fendorf, and Goldberg, 1998). Porter et al., 2004 have reported that under highly oxidizing and moderate pH conditions in the presence of Ca^{+2} ions the precipitation of calcium hydrogen arsenate ($CaHAsO_4$) and calcium arsenate ($Ca_3(AsO_4)_2$).

2.5 Anions in the Soil Environment

Clay minerals, Fe and Al oxides, and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential. For example, Balistrieri and Chao (1987) found the sequence of pH dependent adsorption of anions onto iron oxide to be: (phosphate=silicate=arsenate)>carbonate>sulfate, however, the adsorption capacity for anions is small relative to cation adsorption capacity of soils.

Anions of concern in this study are shown in Figure 2.3 with the corresponding pH ranges of their adsorption on hydrous ferric oxide.

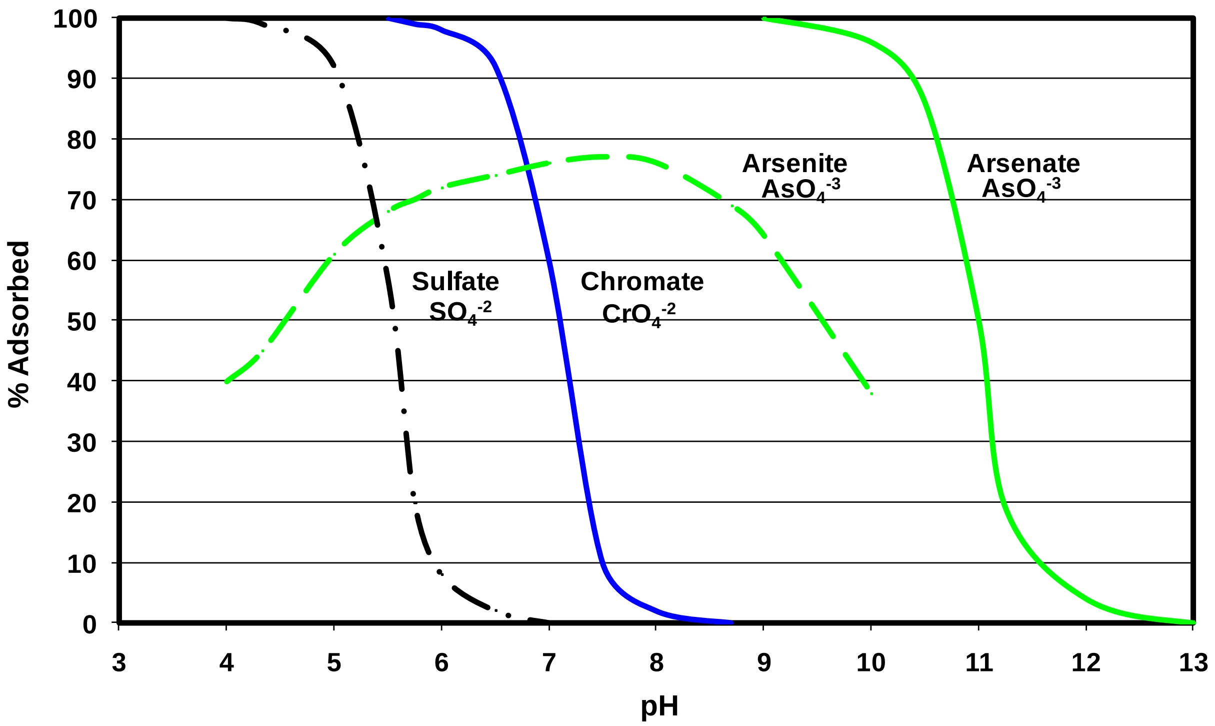


Figure 2.3 – Adsorption of Anions on Hydrous Ferric Oxide
(Adapted from Evanko and Dzombak, 1997)

The presence of inorganic anions (carbonate, phosphate, sulfide, sulfate) in the soil solution can influence the soil's ability to fix metals chemically. These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence. Arsenate (AsO_4^{-3}) is adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979; Neal et al., 1987). Arsenite (AsO_3^{-3}) can adsorb or coprecipitate in anionic form, but it does not form complexes with simple anions such as Cl^- and SO_4^{-2} (Evanko and Dzombak, 1997).

The major Cr(VI) species include chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$). These species are only weakly bound to soil surfaces and are thus easily displaced by other anions, but they precipitate readily in the presence of metal cations (Evanko and Dzombak, 1997).

2.6 Soil Properties, Mechanisms, and Factors Affecting Adsorption and Precipitation Reactions in the Soil/Soil Solution System

Both the exchange adsorption capacity and specific adsorption capacity of a soil are determined by the number and kind of sites available. Adsorption processes are also affected by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water. Sandy soils and/or soils with low pH do not retain metals effectively. For the anionic metals, clay soils containing oxides with low pH are relatively effective in retaining the anions.

The mineral composition of a soil may be a major controlling factor on metals mobility. In a research study of metal mobility through clay minerals, Griffin and Shimp (1978) found the relative mobility of metals through montmorillonite and kaolinite to be: Cr(VI)>As(III)>As(V)>Cu>Cr(III). The presence of hydrous metal oxides of Fe, Al, and Mn in a soil can strongly influence contaminant metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Ellis and Fogg, 1985; Dzombak and Morel, 1987). In a study of the relative mobilities of 11 different trace metals for a wide range of soils, Korte *et al.* (1976) reported that clay soil, containing free iron and manganese oxides, significantly retarded Cr(VI) migration and that hexavalent chromium was found to be the only metal studied that was highly mobile in alkaline soils.

In a column test study by Farmer *et al.*, (2001) a chromium contaminated column was infiltrated with an $FeSO_4$ solution. Instead of reducing the amount of leached Cr(VI), the addition of $FeSO_4$ flushed a large amount of Cr(VI) out of the column. The explanation for this effect is two-fold. First of all, the reduction of Cr(VI) by Fe(II), which readily occurs when these substances are well mixed, does not necessarily take place in a heterogeneous system which is not mixed. Also, in this case, the extremely high pH of the waste material renders Fe(II) immobile by precipitation as soon as it enters the column. It is then unable to react with the Cr(VI), which is transported away from the Fe(II) along with the infiltrating solution. Secondly, the addition of sulfate greatly increases the release of Cr(VI) through competition with anion exchange sites. Previously it had been noted by Zachara et al. (1987) and Zachara et al. (1989) that SO_4^{-2} ion and dissolved inorganic carbon inhibited Cr(VI) adsorption by amorphous iron oxyhydroxide and subsurface soils. The presence of sulfate ion, however, enhanced Cr(VI) adsorption to kaolinite (Zachara et al., 1988).

Copper is retained in soils through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, Cu precipitates are unstable. This may not be the case in waste-soil systems where concentrations are higher and the matrix is more complex and precipitation may be an important mechanism of retention. Cavallaro and McBride (1978) suggested that a clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils while in calcareous soils specific adsorption of Cu onto $CaCO_3$ surfaces may control Cu concentration in solution.

The mobility of As in the soil depends on As(III)/As(V) speciation, as well as the mineralogy of the soil, sediment, or soil solution material (Manning, Fendorf, and Goldberg, 1998). Arsenate, As(V), and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Bodek et al., 1988). Arsenates can be leached easily if the amount of reactive metal in the soil is low. As(V) can also be mobilized under reducing conditions that encourage the formation of As(III), under alkaline and saline conditions, in the presence of other ions that compete for sorption sites, and in the presence of organic compounds that form complexes with arsenic (Smith et al., 1995). The mechanisms at low concentrations have been attributed to specific adsorption, whereas the mechanisms at higher concentrations have been considered to be exchange reactions or precipitation.

Many arsenic compounds sorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. The sorption and co-precipitation with hydrous iron oxides are the most important arsenic removal mechanisms under most environmental conditions (Pierce and Moore, 1982; Krause and Ettel, 1989). Additionally, Elkhatib et al. (1984a) found adsorption of As(III) to be rapid and irreversible on ten soils. They determined, in this study and another study (Elkhatib et al., 1984b), that Fe oxide, redox, and pH were the most important properties in controlling arsenite adsorption by these soils.

As noted above, the mechanisms of adsorption and precipitation are influenced by numerous properties. The following additional information is provided to give greater insight into the effects of oxidation-reduction, competing cations, complex formation, pH, and the effects of co-wastes.

2.6.1 Effect of Oxidation-Reduction

A chemical reaction in which an electron transfer takes place is called an oxidation-reduction process. Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. A measure of the redox potential (electron availability) indicates whether the metals are in an oxidized or reduced state. In general, oxidizing conditions favor retention of metals in soils, while reducing conditions contribute to accelerated migration.

Chemical agents use for remediation of metals in soils must be carefully selected so that they do not further contaminate the treatment area. The primary problem associated with chemical treatment is the nonspecific nature of the chemical reagents. Oxidizing/reducing agents added to the soil matrix to treat one metal will also target other reactive metals and can make them more toxic or mobile (NRC, 1994). Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions (Evanko and Dzombak, 1997). Inorganic Cr and As species undergo oxidizing/reducing reactions while Cu does not; the relevant reactions for Cr and As are discussed below:

Chromium: Chromium exists in two possible oxidation states in soils: trivalent Cr(III) and hexavalent Cr(VI). Forms of Cr(VI) in soils are as chromate ion, $HCrO_4^-$, predominant at pH<6.5, or CrO_4^{-2}, predominant at pH 6.5, and as dichromate, $Cr_2O_7^{-2}$ predominant at higher concentrations (>10mM) and at pH 2-6.

The clay and organic components of soils may influence reduction reactions. Experimentation by James et al., (1995) has supported the hypothesis that the reduction of Cr(VI) to Cr(III) was due to soil properties and not due to the extraction conditions of leaching with distilled water. Soil organic matter has been identified as the electron donor in this reduction reaction (Bartlett and Kimble, 1976; Bloomfield and Pruden, 1980.) Thus, hexavalent chromium can be reduced to Cr(III) under normal soil pH and redox conditions . Bartlett (1991) reported that in natural soils the reduction reaction may be extremely slow, requiring years and Hug et al., (1997) reported that the reduction of Cr(VI) by dissolved organic compounds at pH values from 4-8 is a slow process, occurring on a time scale of days at micromolar and up to months at nanomolar Cr(VI) concentrations. Additionally, the mobility of the resulting Cr(III) is decreased by adsorption to clays and oxide minerals below pH 5 and it has low solubility above pH 5 due to the formation of $Cr(OH)_3$ (Chrotowski et al., 1991). Evanko and Dzombak, (1997) reported that chromium in its Cr(III) form is readily precipitated by hydroxide over a wide range of pH values and that acidification may be used to aid in Cr(VI) reduction to Cr (III).

Since low oxidation-state chemical species can serve as electron donors for the reduction of higher oxidation-state contaminants, this ability can be exploited to remediate metals that are more toxic and mobile in higher oxidation states, such as Cr(VI). Results of column experiments performed by Powell et al. (1994) and batch experiments performed by Cantrell et al. (1995) showed that chromate reduction was enhanced in systems containing iron filings in addition to the natural aquifer material (Evanko and Dzombak, 1997).

The reaction of the reduction of hexavalent chromium, Cr(VI), by Fe(II) is extensively documented in the literature (Eary and Rai, 1988; Ayers et al., 1994; Fendorf and Li, 1996; Buerge and Hug, 1997; Hug et al., 1997). It is widely accepted that the kinetics of this reaction in solution are fast and that in the presence of excess Fe(II) all the Cr(VI) is reduced (Loyaux-Lawniczak et al., 2001). Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{-2} and Fe^{+2} ions under anaerobic conditions often encountered in deeper groundwater (Evanko and Dzombak, 1997). In natural systems, the main factors usually involved in Cr(VI) reduction are Fe(II) in solution or Fe(II)-bearing minerals, sulfides, and organic matter (Loyaux-Lawniczak et al., 2001).

Arsenic: Su and Puls (2001) reported that active remediation of As is often required that may involve conversion of As(III) to As(V), and immobilization of both species by adsorption or coprecipitation. During the remediation process, both pH and the redox are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. As the pH increases or the redox decreases As (III) predominates. The reduced form of arsenic, As(III), is more subject to leaching because of its high solubility, however, the reduction kinetics are slow. Formation of As (III) also may lead to the volatilization of arsine (AsH_3) and methylarsines from soils (Woolson, 1977). Because of the relatively slow redox transformations, both arsenite and arsenate are often found in either redox environment (Masscheleyn et al., 1991; Raven et al., 1998; Song et al., 2006).

Manning and Goldberg (1997) reported that adsorption and oxidation reactions of As(III) at the mineral-water interface are two important factors affecting the fate and transport of arsenic in the environment Also, recovery of adsorbed As from As(III)-treated clay mineral solids showed that oxidation of As(III) to As(V) was enhanced by heterogeneous oxidation on kaolinite and illite surfaces.

Manning and Goldberg (1997) further postulated that because As(V) formation in amorphous aluminum hydroxide suspensions was low, the As(III) oxidation in kaolinite and illite suspensions was caused by heterogeneous reactions with solid phase components other than Al-OH edge sites. Additionally, the SiO_4 tetrahedra, which are major surface components of phyllosilicates, are less reactive than Al-OH function groups toward As(III). Therefore, the As(III) oxidation process with components such as iron and aluminum oxides results in more strongly adsorbed As(V), which would cause a decrease in the mobility of As in the environment.

2.6.2 Effect of Competing Cations

At specific adsorption sites, trace cationic metals are absorbed over major cations (Na^+, Ca^{+2}, Mg^{+2}) and trace anionic metals are absorbed over major anions (SO_4^{-2}). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important (McLean and Bledsoe, 1992).

2.6.3 Effect of Complex Formation

The effect of complex formation on adsorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox. Benjamine and Leckie (1982) stated that the interaction between metal ions and complexing ligands may result in either a complex that is weakly adsorbed to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion. Thus, the presence of complexing ligands may increase metal retention or greatly increase metal mobility.

In systems where the organic ligand adsorbs to the soil surface, metal adsorption may be enhanced by the complexation of the metal to the surface-adsorbed ligand. Haas and Horowitze (1986) found that, in some cases, the presence of organic matter enhanced adsorption by kaolinite, a hydrous aluminum silicate clay. Inorganic cations that cause flocculation (e.g., Ca^{+2} Mg^{+2}, Fe^{+2}, and Al^{+3}) also are thought to provide mutual attraction between the organic matter and soil clays, encouraging the development of clay-organic matter complexes (Brady, 1990).

Studies on metal speciation in soil solution indicate that complexes with dissolved organic matter are significant for metals such as Fe, Al, and Cu (Tack and Verloo, 1995). Khan et al. (1982) found in a study of mobility of metals in soils that Cu > Ni > Pb > Ag >Cd and that the higher mobility of Cu and Ni compared to lead and silver was attributed to their high complexing nature with soluble soil organic matter. Amrhein, et al. (1992) also showed the increased mobility of Cu in the presence of dissolved organic matter. Cu is adsorbed to a greater extent by soils and soil constituents than other heavy metals, with the exception of Pb, however, the high affinity of Cu for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils.

Rai, et al. (1987) concluded that the Cr(III) solubility-controlling solids are thought to be either $Cr(OH)_3$ or Cr(III) coprecipitated with Fe oxides and hydroxides. They also reported that Cr(III) forms hydroxy complexes in natural water, including $Cr(OH)_2^+$, $Cr(OH)^{+2}$, $Cr(OH)_3{}^0$, and $Cr(OH)_4^-$ and that trivalent chromium is readily adsorbed by soils.

The behavior of As(V) in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate As(V), forms insoluble precipitates with iron, aluminum, and calcium, with iron in soils being most effective in controlling arsenate's mobility. On the other hand, arsenite (III) compounds are reported to be 4-10 times more soluble than arsenate compounds and are more mobile. The adsorption of phosphate onto the oxide surfaces increased the negative charge on the oxide surfaces, thus enhancing adsorption of the metal cations. Arsenate adsorption to oxide surfaces produces the same mechanism for increased adsorption of metals.

2.6.4 Effect of pH

The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. The pH of the soil system is a very important parameter, directly influencing sorption/desorption, precipitation/dissolution, complex formation, and oxidation-reduction reactions. In general, maximum retention of cationic metals occurs at $pH>7$ and maximum retention of anionic metals occurs at $pH<7$. Because of the complexity of the soil-waste system, with its many surface types and solution compositions, such a generalization may not hold true. For example, cationic metal mobility has been observed to increase with increasing pH due to the formation of metal complexes with dissolved organic matter. Also, as is true with oxyanions, i.e. arsenic and hexavalent chromium, sorption decreases with decreasing pH (Brady, 1990; Evanko and Dzombak, 1997).

Many adsorption sites in soils are pH dependent, i.e. Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative charged sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{+3} and H^{+}. Jenne (1968) stated that hydrous oxides of Fe and Mn play a principal role in the retention of metals in soils and their solubility is also pH-related. Below pH 6, the oxides of Fe and Mn dissolve, releasing adsorbed metal ions to solution (Essen and El Bassam, 1981). Evanko and Dzombak (1997) reported that the sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased.

Copper: Dzombak and Morel (1990) reported that copper mobility is decreased by sorption to mineral surfaces and Cu^{+2} sorbs strongly to mineral surfaces over a wide range of pH values. This effect is demonstrated graphically in Figure 2.4. It is further reported that the cupric ion, Cu^{+2}, and hydroxide complexes, $CuOH^{+}$ and $Cu(OH)_2$, are also commonly present in soil solution and that in aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species (Evanko and Dzombak, 1997).

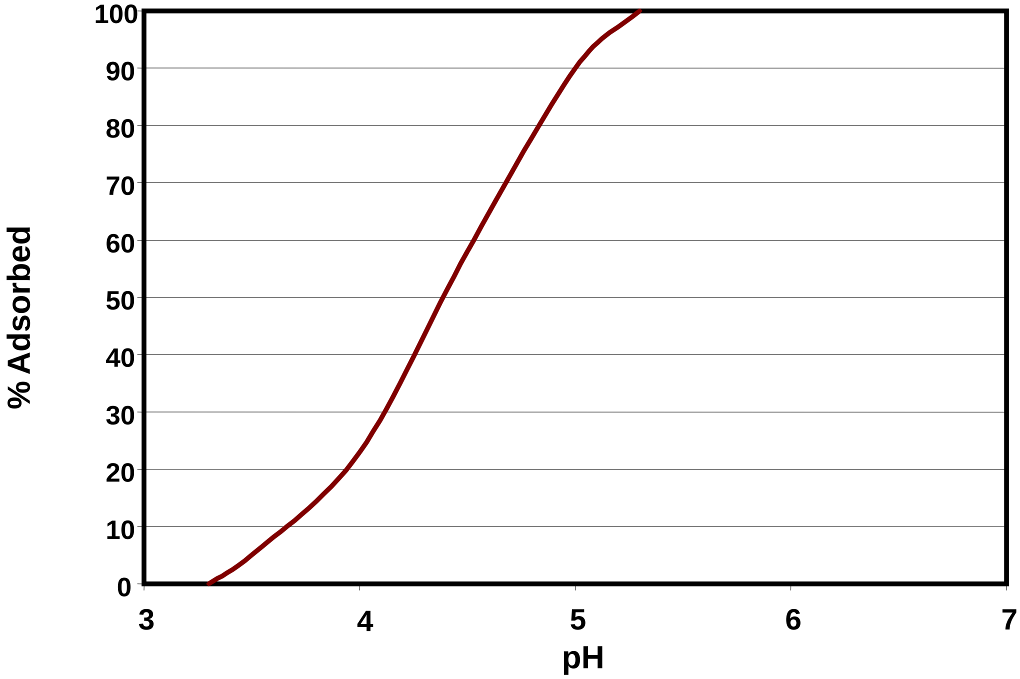


Figure 2.4 - Adsorption of Cu (II) Cation on Hydrous Iron Oxide (Adapted from Dzombak and Morel, 1990)

The solubility of Cu will decrease as pH levels increase, therefore Cu deficiency can occur in soils with pH levels above 7.5. In contrast to Mn, Zn, and Fe, Cu is tightly bound by soil organic matter and as soil organic matter content increases, Cu availability will decrease (Walworth, 1998).

At low pH, H^+ competes with the Cu for complexation with the organic matter. As the pH increases, more of the Cu can be complexed with the organic matter and less is, therefore, adsorbed by the clay fraction of soil. This mechanism has important implications with regard to the practice of liming acid soils to raise the pH and therefore to increase metal retention. But, in soils with significant levels of dissolved organic matter, increasing soil pH may actually mobilize metal due to complex formation with the mobile organic matter. This was confirmed when

Inskeep and Baham (1983) and Baham and Sposito (1986) demonstrated that the adsorption of Cu to montmorillonite clay, in the presence of water-soluble ligands extracted from sludges and various other organic materials, decreased with increasing pH.

Chromium: Chromium, like copper, is bound very strongly by soil particles, especially by soil clays and organic matter. These metals are most strongly bound in near-neutral soils (pH 6-8) and become more soluble in acidic soils (pH less than 5) (Stehouwer, 2001). Smith et al., (1995) report that the leachability of Cr(VI) increases as soil pH increases and Hug et al., (1997) report that the reaction of Cr(VI) with Fe(II) is strongly influenced by pH and organic ligands and at pH values above 5-7, aqueous uncomplexed Cr(III) hydrolyzes to sparsely soluble chromium(III) hydroxides, adsorbs strongly to mineral and organic surfaces, and co-precipitates with other minerals.

Arsenic: Su and Puls (2001) explain As adsorption in terms of ionization of both adsorbates and adsorbents. Their studies examined As adsorption on iron oxide compounds and amorphous iron hydroxide. In the pH range of 3 to 6, As(V) is the predominant species and the major species being adsorbed. The iron oxide surfaces exhibit a net positive charge in this pH range, and adsorption of anionic As(V) is enhanced by coulombic attractions. The net positive charge diminishes as the pH increases to above 5, and approaches zero at pH 7, resulting in maximum adsorption. Both As(V) and As(III) have strong affinities for hydrated iron oxide compounds, and As(III) is adsorbed in much larger amounts than As(V) at pH>7.5 or at high As concentrations in solutions. When the pH is above 9, negatively charged As(III) species become predominant and the oxide surface also becomes negatively charged; thus, electrostatic repulsion results in decreased adsorption.

Manning and Goldberg (1997) noted that minor concentration effects are observed and exceptions occur where high pH and high concentration result in increased As(III) removal from solution. However, they note that between the pH range of 4 to 9, differences between As(III) adsorption on materials due to variations in concentration were typically less than 10%. Additionally, their research showed that homogeneous oxidation of As(III) to As(V) occurs in solutions at or above pH 9.2.

Griffin and Shimp (1978), in a study of As(V) adsorption by kaolinite and montmorillonite clays, found maximum adsorption of As(V) to occur at pH 5, while the adsorption of As(III) increases over a pH range of 3-9. Adsorption of As(V) by aluminum and iron oxides has shown an adsorption maximum at pH 3-4 followed by a gradual decrease in adsorption with increasing pH (Hingston et al., 1971; Andersen et al., 1976).

2.6.5 Effect of Co-Waste

Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the nature of waste residue, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. The use of literature or laboratory data that do not reproduce the specific soil and waste system of a site will not be adequate to describe or predict the behavior of the metals. Data must be site specific and the long-term effects of the association of the waste components must also be considered. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metals will change with the changing soil conditions.

Puls et al., (1991) identified the enhanced transport of metals associated with various wastes due to:

1. facilitated transport caused by metal association with mobile colloidal size particles,
2. formation of metal organic and inorganic complexes that do not sorb to soil solid surfaces,
3. competition with other constituents of waste, both organic and inorganic, for sorption sites, and
4. decreased availability of surface sites caused by the presence of a complex waste matrix.

The following three studies are representative of remediation research conducted on complex waste/soil systems involving As, Cr and Cu metals:

In an experiment to measure hexavalent chromium reduction in soils contaminated with CCA preservative, Song et al. (2006), measured the reduction of Cr(VI) by three soils (sandy, clayey, and organic) in contact with a CCA solution of 2700 mg/L of hexavalent chromium and found that all three soils reduced Cr(VI) concentrations within one month: sandy and clayey soils by 50% and organic soil by almost 100%.

Dagan et al. (2006) performed a laboratory study of the transport of CCA-treated wood leachates through soil columns of three soils (sandy, clayey, and organic). The composition of the CCA leachate solution was as follows: As, 1052 μg/L; Cu, 533 μg/L; Cr, 307 μg/L. After the passage of 80 pore volumes of the leachate the (Cr, Cu, As) metal concentrations (μg/L) of the elutriates were as follows: sandy soil (121,45,479); organic soil (136,87,383); clayey soil (94,40,112). A comparison of the leaching pattern showed that arsenic was the most mobile while copper was the most retained in the soil columns (As>Cr>Cu).

Kumpiene et al. (2008) conducted an overview study of data published in the last five years on the immobilization of As, Cr, and Cu metals in soils. The most extensively studied amendments for As immobilization are Fe containing materials. The immobilization of As occurs through adsorption on Fe oxides by replacing the surface hydroxyl groups with the As ions, as well as by the formation of amorphous Fe(III) arsenates and/or insoluble secondary oxidation minerals. Cr stabilization mainly deals with Cr reduction from its toxic and mobile hexavalent form Cr(VI) to stable in natural environments Cr(III). The reduction is accelerated in soil by the presence of organic matter and divalent iron. Clays, carbonates, phosphates and Fe oxides were the common amendments tested for Cu immobilization. The suggested mechanisms of Cu retention were precipitation of Cu carbonates and oxyhydroxides, ion exchange and formation of ternary cation–anion complexes on the surface of Fe and Al oxy-hydroxides.

2.7 Summary of Application of the Literature Review to Research

The literature review provides insight into fundamental mechanisms and conditions that will produce desired remedial effects upon the system of metals under study.

- ***Cu is bound strongly by soil particles, clays and organic material in the pH 6-8 range and is more soluble in pH <5.*** The adsorption of copper to potential colloidal material has the advantage of placing copper in a reduced mobility environment of flocculation or the disadvantage of producing a possible transport mechanism for increased mobility.
- ***Cr (VI) is reduced to Cr (III) by normal soil in the pH 6-8 range.*** Therefore, the pH conditions of the remediation strategy are an important influence on the oxidation states of chromium resulting in reduced toxicity and mobility of the metal.
- ***Cr (III) mobility is decreased by adsorption to clays and oxide minerals at pH <5.*** Lower pH conditions are conducive to increased adsorption of Cr (III), but lower pH conditions may produce undesirable soil properties.
- ***Cr (III) low solubility above pH 5 due to formation of $Cr(OH)_3$.*** Hydroxide formation produces species that are prone to precipitation and co-precipitation.

- ***Cr (VI) reduction to Cr (III) by Fe(II) decreases almost linearly with pH > 5.5.***
- ***Fe (II) and Cr (VI) over pH 2-13, 1 to 3 equivalents of Fe(II) results in the transformation of Cr (VI) to Cr (III).*** Fe (II) addition by a soil amendment could enhance reduction of Cr (VI) to Cr (III) and serve as a source of iron to the soil matrix and further enhance reactions with Fe and Al oxides.
- ***As and Cr have an affinity for adsorption to iron and aluminum oxides.*** Iron and aluminum oxide compositions in the reactive portion of the soil are potential sites of adsorption reactions.
- ***As (V) forms insoluble precipitates with iron, aluminum, and calcium, with iron in soils being the most effective.*** Enhancing the soil matrix with sources of iron and calcium has potential for increasing adsorption sites for metal anions or precipitation and co-precipitation reactions.
- ***Common cations flocculate soil colloids in the general order of $Al^{+3}>H^{+}>Ca^{+2}$, $Mg^{+2}>K^{+}>Na^{+}$.*** Experimentation with soil amendments containing Ca and Mg cations are thus areas of interest.
- ***Most reactions occur within the clay-size portion of the soil.*** Increasing adsorption to this fraction of the soil will reduce the mobility of metals, therefore research experiments should incorporate a sieved test soil of uniform size in the reactive portion.

CHAPTER III

HYPOTHESES

3.1 Need for Research

The literature review provides strong evidence that soil systems are highly complex due to the chemical and physical nature of soil. The introduction of metal contaminants to these systems poses many questions regarding metals toxicity, mobility, and the degree to which soils will enhance or retard metals mobility when subjected to rainwater-leaching. The multiple factors of Cu, Cr, and As contamination in the environment have the potential for an almost unlimited number of physical and chemical systems to be studied. This dissertation will investigate the burning of CCA-treated wood in residential settings and the generation of CCA-treated wood ash containing toxic metals that have the potential for soil and water contamination.

Adsorption and precipitation are important mechanisms for the control of metals in the soil and water environments. The effectiveness of these mechanisms to immobilize metals may be enhanced by the addition of chemical additives to contaminated soil and water systems. The application of common agricultural chemical amendments may serve as a means of immobilizing metals leaching from soil contaminated with CCA-ash.

Proposed research

The proposed dissertation research work will specifically:

1) Investigate a CCA-treated wood burn site.
2) Quantify the concentrations of CCA-metals in the soil of the burn site.

3) Conduct laboratory experiments to test the mobility of leached CCA-metals in soil.
4) Identify common chemical agricultural amendments which have the potential for reducing the mobility of CCA-metals in soil.
5) Perform laboratory experiments to test the effect upon CCA-metals mobility by the application of the most promising soil amendments identified.

3.2 Hypotheses

The objective of this dissertation research is to determine the mobility of As, Cr, and Cu metals (CCA-metals) undergoing rainwater-leaching from burn sites containing CCA-ash mixed with soil. The literature review indicated that each metal has more than one major species which have varying mobilities in different pH conditions of soil. Therefore, the design and performance of a potential immobilization strategy for these metals will be greatly influenced by the pH conditions resulting from the chemical treatment of soil contaminated by CCA-ash. Studying the results of these chemical treatments will aide in assessing the scope of the problems associated with CCA-metals-contaminated burn sites and the potential for localized remediation strategies. The following hypotheses statements for this dissertation are based on the review of the literature and preliminary analyses.

Hypothesis 1:

CCA-metals in a wood ash/soil system are preferentially associated with soil particle matter and their rainwater-leachability is affected by the soil chemical components.

Prediction 1: CCA-metals are strongly associated with clay, and oxides of aluminum and iron, and organic carbon, therefore soil/CCA-ash mixtures should leach less metal than CCA-ash alone under conditions of rainwater-leaching. Soils are composed of varying sized particles ranging from gravel to sand to silt to clay with varying compositions of organic carbon which increase the ability of soils to adsorb metal contaminants. Since most reactions occur in the clay size fraction which have very high surface areas compared to the other soil components, the significance of the presence of mineral components of clay and oxides of iron and aluminum and organic carbon are of importance to the reduction of metals mobility.

Research Activities 1:

a) Determine the size fraction and mineral composition of the particle components of the test soil used in the study. These results will be used to determine the optimal fractional component of the test soil to use in future experiments

b) Determine the quantity of CCA-metals in a laboratory-prepared CCA-wood ash to be used in the experiments. CCA-ash will be prepared under controlled conditions in order to produce a test ash of reasonably uniform size composition that will result in an acceptable variation of chemical composition in regard to CCA-metals in the ash. The laboratory prepared ash will be analyzed for CCA-metals composition by the use of microwave-assisted acid-digestion methods and ICP analysis.

c) Design and perform batch studies on CCA-ash and test soil/CCA-ash mixtures in order to determine the effect of the enhancement or retardance of soil upon the leachability of CCA-metals from contaminated soil.

Critical Tests 1:

a) Assess the size fraction and mineral components of the test soil. The composition of the major soil components of kaolinitic clay, iron and aluminum oxides, and organic carbon may be determined to better characterize the composition of the soil fraction used in the experiments. The resulting soil composition of the test soil and the test soil fraction used in the study will be graphically presented. If there is a representative composition of mineral clay, oxides of iron and aluminum, and carbon material in the test soil fraction chosen, then the test soil fraction will be acceptable for the study.

b) Assess the CCA-metals composition of the laboratory-prepared CCA-ash. The ICP analysis data will be averaged, the standard deviations determined, the coefficients of variation, and the 95% confidence intervals for the CCA-metals in the sample groups. If there is an acceptable 95% confidence interval for the heterogeneous CCA-ash samples, then the ash will be used for further experimentation.

c) Assess the rainwater-leachability of CCA-metals from CCA-wood ash and the effect upon leachability by the mixing of CCA-ash with the test soil. The ICP analysis data of CCA-metals from the batch study leachates will be averaged, the standard deviations determined, the coefficients of variation, and the 95% confidence intervals will be determined. If the 95% confidence intervals on CCA-metals leachate data and the data trends are significant to show a difference in rainwater-leachability of CCA-ash and test soil/CCA-ash mixtures, then the results will be accepted.

Hypothesis 2:

Burn sites contaminated with metals have the potential for contamination of water as the result of rainwater-leaching of burn sites.

Prediction 2: When CCA-metals are introduced into the environment as the result of the burning of CCA-treated wood waste, the concentrations of CCA-metals in the soil/CCA-ash mixtures are at much higher concentrations than existed in the CCA-treated wood. The resulting CCA-metals contamination at these burn sites will likely overwhelm the natural ability of the soil to retard metals mobility. Therefore, the contamination from concentrated CCA-metals in CCA-ash presents a further potential source for the spread of metals contamination of adjacent soil and water resources.

Research Activities 2:

a) Investigate and design a sample plan for a known burn site where CCA-treated wood has been burned. The site will be measured, photographed, and sample points on the burn site will be recorded on the photographs.

b) Determine the CCA-metals content of the surface and near surface soil samples at the burn site. The CCA-metals distribution at the burn site will be characterized by the samples taken in several locations. The degree of metals mobility from the burn site will be investigated and graphically recorded. The CCA-metals composition data of the samples will be used to design a CCA-metals contaminated test soil media using an uncontaminated test soil and CCA-ash mixture for use in both batch and column leaching studies.

c) Determine relative potential for contamination of adjacent soil and water by leached CCA-metals from a CCA-ash/test soil mixture replicating the burn site concentrations of CCA-metals. A batch study of multiple rainwater-leachings of the replicate burn site CCA-ash/test soil mixture will be conducted to simulate the potential contamination of water by CCA-metals.

Critical Tests 2:

a) The sampling plan will be acceptable if the site investigation shows that the burn area can be clearly delineated in order to both characterize the burn site and the burn site soil to be studied.

b) The sampling plan should use methods which will not contaminate the samples taken at one sampling point by CCA-metals from a previously sampled point on the burn site location. The resulting data will be acceptable if no outlier CCA-metals readings are encountered in the results.

c) The metals distribution model will be accepted if there are no outliers of CCA-metals data both in the horizontal samples taken and the vertical subsurface samples taken at the burn site.

d) The experimental data of the potential for contamination of water from batch rainwater-leaching of CCA-metals will be accepted if the resulting data pass statistical tests.

Hypothesis 3:

Retardance mechanisms within soils are effective means of reducing metals mobility and may be enhanced with amendments in order to further immobilize metals.

Prediction 3: Since CCA-metals mixed with soil are associated with organic carbon material, oxides of iron and aluminum, and mineral clay soil components, the application of appropriate chemical amendments can increase the ability of these soil components to retard the mobility of CCA-metals undergoing rainwater-leaching from a CCA-metals contaminated soil.

Research Activities 3:

a) Design factorial batch leaching experiments to determine the rainwater-leachability of CCA-metals from CCA-ash/test soil, CCA-ash/test soil amended with each chemical amendment or CCA-ash/test soil amended with combinations of chemical amendments.

b) Design and construct several leach columns. Load the columns with southern yellow pine ash and test soil to replicate the wood ash/soil composition of the burn site investigated in this study. The column designs will be tested with water in order to select a column design that will enable column tests to be conducted with an acceptable flow rate.

c) Design factorial column leaching experiments to determine the rainwater-leachability of CCA-metals from CCA-ash/test soil, CCA-ash/test soil amended with each chemical amendment or CCA-ash/test soil amended with combinations of chemical amendments.

Critical Tests 3:

a) Assess the effects of soil amendments upon the batch rainwater-leachability of CCA-metals through multiple leachings. The leached metals data will be analyzed by a table of contrasts for each CCA-metal and all of its amendment combinations.

b) Assess the flow rates of the various column designs to determine the most acceptable column design to be used. Leaching durations should be in the range of 12-24 hours, with no channeling along the walls of the column, and the column soils will not clog during the tests.

c) Assess the effects of the soil amendments upon the rainwater-leaching of CCA-metals from the test soil/CCA-ash column factorial matrix. The data will be compared between duplicate sets of columns leached with an amount of rainwater equivalent to one-year of rainfall at the burn site. The leached metals data will be analyzed by a table of contrasts for each CCA-metal and all of its amendment combinations.

CHAPTER IV

EXPERIMENTAL DESIGN

4.1 Chapter Introduction

The purpose of this chapter is to explain the experimental methods, procedures, apparatus, materials utilized in obtaining and analyzing data for this research project. The methods and apparatus have been derived from previous research and have been modified to the specific needs of these experiments in order to meet the dissertation objectives.

4.2 Quality Control and Quality Assurance

Quality control and quality assurance techniques are used during all parts of this research, including sample collection, laboratory analyses, and data statistical tests. Sampling methods include sampling techniques that will maximize the ability to collect samples reliably and eliminate sample contamination. In order to ensure that the data collected for metals determinations are valid and not a result of contamination or inconsistency, a rigorous quality assurance plan has been developed and implemented.

Sampling containers and other equipment coming into contact with solids and solutions are plastic-ware (fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers). All laboratory sampling equipment and sample containers are carefully cleaned using a three-step procedure: detergent wash and rinse; mineral acid wash (standard nitric acid bath and rinsing procedure); followed by multiple rinses with reagent water. After cleaning and drying, sample containers are sealed with caps, bagged, and stored in the lab until required. All glassware employed in the analyses work is soap washed and rinsed with ASTM Type 2, 17.9 micromho deionized water.

Samples for metals analyses are digested (microwave digestion) prior to analyses and filtered through 0.45 μm metricel membrane filters prior to analyses. Metals analyses are performed using a dual view model Perkin Elmer Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) DV3000. Data quality in this study is guaranteed through the use of blanks (lab blanks, equipment blanks, method blanks, and matrix blanks), NIST standards from two independent sources, spikes (matrix spike) and duplicates (matrix spike duplicates and lab duplicates) and lab replicates. The range of analyte concentrations in the samples will enable selection of appropriate internal standards and delineation of the range and matrix for the calibration solutions. Quality control standards are included at the beginning and end of the analytical run and repeated every ten samples throughout the run in order to ensure accuracy of the analysis. Sufficient matrix blanks are analyzed to determine the LOD/LOQ for each metal during each ICP run.

4.3 Burn Site Investigation

A CCA-treated wood burn site was investigated for levels of contamination by Cu, Cr, and As. In Figure 4.1 we see the general site area with the location of sampling points at B, C, and D, with point B being the location of the burn site and located sixteen feet from the lake edge.

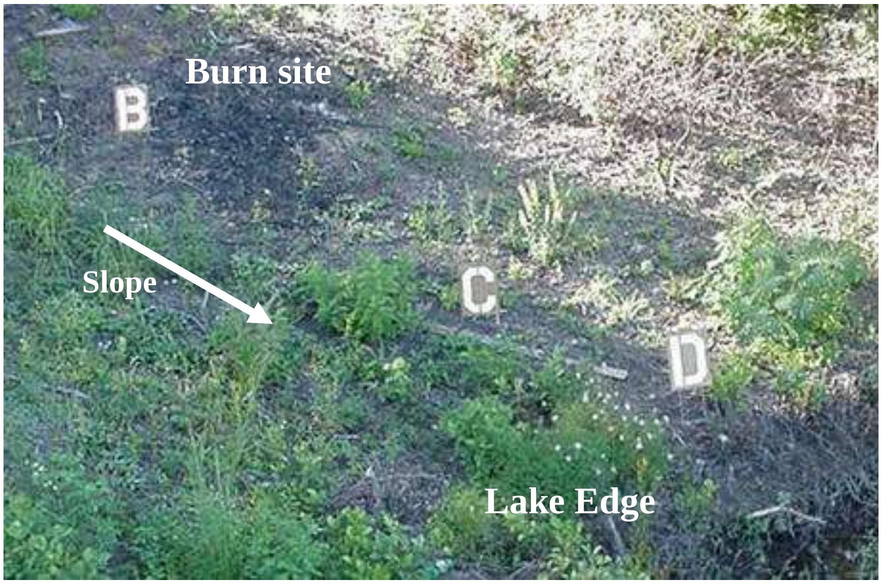


Figure 4.1 – General Area of CCA-wood Burn Site Showing Slope to Lake

4.3.1 Field Sampling Methods

Surface samples – A surface sample is taken at a sample point by gathering several samples from the surface around the point to a depth of 2 inches and mixing to obtain one composite sample.

Core samples – Figure 4.2 shows examples of core samples taken by driving a 2 inch galvanized metal conduit pipe into the sample point. The pipe had no Cu, Cr, or As composition and was washed with lab soap, then rinsed with deionized water. The removed pipe is cut at 3 and 6 inch depths to gather samples to determine depth of soil penetration by the CCA-metals. The sample is taken under dry conditions and the sample used from the core is taken from the interior of the core to eliminate the chance of contamination or contact with the core tool.

Figure 4.2 – Burn Site Area Soil Core Samples

4.4 Experimental Media

4.4.1 Soil Amendments

Figure 4.3 shows the soil amendments studied during this research purchased locally at home improvement and farm supply warehouses: Soil softener (Gypsum) ($CaSO_4$); (AgLime) dolomitic limestone ($CaCO_3$, Mg CO_3); and $FeSO_4$.

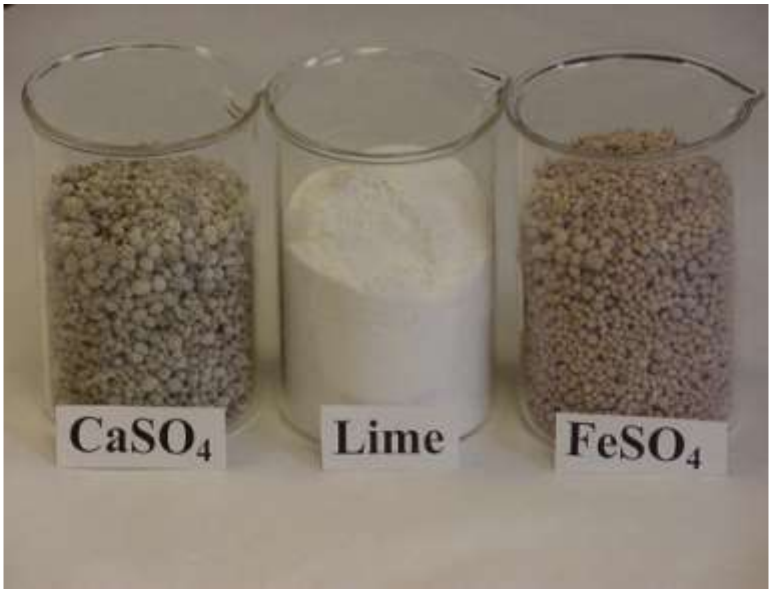


Figure 4.3 – Gypsum ($CaSO_4$), AgLime (Dolomitic Limestone), $FeSO_4$ Soil Amendments

Table 4.1 contains the manufacturer specifications of the three agricultural amendments used in this research.

Table 4.1 – Agricultural Soil Amendments

Chemical	Brand Name	Analysis	% *	Instructions **	Manufacturer
$FeSO_4$	Iron Granules (Soil Acidifier)	Fe from $FeSO_4$	20%	1/4# = 1/2 cup 2-1/2# / 1000 ft^2	Southern Agricultural Insecticides, Inc. Palmetto, FL 34220
$CaSO_4$	Pelletized Gypsum	$CaSO_4 + 2H_2O$	75%	80 - 120# / 1000 ft^2	Imerys
	Soil Conditioner	Ca	18%		100 Mansell Court E.
		S	15%		Roswell, GA 30076
$CaCO_3$	Deco Lawnlime	$CaCO_3$ Equivalent	90%	50 - 100# / 1000 ft^2	Imerys
$MgCO_3$	(AgLime)	CO Equivalent	50%		100 Mansell Court E.
		Derived From:			Roswell, GA 30076
		$CaCO_3$	60%		
		$MgCO_3$	21%		
		CaO	34%		
		MgO	10%		
		Elemental Ca	24%		
		Elemental Mg	6%		

*   Dry wt analysis
** For standard use

4.4.2 Test Soil Preparation

Figure 4.4 shows a sample of the test soil used in the research. The test soil batch was prepared by removing approximately 50 gallons of soil from a soil pile natural to that area and located 200 feet away from and separate from the general area of investigation. The soil was sieved through a U.S.A. Standard Testing Sieve (#4, 4.75 mm, 0.187 in) to remove roots and soil lumps that were too large to be acceptable for use in the modeling experiments. After sieving, approximately 35 gallons of test soil was obtained. The 35-gallon volume of soil was mixed thoroughly by filling 7 buckets with soil and then portioning amounts of each bucket to the test soil barrel. The final test soil used for experiments was sieved through a U.S.A. Standard Testing Sieve (#30, 0.6 mm, 0.0235 in).

The test soil was analyzed for Cu, Cr, and As and the results indicated that the instrument response for Cu, Cr, and As in the test soil was below the instrument response resulting from the analysis of the reagent blanks. The limits of detection for the analysis of the acid leached soil was 25 ppb for Cu, 26 ppb for Cr, and 34 ppb for As.

Figure 4.4 – Sample of the Test Soil used in the Dissertation Research

4.4.3 Test Ash Preparation

A sample of the test CCA-ash produced by burning CCA-treated wood scraps on a large steel grate over a steel catch-pan is shown in Figure 4.5. The newly-treated wood was obtained from Richardson Brothers Wood Preservers, Northport, Alabama. An open-ended 55-gallon steel drum was used as a “stack” to contain the burning and to produce a more efficient burn process. Approximately 2kg of ash was produced. The volume of ash was sieved through a

U.S.A. Standard Testing Sieve (#10, 2.00 mm, 0.0787 in) to remove large unburned cinders. After sieving, the test ash was mixed thoroughly within a 5-gallon plastic bucket. The test ash has a distinctive green-gray color which is indicative of the Cu and Cr content.

Figure 4.5 – Sample of the Test Ash used in the Dissertation Research

4.5 Batch Study Methodology

4.5.1 Leaching Fluids

Deionized Water – ASTM Type 2, 17.9 micromho.

Rainwater – Collected by placing plastic sheeting over a sloping concrete drive. Rainwater is drained into a plastic container and the pH is recorded. Initially the rainwater is stored in a refrigerator for experiments that involved small amounts over a long period of time. Rainwater used in the column study is not stored in the refrigerator due to the continuous nature for rainwater demand during the experiment and the desire to have the rainwater at room temperature.

4.5.2 Batch Study – General Method

Batch studies are the most commonly used technique for sorption studies. Sorption studies are so named because they do not distinguish between adsorption or absorption, or other types of chemical removal processes, such as oxidation, or precipitation.

Advantages of batch studies are:

1. Ease of operation, and
2. Larger numbers of samples may be studied.

Disadvantages of batch studies are:

1. Results are sensitive to the soil:solution ratio used,
2. Soil:solution ratios in actual soil systems cannot be replicated in batch studies, so scaling of data from batch studies to soil systems is uncertain,
3. Results are sensitive to the mixing rate used,
4. Separation techniques may affect results, and
5. Many investigators have found that batch generated data is not adequate to describe the behavior of metals in flow through systems.

The batch study methods utilized in this experimentation are modifications of the US EPA SW-846, Method 1311, Toxicity Characteristic Leaching Procedure. In this modification, a sample of known mass of ash, soil, soil/ash mixture or soil/ash/amendment mixture is placed in an appropriate size polyethylene bottle. The sample is loaded to field-capacity with leaching fluid by adding a measured volume of the fluid to the solid mixture until the solid mixture becomes plastic or becomes a slurry. Field capacity is reached when the drained soil has capillary pores filled with water and micropores filled with air. The wet mixture is allowed to age for 24 hours to reach a reaction equilibrium. The final measured volume of leaching fluid is placed into the bottle and the top is tightly sealed using Teflon tape. Leaching is performed by rotating the jar at 20 RPM in a rotator for 18 ± 2 hours. The rotator, shown in Figure 4.7, is powered by a Baldor Model GP7401 DC Motor, 1/8 HP, and a Baldor DC Drive Control. After leaching is complete, the sample bottle is centrifuged for 20 minutes at 1000 RPM in an International Equipment Company, Model 2XD Centrifuge shown in Figure 4.8 Batch Study Centrifuge. The leachate is removed from the sample bottle by pipette in order to ensure the quality of the leachate by avoiding any colloidal material that may be on the surface of the leachate or any solids deposited on the bottom of the bottle. The leachate is immediately transferred to microwave digestion vessels and acidified for preservation and also to begin the first step of the microwave digestion procedure (US EPA SW-846, Method 3052).

Figure 4.6 – Batch Leaching Study Reactors

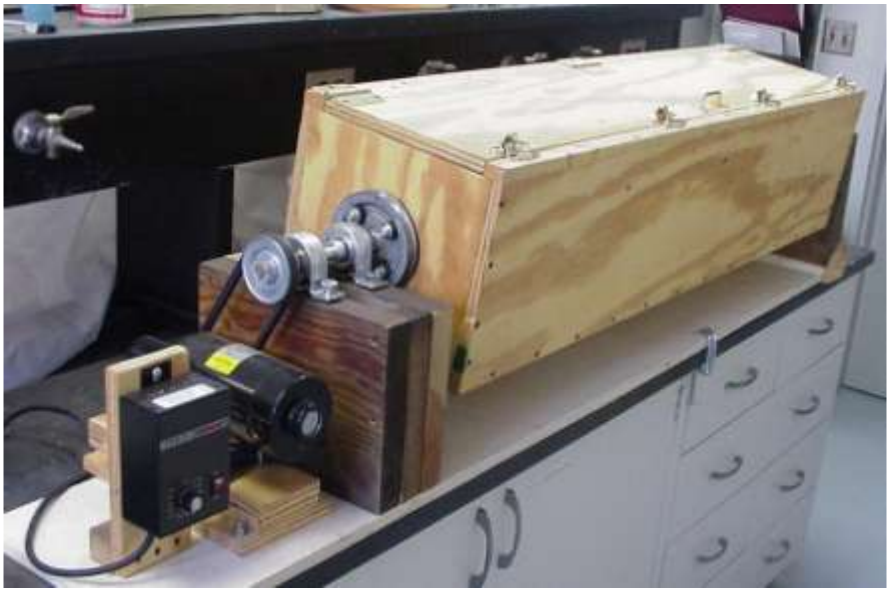


Figure 4.7 – Batch Leaching Study Rotator for Leach Extractions

Figure 4.8 – Batch Leaching Study Centrifuge for Batch Reactors

4.5.3 Batch Study Experiments

The batch experiments are conducted using soil, test ash or soil/test ash mixtures. In the experiment involving the testing the effects of soil amendments and their combinations upon the leaching of CCA metals, as shown in Table 4.2, the experiment involves eight duplicate reactor combinations or a total of sixteen reactors. One set of reactors have only test soil/test CCA-ash, the other seven duplicate sets have test soil/test CCA-ash and either AgLime, $CaSO_4$, $FeSO_4$ or combinations of those amendments. A sequential leaching is conducted to represent multiple leachings to gather preliminary data for the design of column leaching experiments. This batch study is a 2^3 Factorial Design experiment for each of the three metals. That is, the samples are run in duplicate reactors with the three variable "factors" being the content of AgLime, $CaSO_4$, and $FeSO_4$ or their combinations. The response is the mass of leached metal, in total or after each leach, resulting from the rainwater leachings. Comparisons are made between the eight combinations to determine the most effective amendments. Since there are three metal responses, the experiment is actually three nested 2^3 Factorial Design experiments run simultaneously. After examining the results of the three metal responses, a better understanding can be developed of the potentially most effective soil amendments to reduce metals leaching in a future column leaching experiment. The mean values of the duplicate batch leaching are used to compute the main effects and the interaction effects and a standard group error for the experiment according to computations described by Box et al, 2005.

Table 4.2 - Batch Leaching Study Experiment 2^3 Factorial Design Matrix (Table of Contrasts)

Duplicate Batch	Mean	**1 = AgLime** **2 = Gypsum** **3 = Iron Sulfate**						
	I	**1**	**2**	**3**	**12**	**13**	**23**	**123**
1	+	–	–	–	+	+	+	–
2	+	+	–	–	–	–	+	+
3	+	–	+	–	–	+	–	+
4	+	+	+	–	+	–	–	–
5	+	–	–	+	+	–	–	+
6	+	+	–	+	–	+	–	–
7	+	–	+	+	–	–	+	–
8	+	+	+	+	+	+	+	+

4.6 Column Study Methodology

4.6.1 Leaching Fluid

Rainwater – Collected by placing plastic sheeting over a sloping concrete drive. Rainwater is drained into a plastic container and the pH recorded. The rainwater used in the column study, approximately 20 L in a plastic carboy, is not stored in the refrigerator due to the continuous demand for rainwater during the experiment and the desire to have the rainwater at room temperature.

4.6.2 Column Study – General Method

Column studies are less commonly used in sorption studies than are batch studies.

Advantages of column studies are:

1. Low soil:solution ratios can be used,
2. Separation of the soil and solution phase is not required,

3. Mechanical mixing is not required, and
4. Column studies more closely simulate field conditions than batch studies.

Disadvantages of column studies are:

1. Results depend on flow rates used,
2. Columns are difficult to set-up and maintain,
3. Uniform packing of the column is difficult often leading to channel flow, and
4. Fewer columns can be operated at one time compared with the number of batch reactors.

The test columns used in this dissertation research depart from the more common method of operation of columns used for sorption studies. Commonly, a column media is studied by the controlled upward flow of a fluid through the column. The fluid containing a known amount of a material enters the column at the bottom and samples are taken of the fluid as it exits the column at the top. Analysis of the exiting fluid enables the experimentor to determine the amount of the material being sorbed versus time and volume by the column media. In this dissertation research, the column media is studied for its reactions with rainwater flowing by gravity in individual "batches" representing individual precipitation events from the top of the column and exiting the bottom of the column. The leaching of metals from the column media versus time and volume is the focus of this experiment.

4.6.3 Column Composition

A schematic of the test columns, polycarbonate cylinders that are fabricated from fluorescent tube protectors, is shown in Figure 4.9. The column dimensions are 4.2 cm in diameter and 61 cm in length. Each tube protector has two removable ends. One of these ends was used with landscape fabric to produce a bottom end seal of the column. This end seal is held in place by a stainless steel hose clamp fastened around the polycarbonate cylinder at the location of the end seal. The test columns are placed vertically in a wooden rack as shown in Figure 4.10.

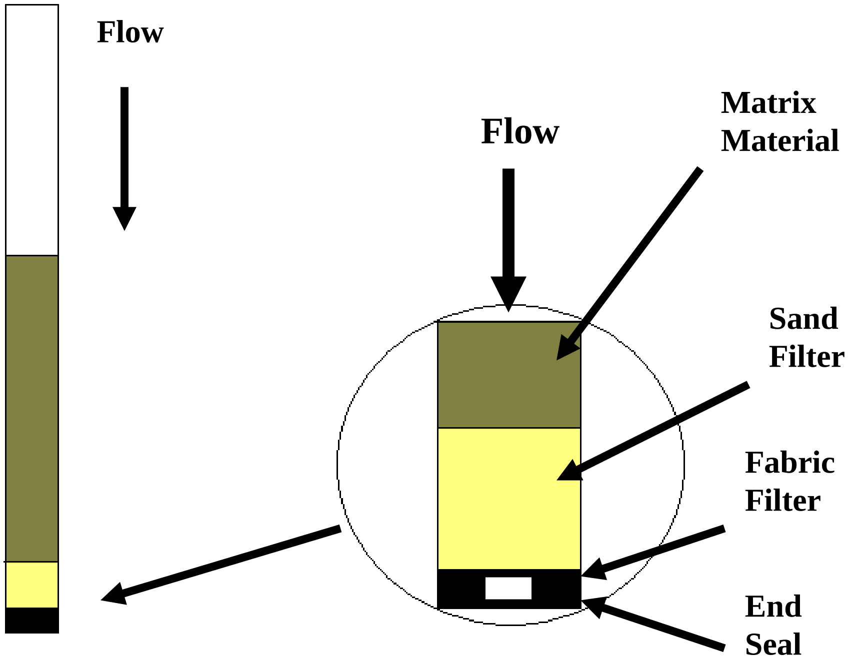


Figure 4.9 – Schematic of Test Column

Figure 4.10 Column Leaching Study in Operation

4.6.4 Column Experiment Design

The column leaching experiment is designed to determine the effects of a controlled rainwater leach of eight sets of duplicate test soil/CCA-ash columns designed to closely replicate the Cu, Cr, and As concentrations in the soil at the burn site. The duplicate columns of eight combinations of test soil/CCA-ash and the amendments AgLime, $CaSO_4$, and $FeSO_4$ and amendment combinations are leached with nineteen leach “episodes” of rainwater to simulate the annual rainfall in the area.

4.6.5 Column Factorial Analysis

The factorial design of the column experiment is shown in Table 4.3. The experiment involves the effects of the use or nonuse of the three amendments and their combinations. The effects being studied are the relative magnitudes of the resulting leached masses of each of the three CCA-metals (Cu, Cr, As).

Table 4.3 – Column Leaching Experiment 2^3 Factorial Design Matrix (Table of Contrasts)

Duplicate Batch	Mean	**1 = AgLime** **2 = Gypsum** **3 = Iron Sulfate**						
	I	**1**	**2**	**3**	**12**	**13**	**23**	**123**
1	+	–	–	–	+	+	+	–
2	+	+	–	–	–	–	+	+
3	+	–	+	–	–	+	–	+
4	+	+	+	–	+	–	–	–
5	+	–	–	+	+	–	–	+
6	+	+	–	+	–	+	–	–
7	+	–	+	+	–	–	+	–
8	+	+	+	+	+	+	+	+

The resulting data are analyzed using a Table of Constrasts to determine a mathematical model that will represent the effects of interactions of amendments upon the leaching of Cu, Cr, and As. The mathematical model for effects of an amendment or amendment combinations can be computed using a system of matrix computations using the mean values of the leached mass data and a final computation of the effects and standard group error (Box et al., 2005).

4.7 Data Analysis

4.7.1 Basic Characterization Experiments Data Analysis

The following characterization experiments were performed to determine the relative leaching characteristics of the experimental media and descriptive statistics were evaluated to measure the quality of the data and experimental procedures.

1. Metal Mass Analysis of CCA-ash Sample
2. TCLP Leach of CCA-ash Sample
3. Data of Rainwater-leach of CCA-ash, CCA-ash/Test Soil

Descriptive Statistics

- Standard deviation (SD)
- Coefficient of variation (CV)
- 95% Confidence Interval (95% CI)

4.7.2 Statistical Tests for Batch and Column Leaching Study Data

Mathematical Computation Procedure for Table of Contrasts for Factorial Designs

- Box et al., 2005
- Page 186, Section 5.9 Table of Contrasts

ANOVA Analysis for Batch and Column Leaching Factorial Designs

- Design-Expert 8.0.4.1 Program, Design-Ease, Inc.

4.8 Analytical Procedures

Below is a list of the methods and auxiliary procedures used:

- US EPA SW-846 Method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.
- US EPA SW-846 Method 3051, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.
- US EPA SW-846 Method 1311, Toxic Characteristic Leaching Procedure.
- pH of Water – ThermoOrion pH Meter, Model 520.
- pH of Soil – ThermoOrion pH Meter, Model 520. Soil pH, Soil Science Society of America, Methods of Soil Analysis, Part 3-Chemical Methods, p 487.
- Carbon Content and Organic Carbon Content of Soil – Loss On Ignition Method, Soils Science Society of America, Book Series: 5, Methods of Soil Analysis, Part 3-Chemical Methods, p1004.
- Bulk Density Determinations– *The Nature and Properties of Soils*, Brady, p103.
- ICP-OES Analysis by Elizabeth Graham, PhD
  Manager, Geochemical Laboratory
  Department of Geological Sciences
  The University of Alabama
  Tuscaloosa, Alabama

4.9 Conclusions

The experimental design of this dissertation research has been planned to produce data that is reproducible within acceptable confidence intervals. From the initial characterization sampling in the field and laboratory to the preparation of experimental media to the quality assurance/quality control during batch and column leaching experiments, careful procedures have been undertaken to create a controlled research study.

CHAPTER V

EFFECTS OF SOIL COMPONENTS AND LIMING EFFECT OF CCA-WOOD ASH UPON LEACHING OF Cu, Cr, AND As FROM CCA-WOOD ASH IN ULTISOL SOIL

Abstract

The burning of wood that has been chemically treated with chromated copper arsenate (CCA) produces an ash containing high concentrations of copper, chromium, and arsenic (CCA-metals). The rainwater-leaching of these metals from burn sites can produce increased soil and water contamination. Soil systems have varying natural abilities to retard leaching and they also impact metals speciation and toxicity, through sorption, conversion and sedimentation related mechanisms. Recent regulations restricting the use of CCA-treatment have resulted in increased quantities of CCA-treated lumber entering the waste stream, making the study of metals leaching from CCA-wood ash and soil/CCA-wood ash systems to be important areas of investigation.

Wood ash composition, soil composition, and CCA-metals speciation are all important factors determining the degree of the metal mobility in a soil system containing metals leached from CCA-wood ash. The CCA-metals composition of CCA-wood ash was determined by analytical methods. Both pH and batch leaching studies were used to postulate mobility mechanisms within the CCA-wood ash/soil system. The contrasting effects of untreated-wood ash and CCA-wood ash on soil components is presented in order to assess the potential for enhancement of immobilization mechanisms that increase the soil system retardance of CCA-metals mobility.

Results of this investigation show that the Ultisol test soil retards the mobility of As and Cr compared to CCA-wood ash alone, while Cu mobility is increased in the presence of the Ultisol test soil. Experimental results show that the alkalinity of a CCA-wood ash/Ultisol soil system is lower than that of an untreated-wood ash/Ultisol soil system. This indicates a difference in chemical composition and the potential consumption of hydroxyl ions during treatment by the retardance mechanisms affecting Cr and As mobility. Therefore, the study of these contaminated soil systems and the potential enhancement of immobilization mechanisms are important areas of investigation.

Keywords: Arsenic, Chromium, Copper, Retardance, Liming Effect, CCA-wood ash treatment

5.1 Introduction

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 humid climate and the increased presence of parasitic insects on untreated wood in this region (Solo-Gabriele et al., 1999). Increasingly larger quantities of used CCA-wood are entering the waste stream due to a combination of factors that include; normal end of the service life; design changes (Cooper, 1993; McQueen and Stevens, 1998; Clausen, 2000; Wu, 2000); a restrictive ban on future CCA-wood use in domestic settings (Federal Register, 2003) and an associated increased public awareness of health concerns related to CCA-wood use. The disposal of weathered and scrap CCA-wood by onsite burning, producing an ash that poses a potential threat to humans and the environment, is discouraged but remains a pathway for the release of Cu, Cr and As (CCA-metals) (Solo-Gabriele et al, 1999). Low levels of these compounds have been long recognized as causing environmental problems. At the $\mu g\ L^{-1}$ 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 (Winner, 1984; Korte and Fernando, 1991; LaGrega et al., 1994; Palmer and Puls, 1994; Raven et al., 1998; Solo-Gabriele et al., 1999).

The interaction of wood ash with soil in a wood ash/soil system is complex. Factors such as soil chemical composition, organic carbon content, pH, solution complex formation, type and aqueous speciation of metal, metal concentration, liquid:solid(soil) ratio, climatic, and geologic conditions play a role in the movement of the metal species from the wood ash and soil mixture (US EPA, 1992; Evanko and Dzombak, 1997). The effects of each metal species present are dependent, in part, upon the valence state of the metal (Helsen et al., 2003). Oxidation-reduction reactions of metals occur naturally within the soil and can increase or decrease their mobility in the soil system (NRC, 1994). High concentrations of metals tend to overwhelm the natural ability of the soil to change the valence state of metal species, therefore, a study of the contaminated soil systems may lead to chemical soil amendments that will increase the rate and extent of remediation processes (Evanko and Dzombak, 1997; Harden, 2005).

Studies have been performed to assess the individual behavior of Cr, Cu, and As in soils. Carey et al. (1996) and Khaodhiar et al. (2000) studied Cu, Cr, and As sorption in individual or mixed-metal systems on natural soils and iron oxide-coated sands, respectively. Lund and Fobian (1991) and Stilwell and Gorny (1997) evaluated the distribution of these metals in various horizons of CCA-contaminated soils. Song et al (2006) studied Cr speciation in discarded CCA-wood and ash and Kumpiene et al (2008) conducted a review of stabilization of As, Cr, Cu, Pb and Zn in soil. However, to our knowledge, a comparative study of the physical and chemical parameters of ash from untreated-wood and CCA-wood have not been conducted in regard to the retardance ability of soil in contact with a measured high concentration of CCA-metals replicating that of a burn site known to be contaminated with CCA-wood ash.

Under laboratory conditions, using batch leaching and pH studies, CCA-metals concentrations in an Ultisol soil/CCA-wood ash mixture at a burn site in Tuscaloosa County, Alabama were replicated in order to measure the physical and chemical parameters affecting retardance of rainwater-leached metals in CCA-wood ash and in an Ultisol test soil/CCA-wood ash system. Untreated-wood ash and CCA-wood ash were experimentally tested for alkalinity characteristics that influence their pH and the pH of the soil/wood ash systems.

5.1.1 Experimental Soil System Components and Properties

The properties of soil system components investigated in this study are reported below. The components being Ultisol soil as a test soil, wood ash from untreated Southern Yellow pine wood (untreated-wood ash), and wood ash from CCA-treated Southern Yellow pine wood (CCA-wood ash).

Ultisol Test Soil

Ultisol soil is the dominant soil order in the Southeastern U.S. and comprises 12.9% of the soil in the U.S. The soil forms under humid, tropical conditions primarily by the weathering of clay minerals and the leaching of base-forming cations. Table 5.1 compares Ultisols with other soil orders in the United States. Observe that Ultisols have the highest percentage of base-forming cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) of the soil orders that are high (>50%) in acid-forming cations (H^{+} and Al^{+3}). Ultisols have a low cation exchange capacity (CEC). CEC is the sum total of the exchangeable cations that a soil can adsorb, therefore a measure of the relative amounts of different colloids in the soil and the CEC of these colloids. Ultisols are dominated by kaolinitic clay and lesser so by oxides of Fe and Al (Brady and Weil, 2002).

Table 5.1 - Soil Orders in the United States (percentages of major cations)

Soil Order	Typical location	H^+ and Al^{+3}	Ca^{+2}	Mg^{+2}	K^+	Na^+
Oxisols	Hawaii	85	10	3	2	tr
Spodosols	New England	80	15	3	2	tr
Ultisols	**Southeast U.S.**	**65**	**25**	**6**	**3**	**1**
Alfisols	PA to WI	45	35	13	5	2
Vertisols	AL to TX	40	38	15	5	2
Mollisols	Midwest U.S.	30	43	18	6	3
Aridisols	Southwest U.S.	□	65	20	10	5

The percentage figures are based on the sum of the cation equivalents taken as 100
Al^{+3} adsorption includes that of complex aluminum hydroxy ions
Adapted from Brady & Weil, 2002

Untreated-wood Ash

Untreated-wood ash is composed of complex and heterogeneous materials ranging from charcoal to metal carbonates, oxides, and hydroxides. At lower temperatures of combustion, carbonates dominate the ash, while at higher temperatures, oxides are the dominant ash components. Misra et al., 1993 determined $CaCO_3$, $K_2Ca(CO_3)_2$, $Ca(OH)_2$ to be the dominant compounds at 600˚ C and Ca_2MnO_4, CaO, Mg_6MnO_8, $K_2Ca_2(SO_4)_3$ to be dominant at 1300˚ C. Etiegni and Campbell (1991) determined that carbonates and bicarbonates predominate with temperatures below 500˚ C, oxides above 1000˚ C and soluble alkalinity originated from hydroxides (92%) and carbonates (8%).

CCA-wood Ash

CCA-wood ash is composed of even more complex and heterogeneous materials than the ash of untreated-wood. The most common CCA-treatment solution used to treat CCA-wood products was composed of 47.5 % arsenic pentoxide (As_2O_5), 34% chromic acid (CrO_3), and 18.5% copper oxide (CuO) (Solo-Gabriele et al., 1999). The resulting CCA-wood contains predominantly chromium arsenate ($CrAsO_4$) with Cu^{+2} attached to wood organic compounds. When the CCA-wood is burned, As compounds are converted to As_2O_3 and the As(III) and As(V) oxyanions of AsO_3^{-3} and AsO_4^{-3}, Cr compounds are converted to Cr_2O_3 and the Cr(III) cation Cr^{+3} and Cr(VI) oxyanion CrO_4^{-2}, and Cu^{+2} cations are converted in part to CuO in the CCA-wood ash (Helsen et al, 2003). Chromium species present in CCA-wood ash are largely the less toxic Cr(III) with the more toxic Cr(VI) averaging 4 to 7% (Song et al., 2006). The CCA-treatment solution contains Cr(VI) and is partly converted to Cr(III) during the wood treatment process. Depending upon combustion conditions, a portion of the Cr(III) may be oxidized to Cr(VI) and under pyrolysis conditions of low oxygen Cr(VI) converted to Cr(III) in the CCA-wood ash (Helsen et al., 2003).

Arsenic species in CCA-wood ash are both the more toxic As(III) and the less toxic As(V). The As(V) species is found in the CCA-treatment solution and in the CCA-wood and after pyrolysis of the CCA-wood both the As(III) and As(V) species are found in the CCA-wood ash (Helsen et al., 2003).

Copper oxide, CuO, in CCA-wood ash is the dominant copper compound resulting from a cycle beginning with water-insoluble but acid-soluble CuO reacting with chromic acid, CrO_3, and arsenic pentoxide, As_2O_3, to form the CCA-treatment solution. During combustion, Cu^{+2} attached to wood organic material is converted to water-insoluble CuO with residual Cu^{+2} remaining in the unburned or partially burned wood components and associated with complex metal oxides, hydroxides, and carbonates.

Alkalinity of CCA-wood Ash and Untreated-wood Ash

Due to the increase in chemical complexity of CCA-wood ash compared to untreated-wood ash, the resulting difference in the degree of alkalinity and its effect upon the pH of Ultisol test soil/CCA-metals/soil solution systems are important areas of investigation. The liming effect (neutralizing value) of wood ash is the capacity of a liming agent to neutralize soil system acidity and results from combustion compounds, which are dominantly alkali oxides that readily hydrolyze with water to produce an alkaline pH solution. The potential pH range of soil systems is affected by the alkalinity contribution from the ashes of wood. Increases in pH of soil systems may increase the attraction forces of soil components for metal ions in the soil solution (Brady and Weil, 2002). Thus, it is important to assess any differences between the liming effects of wood ash and CCA-wood ash upon the test soil system.

Ash generated from combustion of wood at the approximate temperature of 600˚ C is composed primarily of alkali earth metal carbonates, oxides, and hydroxides with $CaCO_3$ being dominant. As temperatures of burning approach 900˚ C there is an increase in proportions of alkali earth metal oxides that readily hydrolyze to hydroxides and are the most effective source of alkalinity (Etiegni and Campbell, 1991).

5.2 Methods and Materials

5.2.1 Analytical Methods

The metals content of CCA-wood ash, CCA-wood ash/soil mixtures, and batch rainwater leachates were determined by acid microwave digestion (HNO_3) analyses in a MARS-X microwave using Methods 3015 and 3051 (US EPA, 1996). Leachates from Methods 3015 and 3051 were analyzed by the Geochemical Laboratory, Department of Geological Sciences, The University of Alabama, Tuscaloosa using inductively coupled plasma atomic emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 3000DV) to determine the concentrations of Cu, Cr, and As using Methods 3015 and 3051 (US EPA, 1996). 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} of ash 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 (LOI) method 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, ash, and soil/ash 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. Deionized water was ASTM Type 2, 17.9 micromho. All metal results are stated on a mass basis unless otherwise noted. Sieve analyses were performed using a Rota-Tap machine for 20 minutes and using ASTM sieves. The determination of neutralizing (liming effect) and reactivity values were performed according to laboratory procedures of Faithfull, 2002. The test soil was extracted for cations using Mehlich 1 and deionized water by the Soil Testing Laboratory of Auburn University, Auburn, Alabama.

5.2.2 Experimental Media Preparation

Ultisol Test Soil

Topsoil was employed as the test soil and was analyzed for Cu, Cr, and As to establish baseline metals concentrations. The analysis of CCA-metals in the test soil was below detection limits and the measured pH of the soil was 6.9. The total carbon content of the soil was analyzed to be 2 percent, which is consistent with the carbon content reported by the USDA Soil Survey. The soil at this location was classified by the USDA as Paleudult Ultisol with a 10-15 centimeter layer of sandy clay loam of 2-33% clay and 0.5-2% organic matter (U.S. Department of Agriculture, 1981) underlain by impermeable kaolinitic clay over fractured rock. The soil was sieved through a number 30 sieve (0.6 mm) to increase particle uniformity and remove large particles. The prepared soil was analyzed for extractable cations by the Soil Testing Laboratory of Auburn University, Auburn, Alabama using soil extraction with Mehlick 1 and deionized water.

CCA-wood Ash

The CCA-wood ash was prepared under controlled burn conditions by burning scrap CCA-wood on a metal grate over a metal catch-pan and then sieving the ash through a number 10 (2.00 mm) sieve to remove large unburned cinders. The combustion temperature was about 600˚ C for 1 hour under an initial condition of normal-oxygen combustion to a final condition of low-oxygen pyrolysis. The ash was used in the experimentation as CCA-wood ash or in the preparation of the test soil/CCA-wood ash mixture. Analysis conducted in triplicate as described in Section 2.1 was (mg metal g^{-1} ash ± 95% confidence interval): Cu (86.3±11.3); Cr (76.7±16.0); As (69.6±2.1). 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.

Test Soil/CCA-wood Ash Mixture

The test soil/CCA-wood ash mixture was produced by mixing Ultisol test soil with CCA-wood ash at a mass ratio of 5.28:1 to replicate soil-ash metal concentrations in the topsoil layer at a CCA-wood burn site previously investigated by Harden, 2005. The resulting approximate metal concentrations in the mixture were (metal mg g^{-1} test mixture ± 95% confidence interval): Cu (13.7±1.8); Cr (12.2±2.6); As (11.1±0.3) and were found to closely approximate the field conditions of Cu (14.5±0.2), Cr (17.4±0.6), and As (12.2±0.5) (Harden, 2005).

Untreated-wood Ash

The untreated-wood ash was prepared under controlled burn conditions by burning scrap untreated Southern Yellow Pine wood on a steel grate over a steel catch-pan and the resulting ash sieved through a number 10 (2.00 mm) sieve to remove large unburned cinders with care taken to ensure that there was no contamination with CCA-metals. Combustion temperature approximated 600˚ C for 1 hour under an initial condition of normal-oxygen combustion to a final condition of low-oxygen pyrolysis. The ash was used in the experimentation as untreated-wood ash or in the preparation of the test soil/untreated-wood ash mixture.

Test Soil/Untreated-wood Ash Mixture

The test soil/untreated-wood ash mixture was produced by mixing Ultisol test soil with untreated-wood ash at a mass ratio of 5.28:1, the same proportions as the test soil/CCA-wood ash mixture used in this study and the study by Harden, 2005.

5.2.3 Batch Leaching

Batch leaching with rainwater was used to determine the mobility of CCA-metals leaching from CCA-wood ash and from a mixture of CCA-wood ash and the Ultisol test soil. Additionally, pH changes were recorded during the sequential deionized-water leaching of Ultisol test soil, CCA-wood ash, untreated-wood ash and their mixtures.

Duplicate batch leachings were conducted by wetting to field-capacity known masses of CCA-wood ash, untreated-wood ash, Ultisol test soil or their mixtures with a measured volume of rainwater or deionized water to form a slurry in a 250-mL acid-washed polyethylene bottle reactor and then aged for 24 hours to reach reaction equilibrium under wet soil conditions. After the appropriate water was added to produce the final liquid volume, the reactor was tumbled at 20 RPM for 18 ± 2 hours, centrifuged for 20 minutes at 1000 RPM, and the leachate drawn off by pipette for metal analysis according to Method 1311 (US EPA, 1996) or the pH was determined for each sequential leaching. .

5.2.4 Experiment Flow Chart

Particle Size Distribution of Study Media

Sieve Analysis of:

- **Ultisol Test Soil – 25g**
- **Untreated-wood Ash – 10g**
- **CCA-wood Ash – 10g**
- **Gypsum – 70g**

CCA-wood Ash Composition

Acid-microwave digestion and ICP-OES analysis for CCA-metals and the calculation of the CCA-metal oxides content.

Determination of:

- **CCA-metals**
- **CCA-metal Oxides**

Extraction of Mobile Cations

Mobile cations determined by an extraction of the soil sample with Mehlich I (acid) and compared to an extraction with deionized water

Acid and Deionized Water Leaching of:

- **Ultisol Test Soil**

Liming Characteristics of Wood Ash

Determination of the acid Neutralizing Value and the Reactivity of each sample using the methods of Faithful, 2002.

- **Untreated-wood Ash**
- **CCA-wood Ash**

Liming Effect Upon the pH of Ultisol Test Soil

Determination of the pH ranges of untreated-wood ash, CCA-wood ash, Ultisol test soil and their mixtures during a sequential deionized water leaching.

- **Untreated-wood Ash**
- **CCA-wood Ash**
- **Ultisol test soil**

Retardance of Leached CCA-metals

Determination of the retardance of the soil upon the rainwater-leaching of CCA-metals from CCA-wood ash compared to the rainwater-leaching of CCA-wood ash alone.

- **Ultisol Soil – 8.25g**
- **CCA-wood Ash – 1.45g**
- **Rainwater – 130mL**

5.3 Results and Discussion

The results presented in this paper include the sieve analysis of the particle size distribution of the experimental media, determination of the CCA-metals and CCA-metal oxide composition of CCA-wood ash, determination of the extractable cations from the Ultisol test soil, determination of the liming characteristics of untreated-wood ash and CCA-wood ash, determination of the liming effect upon Ultisol test soil by untreated-wood ash and by CCA-wood ash, and determination of the amount of retardance of rainwater-leached CCA-metals by the Ultisol test soil.

5.3.1 Particle Size Distribution of Experimental Media

Most reactions occur within the clay-size portion (< 5 microns) of the soil due to their very large surface areas per mass because of the small size of the individual particles. Fine colloidal clay-size particles have about 10,000 times as much surface area as the same mass of medium sand-size particles. The specific surface of colloidal clay-size particles range from about 10 to 1000 square meters per gram (m^2 g^{-1}) compared to 1 and 0.1 m^2 g^{-1} for the smallest silt and fine sand-size particles. Since the adsorption of water, ions, and gas and the attraction of particles for each other are all surface phenomena, the very high specific surface of clay-size particles is significant in determining soil reaction properties (Brady, 1990).

Particle size distribution can influence the level of metal contamination in a soil. Since fine particles are more reactive and have a higher surface area than coarser material, the fine fraction of a soil often contains the majority of the contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of metal remediation technologies or retardance by the soil (Dzombak et al., 1994). However, the relative abundance of the soil particles by size will affect their relative importance, but the surface area usually is still very significant for the smaller particles found in most soils.

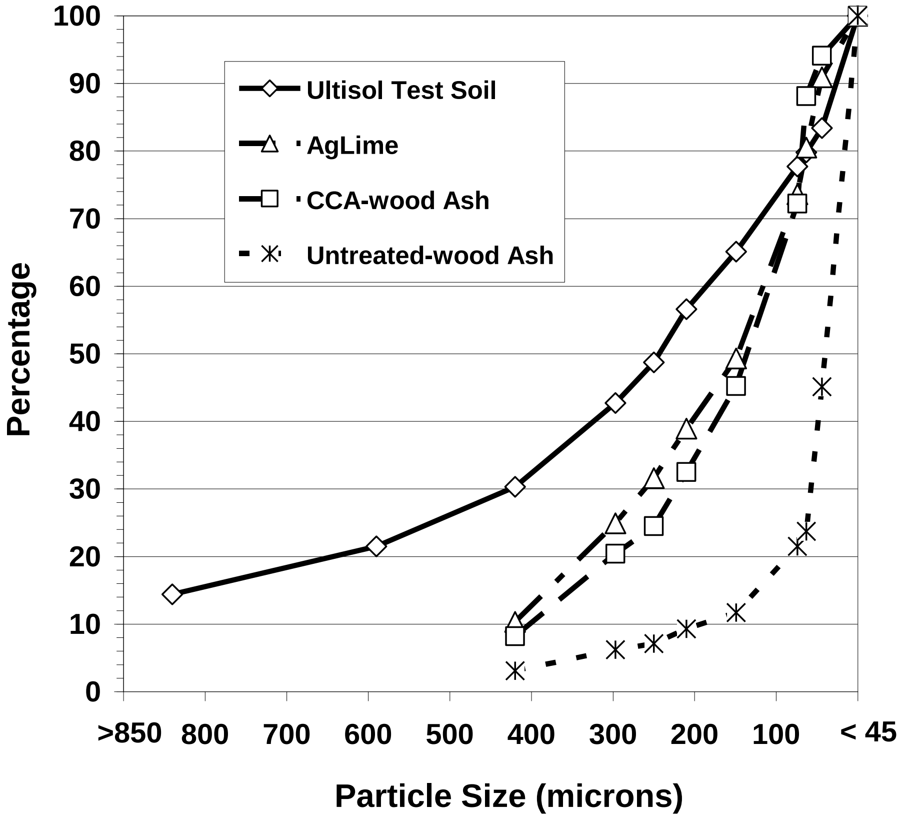
Figure 5.1 represents the particle size distribution results from the sieve analysis of the experimental media compared to agricultural lime (AgLime – Imery's, Roswell, GA). Over the particle size range of <425 microns to <45 microns untreated-wood ash was measured as having the largest percent (80%) of the sample <75 microns compared to the CCA-wood ash and AgLime samples that measured almost equivalent percentages in all particle size ranges. The Ultisol test soil has approximately one-third of its particle size distribution in the larger size range of 425 microns up to 2000 microns.

In the <45 micron size portion of the samples, both AgLime and CCA-wood ash are <10% of the samples, Ultisol test soil is approximately 20%, and untreated-wood ash is >50%. From this larger percentage (>50%) it is assumed that untreated-wood ash will have the largest amount of <5 micron particles available for reaction with the <5 micron portion of the Ultisol test soil.

Figure 5.1 – Percentage Mass vs Particle Size of Experimental Media

5.3.2 CCA-metals and CCA-metal Oxide Composition of CCA-wood Ash

Figure 5.2 represents analytical results of the CCA-metals mass composition of triplicate samples of CCA-wood ash used in the experiments compared to the computed CCA- metal oxide composition of CCA-wood ash. The total CCA-metals composition of the ash sample is 23% (232.6 mg $g^{-1}$of ash), determined by microwave digestion and ICP-OES analysis. Individually, the Cu, Cr, and As masses were determined to be 86, 76, and 70 mg g^{-1} of ash, respectively.



The most common simple oxides of Cu, Cr, and As in the CCA-wood ash are as follows: CuO; Cr_2O_3, CrO_4^{-2}; As_2O_3, AsO_3^{-3}, AsO_4^{-3} (Helsen et al, 2003). The formula weights of these compounds were used to calculate the approximate CCA-metal oxides percentage of 44.7% (446.9 mg g^{-1}) of CCA-wood ash. Cr, As, and Cu approximate 19.6 %, 14.3%, and 10.8% of the mass Oxide compounds of of CCA-wood ash. From these mass approximations it can be concluded that CCA-wood ash has nearly 45% less mass of liming compounds (ie. Calcium oxides, etc.) compared to untreated-wood ash.

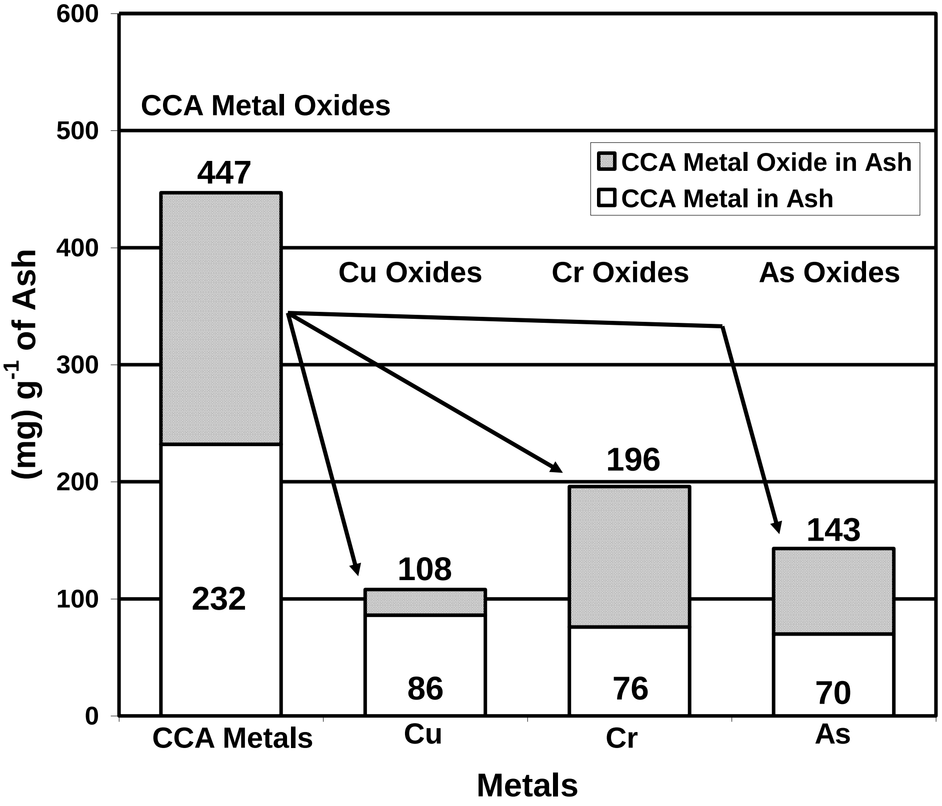


Figure 5.2 - CCA-metals and CCA-metal Oxide Composition of CCA-wood Ash

5.3.3 Extraction of Mobile Cations from the Ultisol Test Soil

Extractions of the cations from the Ultisol test soil was performed for the purpose of assessing the mobility of the cations that play important roles in the determination of soil system pH. Some mobile cations (ie. Ca^{+2}, Fe^{+2}) are important factors in soil systems and may lead to an increase in adsorption, precipitation or redox reactions. Two extractions of separate test soil samples were conducted; one using the Mehlich 1 method and the other using deionized water.

The Mehlich 1 solution, an acid solution, was used to determine the total amount of extractable cations in the Ultisol test soil resulting from leaching by an aggressive leaching solution. Table 5.2 shows that species containing Al, Ca, Mn, and Mg dominate the results of the

Mehlich 1 extraction. Silicate clays in soil vary widely in their chemical composition, some are relatively simple aluminosilicates, while others contain in their crystal structures varying quantities of iron, magnesium, potassium, and other elements. The surface of the kaolinitic clay of the Ultisol test soil holds small, but significant, quantities of cations. Also, the content of iron and aluminum oxides plays a prominent role in adsorption in the soil system (Brady, 1990).

The soil extraction using deionized water under controlled leaching conditions determined the readily leachable cations in the Ultisol test soil. Species containing Al, Fe, Na and K were the highest concentrations with Al and Fe being the highest concentrations, therefore showing further evidence of the dominant role these species play in reactions within the soil solution. The presence of hydrous metal oxides of Fe and Al in a soil can strongly influence contaminant metal concentrations because they can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Dzombak and Morel, 1987; Reed and Cline, 1994).

Table 5.2 - Ultisol Test Soil Mobile Cation Extraction Data (ppm in soil)

Leach	Ca	K	Mg	Al	Fe	Mn	Na
Mehlich 1	292	74	110	410	42	242	74
H_2O	3	32	6	79	64	3	57
ppm in soil							

5.3.4 Liming Characteristics of Untreated-wood Ash and CCA-wood Ash

The liming effect (neutralizing value) of the wood ash is an important characteristic because the liming effect acts to raise the pH of an acidic soil. The capacity of a liming agent to neutralize soil acidity depends on its content of soluble and hydrolyzable bases such as oxides, hydroxides, carbonates, and silicates. In these reactions cations such as calcium, magnesium, and potassium are the interactive counter-ions (Nurmesniemi et al, 2004).

Table 5.3 shows that the measured liming effect, or neutralizing value (NV), of untreated-wood ash used in this study averaged 44.5 % of $CaCO_3$ equivalent compared to an average of 11.7% for CCA-wood ash. These values may be compared to the measured liming effect for AgLime of 49.8% $CaCO_3$ equivalent in this study to wood fly ash of 41.2 % $CaCO_3$ equivalent by (Nurmesniemi et al, 2004) and 50.0% $CaCO_3$ equivalent for coal fly ash (Adriano et al, 2002).

The reactivity (r_{ac}) of untreated-wood ash and CCA-wood ash was measured in order to assess the speed and effectiveness of the neutralizing potential of the liming compounds in each ash. The results show an average reactivity of 33.8% $CaCO_3$ equivalent for untreated-wood ash while CCA-wood ash was measured at an average of 18.7%. Using the data for neutralizing values (NV) and reactivities (r_{ac}), the "fast acting" capacities (r_{ac}/NV) of untreated-wood ash and CCA-wood ash were calculated as an average of 78.4% and 161% $CaCO_3$ equivalent, respectively.

The explanation for the difference in liming effect between untreated-wood ash and CCA-wood ash is two-fold. First, as shown in Section 5.3.2, the CCA-wood ash in this study is composed of an analytically determined 23.2% CCA-metals and a corresponding calculated approximation of 44.7% CCA-metal oxides, therefore the CCA-wood ash should contain less mass of reactive alkali metal oxides.

Second, the greater "fast acting" capacity of CCA-wood ash could be attributed to a larger proportion of more reactive oxides in the alkali metal oxides of the CCA-wood ash, compared to the reactive oxides of the untreated-wood ash.

As a result, untreated-wood ash has four times the neutralizing value compared to CCA-wood ash, while CCA-wood ash has twice the reactivity and “fast acting” capacity of untreated-wood ash. Untreated-wood ash is shown to be essentially equivalent to AgLime in the characteristics of neutralizing value, reactivity, and “fast acting” capacity.

Table 5.3 - Liming Characteristics of Untreated-wood Ash and CCA-wood Ash
(value +/- standard deviation)

	Neutralizing Value (NV) (Liming Effect - % $CaCO_3$)	Reactivity (r_{ac})	r_{ac}/NV ("fast acting" capacity)
Untreated-wood Ash	44.5 ± 3.2	33.8 ± 7.5	78.4 ± 0.18
CCA-wood Ash	11.7 ± 0.7	18.7 ± 1.6	161 ± 0.16
AgLime	49.8 ± 1.8	39.2 ± 2.1	78.9 ± 0.05

5.3.5 Liming Effect upon Ultisol Test Soil by Untreated-wood Ash and by CCA-wood Ash

Figure 5.3 presents the plot of pH versus leach test sequence number during five sequential deionized-water batch leachings of Ultisol test soil, untreated-wood ash, CCA-wood ash, and mixtures of Ultisol test soil/untreated-wood ash and Ultisol test soil/CCA-wood ash. Results indicate that there is a distinct difference between the pH measurements of the leachates from untreated-wood ash, the CCA-wood ash, and the leachates from the mixtures of each with Ultisol test soil. Untreated-wood ash is significantly more alkaline than CCA-wood ash and the resulting soil solution pH is quite different when mixed with the Ultisol test soil. The pH of the batch leachates from untreated-wood ash (filled circles) and test soil (filled squares) are compared to the pH of the leachates from the mixture of Ultisol test soil/untreated-wood ash (filled triangles) which exhibits a uniform pH 10 leachate. Untreated-wood ash leached over the range of pH 9 to 11 while Ultisol test soil leached over the range of 6.7 to 8.

The Ultisol test soil/untreated-wood ash mixture pH of 10 represents the effect of the alkalinity from untreated-wood ash to increase the pH of the Ultisol test soil solution when it is mixed with untreated-wood ash and is representative of a soil solution in which the dominant liming reaction is:

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^- \qquad (1)$$

The pH of the batch leachates of CCA-wood ash (open circles) and Ultisol test soil (filled squares) are compared to the leachates from the mixture of Ultisol test soil/CCA-wood ash (open triangles). The Ultisol test soil and the Ultisol test soil/CCA-wood ash mixture both leach over the same pH 6.7 to 8 range, an indication of a weaker liming ability of CCA-wood ash. An additional factor affecting this pH trend could be the removal of hydroxide ions from the soil solution by chemical reaction and precipitation, evidenced by Cr(III) cations reacting with hydroxyl ions to form precipitates of chromium hydroxides.

The importance of the pH 6.7 to 8 range for the leaching of the Ultisol test soil/CCA-wood ash mixture can be seen in the pH data for retardance mechanisms of the Cr and As species. The basic pH data for adsorption on hydrous ferric oxide or precipitation can be briefly summarized as follows: Cr(VI), <7.5; Cr(III), >5-7; As(V), <9; As(III), 8-6.5 (Evanko and Dzombak, 1997; Hug et al, 1997).

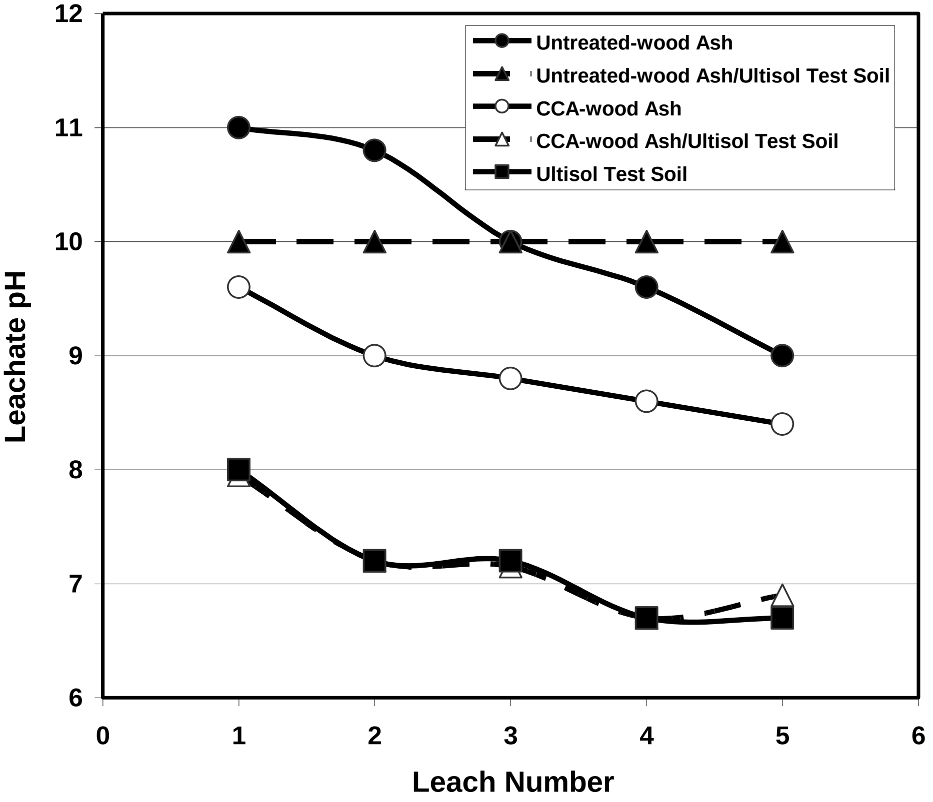


Figure 5.3 - pH of Sequential Leaching of Experimental Media

5.3.6 Retardance of Rainwater-leaching of CCA-metals by the Ultisol Test Soil

The main objective of this experiment was to determine the potential of the Ultisol test soil to inhibit or promote the rainwater-leaching of CCA-metals from an Ultisol test soil/CCA-wood ash mixture compared to the rainwater-leaching of CCA-wood ash alone. Triplicate CCA-wood ash samples were leached and triplicate Ultisol test soil/CCA-wood ash samples were leached to simulate a rainwater-leaching event as described earlier in Section 5.2.3 Batch Leaching. The resulting data is plotted in Figure 5.4 and the statistical summary of the data is presented in Table 5.4. Data generated from this experiment indicates that the mobility of Cr and As is lowered in the presence of Ultisol test soil, while Cu mobility is increased. During the rainwater-leach, the Ultisol test soil/CCA-wood ash mixture retarded the leaching of Cr and As by 75% and 74% respectively, but enhanced Cu leaching by 280% compared to CCA-wood ash alone.

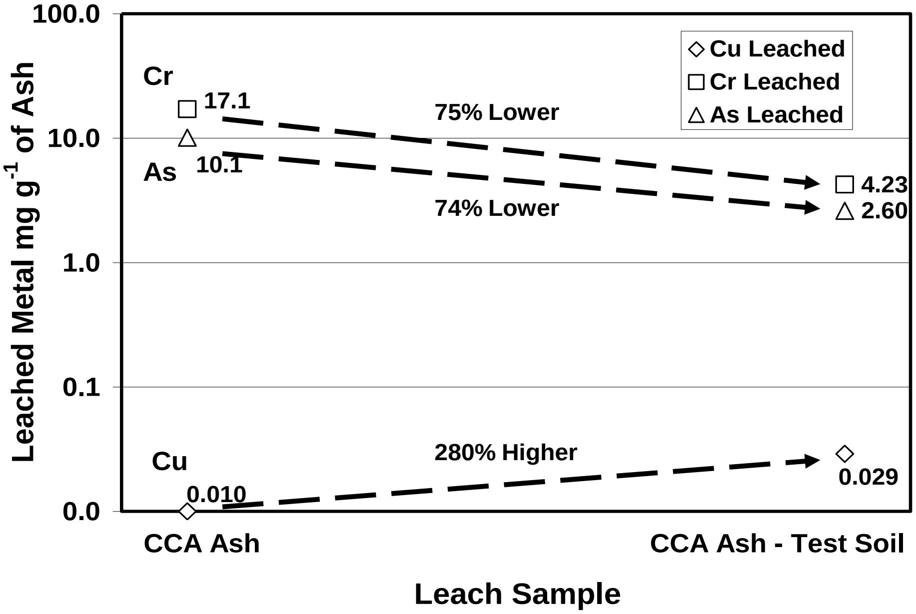


Figure 5.4 - Rainwater-leaching of CCA-wood ash and CCA-wood ash/Ultisol Test Soil

Table 5.4 - Descriptive Statistical Summary of Batch Rainwater-leaching Experiment

Mass (mg metal g^{-1} ash)	**Cu**	**Cr**	**As**
CCA-wood Ash Leach			
Sample 1	0.01	17.2	10.5
Sample 2	0.01	16.4	9.9
Sample 3	0.01	17.7	10.1
Mean	0.01	17.1	10.1
Standard Deviation	0	0.66	0.31
Coefficient of Variation	0	3.90%	3.10%
Confidence Interval 95%	0.010±0.000	17.1±1.63	10.1±0.80
Ultisol Soil/CCA-wood Ash Leach			
Sample 1	0.032	4.23	2.7
Sample 2	0.026	4.1	2.53
Sample 3	0.028	4.34	2.57
Mean	0.029	4.23	2.6
Standard Deviation	0.003	0.12	0.09
Coefficient of Variation	10.30%	2.80%	3.50%
Confidence Interval 95%	0.029±0.007	4.23±0.29	2.60±0.22

The retardance of the mobility of leached Cr and As species resulting from the mixing of CCA-wood ash with Ultisol test soil is likely due to adsorption of Cr and As to the mineral components of the kaolinitic clay and to organics in the soil, with the presence of Al and Fe oxides being dominant (Evanko and Dzombak, 1997; Manning and Goldberg, 1997). The mobility of Cu significantly increases as Cu^{+2} species become bound to mobile organic material in the Ultisol soil solution (Tipping et al., 1983; Lehmann and Harter, 1984; and Davis, 1984).

5.4 Conclusions

Experimental results of this investigation show that the Ultisol test soil retards the mobility of As and Cr compared to CCA-wood ash alone, while Cu mobility is increased in the presence of the Ultisol test soil and is likely due to complexation with mobile organic matter. The retardance effect of the Ultisol test soil was a 75% and 74% reduction of Cr and As mobility, respectively. Cu mobility was increased by 280%, but at a mass concentration two orders of magnitude less than the mobility of Cr and As. Therefore, the mobility of CCA-metals in CCA-wood ash followed the order of Cr > As > Cu, while the retardance of mobility of CCA-metals in the Ultisol test soil/CCA-wood ash mixture followed the order of Cr=As with Cu mobility increasing.

The alkalinity of a CCA-wood ash/Ultisol soil system is lower than that of an untreated-wood ash/Ultisol soil system, indicating a difference in chemical composition and the potential consumption of hydroxyl ions during mechanisms of the retardance of Cr and As mobility. Untreated-wood ash was determined to have four times the liming effect (neutralizing value) than that of CCA-wood ash, but equivalent to an agricultural lime soil amendment (AgLime). The reactivities of untreated-wood ash and AgLime were determined to be equal and twice the magnitude of CCA-wood ash, while the “fast acting” capacities of untreated-wood ash and AgLime were found to be equal and half of the magnitude of CCA-wood ash, respectively.

The CCA-wood ash used in the study was determined to be composed of 23% CCA-metals and that mass of CCA-metals was calculated to represent a CCA-wood ash that contains 45% CCA-metal oxides. A sieve analysis concluded that while CCA-wood ash and AgLime had the same particle size distribution, the particle size distribution of untreated-wood ash was four times greater (80% compared to 20%) than CCA-wood ash and AgLime in the <75 micron particle size range where greater reactions occur.

Deionized water leaching of Ultisol soil indicates that Al, Fe, Na, and K cation species are readily leachable with Al and Fe species being the dominant cation concentrations. Sequential deionized-water leaching of mixtures of Ultisol test soil/CCA-wood ash and Ultisol test soil/untreated-wood ash resulted in a pH range of 6.7-8 and a constant pH of 10, respectively.

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APPENDIX V-A

V-A–1 Percentage by Mass of Experimental Media

Sieve No.	10	20	30	40	50	60	70	100	200	230	325	End
Microns	2000	840	590	420	297	250	210	149	74	63	44	0
Wood Ash				3.1	6.2	7.1	9.3	11.7	21.5	23.7	45.1	100%
CCA Ash				8.2	20.4	24.5	32.5	45.2	72.2	88.1	94.1	100%
AgLime				10.3	24.9	31.6	38.9	49.3	73.6	80.5	90.9	100%
Soil		14.4	21.5	30.3	42.7	48.7	56.6	65.1	77.7	79.8	83.4	100%

CHAPTER VI

THE APPLICATION OF SOIL AMENDMENTS TO THE RETARDANCE OF RAINWATER-LEACHED METALS FROM CCA-TREATED WOOD ASH IN SOIL

Abstract

The burning of wood treated with chromated copper arsenate (CCA) produces an ash that contains high concentrations of copper, chromium, and arsenic. The subsequent leaching of these metals from burn sites can produce soil and water contamination. Soils have varying natural abilities to reduce leaching and impact metals speciation and toxicity, by sorption, conversion and sedimentation related mechanisms. Recent regulations have resulted in increased quantities of CCA-treated lumber entering the waste stream, making the study of metals leaching from ash, and the amendment of soils to more effectively immobilize metals, important areas of investigation.

The performance of various soil amendments to immobilize or retard Cu, Cr, and As species in soil/CCA-ash mixtures was studied. The amendments evaluated were agricultural lime ($CaCO_3/MgCO_3$), soil softener ($CaSO_4 \cdot 2H_2O$), and iron sulfate ($FeSO_4$). Results of this investigation show that native soil alone retards the mobility of As and Cr, amendments applied alone or in combinations further retard metal mobility compared to the control soil/CCA-ash mixture. The $CaSO_4$ soil amendment is most effective in reducing the rainwater leaching of Cr and As from CCA-ash in soil reducing the mobility by 72.4% and 77.3%, respectively, compared to the control soil-ash mixture. Cu mobility is increased in the presence of the native soil and by all amendments.

Keywords: Arsenic, Chromium, Copper, Immobilization, Remediation, Transport

6.1 Introduction

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 (Cooper, 1993; McQueen and Stevens, 1998; Clausen, 2000; Wu, 2000); a ban on CCA-treated wood use in domestic settings (Federal Register, 2003) and an associated increased public awareness of health concerns. The Southeastern region of the U.S. has been the largest producer and user of CCA-treated wood due to the climatic and parasitic pressures on untreated wood in this region (Solo-Gabriele et al., 1999). A common practice is to dispose of CCA-treated wood by onsite burning, producing an ash that poses a potential threat to humans and the environment (Solo-Gabriele et al., 1999).

CCA-treated wood ash is a source of heavy metals, primarily Cu, Cr and As. At the $\mu g\ L^{-1}$ 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 (Winner, 1984; Korte and Fernando, 1991; LaGrega et al., 1994; Palmer and Puls, 1994; Raven et al., 1998; Solo-Gabriele et al., 1999).

Combustion conditions can effect the Cr speciation in CCA-ash with a portion of the predominant Cr(III) converting to Cr(VI) (Helsen et al., 1997). The resulting ash, although still largely Cr(III), will have varying Cr(VI) concentrations influenced by the degree of the wood treatment, with a range of 4-7% (Song et al., 2006).

Arsenic species in CCA-treated wood ash are both the more toxic As(III) and the less toxic As(V). The As(V) species is found in the CCA-treated wood and after pyrolysis the As(III) and As(V) species are found in the wood ash (Helsen et al., 1997)

The interaction of CCA-treated wood ash with soil is complex. Factors such as soil chemical composition, organic content, pH, solution complex formation, climatic, and geologic conditions play a role in the movement of the metal species from the CCA-treated wood ash and soil mixture (US EPA, 1992; Evanko and Dzombak, 1997). The adverse effects of each metal species present are dependent, in part, upon the valence state of the metal (Helsen et al., 1997). Oxidation-reduction reactions of metals occur naturally within the soil and can change the species to a less toxic and less available metal species (NRC, 1994). High concentrations of metals 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 effectiveness of various soil amendments to immobilize and retard CCA-metal species using agricultural lime ($CaCO_3/MgCO_3$), soil softener ($CaSO_4 \cdot 2H_2O$), and iron sulfate ($FeSO_4$) was studied. These soil amendments were chosen due to availability, current application as soil supplements, and potential to enhance chemical reactions that reduce the mobility of metal species within the soil (Brady, 1990). A CCA-treated wood burn site in Tuscaloosa County, Alabama was investigated to determine baseline conditions and obtain data for a laboratory study (Harden, 2005). Soil/CCA-treated wood ash burn site conditions were then replicated under laboratory conditions using batch and soil column leaching studies and pH studies.

6.2 Methods and Materials

6.2.1 Site Description

A CCA-treated wood burn site located on the shoreline of Lake Tuscaloosa, a 5,900 acre municipal water reservoir located in Tuscaloosa County, Alabama was selected as a typical case study. 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 Lake Tuscaloosa 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. The 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.

6.2.2 Analytical Methods

The metals content of CCA-ash and CCA-ash/soil mixtures were determined by acid microwave digestion (HNO_3) analyses using Methods 3015 and 3051 (US EPA, 1996). The Toxic Characteristic Leaching Procedure (TCLP) Method 1311 was used to provide a regulatory context to the ash (US EPA, 1996). Leachates and TCLP extracts were analyzed with inductively coupled plasma atomic emission spectrophotometry (ICP-OES, Optima 3000DV) to determine the concentrations of Cu, Cr, and As. 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 of ash for soil/ash and ash as necessary. The carbon and organic carbon content of the native soil was determined by the loss on ignition (LOI) method and the soil pH values were determined by standard 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 metal results are stated on a mass basis unless otherwise noted.

6.2.3 Characterization of Burn Site Soil and Ash

Sampling Methods and Burn Site Soil/CCA-ash Characterization

A CCA-metals concentration gradient profile was obtained by taking surface and core soil samples from the burn site (0 meter sample point) and also at sites up-gradient (-4 meter sample point) and down-gradient (3, 5, and 6 meter sample points). Several surface samples taken at the center of the burn site down to a depth of 5 centimeters were combined to obtain one composite sample. This composite sample was used to determine metal concentrations used in the experimental soil columns and establish the soil:ash ratio used in preparation of the laboratory control soil/CCA-ash mixture.

Burn site surface samples were dark gray in color indicating the presence of ash in the topsoil. Deeper samples were taken by driving a 5 centimeter diameter metal pipe into the soil. The soil cores were cut at 7.5 and 15 centimeter depths. Samples were taken from the interior of the core to eliminate potential wall effects. All samples were taken under fair-weather conditions. Samples were analyzed for CCA-metals as described in Section 6.2.2 and soil/CCA-metals ratios were determined.

Up-gradient Control Soil

Topsoil, located 100 meters up-gradient from the burn site, was employed as the control soil and was analyzed for Cu, Cr, and As to establish baseline metals concentrations. All levels of CCA-metals in the control soil were below detection limits and the measured pH of the soil was 6.9. The total carbon content of the soil was analyzed to be 2 percent, which is consistent with the carbon content reported by the USDA Soil Survey. The soil at this location was classified by the USDA as Paleudult Ultisol with a 10-15 centimeter layer of sandy clay loam of 2-33% clay and 0.5-2% organic matter (U.S. Department of Agriculture, 1981) underlain by impermeable kaolinitic clay over fractured rock. The soil was sieved through a number 30 sieve (0.6 mm) to increase particle uniformity and remove large particles that could cause column channeling.

6.2.4 Experimental Media Preparation

CCA-ash

The CCA-ash was prepared under controlled burn conditions by burning scrap CCA-treated wood on a metal grate over a metal catch-pan and then sieved through a number 10 (2.00 mm) sieve to remove large unburned cinders. Combustion temperature approximated 600˚ C for 1 hour under an initial condition of normal-oxygen combustion to a final condition of low-oxygen pyrolysis. The ash was used in the preparation of the control soil/CCA-ash and amended control soil/CCA-ash mixtures. Analysis conducted in triplicate as described in Section 2.2 was (mg metal g^{-1} ash ± 95% confidence interval): Cu (86.3±24.8); Cr (76.7±34.9); As (69.6±4.6). 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. The other major components of the wood ash are oxides and carbonates of Ca, K, and Mg (Demeyer et al., 2001).

Control Soil/CCA-ash Mixture

The control soil/ash mixture was produced by mixing up-gradient control soil with CCA-ash at a mass ratio of 5.28:1 to replicate soil-ash metal concentrations in the topsoil layer at the burn site. The resulting approximate metal concentrations in the mixture were (metal mg g^{-1} control mixture ± 95% confidence interval): Cu (13.7±4.0); Cr (12.2±5.6); As (11.1±0.7) and were found to closely approximate the field conditions of Cu (14.5±0.5), Cr (17.4±1.4), and As (12.2±1.2).

Alone and in combinations the three soil amendments ($FeSO_4$, $CaSO_4$ and $CaCO_3$) were added to the control soil/CCA-ash mixture. The commercial soil amendments used were: $FeSO_4$ as iron sulfate granules (20% Fe); $CaSO_4 \cdot 2H_2O$ as pelletized gypsum (75% $CaSO_4 \cdot 2H_2O$); and $CaCO_3$ as agricultural lime (AgLime) (60% $CaCO_3$ and 21% $MgCO_3$).

6.2.5 Batch Study Design

Replicate batch studies were conducted by wetting to field-capacity known masses of sample with a measured volume of rainwater to form a slurry in a polyethylene bottle reactor and then aged for 24 hours to reach reaction equilibrium under wet soil conditions. After a final measured volume of rainwater was added, the reactor was tumbled at 20 RPM for 18 ± 2 hours, centrifuged for 20 minutes at 1000 RPM, and the leachate drawn off by pipette for analysis according to Method 1311 (US EPA, 1996). The ratio of solid/water used for the measurements ranged from an initial leach of 1/6.7 to 1/10.3 for subsequent leachings.

6.2.6 Column Experiment Design and Stoichiometry

Literature studies of redox-stoichiometric adsorption data were used to establish minimum soil amendment/metal mass ratios for the 2^3 Factorial Design of column experiments (Box et al., 1978). For example, an adsorption study determined that three equivalents of Fe(II) are required to reduce Cr(VI) (Buerge and Hug, 1997). Subsequently the mass ratio of amendment added to total CCA-metals present ranged from 3:1 when one amendment was studied to 9:1 when all three amendments were studied in combination (Harden, 2005).

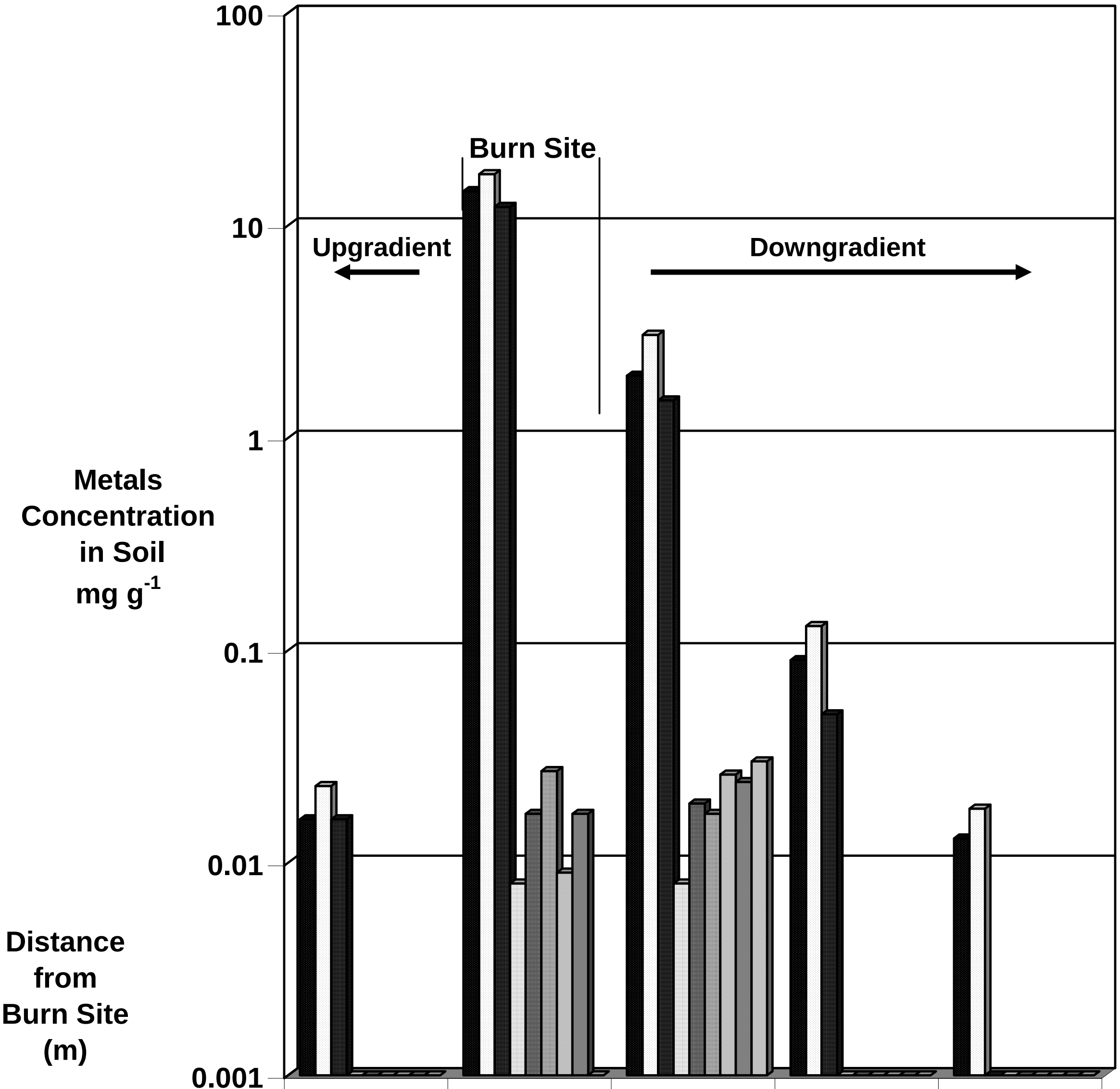
Accelerated leach experiments were used to determine the effects of controlled rainwater leaching events. The experiments were performed using duplicate sets of control soil/CCA-ash columns designed to closely replicate the soil conditions at the burn site. The column tests were a 2^3 Factorial Design for each of the three metals (Box et al., 1978), therefore, the samples were run in duplicate columns with the three variable factors being AgLime, $CaSO_4$, and $FeSO_4$ amendments and all combinations of these amendments, resulting in a total of 16 columns. Under laboratory conditions rainwater flowed by gravity from the top of the column and was collected as it exited the column. Average flow rate for the columns was 6 mL hr^{-1} and each column leach event was 12-24 hours duration. Data collected was the mass of each metal leached from individual leachings and the cumulative results of nineteen leach events for each column. Each polycarbonate column was 4.2 cm in diameter and 61 cm in length and contained 231 g of control soil, 49 g CCA-ash, and 68 g of each amendment when used alone or in combination with other amendments. These proportions of soil amendments to CCA-ash were established from calculations described previously to provide for potential stoichiometric conversion. Leach event volumes ranged from an initial 45 mL volume to subsequent 100 mL volumes equal to 3.2-7.2 cm height in the column 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 metal 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 total mass of metal leached and the pH trends resulting from the addition of amendment.

6.3 Results and Discussion

Results presented include baseline characterization of the burn site soil, CCA-metals analysis of the laboratory-prepared CCA-ash, and the control soil-ash mixture and both batch and column rainwater leaching studies of CCA-metals from the control soil/CCA-ash/amendment mixtures.

6.3.1 CCA-ash Metals Occurrence at the CCA-treated Wood Burn Site

Figure 6.1 represents the metals distribution in the CCA-ash/soil mixture at the burn site. Spatially variable surface and depth samples were taken in a line extending from the lakeshore sediment located 6 meters down-gradient from the burn site, through the burn site (0 meters data point) to the up-gradient area located 4 meters from the burn site. The burn site samples (0 meters data point), analyzed in triplicate by microwave digestion and ICP-OES, revealed that metals concentrations in the soil/ash (mg metal g^{-1} soil/ash ± 95% confidence interval) were: Cu (14.5±0.5); Cr (17.4±1.4); As (12.2±1.2). The data indicate that the metals concentrations were highest at the center of the burn site with lower concentrations appearing down-gradient toward the lakeshore. This is assumed to be the result of leached metals moving down-gradient and the 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, whereas in all other areas sampled the metals were confined to the upper 5 centimeters of topsoil. Up-gradient metals concentrations (-4 meter data point) were all low (<0.025 mg g^{-1}) and assumed to result from airborne ash during the burn process.



Metal Conc. mg g^{-1} with Sample Depth (cm)

Distance from Burn Site (m)	-4	0	3	5	6
■ 5 cm Cu	0.016	14.5	1.96	0.090	0.013
□ 5 cm Cr	0.023	17.4	3.05	0.130	0.018
■ 5 cm As	0.016	12.2	1.50	0.050	0.001
□ 7.5 cm Cu	<LOD	0.008	0.008	<LOD	<LOD
▨ 7.5 cm Cr		0.017	0.019		
▨ 7.5 cm As		0.027	0.017		
□ 15 cm Cu		0.009	0.026		
▨ 15 cm Cr		0.017	0.024		
□ 15 cm As		<LOD	0.030		

Figure 6.1 - Metals Distribution in the Topsoil at the Burn Site

6.3.2 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 (mg L^{-1} ± 95% confidence intervals) yielded: Cu (6.72±0.713); Cr (0.719±0.057); As (578±44.7). The data shows that As concentration is two orders of magnitude above the RCRA limit of 5.0 mg L^{-1} while Cr concentration is 0.719 mg L^{-1} which is below the 5.0 mg L^{-1} RCRA limit for Cr(VI). The TCLP concentration 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. Under RCRA terminology, "generators" of CCA-ash are therefore subject to RCRA regulations though household generators are exempt. Although TCLP analyses yield data that is useful in a regulatory context, the TCLP leach conditions of pH 4.93 (acetic acid and NaOH addition) are unlikely to accurately model the expected results from rainwater leaching of metals from CCA-ash. It is known that hydroxyl species of Cr precipitate at pH 4.5 and complete precipitation occurs at pH 5.5, thus Cr mobility and concentration levels under these leach conditions may not well model the expected results from a rainwater leach of CCA-ash. An additional source of hydroxyl ions has been added to the system, precipitation of Cr(III) has been increased, while mobile Cr(VI) becomes a more dominant species in the leachate (Harden, 2005; Song et al., 2006; FRTR, 2008).

6.3.3 Batch Rainwater Leaching of Unamended CCA-ash and Soil/CCA-ash Mixture

The main objective of this experiment was to determine the potential of unamended soil-ash mixture to inhibit or promote the rainwater leaching of metals compared to ash alone.

Triplicate ash samples were leached and triplicate soil-ash samples were leached then re-leached to simulate multiple wet weather events as described earlier in 2.5 Batch Study Design, the resulting data, including error bars, is presented in Figure 6.2. Data generated from this experiment indicates that the mobility of Cr and As is lowered in the presence of soil while Cu mobility is increased. During the first leach the soil-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 releaching 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 ash alone. Conversely, an increase of 1550% was recorded in the leached mass of Cu.

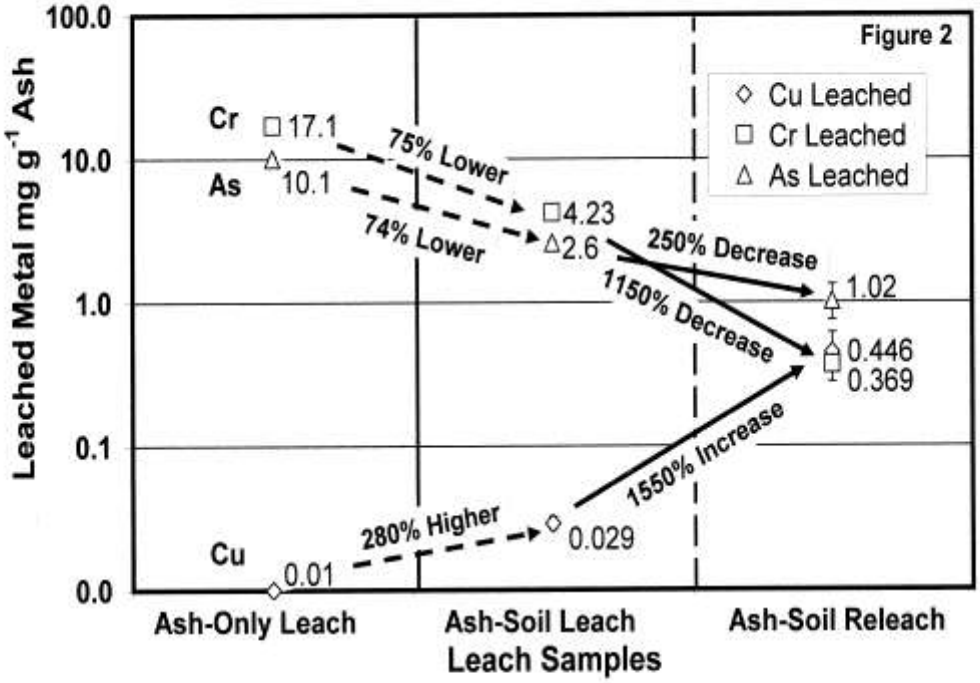


Figure 6.2 – Impact of Unamended Soil on the Rainwater-leaching of CCA-metals

Mass Transfer Mechanisms

The retardance of Cr and As by mixing CCA-ash with soil is likely due to adsorption of Cr and As to the mineral components of the kaolinitic clay, organics in the soil, and the presence of the Al and Fe oxides which may lower the metals mobility during the first leach of soil/CCA-ash mixture compared to the leach of CCA-ash alone (Evanko and Dzombak, 1997; Manning and Goldberg, 1997). As supported by Stollenwerk and Grove, 1985, describing nonspecific adsorption, Cr had the largest leached mass during the first leach of soil/CCA-ash mixture 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 this mobile organic matter from the soil, an increased mass of Cu leaches from the soil/CCA-ash mixture. During this depletion, release of Cu from surface adsorption sites in the soil decreases and release from inner-sphere adsorption sites becomes the dominant mechanism of Cu mobility as supported by Tipping et al., 1983; Davis, 1984; and Lehmann and Harter, 1984. .

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

Figure 6.3 represents the metals mass composition of triplicate samples of the CCA-ash used in the experiments compared to rainwater leached metals. The 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 ICP-OES analysis.

During a first leach by rainwater of the CCA-ash sample mixed with soil the total mass of those metals leached was 6.9 mg g^{-1}ash with individual leachings of Cu 0.03 mg g^{-1}, Cr 4.2 mg g^{-1}, and As 2.6 mg g^{-1}as shown by the white portions of each bar in Figure 6.3. In summary, data in Figure 6.3 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 total mass of each metal in the ash represents approximately one-third of the total mass of Cu, Cr, and As as seen by similar height bars for metals in Figure 6.3. Also note that each of these three groups is compared to the corresponding mass of Cu, Cr, and As leached during a first leach of the sample by rainwater. Of the three metals, the leached mass during the first leach follows the order: Cr > As > Cu.

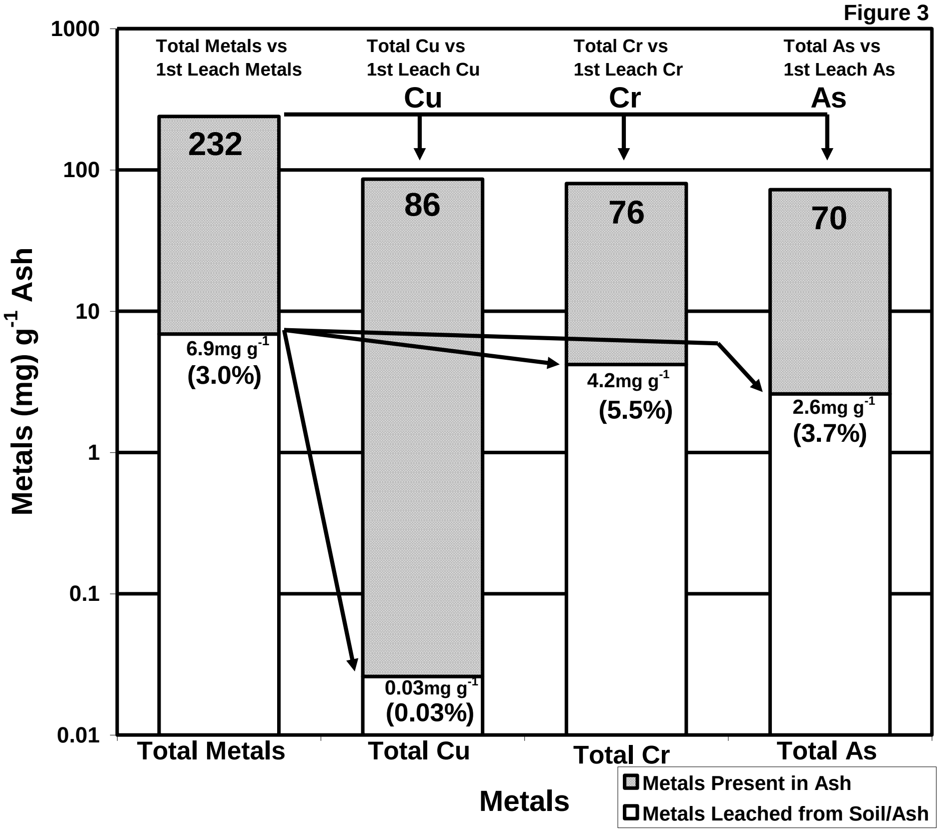


Figure 6.3 - Mass Compositions of CCA-metals in CCA-ash and the Rainwater-leached Metals from a Control Soil/CCA-ash Mixture

Evaluation of Potential Contamination of Water by Leached CCA-metals

Table 6.1 presents a comparison of the mass of Cu, Cr, and As metals leached during a batch study of the potential CCA- metals contamination of water and the regulatory contamination levels. Batch studies were performed to evaluate the potential for metals release into rainwater runoff until equilibrium is reached at a burn site as described in 2.5 Batch Study Design. The data trend shows that Cu, Cr, and As metals in an unamended 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 and standards for toxicity to freshwater clams (Harrison et al., 1984). That contamination potential trend in L of water contaminated per gram of CCA-ash is: As, 469 L g^{-1} > Cu, 113 L g^{-1} > Cr, 29 L g^{-1}.

Table 6.1 – Potential Contamination of Water by CCA-metals

Potential Contamination of Water by Soil/CCA-Ash

Batch Leach (5 Leachings) **Table 1**

1.45 g CCA-Ash, 8.25 g Control Soil, 465 mL Total Rainwater Volume

Metal	Leached (μg g^{-1}ash)	Regulatory Level (μg L^{-1})	L g^{-1} ash
Cu	1130	10*	113***
Cr	2900	100**	29***
As	4700	10**	469***

* Cu based on toxicity to freshwater clams Harrison, et al. 1984
** SDWA-MCL
*** Volume of Water Contaminated to Regulatory Level

6.3.4 Column Rainwater Leaching of Amended and Unamended Soil/CCA-ash Combinations

Effect of Soil Amendments on pH and Metals Mobility During Rainwater Leaching

System pH conditions and amendment combinations have varying effects on the leaching of Cu, Cr, and As. Figure 6.4 presents a plot of leachate pH versus rainwater leach number from duplicates of the eight soil/CCA-ash/amendment combinations. The Control, AgLime, $CaSO_4$, and AgLime/$CaSO_4$ combinations are weakly basic systems that become more neutral as the columns reach equilibrium. The combinations $FeSO_4$/AgLime and $FeSO_4$/AgLime/$CaSO_4$ are initially strongly acidic but quickly trend toward neutral pH, due to the buffering effect of $CaCO_3$. The $FeSO_4$ and $FeSO_4$/$CaSO_4$ combinations are strongly acidic and remain acidic to equilibrium. The weakly basic systems (Control, AgLime, $CaSO_4$, and AgLime/$CaSO_4$) exhibit relatively low mobility of metals while all the strongly acidic combinations containing $FeSO_4$

have initially high mobility of Cu and As with the combinations $FeSO_4$/AgLime and $FeSO_4$/AgLime/$CaSO_4$ becoming less mobile as the pH moves toward equilibrium near neutral pH.

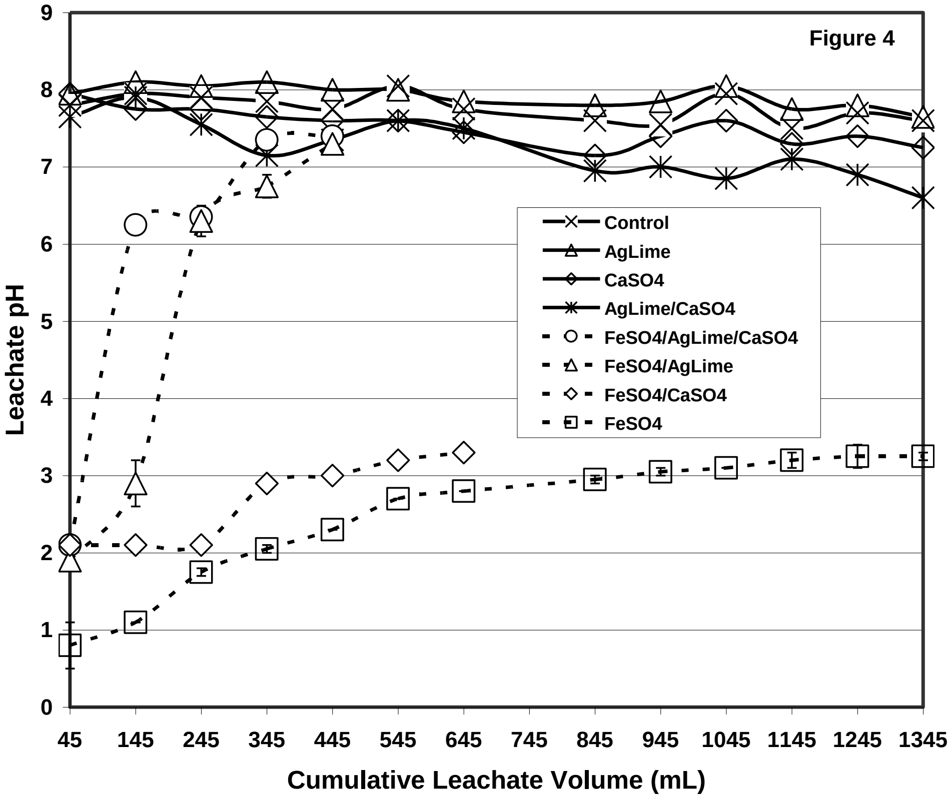


Figure 6.4 – pH Variation in the Column Leaching of Control Soil/CCA-ash with Amendments and Amendment Combinations

Figure 6.5a represents Leach #1 data of the mass of metals leached in the column studies. All systems had neutral or negative effects on the retardance of Cu. AgLime had no effect on Cu leached, while the $CaSO_4$ and AgLime/$CaSO_4$ combinations exhibited similar impacts on Cu mobility with leached masses nearly two orders of magnitude greater than the Control. This relationship is evidence of the binding mechanism of Cu to organic material in the soil and the adsorption to hydroxide, carbonate and bicarbonate ions of wood ash, while $CaSO_4$ supplies Ca^{+2}

ions that displace Cu^{+2} ions from organic material and surface adsorption sites of soil (Lehmann and Harter, 1984; Cavallero and McBride, 1978).

All $FeSO_4$ combinations fall within the very acidic pH range of 0.8-2.1 and leach more Cu and As and less Cr than the Control. In addition all $FeSO_4$ systems show little overall variation in their effect on metals leaching.

Amendment combinations without $FeSO_4$ addition are observed in the weakly basic pH range of 7.6-8.0. Comparing the Cr leaching of the combinations in this pH range of 7.6-8.0 to the four $FeSO_4$ addition combinations in the pH range of 0.8-2.1, observe that $CaSO_4$ and AgLime/$CaSO_4$ combinations leached masses are an order of magnitude greater while Control and AgLime combinations are two orders of magnitude greater. Therefore, $CaSO_4$ and AgLime/$CaSO_4$ combinations are more effective amendments in Cr leach reduction for a non-acidic pH range. In this pH range of 7.6-8.0 Cr(III) hydrolyzes to sparsely soluble chromium hydroxides, adsorbs strongly to mineral and organic surfaces, and coprecipitates with other minerals (Hug et al., 1997).

The As leached masses of the combinations in this pH range of 7.6-8.0 are nearly identical and over an order of magnitude lower than the masses of the combinations with $FeSO_4$ additions. Su and Puls (2001) explain this adsorption of As in terms of both ionization of adsorbates and adsorbents which reaches its maximum adsorption at pH 7 for As(III) and for As(V) at pH <8.5.

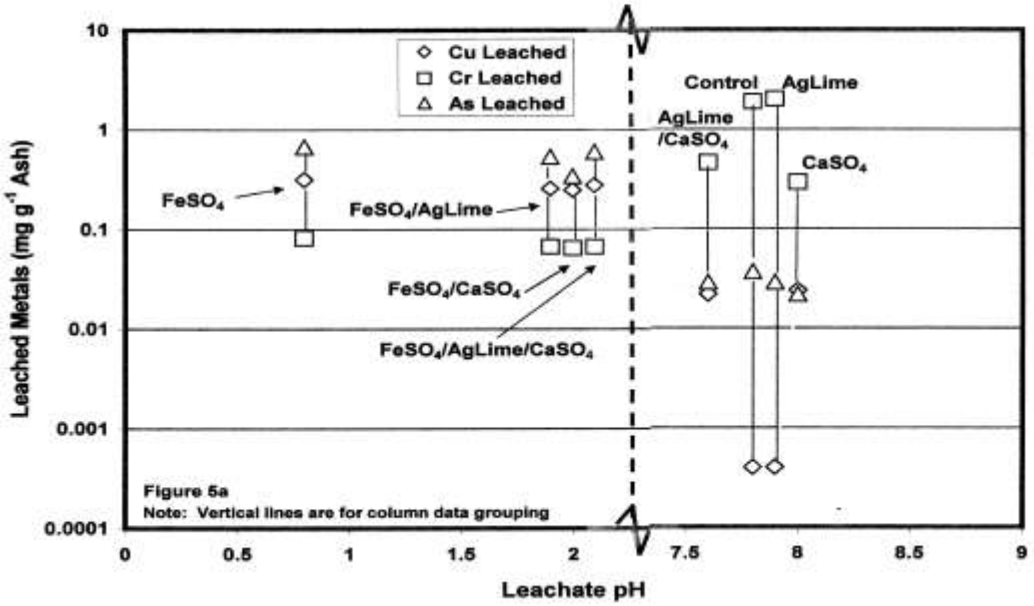


Figure 6.5a - Column Study Leach #1 – Mass CCA-metals Leached for each Amendment and Amendment Combinations with Leachate pH

Figure 6.5b represents Leach #5 data of the mass of metals leached in the column studies.. Comparing Leach #5 to Leach #1 (Figure 6.5a) observe that the $FeSO_4$-only system continues to leach metals at the same rate under very acidic conditions, whereas all other $FeSO_4$ amendment combinations leach all three metals at a lower rate, a result of the mobile metal concentrations having been leached out as each system moves toward pH 7. As the pH tends toward pH 7 and above, the adsorption strength on surface sites increases and the mobility of the remaining metals is reduced (Su and Puls, 2001). This is demonstrated by an arc from $FeSO_4$ at pH 2.3 through $FeSO_4/CaSO_4$ and $FeSO_4$/AgLime/$CaSO_4$ to $FeSO_4$/AgLime at pH 7.3, shown as a dashed line on Figure 6.5b.

Comparing Leach #5 to #1 of all non-$FeSO_4$ combinations (pH 7.3-8.1) observe that leached Cu mass has been lowered by an order of magnitude in the combinations of $CaSO_4$ and AgLime/$CaSO_4$ resulting in identical leached masses among the four combinations, Control, AgLime, $CaSO_4$ and AgLime/$CaSO_4$. This relationship shows that mobile Cu in AgLime and

$CaSO_4$ combinations has been leached out by Leach #5. The mobility of Cu in these two combinations may be a result of Ca^{+2} ions competing with Cu^{+2} ions at adsorption sites and the depletion of Cu-bound mobile organic material as supported by the literature (Lehmann and Harter, 1984; Amrhein, et al., 1992; Evanko and Dzombak, 1997).

By Leach #5, the Cr leaching has been reduced by one to two orders of magnitude. Combinations containing only $FeSO_4$ leach the same mass of Cr across the five leachings.

Observe that the As leach mass of Leach #5 is the same magnitude for $CaSO_4$ and AgLime/$CaSO_4$ compared to Leach #1, while the Control and AgLime combinations of Leach #5 produce an order of magnitude increase in leached mass compared to Leach #1. This depletion of adsorbed As in the Control and AgLime combinations is due to the depletion of the mobile As and the adsorbing power of the soil on the remaining As. The AgLime/$CaSO_4$ and $CaSO_4$ combinations continue to leach As at the same rate due to an excess of Ca^{+2} ions that maintain the adsorbing power of the soil particles (Brady, 1990). The even leaching rate of As is indicative that the operative amendment in the combinations is $CaSO_4$ with AgLime having little or no effect upon leaching rate.

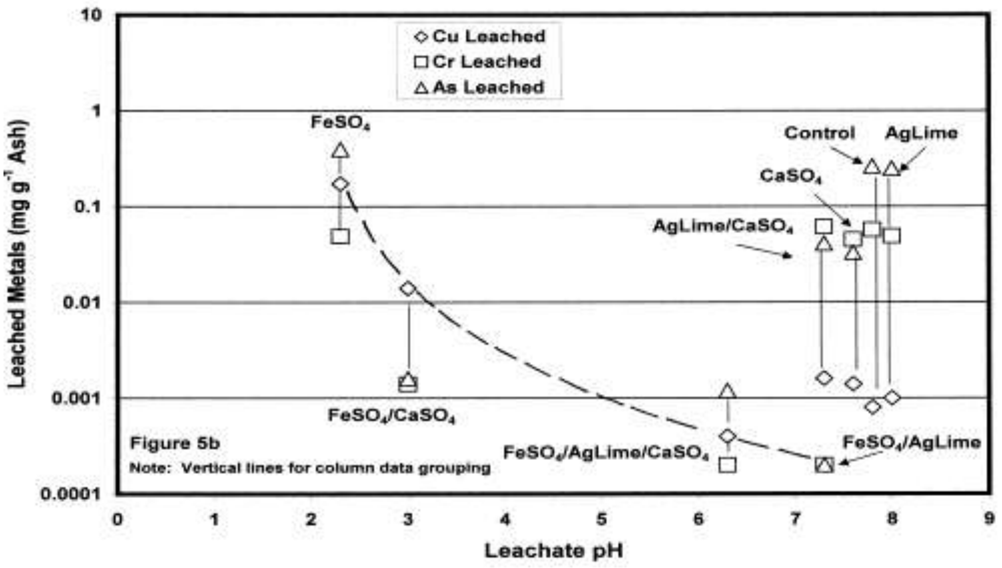


Figure 6.5b - Column Study Leach #5 - Mass CCA-metals Leached for each Amendment and Amendment Combinations with Leachate pH

Evaluation of Amendment Performance

System pH conditions and amendment combinations have varying effects on the leaching of Cu, Cr, and As. With serial leachings of the soil/CCA-ash/amendment combinations, the rates of metals mobility and system pH change in varying degrees. To compare systems over several leachings, the leach mass data of column leachings #1 and #5 were combined to produce a performance measure for the amendment combinations compared to the control soil.

Figure 6.6 indicates that the $CaSO_4$ amendment, filled squares in Figure 6.6, was the most effective in reducing the leaching of Cr and As compared to the control soil/CCA-ash, followed by the AgLime/$CaSO_4$ amendment combination, astrics on Figure 6.6. All combinations had a neutral to detrimental effect on Cu mobility. Amendment combinations containing $FeSO_{4,}$ filled triangles on Figure 6.6, are most effective in decreasing the leaching of Cr but unfortunately also have the greatest effect in increasing As mobility.

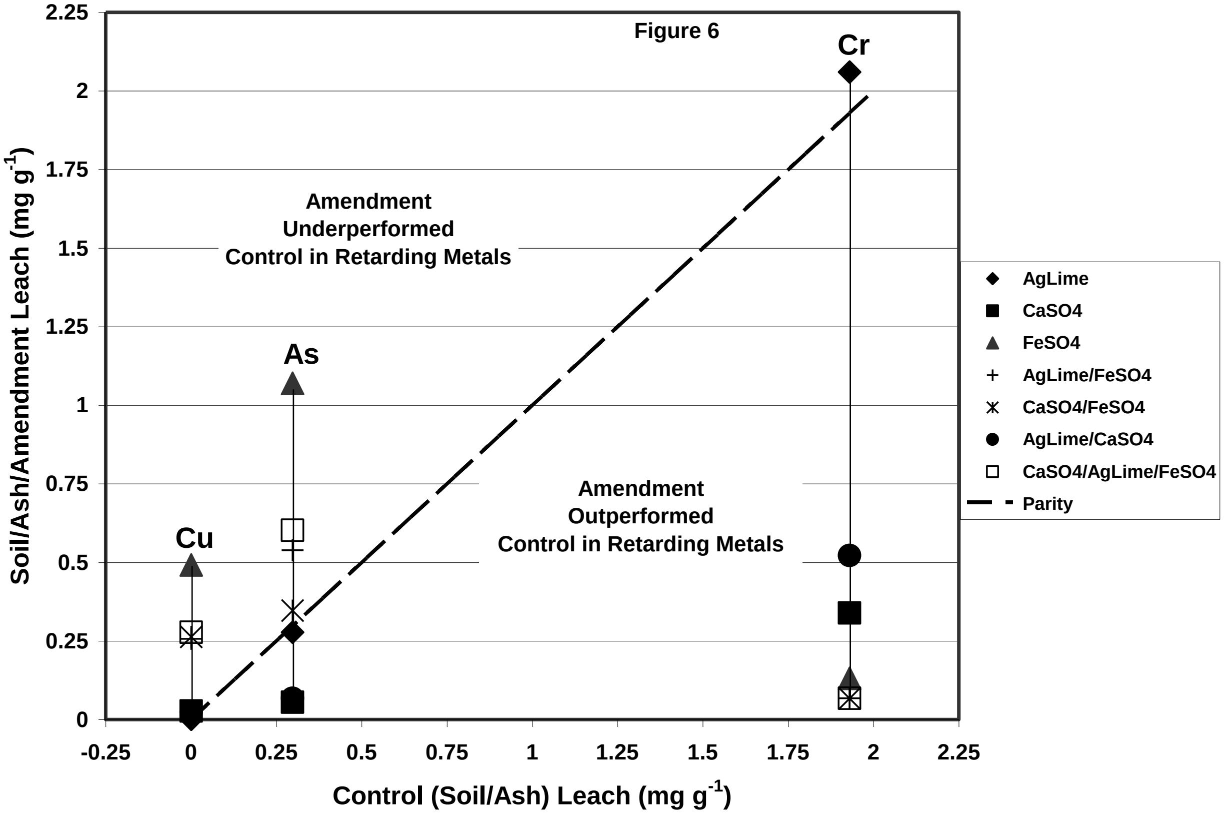


Figure 6.6 – Evaluation of Metals Leached from Amended Soil/CCA-ash (mg/g) vs Control (Soil/CCA-ash) for Leaches #1 and #5

Using metals leaching data and data generated by interpolating between analyses leach data a projection of the effect of the amendment upon the leaching of metals over a one-year period of rainfall was performed. The results are presented in Figures 6.7a (Cr), 6.7b (As), and 6.7c (Cu), the graphic presentations of the Simulated One-Year Leach of Cu, Cr, and As – Control vs Amendments. These projections extend to 1845 mL of rainwater, the equivalent of 19 rainfall events or one year of rainfall (130 cm.) at the burn site.

The data and Figure 6.7a show that Cr leaches the highest mass over the short-term and is greatly retarded by the amendments $FeSO_4/CaSO_4$ (open circles) and $CaSO_4$ (open triangles) over the Control mixture (filled squares).

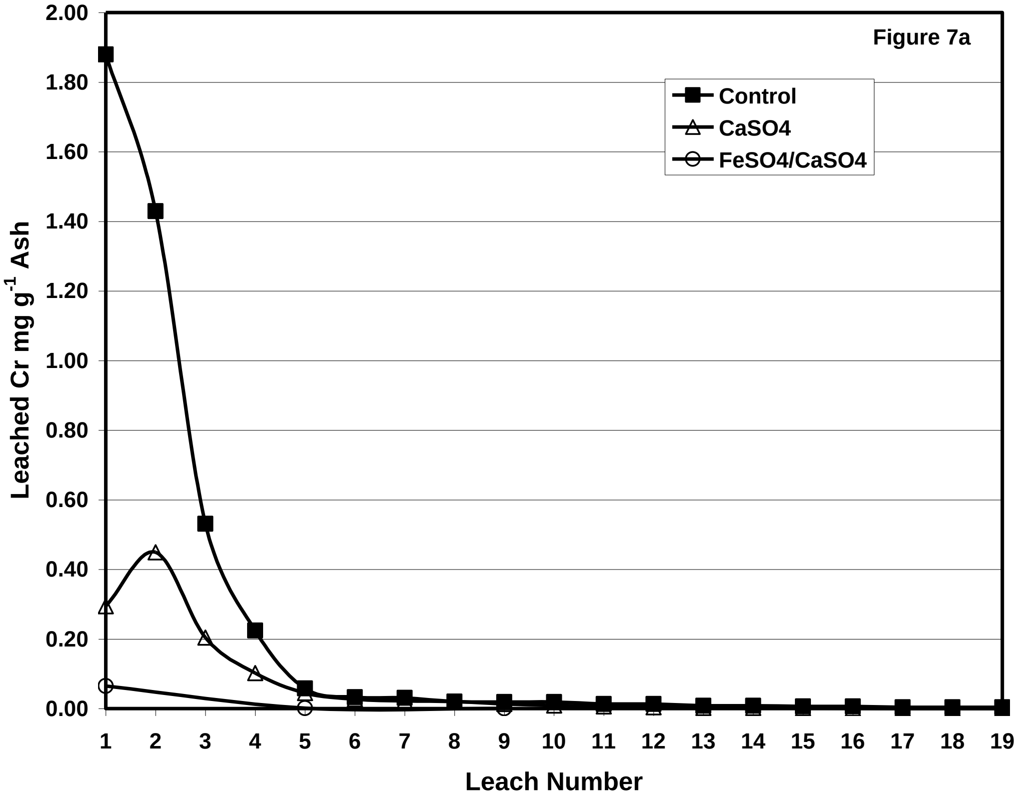


Figure 6.7a – Simulated One-Year Mass Leach of Cr – Control vs Amendments

The data and Figure 6.7b support the conclusion that As mass leaching in the Control mixture (filled squares) is high in the short-term and significant in the long-term, and that the amendments $CaSO_4$ (open triangles) and AgLime/$CaSO_4$ (open circles) produce significant reductions in short-term and long-term As leaching.

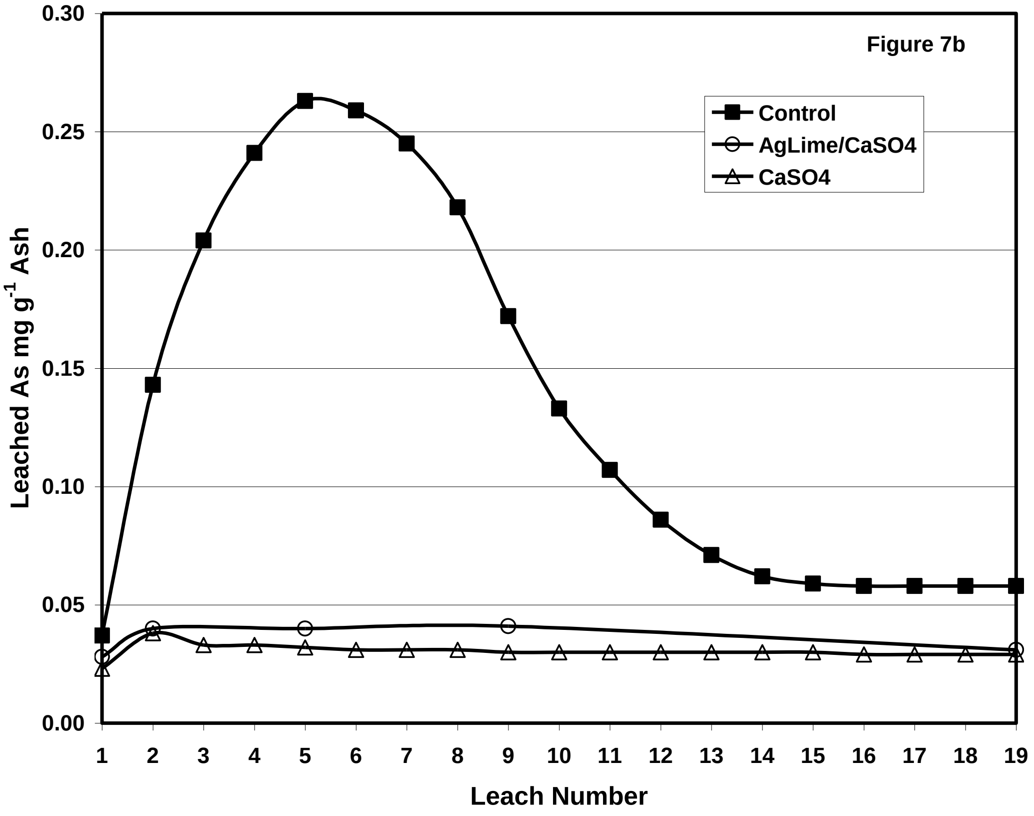


Figure 6.7b – Simulated One-Year Mass Leach of As – Control vs Amendments

The data and Figure 6.7c show that $CaSO_4$ amendment (open triangles) will produce greater Cu leaching in the short-term compared to the Control (filled squares) while the AgLime amendment (open circles) will produce a reduction of Cu leaching during the short-term over the Control.

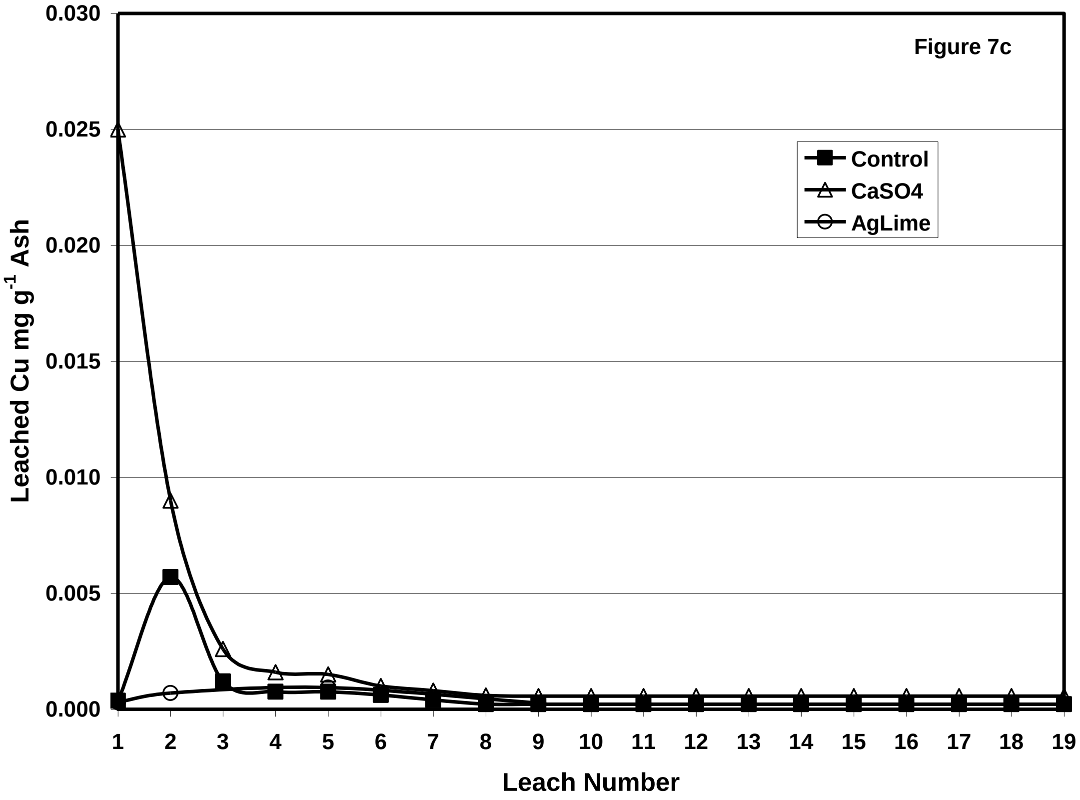


Figure 6.7c – Simulated One-Year Mass Leach of Cu – Control vs Amendments

The simulated one-year cumulative mass leach of metals (mg g^{-1}) from the soil/CCA-ash without amendment is as follows: Cu, 0.012; Cr, 4.31; As, 2.53. The resulting simulated one-year cumulative mass leach of metals (mg g^{-1}) from the soil/CCA-ash with $CaSO_4$ amendment is as follows: Cu, 0.048; Cr, 1.20; As, 0.578. Note 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 72.4% and 77.3% reduction in the leaching of Cr and As and therefore significant reductions in the mass of leached metal.

Figure 6.8 compares the Simulated One-Year Mass Leach of Cu, Cr, and As after amendment with $CaSO_4$. The figure indicates that Cr (filled squares) has the largest initial leaching after amendment with $CaSO_4$ while As (filled triangles) is the most retarded. The results of these studies of retardation and mobility show the fate of metals in amended CCA-ash/soil systems correlates well with non-ash metal/soil system literature.

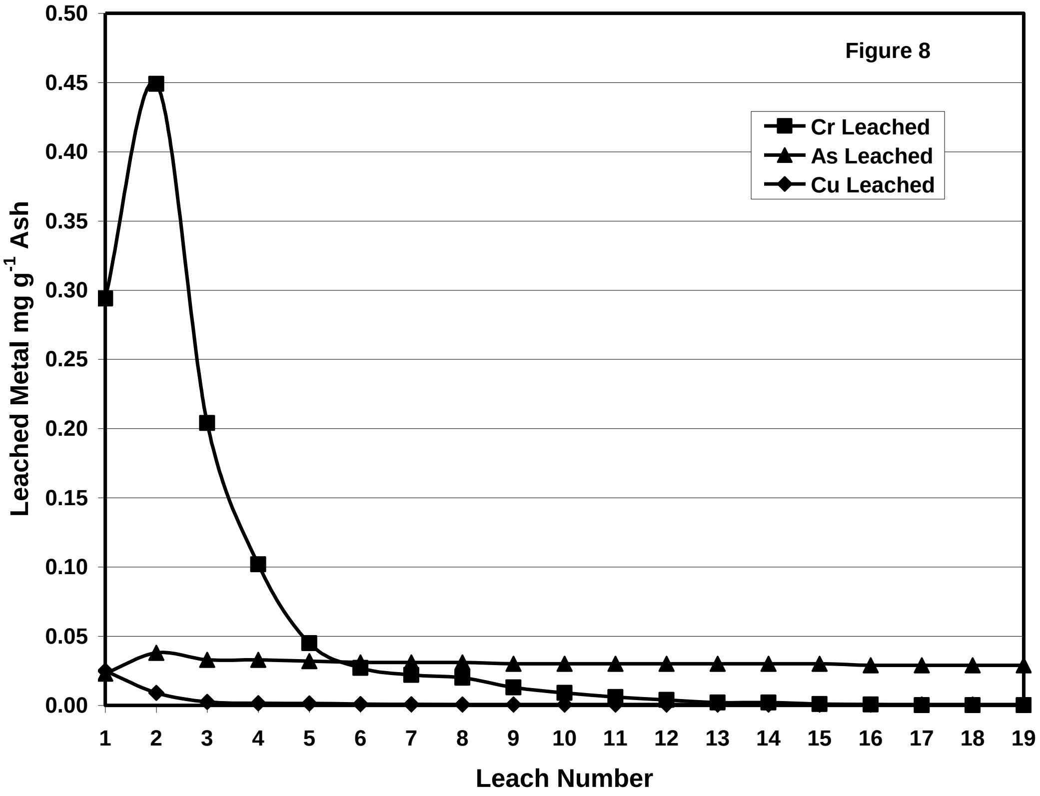


Figure 6.8 – Simulated One-Year Mass Leach of Cu, Cr, As – $CaSO_4$ Amended Soil

6.4 Conclusions

The use of $CaSO_4$ 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-ash burn sites.

Unamended soil/CCA-ash mixture exhibits the potential for retardance of CCA-metals during rainwater leaching through natural attenuation compared to CCA-ash leaching alone. System pH conditions and amendment combinations have varying effects on the leaching of Cu, Cr, and As.

Eight different amendments and a control soil/CCA-ash mixture had either little effect or increased the Cu mobility over CCA-ash alone (up to 400%). $CaSO_4$ and $FeSO_4$/ $CaSO_4$ amendments performed best for Cr retardation (up to 72.4%) and $CaSO_4$ and $CaSO_4$ /AgLime amendments performed best for reducing As mobility (up to 77.3%) over the control soil/CCA-ash mixture. Although mixtures containing $FeSO_4$ performed well in retarding Cr, $FeSO_4$ and all amendment combinations with $FeSO_4$ increased the leaching of As.

Of the mixtures studied, the $CaSO_4$ amendment acting alone was found to be the most effective amendment for the overall retardation of Cr and As mobility. The $CaSO_4$/AgLime combination was a close second in As and Cr reduction. $CaSO_4$ as a reactive soil amendment for the treatment of soils containing Cr and As metals results in significant rates of reduction of metals mobility, approaching 80% compared to unamended soil/CCA-ash mixtures over a simulated one-year leaching period.

An optimization study revealed that a ratio of 3:1 of $CaSO_4$ to metals mass was most effective in reducing the mobility of Cr and As metals. Use of a higher ratio would serve as a source for Ca^{+2} ions and should guarantee long-term stabilization while maintaining the pH in the 7.3-8.0 range.

Acknowledgment

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APPENDIX VI-A

VI-A-1 Column Leaching Study Data

Column Study Data	Leach No.																		
pH and Leached Metals	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
NS=No Sample	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**	**mg**
ND=Not Determined	**Cu Cr As**	**Cu Cr As**			**Cu Cr As**				**Cu Cr As**										**Cu Cr As**
Sample No.	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**
Soil/Ash (S/A)	**0.019 104 1.72**				**0.038 2.96 13.0**				**0.008 1.13 8.64**										
1	7.8	8.0	7.8	7.8	7.7	8.1	7.7	ND	7.5	7.4	7.9	7.5	7.7	7.5	ND	ND	ND	ND	ND
Soil/Ash (S/A)	**0.016 81.0 1.94**				**0.036 2.67 12.7**				**0.014 0.770 8.22**										
2	7.8	7.9	8.0	7.9	7.8	8.0	7.8	ND	7.7	7.7	8.0	7.5	7.7	7.7	ND	ND	ND	ND	ND
S/A Lime	**0.016 103 1.73**				**0.044 2.46 12.0**				**0.012 0.850 8.36**										
3	7.9	8.1	8.0	8.1	8.0	8.0	7.8	ND	7.8	7.8	8	7.7	7.8	7.6	ND	ND	ND	ND	ND
S/A Lime	**0.013 94.8 1.15**				**0.048 2.30 12.4**				**0.014 0.630 7.92**										
4	8.0	8.1	8.1	8.1	8.0	8.0	7.9	ND	7.8	7.9	8.1	7.8	7.8	7.7	ND	ND	ND	ND	ND
S/A CaSO4	**1.27 14.7 1.12**	**0.440 27.0 1.78**			**0.070 2.23 1.53**				**0.028 0.640 1.42**										**0.018 0.009 1.40**
5	8.0	8.0	7.8	7.7	7.6	7.6	7.4	ND	7.1	7.4	7.6	7.3	7.4	7.3	ND	ND	ND	ND	ND
S/A CaSO4	**1.21 14.1 1.10**	**0.440 17.0 1.90**			**0.076 2.18 1.62**				**0.029 0.630 1.49**										**0.020 0.010 1.44**
6	7.9	7.5	7.7	7.6	7.6	7.6	7.5	ND	7.2	7.4	7.6	7.3	7.4	7.2	ND	ND	ND	ND	ND
S/A FeSO4	**15.0 3.76 30.9**				**8.46 2.43 19.4**				**0.470 0.077 0.085**										
7	1.1	1.1	1.7	2.0	2.3	2.7	2.8	ND	3.0	3.1	3.1	3.3	3.4	3.2	ND	ND	ND	ND	ND
S/A FeSO4	**16.2 4.23 35.3**				**8.46 2.43 19.4**				**0.450 0.078 0.112**										
8	0.5	1.1	1.8	2.1	2.3	2.7	2.8	ND	2.9	3.0	3.1	3.1	3.1	3.3	ND	ND	ND	ND	ND
S/A FeSO4/Lime	**9.90 2.91 23.0**				**0 0 0.010**														
9	2.0	3.2	6.5	6.9	7.2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/Lime	**15.3 3.63 29.8**				**0 0.010 0.010**														
10	1.8	2.6	6.1	6.6	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/CaSO4	**12.6 3.42 10.9**				**0.750 0.060 0.100**				**0.470 0.030 0.080**										
11	2.1	2.1	2.1	2.9	3	3.2	3.3	ND	ND	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/CaSO4	**11.7 2.97 22.9**				**0.660 0.080 0.060**				**0.090 0.004 0.020**										
12	2.1	2.1	2.1	2.9	3.0	3.2	3.3	ND	ND	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A Lime/CaSO4	**1.09 21.2 1.29**	**0.620 26.4 2.10**			**0.083 3.16 1.80**				**0.034 0.680 1.88**										**0.010 0.010 1.52**
13	7.4	7.9	7.5	7.0	7.3	7.6	7.5	ND	6.8	6.9	6.8	7.0	6.8	6.4	ND	ND	ND	ND	ND
S/A Lime/CaSO4	**1.15 24.0 1.43**	**0.580 27.8 2.48**			**0.079 2.83 2.13**				**0.029 0.710 2.10**										**0.010 0.010 1.55**
14	7.9	7.9	7.6	7.3	7.4	7.6	7.5	ND	7.1	7.1	6.9	7.2	7.0	6.8	ND	ND	ND	ND	ND
S/A FeSO4/Lime/CaSO4	**13.9 3.36 29.2**	**2.10 0.490 3.50**			**0.020 0 0.040**														
15	2.1	6.2	6.3	7.4	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/Lime/CaSO4	**13.2 3.29 29.7**	**0.180 0.030 0.220**			**0.020 0 0.070**														
16	2.1	6.3	6.4	7.3	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

CHAPTER VII

THE APPLICATION OF $CaSO_4$ SOIL AMENDMENT TO THE RETARDANCE OF RAINWATER-LEACHED METALS FROM CCA-TREATED WOOD ASH IN SOIL

Abstract

The burning of wood treated with chromated copper arsenate (CCA) produces a toxic ash that is highly concentrated with As, Cr and Cu metals. The subsequent leaching of these metals from burn sites can produce soil and water contamination. Soils have varying natural abilities to reduce leaching and impact metals speciation and toxicity, by sorption, conversion and sedimentation related mechanisms.

The goal of this research has been to determine the effectiveness of various soil amendments in the immobilization/retardance of As, Cr, and Cu species in ash produced from the burning of CCA-treated lumber, and enhance our understanding of the role of amendments in the leaching of As, Cr, and Cu metals in a soil contaminated with CCA-ash. Soil softener ($CaSO_4 \cdot 2H_2O$) was evaluated for potential application as a low-cost method of reducing the mobility of these toxic metals. Results of the investigation shows that although the control host soil retards the mobility of As & Cr, the $CaSO_4$ soil amendment further retards metals mobility by (72.4% and 77.3%), respectively compared to the control soil-ash mixture. Cu mobility is increased by the presence of soil and by $CaSO_4$ amendment but at a much smaller mass rate.

7.1 Introduction and 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 its use in domestic settings and an associated increased public awareness of the related health concerns. The Southeastern region of the U.S. has been the largest producer and user of CCA-treated wood due to the climatic and parasitic pressures on untreated wood in this region (Solo-Gabriele et al., 1999). It is a common practice for this wood to be disposed of by onsite burning, producing a toxic ash that poses a threat to humans and the environment (Solo-Gabriele et al., 1999).

CCA-treated wood ash is a source of toxic metals, primarily copper, chromium and arsenic. Copper species are toxic to marine algae and macro-invertebrates (Harrison et al., 1983). 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 content, pH, solution complex formation, climatic and geologic conditions play a role in the movement of the metal species from the CCA-wood ash and soil mixture (Evanko and Dzombak, 1997). The adverse effects of each metal species present are dependent, in part, upon the valence state of the metal (Helsen et al., 1997). Oxidation-reduction reactions of the metals occur naturally with the soil and can change the species to a less toxic metal species (NRC, 1994). Concentrations of toxic metals 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 in the immobilization/retardance of CCA-metal species. A CCA burn site was investigated to determine baseline conditions and obtain data for the lab study. Soil/CCA-treated wood ash burn site conditions were then replicated under laboratory conditions using batch and soil column leaching studies and pH studies. The results of amendment with soil softener ($CaSO_4 \cdot 2H_2O$) will be reported in this paper.

7.2 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. This reservoir serves as the main source of water for a population of approximately 125,000. It is also a major local recreational area, with over 3,000 permitted residential sites within its shoreline that use various amounts of treated wood for decks, boathouses, piers and retaining walls.

The study site is a residential lot with a history of scrap CCA-treated wood burning at a central location on the lot. This burn site is located on ground that has a slope angle of 15 degrees and drains 6 meters into Lake Tuscaloosa. Potential paths of metals contamination are by direct runoff and soil infiltration.

7.3 Methods and Materials

7.3.1 Analytical Methods

The metals content of the CCA-ash and the CCA-ash contaminated soil were determined by acid microwave digestion (HNO_3) analyses (EPA SW-846 Methods 3015 and 3051). The Toxic Characteristic Leaching Procedure (TCLP) (EPA SW-846 Method 1311) was used to provide regulatory context to the waste ash. Leachates and TCLP extracts were analyzed with inductively coupled plasma atomic emission spectrophotometry (ICP-OES) to determine the concentrations of As, Cr, and Cu. The carbon and organic carbon content of the test soil was determined by the loss on ignition method (LOI-Chemical Methods, Soil Science Society of America). The soil pH values were determined by standard methods (Soil pH-Chemical Methods, Soil Science Society of America). The pH values for soil and column leachates were determined with a ThermoOrion pH Meter, Model 520. All metals results are stated on a mass basis unless otherwise noted.

7.3.2 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 metals contaminations in the soil columns and establish the ratio of soil:ash used in preparation of the laboratory test soil.

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.

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

Uncontaminated Test 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.

Test CCA-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/ash control and amended soil mixtures.

Test Media Preparation

The test soil/ash mixture (control) was produced by mixing test soil with CCA-ash in the ratio of 5.28:1 to replicate soil-ash metal concentrations in the topsoil layer at the burn site. The resulting metal concentrations in the mixture were (metal mg g^{-1} control mixture ± 95% confidence interval): As (11.1±0.7); Cr (12.2±5.6); Cu (13.7±4.0). The amended test soil was prepared by adding $CaSO_4 \cdot 2H_2O$ to the control soil-ash mixture.

7.4 Column Experiment Design and Stoichiometry

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

Accelerated leach experiments, 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 pH 4.6 rainwater used in the experimentation was collected under controlled conditions. 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 $CaSO_4 \cdot 2H_2O$ amended test soil.

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 soil amendment. These proportions of soil amendment to CCA-ash were established from calculations described previously to provide for stoichiometric conversion.

7.5 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 soil amendment mixtures.

7.5.1 Ash Metals Characterization and Occurrence at the CCA Burn Site

Laboratory ash samples, analyzed in triplicate by microwave digestion and ICP-OES, revealed that metals concentrations in the ash (mg metal g^{-1} ash ± 95% confidence interval) were: As (69.6±4.6); Cr (76.7±34.9); Cu (86.3±24.8) for a total ash CCA-metals mass of 232.6 mg metals g^{-1} ash. The ICP limits of detection (LOD) were as follows: As, 0.034 mg L^{-1}; Cr, 0.026 mg L^{-1}; Cu, 0.025 mg L^{-1}. 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 mg g^{-1}; Cr, 17.4 mg g^{-1}; Cu 14.5 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, whereas in all other areas sampled the metals were confined to the upper 5 centimeters of topsoil. Up-gradient metals concentrations were all low (<0.025 mg g^{-1}).

7.5.2 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 (mg L^{-1} ± 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 though 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.

7.5.3 Batch Rainwater-leaching of Unamended CCA-ash and Test Soil/CCA-ash Mixture

The main objective of this experiment was to determine the potential of unamended test soil-ash mixture to inhibit or promote the rainwater leaching of metals compared to 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 ash samples were leached and triplicate soil-ash samples were leached then re-leached to simulate wet weather events as described earlier. Data generated from this experiment indicates that the mobility of Cr and As is significantly lowered in the presence of the test soil while Cu mobility is increased. During the first leach the soil-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 releaching 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 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 Metals from Test Soil/CCA-ash Mixture

The 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 the first rainwater-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 toxic contamination of water 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 soil/CCA-ash mixture is: As, 469 Lg^{-1}; Cr, 29 Lg^{-1}; Cu, 113 Lg^{-1}.

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

Effect of Soil Amendments on pH and Metals Mobility During Rainwater-leaching

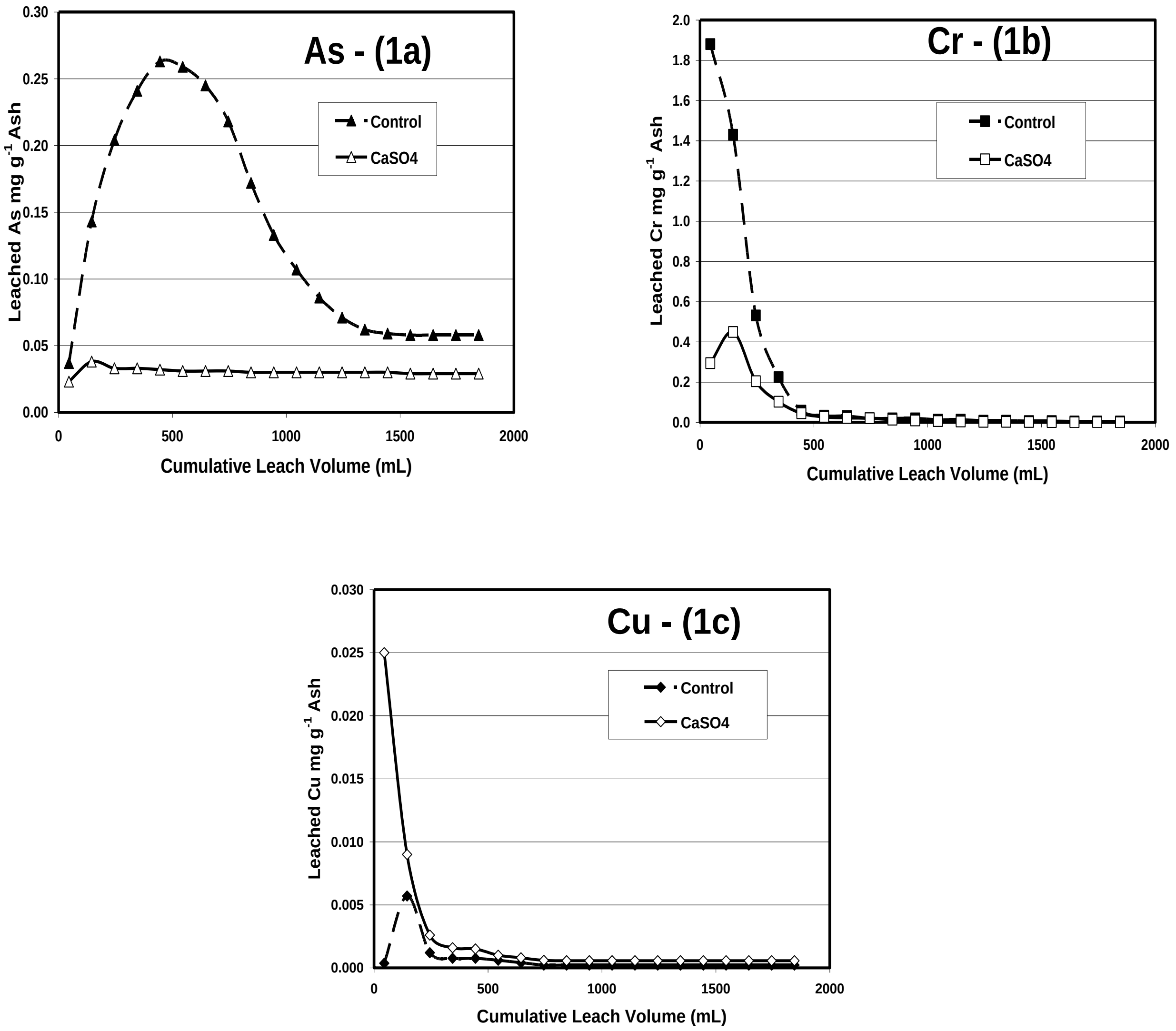
System pH conditions and amendment combinations have varying effects on the leaching of As, Cr, and Cu. The Control and $CaSO_4$ combinations are weakly basic systems (7.3-8.0 pH) that become more neutral as the columns reach equilibrium and exhibit relatively low mobility of metals.

The $CaSO_4$ amended test soil exhibited similar impacts on Cu mobility with leached masses nearly two orders of magnitude greater than the Control. This relationship is evidence of the binding mechanism of Cu to organic material in the soil and the adsorption to $CaCO_3$ in the ash, while $CaSO_4$ supplies Ca^{+2} ions that displace Cu^{+2} ions from organic material and surface adsorption sites of soil (Lehmann and Harter, 1984). In this pH range of 7.3-8.0 Cr hydrolyzes to sparsely soluble chromium hydroxides, adsorbs strongly to mineral and organic surfaces, and coprecipitates with other minerals (Hug et al., 1997). Su and Puls (2001) explain this adsorption of As in terms of both ionization of adsorbates and adsorbents which reaches its maximum adsorption at pH 7.

Evaluation of Amendment Performance

Using measured metals leaching data and data interpolated from intermittent leaching trends it is possible to produce a projection of the effect of the $CaSO_4$ amendment upon the leaching of the As, Cr, and Cu metals over a simulated one-year period of rainfall and is presented in Figures 7.1a, 7.1b, and 7.1c, the graphic presentations of the Simulated One-Year Leach of As, Cr, and Cu – Control vs $CaSO_4$ Amendment. These projections extend to 1845 mL of rainwater, the equivalent of 19 rainfall “episodes” of the research project or one year of rainfall (130 cm.) at the contaminated 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 $CaSO_4$ amendment is as follows: As, 0.578; Cr, 1.20; Cu, 0.048. It is noted that the mass leaching data percentages project a 390% increase of Cu leaching, but this represents a small relative mass of Cu compared to Cr and As masses. The data also reflects a 72.4% and 77.3% reduction in the leaching of Cr and As and therefore significant reductions in the mass of leached metal. The figures indicate that Cr has the largest remaining initial leaching after amendment with $CaSO_4$ while As is the most retarded. The results of these studies of retardation and mobility show the fate of metals in amended CCA-ash/soil systems correlates well with non-ash metal/soil system literature.



Figures 7.1a,7.1b,7.1c – Simulated One-Year Mass Leach of As, Cr, Cu – Control vs $CaSO_4$ Amendment (Harden, 2005)

7.6 Conclusions

The use of gypsum soil-softener ($CaSO_4 \cdot 2H_20$) acting as a stabilizing agent within the pH 7.3-8.0 range may be an economically feasible soil amendment for the stabilization of Cr and As from a heavily contaminated soil while also preventing potential contamination of water by leached metals.

The unamended soil/CCA-ash mixture exhibits the potential for retardance of CCA-ash metals during rainwater leaching through natural attenuation compared to CCA-ash leaching alone. Amendment with ($CaSO_4 \cdot 2H_2O$) increased the Cu mobility over CCA-ash alone.

The $CaSO_4$ as a reactive soil amendment for the treatment of soils contaminated by Cr and As metals results in significant rates of reduction of metals mobility, nearly 80% compared to unamended CCA-metals contaminated soil, over a simulated one-year leaching period, and in cases in which initial high metals concentrations in the soil leach at very high rates.

An optimization study revealed that a ratio of 3:1 of gypsum to metals mass was most effective in reducing the mobility of Cr and As metals. Use of a higher ratio would serve as a source for Ca^{+2} ions and should guarantee long-term stabilization while maintaining the pH in the 7.3-8.0 range.

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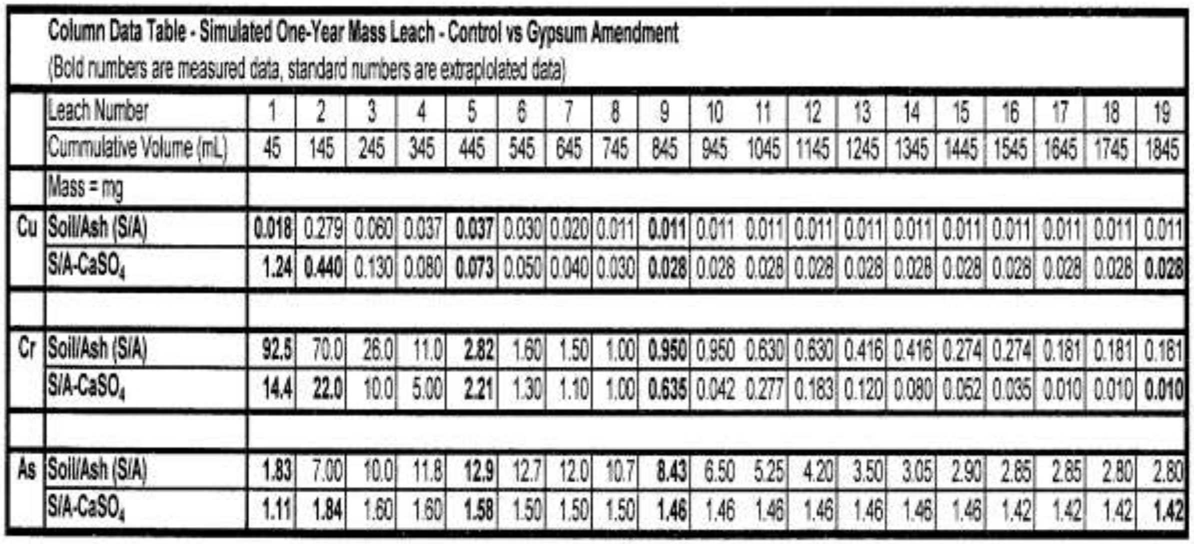
APPENDIX VII-A

VII –A- 1 Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment



Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment

(Bold numbers are measured data, standard numbers are extraplolated data)

	Leach Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Cummulative Volume (mL)	45	145	245	345	445	545	645	745	845	945	1045	1145	1245	1345	1445	1545	1645	1745	1845
	Mass = mg																			
Cu	**Soil/Ash (S/A)**	**0.018**	0.279	0.060	0.037	**0.037**	0.030	0.020	0.011	**0.011**	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
	S/A-CaSO$_4$	**1.24**	**0.440**	0.130	0.080	**0.073**	0.050	0.040	0.030	**0.028**	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	**0.028**
Cr	**Soil/Ash (S/A)**	**92.5**	70.0	26.0	11.0	**2.82**	1.60	1.50	1.00	**0.950**	0.950	0.630	0.630	0.416	0.416	0.274	0.274	0.181	0.181	0.181
	S/A-CaSO$_4$	**14.4**	**22.0**	10.0	5.00	**2.21**	1.30	1.10	1.00	**0.635**	0.042	0.277	0.183	0.120	0.080	0.052	0.035	0.010	0.010	**0.010**
As	**Soil/Ash (S/A)**	**1.83**	7.00	10.0	11.8	**12.9**	12.7	12.0	10.7	**8.43**	6.50	5.25	4.20	3.50	3.05	2.90	2.85	2.85	2.80	2.80
	S/A-CaSO$_4$	**1.11**	**1.84**	1.60	1.60	**1.58**	1.50	1.50	1.50	**1.46**	1.46	1.46	1.46	1.46	1.46	1.46	1.42	1.42	1.42	**1.42**

CHAPTER VIII

EVALUATION OF GYPSUM AS A RETARDANT IN THE LEACHING OF METALS FROM CCA-TREATED WOOD BURN SITES

Abstract

Agricultural lime, gypsum and various gypsum-like by-products have long been applied to soil surfaces as ameliorants of soil acidity and aluminum and manganese toxicity. In this research, gypsum is evaluated as a soil amendment for the purpose of retarding the rainwater-leaching of Cu, Cr, and As species from CCA-treated wood burn sites. The burning of wood that has been chemically treated with chromated copper arsenate (CCA) produces an ash containing high concentrations of copper, chromium, and arsenic (CCA-metals). The rainwater-leaching of these metals from burn sites can produce increased soil and water contamination. Soils have varying natural abilities to retard leaching and they also impact metals speciation and toxicity, through sorption, conversion and sedimentation related mechanisms. Recent regulations restricting the use of CCA-treatment have resulted in increased quantities of CCA-treated lumber entering the waste stream, making the study of metals leaching from CCA-ash and soil/CCA-ash systems and metal retardance to be important areas of investigation.

Results of this investigation show that native soil alone retards the mobility of As and Cr compared to CCA-ash alone, and that gypsum amendment application further retards As and Cr mobility. Gypsum soil amendment reduced the rainwater-leaching of Cr and As from CCA-ash, the reduction in mobility is 72% for Cr and 77% for As compared to the unamended soil/CCA-ash mixture. Cu mobility is increased in the presence of the soil and by gypsum amendment of

the soil/CCA-ash mixture. The optimum retardance of CCA-metals resulting from gypsum amendment of soil/CCA-ash mixtures was determined during a batch leaching study to be at the 3:1 mass ratio of gypsum to CCA-metals in the CCA-ash.

Keywords: Arsenic, Chromium, Copper, Immobilization, Soil

8.1 Introduction

In situ stabilization of metals in contaminated soils by addition of industrial by-products is an attractive remediation technique. In this research paper, gypsum in the form of an agricultural soil amendment was evaluated in laboratory experiments for its potential to retard the rainwater-leaching of CCA-metals from a soil/CCA-ash mixture.

A literature review of similar articles regarding the amendment of soil and metals-contaminated soil revealed other research that evaluated the effects of gypsum and gypsum-rich industrial by-products upon metal availability and leachability. Vizcayno, et al (2001) studied the effects of gypsum upon soil and the resulting extractable forms of Al; Ishak, et al (2002) studied the effects of flue-gas gypsum upon the physical parameters of soils of the southeastern U.S.; Illera, et al (2004a) studied the effects of gypsum and gypsum-rich industrial by-products upon the immobilization of heavy metals; and Illera, et al (2004b) studied the effects of gypsum and gypsum-rich industrial by-products on the release of exchangeable Al from soil.

Gypsum is an evaporite mineral most commonly found in layered sedimentary deposits in association with halite, anhydrite, sulfur, calcite and dolomite. Gypsum ($CaSO_4 \cdot 2H_2O$) is very similar to Anhydrite ($CaSO_4$). The chemical difference is that gypsum contains two waters and anhydrite is without water. Gypsum is the most common sulfate mineral. Gypsum uses include: manufacture of wallboard, cement, plaster of Paris, soil conditioning, a hardening retarder in

Portland cement. Researchers, mainly in the southeastern United States, Brazil, and South Africa, have found that gypsum can ameliorate aluminum toxicity despite the fact that it does not increase soil pH (Brady and Weil, 2002).

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 service life; design changes (Cooper, 1993; McQueen and Stevens, 1998; Clausen, 2000; Wu, 2000) a restrictive ban on future CCA-treated wood 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 products due to the adverse effects of the hot and humid climate and 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 potential threat to humans and the environment (Solo-Gabriele et al, 1999).

CCA-ash is a source of heavy metals, primarily Cu, Cr and As compounds, that have been long recognized as causing environmental problems. At the μg/L 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 (Winner, 1984; Korte and Fernando, 1991; LaGrega et al., 1994; Palmer and Puls, 1994; Raven et al., 1998; Solo-Gabriele et al., 1999). A previous study by Harden (2005) and reported by Harden and Johnson (2009) showed that a CCA-ash/soil sample subjected to rainwater-leaching exhibited the potential contamination of water beyond the regulatory limits in the order of: As, 469 L g^{-1} Ash > Cu, 113 L g^{-1} Ash > Cr, 29 L g^{-1} Ash.

The oxidation states of arsenic and chromium species exhibit a significant influence on the mobility of the metals. Combustion conditions of temperature and oxygen supply during the burning of CCA-treated wood can effect the Cr speciation in the CCA-ash with a portion of the predominant Cr(III) converting to the much more toxic Cr(VI) form (Helsen et al, 2003). The resulting ash, although still largely Cr(III), will have varying Cr(VI) concentrations influenced by the degree of the initial CCA-treatment of the wood, along with the combustion conditions. Resulting Cr(VI) ash content ranging from 4 to 7% has been reported by Song et al., (2006). The Cr(VI) species, besides being more toxic, is also more soluble and therefore more mobile in the the environment compared to Cr(III).

Arsenic species in CCA-treated wood ash are both the more toxic As(III) and the less toxic As(V), with As(III) being more soluble and mobile in the environment. The As(V) species is found in the CCA-treatment solution and in the treated wood and after pyrolysis of the scrap wood (thermochemical decomposition at an elevated temperature in the absence of oxygen), some of the As(V) is converted to the As(III) species in the CCA-ash (Helsen et al., 2003). Lida, et al. (2004) reported XRD results of a number of incineration products of CCA-treated wood over the temperature range of 600-900 ˚C to include: Cr_2O_3, As_2O_3, $Cu_3AsO_4(OH)_3$, $CuCr_2O_4(OH)_3$ and $CuCr_2O_4 \cdot 2H_2O$.

Arsenic pentoxide (As_2O_5) and CuO are dissolved in chromic acid to produce the CCA-treatment solution (Solo-Gabriele, et al, 1999). The ash resulting from the burned CCA-wood has almost all copper in the form of CuO, which was reported by Palmer and Benezeth (2004) to be very sparsely water-soluble at 25° C.

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 within a soil system can change these metals to more or less toxic and available metal species (NRC, 1994). Song et al, (2006) showed significant reduction of Cr(VI) to Cr(III) when mixed with soil and Georgiadis et al (2006) noted the potential oxidation of As(III) to As(V) in soil. The resulting interaction of CCA-wood ash and its CCA-metal species with soil is a complex system. 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 (US EPA, 1992; Evanko and Dzombak, 1997). A significant problem occurs when high concentrations of metals at 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 effectiveness of a soil amendment to immobilize and retard CCA-metal species using gypsum soil softener ($CaSO_4 \cdot 2H_2O$) was studied as a part of this research. This soil amendment was chosen due to availability, current application as a soil supplement, and potential to enhance chemical reactions that reduce the mobility of metal species within the soil (Brady, 1990). A previously investigated CCA-treated wood burn site in Tuscaloosa County, Alabama was used for baseline conditions of a laboratory study (Harden, 2005). The maximum CCA- metal concentrations (metal mg g^{-1}soil/CCA-ash ± 95% confidence interval) at this site were reported by Harden and Johnson (2009) to be: Cu (14.5±0.2), Cr (17.4±0.6), and As (12.2±0.5). Soil/CCA-treated wood ash burn site conditions and CCA-metal concentrations were replicated under laboratory conditions to conduct batch and soil column leaching studies and pH studies.

8.2 Methods and Materials

8.2.1 Analytical Methods

The metals content of CCA-ash and CCA-ash/Ultisol soil mixtures were determined by acid microwave digestion (HNO_3) analyses in a MARS-X microwave using Methods 3015 and 3051 (US EPA, 1996). Leachates and microwave digestion extracts were analyzed with inductively coupled plasma-atomic emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 3000DV) to determine the concentrations of Cu, Cr, and As using Methods 3015 and 3051 (US EPA, 1996).. 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} of ash for soil/ash and ash as necessary. The total carbon and organic carbon content of the native soil was determined by the loss on ignition (LOI) method 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. Deionized water used as the leaching fluid in the Gypsum Optimization Study was ASTM Type 2, 17.9 micromho. All metal results are stated on a mass basis unless otherwise noted.

8.2.2 Characterization of the Soil and Soil/Ash Mixture

Control Soil

Topsoil, located 100 meters up-gradient from the burn site, was employed as the control soil and was analyzed for Cu, Cr, and As to establish baseline metals concentrations with no detectable concentrations of the CCA-metals found (Harden, 2005). The total carbon content of the soil was analyzed to be 2 percent, which is consistent with the carbon content reported by the USDA Soil Survey. The soil at this location was classified by the USDA as Paleudult Ultisol with a 10-15 centimeter layer of sandy clay loam of 2-33% clay and 0.5-2% organic matter underlain by impermeable kaolinitic clay over fractured rock. Specifically, the soil is described as yellow-brown to medium brown, fine grain to silt, predominantly fine grain, subangular, 70% quartz, 20% very fine clay, 10% very fine to silt, dark brown-black minerals (United States Department of Agriculture, 1981). The soil was sieved through a number 30 sieve (0.6 mm) to increase particle uniformity and remove large particles that could cause column channeling.

CCA-ash

The CCA-ash was prepared under controlled burn conditions by burning scrap CCA-treated wood on a metal grate over a metal catch-pan and then sieved through a number 10 (2.00 mm) sieve to remove large unburned cinders. The combustion temperature was about 600° C for 1 hour under an initial condition of normal-oxygen combustion to a final condition of low-oxygen pyrolysis. The ash was used in the preparation of the soil/CCA-ash and amended soil/CCA-ash mixtures. Analyses were conducted in triplicate, as described in Section 8.2.1. The metal content of the ash used in these mixtures was (mg metal/g ash ± 95% confidence interval): Cu (86.3±11.3); Cr (76.7±16.0); As (69.6±2.1). 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. The other major components of the wood ash are complex oxides and carbonates of Ca, K, and Mg with minor components of Cu, Cr, and As. (Demeyer et al., 2001).

Soil/CCA-ash Mixture

The soil/CCA-ash mixture was produced by mixing Ultisol control soil with CCA-ash at a mass ratio of 5.28:1 to replicate soil-ash metal concentrations in the topsoil layer at the burn site. The resulting approximate metal concentrations in the mixture were (metal mg/g control mixture ± 95% confidence interval): Cu (13.7±1.8); Cr (12.2±2.6); As (11.1±0.3) and were found to closely approximate the field conditions reported by Harden and Johnson (2009) of Cu (14.5±0.2), Cr (17.4±0.6), and As (12.2±0.5).

Gypsum-amended Soil/CCA-ash Mixture

The gypsum soil amendment ($CaSO_4 \cdot 2H_2O$) was added to the soil/CCA-ash mixture to produce the amended soil/CCA-ash mixture used in the experimentation. The gypsum soil amendment used (Table 8.1) was commercial grade pelletized gypsum that was crushed and sieved through a number 10 (2.00 mm) sieve. The manufacturer, Imery's, 100 Mansel Court E., Roswell, GA 30076, listed the gypsum analysis as follows: $CaSO_4 \cdot 2H_2O$, 75%; Ca, 18%; S, 15%.

8.2.3 Batch Leaching

Batch leaching with rainwater was used to determine the mobility of CCA-metals leaching from CCA-ash, a mixture of CCA-ash and the Ultisol control soil, and from mixtures of gypsum-amended Ultisol control soil/CCA-ash. Additionally, pH changes were recorded during the sequential deionized-water leaching of Ultisol soil/CCA-ash mixtures. Duplicate batch leachings were conducted by wetting to field-capacity known masses of sample mixtures with a measured volume of rainwater or deionized water to form a slurry in a 250-mL acid-washed polyethylene bottle reactor and then aged for 24 hours to reach reaction equilibrium under wet soil conditions. After the appropriate water was added to produce the final liquid volume, the reactor was tumbled at 20 RPM for 18 ± 2 hours, centrifuged for 20 minutes at 1000 RPM, and the leachate drawn off by pipette for metal analysis according to Method 1311 (US EPA, 1996) or the pH was determined for each sequential leaching.

Optimization Study Design

Literature studies of redox-stoichiometric adsorption data were used to establish minimum soil amendment/metal mass ratios for the column experiment. An adsorption study determined that three equivalents of divalent cations are required to reduce common metal species (Buerge and Hug, 1997). In order to provide additional data to confirm the use of the 3:1 ratio a batch study of gypsum-amended soil/CCA-ash mixtures was conducted.

8.2.4 Column Experiment Design and Stoichiometry

In traditional column studies, a media is studied by the controlled upward flow of a fluid through the column. The fluid containing a known amount of material enters the column at the bottom and samples are taken as the fluid exits the column at the top. Data on sorption vs. contact time is therefore available by varying the flow rate. During this research, the column media was examined to determine its reactions with rainwater flowing by gravity through the column in individual “batches.” Each batch represented a precipitation event entering the top of the column and exiting the bottom of the column, with the media in the column being the soil and ash mixtures undergoing leaching as the rainwater infiltrated the soil. The leaching of the metals from the column media versus simulated rainfall amount is the focus of these experiments.

Literature studies of redox-stoichiometric adsorption data and the results of the gypsum optimization study were used to establish minimum gypsum amendment/CCA-metal mass ratios for the design of the column experiment. This accelerated leach experiment was used to determine the effects of controlled rainwater leaching events. The experiment was performed using duplicate sets of soil/CCA-ash columns designed to closely replicate the soil conditions at the burn site. The column tests were run using duplicate sets of columns, with the two variable factors being soil/CCA-ash mixture alone, or amended with gypsum, resulting in a total of 4 columns. Under laboratory conditions, rainwater flowed by gravity from the top of the column and was collected as it exited the column. The average flow rate for the 4.2 cm diameter columns was 6 mL hr^{-1} (resulting in an infiltration rate of 4.3 mm/hr) and each column leach event was 12-24 hours in duration. Data collected was the mass of each metal leached from individual leaching events and the cumulative results of nineteen leach events for each column. Each polycarbonate column was 4.2 cm in diameter and 61 cm in length and contained 231 g of control soil, 49 g CCA-ash, and 68g of gypsum amendment (when gypsum was also added). These proportions of gypsum soil amendment to CCA-ash were established from calculations described previously to provide for potential stoichiometric conversion. Leach event volumes ranged from an initial 45 mL volume to subsequent 100 mL volumes equal to 3.2-7.2 cm height in the column 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 metal 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 total mass of metal leached and the pH trends resulting from the addition of the gypsum amendment.

8.2.5 Experiment Flow Chart

Batch Rainwater-Leaching of CCA-Ash and a Sequential (5) Rainwater-Leaching of a Soil/CCA-Ash Mixture

Purpose: To determine the natural attenuation of soil upon the leaching of CCA-metals from a soil/CCA-ash mixture compared to the leaching of CCA-ash alone. The leaching trend from sequential leaching of a soil/CCA-ash mixture is studied.

Triplicate Samples
Soil/CCA-ash mixture of 8.25 g soil/1.45 g CCA-ash
Rainwater Leachings – 130 mL

⇩

Sequential (5) Batch Rainwater-Leaching of Unamended and Gypsum-Amended Soil/CCA-Ash Mixtures

Purpose: To determine the rainwater-leaching trends of a gypsum-amended and unamended soil/CCA-ash mixture.

Duplicate samples
Soil/CCA-ash mixture of 4.12 g Soil/0.75 g CCA-ash
Gypsum amendment (1.0 g) when added.
Initial leach volume (65 mL), leach 2-5 (100 mL).

⇩

Gypsum Optimization Study

Purpose: Conduct a deionized-water batch leaching study to determine the optimum ratio of gypsum amendment to CCA-metals in a soil/CCA-ash mixture.

Duplicate Samples
Soil/CCA-ash Mixtures of 400 mg soil/85 mg CCA-ash
Mixtures are amended with 0, 25, 100 and 400 mg of gypsum
Each leach contains 10 mL deionized-water

Column Rainwater-Leaching of Gypsum-Amended and Unamended Soil/CCA-Ash Mixtures

Purpose: To determine the rainwater-leaching of CCA-metals from gypsum-amended and unamended soil/CCA-ash columns.

Duplicate columns
Two columns: 231 g soil, 49 g CCA-ash
Two columns: 231 g soil, 49 g CCA-ash and 68 g of gypsum
Leach events: 19 events = 1845 mL of rainwater

8.3 Results and Discussion

The results of several batch experiments and a column experiment are presented in order to better characterize the retardance ability for rainwater-leached CCA-metals by Ultisol soil and by unamended and gypsum-amended Ultisol soil/CCA-ash mixtures.

8.3.1 Batch Rainwater-leaching of CCA-Ash and Sequential Rainwater-leaching of an Ultisol Soil/CCA-ash Mixture

The main objective of this experiment was to determine the potential of an Ultisol soil/CCA-ash mixture to inhibit or promote the rainwater-leaching of CCA-metals compared to the rainwater-leaching of CCA-ash alone, to evaluate the leaching trends for the Ultisol soil/CCA-ash mixtures, and to further evaluate the CCA-metals concentrations resulting from a sequential rainwater-leaching of an Ultisol soil/CCA-ash mixture. Triplicates of CCA-ash were leached and triplicates of an Ultisol soil/CCA-ash mixture were sequentially leached to simulate multiple wet weather events as described earlier in 2.3 Batch Leaching. The resulting data, including error bars, is presented in Figure 8.1. Data generated from this experiment indicates that the mobility of Cr and As is lowered in the presence of soil while Cu mobility is increased. During the first leach the soil/ash mixture retarded the leaching of Cr and As by 75% and 74% respectively (Cr: 17.1 to 4.23 mg g^{-1} CCA-ash; As: 10.1 to 2.60 mg g^{-1} CCA-ash), but enhanced Cu leaching by 280% (0.010 to 0.029 mg g^{-1} CCA-ash) compared to the leaching of CCA-ash alone. Subsequent releaching of the soil/CCA-ash mixture resulted in a cumulative decrease of 250% (2.60 to 1.02 mg g^{-1} CCA-ash) in the leached mass of As and 1150% (4.23 to 0.369 mg g^{-1} CCA-ash) in the leached mass of Cr compared to the leaching of CCA-ash alone. Conversely, an increase of 1550% (0.029 to 0.446 mg g^{-1} CCA-ash) was recorded in the leached mass of Cu.

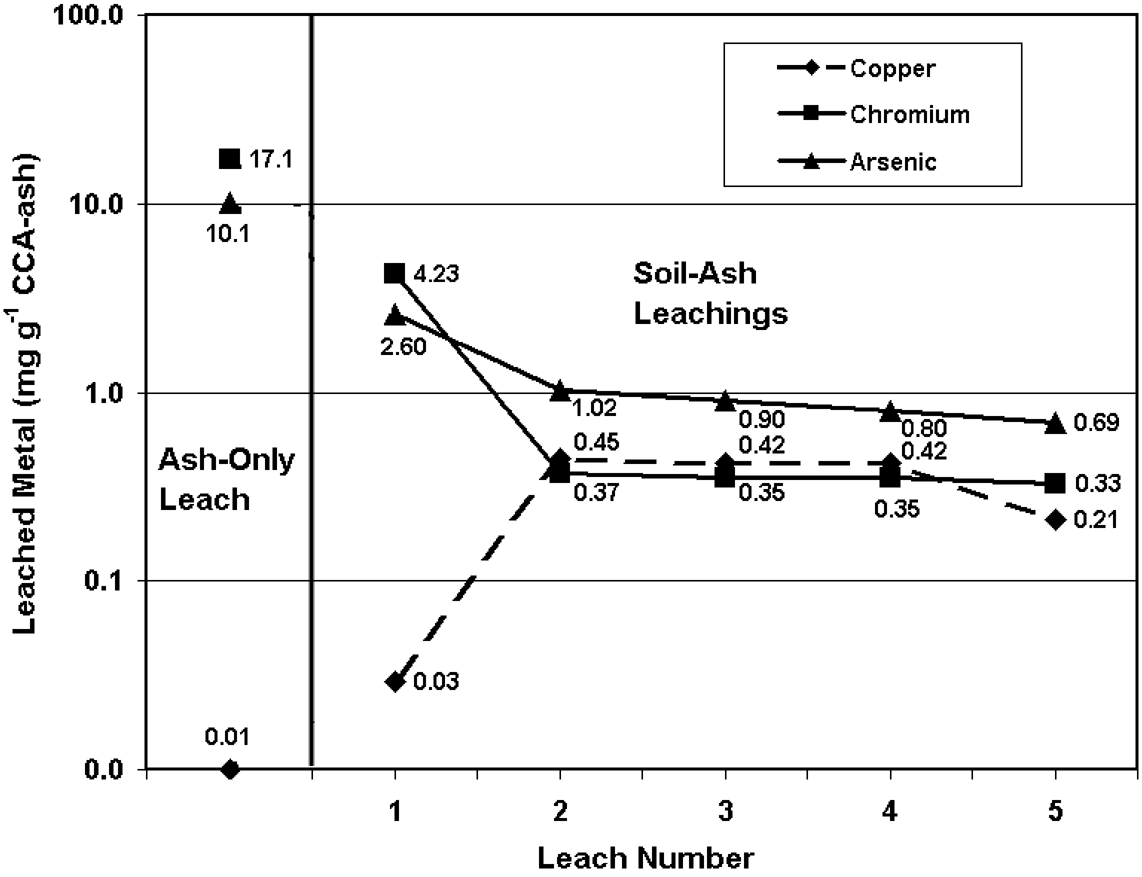


Figure 8.1- Impact of Unamended Soil on the Rainwater-leaching of CCA-metals

<u>Mass Transfer Mechanisms</u>

The retardance of Cr and As by mixing CCA-ash with soil is likely due to adsorption of Cr and As to the mineral components of the kaolinitic clay, organics in the soil, and the presence of Al and Fe oxides which may lower the CCA-metals mobility during the first leach of soil/CCA-ash mixture compared to the leach of CCA-ash alone (Evanko and Dzombak, 1997; Manning and Goldberg, 1997). As supported by Stollenwerk and Grove (1985), describing nonspecific adsorption, Cr had the largest leached mass during the first leach of soil/CCA-ash mixture 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 this mobile organic matter from the soil, an increased mass of Cu leaches from the soil/CCA-ash mixture. During this depletion, release of Cu from surface adsorption sites in the soil decreases and release from inner-sphere adsorption sites becomes the dominant mechanism of Cu mobility as supported by Tipping et al., 1983; Davis, 1984; and Lehmann and Harter, 1984.

8.3.2 Batch Rainwater-leaching of Unamended (Control) and Gypsum-amended (Gypsum) Soil/CCA-ash Mixtures

Figures 8.2a, 8.2b, and 8.2c show the relative retardance of Cr, As, and Cu resulting from the addition of the gypsum amendment to the soil/CCA-ash mixture during the batch rainwater-leaching. Figure 8.2a shows that, although amendment with gypsum results in an overall retardance of Cr mobility, both the Control and Gypsum mixtures have an initial large leaching of Cr followed by a depletion of mobile Cr in successive leachings.

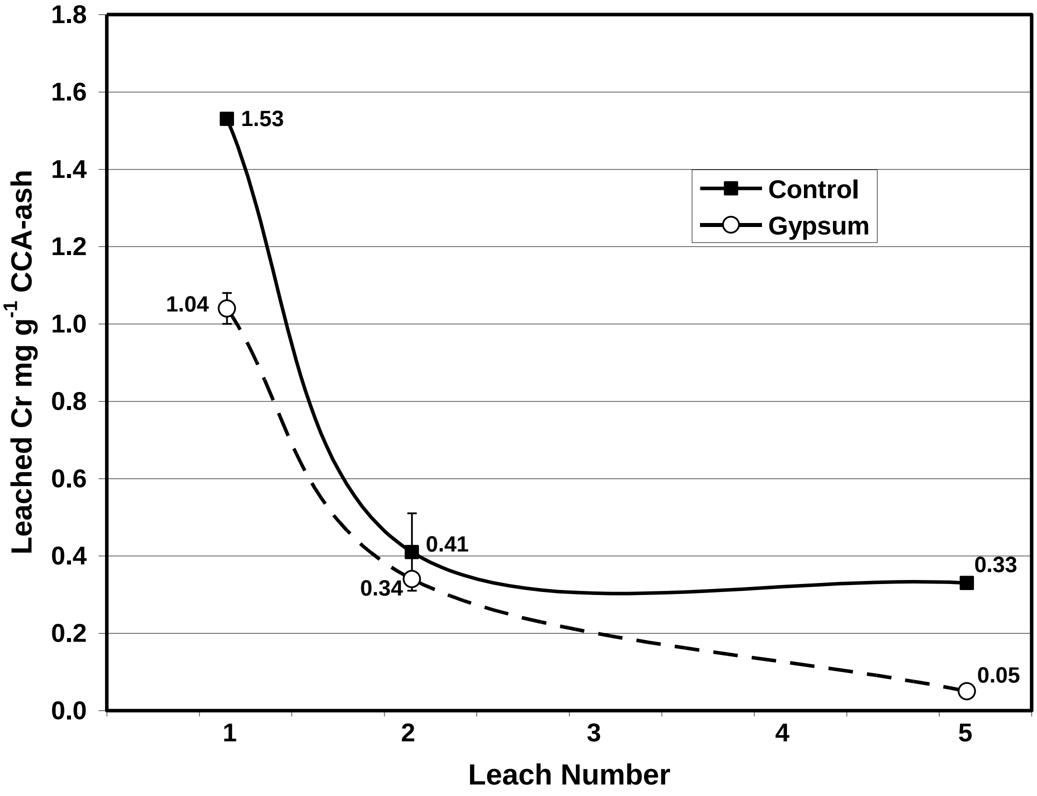


Figure 8.2a - Cr Batch-leached from Control and Gypsum-amended Soil/CCA-ash (with error bars)

Figure 8.2b shows that the Gypsum-amended soil/CCA-ash exhibits an overall trend for retardance of As leaching compared to the Control.

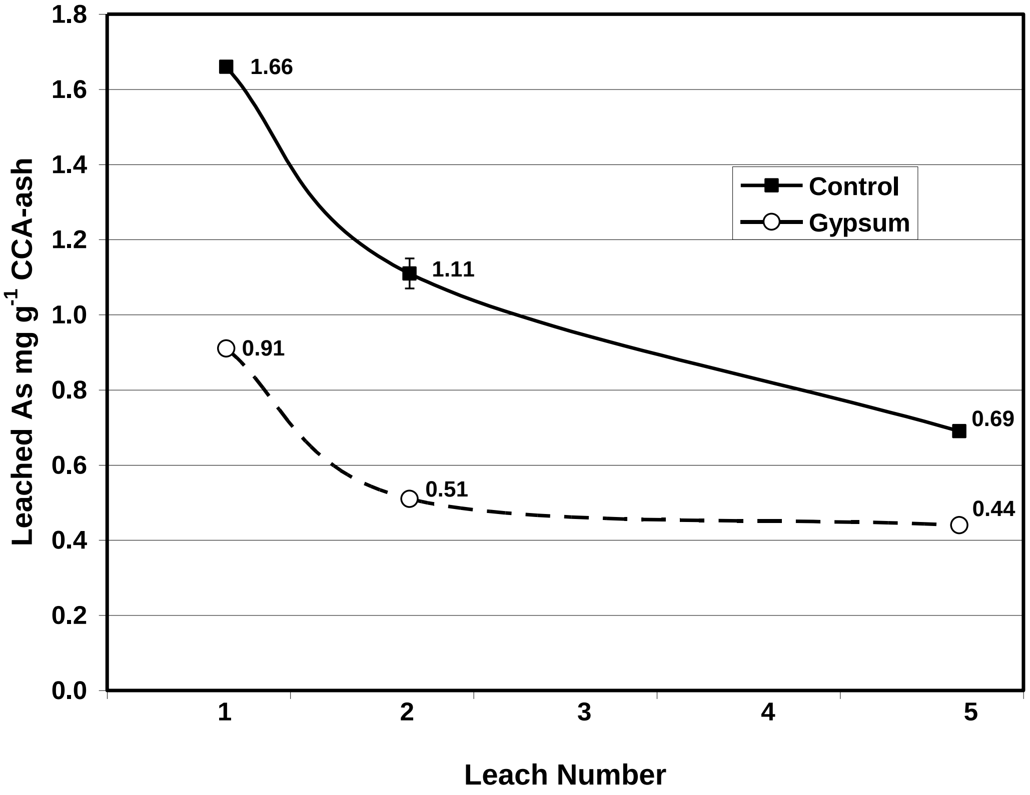


Figure 8.2b - As Batch-leached from Control and Gypsum-amended Soil/CCA-ash (with error bars)

Figure 8.2c shows that Cu mobility is high in the Control due to binding with mobile colloids while the Gypsum exhibits a high degree of retardance of Cu probably due to increased flocculation of colloids or binding of Cu to soil components.

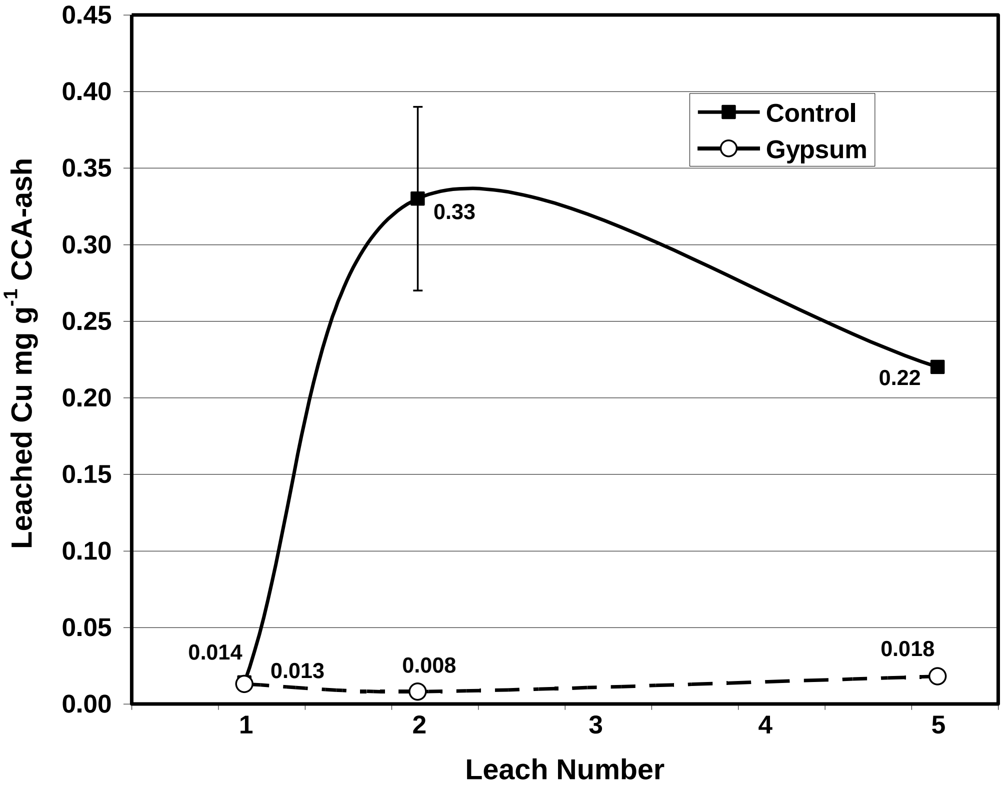


Figure 8.2c - Cu Batch-leached from Control and Gypsum-amended Soil/CCA-ash (with error bars)

8.3.3 Gypsum Optimization Study

A batch leach study was performed to determine a potential stoichiometric or optimum mass ratio of gypsum:CCA-ash needed to reduce the leaching of Cu, Cr, and As from a known mass of the CCA-metals in a soil/CCA-ash mixture. This study used duplicate 100 mL acid-washed bottles and a 10 mL deionized water leaching of the soil/CCA-ash and soil/CCA-ash with various mass ratios of gypsum:CCA-metals.

Each soil/CCA-ash sample used in the optimization study contained 19.6 mg total mass of Cu, Cr, and As. The sample was leached with deionized water and the resulting leached mass of each metal was plotted versus gypsum mass additions of 0, 25, 100 and 400 mg per 485 mg of soil/CCA-ash mixture which contained 85.4 mg CCA-ash equivalent to 19.6 mg CCA metals. Figure 8.3 compares the effect upon leaching of metals by the addition of gypsum in mass ratios of 1:1, 4:1, and 16:1 to the mass of total CCA-metals present in the soil/CCA-ash sample. The changes in the slopes of the Cr and As curves indicate that a gypsum addition ratio in the range of 1:1 to 4:1 should be most reasonable and effective. Over the 1:1 to 4:1 range, the Cr curve has a uniformly steep slope indicating Cr retardance while the As curve has its maximum slope at the 1:1 ratio with a lesser, but uniform slope, toward the 4:1 ratio. Amendment with gypsum supplies Ca^{+2} cations to the soil solution that increase the concentration of surface adsorbed calcium ions. This increased calcium adsorption produces greater complexation, surface adsorption, and precipitation of As and Cr anions. The small increase in leaching of Cu^{+2} cations and Cu hydroxyl complexes results from the competition of Ca^{+2} cations for tightly held surface and inner-sphere adsorption sites on clay and organic material in the soil (Lehmann and Harter, 1984; Dzombak and Morel, 1990). Further decrease in the leaching of Cr and As at the 400 mg of gypsum addition is most likely due to a dilution effect of the increased amount of solute in the system and the saturation of Ca^{+2} cations in the adsorption mechanism of the soil clays. This saturation at adsorption sites also contributes to an increased leaching of Cu. The smaller magnitude but continued reduction in mobility of Cr and As over the 4:1 to 16:1 ratio range does not justify the increase in mobility of Cu.

From Figure 8.3 it is noted that the Cu leached mass is not distinctly different between the samples with 0, 25, and 100 mg of gypsum addition. The 400 mg gypsum addition samples leached a greater mass of Cu and are distinctly different from the other samples with gypsum. It is also noted that the 0 and 25 mg gypsum addition samples have the same magnitude of Cr mass leaching. The samples with 100 and 400 mg of gypsum addition are distinctly different from each other and the 0 and 25 mg addition samples.

The data for As leached mass is distinctly different between the 0, 25, 100, and 400 mg gypsum addition samples. The data shows that the 1:1 to 4:1 ratios of addition of gypsum will be the most efficient addition range with 3:1 being the optimum ratio. The 1:1 to 4:1 ratios that exhibit the range of percent reductions in Cr (+3 % to -19%) and As (-33% to - 45%) are significant while still maintaining a dominant soil environment. Beyond the 4:1 addition ratio Cu begins to leach at unacceptably high levels (+700%).

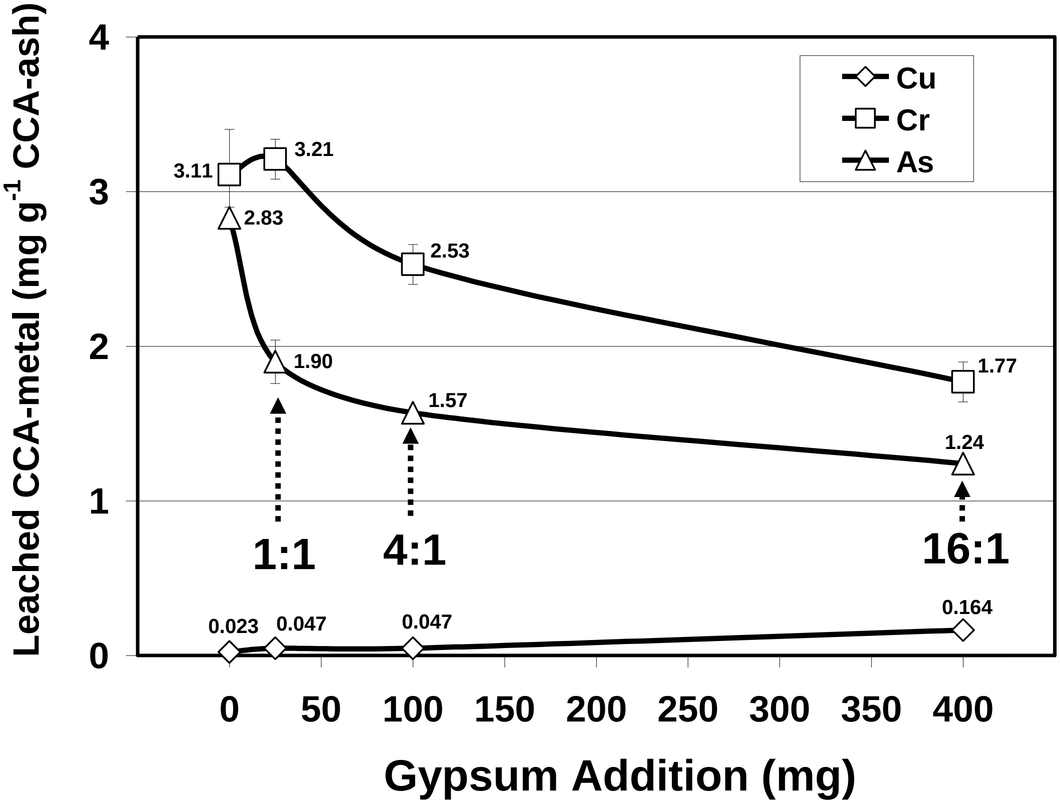


Figure 8.3 - Gypsum Optimization Study – Metal Mass vs Mass Gypsum Addition (with error bars)

8.3.4 Column Rainwater-leaching of Gypsum-amended and Unamended Soil/CCA-ash Mixtures

The pH conditions in soil are very important to the rainwater-leaching mobility of soil components and metal ions. In this research, column study pH is affected only slightly by the addition of gypsum amendment. The soil/CCA-ash column ranged from pH 7.6-8.0 while the soil/CCA-ash/gypsum amendment column ranged from pH 7.3-8.0.

Evaluation of Gypsum Amendment Performance

Using metals leaching data and data generated by interpolating between analyses leach data a projection of the effect of the gypsum amendment upon the leaching of metals over a one-year period of rainfall was performed. The results are presented in Figures 8.4a (Cr), 8.4b (As), and 8.4c (Cu), the graphic presentations of the Simulated One-Year Leach of Cr, As, and Cu – Control vs Gypsum Amendment. These projections extend to 1845 mL of rainwater, the equivalent of 19 rainfall events or one year of rainfall (130 cm.) at the burn site.

The data and Figure 8.4a show that Cr leaches the highest mass over the short-term and is greatly retarded by the Gypsum amendment (open squares) compared to the Control mixture (filled squares). Over the pH range of 7.6-8.0 the dominant Cr(III) reaction involves hydrolysis of chromium to sparsely soluble chromium hydroxides, strong adsorption to mineral and organic surfaces, and coprecipitation with other minerals (Hug et al., 1997). Gypsum addition to the soil system enhances the mechanisms whereby hydroxyl radical concentrations are increased in the soil solution resulting in increased precipitation of chromium hydroxides (Harden, 2005).

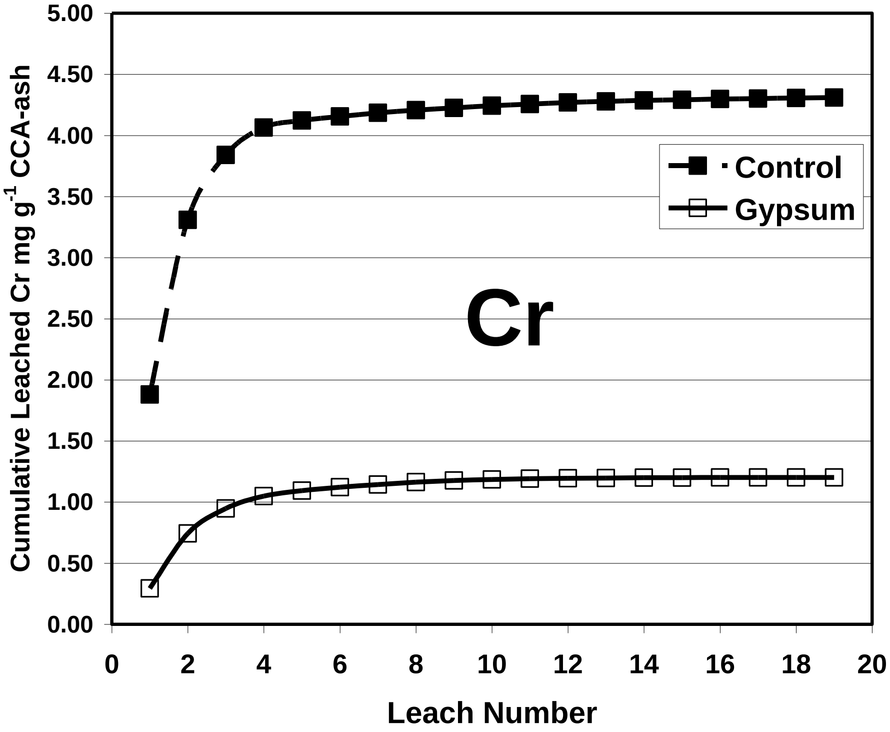


Figure 8.4a - Simulated One-Year Mass Leach of Cr – Control vs Gypsum Amendment

The data and Figure 8.4b support the conclusion that As mass leaching in the Control mixture (filled triangles) is high in the short-term and significant in the long-term, and that the Gypsum amendment (open triangles) produces significant reductions in both short-term and long-term As leaching as evidenced by the linear nature of the curve representing cumulative leaching of arsenic. This mechanism is evidence of the uniform release of leached arsenic after amendment with gypsum and is indicative of two mechanisms which have immobilized arsenic. In the first mechanism, Su and Puls (2001) explain the adsorption of arsenic in terms of both ionization of adsorbates and adsorbents which reaches a maximum adsorption at pH 7 for As(III) and for As(V) at pH <8.5. Amendment with gypsum increases the ionization of adsorption surfaces resulting in increased adsorption and coprecipitation mechanisms (Harden, 2005). In the second and associated mechanism, amendment with gypsum results in the coprecipitation and precipitation of sparsely soluble calcium arsenates (Magalhaes, 2002).

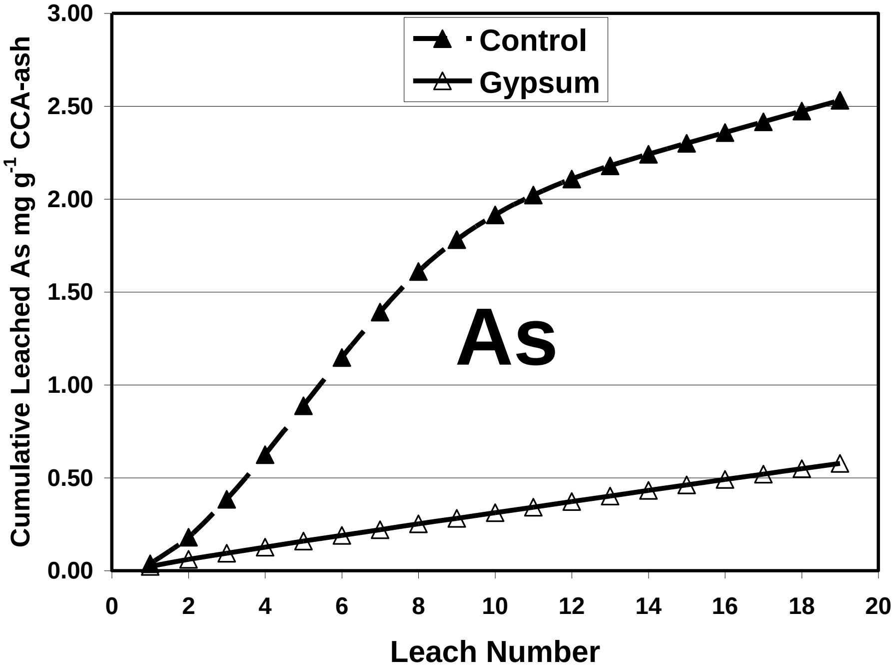


Figure 8.4b - Simulated One-Year Mass Leach of As – Control vs Gypsum Amendment

The data and Figure 8.4c show that Gypsum amendment (open diamonds) will produce greater Cu leaching in the short-term compared to the Control (filled diamonds).

The increased mobility of Cu in the Gypsum combination results from Ca^{+2} ions competing with Cu^{+2} ions at adsorption sites and the increased rate of depletion of Cu-bound mobile organic material as supported by the literature (Lehmann and Harter, 1984; Amrhein, et al., 1992; Evanko and Dzombak, 1997). The increased mobility due to the gypsum amendment of the column study is directly opposite of the finding of retardance of mobility due to addition of gypsum in the batch study. This anomaly will be covered in greater detail in 3.5 Comparison of Leachate Concentrations of Column and Batch Studies.

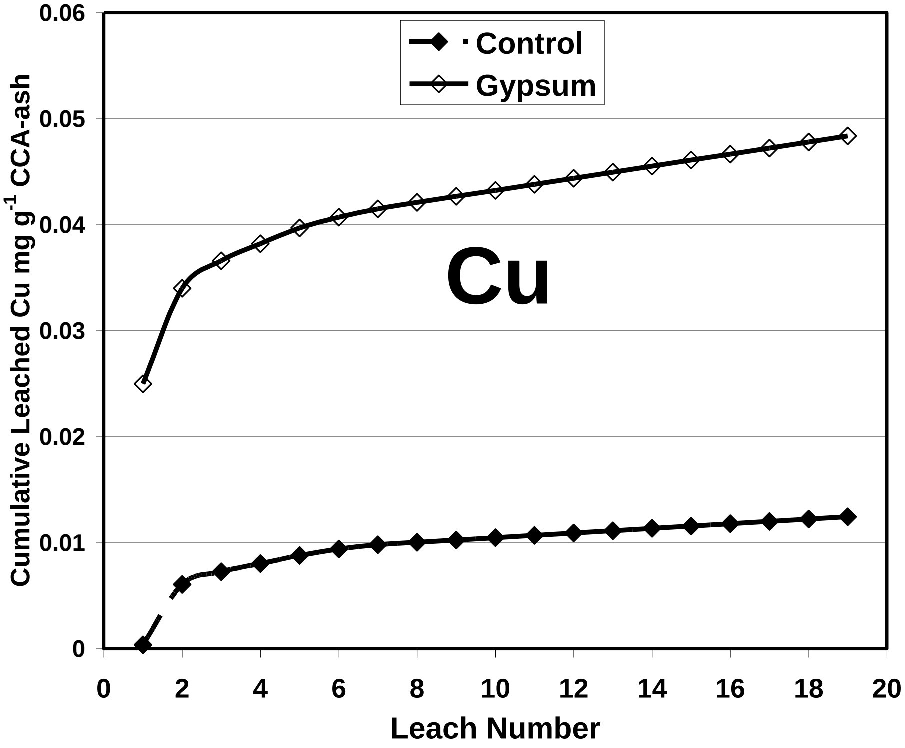


Figure 8.4c - Simulated One-Year Mass Leach of Cu – Control vs Gypsum Amendment

The simulated one-year cumulative mass leach of metals (mg/g) from the soil/CCA-ash without amendment is as follows: Cu, 0.012; Cr, 4.31; As, 2.53. The resulting simulated one-year cumulative mass leach of metals (mg/g) from the soil/CCA-ash with gypsum amendment is as follows: Cu, 0.048; Cr, 1.20; As, 0.578. Note 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 leached metal.

8.3.5 Comparison of Leachate Concentrations of Column and Batch Studies

Figure 8.5a shows that As leachate concentrations from the large CCA-ash mass Control column of the column study were very high (40.6 to 128 mg/L) while the As leachate concentrations in the Gypsum column were greatly retarded (24.6 to 15.8 mg/L). The Gypsum column leachate As concentrations followed the same As concentration trend as the batch study with the Control-Batch As concentration being equal to the Gypsum-Column and the Batch-Gypsum As concentration being retarded.

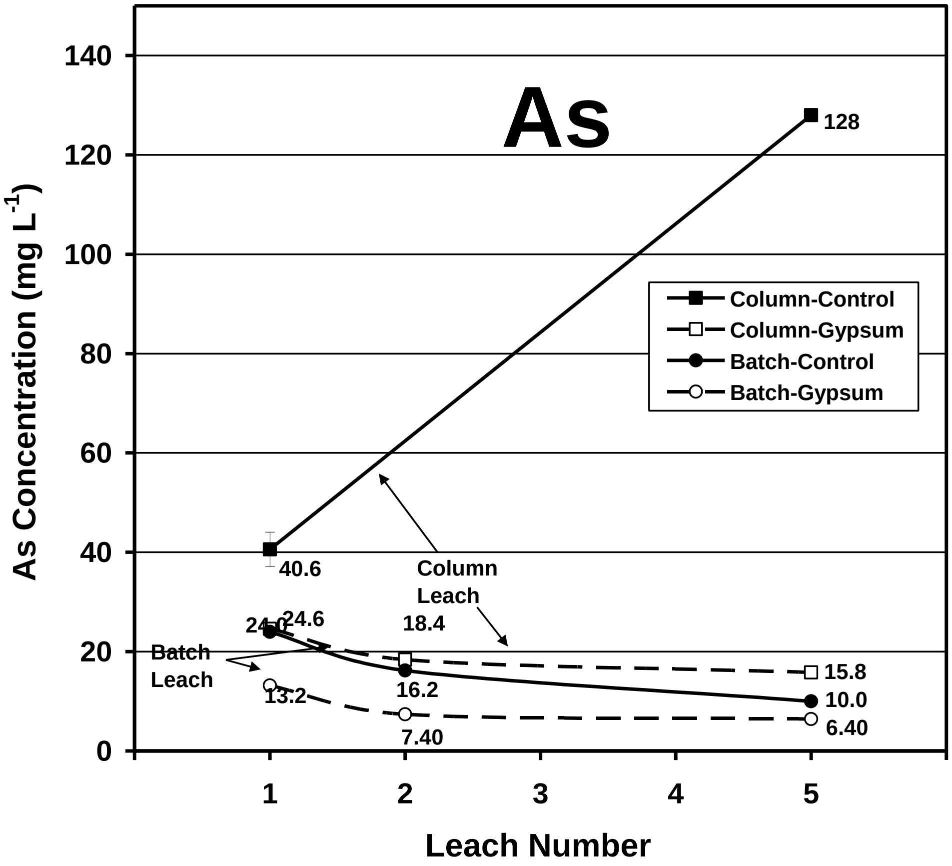


Figure 8.5a - As Leachate Concentrations of Column and Batch Studies

Figure 8.5b shows that the Cr leachate concentrations of the Column and Batch studies exhibit the same leaching trend with the concentrations being two orders of magnitude higher in the Column study compared to the Batch study. The high Cr concentration of the Column-Control shows a large concentration decrease in response to gypsum amendment (Column-Gypsum).

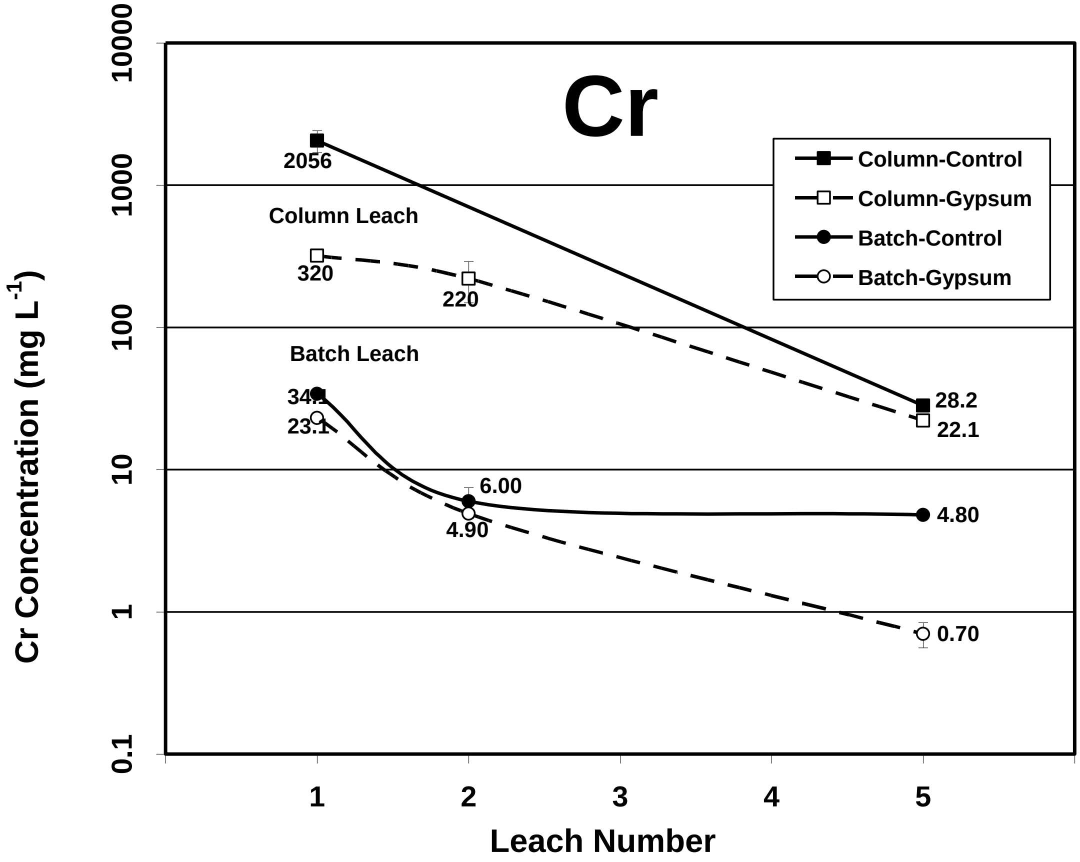


Figure 8.5b - Cr Leachate Concentrations of Column and Batch Studies

Figure 8.5c shows a Cu concentration anomaly between the Column and Batch studies. The Column-Control data shows a uniform Cu concentration (0.39 to 0.27 mg/L) while the Column-Gypsum data shows a relatively large Cu concentration in the initial leach (27.6 mg/L). In contrast, the Cu concentration trend of the Batch-Control shows a large increase while the Batch-Gypsum shows a Cu concentration decrease.

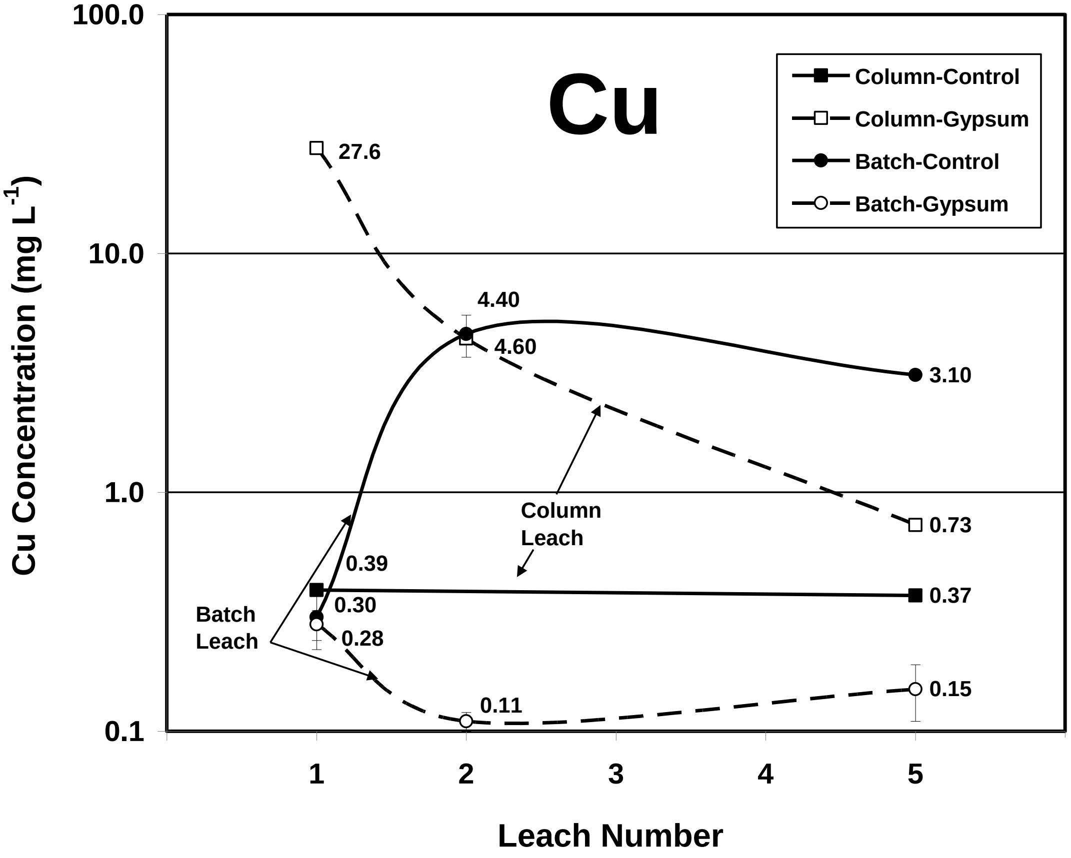


Figure 8.5c - Cu Leachate Concentrations of Column and Batch Studies

The Cu retardance anomaly between the Batch and Column studies is highly influenced by the solids to liquid ratios of each study. Table 8.1 shows that the solid:liquid ratio of the Column study is much higher than that of the Batch study. Under the Batch study conditions, gypsum is effectively retarding Cu mobility by increased flocculation and adsorption to soil particle surfaces while gypsum in the Column study is forcing adsorbed Cu from adsorption sites in the soil due to increased competition from Ca^{+2} ions.

Table 8.1 - Column and Batch Study Experimental Media Ratios

Column Leach	Soil	Gypsum	CCA-ash
	231g	68g	40g
Solids Ratio (to ash)	4.7	1.4	1
Solid:Liquid Ratio 3.4:1 100mL Leachate			
Batch Leach	Soil	Gypsum	CCA-ash
	4.125g	1.00g	0.725g
Solids Ratio (to ash)	5.7	1.4	1
Solid:Liquid Ratio 0.06:1 100mL Leachate			

8.4 Conclusions

The use of gypsum 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 leaching from CCA-ash at CCA-treated wood burn sites.

Unamended soil/CCA-ash mixtures exhibit the potential for retardance of CCA-metals during rainwater-leaching through natural attenuation compared to the rainwater-leaching of CCA-ash alone.

Gypsum amendment of a soil/CCA-ash mixture in a leaching column had little effect or increased the Cu mobility over CCA-ash alone. Gypsum amendment of soil/CCA-ash mixtures reduced As mobility up to 77% and Cr mobility by up to 72% over the unamended soil/CCA-ash mixture. Gypsum as a reactive soil amendment for the treatment of soils containing Cr and As metals results in reduction of CCA-metals mobility, approaching 80% compared to unamended soil/CCA-ash mixtures over a simulated one-year rainwater-leaching period.

Gypsum amendment was shown to retard the mobility of Cu in a batch study while increasing the mobility of Cu in a simulated one-year rainwater-leaching study.

An gypsum optimization study revealed that a ratio of 3:1 of gypsum to CCA-metals mass was most effective in reducing the mobility of Cr and As metals. Use of a higher ratio would serve as a source for Ca^{+2} ions and should guarantee long-term stabilization while maintaining the pH in the 7.3-8.0 range.

Acknowledgment

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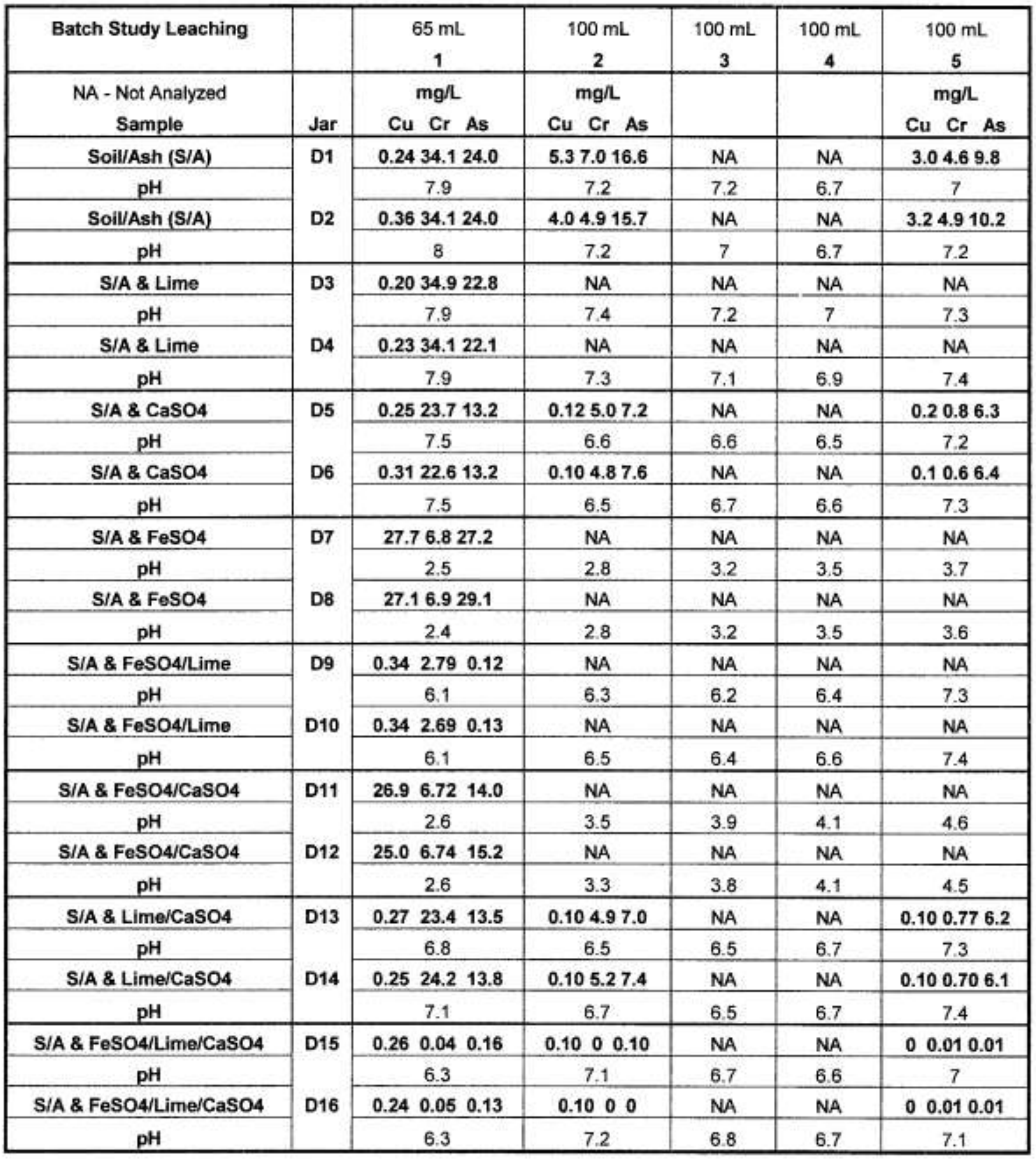
APPENDIX VIII-A

VIII-A-1 – Data for Impact of Unamended Soil on the Rainwater-leaching of CCA-metals

Batch Leach Data	**Cu** mg g^{-1} CCA-ash	**Cr** mg g^{-1} CCA-ash	**As** mg g^{-1} CCA-ash
CCA-Ash Leach			
3-20-02-4	0.010	17.2	10.5
3-20-02-5	0.010	16.4	9.90
3-20-02-6	0.010	17.7	10.1
Mean	**0.010**	**17.1**	**10.1**
Standard Deviation	0.000	0.66	0.31
Coefficient Variation (%)	0.00	3.9	3.1
Confidence Interval 95%	0.010±0.000	17.1±1.63	10.1±0.80
Test Soil/CCA-Ash Leach			
3-18-02-1	0.032	4.23	2.70
3-18-02-2	0.026	4.10	2.53
3-18-02-3	0.028	4.34	2.57
Mean	**0.029**	**4.23**	**2.60**
Standard Deviation	0.003	0.12	0.09
Coefficient Variation (%)	10.3	2.8	3.5
Confidence Interval 95%	0.029±0.007	4.23±0.29	2.60±0.22
Test Soil/CCA-Ash Releach (2)			
3-20-02-1	0.345	0.38	0.76
3-20-02-2	0.379	0.28	0.97
3-20-02-3	0.621	0.45	1.35
Mean	**0.448**	**0.37**	**1.02**
Standard Deviation	0.150	0.09	0.30
Coefficient Variation (%)	33.5	24.3	29.4
Confidence Interval 95%	0.448±0.374	0.37±0.22	1.02±0.74
Test Soil/CCA-Ash Releach (3)	Interpolated from chart		
Test Soil/CCA-Ash Releach (4)	Interpolated from chart		
Test Soil/CCA-Ash Releach (5)			
3-20-02-1	0.207	0.32	0.68
3-20-02-2	NA	NA	NA
3-20-02-3	0.221	0.34	0.70
Mean	**0.214**	**0.33**	**0.69**
Standard Deviation	0.010	0.02	0.02
Coefficient Variation (%)	4.7	6.1	1.4
Confidence Interval 95%	0.214±0.010	0.33±0.03	0.69±0.03

VIII-A-2 – Batch Study Leaching Data including Batch Rainwater-Leaching of Unamended(Control) and Gypsum-Amended (Gypsum) Soil/CCA-ash Mixtures



Batch Study Leaching		65 mL 1	100 mL 2	100 mL 3	100 mL 4	100 mL 5
NA - Not Analyzed Sample	Jar	mg/L Cu Cr As	mg/L Cu Cr As			mg/L Cu Cr As
Soil/Ash (S/A)	D1	0.24 34.1 24.0	5.3 7.0 16.6	NA	NA	3.0 4.6 9.8
pH		7.9	7.2	7.2	6.7	7
Soil/Ash (S/A)	D2	0.36 34.1 24.0	4.0 4.9 15.7	NA	NA	3.2 4.9 10.2
pH		8	7.2	7	6.7	7.2
S/A & Lime	D3	0.20 34.9 22.8	NA	NA	NA	NA
pH		7.9	7.4	7.2	7	7.3
S/A & Lime	D4	0.23 34.1 22.1	NA	NA	NA	NA
pH		7.9	7.3	7.1	6.9	7.4
S/A & CaSO4	D5	0.25 23.7 13.2	0.12 5.0 7.2	NA	NA	0.2 0.8 6.3
pH		7.5	6.6	6.6	6.5	7.2
S/A & CaSO4	D6	0.31 22.6 13.2	0.10 4.8 7.6	NA	NA	0.1 0.6 6.4
pH		7.5	6.5	6.7	6.6	7.3
S/A & FeSO4	D7	27.7 6.8 27.2	NA	NA	NA	NA
pH		2.5	2.8	3.2	3.5	3.7
S/A & FeSO4	D8	27.1 6.9 29.1	NA	NA	NA	NA
pH		2.4	2.8	3.2	3.5	3.6
S/A & FeSO4/Lime	D9	0.34 2.79 0.12	NA	NA	NA	NA
pH		6.1	6.3	6.2	6.4	7.3
S/A & FeSO4/Lime	D10	0.34 2.69 0.13	NA	NA	NA	NA
pH		6.1	6.5	6.4	6.6	7.4
S/A & FeSO4/CaSO4	D11	26.9 6.72 14.0	NA	NA	NA	NA
pH		2.6	3.5	3.9	4.1	4.6
S/A & FeSO4/CaSO4	D12	25.0 6.74 15.2	NA	NA	NA	NA
pH		2.6	3.3	3.8	4.1	4.5
S/A & Lime/CaSO4	D13	0.27 23.4 13.5	0.10 4.9 7.0	NA	NA	0.10 0.77 6.2
pH		6.8	6.5	6.5	6.7	7.3
S/A & Lime/CaSO4	D14	0.25 24.2 13.8	0.10 5.2 7.4	NA	NA	0.10 0.70 6.1
pH		7.1	6.7	6.5	6.7	7.4
S/A & FeSO4/Lime/CaSO4	D15	0.26 0.04 0.16	0.10 0 0.10	NA	NA	0 0.01 0.01
pH		6.3	7.1	6.7	6.6	7
S/A & FeSO4/Lime/CaSO4	D16	0.24 0.05 0.13	0.10 0 0	NA	NA	0 0.01 0.01
pH		6.3	7.2	6.8	6.7	7.1

VIII-A-3 – Data for Gypsum Optimization Study

Gypsum (mg)	Cu* (mg g^{-1} CCA-ash)	Percent Change	Cr* (mg g^{-1} CCA-ash)	Percent Change	As* (mg g^{-1} CCA-ash)	Percent Change
0	0.023 ± 0		3.11 ± 0.293		2.83 ± 0.070	
25	0.047 ± 0.023	0	3.21 ± 0.129	3	1.90 ± 0.141	-33
100	0.047 ± 0.023	0	2.53 ± 0.129	-19	1.57 ± 0.012	-45
400	0.164 ± 0.012	700	1.77 ± 0.129	-43	1.24 ± 0.012	-56

* Duplicate samples

VIII-A-4 – Data for Column Rainwater-Leaching of Gypsum-Amended andUnamendedSoil/CCA-Ash Mixtures

	Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment																			
	(Bold numbers are measured data, standard numbers are extraplolated data)																			
	Leach Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Cummulative Volume (mL)	45	145	245	345	445	545	645	745	845	945	1045	1145	1245	1345	1445	1545	1645	1745	1845
	Mass = mg																			
Cu	**Soil/Ash (S/A)**	**0.018**	0.279	0.060	0.037	**0.037**	0.030	0.020	0.011	**0.011**	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
	S/A-CaSO$_4$	**1.24**	**0.440**	0.130	0.080	**0.073**	0.050	0.040	0.030	**0.028**	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	**0.028**
Cr	**Soil/Ash (S/A)**	**92.5**	70.0	26.0	11.0	**2.82**	1.60	1.50	1.00	**0.950**	0.950	0.630	0.630	0.416	0.416	0.274	0.274	0.181	0.181	0.181
	S/A-CaSO$_4$	**14.4**	**22.0**	10.0	5.00	**2.21**	1.30	1.10	1.00	**0.635**	0.042	0.277	0.183	0.120	0.080	0.052	0.035	0.010	0.010	**0.010**
As	**Soil/Ash (S/A)**	**1.83**	7.00	10.0	11.8	**12.9**	12.7	12.0	10.7	**8.43**	6.50	5.25	4.20	3.50	3.05	2.90	2.85	2.85	2.80	2.80
	S/A-CaSO$_4$	**1.11**	**1.84**	1.60	1.60	**1.58**	1.50	1.50	1.50	**1.46**	1.46	1.46	1.46	1.46	1.46	1.46	1.42	1.42	1.42	**1.42**

VIII-A-5 – Data for Comparison of Leachate Concentrations of Column and Batch Studies

Batch Leach	**Mixture**	**#1**	**#2**	**#5**
Cr	Control	34.1±0	6.00±1.48	4.80±0.21
(mg L^{-1})	Gypsum	23.1±0.78	4.90±0.14	0.70±0.14
As	Control	24.0±0	16.2±0.63	10.0±0.28
(mg L^{-1})	Gypsum	13.2±0	7.40±0.28	6.40±0.07
Cu	Control	0.30±0.08	4.60±0.92	3.10±0.14
(mg L^{-1})	Gypsum	0.28±0.04	0.11±0.01	0.15±0.07
Column Leach	**Mixture**	**#1**	**#2**	**#5**
Cr	Control	2056±360	NA	28.2±2.05
(mg L^{-1})	Gypsum	320±9.5	220±71	22.1±0.35
As	Control	40.6±3.46	NA	128±2.12
(mg L^{-1})	Gypsum	24.6±0.35	18.4±0.84	15.8±0.64
Cu	Control	0.39±0	NA	0.37±0.01
(mg L^{-1})	Gypsum	27.6±0.91	4.40±0	0.73±0.04

CHAPTER IX

MASS TRANSFER MECHANISMS OF GYPSUM RETARDANCE OF RAINWATER-LEACHED METALS FROM CCA-WOOD ASH IN SOIL

Abstract

Copper, chromium, and arsenic metals are highly concentrated in the ash produced from the burning of wood treated with chromated copper arsenate (CCA) preservative. Leaching of these metals from CCA-wood burn sites can produce soil and water contamination. Soils have varying natural abilities to reduce leaching and they also impact metals speciation and toxicity, through sorption, conversion and sedimentation related mechanisms. Therefore, enhancing the efficiency of these mechanisms may be an important approach to the remediation of these metals at ash contaminated locations.

This study evaluated the performance of using a gypsum soil amendment ($CaSO_4 \cdot 2H_2O$) to immobilize or retard the leaching of high concentrations of Cu, Cr, and As species in a soil/CCA-wood ash mixture, and reports the various retardation mechanisms operating in the soil system. Results of this investigation show that native soil alone retards the mobility of As and Cr, while the gypsum amendment application further retards metal mobility when compared to the unmodified soil/CCA-wood ash mixture. The gypsum soil amendment is very effective in reducing the rainwater-leaching of Cr and As from the CCA-wood ash in soil by reducing the mobility of these metals by 72% and 77%, respectively, compared to the soil/CCA-wood ash mixture alone. However, Cu mobility is increased when the CCA-ash is mixed with the soil and when the mixture is amended with gypsum.

A mechanistic pathway diagram was developed for this paper as an aid to explain the retardance processes affecting the mobility of CCA-metals in a soil/CCA-wood ash/soil solution system containing kaolinitic clay, Fe and Al oxides, and organic carbon material as the major reactive soil components. This pathway diagram fit the synergistic conditions of the multiple soil components and mechanisms of the system being studied.

Keywords: Arsenic, Chromium, Copper, Retardance, Sorption, CCA-treated wood ash

9.1 Introduction

Chromium and arsenic metals make their way into the soil and water environments from both anthropogenic sources (mining, agriculture, coal burning, wood preservation) and natural occurrences (weathering of metal-bearing minerals). Wood treated with chromated copper arsenate (CCA) preservative has been a major source for the introduction of these metals into the residential setting and potentially into the soil and water environments.

Increasing quantities of used CCA-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 (Cooper, 1993; McQueen and Stevens, 1998; Clausen, 2000; Wu, 2000); a ban on future CCA-wood use in domestic settings (Federal Register, 2003) and an associated increased public awareness of health concerns related to CCA-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-wood by onsite burning, producing an ash that poses a potential threat to humans and the environment (Solo-Gabriele et al, 1999).

Low levels of these compounds have been long recognized as causing environmental problems. At the $\mu g\ L^{-1}$ 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 (Winner, 1984; Korte and Fernando, 1991; LaGrega et al., 1994; Palmer and Puls, 1994; Raven et al., 1998; Solo-Gabriele et al., 1999).

The ash remaining after the burning of CCA-wood is a source of heavy metals, primarily Cu, Cr and As, that may enter the environment (Polandt et al., 1993; Solo-Gabriele et al., 2002; Lida et al., 2004). A previous study by Harden (2005) established that CCA-wood ash is composed of approximately one-quarter by mass of CCA-metals, with the mass of Cu, Cr, and As each approximately one-third of the total mass of CCA-metals . The study also found that Cr in a CCA-metals/Ultisol soil mixture was the most leached by rainwater, followed by As, with Cu being the least mobile at significantly lower leachate concentrations**.** Additionally, the previous study found that As and Cr mobility was reduced by 75% compared to the CCA-wood ash alone when the CCA-wood ash was mixed with an Ultisol soil, evidence of the natural attenuation of metals mobility by a soil.

The oxidation states of arsenic and chromium species exhibit a significant influence on the mobility of the metals. Combustion conditions of temperature and oxygen supply during the burning of CCA-wood can effect the Cr speciation in the CCA-wood ash with a portion of the predominant Cr(III) converting to the much more toxic Cr(VI) form (Helsen et al., 2003). The resulting ash, although still largely Cr(III), will have varying Cr(VI) concentrations influenced by the degree of the initial CCA-treatment of the wood, along with the combustion conditions. Resulting Cr(VI) ash content ranging from 4 to 7% has been reported by Song et al., (2006). The Cr(VI) species, besides being more toxic, is also more soluble and therefore more mobile in the environment compared to Cr(III).

Arsenic species in CCA-wood ash are both the more toxic As(III) and the less toxic As(V), with As(III) being more soluble and mobile in the environment. The As(V) species is found in the CCA-wood and after pyrolysis of the scrap wood (thermochemical decomposition at an elevated temperatures in the absence of oxygen), some of the As(V) is converted to the As(III) species in the CCA-wood ash (Helsen et al., 2003).

Copper, in the form of CuO, is dissolved in an acidic solution (chromic acid) with arsenic pentoxide to produce the CCA-treatment solution (Solo-Gabriele, et al., 1999). The CCA-wood ash resulting from the burned CCA-wood has almost all copper present in the form of CuO, which has been found by Palmer and Benezeth (2004) to be very sparsely water-soluble at 25˚ C.

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 within a soil system can change these metals to more or less toxic and available metal species (NRC, 1994). Song et al, (2006) showed significant reduction of Cr(VI) to Cr(III) when mixed with soil and Georgiadis et al (2006) noted the potential oxidation of As(III) to As(V) in soil. The resulting interaction of CCA-wood ash and its CCA-metal species with soil is a complex system. 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 (US EPA, 1992; Evanko and Dzombak, 1997). A significant problem occurs when high concentrations of metals at 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 effectiveness of a soil amendment to immobilize and retard CCA-metal species using gypsum soil softener ($CaSO_4 \cdot 2H_2O$) was studied as part of this research. This soil amendment was chosen due to availability, current application as a soil supplement, and potential to enhance chemical reactions that reduce the mobility of metal species within the soil. A CCA-wood burn site in Tuscaloosa County, Alabama was previously investigated to determine baseline conditions and obtain data for a laboratory study (Harden, 2005). Ultisol soil/CCA-wood ash burn site conditions were then replicated under laboratory conditions using batch and soil column leaching studies and pH studies. According to the University of Idaho, Ultisol soils are strongly leached, acidic forest soils having relatively low fertility. They are found primarily in humid temperate and tropical areas of the world. Intense weathering of the primary minerals has occurred, and much of the Ca, Mg, and K have been leached. Ultisol soils have a subsurface horizon in which clays have accumulated, often with strong yellowish or reddish colors resulting from the presence of Fe oxides. The red clay soils of the southeastern United States are examples of Ultisol soils (http://soils.cals.uidaho.edu/soilorders/ultisols.htm).

The results of this laboratory study were incorporated into the study of the surface complexation and surface precipitation mechanisms of the CCA-wood ash/Ultisol soil system in order to support the hypothesized mechanisms whereby gypsum retarded the mobility of Cr and As species. The soil system mechanisms describe the retardance of CCA-metals in an Ultisol soil/CCA-wood ash/soil solution system containing kaolinitic clay, Fe and Al oxides, and organic carbon material. These surface complexation and surface precipitation mechanisms fit the synergistic conditions of the multiple components and reactions within the system and support the mobility retardance hierarchy of Cr > As > Cu species reported by Harden (2005).

Several notable studies have been reported specifically related to CCA-contamination of soil. Among these are articles concerning the influence of soil composition (Balasoiu, et al., 2001) and a review of published journal articles concerning the stabilization of As, Cr, and Cu in soil by amendments (Kumpiene, et al., 2008). To our knowledge, there has not been published a detailed study of the retardance mechanisms and effectiveness of the stabilization of high concentrations of CCA-ash in soil by the use of gypsum amendments.

The study of soil systems containing waste materials are important areas of investigation that may reveal pathways to the formulation of new, efficient, and cost-effective means of retardance of the mobility of waste materials in soil. The use of literature or laboratory data that do not reproduce the specific soil and waste system of the site will not be adequate to describe or predict the behavior of the metals. Data must be site specific and the long-term effects of the association of the waste components must also be considered, therefore this study reproduced site specific conditions in the laboratory and followed the long-term effects of the association of Cu, Cr, and As rainwater-leaching from an Ultisol soil/CCA-wood ash matrix.

9.2 Methods and Materials

9.2.1 Site Description

A CCA-wood burn site located on the shoreline of Lake Tuscaloosa, a 5,900 acre municipal water reservoir located in Tuscaloosa County, Alabama was selected as a typical case study. 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 Lake Tuscaloosa, 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-wood burning at a single burn site during the construction of two boathouses, a pier, and a deck. The 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. The climate in the area is humid subtropical with temperatures ranging from an average high of 24.4˚ C to an average low of 11.1˚ C with an average rainfall of 130 centimeters.

9.2.2 Analytical Methods

The metals content of CCA-wood ash and CCA-wood ash/Ultisol soil mixtures were determined by acid microwave digestion (HNO_3) analyses in a MARS-X microwave using Methods 3015 and 3051 (US EPA, 1996). Leachates and microwave digestion extracts were analyzed with inductively coupled plasma-atomic emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 3000DV) to determine the concentrations of Cu, Cr, and As using Methods 3015 and 3051 (US EPA, 1996).. 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} of ash for soil/ash and ash as necessary. The total carbon and organic carbon content of the native soil was determined by the loss on ignition (LOI) method 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 metal results are stated on a mass basis, unless otherwise noted.

9.2.3 Characterization of Burn Site Soil and Ash

Sampling Methods and Burn Site Soil/CCA-wood Ash Characterization

A CCA-metals concentration gradient profile was obtained by taking surface and core soil samples from the 2.5 m diameter burn site (0 meter sample point) and also at sites up-gradient (-4 meter sample point) and down-gradient (3, 5, and 6 meter sample points). Several surface samples taken at the center of the burn site down to a depth of 5 centimeters were combined to obtain one composite sample. This composite sample was used to determine metal concentrations used in the experimental soil columns and establish the soil:ash ratio used in preparation of the laboratory soil/CCA-wood ash mixture.

Burn site surface samples were dark gray in color, indicating the presence of wood ash in the topsoil. Deeper samples were taken by driving a 5 centimeter diameter metal pipe into the soil. The soil cores were cut at 7.5 and 15 centimeter depths. Samples were taken from the interior of the core to eliminate potential wall effects. All samples were taken under fair-weather conditions. Samples were analyzed for CCA-metals as described in Section 9.2.2 and Ultisol soil/CCA-metals ratios were determined.

Up-gradient Control Soil

Topsoil, located 100 meters up-gradient from the burn site, was employed as the control soil and was analyzed for Cu, Cr, and As to establish baseline metals concentrations for the local native soils. All levels of CCA-metals in the control soil were below detection limits and the measured pH of the soil was 6.9. The total carbon content of the soil was analyzed to be 2 percent, which is consistent with the carbon content reported by the USDA Soil Survey. The soil at this location was classified by the USDA as Paleudult Ultisol with a 10-15 centimeter layer of sandy clay loam of 2-33% clay and 0.5-2% organic matter (U.S. Department of Agriculture,

1981) underlain by impermeable kaolinitic clay over fractured rock. The soil was sieved through a number 30 sieve (0.6 mm) to increase particle uniformity and remove large particles that could cause column channeling.

9.2.4 Experimental Media Preparation

CCA-wood Ash

The CCA-wood ash was prepared under controlled burn conditions by burning scrap CCA-wood on a metal grate over a metal catch-pan and then sieved through a number 10 (2.00 mm) sieve to remove large unburned cinders. The combustion temperature was about 600˚ C for 1 hour under an initial condition of normal-oxygen combustion to a final condition of low-oxygen pyrolysis. The ash was used in the preparation of the soil/CCA-wood ash and amended soil/CCA-wood ash mixtures. Analyses were conducted in triplicate, as described in Section 9.2.2. The metal content of the ash used in these mixtures was (mg metal g^{-1} ash ± 95% confidence interval): Cu (86.3±11.3); Cr (76.7±16.0); As (69.6±2.1). 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. The other major components of the wood ash are oxides and carbonates of Ca, K, and Mg (Demeyer et al., 2001).

Soil/CCA-wood Ash Mixture

The soil/CCA-wood ash mixture was produced by mixing up-gradient soil with CCA-wood ash at a mass ratio of 5.28:1 to replicate soil-ash metal concentrations in the topsoil layer at the burn site. The resulting approximate metal concentrations in the mixture were (metal mg g^{-1} control mixture ± 95% confidence interval): Cu (13.7±1.8); Cr (12.2±2.6); As (11.1±0.3) 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 ($CaSO_4 \cdot 2H_2O$) was added to the soil/CCA-wood ash mixture to produce the amended soil/CCA-wood ash mixture used in the experimentation. The gypsum soil amendment used was commercial grade pelletized gypsum (Imery's, Roswell, GA) that was crushed and sieved through a number 10 (2.00 mm) sieve. .

9.2.5 Column Experiment Design and Stoichiometry

In traditional column studies, a media is studied by the controlled upward flow of a fluid through the column. The fluid containing a known amount of material enters the column at the bottom and samples are taken as the fluid exits the column at the top. Data on sorption vs. contact time is therefore available by varying the flow rate. During this research, the column media was examined to determine its reactions with rainwater flowing by gravity through the column in individual "batches." Each batch represented a precipitation event entering the top of the column and exiting the bottom of the column, with the media in the column being the soil and ash mixtures undergoing leaching as the rainwater infiltrated the soil. The leaching of the metals from the column media versus rainfall amount is the focus of these experiments.

Literature studies of redox-stoichiometric adsorption data were used to establish minimum soil amendment/metal mass ratios for the design of column experiments. For example, an adsorption study determined that three equivalents of divalent cations are required to reduce Cr(VI) species (Buerge and Hug, 1997). Subsequently, the mass ratio of gypsum amendment added to total CCA-metals present was 3:1 (Harden, 2005).

Accelerated leach experiments were used to determine the effects of controlled rainwater leaching events. The experiments were performed using duplicate sets of soil/CCA-wood ash columns designed to closely replicate the soil conditions at the burn site. The column tests were run in duplicate columns, with the two variable factors being soil/CCA-wood ash mixture alone, or amended with gypsum, resulting in a total of 4 columns. Under laboratory conditions, rainwater flowed by gravity from the top of the column and was collected as it exited the column. The average flow rate for the 4.2 cm diameter columns was 6 mL hr^{-1} (resulting in an infiltration rate of 4.3 mm/hr) and each column leach event was 12-24 hours in duration. Data collected was the mass of each metal leached from individual leaching events and the cumulative results of nineteen leach events for each column. Each polycarbonate column was 4.2 cm in diameter and 61 cm in length and contained 231 g of control soil, 49 g CCA-wood ash, and 68g of gypsum amendment (when gypsum was also added). These proportions of gypsum soil amendment to CCA-wood ash were established from calculations described previously to provide for potential stoichiometric conversion. Leach event volumes ranged from an initial 45 mL volume to subsequent 100 mL volumes equal to 3.2-7.2 cm height in the column 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 metal 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 total mass of metal leached and the pH trends resulting from the addition of the gypsum amendment.

9.3 Results and Discussion

Results presented include a baseline characterization of the burn site soil, column rainwater-leaching studies of soil/CCA-wood ash and soil/CCA-wood ash amended with gypsum, and a mechanistic pathway diagram (Figure 9.3) of the retardance processes in a CCA-wood ash/soil/soil-solution system and the effects of amending the system with gypsum.

9.3.1 CCA-wood Ash/CCA-metals Occurrence at the CCA-wood Burn Site

Tables 9.1 and 9.2 show the locations of the burn site sample points and the metals distribution in the CCA-wood ash/Ultisol soil mixture at each location.

Table 9.1 - Locations of Burn Site Sample Points

Sample Points					
↓	↓	↓	↓	↓	
-4m	**0m**	**3m**	**5m**	**6m**	Lake
Updip	Burn Site				Downdip→

Spatially variable surface samples analyzed in triplicate and depth samples analyzed as singlets were taken in a line extending from the lakeshore sediment located 6 meters down-gradient from the burn site, through the burn site (0 meters data point) to the up-gradient area located 4 meters from the burn site. The surface soil samples of the burn site (0 meters data point), analyzed by microwave digestion and ICP-OES, revealed that the metals concentrations in the soil/ash (mg metal g^{-1} soil/ash ± 95% confidence interval) were: Cu (14.5±0.2); Cr (17.4±0.6); As (12.2±0.5). The data indicate that the metals concentrations were highest at the center of the burn site with lower concentrations appearing down-gradient toward the lakeshore. This is assumed to be the result of leached metals moving down-gradient and the 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, whereas in all other areas sampled, the metals were confined to the upper 5 centimeters of topsoil. Up-gradient metals concentrations (-4 meter data point) were all low (<0.025 mg g^{-1}) and assumed to result from airborne ash during the burn process.

Table 9.2 - Metals Distribution in the Topsoil at the Burn Site

			Distance from Burn Site (m)				
			-4	**0**	**3**	**5**	**6**
Metal Conc. (mg g^{-1}) with Sample Depth	**Cu**	0-5 cm	0.016±0.001	14.5±1.10	1.96±0.03	0.090±0.005	0.013±0.001
		7.5 cm	<0.004	0.008	0.008	<0.004	<0.004
		15 cm	<0.004	0.009	0.026	<0.004	<0.004
	Cr	0-5 cm	0.023±0.004	17.4±1.37	3.05±0.30	0.130±0.005	0.018±0.003
		7.5 cm	<0.002	0.017	0.019	<0.002	<0.002
		15 cm	<0.002	0.017	0.024	<0.002	<0.002
	As	0-5 cm	0.016±0.01	12.2±0.95	1.50±0.01	0.050±0.01	<0.007
		7.5 cm	<0.007	0.027	0.017	<0.007	<0.007
		15 cm	<0.007	<0.007	0.030	<0.007	<0.007
0-5 cm Samples are triplicate analyses; 7.5 & 15 cm Samples are single analysis							

9.3.2 Column Rainwater-leaching of Gypsum-amended and Unamended Control Soil/CCA-wood Ash Mixtures

System pH conditions and the gypsum amendment have varying effects on the leaching of Cu, Cr, and As. With serial leaching of the Control Columns (soil/CCA-wood ash) and Gypsum Columns (soil/CCA-wood ash/gypsum), the rates of CCA-metals mobility and the system pH change. The Control Column leachates ranged from an initial pH of 8.0 to a final pH of 7.6 while Gypsum Column leachates had an initial pH of 8.0 and a final pH of 7.3.

Evaluation of Gypsum Amendment Performance

Using CCA-metals leaching data and data generated by interpolating between analyses leach data points a projection of the effect of the gypsum amendment upon the leaching of CCA-metals over a one-year period of rainfall was performed. The results are presented in Figures 9.1a (Cr), 9.1b (As), and 9.1c (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 (130 cm) at the burn site.

The data plotted on Figure 9.1a show that Cr leaches the highest relative mass compared to As and Cu over the short-term and is greatly retarded by the gypsum amendment (open squares) over the control (filled squares). This is likely because over the pH range of 8.0-7.6, Cr(III) hydrolyzes to sparsely soluble chromium hydroxides, adsorbs strongly to mineral and organic surfaces, and coprecipitates with other minerals, as reported by Hug et al., (1997). Adding the gypsum amendment to the CCA-wood ash/soil mixture results in increased hydroxyl radical concentrations in the soil solution by displacing the hydroxyl radicals from the adsorption sites. An increased precipitation of chromium hydroxide therefore occurs (Harden, 2005).

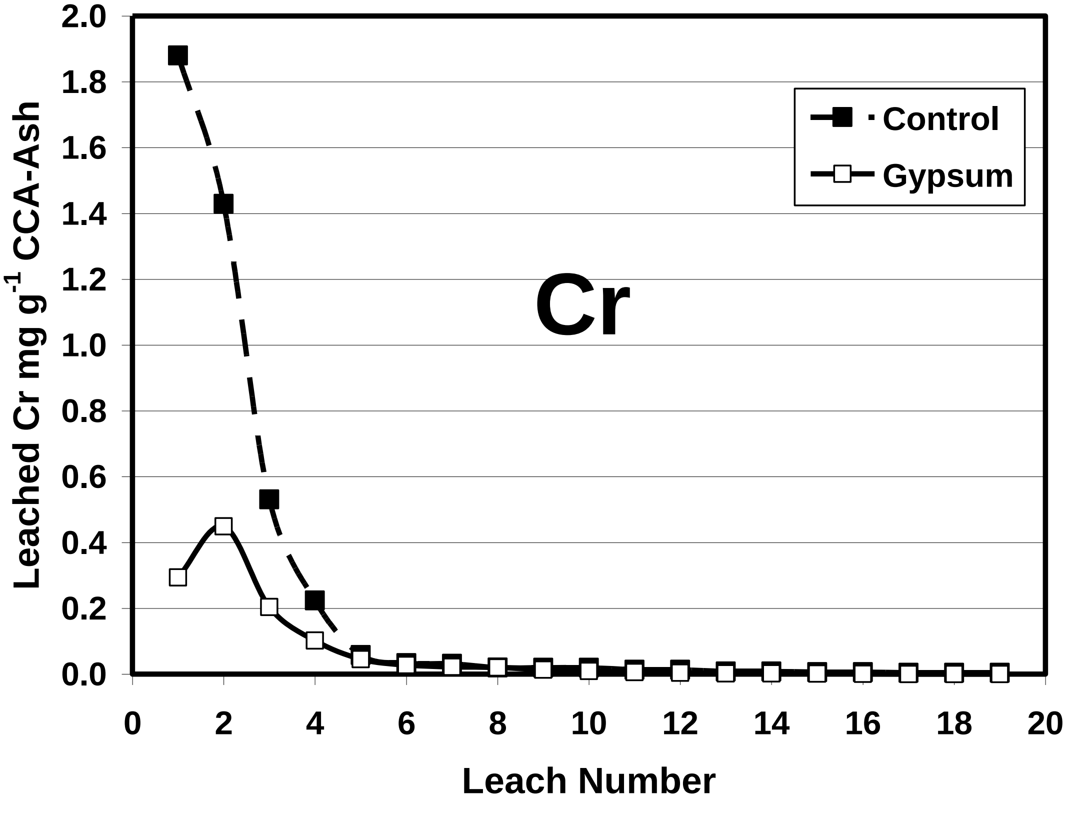


Figure 9.1a – Simulated One-Year Mass Leach of Cr – Control vs Gypsum Amendment

The data plotted on Figure 9.1b support the conclusion that As mass leaching in the control mixture (filled triangles) is very high in the short-term and remains significant in the long-term. The gypsum amendment (open triangles) produces significant reductions in both short-term and long-term As leaching. Using gypsum as an amendment increases the ionization of the adsorption surfaces resulting in increased adsorption and coprecipitation mechanisms (Harden, 2005). This is also described by Su and Puls (2001) who explained the adsorption of As in terms of both ionization of adsorbates and adsorbents which reaches a maximum adsorption at pH 7 for As(III) and for As(V) at pH <8.5.

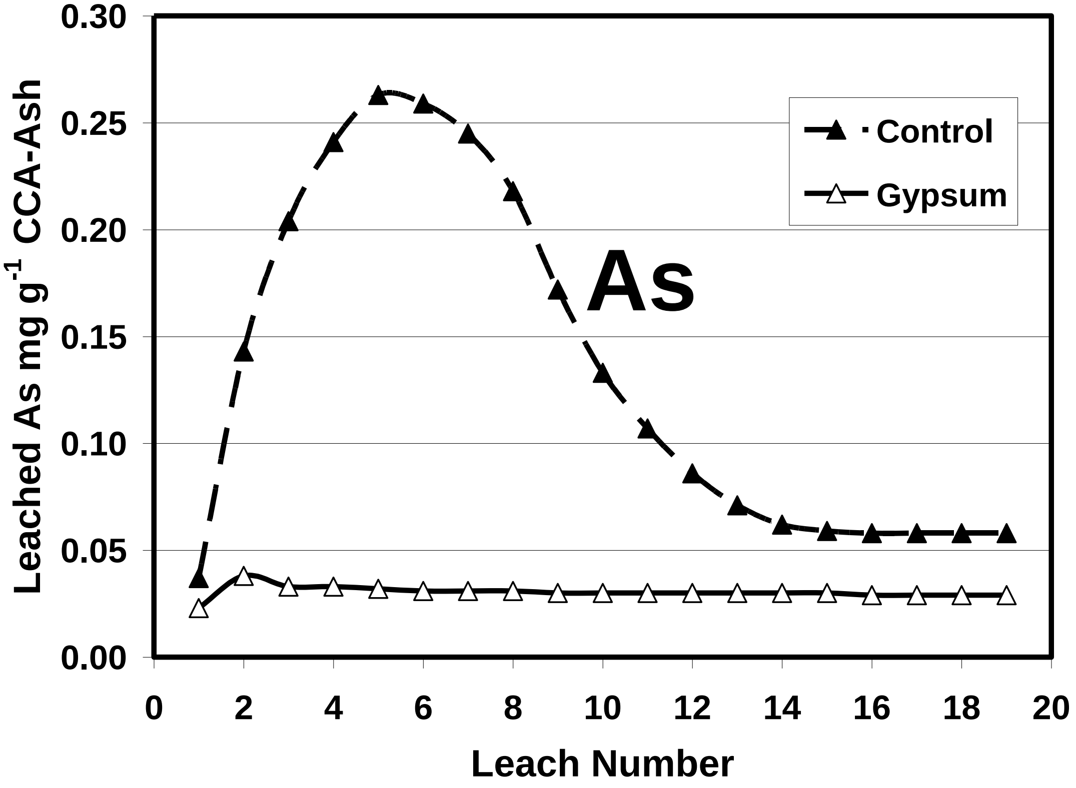


Figure 9.1b – Simulated One-Year Mass Leach of As – Control vs Gypsum Amendment

The data plotted in Figure 9.1c show that the use of the gypsum amendment (open diamonds) produces greater Cu leaching in the short-term compared to the control condition (filled diamonds). The increased mobility of Cu in the gypsum mixture results from Ca^{+2} ions competing with Cu^{+2} ions at adsorption sites and the increased rate of depletion of Cu-bound mobile organic material, as previously described in the literature by Lehmann and Harter (1984) in their assessment of copper-soil bond strength; Amrheim, et al (1992) in their study of metal mobility in roadside soil; and Evanko and Dzombak (1997) in their study of the remediation of metals-contaminated soils.

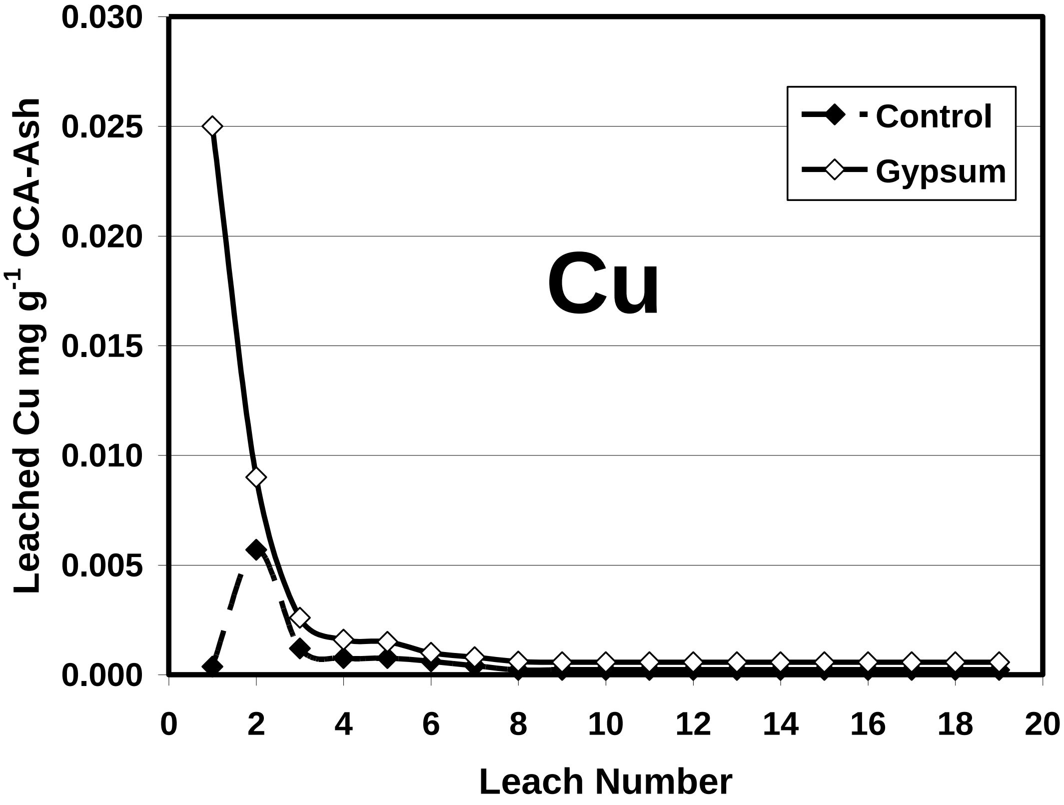


Figure 9.1c – Simulated One-Year Mass Leach of Cu – Control vs Gypsum Amendment

As shown in Table 9.3, the simulated one-year cumulative mass leaching of metals (mg g^{-1}) from the soil/CCA-wood ash, without amendments, is as follows: Cu, 0.012; Cr, 4.31; As, 2.53. The resulting simulated one-year cumulative mass leaching of metals (mg g^{-1}) from the soil/CCA-wood ash, with the gypsum amendment, is as follows: Cu, 0.048; Cr, 1.20; As, 0.578.

Table 9.3 - CCA-wood Ash Composition and Mass of Metals Leached (mg g^{-1} ash)

	Cu	Cr	As
CCA-wood Ash	**86**	**76**	**70**
Leached - Control	**0.012**	**4.31**	**2.53**
Leached - Gypsum	**0.048**	**1.2**	**0.58**

Note that the mass leaching data percentages project a 400% increase of Cu leaching with the use of gypsum, but this represents a small relative mass of Cu compared to Cr and As masses. The data also reflects very important 72% and 77% reductions in the leaching of Cr and As with the use of the gypsum amendment.

9.3.3 Retardance Mechanisms of Gypsum Amendment of Ultisol Soil/ CCA-wood Ash

The Ultisol soil/CCA-wood ash/soil solution is a highly complex, synergistic system involving adsorption, ion exchange, complexation with humic substances and precipitation/coprecipitation reactions. The surface soil from the burn site is a soil of relatively low (3.65)cation exchange capacity (CEC), the sum total of exchangeable cations that a soil may absorb, and is characterized by kaolinite clay, oxides of Al and Fe, and humic substances (U.S. Department of Agriculture, 1981). The amount of soil organic matter in this mineral soil produces a significant increase in the CEC, the Ultisol control soil used having a measured 2% carbon content (Harden, 2005). Brady and Weil (2002) state that Ultisol soil is relatively high (65%) in H^{+}, Al^{+3} and (25%) in Ca^{+2}, the major adsorbed cations on soil surfaces, and the soil has less than 35% of the CEC satisfied with “base-forming” metallic cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}, NH_4^{+}), with 65% associated with the organic matter.

Tightly held H^{+} and Al^{+3} cations in the Ultisol soil will inhibit dispersion, as the ability of common cations to flocculate soil colloids is in the order of $Al^{+3} > H^{+} > Ca^{+2}, Mg^{+2} > K^{+} > Na^{+}$. Furthermore, the relative concentrations of flocculating inorganic cations (ie. Ca^{+2}) in the soil solution will determine the degree to which adsorption occurs by increasing mutual attraction between the organic matter and soil clay, encouraging the development of clay-organic matter complexes (Brady and Weil, 2002), thus the use of the gypsum amendment will increase the formation of complexes and flocculation.

The soil solution consists of freely-moving water dipoles together with solvated ions and complexes. Reactions at the interface of the soil solution and the soil surface result in atomic reorganization in both phases that then change the magnitude of the surface charge. The permanent structural charges of hydrous oxide minerals, like Fe and Al oxides, and simple layer silicates, like kaolinite, are close to zero. The pH for the point of zero charge for kaolinite is 4.6, thus there is an increase in negative surface charges on kaolinitic clays when the soil system operates at basic pH ranges (Brady, 1990). The attraction of ions to surface charges on clays were confirmed by Griffin and Shimp (1978) who found the relative mobility of these metals through kaolinite to be: Cr(VI) > As(III) > As(V) > Cu > Cr(III).

From the above sequence, Cr(III) would be preferentially accumulated in the kaolinite clay fraction (Loyaux-Lawniczak et al., 2001). A basic pH (hydroxyl-rich) soil solution therefore results in a dominant $Cr(OH)_3$ precipitation and co-precipitation reaction (Harden, 2005). More specifically, at pH values above 7, aqueous uncomplexed Cr(III) hydrolyzes to sparsely soluble chromium (III) hydroxides, adsorbs strongly to mineral and organic surfaces, and co-precipitates with other minerals, a reaction that is strongly influenced by pH and organic ligands (Hug et al., 1997). On the other hand, Cr(VI) species are only weakly bound to soil surfaces and are thus easily displaced by other anions (Evanko and Dzombak, 1997). Reduction of Cr(VI) to Cr(III) may occur due to soil properties (James et al., 1995) with soil organic matter being identified as the electron donor in this reaction (Bartlett and Kimble, 1976; Bloomfield and Pruden, 1980). The reduction of Cr(VI) has been reported to be an extremely slow process, requiring months to years (Bartlett, 1991**;** Hug et al., 1997). However, this process can be accelerated by the presence of Fe(II) in solution, or Fe(II)-bearing minerals and organic matter, such as can be found in an Ultisol soil (Loyaux-Lawniczak et al., 2001).

Arsenic is bound to soil particles, but in general is not held as tightly as Cr or Cu. Thus, As tends to be somewhat more mobile in soil (Stehouwer, 2001) and undergoes adsorption reactions on mineral surfaces, especially iron and aluminum oxide (Manning et al., 1998). Iron oxide surfaces have a high affinity for As(V), capable of forming inner-sphere bidentate, binuclear As(V)-Fe(III) complexes and a similar mechanism for As(III) inner-sphere adsorption (Lumsdon and Evans, 1994; Fendorf et al., 1997; Manning et al., 1998). Arsenate (AsO_4^{-3}) is adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979; Neal et al., 1987), and forms insoluble precipitates with iron, aluminum, and calcium. Anderson et al.(1976) reported significant adsorption of As(V) on precipitated aluminum hydroxide, a function of pH-induced electrical surface charges. Arsenite (AsO_3^{-3}) adsorbs or coprecipitates in its anionic form (Evanko and Dzombak, 1997) and is adsorbed in much larger amounts than As(V) at pH > 7.5, or at high concentrations in solution than As(V).

According to Wu et al. (2001), copper is preferentially complexed with the organic components and clay-organic complexes of soil and soil solutions. The adsorption of Cu^{+2} on mineral surfaces may be suppressed in a basic pH soil solution by the formation of strong solution complexes with mobile humic acids and copper hydroxides (Tipping et al., 1983; Davis, 1984). Lehmann and Harter (1984) report that rapidly-released Cu^{+2} is loosely held on soil surfaces and slowly-released Cu^{+2} is held by tightly bound sites.

Electric Double Layer Model

Figure 9.2 (Adapted after Mitchell and Soga, 2005) presents a theoretical distribution of the cations and anions in the Ultisol soil solution-soil surface interface. A net negative charge at the interface between the colloid surface (Negatively Charged Surface) and the soil solution may be produced by ions in solution and those at the surface. In kaolinite, surface hydroxyl ions are attached to the silicon and aluminum cations in the clay mineral layers. In basic solutions, a proton may be lost from the surface hydroxyl group (OH^-) by either or both of the following reactions (1 and 2):

$$\text{Si-OH} + OH^- \rightarrow \text{Si-O}^- + H_2O \qquad (1)$$

$$\text{Al-OH} + OH^- \rightarrow \text{Al-O}^- + H_2O \qquad (2)$$

These reactions result in a negative contribution to the surface electrical charge with the increasing pH of the system and the resulting total net charge being the sum of the permanent structural charge and the charge due to surface reactions with the solution.

Counter ions, ie. Ca^{+2}, accumulate near the Ultisol soil solution-surface interface, thus creating an electric double layer composed of an inner layer (Stern layer) attached to the surface by electrostatic forces, or by the formation of complexes and an outer layer (Gouy layer) where ions diffuse into the solution. The distance between the solution-surface interface and the center of charge within the outer layer is proportional to the square root of the ionic strength of the solution (Mitchell and Soga, 2005).

Increasing the pH-influenced negatively charged attraction forces on the soil surface, and increasing the concentrations of certain counter ions in the soil solution, will result in an increase in the distance to the center of charge from the soil surface. From Figure 9.2, it is noted that an increase in the concentration of cations (ΔI_C) in the Gouy layer produces a corresponding equilibrium-driven increase in the concentration of anions (ΔI_A) in the layer, a result of the increase in the distance (Δd) to the center of charge in the layer.

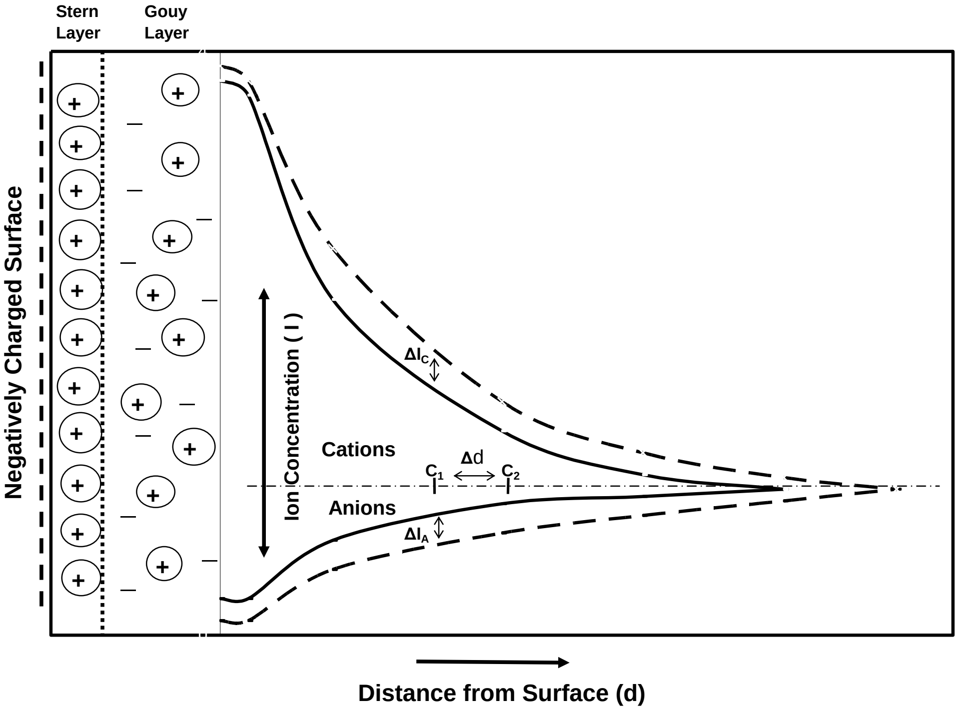


Figure 9.2 – Electric Double Layer Model of the Gypsum Retardance Mechanism (Adapted after Bradl, 2002; Mitchell and Soga, 2005)

Ultisol Soil/CCA-wood Ash/Soil Solution System

In the Ultisol soil/CCA-wood ash/soil solution system represented in Figure 9.3, Metal Retarding Mechanism Pathways of Soil/CCA-wood Ash/Soil Solution System, a number of reaction mechanisms dominate the multitude of reactions within the system.

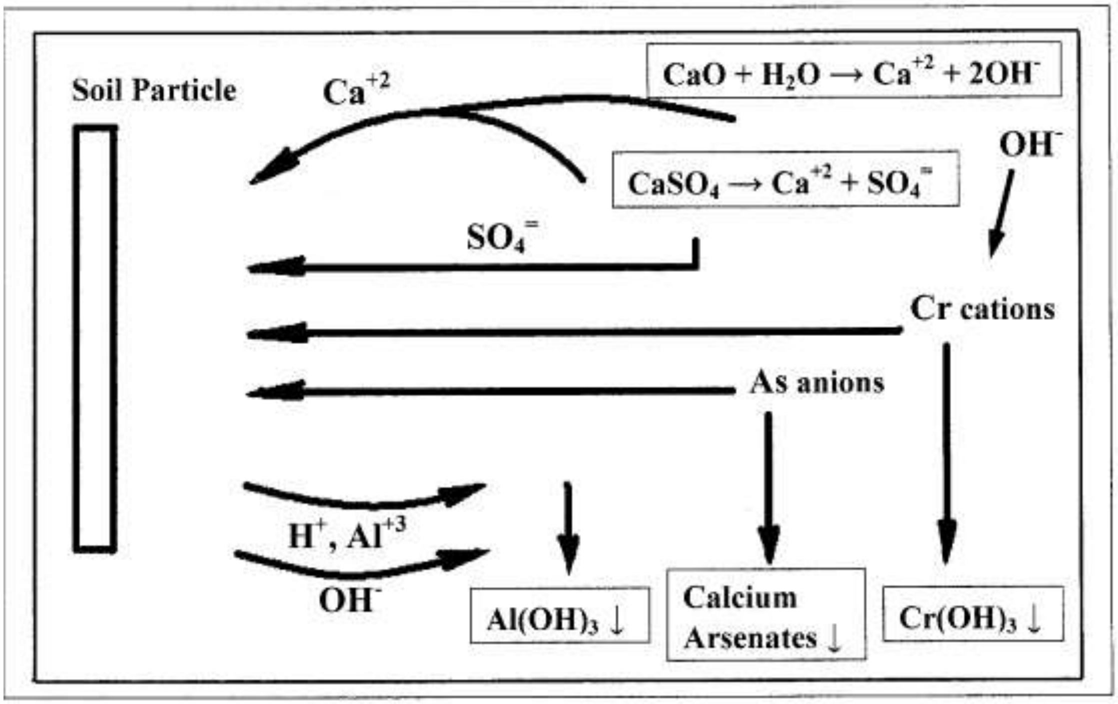


Figure 9.3 – Metal Retarding Mechanism Pathways of Soil/CCA-wood Ash/Soil Solution System

A major mechanism involves the liming effect of the CCA-wood ash whose major liming compounds are CaO, KO, and MgO, with CaO being the most abundant(Etiegni and Campbell, 1991). Hydrolyzing reactions of these compounds with water result in alkaline hydroxides which freely dissociate, as shown in Equation (3).

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^- \qquad (3)$$

The resulting calcium-ion-rich alkaline solution reacts with clay and humus substances in the soil with calcium ions displacing hydrogen and aluminum ions on soil particle surfaces. The precipitation of aluminum hydroxide and an increase in the pH of the soil and soil solution, then occurs, as shown in Equation (4).

$$\begin{array}{r|l} \text{Clay or} & H^+ \\ \text{Humus} & A^{+3} \end{array} + 2Ca^+ + 4OH^- \rightarrow \begin{array}{r|l} \text{Clay or} & Ca^{+2} \\ \text{Humus} & Ca^{+2} \end{array} + Al(OH)_3 \downarrow + H_2O \qquad (4)$$

Amendment of the System with Gypsum

The adsorption of species of As, Cr, and Cu on heterogeneous soil particles in the Ultisol soil/CCA-wood ash/soil solution system is complex in that many mechanisms are possible involving metal cation and anion sorption reactions. According to Brady and Weil (2002), amending a soil system with gypsum, a neutral salt, does not raise the soil pH, and so does not increase the CEC of the soil. Gypsum is known to increase the concentration of Ca^{+2} cations in the soil solution with an associated reduction in the concentration of Al^{+3} cations, both in the soil solution and on the soil exchange complexes. Although not increasing the CEC, Ca^{+2} cations from gypsum will increase the efficiency of the existing CEC, in part due to the soil structure modification and increase in the soil infiltration rate (Borselli et al, 1996; Brady and Weil, 2002). This increase in CEC efficiency results directly from the Ca^{+2} cations released from the gypsum by replacing Al^{+3} cations from exchange sites, as in equation (4).

Reaction of sulfate ions with Fe/Al soil substances results in the release of additional hydroxyl ions into the soil solution, as in Equation (5).

$$\begin{array}{llll} \text{Fe/Al Soil } |\text{- OH} & + Ca^{+2} + SO_4^{-2} \rightarrow & \text{Fe/Al Soil } |{=}SO_4 + Ca^{+2} + 2OH^{-} & \quad (5) \\ \text{Substances } | \text{–OH} & & \text{Substances}| & \end{array}$$

The free hydroxyl ions formed may react with Al^{+3} cations in the soil solution to form an insoluble $Al(OH)_3$ precipitate, thereby reducing the concentration of Al^{+3} cations while increasing the relative concentration of Ca^{+2} cations in the soil solution, as in Equation (6).

$$3Ca^{+2} + 6OH^{-} + 2Al^{+3} \rightarrow 2Al(OH)_3 \downarrow + 3Ca^{+2} \qquad (6)$$

A further probable mechanism of Al^{+3} cation removal is the direct, or indirect, reaction of the released aluminum ion with the sulfate ion to form $AlSO_4^{-}$ ions.

Brady and Weil (2002) further state that as Al^{+3} cations are removed from the soil surface and precipitated as $Al(OH)_3$, Ca^{+2} cations in the soil solution then have a greater affinity for attachment to exchange sites. The order of strength of adsorption for the most common cations is: $Al^{+3}>Ca^{+2}>Mg^{+2}>K^{+}=NH_4^{+}>Na^{+}$. The less tightly held cations oscillate farther from the soil colloid surface and therefore are the most likely to be displaced into the soil solution and carried away by leaching. Thus, soil colloids in humid regions are dominated by Al^{+3} (and other aluminum ions) and Ca^{+2} ions.

By amendment with gypsum, the relative concentration of Ca^{+2} cations increases in the diffuse (Gouy) layer, the resulting increased electrical attraction of anions to the Stern layer results in an increase in sorption processes and co-precipitation. The gypsum amendment of the Ultisol soil/CCA-wood ash serves as a source for Ca^{+2} cations that move into the soil solution creating a concentration gradient that drives the soil system reactions toward the attachment of Ca^{+2} cations to the soil surfaces and soil complexes. The resulting increase in the concentration of Ca^{+2} cations in the soil solution and attachment to soil surfaces results in a corresponding increase in the electrical forces attracting anions to the soil surfaces.

These mechanisms which are hypothesized to be attributable to the Ca^{+2} source are influenced by the effective solubility of gypsum in the soil/CCA-wood ash/soil solution system. The solubility of gypsum (2.4 g L^{-1}) is 150 times lower than NaCl (359 g L^{-1}) but two orders of magnitude greater than the solubility of $CaCO_3$ (0.01 g L^{-1}) in pure water at 25° C (Lange, 1961). According to Klimchouk (2000), the solubility of gypsum is increased by the presence of foreign ions, and decreased by high ion concentrations of the solution and, furthermore, the consumption of sulfate ion will rejuvenate gypsum solubility. Therefore, it is postulated that the consumption of sulfate ions by the mechanisms of sulfate reaction with Fe/Al soil substances and by the leaching of sulfate ions from the soil system will drive the system reaction toward continued solubility of ions from the Ca^{+2} source.

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 and gypsum mixtures are weakly basic systems (pH 8.0 and 7.3 respectively) that become nearly neutral as the leached columns reach equilibrium and exhibit relatively low concentrations of mobile CCA-metals in the leachate.

Metal hydroxides, being amphoteric, are increasingly soluble at both low and high pH values; the point of minimum solubility (optimum pH for precipitation) occurs at different pH values for every metal. According to Ayres, et al. (1994), the minimum solubility for Cu and Cr hydroxides occurs at pH 8.1 and 8.5 respectively. At other pH values, remaining soluble hydroxides will start to dissolve into solution as the pH changes, resulting in an increase in metal concentration in the leachate. Therefore, the soil/CCA-wood ash/soil solution system pH (7.3 to 8.0) is highly favorable to hydroxide precipitation reactions and low hydroxide solubility.

Arsenic is bound to soil particles, but in general is not held as tightly as Cr or Cu, thus tending to be more mobile in soil (Stenhouwer, 2001). Arsenite, As (III), the dominant form of arsenic in CCA-wood ash is more toxic and more mobile than the arsenate, As (V), which may be present. Su and Puls (2001) explain the mechanism of the adsorption of As in terms of both ionization of adsorbates and adsorbents which reaches its maximum adsorption around pH 7. With this mechanism, arsenate oxyanions such as $HAsO_4^{-2}$, may release OH^- ions from the surface upon complexation, forming inner-sphere complexes which predominantly involve coordinate-covalent bonding (Apak, 2002). Arsenite (AsO_3^{-3}), the dominant As (III) species under these conditions, adsorbs or coprecipitates in anionic form, but it does not form complexes with simple anions such as SO_4^{-2} and the percent adsorbed on iron oxide reaches a maximum of 75% around pH 7.8 (Evanko and Dzomback, 1997). This finding evidences the need to enhance anionic sorption processes of soil clays, humic substances, and Fe/Al soil substances, for example, by the addition of an amendment to the contaminated soil. Thus, amending the contaminated soil with gypsum and the resulting increased concentration of Ca^{+2} cations at the sorption surfaces, potentially results in the precipitation of less mobile solid calcium arsenates (Bothe and Brown, 1999).

In the pH range of 7.3 to 8.0, Cr (III), the dominant chromium cation resulting from pyrolysis of CCA-wood, hydrolyzes to sparsely soluble chromium hydroxides, adsorbs strongly to mineral and organic surfaces, and coprecipitates with other minerals (Hug et al., 1997). Therefore, increasing the electrical charges on surfaces in the system and increasing the concentration of hydroxyl ions results in reduced Cr(III) mobility. The remaining mobile chromium, Cr(VI), may leach from the system or be reduced to Cr(III) and sorb and/or precipitate.

At pH < 7, Cu^{+2} adsorption ranges from inner-sphere, bidentate complexes on layered silicate surfaces of kaolinite, to outer-sphere complexes with humic substances, both exhibiting high-energy bonding. For the near neutral-to-slightly alkaline pH range (7.3-8.0) of the Ultisol soil/CCA-wood ash/soil solution system, solubility and complexation reactions may be superimposed on adsorption processes resulting in increased mobility of complexes and the formation of copper hydroxides (Apak, 2002). The gypsum amended Ultisol soil/CCA-wood ash column (Gypsum) exhibited similar impacts on Cu mobility with leached masses nearly two orders of magnitude greater than the control mixture column. This result is evidence of the binding mechanism of Cu to organic material in the Ultisol soil and the adsorption to hydrolyzing reaction byproducts of CaO, KO, MgO and $CaCO_3$ in the ash. This occus as the gypsum amendment supplies solvated Ca^{+2} ions that displace Cu^{+2} ions from organic materials and surface adsorption sites of the Ultisol soil and CCA-wood ash (Cavallero and McBride, 1978; Lehmann and Harter, 1984). Apak (2002) states that above pH 7, the relative abundance of anionic forms of humic acid increase in aqueous solutions, thus resulting in increased mobility of cationic Cu^{+2} bound to mobile organic material. Also, Baham and Sposito (1986) and Inskeep and Baham (1983) demonstrated that adsorption of Cu^{+2} to clay, in the presence of water-soluble ligands, decreased with increasing pH.

9.4 Conclusions

The use of gypsum acting as a stabilizing agent within the pH 7.3 to 8.0 range may be a feasible soil amendment for the treatment of Cr and As in the soil and ash at CCA-wood burn sites. However, the increased leaching of Cu may cause problems.

The Ultisol control soil component of the unamended Ultisol soil/CCA-wood ash mixtures exhibits the potential for retardance of the mobility of two of the CCA-metals, chromium and arsenic, during rainwater-leaching as compared to the leaching of CCA-wood ash alone.

Gypsum amendment of the Ultisol soil/CCA-wood ash mixture had little effect or increased the Cu mobility compared to the leaching of CCA-wood ash alone. Gypsum amendment of the Ultisol soil/CCA-wood ash mixture reduced As mobility by 77% and Cr mobility by 72% over the unamended soil/CCA-wood ash mixture during a simulated leaching period of one-year of rainfall.

A mechanistic pathway diagram of metal retarding mechanisms was postulated for the CCA-metals in an Ultisol soil/CCA-wood ash/soil solution system containing kaolinitic clay, Fe and Al oxides, and organic carbon material, with gypsum amendments. These surface complexation and surface precipitation mechanisms fit the synergistic conditions of the multiple factors and reactions within the Ultisol soil/CCA-wood ash/soil solution system. These mechanisms support the conclusions that amendment of the Ultisol soil/CCA-wood ash/soil solution system with gypsum results in enhanced Cr and As sorption processes at the soil surface, increased flocculation and precipitation of aluminum and chromium hydroxides, and the possible precipitation of solid calcium arsenates. The net result of these mechanisms upon the effects of rainwater-leaching is increased retardance of chromium and arsenic mobility in the system, but with possible increased leaching of copper.

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APPENDIX IX-A

IX-A-1 Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment

	Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment																			
	(Bold numbers are measured data, standard numbers are extraplolated data)																			
	Leach Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Cummulative Volume (mL)	45	145	245	345	445	545	645	745	845	945	1045	1145	1245	1345	1445	1545	1645	1745	1845
	Mass = mg																			
Cu	**Soil/Ash (S/A)**	**0.018**	0.279	0.060	0.037	**0.037**	0.030	0.020	0.011	**0.011**	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
	S/A-$CaSO_4$	**1.24**	**0.440**	0.130	0.080	**0.073**	0.050	0.040	0.030	**0.028**	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	**0.028**
Cr	**Soil/Ash (S/A)**	**92.5**	70.0	26.0	11.0	**2.82**	1.60	1.50	1.00	**0.950**	0.950	0.630	0.630	0.416	0.416	0.274	0.274	0.181	0.181	0.181
	S/A-$CaSO_4$	**14.4**	**22.0**	10.0	5.00	**2.21**	1.30	1.10	1.00	**0.635**	0.042	0.277	0.183	0.120	0.080	0.052	0.035	0.010	0.010	**0.010**
As	**Soil/Ash (S/A)**	**1.83**	7.00	10.0	11.8	**12.9**	12.7	12.0	10.7	**8.43**	6.50	5.25	4.20	3.50	3.05	2.90	2.85	2.85	2.80	2.80
	S/A-$CaSO_4$	**1.11**	**1.84**	1.60	1.60	**1.58**	1.50	1.50	1.50	**1.46**	1.46	1.46	1.46	1.46	1.46	1.46	1.42	1.42	1.42	**1.42**

CHAPTER X

CONCLUSIONS

10.1 Research Objectives

The overall objective of this research was to evaluate the mobility of As, Cr, and Cu metals (CCA-metals) undergoing rainwater-leaching from burn sites containing CCA-ash mixed with soil and to determine the effectiveness of adding agricultural soil amendments individually or in combinations to retard the rainwater-leaching of the CCA-metals. This research advances the understanding of the leaching of CCA-metals from soil contaminated with the ash of CCA-treated wood, the understanding of the pH conditions in this contaminated soil system, and the understanding of soil conditions that promote or retard the leaching of CCA-metals.

The objective was met by: (1) investigating a CCA-treated wood burn site and quantifying the concentrations of CCA-metals in the soil of the burn site; (2) determining the CCA-metals concentrations in laboratory-prepared CCA-ash and the physical and chemical characteristics of CCA-ash and the native soil at the burn site area; (3) identifying common chemical agricultural amendments (AgLime, Gypsum, and Iron Sulfate) which have the potential for reducing the mobility of CCA-metals in soil; (4) conducting laboratory batch rainwater-leaching experiments to determine the potential retardance of amendments upon leached CCA-metals in soil and the pH conditions and; (5) conducting a simulated one-year laboratory column rainwater-leaching experiment to determine the potential retardance of CCA-metals by unamended and amended soil/CCA-ash mixtures.

Research activities and questions supporting the overall objective were as follows:

(1) Investigating a CCA-treated wood burn site and quantifying the concentrations of CCA-metals in the soil of the burn site was accomplished by collecting surface soil samples and taking subsurface core samples. Specific questions were: (a) What are the concentrations of As, Cr, and Cu in the contaminated soil at the burn site? (b) What was the extent of CCA-metals movement both horizontally over the surface and vertically in the soil column at the burn site?

(2) Determining the CCA-metals concentrations in laboratory-prepared CCA-ash and the physical and chemical characteristics of CCA-ash and the native Ultisol soil at the burn site area by the use of analytical methods for characterizing solid wastes, pH measurements, and sieve analysis. Specific questions were: (a) What are the concentrations of Cu, Cr, and As in CCA-ash? (b) What are the pH conditions of the rainwater-leaching of CCA-ash, native Ultisol soil, and their mixtures? (c) What are the distributions of particle sizes in the most reactive portions of CCA-ash and native Ultisol soil?

(3) Identifying common chemical agricultural amendments (AgLime, Gypsum, and Iron Sulfate) which have the potential for reducing the mobility of CCA-metals in soil through an extensive literature review. Specific questions were: (a) What agricultural amendments are in common use and are chemically associated with compounds that previous research has shown to affect the mobility or oxidation states of Cu, Cr, and As compounds? (b) What affect did the agricultural amendments have upon the soil pH conditions?

(4) Conducting in the laboratory batch rainwater-leaching experiments to determine the potential retardance by unamended soil/CCA-ash and by amended soil/CCA-ash upon leached CCA-metals and the pH conditions by designing 2^3 factorial batch experiments replicating soil:CCA-ash mass ratios that duplicate the Cu, Cr, and As concentrations at the burn site. Specific questions were: (a) What amendments or amendment combinations were potentially most effective in retarding the leaching of CCA-metals? (b) What are the initial pH and the pH trends of the amendments and amendment combinations? (c) What effect does a solvent-rich leaching have upon the retardance of CCA-metals by the amendments or amendment combinations?

(5) Conducting in the laboratory a simulated one-year column rainwater-leaching experiment to determine the potential retardance of CCA-metals by unamended soil/CCA-ash and by amended soil/CCA-ash mixtures and their pH trends by designing 2^3 factorial column experiments replicating soil:CCA-ash mass ratios that duplicate the Cu, Cr, and As concentrations at the burn site. Specific questions were: (a) What amendments or amendment combinations were potentially most effective in retarding the leaching of CCA-metals from the test columns? (b) What are the initial leachate pH and the pH trends of the unamended test columns and test columns containing amendments and amendment combinations? (c) What effect does a low solvent:solids ratio of the test columns have upon the retardance of CCA-metals by the amendments or amendment combinations?

10.2 Table of Contrasts and ANOVA Analysis of Batch and Column Leaching Data

The data resulting from the batch and column leaching factorial experiments was analyzed by computing a table of contrasts for the factorial experiments and by using the Design-Expert 8.0.4.1software to compute an ANOVA that evaluated the significance of the experimental results. Table of Contrasts results and ANOVA results for each CCA-metal in the batch leaching and column leaching studies are presented in the following tables to aid in comparing the effects calculated by each method. Additional supporting matrix computations for the Table of Contrasts and the Design-Expert ANOVA plot results for the Normal Probability Plot of Effects, Normal Probability Plot of Residuals, and Plot of Residuals vs Run are located in Appendix A-X.

In Table 10.1 for the batch leaching of As there is adequate confirmation between the two analyses that AgLime, Gypsum and Iron Sulfate have significant retardance main effects upon As mobility and AgLime/Iron Sulfate has a two-factor interaction effect. Additional supporting material is located in Appendix X; X-A-8, X-A-11 and X-A-23.

Table 10.1 – Comparison of Table of Contrasts and ANOVA for Batch As Results

As Batch Leaching	**Table of Contrasts Effect**	**ANOVA Effect**	**ANOVA p**	**ANOVA Model**	**ANOVA % Contribution**
		Model	< 0.0001	**R =**	
Average Effect	0.95 ± 0.01	0.95 ± 0.05		**0.95**	
Main Effects					
AgLime	**-0.71 ± 0.02**	**-0.35 ± 0.05**	0.0001	**-0.35**	31.4
Gypsum	**-0.54 ± 0.02**	**-0.27 ± 0.05**	0.0002	**-0.27**	18.1
Iron Sulfate	**-0.49 ± 0.02**	**-0.25 ± 0.05**	0.0005	**-0.25**	15.2
Two-Factor Interactions					
AgLime/Gypsum	0.25 ± 0.02				
AgLime/Iron Sulfate	**-0.67 ± 0.02**	**-0.34 ± 0.05**	< 0.0001	**-0.34**	28.3
Gypsum/Iron Sulfate	0.10 ± 0.02				
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	0.19 ± 0.02				

The analyses results in Table 10.2 show that for the batch study Iron Sulfate exhibits the dominant retardance effect upon Cr mobility and that Gypsum has a lesser, but significant retardance interaction with Cr. Additional supporting material is located in Appendix X; X-A-8, X-A-12 and X-A-24.

Table 10.2 – Comparison of Table of Contrasts and ANOVA for Batch Cr Results

Cr Batch Leaching	**Table of Contrasts Effect**	**ANOVA Effect**	**ANOVA p**	**ANOVA Model**	**ANOVA % Contribution**
		Model	< 0.0001	**R =**	
Average Effect	1.07 ± 0.005	1.07 ± 0.04		**1.07**	
Main Effects					
AgLime	-0.16 ± 0.01				
Gypsum	**-0.40 ± 0.01**	**-0.20 ± 0.04**	0.0002	**-0.20**	5.46
Iron Sulfate	**-1.61 ± 0.01**	**-0.81 ± 0.04**	< 0.0001	**-0.81**	89.0
Two-Factor Interactions					
AgLime/Gypsum	-0.04 ± 0.01				
AgLime/Iron Sulfate	-0.19 ± 0.01				
Gypsum/Iron Sulfate	**0.31 ± 0.01**	**0.15 ± 0.04**	0.0014	**0.15**	3.25
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	-0.05 ± 0.01				

The analysis results in Table 10.3 show that for the batch study AgLime and Iron Sulfate have significant main effects and a two-factor effect upon Cu mobility. AgLime and AgLime/Iron Sulfate retard Cu mobility while Iron Sulfate increases mobility. Although Gypsum/Iron Sulfate does not compute to have a significant main effect, the experimental data shows that it increases Cu mobility equivalent to Iron Sulfate. Additional supporting material is located in Appendix X; X-A-8, X-A-13 and X-A-25.

Table 10.3 – Comparison of Table of Contrasts and ANOVA for Batch Cu Results

Cu Batch Leaching	**Table of Contrasts**	**ANOVA**	**ANOVA**	**ANOVA**	**ANOVA**
	Effect	**Effect**	**p**	**Model**	**% Contribution**
		Model	< 0.0001	**R =**	
Average Effect	0.45 ± 0.005	5.68 ± 0.18		**5.68**	
Main Effects					
AgLime	**-0.86 ± 0.01**	**1.76 ± 0.18**	< 0.0001	**1.76**	36.3
Gypsum	-0.03 ± 0.01				
Iron Sulfate	**0.86 ± 0.01**	**-1.76 ± 0.18**	< 0.0001	**-1.76**	36.3
Two-Factor Interactions					
AgLime/Gypsum	0.03 ± 0.01				
AgLime/Iron Sulfate	**-0.86 ± 0.01**	**1.40 ± 0.18**	< 0.0001	**1.40**	22.8
Gypsum/Iron Sulfate	-0.03 ± 0.01				
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	0.03 ± 0.01				

Table 10.4 shows that Gypsum, Iron Sulfate, and the interaction effect of AgLime/Gypsum have significant effect upon Cr mobility.in the column leaching study. Gypsum and AgLime/Gypsum have significant retardance effects while Iron Sulfate and all combinations with Iron Sulfate have significant retardance effects confirmed by experimental data results. Additional supporting material is located in Appendix X; X-A-17, X-A-19 and X-A-27.

Table 10.4 – Comparison of Table of Contrasts and ANOVA for Column Cr Results

Cr **Column Leaching**	**Table of Contrasts** **Effect**	**ANOVA** **Effect**	**ANOVA** **p**	**ANOVA** **Model**	**ANOVA** **% Contribution**
		Model	< 0.0001	**R =**	
Average Effect	31.9 ± 0.8	31.9 ± 1.5		**31.9**	
Main Effects					
AgLime	**-6.6 ± 1.6**				
Gypsum	**-41.1 ± 1.6**	**-19.7 ± 1.5**	< 0.0001	**-19.7**	25.0
Iron Sulfate	**-46.1 ± 1.6**	**-27.8 ± 1.5**	< 0.0001	**-27.8**	50.0
Two-Factor Interactions					
AgLime/Gypsum	**1.53 ± 1.6**	**19.0 ± 1.5**	< 0.0001	**19.0**	23.2
AgLime/Iron Sulfate	-4.6 ± 1.6				
Gypsum/Iron Sulfate	40.0 ± 1.6				
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	9.7 ± 1.6				

Table 10.5 shows that Gypsum, AgLime/Gypsum, and Iron Sulfate have significant effect upon As mobility.in the column leaching study. Gypsum and AgLime/Gypsum have significant retardance effects while Iron Sulfate and all combinations containing Iron Sulfate result in increased leaching of As confirmed by experimental data results. Additional supporting material is located in Appendix X; X-A-17, X-A-18 and X-A-26.

Table 10.5 – Comparison of Table of Contrasts and ANOVA for Column As Results

As Column Leaching	**Table of Contrasts Effect**	**ANOVA Effect**	**ANOVA p**	**ANOVA Model**	**ANOVA % Contribution**
		Model	< 0.0001	**R =**	
Average Effect	20.1 ± 0.046	4.11 ± 0.11		**4.11**	
Main Effects					
AgLime	21.4 ± 0.93				
Gypsum	**11.1 ± 0.93**	**-0.87 ± 0.11**	< 0.0001	**-0.87**	24.3
Iron Sulfate	**-2.1 ± 0.93**	**1.36 ± 0.11**	< 0.0001	**1.36**	59.0
Two-Factor Interactions					
AgLime/Gypsum	**10.4 ± 0.93**	**0.49 ± 0.11**	0.0008	**0.49**	7.6
AgLime/Iron Sulfate	-3.7 ± 0.93				
Gypsum/Iron Sulfate	-2.9 ± 0.93				
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	-15.6 ± 0.93	0.40 ± 0.11	0.0035	**0.40**	5.0

Table 10.6 shows that all amendments and amendment combinations either have no retardance effect or increase the mobility of Cu in the column leaching study. Iron Sulfate and all combinations containing Iron Sulfate result in increased leaching of Cu confirmed by experimental data results. Additional supporting material is located in Appendix X; X-A-17, X-A-20 and X-A-28.

Table 10.6 – Comparison of Table of Contrasts and ANOVA for Column Cu Results

Cu Column Leaching	**Table of Contrasts Effect**	**ANOVA Effect**	**ANOVA p**	**ANOVA Model**	**ANOVA % Contribution**
		Model	< 0.0001	**R =**	
Average Effect	8.2 ± 0.17	8.22 ± 0.67		**8.22**	
Main Effects					
AgLime	8.7 ± 0.35				
Gypsum	10.0 ± 0.35				
Iron Sulfate	**3.7 ± 0.35**	**7.57 ± 0.67**	< 0.0001	**7.57**	81.8
Two-Factor Interactions					
AgLime/Gypsum	0.02 ± 0.35	1.51 ± 0.67	0.0478	**1.51**	3.2
AgLime/Iron Sulfate	-2.7 ± 0.35				
Gypsum/Iron Sulfate	-5.6 ± 0.35				
Three-Factor Interactions					
AgLime/Gypsum/Iron Sulfate	-8.4 ± 0.35	1.53 ± 0.67	0.0449	**1.53**	3.4

10.3 Summary of Findings

10.3.1 Hypothesis 1:

CCA-metals in a wood ash/soil system are preferentially associated with soil particle matter and their rainwater-leachability is affected by the soil chemical components

1) CCA-ash and AgLime had the same particle size distribution range of 425 to <45 microns while untreated-wood ash had a particle size distribution four times greater in the <75 micron particle size

2) CCA-ash used in this research was determined to be composed of 23% CCA-metals and that mass of CCA-metals represents a CCA-ash that contains approximately 45% by mass of CCA-metal oxides

3) Ultisol test soil when mixed with CCA-ash retards the rainwater-leaching of As and Cr, by 75% and 74% compared to the rainwater-leaching of CCA-ash alone

4) Cu mobility from rainwater-leaching of CCA-ash is increased by the presence of Ultisol test soil

5) Ultisol test soil extraction with deionized water determined the readily leachable cations to be species of Al, Fe, Na, and K with Al and Fe being the highest concentrations

6) The alkalinity of a CCA-ash/Ultisol soil system is lower than that of an untreated-wood ash/Ultisol soil system with untreated-wood ash exhibiting a liming effect four times that of CCA-ash

7) The reactivity of untreated-wood ash and AgLime were determined to be equal and twice the magnitude of CCA-ash

8) The "fast acting" capacities of untreated-wood ash and AgLime were found to be equal and half of the magnitude of CCA-ash

9) Ultisol test soil/CCA-ash rainwater-leached over a pH range of 6.7-8 while Ultisol test soil/untreated-wood ash rainwater-leached at a constant pH 10

10.3.2 Hypothesis 2:

Burn sites contaminated with metals have the potential for contamination of water as the result of rainwater-leaching of burn sites

1) A CCA-ash/Ultisol test soil mixture was shown to have the potential for the contamination of water with high concentrations of As, Cu, and Cr in excess of regulatory limits and the contamination potential followed the order As > Cu > Cr

2) A CCA-treated wood burn site was shown to have high concentrations of CCA-metals on the surface soil, little vertical penetration in the soil column, and horizontal migration of surface CCA-metals downgradient from the burn site

3) The CCA-treated wood burn site sampling plan was found acceptable with not sample contamination and no data outliers

10.3.3 Hypothesis 3:

Retardance mechanisms within soils are effective means of reducing metals mobility and may be enhanced with amendments in order to further immobilize metals

1) For the batch rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed significant main effects for As retardance resulting from use of the amendments AgLime, Gypsum, and Iron Sulfate and from the two-factor interaction effect of AgLime/Iron Sulfate

2) For the batch rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed significant main effects for Cr retardance resulting from use of the amendments Iron Sulfate and Gypsum and from the two-factor interaction effect of Gypsum/Iron Sulfate

3) For the batch rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed significant main effects for Cu mobility retardance resulting from use of the amendment AgLime and increased mobility from use of the amendment Iron Sulfate while the two-factor interaction of AgLime/Iron Sulfate computed as a reduction in Cu mobility

4) For the batch rainwater-leaching study, Ultisol test soil/CCA-ash mixtures amended by three different amendments and four different amendment combinations had either little effect or increased the Cu mobility compared to the rainwater-leaching of the Ultisol test soil/CCA-ash mixture

5) An optimization batch-leaching study revealed that a mass ratio of 3:1 of Gypsum amendment to CCA-metals was most effective in reducing the leaching mobility of Cr and As metals while the study also revealed that Cu leaching mobility was increased by the additions of Gypsum

6) Prototype columns of soil, sand, and wood ash materials were constructed, flow-tested to determine the best column design and the most efficient mass of column media necessary to produce leaching retention times of 12 to 24 hours, and the design for Column 5 was determined to have the required soil to ash mass ratio of 4.6:1, an efficient and reproducible construction design, and uniform flow rates and retention times of 12 to 20 hours

7) For the column rainwater-leaching study, all amendment combinations containing iron sulfate fall within the very acidic pH range of 0.8-2.1 and leach more Cu and As and less Cr than the unamended Ultisol soil/CCA-ash mixture

8) For the column rainwater-leaching study, Gypsum and AgLime/Gypsum amendments are more effective for Cr retardance in a non-acidic pH range of 7.6-8

9) For the column rainwater-leaching study, Gypsum and Iron Sulfate/ Gypsum amendments of Ultisol soil/CCA-ash mixtures performed best for Cr retardation (up to

72%) and Gypsum and Gypsum /AgLime amendments performed best for reducing As leaching (up to 77%) over the unamended Ultisol soil/CCA-ash mixture

10) For the column rainwater-leaching study, although Ultisol soil/CCA-ash mixtures containing Iron Sulfate performed well in retarding Cr, Iron Sulfate and all amendment combinations with Iron Sulfate increased the leaching of As

11) For the column rainwater-leaching study, Gypsum amendment acting alone upon the Ultisol soil/CCA-ash mixtures was found to be the most effective amendment for the overall retardation of Cr and As leaching

12) For the column rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed the main effect of Gypsum to reduce As mobility and Iron Sulfate to increase As mobility

13) For the column rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed notable retardance of Cr mobility for the main effects of Gypsum and Iron Sulfate

14) For the column rainwater-leaching study, a 2^3 Factorial Table of Contrasts computed a notable increase in Cu mobility due to the main effect of Iron Sulfate

15) Cu retardance resulted from the gypsum amendment in the high liquid:solids ratio of the batch rainwater-leaching study while the low liquid:solids ratio of the column rainwater-leaching study resulted in increased mobility of Cu

10.3.4 Conclusions of Research

The column rainwater-leaching study resulted in data that proves that the addition of agricultural soil amendments to soil contaminated with CCA-ash is potentially a feasible means of retarding the rainwater-leaching mobility of Cu, Cr, and As species. The study has shown that addition of the gypsum to the Ultisol soil/CCA-ash mixture will produce significant and continued retardance of the rainwater-leaching of As and Cr species. Retardance of As and Cr leaching is 77% and 72%, respectively, while Cu leaching was increased by up to 400%. Gypsum supplies a source of Ca^{+2} ions and pH conditions that modify surface conditions at adsorption sites of the soil structure resulting in enhanced adsorption and precipitation mechanisms. Experimental results indicate that gypsum addition in the ratio 3:1 of gypsum to CCA-metals mass in the CCA-ash will result in significant reductions in leaching of As and Cr species and will should enhance remediation of the species by the Ultisol soil matrix materials. These findings may be utilized to plan for the amendment of soil/CCA-ash with the optimum amount of gypsum in order to enhance adsorption, precipitation, and remediation of the leaching As and Cr species.

10.4 Engineering Significance of Research

There is a growing need to understand the deleterious effects of the waste materials that result from the use of treated-wood products. As new treatment methods evolve and older treated-wood products enter the waste stream there is a need to examine the effects of these discarded wastes upon the soil and water environments.

The disposal of CCA-treated wood waste is projected to be an ever increasing problem. Means of stabilizing and attenuating the release of toxic metal species that result from improper disposal methods (ie. burning) will become more attractive alternatives to massive cleanup efforts at small soil contaminated sites. Remedial means employed at residential construction and demolition sites will become more viable than the option of doing nothing to the soil at sites contaminated with CCA-ash and CCA-metal species. The investigation of alternative methods of stabilization and toxicity reduction of CCA-metals may be much better alternatives than the option of landfilling the contaminated soil.

10.5 Future Work and Recommendations

There are three areas of this research that appear to warrant further study. First, a more detailed study of the stoichiometry of the reaction of the gypsum amendment with Ultisol soil/CCA-treated wood ash should be undertaken. The gypsum amendment has proved to be effective in this research, but the concentration threshold needs to be examined in more detail; that is, what are the effective concentration ranges of gypsum addition and what are the effects upon individual components of the Ultisol soil/CCA-ash system? It is known that the structures of kaolinitic clay, iron and aluminum oxides, and organic materials within the Ultisol soil are major components of metals retardance mechanisms. The modification of these structures by reaction with gypsum in a soil system offers the potential for research into further enhancement of soil retardance mechanisms.

Second, the potential and effectiveness of the addition of a source of Fe^{+2} to the gypsum amendment should be investigated. If the addition of a source of Fe^{+2} does not change the pH range of the soil mechanism reactions then the resulting retardance of leached metals and changes in oxidation states of retarded metals, particularly chromium, may be enhanced. Evanko and Dzomback (1997) reported that the addition of iron fillings to a soil matrix material would enhance the chromium reduction from Cr(VI) to Cr(III). It has been shown that the controlling solids for Cr adsorption are either $Cr(OH)_3$ reactions or Cr(III) in coprecipitation with Fe oxides and hydroxides (Rai, *et al*, 1987). Furthermore, iron fillings have been reported to be a source of Fe^{+2} for supplementing Fe oxide matrix materials of soils and will enhance the adsorption ability of that matrix (EPA, 1991). This potential addition of an Fe^{+2} source to the gypsum amendment could further attenuate the Cr leach spike that is characteristic of initial Cr leaching in this and other research studies.

Third, an area that warrants further research concerns the valence states of the metals within the CCA-ash, the test soil/CCA-ash mixture and the test soil/CCA-ash/amendment combinations. Such a study would involve both the rainwater leachate and the residual mixture solids after leaching. This study would determine the oxidation-reduction states during the natural remediation by the test soil and during the remediation by the amendment concentrations and combinations. Research in this area could be used to better assess the performance of newly formulated additives, ie. additives containing Fe^{+2} combined with the gypsum amendment.

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APPENDIX X

X-A-1 Percentages by Mass of the Particle Size Distribution of Experimental Media

	Sieve No.	20	30	40	50	60	70	100	200	230	325	
Sample	Microns	2000	840	590	420	297	250	210	149	74	44	
10g	Wood Ash			3.1	6.2	7.1	9.3	11.7	21.5	23.7	45.1	100%
10g	CCA Ash			8.2	20.4	24.5	32.5	45.2	72.2	88.1	94.1	100%
73g	AgLime			10.3	24.9	31.6	38.9	49.3	73.6	80.5	90.9	100%
25g	Soil	14.4	21.5	30.3	42.7	48.7	56.6	65.1	77.7	79.8	83.4	100%

X-A-2 Liming Characteristics of Untreated-wood Ash and CCA-wood Ash (value +/- standard deviation)

	Neutralizing Value (NV)	Reactivity	r_{ac}/NV
	(Liming Effect - % $CaCO_3$)	(r_{ac})	("fast acting" capacity)
Untreated-wood Ash	44.5±3.2	33.8±7.5	78.4±0.18
CCA-wood Ash	11.7±0.7	18.7±1.6	161±0.16
AgLime	49.8±1.8	39.2±2.1	78.9±0.05

X-A-3 Ultisol Test Soil Mobile Cation Extraction Data (ppm in soil)

Leach	Ca	K	Mg	Al	Fe	Mn	Na
Mehlich 1	292	74	110	410	42	242	74
H_2O	3	32	6	79	64	3	57
ppm in soil							

X-A-4 pH Data for the Sequential Leaching of Experimental Media

Leach	1	2	3	4	5
Wood Ash	11	10.8	10	9.6	9.0
CCA-Ash	9.6	9.0	8.8	8.6	8.4
Test Soil	8	7.2	7.2	6.7	6.7
CCA-Ash/Test Soil	8.0	7.2	7.2	6.7	6.9
Wood Ash/Test Soil	10	10	10	10	10

X-A-5 Distribution of CCA-metals at the Burn Site

			Distance from Burn Site (m)				
			-4	**0**	**3**	**5**	**6**
Metal Conc. (mg g^{-1}) with Sample Depth	**Cu**	0-5 cm	0.016±0.001	14.5±1.10	1.96±0.03	0.090±0.005	0.013±0.001
		7.5 cm	<0.004	0.008	0.008	<0.004	<0.004
		15 cm	<0.004	0.009	0.026	<0.004	<0.004
	Cr	0-5 cm	0.023±0.004	17.4±1.37	3.05±0.30	0.130±0.005	0.018±0.003
		7.5 cm	<0.002	0.017	0.019	<0.002	<0.002
		15 cm	<0.002	0.017	0.024	<0.002	<0.002
	As	0-5 cm	0.016±0.01	12.2±0.95	1.50±0.01	0.050±0.01	<0.007
		7.5 cm	<0.007	0.027	0.017	<0.007	<0.007
		15 cm	<0.007	<0.007	0.030	<0.007	<0.007
0-5 cm Samples are triplicate analyses; 7.5 & 15 cm Samples are single analysis							

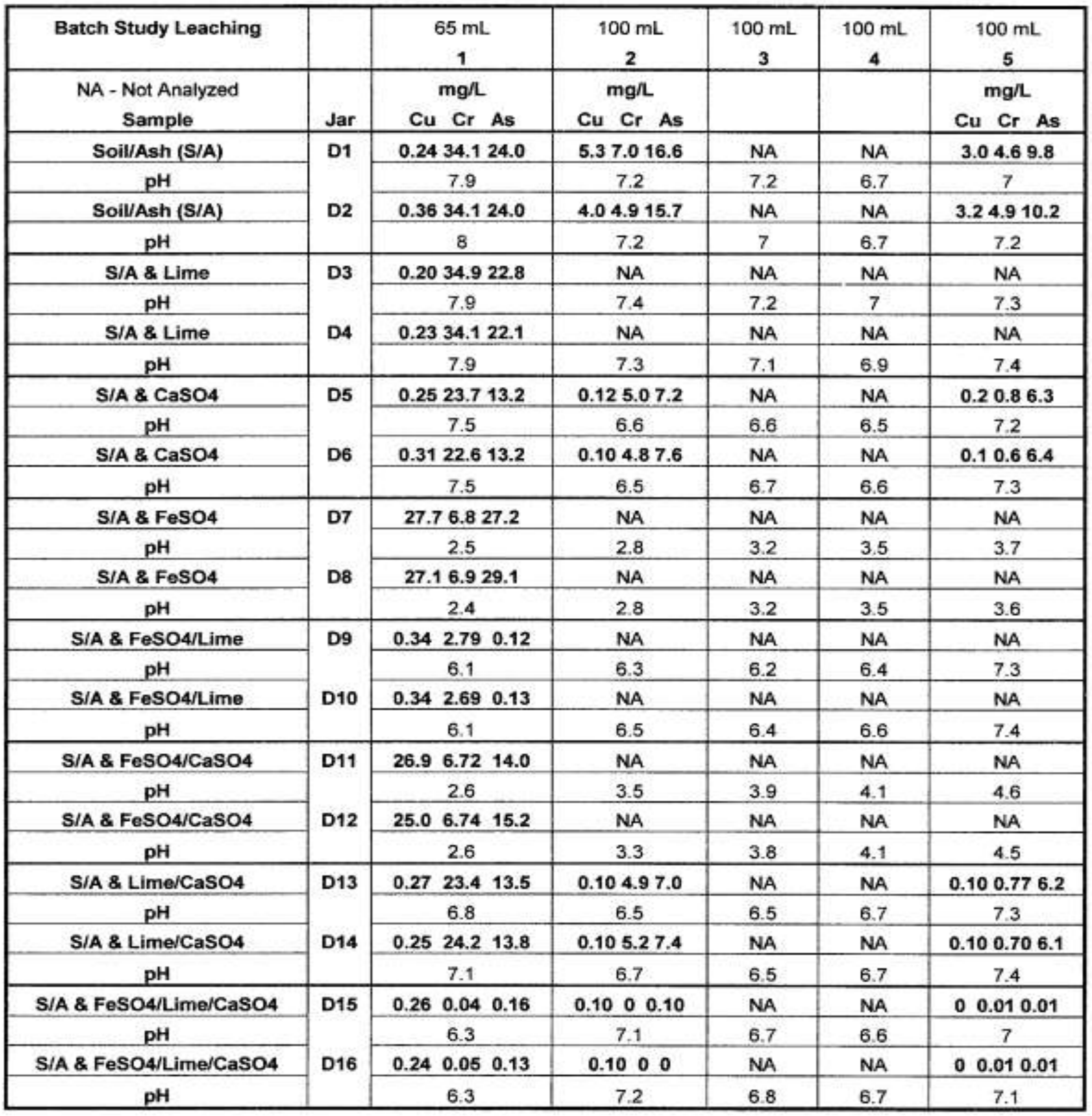
X-A-6 Data and Statistical Summary of Rainwater-leaching Experiment

Mass (mg metal g^{-1} ash)		**Cu**	**Cr**	**As**
CCA-wood Ash Leach				
Sample 1		0.010	17.2	10.5
Sample 2		0.010	16.4	9.90
Sample 3		0.010	17.7	10.1
Mean		0.010	17.1	10.1
Standard Deviation		0	0.66	0.31
Coefficient of Variation		0	3.9%	3.1%
Confidence Interval	95%	0.010±0.000	17.1±1.63	10.1±0.80
Ultisol Soil/CCA-wood Ash Leach				
Sample 1		0.032	4.23	2.70
Sample 2		0.026	4.10	2.53
Sample 3		0.028	4.34	2.57
Mean		0.029	4.23	2.60
Standard Deviation		0.003	0.12	0.09
Coefficient of Variation		10.3%	2.8%	3.5%
Confidence Interval	95%	0.029±0.007	4.23±0.29	2.60±0.22

X-A-7 Bulk Density of Ultisol Soil and CCA-wood Ash

Bulk Density	**(g cc^{-1})**
Ultisol Test Soil	1.19
CCA-wood Ash	0.165

X-A-8 Batch Leaching Study Raw Data



Batch Study Leaching		65 mL 1	100 mL 2	100 mL 3	100 mL 4	100 mL 5
NA - Not Analyzed Sample	Jar	mg/L Cu Cr As	mg/L Cu Cr As			mg/L Cu Cr As
Soil/Ash (S/A)	D1	0.24 34.1 24.0	5.3 7.0 16.6	NA	NA	3.0 4.6 9.8
pH		7.9	7.2	7.2	6.7	7
Soil/Ash (S/A)	D2	0.36 34.1 24.0	4.0 4.9 15.7	NA	NA	3.2 4.9 10.2
pH		8	7.2	7	6.7	7.2
S/A & Lime	D3	0.20 34.9 22.8	NA	NA	NA	NA
pH		7.9	7.4	7.2	7	7.3
S/A & Lime	D4	0.23 34.1 22.1	NA	NA	NA	NA
pH		7.9	7.3	7.1	6.9	7.4
S/A & CaSO4	D5	0.25 23.7 13.2	0.12 5.0 7.2	NA	NA	0.2 0.8 6.3
pH		7.5	6.6	6.6	6.5	7.2
S/A & CaSO4	D6	0.31 22.6 13.2	0.10 4.8 7.6	NA	NA	0.1 0.6 6.4
pH		7.5	6.5	6.7	6.6	7.3
S/A & FeSO4	D7	27.7 6.8 27.2	NA	NA	NA	NA
pH		2.5	2.8	3.2	3.5	3.7
S/A & FeSO4	D8	27.1 6.9 29.1	NA	NA	NA	NA
pH		2.4	2.8	3.2	3.5	3.6
S/A & FeSO4/Lime	D9	0.34 2.79 0.12	NA	NA	NA	NA
pH		6.1	6.3	6.2	6.4	7.3
S/A & FeSO4/Lime	D10	0.34 2.69 0.13	NA	NA	NA	NA
pH		6.1	6.5	6.4	6.6	7.4
S/A & FeSO4/CaSO4	D11	26.9 6.72 14.0	NA	NA	NA	NA
pH		2.6	3.5	3.9	4.1	4.6
S/A & FeSO4/CaSO4	D12	25.0 6.74 15.2	NA	NA	NA	NA
pH		2.6	3.3	3.8	4.1	4.5
S/A & Lime/CaSO4	D13	0.27 23.4 13.5	0.10 4.9 7.0	NA	NA	0.10 0.77 6.2
pH		6.8	6.5	6.5	6.7	7.3
S/A & Lime/CaSO4	D14	0.25 24.2 13.8	0.10 5.2 7.4	NA	NA	0.10 0.70 6.1
pH		7.1	6.7	6.5	6.7	7.4
S/A & FeSO4/Lime/CaSO4	D15	0.26 0.04 0.16	0.10 0 0.10	NA	NA	0 0.01 0.01
pH		6.3	7.1	6.7	6.6	7
S/A & FeSO4/Lime/CaSO4	D16	0.24 0.05 0.13	0.10 0 0	NA	NA	0 0.01 0.01
pH		6.3	7.2	6.8	6.7	7.1

X-A-9 Batch Leaching Study – pH Measurements

Jar Study - pH Measurements						
	Jar No.	1	2	3	4	5
Soil/Ash (S/A)	1	7.90	7.20	7.26	6.72	6.96
	2	7.95	7.15	7.03	6.72	7.16
S/A-Lime	3	7.88	7.38	7.16	7.00	7.30
	4	7.94	7.30	7.13	6.88	7.41
S/A-CaSO4	5	7.46	6.62	6.63	6.53	7.16
	6	7.48	6.46	6.70	6.55	7.28
S/A-FeSO4	7	2.45	2.80	3.25	3.52	3.69
	8	2.40	2.76	3.24	3.45	3.63
S/A-FeSO4/Lime	9	6.07	6.30	6.23	6.39	7.34
	10	6.14	6.53	6.43	6.58	7.37
S/A-FeSO4/CaSO4	11	2.65	3.53	3.88	4.11	4.57
	12	2.60	3.30	3.84	4.11	4.53
S/A-Lime/CaSO4	13	6.83	6.47	6.47	6.67	7.34
	14	7.10	6.70	6.50	6.68	7.38
S/A-CaSO4/Lime/FeSO4	15	6.32	7.10	6.72	6.62	7.02
	16	6.34	7.21	6.76	6.71	7.05

X-A-10 – Data for Gypsum Optimization Study

$CaSO_4$ (mg)	Cu * Average	± Range	Percent Change	Cr * Average	± Range	Percent Change	As * Average	± Range	Percent Change
0	0.002	0		0.266	0.025		0.242	0.006	
25	0.004	0.002	0	0.274	0.011	3	0.162	0.012	-33
100	0.004	0.002	0	0.216	0.011	-19	0.134	0.001	-45
400	0.014	0.001	700	0.151	0.011	-43	0.106	0.001	-56
* Duplicate samples									
± Difference in mg leached high-low									

X-A-11 As - Batch Leaching Study – 2^3 Factorial Table of Contrasts and Summary

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

As

	I	1	2	3	12	13	23	123	Yield Average	d (est)	Estimated Variance $\sum S^2 = \sum d^2/2$
1	+	-	-	-	+	+	+	-	1.56	0	0
2	+	+	-	-	-	-	+	+	1.46	0.04	0.0008
3	+	-	+	-	-	+	-	+	0.86	0	0.00
4	+	+	+	-	+	-	-	-	0.89	0.02	0.0002
5	+	-	-	+	+	-	-	+	1.83	0.12	0.0072
6	+	+	-	+	-	+	-	-	0.01	0	0
7	+	-	+	+	-	-	+	-	0.95	0.08	0.0032
8	+	+	+	+	+	+	+	+	0.01	0	0
	7.57	-2.83	-2.15	-1.97	1.01	-2.69	0.39	0.75	7.57		0.0114
Divisor	8	4	4	4	4	4	4	4			$\sum S^2$
	0.95	-0.71	-0.54	-0.49	0.25	-0.67	0.10	0.19			

Estimate of Variance **As**

$S^2 = \sum S^2/8 = 0.011/8$

$S^2 = 0.001$

Variance of an Effect

$V(\text{effect}) = S^2/4 = 0.001/4$

V(effect) = 0.00025

Standard Error of Effect

SE(effect) = √ V(effect) = √ (0.00025)

SE(effect) = 0.02

Average Effect	0.95 ± 0.01
Main Effects	
AgLime	**-0.71 ± 0.02**
Gypsum	**-0.54 ± 0.02**
Iron Sulfate	**-0.49 ± 0.02**
Two-Factor Interactions	
AgLime/Gypsum	0.25 ± 0.02
AgLime/Iron Sulfate	**-0.67 ± 0.02**
Gypsum/Iron Sulfate	0.10 ± 0.02
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	0.19 ± 0.02

X-A-12 Cr - Batch Leaching Study – 2^3 Factorial Table of Contrasts and Summary

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

Cr

	I	**1**	**2**	**3**	**12**	**13**	**23**	**123**	**Yield Average**	**d (est)**	**Estimated Variance $\sum S^2 = \sum d^2/2$**
1	+	-	-	-	+	+	+	-	**2.22**	**0**	**0**
2	+	+	-	-	-	-	+	+	**2.24**	**0.05**	**0.001**
3	+	-	+	-	-	+	-	+	**1.51**	**0.07**	**0.002**
4	+	+	+	-	+	-	-	-	**1.54**	**0.05**	**0.001**
5	+	-	-	+	+	-	-	+	**0.44**	**0.01**	**0.00**
6	+	+	-	+	-	+	-	-	**0.18**	**0**	**0**
7	+	-	+	+	-	-	+	-	**0.44**	**0**	**0**
8	+	+	+	+	+	+	+	+	**0.003**	**0.00**	**0**
	8.57	**-0.65**	**-1.59**	**-6.45**	**-0.17**	**-0.75**	**1.23**	**-0.19**	**8.57**		**0.004**
Divisor	**8**	**4**	**4**	**4**	**4**	**4**	**4**	**4**			$\sum S^2$
	1.07	**-0.16**	**-0.40**	**-1.61**	**-0.04**	**-0.19**	**0.31**	**-0.05**			

Estimate of Variance **Cr**

$S^2 = \sum S^2/8 = 0.004/8$

$S^2 = 0.0005$

Variance of an Effect

$V(\text{effect}) = S^2/4 = 0.0005/4$

V(effect) = 0.000125

Standard Error of Effect

SE(effect) = √ V(effect) = √ (0.000125)

SE(effect) = 0.01

Average Effect	1.07 ± 0.005
Main Effects	
AgLime	-016 ± 0.01
Gypsum	**-0.40 ± 0.01**
Iron Sulfate	**-1.61 ± 0.01**
Two-Factor Interactions	
AgLime/Gypsum	-0.04 ± 0.01
AgLime/Iron Sulfate	-0.19 ± 0.01
Gypsum/Iron Sulfate	**0.31 ± 0.01**
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	-0.05 ± 0.01

X-A-13 Cu - Batch Leaching Study – 2^3 Factorial Table of Contrasts and Summary

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

Cu

	I	1	2	3	12	13	23	123	Yield Average	d (est)	Estimated Variance $\sum S^2 = \sum d^2/2$
1	+	-	-	-	+	+	+	-	0.02	0	0
2	+	+	-	-	-	-	+	+	0.015	0.005	0.00001
3	+	-	+	-	-	+	-	+	0.02	0	0.00
4	+	+	+	-	+	-	-	-	0.02	0	0
5	+	-	-	+	+	-	-	+	1.8	0.00	0
6	+	+	-	+	-	+	-	-	0.02	0.00	0
7	+	-	+	+	-	-	+	-	1.68	0.1	0.00500
8	+	+	+	+	+	+	+	+	0.02	0.00	0
	3.58	-3.44	-0.12	3.44	0.12	-3.44	-0.12	0.12	3.58		0.005
Divisor	8	4	4	4	4	4	4	4			$\sum S^2$
	0.45	-0.86	-0.03	0.86	0.03	-0.86	-0.03	0.03			

Estimate of Variance **Cu**

$S^2 = \sum S^2/8 = 0.005/8$

$S^2 = 0.000625$

Variance of an Effect

V(effect) = $S^2/4 = 0.000625/4$

V(effect) = 0.00016

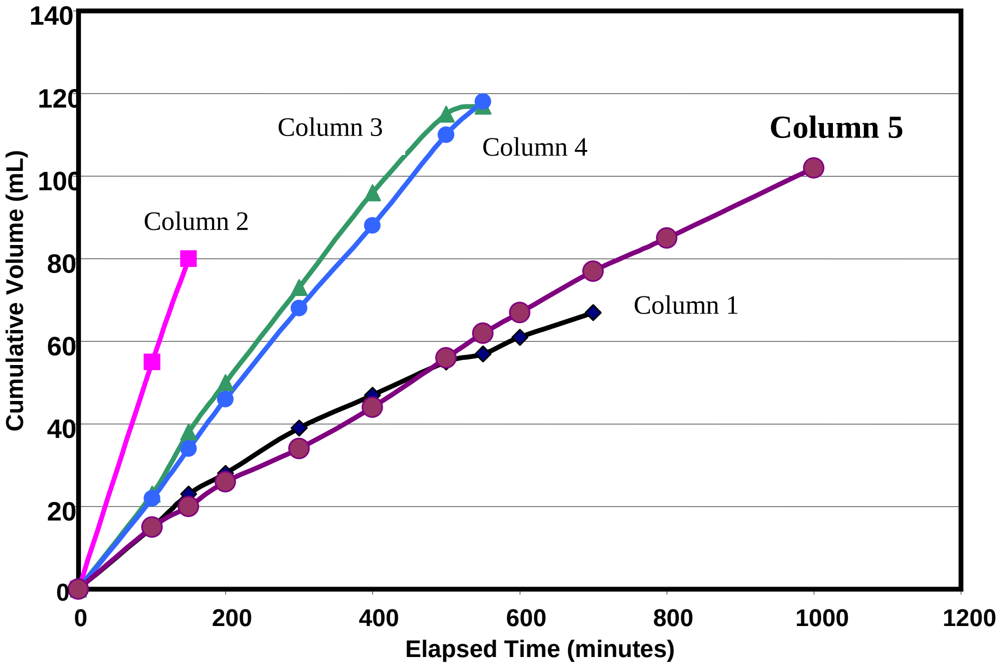
Standard Error of Effect

SE(effect) = √ V(effect) = √ (0.00016)

SE(effect) = 0.01

Average Effect	0.45 ± 0.005
Main Effects	
AgLime	**-0.86 ± 0.01**
Gypsum	-0.03 ± 0.01
Iron Sulfate	**0.86 ± 0.01**
Two-Factor Interactions	
AgLime/Gypsum	0.03 ± 0.01
AgLime/Iron Sulfate	**-0.86 ± 0.01**
Gypsum/Iron Sulfate	- 0.03 ± 0.01
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	0.03 ± 0.01

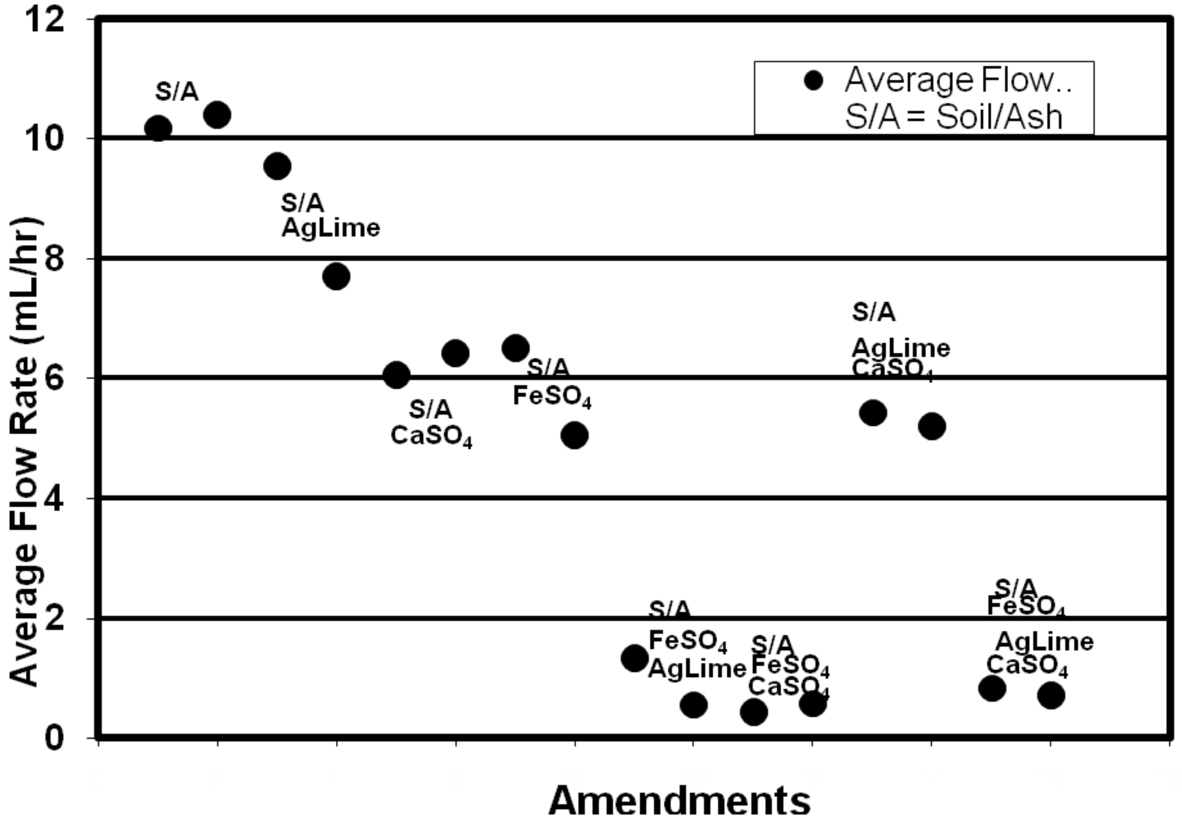
X-A-14 Column Design Flow Test Chart



X-A-15 Column Design Test Data

Column Design Test Data																			
Column 1	Time	0	15	40	45	55	65	135	340	705									
Cumulative	Volume	0	1	4	6	7	7.5	20	43	67									
Volume	80 mls																		
Composition:		Soil	230 g	6.75"															
		Sand Plug	100 g	2.75"															
Column 2	Time	0	15	30	40	45	55	65	135										
Cumulative	Volume	0	9	20	27	28	32	37	73										
Volume	80 mls																		
Composition:		Soil/Sand Mix		170 g	Soil	60g	Sand												
		Sand Plug	100 g																
Column 3	Time	0	140	190	225	270	290	305	480	520	545								
Cumulative	Volume	0	37	45	59	62	66.5	74	114	115	118								
Volume	115 mls																		
Composition:		Soil/Ash Mix		330 g	Soil	272 g	Ash	58 g											
		Sand Plug	145 g																
Column 4	Time	0	60	90	135	150	165	180	210	245	255	285	315	345	390	425	470	480	505
Cumulative	Volume	0	15	20	30	34	38	41	48	56	58	64	71	78	86	93	104	105	110
Volume	115 mls																		
Composition:		Soil/Ash/Sand Mix		330 g	Soil	238 g	Ash	51 g	Sand	41 g									
		Sand Plug	145 g																
Column 5	Time	0	30	50	115	130	220	270	335	370	390	460	490	585	630	650	675	750	1000
Cumulative	Volume	0	4	7	16	17	28	33	37	40	42	52	55	66	72	75	77	80	101
Volume	115 mls																		
Composition:		Soil	428 g																
		Ash	96 g																
		Sand Plug	100 g	40/20/40 Plug															

X-A-16 Column Leaching Study – Average Column Flow Rate vs Amendment



X-A-17 Column Leaching Study Raw Data

Column Study Data	Leach No.																		
pH and Leached Metals	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
NS=No Sample	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
ND=Not Determined	Cu Cr As	Cu Cr As			Cu Cr As				Cu Cr As										Cu Cr As
Sample No.	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
Soil/Ash (S/A)	0.019 104 1.72				0.038 2.96 13.0				0.008 1.13 8.64										
1	7.8	8.0	7.8	7.8	7.7	8.1	7.7	ND	7.5	7.4	7.9	7.5	7.7	7.5	ND	ND	ND	ND	ND
Soil/Ash (S/A)	0.016 81.0 1.94				0.036 2.67 12.7				0.014 0.770 8.22										
2	7.8	7.9	8.0	7.9	7.8	8.0	7.8	ND	7.7	7.7	8.0	7.5	7.7	7.7	ND	ND	ND	ND	ND
S/A Lime	0.016 103 1.73				0.044 2.46 12.0				0.012 0.850 8.36										
3	7.9	8.1	8.0	8.1	8.0	8.0	7.8	ND	7.8	7.8	8	7.7	7.8	7.6	ND	ND	ND	ND	ND
S/A Lime	0.013 94.8 1.15				0.048 2.30 12.4				0.014 0.630 7.92										
4	8.0	8.1	8.1	8.1	8.0	8.0	7.9	ND	7.8	7.9	8.1	7.8	7.8	7.7	ND	ND	ND	ND	ND
S/A CaSO4	1.27 14.7 1.12	0.440 27.0 1.78			0.070 2.23 1.53				0.028 0.640 1.42										0.018 0.009 1.40
5	8.0	8.0	7.8	7.7	7.6	7.6	7.4	ND	7.1	7.4	7.6	7.3	7.4	7.3	ND	ND	ND	ND	ND
S/A CaSO4	1.21 14.1 1.10	0.440 17.0 1.90			0.076 2.18 1.62				0.029 0.630 1.49										0.020 0.010 1.44
6	7.9	7.5	7.7	7.6	7.6	7.6	7.5	ND	7.2	7.4	7.6	7.3	7.4	7.2	ND	ND	ND	ND	ND
S/A FeSO4	15.0 3.76 30.9				8.46 2.43 19.4				0.470 0.077 0.085										
7	1.1	1.1	1.7	2.0	2.3	2.7	2.8	ND	3.0	3.1	3.1	3.3	3.4	3.2	ND	ND	ND	ND	ND
S/A FeSO4	16.2 4.23 35.3				8.46 2.43 19.4				0.450 0.078 0.112										
8	0.5	1.1	1.8	2.1	2.3	2.7	2.8	ND	2.9	3.0	3.1	3.1	3.1	3.3	ND	ND	ND	ND	ND
S/A FeSO4/Lime	9.90 2.91 23.0				0 0 0.010														
9	2.0	3.2	6.5	6.9	7.2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/Lime	15.3 3.63 29.8				0 0.010 0.010														
10	1.8	2.6	6.1	6.6	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/CaSO4	12.6 3.42 10.9				0.750 0.060 0.100				0.470 0.030 0.080										
11	2.1	2.1	2.1	2.9	3	3.2	3.3	ND	ND	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/CaSO4	11.7 2.97 22.9				0.660 0.080 0.060				0.090 0.004 0.020										
12	2.1	2.1	2.1	2.9	3.0	3.2	3.3	ND	ND	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A Lime/CaSO4	1.09 21.2 1.29	0.620 26.4 2.10			0.083 3.16 1.80				0.034 0.680 1.88										0.010 0.010 1.52
13	7.4	7.9	7.5	7.0	7.3	7.6	7.5	ND	6.8	6.9	6.8	7.0	6.8	6.4	ND	ND	ND	ND	ND
S/A Lime/CaSO4	1.15 24.0 1.43	0.580 27.8 2.48			0.079 2.83 2.13				0.029 0.710 2.10										0.010 0.010 1.55
14	7.9	7.9	7.6	7.3	7.4	7.6	7.5	ND	7.1	7.1	6.9	7.2	7.0	6.8	ND	ND	ND	ND	ND
S/A FeSO4/Lime/CaSO4	13.9 3.36 29.2	2.10 0.490 3.50			0.020 0 0.040														
15	2.1	6.2	6.3	7.4	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
S/A FeSO4/Lime/CaSO4	13.2 3.29 29.7	0.180 0.030 0.220			0.020 0 0.070														
16	2.1	6.3	6.4	7.3	7.4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

X-A-18 As - Column Leaching Study – 2^3 Factorial Table of Contrasts

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

	I	1	2	3	12	13	23	123	Yield Average	d (est)	As Column Estimated Variance $\sum S^2 = \sum d^2/2$
1	+	-	-	-	+	+	+	-	**14.6**	**0.05**	**0.001**
2	+	+	-	-	-	-	+	+	**13.6**	**0.05**	**0.001**
3	+	-	+	-	-	+	-	+	**2.6**	**0.05**	**0.001**
4	+	+	+	-	+	-	-	-	**53.7**	**2.7**	**3.6**
5	+	-	-	+	+	-	-	+	**3.5**	**0.40**	**0.08**
6	+	+	-	+	-	+	-	-	**26.4**	**3.40**	**5.8**
7	+	-	+	+	-	-	+	-	**16.9**	**6.0**	**18.0**
8	+	+	+	+	+	+	+	+	**29.4**	**0.20**	**0.02**
	160.7	**85.5**	**44.5**	**-8.3**	**41.7**	**-14.7**	**-11.7**	**-62.5**	**160.7**		**27.5**
Divisor	**8**	**4**	**4**	**4**	**4**	**4**	**4**	**4**			**$\sum S^2$**
	20.1	**21.4**	**11.1**	**-2.08**	**10.4**	**-3.68**	**-2.90**	**-15.6**			

Estimate of Variance	**As Column**
$S^2 = \sum S^2/8 = 27.5/8$	
$S^2 = 3.44$	
Variance of an Effect	
$V(\text{effect}) = S^2/4 = 3.44/4$	
$V(\text{effect}) = 0.86$	
Standard Error of Effect	
$SE(\text{effect}) = \sqrt{V(\text{effect})} = \sqrt{(0.86)}$	
$SE(\text{effect}) = 0.93$	
Average Effect	20.1 ± 0.46
Main Effects	
AgLime	21.4 ± 0.93
Gypsum	**11.1 ± 0.93**
Iron Sulfate	-2.1 ± 0.93
Two-Factor Interactions	
AgLime/Gypsum	**10.4 ± 0.93**
AgLime/Iron Sulfate	-3.7 ± 0.93
Gypsum/Iron Sulfate	- 2.9 ± 0.93
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	**-15.6 ± 0.93**

X-A-19 Cr - Column Leaching Study – 2^3 Factorial Table of Contrasts

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

	I	1	2	3	12	13	23	123	Yield Average	d (est)	Cr Column Estimated Variance $\sum S^2 = \sum d^2/2$
1	+	-	-	-	+	+	+	-	95.4	11.6	67.3
2	+	+	-	-	-	-	+	+	101.6	4.4	9.7
3	+	-	+	-	-	+	-	+	16.6	0.3	0.04
4	+	+	+	-	+	-	-	-	6.4	0.2	0.02
5	+	-	-	+	+	-	-	+	25.6	1.2	0.7
6	+	+	-	+	-	+	-	-	3.2	0.4	0.08
7	+	-	+	+	-	-	+	-	3.3	0.2	0.0
8	+	+	+	+	+	+	+	+	3.4	0.05	0.001
	256	-26.3	-166	-185	6.1	-18.3	151.9	38.9	256		77.9
Divisor	8	4	4	4	4	4	4	4			$\sum S^2$
	31.9	-6.6	-41.5	-46.1	1.53	-4.60	40.0	9.7			

Estimate of Variance	**Cr Column**
$S^2 = \sum S^2/8 = 77.9/8$	
$S^2 = 9.73$	
Variance of an Effect	
$V(\text{effect}) = S^2/4 = 9.73/4$	
V(effect) = 2.43	
Standard Error of Effect	
$SE(\text{effect}) = \sqrt{V(\text{effect})} = \sqrt{(2.43)}$	
SE(effect) = 1.56	
Average Effect	31.9 ± 0.8
Main Effects	
AgLime	-6.6 ± 1.6
Gypsum	**-41.5 ± 1.6**
Iron Sulfate	**-46.1 ± 1.6**
Two-Factor Interactions	
AgLime/Gypsum	**1.53 ± 1.6**
AgLime/Iron Sulfate	-4.6 ± 1.6
Gypsum/Iron Sulfate	**40.0 ± 1.6**
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	**9.7 ± 1.6**

X-A-20 Cu - Column Leaching Study – 2^3 Factorial Table of Contrasts

1 = AgLime
2 = Gypsum
3 = Iron Sulfate

Cu Column

	I	1	2	3	12	13	23	123	Yield Average	d (est)	Estimated Variance $\sum S^2 = \sum d^2/2$
1	+	-	-	-	+	+	+	-	**0.06**	**0**	**0**
2	+	+	-	-	-	-	+	+	**0.06**	**0**	**0**
3	+	-	+	-	-	+	-	+	**1.3**	**0**	**0**
4	+	+	+	-	+	-	-	-	**24.1**	**0.6**	**0.18**
5	+	-	-	+	+	-	-	+	**1.2**	**0.0**	**0**
6	+	+	-	+	-	+	-	-	**12.6**	**2.7**	**3.6**
7	+	-	+	+	-	-	+	-	**12.9**	**0.5**	**0.12**
8	+	+	+	+	+	+	+	+	**13.6**	**0.4**	**0.08**
	65.8	**34.9**	**40.0**	**14.8**	**0.10**	**-10.7**	**-22.6**	**-33.5**	**65.8**		**4.0**
Divisor	**8**	**4**	**4**	**4**	**4**	**4**	**4**	**4**			$\sum S^2$
	8.2	**8.7**	**10**	**3.7**	**0.02**	**-2.7**	**-5.6**	**-8.4**			

Estimate of Variance	**Cu Column**
$S^2 = \sum S^2/8 = 4.0/8$	
$S^2 = 0.50$	
Variance of an Effect	
$V(\text{effect}) = S^2/4 = 0.50/4$	
V(effect) = 0.125	
Standard Error of Effect	
$SE(\text{effect}) = \sqrt{V(\text{effect})} = \sqrt{(0.125)}$	
SE(effect) = 0.35	
Average Effect	8.2 ± 0.17
Main Effects	
AgLime	8.7 ± 0.35
Gypsum	**10.0 ± 0.35**
Iron Sulfate	**3.7 ± 0.35**
Two-Factor Interactions	
AgLime/Gypsum	**0.02 ± 0.35**
AgLime/Iron Sulfate	-2.7 ± 0.35
Gypsum/Iron Sulfate	**-5.6 ± 0.35**
Three-Factor Interactions	
AgLime/Gypsum/Iron Sulfate	**-8.4 ± 0.35**

X-A-21 Data for Column Rainwater-Leaching of Gypsum-Amended and Unamended Soil/CCA-Ash Mixtures

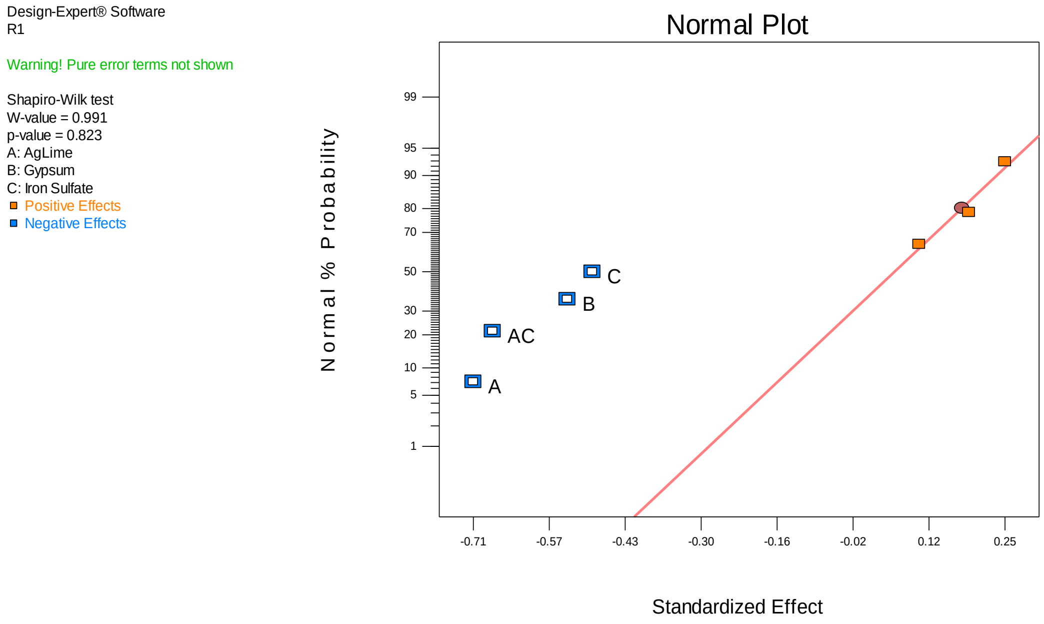
Column Data Table - Simulated One-Year Mass Leach - Control vs Gypsum Amendment
(Bold numbers are measured data, standard numbers are extraplolated data)

	Leach Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Cummulative Volume (mL)	45	145	245	345	445	545	645	745	845	945	1045	1145	1245	1345	1445	1545	1645	1745	1845
	Mass = mg																			
Cu	**Soil/Ash (S/A)**	**0.018**	0.279	0.060	0.037	**0.037**	0.030	0.020	0.011	**0.011**	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
	S/A-$CaSO_4$	**1.24**	**0.440**	0.130	0.080	**0.073**	0.050	0.040	0.030	**0.028**	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	**0.028**
Cr	**Soil/Ash (S/A)**	**92.5**	70.0	26.0	11.0	**2.82**	1.60	1.50	1.00	**0.950**	0.950	0.630	0.630	0.416	0.416	0.274	0.274	0.181	0.181	0.181
	S/A-$CaSO_4$	**14.4**	**22.0**	10.0	5.00	**2.21**	1.30	1.10	1.00	**0.635**	0.042	0.277	0.183	0.120	0.080	0.052	0.035	0.010	0.010	**0.010**
As	**Soil/Ash (S/A)**	**1.83**	7.00	10.0	11.8	**12.9**	12.7	12.0	10.7	**8.43**	6.50	5.25	4.20	3.50	3.05	2.90	2.85	2.85	2.80	2.80
	S/A-$CaSO_4$	**1.11**	**1.84**	1.60	1.60	**1.58**	1.50	1.50	1.50	**1.46**	1.46	1.46	1.46	1.46	1.46	1.46	1.42	1.42	1.42	**1.42**

X-A-22 Data for Comparison of Leachate Concentrations of Column and Batch Studies

Batch Leach	**Mixture**	**#1**	**#2**	**#5**
Cr	Control	34.1±0	6.00±1.48	4.80±0.21
(mg L^{-1})	Gypsum	23.1±0.78	4.90±0.14	0.70±0.14
As	Control	24.0±0	16.2±0.63	10.0±0.28
(mg L^{-1})	Gypsum	13.2±0	7.40±0.28	6.40±0.07
Cu	Control	0.30±0.08	4.60±0.92	3.10±0.14
(mg L^{-1})	Gypsum	0.28±0.04	0.11±0.01	0.15±0.07
Column Leach	**Mixture**	**#1**	**#2**	**#5**
Cr	Control	2056±360	NA	28.2±2.05
(mg L^{-1})	Gypsum	320±9.5	220±71	22.1±0.35
As	Control	40.6±3.46	NA	128±2.12
(mg L^{-1})	Gypsum	24.6±0.35	18.4±0.84	15.8±0.64
Cu	Control	0.39±0	NA	0.37±0.01
(mg L^{-1})	Gypsum	27.6±0.91	4.40±0	0.73±0.04

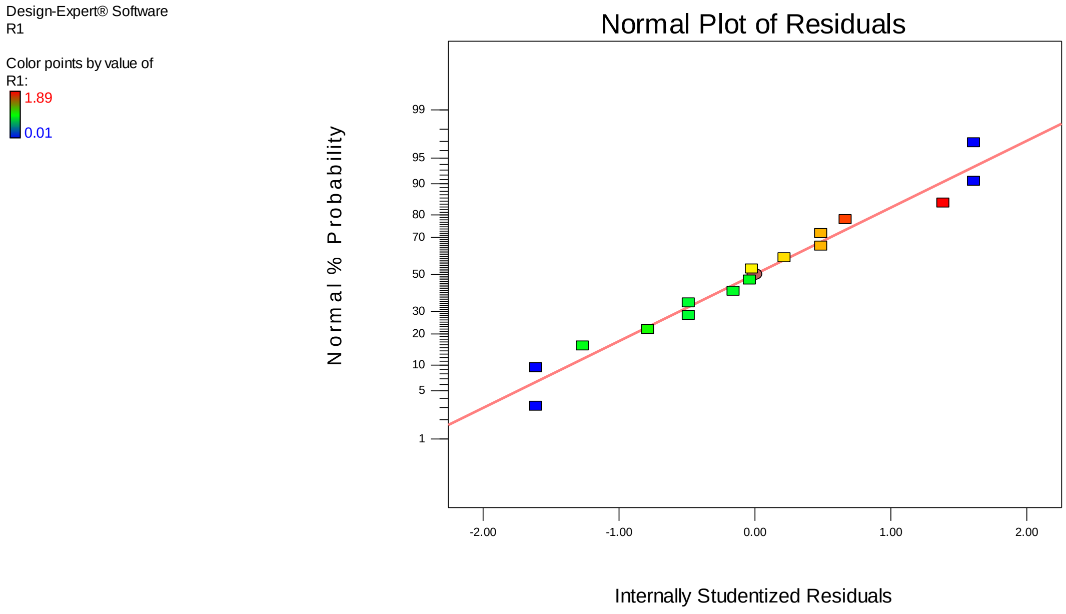
X-A-23 Batch – As - ANOVA



Design-Expert® Software
R1

Warning! Pure error terms not shown

Shapiro-Wilk test
W-value = 0.991
p-value = 0.823
A: AgLime
B: Gypsum
C: Iron Sulfate
🟧 Positive Effects
🟦 Negative Effects



Design-Expert® Software
R1

Color points by value of
R1:
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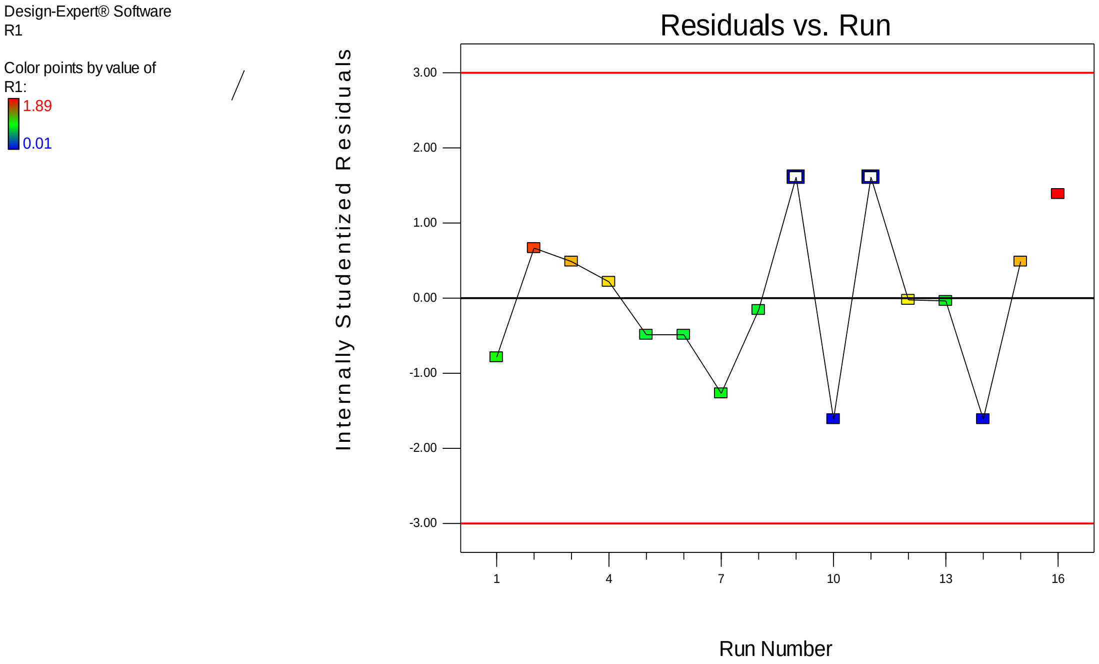
0.01

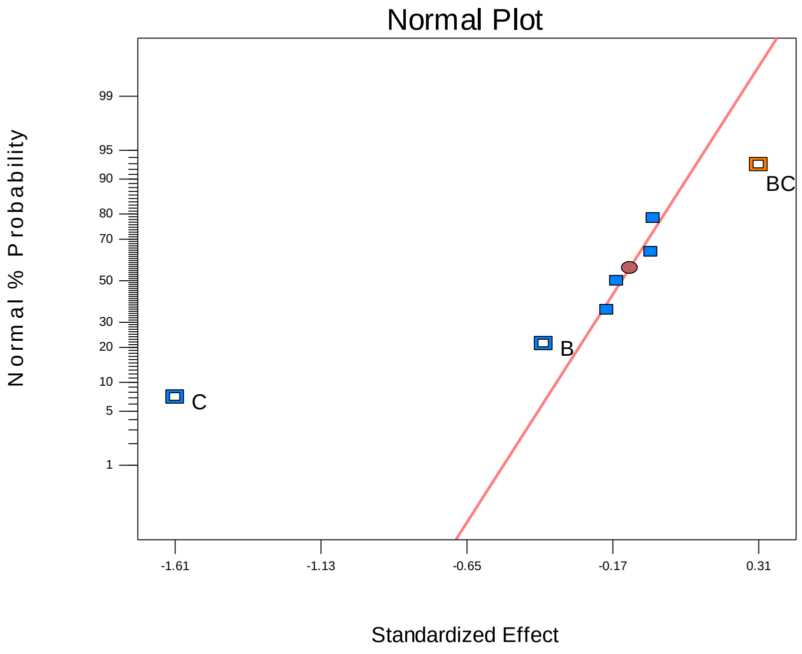

Design-Expert® Software
R1
Color points by value of R1:
1.89
0.01
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

X-A-24 Batch – Cr – ANOVA

Design-Expert® Software
R1

Warning! Pure error terms not shown

Shapiro-Wilk test
W-value = 0.842
p-value = 0.202
A: AgLime
B: Gypsum
C: Iron Sulfate
■ Positive Effects
■ Negative Effects



Design-Expert® Software
R1

Color points by value of
R1:
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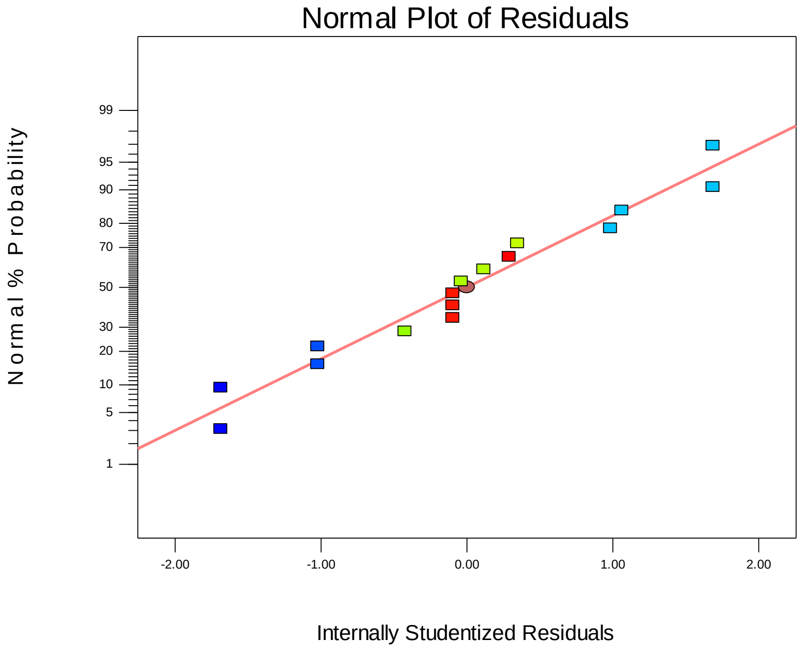
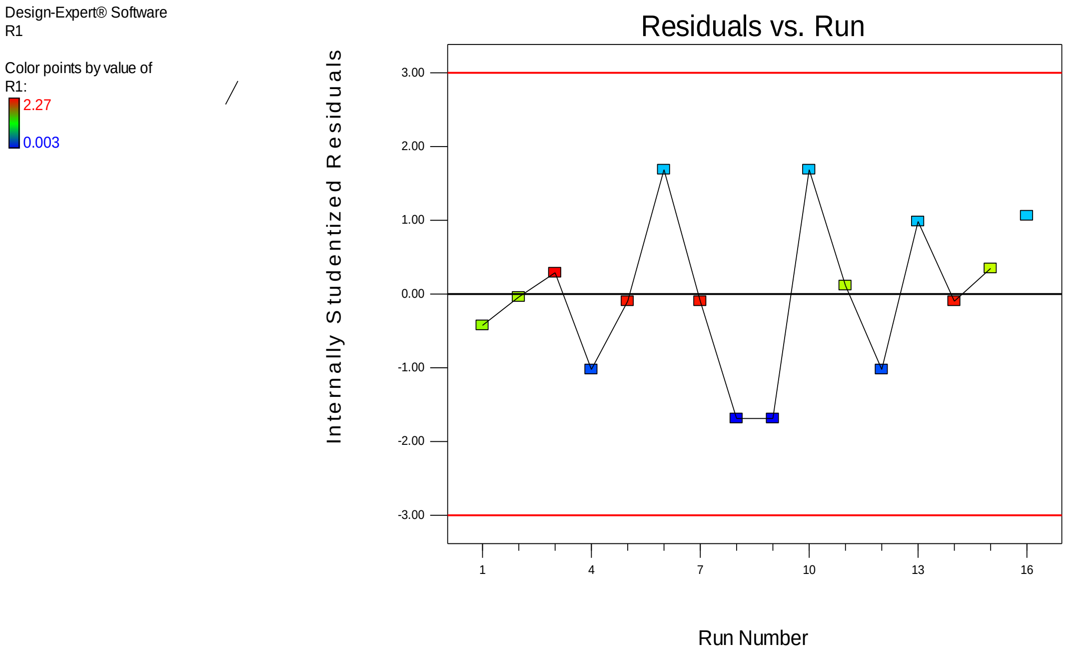
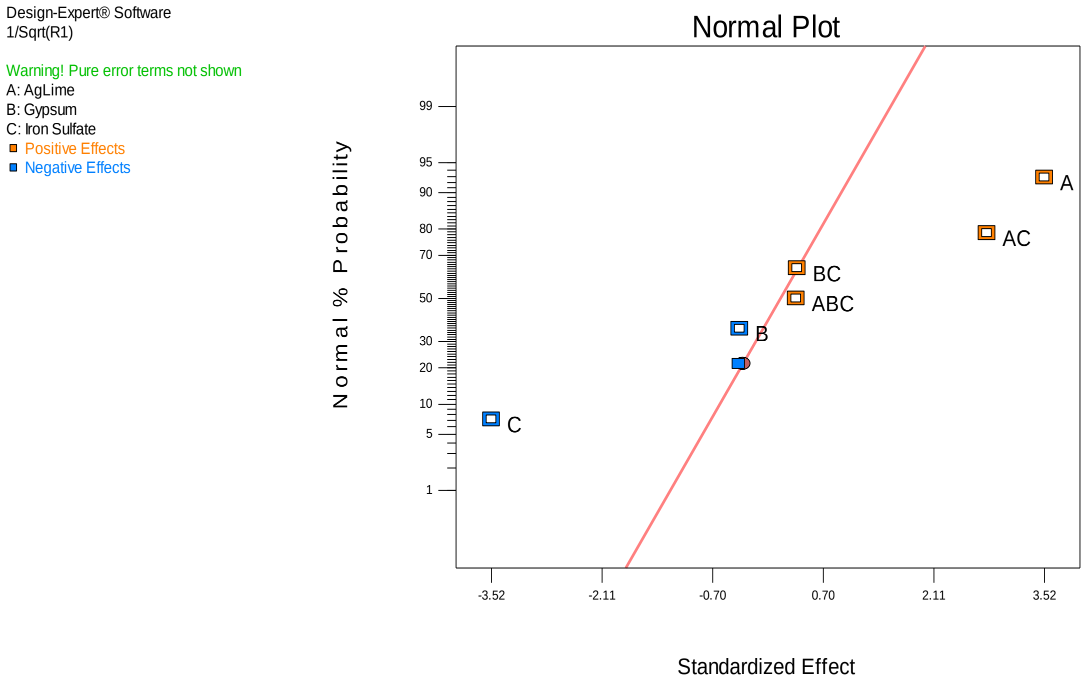
0.003

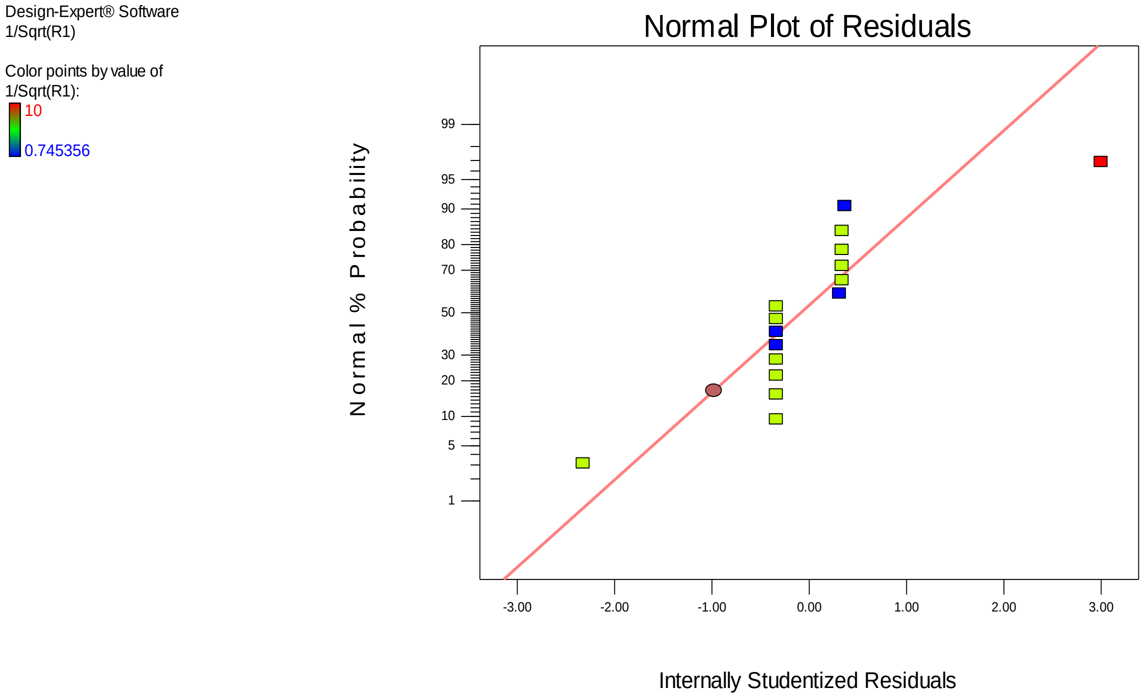


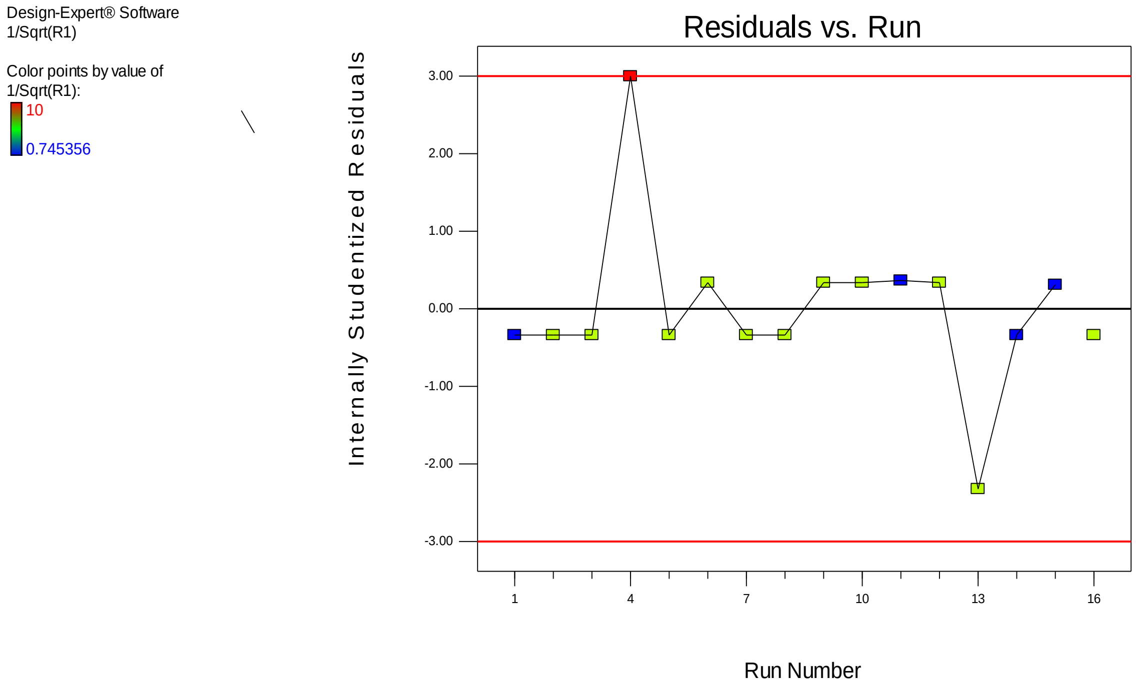


Design-Expert® Software
R1
Color points by value of
R1:
2.27
0.003
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

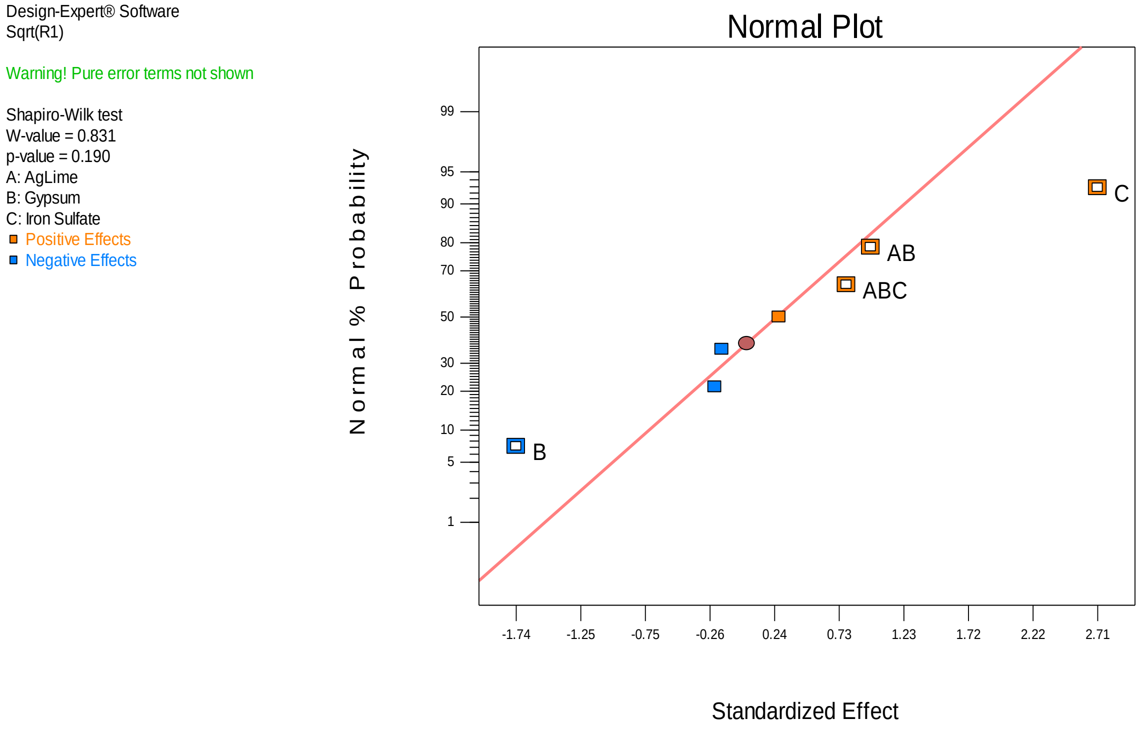
X-A-25 Batch – Cu – ANOVA

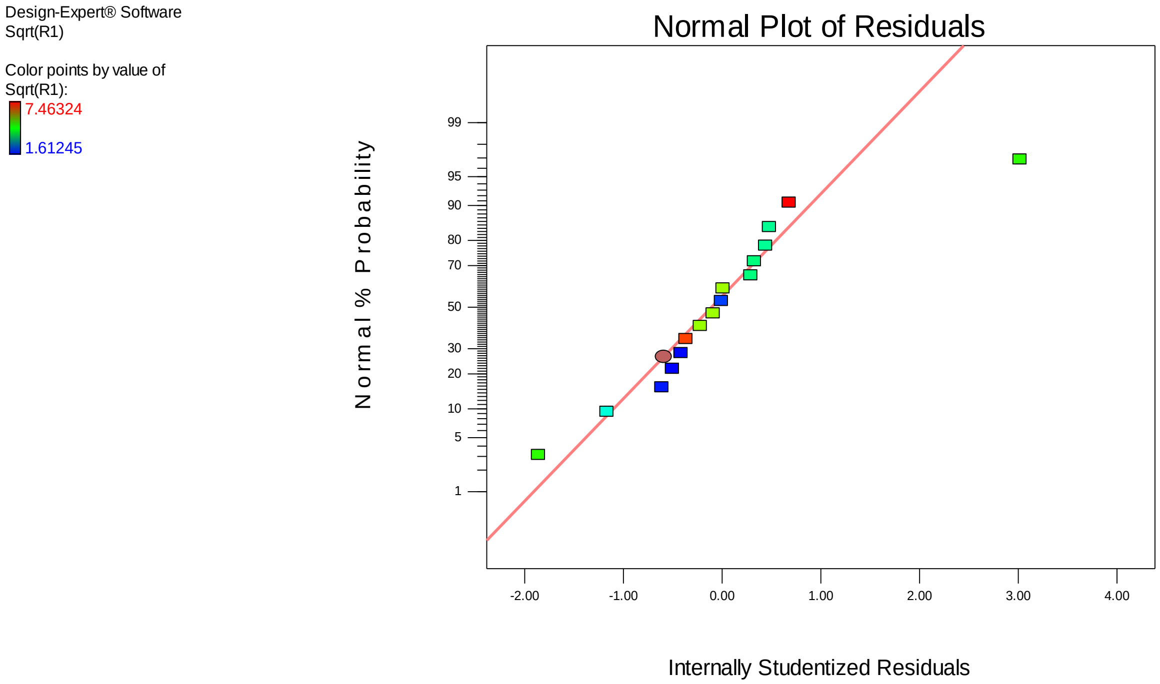


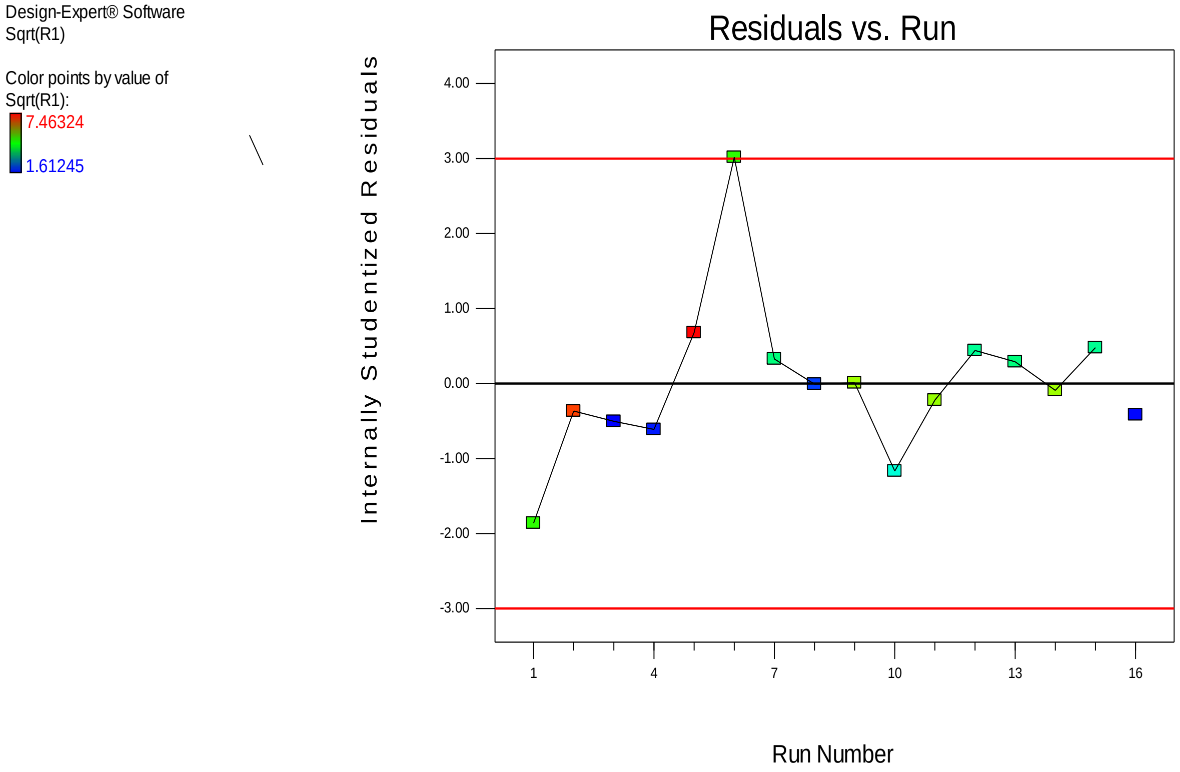



Design-Expert® Software
1/Sqrt(R1)
Color points by value of
1/Sqrt(R1):
10
0.745356
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

X-A-26 Column – As – ANOVA






Design-Expert® Software
Sqrt(R1)
Color points by value of
Sqrt(R1):
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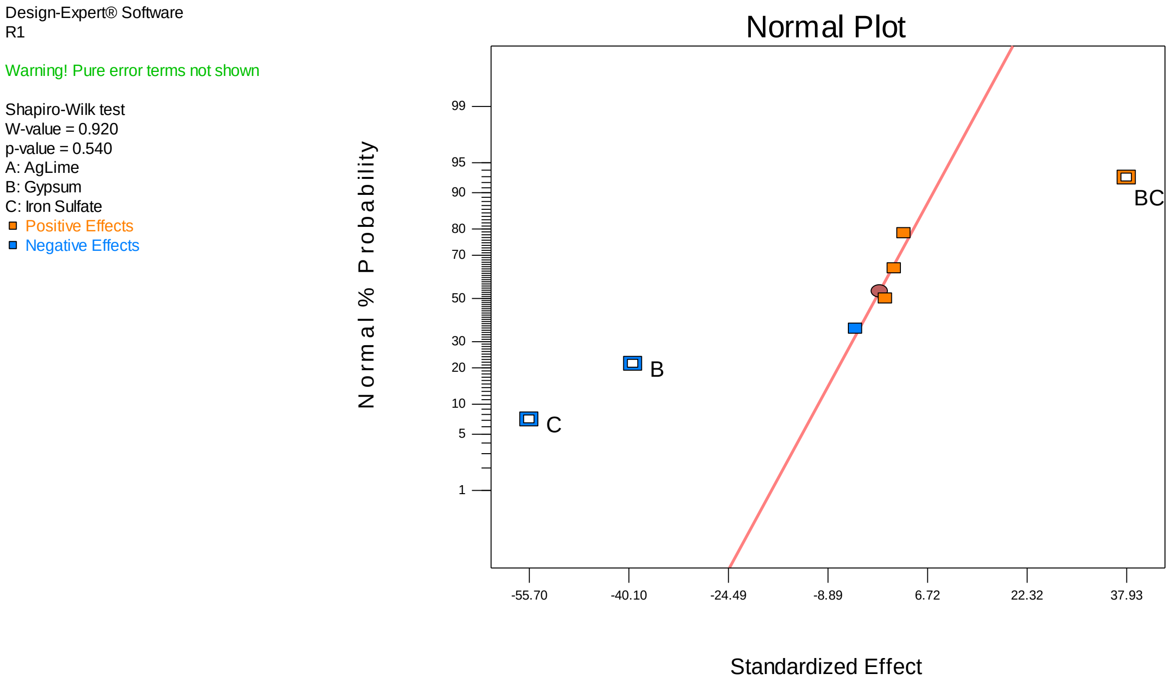
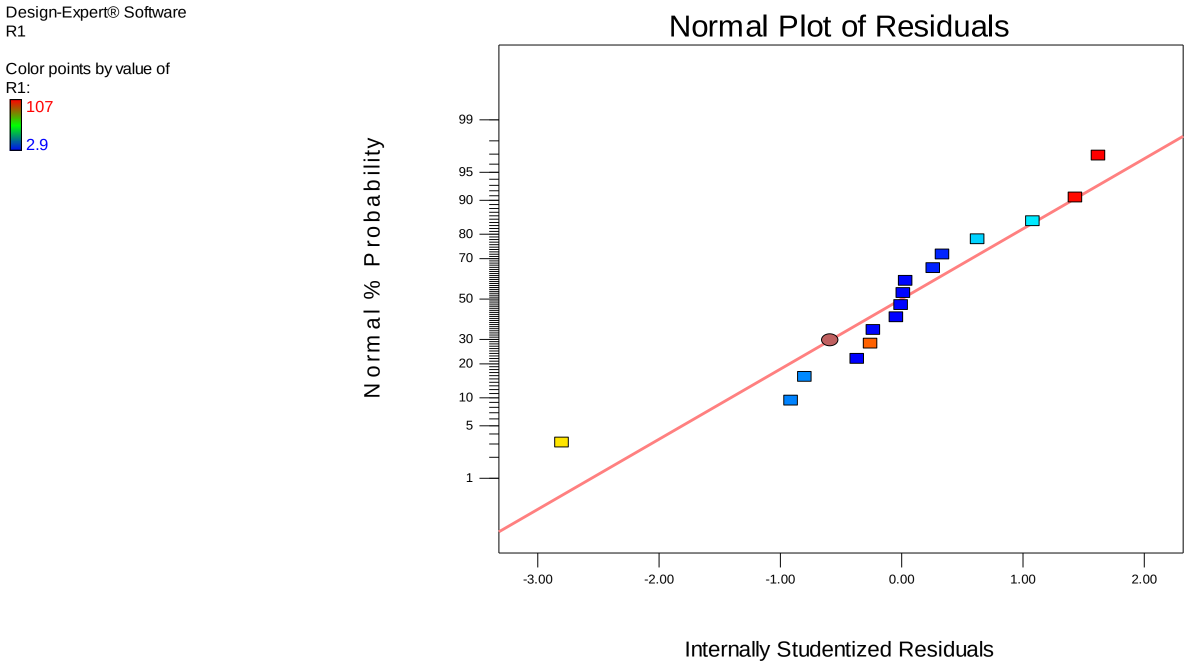
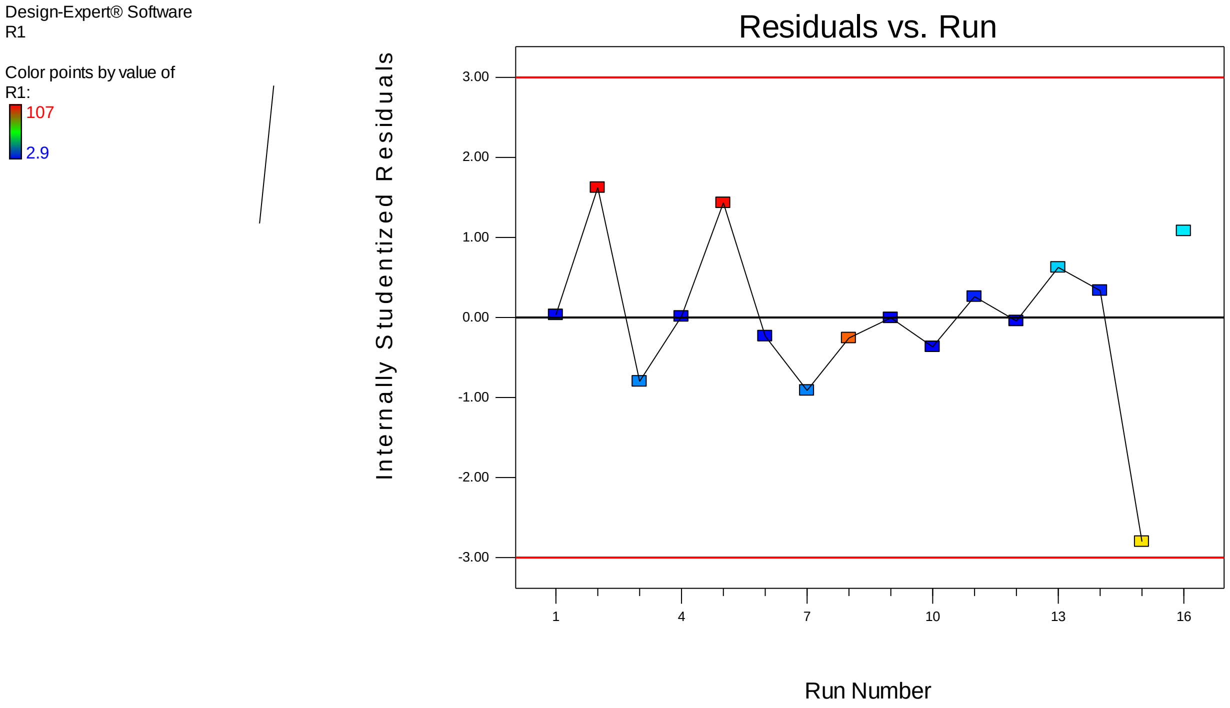
1.61245
Residuals vs. Run
Internally Studentized Residuals
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

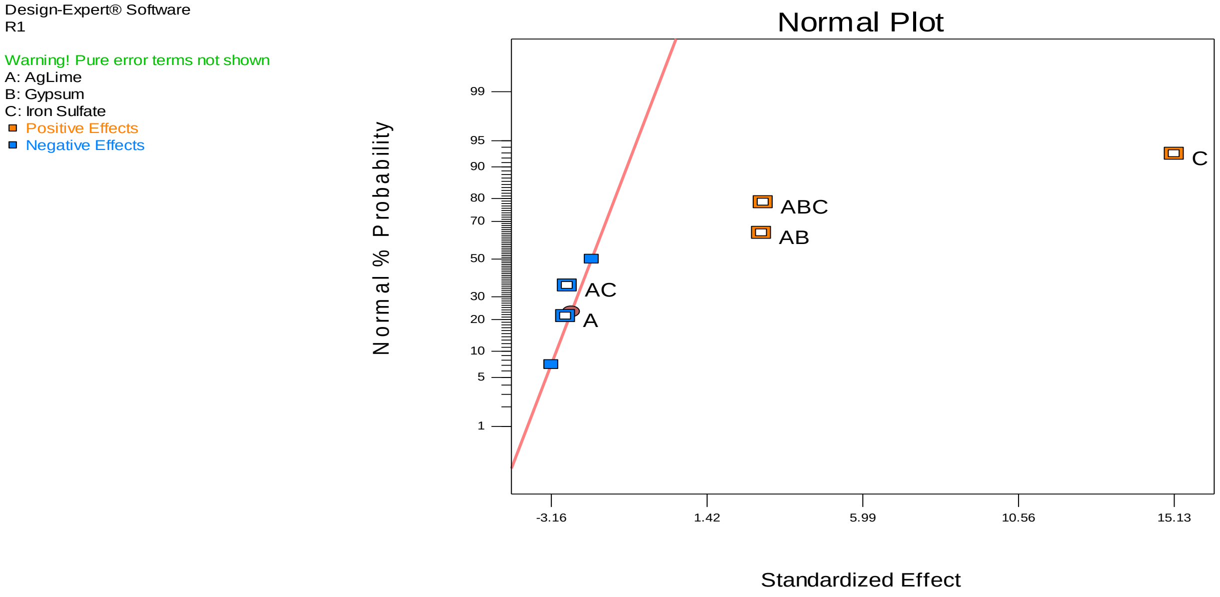
X-A-27 Column – Cr – ANOVA

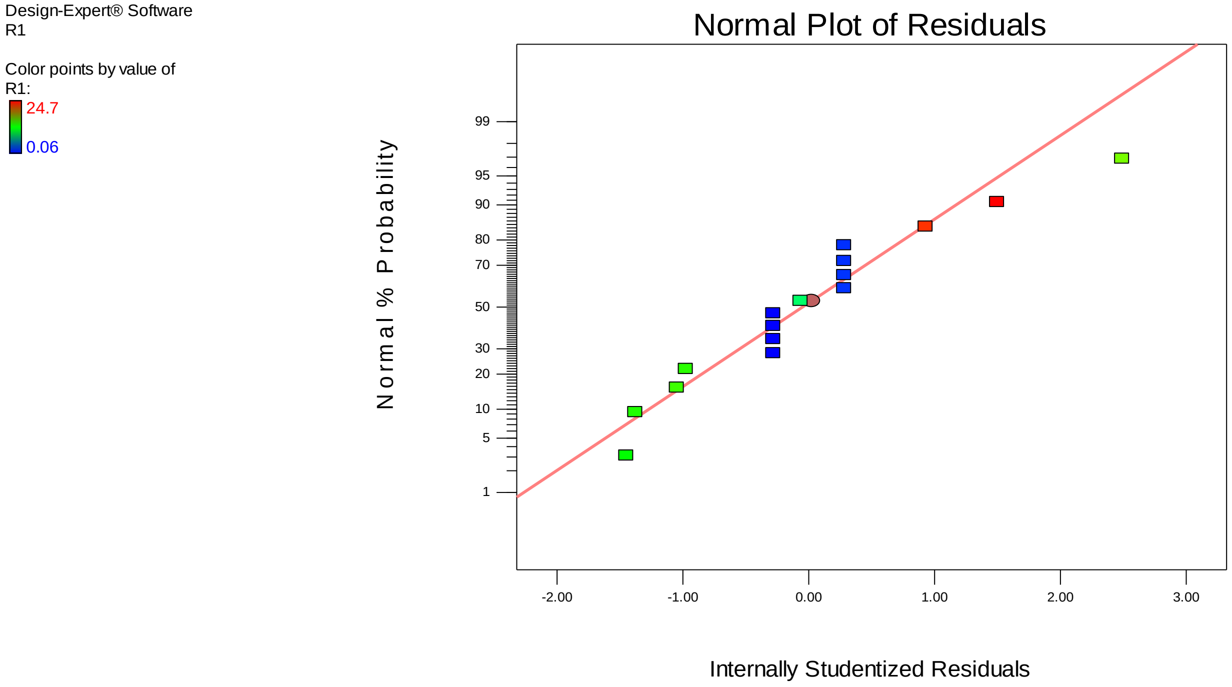


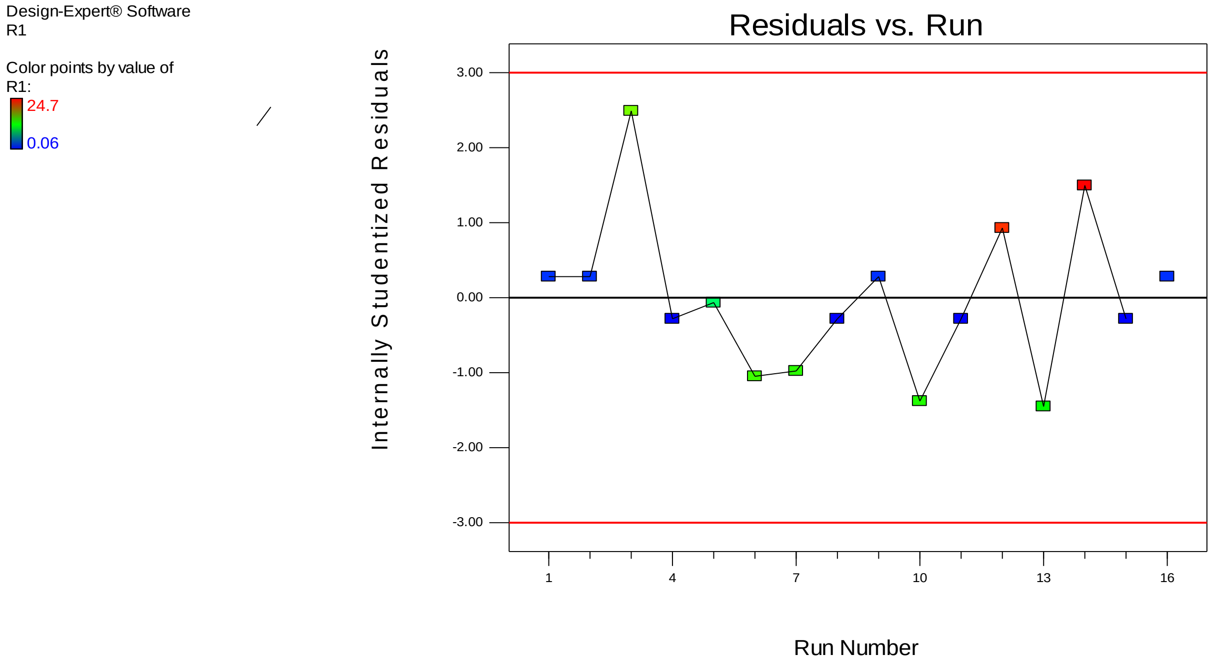



Design-Expert® Software
R1
Color points by value of
R1:
107
2.9
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

X-A-28 Column – Cu – ANOVA






Design-Expert® Software
R1
Color points by value of
R1:
24.7
0.06
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
4
7
10
13
16
Run Number

X-A-29 Data Results for ICP-OES Analysis of Samples for Research

Metals analyses are performed using a dual view model Perkin Elmer Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) DV3000. Data quality in this study is guaranteed through the use of blanks (lab blanks, equipment blanks, method blanks, and matrix blanks), NIST standards from two independent sources, spikes (matrix spike) and duplicates (matrix spike duplicates and lab duplicates) and lab replicates. The range of analyte concentrations in the samples will enable selection of appropriate internal standards and delineation of the range and matrix for the calibration solutions. Quality control standards are included at the beginning and end of the analytical run and repeated every ten samples throughout the run in order to ensure accuracy of the analysis. Sufficient matrix blanks are analyzed to determine the LOD/LOQ for each metal during each ICP run.

<u>**090301ce.csv**</u> <u>**090301S**</u>

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	ppm
lod	0.020	0.002	0.005	0.064	ppm
loq	0.067	0.007	0.010	0.180	ppm

0.050 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	3.530	-1.803	0.426	12.357

0.250 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	5.652	-1.833	-6.358	-3.146

0.500 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	5.129	-1.824	-6.704	-7.406

1.00 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	3.841	1.495	-3.780	-7.967

5.00 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	2.082	0.978	-3.480	-4.717

10.00 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	0.969	1.173	-3.308	-4.241

20.00 PPM HP	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
%difference	-0.574	1.200	-2.561	-2.920

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
BLANK 7-22-01B	1.010	0.002	<lod	<lod	ppm
7-22-01-1 ASH		6.817	0.722	578.475	ppm
7-22-01-2 ASH		6.690	0.714	574.696	ppm
7-22-01-3 ASH		6.271	0.679	545.842	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
BLANK 8-21-01-B	1.010	0.031	0.023	<lod	ppm
8-21-01-2 ASH DGN		227.684	339.626	283.236	ppm
8-21-01-3 ASH DGN		242.010	363.372	297.449	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-26-01-1 UPDIPSOIL	1.788	0.102	0.165	0.083	ppm
8-26-01-3 UPDIPSOIL	1.469	0.077	0.099	0.083	ppm
8-26-01-5 ASH/SOIL		61.004	72.206	53.028	ppm
8-26-01-6 ASH/SOIL		56.556	68.954	48.724	ppm
8-26-01-7 ASH/SOIL		52.293	61.900	45.311	ppm

090301R3

Sample ID	Analyte Name	Conc (Calib)	RSD (Conc)	Calib Units
Calib Blank 1	Y 371.029		0.4734349	mg/L
Calib Blank 1	Cu 327.393		0	mg/L
Calib Blank 1	Cr 267.716		0	mg/L
Calib Blank 1	As 188.979		0	mg/L
Calib Std 1	Y 371.029		0.2112638	mg/L
Calib Std 1	Cu 327.393		0	mg/L
Calib Std 1	Cr 267.716		0	mg/L
Calib Std 1	As 188.979		0	mg/L
Calib Std 6	Y 371.029		2.5974434	mg/L
Calib Std 6	Cu 327.393		0	mg/L
Calib Std 6	Cr 267.716		0	mg/L
Calib Std 6	As 188.979		0	mg/L
Calib Std 7	Y 371.029		3.43E-02	mg/L
Calib Std 7	Cu 327.393		1.32E-06	mg/L
Calib Std 7	Cr 267.716		1.32E-06	mg/L
Calib Std 7	As 188.979		1.32E-06	mg/L
BLANK	Y 371.029	1.01275367	0.1299229	mg/L
BLANK	Cu 327.393	1.05E-04	1972.5344	mg/L
BLANK	Cr 267.716	3.00E-03	39.338721	mg/L
BLANK	As 188.979	1.69E-02	58.869736	mg/L
BLANK 7-22-01B	Y 371.029	1.01001636	0.5684789	mg/L
BLANK 7-22-01B	Cu 327.393	2.14E-03	72.302797	mg/L
BLANK 7-22-01B	Cr 267.716	4.24E-03	45.982259	mg/L
BLANK 7-22-01B	As 188.979	2.20E-02	52.623716	mg/L
BLANK	Y 371.029	1.01044018	0.4635967	mg/L
BLANK	Cu 327.393	-2.03E-03	34.575524	mg/L

BLANK	Cr 267.716	4.58E-03	66.244552	mg/L
BLANK	As 188.979	1.67E-02	124.09142	mg/L
BLANK	Y 371.029	1.00664644	0.2922635	mg/L
BLANK	Cu 327.393	-9.25E-04	113.45958	mg/L
BLANK	Cr 267.716	2.63E-03	25.02959	mg/L
BLANK	As 188.979	-3.51E-03	525.07803	mg/L
BLANK 8-21-01-B	Y 371.029	1.01039052	0.2649481	mg/L
BLANK 8-21-01-B	Cu 327.393	3.09E-02	1.732995	mg/L
BLANK 8-21-01-B	Cr 267.716	2.28E-02	5.1057941	mg/L
BLANK 8-21-01-B	As 188.979	3.09E-02	52.435616	mg/L
BLANK	Y 371.029	0.9979089	1.0039862	mg/L
BLANK	Cu 327.393	-6.15E-04	255.73024	mg/L
BLANK	Cr 267.716	1.95E-03	90.976403	mg/L
BLANK	As 188.979	-1.18E-02	308.2994	mg/L
BLANK	Y 371.029	0.99370375	0.626512	mg/L
BLANK	Cu 327.393	-6.57E-04	120.4486	mg/L
BLANK	Cr 267.716	2.89E-03	39.386719	mg/L
BLANK	As 188.979	2.27E-02	113.53982	mg/L
BLANK	Y 371.029	1.00468368	0.4744277	mg/L
BLANK	Cu 327.393	-1.64E-03	108.83992	mg/L
BLANK	Cr 267.716	2.73E-03	84.589136	mg/L
BLANK	As 188.979	5.04E-03	424.54002	mg/L
BLANK	Y 371.029	1.00142746	0.3536419	mg/L
BLANK	Cu 327.393	-1.55E-03	91.158214	mg/L
BLANK	Cr 267.716	2.85E-03	68.944072	mg/L
BLANK	As 188.979	3.22E-02	16.731568	mg/L
BLANK	Y 371.029	0.99717437	0.3779725	mg/L
BLANK	Cu 327.393	-1.92E-03	63.681006	mg/L
BLANK	Cr 267.716	2.89E-03	64.326623	mg/L
BLANK	As 188.979	3.54E-02	96.728335	mg/L

<u>090301ce.csv</u> **John Harden**

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	ppm
BLANK	1.013	0.000	0.003	0.017	
	1.010	-0.002	0.005	0.017	
	1.007	-0.001	0.003	-0.004	
	0.998	-0.001	0.002	-0.012	
	0.994	-0.001	0.003	0.023	
	1.005	-0.002	0.003	0.005	
	1.001	-0.002	0.003	0.032	
	0.997	-0.002	0.003	0.035	

average	1.003	-0.001	0.003	0.014	ppm
stdev	0.007	0.001	0.001	0.017	ppm
lod	0.020	0.002	0.005	0.064	ppm
loq	0.067	0.007	0.010	0.180	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
0.050 PPM HP	1.032	0.049	0.050	0.058	ppm
	1.039	0.049	0.050	0.054	ppm
average	1.035	0.049	0.050	0.056	ppm
stdev	0.005	0.000	0.000	0.002	ppm
%rsd	0.518	0.463	0.080	4.265	ppm
%difference	3.530	-1.803	0.426	12.357	
actual	1.000	0.050	0.050	0.050	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
0.250 PPM HP	1.056	0.246	0.233	0.241	ppm
	1.057	0.245	0.236	0.243	ppm
average	1.057	0.245	0.234	0.242	ppm
stdev	0.000	0.001	0.002	0.002	ppm
%rsd	0.026	0.329	0.870	0.641	ppm
%difference	5.652	-1.833	-6.358	-3.146	
actual	1.000	0.250	0.250	0.250	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
0.500 PPM HP	1.049	0.492	0.465	0.456	ppm
	1.053	0.490	0.468	0.470	ppm
average	1.051	0.491	0.466	0.463	ppm
stdev	0.003	0.002	0.002	0.010	ppm
%rsd	0.277	0.323	0.409	2.121	ppm
%difference	5.129	-1.824	-6.704	-7.406	
actual	1.000	0.500	0.500	0.500	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
1.00 PPM HP	1.041	1.006	0.979	0.930	ppm
	1.035	1.018	0.960	0.908	ppm
	1.039	1.021	0.948	0.923	ppm
average	1.038	1.015	0.962	0.920	ppm
stdev	0.003	0.008	0.015	0.011	ppm
%rsd	0.275	0.813	1.607	1.201	ppm
%difference	3.841	1.495	-3.780	-7.967	
actual	1.000	1.000	1.000	1.000	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
5.00 PPM HP	1.025	5.039	4.896	4.832	ppm
	1.020	5.028	4.809	4.747	ppm
	1.018	5.079	4.773	4.713	ppm
average	1.021	5.049	4.826	4.764	ppm
stdev	0.004	0.027	0.064	0.061	ppm

%rsd	0.358	0.534	1.319	1.285	ppm
%difference	2.082	0.978	-3.480	-4.717	
actual	1.000	5.000	5.000	5.000	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
10.00 PPM HP	1.013	10.102	9.782	9.704	ppm
	1.008	10.114	9.594	9.481	ppm
	1.008	10.136	9.632	9.542	ppm
average	1.010	10.117	9.669	9.576	ppm
stdev	0.003	0.017	0.099	0.116	ppm
%rsd	0.271	0.169	1.027	1.207	ppm
%difference	0.969	1.173	-3.308	-4.241	
actual	1.000	10.000	10.000	10.000	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
20.00 PPM HP	0.997	20.170	19.712	19.742	ppm
	0.993	20.206	19.395	19.233	ppm
	0.993	20.345	19.356	19.273	ppm
average	0.994	20.240	19.488	19.416	ppm
stdev	0.003	0.093	0.195	0.283	ppm
%rsd	0.264	0.457	1.000	1.457	ppm
%difference	-0.574	1.200	-2.561	-2.920	
actual	1.000	20.000	20.000	20.000	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
BLANK 7-22-01B	1.010	0.002	0.004	0.022	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
7-22-01-1 ASH DF10	0.996	0.682	0.072	57.243	ppm
		6.817	0.722	572.431	ppm
7-22-01-1 ASH DF100	1.004	0.069	0.005	5.785	ppm
7-22-01-1 ASH		6.817	0.722	578.475	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
7-22-01-2 ASH DF10	0.999	0.669	0.071	56.888	ppm
		6.690	0.714	568.884	ppm
7-22-01-2 ASH DF100	1.011	0.067	0.003	5.747	ppm
				574.696	ppm
7-22-01-2 ASH		6.690	0.714	574.696	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
7-22-01-3 ASH DF10	1.001	0.627	0.068	55.798	ppm
		6.271	0.679	557.985	ppm
7-22-01-3 ASH DF100	1.016	0.063	0.002	5.458	ppm
				545.842	ppm
7-22-01-3 ASH		6.271	0.679	545.842	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
BLANK 8-21-01-B	1.010	0.031	0.023	0.031	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-21-01-1 ASH DGN DF100	1.003	2.311	3.520	2.923	ppm
8-21-01-1 ASH DGN		231.142	351.988	292.281	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-21-01-2 ASH DGN DF100	1.008	2.277	3.396	2.832	ppm
8-21-01-2 ASH DGN		227.684	339.626	283.236	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-21-01-3 ASH DGN DF100	1.020	2.420	3.634	2.974	ppm
8-21-01-3 ASH DGN		242.010	363.372	297.449	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-26-01-1 UPDIPSOIL	1.788	0.102	0.165	0.083	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-26-01-3 UPDIPSOIL	1.469	0.077	0.099	0.083	ppm

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979	
8-26-01-5 ASH/SOIL DF100	1.016	0.610	0.722	0.530	ppm
8-26-01-5 ASH/SOIL		61.004	72.206	53.028	ppm
8-26-01-6 ASH/SOIL DF100	1.003	0.566	0.690	0.487	ppm
8-26-01-6 ASH/SOIL		56.556	68.954	48.724	ppm
8-26-01-7 ASH/SOIL DF100	1.015	0.523	0.619	0.453	ppm
8-26-01-7 ASH/SOIL		52.293	61.900	45.311	ppm

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	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
0.050 PPM HP	1.089	0.051	0.056	0.042
	1.027	0.052	0.049	0.034
	1.121	0.050	0.050	0.026
	1.033	0.052	0.050	0.060
AVERAGE	1.067	0.051	0.051	0.040
STDEV	0.045	0.001	0.003	0.014
%RSD	4.245	2.429	6.012	35.397
%DIFFERENCE	6.727	2.597	2.464	-19.077
ACTUAL	1.000	0.050	0.050	0.050

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
0.250 PPM HP	1.158	0.242	0.260	0.249
	1.047	0.252	0.242	0.231
	1.177	0.241	0.257	0.241
	1.060	0.252	0.243	0.228
AVERAGE	1.110	0.247	0.250	0.237
STDEV	0.066	0.006	0.009	0.010
%RSD	5.964	2.381	3.640	4.084
%DIFFERENCE	11.035	-1.293	0.182	-5.052
ACTUAL	1.000	0.250	0.250	0.250

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
0.500 PPM HP	1.234	0.469	0.533	0.503
	1.051	0.497	0.482	0.459
	1.259	0.467	0.518	0.467
	1.095	0.492	0.484	0.460
AVERAGE	1.160	0.481	0.504	0.472
STDEV	0.103	0.015	0.025	0.021
%RSD	8.838	3.170	5.003	4.340
%DIFFERENCE	15.976	-3.721	0.855	-5.507
ACTUAL	1.000	0.500	0.500	0.500

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
1.00 PPM HP	1.056	1.005	0.966	0.990
	1.213	0.951	1.046	0.986
	1.097	0.981	0.978	0.944
	1.053	0.999	0.955	0.925
AVERAGE	1.105	0.984	0.986	0.961
STDEV	0.075	0.024	0.041	0.032
%RSD	6.804	2.473	4.153	3.280
%DIFFERENCE	10.477	-1.590	-1.354	-3.884
ACTUAL	1.000	1.000	1.000	1.000

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
5.00 PPM HP	1.137	4.760	5.109	5.027
	1.101	4.812	5.018	4.922
	1.045	4.927	4.833	4.755
	1.037	4.977	4.765	4.670
AVERAGE	1.080	4.869	4.931	4.844
STDEV	0.048	0.100	0.160	0.161
%RSD	4.404	2.062	3.235	3.320
%DIFFERENCE	8.012	-2.621	-1.379	-3.128
ACTUAL	1.000	5.000	5.000	5.000

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
10.00 PPM HP	1.057	9.733	10.081	10.027
	1.048	9.805	9.899	9.788
	1.016	9.895	9.551	9.485
	1.020	9.890	9.399	9.316
AVERAGE	1.035	9.831	9.733	9.654
STDEV	0.020	0.077	0.313	0.316
%RSD	1.942	0.784	3.212	3.275
%DIFFERENCE	3.527	-1.694	-2.674	-3.458
ACTUAL	1.000	10.000	10.000	10.000

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
20.00 PPM HP	1.008	18.826	18.860	18.963
	0.992	19.212	18.596	18.667
	0.979	19.083	18.064	18.209
	1.070	18.462	19.209	18.585
AVERAGE	1.012	18.896	18.682	18.606
STDEV	0.040	0.331	0.483	0.311
%RSD	3.988	1.750	2.583	1.670
%DIFFERENCE	1.249	-5.521	-6.589	-6.971
ACTUAL	1.000	20.000	20.000	20.000

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
BLANK	1.028	0.001	0.003	-0.004
	1.019	0.000	0.002	-0.001
	1.025	0.001	0.003	-0.005
	1.002	0.001	0.003	-0.007
	1.009	0.001	0.005	-0.004
	1.106	0.003	0.001	-0.003
	1.023	0.000	0.003	0.004
AVERAGE	1.031	0.001	0.003	-0.003
STDEV	0.034	0.001	0.002	0.005
LOD	0.103	0.005	0.008	0.014
LOQ	0.343	0.016	0.019	0.046

	Y 371.029	Cu 327.393	Cr 267.716	As 188.979
8-29-01 1 DF4	1.043	0.007	<LOD	<LOD
8-29-01 1		0.028	<LOD	<LOD
8-29-01 2 DF4	1.036	<LOD	<LOD	<LOD
8-29-01 2		<LOD	<LOD	<LOD
8-29-01 3 DF4	1.031	<LOD	<LOD	<LOD
8-29-01 3		<LOD	<LOD	<LOD
8-29-01 4 DF4	1.029	<LOD	<LOD	<LOD

8-29-01 4		<LOD	<LOD	<LOD
8-29-01 5 DF4	1.025	0.005	<LOD	<LOD
8-29-01 5		0.019	<LOD	<LOD
8-29-01 6 DF4	1.026	0.005	<LOD	<LOD
8-29-01 6		0.022	<LOD	<LOD
8-29-01 7 DF4	1.022	<LOD	<LOD	<LOD
8-29-01 7		<LOD	<LOD	<LOD
8-29-01 8 DF4	1.023	<LOD	<LOD	<LOD
8-29-01 8		<LOD	<LOD	<LOD
8-29-01 B BLANK DF4	1.044	<LOD	<LOD	<LOD
8-29-01 B BLANK		<LOD	<LOD	<LOD
8-31-01 1 DF2	1.461	5.267	9.007	4.003
8-31-01 1		10.533	18.015	8.006
8-31-01 2 DF2	1.343	4.649	6.939	3.522
8-31-01 2		9.297	13.878	7.043
8-31-01 2% OPTIMA HNO3DF2	0.990	<LOD	<LOD	<LOD
8-31-01 2% OPTIMA HNO3DF2		<LOD	<LOD	<LOD
8-31-01 3 DF2	1.289	4.209	6.076	3.283
8-31-01 3		8.419	12.151	6.566
8-31-01 4 DF2	1.114	0.033	0.042	0.018
8-31-01 4		0.067	0.083	0.035
8-31-01 5 DF2	1.100	0.032	0.050	<LOD
8-31-01 5		0.064	0.101	<LOD
8-31-01 6 DF2	1.112	0.031	0.043	<LOD
8-31-01 6		0.063	0.086	<LOD
8-31-01 B BLANK DF2	1.174	<LOD	<LOD	<LOD
8-31-01 B BLANK		<LOD	<LOD	<LOD
9-13-01 1 DF2	1.325	0.035	0.040	<LOD
9-13-01 1		0.069	0.080	<LOD
9-13-01 2 DF2	1.352	0.037	0.041	0.015
9-13-01 2		0.073	0.081	0.031
9-13-01 3 DF2	1.267	0.031	0.028	<LOD
9-13-01 3		0.063	0.057	<LOD

9-24-01 1 DF2	0.974	0.022	0.015	<LOD
9-24-01 1		0.044	0.029	<LOD
9-24-01 2 DF2	1.147	0.024	0.009	<LOD
9-24-01 2		0.047	0.018	<LOD
9-24-01 3 DF2	1.366	0.019	0.041	0.066
9-24-01 3		0.039	0.082	0.131
9-24-01 4 DF2	1.224	0.020	0.045	0.027
9-24-01 4		0.040	0.091	0.054
9-24-01 5 DF2	1.253	0.021	0.041	<LOD
9-24-01 5		0.042	0.082	<LOD
9-24-01 6 DF2	1.236	0.060	0.100	0.071
9-24-01 6		0.120	0.201	0.142
9-24-01 7 DF2	0.996	<LOD	<LOD	<LOD
9-24-01 7		<LOD	<LOD	<LOD
9-24-01 8 DF2	1.209	0.226	0.335	0.126
9-24-01 8		0.452	0.671	0.253

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	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
0.050 PPM HP	1.014	1.016	0.053	0.052	0.042	0.054	0.049	0.048	mg/L
	1.018	1.016	0.052	0.05	0.044	0.056	0.048	0.049	mg/L
	1.021	1.016	0.05	0.048	0.04	0.052	0.046	0.047	mg/L
	1.02	1.02	0.05	0.049	0.042	0.054	0.046	0.048	mg/L
average	1.018	1.017	0.051	0.05	0.042	0.054	0.047	0.048	mg/L
stdev	0.003	0.002	0.001	0.002	0.002	0.002	0.001	0.001	mg/L
%rsd	0.303	0.195	2.576	3.045	4.081	2.986	3.016	2.073	mg/L
%difference	1.816	1.676	2.48	-0.347	-15.876	8.357	-5.265	-4.435	
actual	1	1	0.05	0.05	0.05	0.05	0.05	0.05	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
0.250 PPM HP	1.03	1.031	0.266	0.258	0.256	0.256	0.249	0.245	mg/L
	1.028	1.028	0.265	0.255	0.255	0.255	0.247	0.245	mg/L
	1.034	1.035	0.262	0.251	0.246	0.247	0.244	0.24	mg/L
	1.035	1.04	0.262	0.253	0.251	0.251	0.244	0.24	mg/L
average	1.032	1.033	0.264	0.254	0.252	0.252	0.246	0.243	mg/L
stdev	0.003	0.005	0.002	0.003	0.004	0.004	0.002	0.003	mg/L
%rsd	0.334	0.491	0.901	1.099	1.757	1.656	0.936	1.161	mg/L
%difference	3.166	3.324	5.434	1.669	0.821	0.827	-1.656	-2.964	
actual	1	1	0.25	0.25	0.25	0.25	0.25	0.25	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
0.500 PPM HP	1.034	1.033	0.533	0.514	0.516	0.501	0.494	0.487	mg/L
	1.038	1.036	0.534	0.51	0.513	0.498	0.494	0.483	mg/L
	1.033	1.037	0.531	0.507	0.497	0.483	0.492	0.482	mg/L
	1.04	1.039	0.527	0.505	0.512	0.497	0.487	0.479	mg/L
average	1.036	1.036	0.531	0.509	0.51	0.495	0.492	0.483	mg/L
stdev	0.003	0.002	0.003	0.004	0.008	0.008	0.003	0.003	mg/L
%rsd	0.33	0.226	0.611	0.763	1.645	1.597	0.659	0.657	mg/L
%difference	3.626	3.627	6.276	1.757	1.905	-1.06	-1.604	-3.421	
actual	1	1	0.5	0.5	0.5	0.5	0.5	0.5	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
1.00 PPM HP	1.028	1.032	1.066	1.035	1.058	1.012	0.992	0.985	mg/L
	1.033	1.031	1.058	1.028	1.04	0.994	0.983	0.976	mg/L
	1.03	1.03	1.054	1.019	1.034	0.989	0.98	0.971	mg/L
	1.027	1.031	1.048	1.018	1.022	0.978	0.977	0.971	mg/L
average	1.03	1.031	1.056	1.025	1.039	0.993	0.983	0.976	mg/L
stdev	0.002	0.001	0.008	0.008	0.015	0.014	0.007	0.007	mg/L
%rsd	0.24	0.111	0.723	0.809	1.433	1.412	0.694	0.685	mg/L
%difference	2.961	3.096	5.645	2.493	3.868	-0.664	-1.701	-2.423	
actual	1	1	1	1	1	1	1	1	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
5.00 PPM HP	1.023	1.029	5.273	5.162	5.291	5	4.904	4.918	mg/L
	1.022	1.038	5.26	5.143	5.232	4.945	4.886	4.923	mg/L
	1.021	1.02	5.225	5.12	5.193	4.908	4.827	4.858	mg/L
	1.028	1.028	5.168	5.096	5.183	4.899	4.794	4.832	mg/L
average	1.023	1.029	5.231	5.13	5.225	4.938	4.853	4.883	mg/L
stdev	0.003	0.007	0.047	0.029	0.049	0.046	0.051	0.045	mg/L
%rsd	0.318	0.703	0.898	0.558	0.935	0.932	1.053	0.921	mg/L
%difference	2.345	2.891	4.627	2.605	4.494	-1.237	-2.945	-2.341	
actual	1	1	5	5	5	5	5	5	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
10.00 PPM HP	1.007	1.009	10.472	10.338	10.62	10.023	9.725	9.858	mg/L
	1.008	1.001	10.326	10.295	10.509	9.918	9.605	9.754	mg/L
	1.004	0.995	10.366	10.241	10.436	9.849	9.557	9.695	mg/L
	1.006	1.012	10.338	10.221	10.416	9.83	9.595	9.734	mg/L
average	1.006	1.004	10.375	10.274	10.495	9.905	9.62	9.76	mg/L
stdev	0.002	0.008	0.067	0.053	0.092	0.087	0.073	0.07	mg/L
%rsd	0.173	0.771	0.641	0.517	0.881	0.88	0.757	0.712	mg/L
%difference	0.616	0.442	3.754	2.738	4.954	-0.949	-3.797	-2.396	
actual	1	1	10	10	10	10	10	10	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
20.00 PPM HP	0.986	0.983	20.968	20.889	21.505	20.28	19.351	19.682	mg/L
	0.981	0.979	20.998	20.852	21.352	20.136	19.387	19.68	mg/L

	0.974	0.979	20.82	20.722	21.161	19.956	19.387	19.739	mg/L
	0.981	0.988	20.85	20.667	21.131	19.928	19.173	19.66	mg/L
average	0.98	0.982	20.909	20.783	21.287	20.075	19.324	19.69	mg/L
stdev	0.005	0.004	0.087	0.105	0.175	0.165	0.103	0.034	mg/L
%rsd	0.49	0.415	0.417	0.507	0.822	0.822	0.531	0.174	mg/L
%difference	-1.962	-1.753	4.546	3.913	6.436	0.375	-3.378	-1.548	
actual	1	1	20	20	20	20	20	20	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
BLANK	1.008	1.008	0	-0.003	-0.01	0.005	-0.001	-0.003	mg/L
	1.019	1.014	-0.003	-0.001	-0.01	0.005	-0.003	-0.001	mg/L
	1.017	1.015	-0.003	-0.003	-0.015	0.001	-0.003	-0.001	mg/L
	1.017	1.012	-0.003	-0.001	-0.016	0	-0.003	-0.001	mg/L
	1.014	1.005	-0.004	-0.002	-0.008	0.007	-0.004	0	mg/L
	1.013	1.01	-0.003	-0.002	-0.006	0.009	-0.004	-0.001	mg/L
	1.014	1.012	-0.004	-0.004	-0.007	0.008	-0.003	-0.001	mg/L
average	1.015	1.011	-0.003	-0.002	-0.01	0.005	-0.003	-0.001	mg/L
stdev	0.004	0.003	0.001	0.001	0.004	0.004	0.001	0.001	mg/L
lod	0.011	0.01	0.004	0.003	0.011	0.016	0.003	0.002	mg/L
loq	0.035	0.035	0.013	0.009	0.038	0.041	0.01	0.007	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
3-14-02-1 df2	1.123	1.107	0.846	0.77	0.685	0.66	0.776	0.724	mg/L
3-14-02-1			1.693	1.541	1.371	1.321	1.551	1.448	mg/L
3-14-02-2 df2	1.044	1.044	0.06	6.786	3.563	3.372	0.054	6.406	mg/L
3-14-02-2			0.12	13.572	7.125	6.744	0.108	12.813	mg/L
3-14-02-3 df2	1.051	1.054	0.037	6.559	2.955	2.799	0.033	6.22	mg/L
3-14-02-3			0.073	13.118	5.909	5.598	0.066	12.44	mg/L
3-14-02-4 df2	1.037	1.035	0.072	2.179	1.333	1.271	0.067	2.062	mg/L
3-14-02-4			0.144	4.358	2.667	2.542	0.134	4.124	mg/L
3-14-02-5 df2 *	2.496	2.474	13.569	3.883	17.354	16.368	12.528	3.655	mg/L
3-14-02-5			27.139	7.765	34.708	32.737	25.055	7.309	mg/L
3-14-02-6 df2	1.037	1.044	0.044	0.828	0.081	0.09	0.041	0.788	mg/L
3-14-02-6			0.089	1.657	0.161	0.181	0.082	1.576	mg/L
3-14-02-7 df2 *	2.157	2.172	11.766	0.988	0.037	0.05	10.941	0.944	mg/L
3-14-02-7			23.533	1.976	0.075	0.1	21.882	1.888	mg/L
3-14-02-8 df2	1.04	1.043	0.038	4.427	1.782	1.694	0.036	4.197	mg/L
3-14-02-8			0.076	8.853	3.563	3.387	0.073	8.394	mg/L
3-14-02-9 df2	1.032	1.036	0.035	0.827	0.146	0.153	0.033	0.79	mg/L
3-14-02-9			0.07	1.655	0.293	0.305	0.066	1.58	mg/L

3-14-02-10 df2	1.185	1.177	3.32	0.358	-0.006	0.009	3.08	0.339	mg/L
3-14-02-10			6.64	0.716	<lod	0.017	6.161	0.677	mg/L
3-14-02-B df2	1.016	1.013	0	-0.003	-0.01	0.005	0	-0.001	mg/L
3-14-02-B			<lod	<lod	<lod	<lod	<lod	<lod	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
3-18-02 1 7.81 df2	1.011	1.031	0.084	11.002	6.946	6.56	0.077	10.236	mg/L
3-18-02 1 7.81			0.169	22.005	13.892	13.121	0.154	20.471	mg/L
3-18-02 2 7.81 df2	1.053	1.058	0.067	10.578	6.538	6.175	0.064	10.026	mg/L
3-18-02 2 7.81			0.135	21.156	13.075	12.351	0.127	20.051	mg/L
3-18-02 3 7.81 df2	1.054	1.052	0.071	11.227	6.64	6.272	0.065	10.577	mg/L
3-18-02 3 7.81			0.142	22.454	13.28	12.544	0.131	21.154	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
3-20-02 1 7.47 df2	1.09	1.095	0.899	0.952	1.926	1.83	0.838	0.907	mg/L
3-20-02 1 7.47			1.797	1.905	3.852	3.659	1.676	1.814	mg/L
3-20-02 2 7.47 df2	1.079	1.087	0.976	0.709	2.525	2.394	0.907	0.674	mg/L
3-20-02 2 7.47			1.952	1.417	5.05	4.788	1.813	1.348	mg/L
3-20-02 3 7.47 df2	1.097	1.099	1.612	1.191	3.429	3.246	1.49	1.124	mg/L
3-20-02 3 7.47			3.224	2.382	6.858	6.492	2.98	2.249	mg/L
3-20-02 4 9.63 df2	1.015	1.043	0.006	9.975	5.999	5.668	0.005	9.204	mg/L
3-20-02 4 9.63			0.012	19.949	11.999	11.336	0.011	18.408	mg/L
3-20-02 5 9.63 df2	1.021	1.047	0.005	9.546	5.659	5.347	0.007	8.751	mg/L
3-20-02 5 9.63			0.01	19.093	11.317	10.694	0.013	17.503	mg/L
3-20-02 6 9.63 df2	1.012	1.028	0.013	10.027	5.813	5.492	0.011	9.359	mg/L
3-20-02 6 9.63			0.025	20.055	11.626	10.985	0.022	18.719	mg/L

	Y 371.029	Y AXIAL	Cu 327.393	Cr 267.716	As 188.979	As AXIAL	Cu AXIAL	Cr AXIAL	
3-31-02 1 TCLP df4	1.058	1.05	6.204	1.182	3.031	2.87	5.705	1.114	mg/L
3-31-02 1 TCLP			24.817	4.728	12.122	11.482	22.821	4.455	mg/L
3-31-02 2 TCLP df4	1.056	1.046	3.286	0.573	2.211	2.098	2.985	0.537	mg/L
3-31-02 2 TCLP			13.145	2.294	8.844	8.392	11.941	2.149	mg/L
3-31-02 3 TCLP df4	1.032	1.028	0.792	0.335	1.352	1.289	0.732	0.317	mg/L
3-31-02 3 TCLP			3.17	1.34	5.409	5.156	2.927	1.27	mg/L
3-31-02 4 DI WATER df4	1.033	1.019	0.235	0.171	1.046	1	0.216	0.161	mg/L
3-31-02 4 DI WATER			0.94	0.685	4.184	4.001	0.864	0.644	mg/L
3-31-02 5 DI	1.043	1.037	0.623	0.232	1.061	1.015	0.575	0.221	mg/L

WATER df4									
3-31-02 5 DI WATER			2.494	0.929	4.245	4.058	2.301	0.882	mg/L
3-31-02 7 TCLP df4	1.048	1.045	2.828	0.361	1.8	1.711	2.635	0.343	mg/L
3-31-02 7 TCLP			11.312	1.443	7.201	6.845	10.538	1.372	mg/L
3-31-02 8 TCLP df4	1.054	1.048	3.305	0.448	2.151	2.041	3.034	0.42	mg/L
3-31-02 8 TCLP			13.22	1.791	8.602	8.165	12.135	1.68	mg/L
3-31-02 9 DI WATER df4	1.028	1.027	0.894	0.176	1.205	1.15	0.826	0.169	mg/L
3-31-02 9 DI WATER			3.576	0.705	4.822	4.602	3.302	0.674	mg/L
3-31-02 B DI WATER df4	1.016	1.014	0	-0.001	-0.009	0.006	0	0	mg/L
3-31-02 B DI WATER			<lod	<lod	<lod	<lod	<lod	<lod	mg/L
3-31-02 5 RAINWATER df4	1.025	1.025	-0.004	-0.002	-0.013	0.002	-0.003	-0.001	mg/L
3-31-02 5 RAINWATER			<lod	<lod	<lod	<lod	<lod	<lod	mg/L
3-31-02 6 RAINWATER df4	1.043	1.024	0.623	0.237	0.965	0.924	0.569	0.223	mg/L
3-31-02 6 RAINWATER			2.491	0.949	3.86	3.696	2.277	0.89	mg/L
3-31-02 10 RAINWATER df4	1.039	1.03	0.795	0.14	1.021	0.977	0.728	0.132	mg/L
3-31-02 10 RAINWATER			3.18	0.56	4.084	3.907	2.911	0.527	mg/L
3-31-02 11 RAINWATER df4	1.031	1.03	0.857	0.144	0.975	0.934	0.794	0.136	mg/L
3-31-02 11 RAINWATER			3.429	0.576	3.901	3.734	3.178	0.543	mg/L

* these values are not accurate as indicated by the value of the internal standard. The autosampler probably missed the tube and I didn't catch it.

the first values were measured radially, and the second axially. All appear to be good with the exception of As<0.050 mg/l when measured radially.

JH071402

Sample ID	Analyte Name	Conc (Calib)	RSD (Conc)	Calib Units
Calib Blank 1	Y 371.029		0.674939978	mg/L
Calib Blank 1	Y AXIAL		0.304551801	mg/L
Calib Blank 1	Cu 327.393		0	mg/L
Calib Blank 1	Cr 267.716		0	mg/L
Calib Blank 1	As 188.979		0	mg/L
Calib Blank 1	As AXIAL		0	mg/L
Calib Blank 1	Cu AXIAL		0	mg/L
Calib Blank 1	Cr AXIAL		0	mg/L

Calib Std 1	Y 371.029		0.755551409	mg/L
Calib Std 1	Y AXIAL		0.391064239	mg/L
Calib Std 1	As AXIAL		1.32E-06	mg/L
Calib Std 1	Cu AXIAL		1.32E-06	mg/L
Calib Std 1	Cr AXIAL		1.32E-06	mg/L
Calib Std 2	Y 371.029		1.168004965	mg/L
Calib Std 2	Y AXIAL		0.61024187	mg/L
Calib Std 2	As AXIAL		0	mg/L
Calib Std 2	Cu AXIAL		0	mg/L
Calib Std 2	Cr AXIAL		0	mg/L
Calib Std 3	Y 371.029		0.433575003	mg/L
Calib Std 3	Y AXIAL		0.291377241	mg/L
Calib Std 3	As AXIAL		0	mg/L
Calib Std 3	Cu AXIAL		0	mg/L
Calib Std 3	Cr AXIAL		0	mg/L
Calib Std 4	Y 371.029		0.613003507	mg/L
Calib Std 4	Y AXIAL		0.478954089	mg/L
Calib Std 4	Cu 327.393		0	mg/L
Calib Std 4	Cr 267.716		0	mg/L
Calib Std 4	As 188.979		0	mg/L
Calib Std 4	As AXIAL		0	mg/L
Calib Std 4	Cu AXIAL		0	mg/L
Calib Std 4	Cr AXIAL		0	mg/L
Calib Std 5	Y 371.029		0.307877625	mg/L
Calib Std 5	Y AXIAL		0.536578655	mg/L
Calib Std 5	Cu 327.393		0	mg/L
Calib Std 5	Cr 267.716		0	mg/L
Calib Std 5	As 188.979		0	mg/L
Calib Std 6	Y 371.029		0.131478441	mg/L
Calib Std 6	Y AXIAL		0.51136778	mg/L
Calib Std 6	Cu 327.393		0	mg/L
Calib Std 6	Cr 267.716		0	mg/L
Calib Std 6	As 188.979		0	mg/L
Calib Std 7	Y 371.029		0.345229988	mg/L
Calib Std 7	Y AXIAL		0.561092197	mg/L
Calib Std 7	Cu 327.393		0	mg/L
Calib Std 7	Cr 267.716		0	mg/L
Calib Std 7	As 188.979		0	mg/L
Reagent Blank 1	Y 371.029	1.00250345	0.281521348	mg/L
Reagent Blank 1	Y AXIAL	1.00334305	0.357415456	mg/L
Reagent Blank 1	Cu 327.393	-3.22E-03	25.69038578	mg/L
Reagent Blank 1	Cr 267.716	4.01E-02	2.055305091	mg/L
Reagent Blank 1	As 188.979	4.90E-02	6.971390769	mg/L

Reagent Blank 1	As AXIAL	4.47E-04	201.1195765	mg/L
Reagent Blank 1	Cu AXIAL	1.89E-04	189.4234761	mg/L
Reagent Blank 1	Cr AXIAL	-1.03E-03	13.68304118	mg/L
BLANK	Y 371.029	1.00062657	0.256327813	mg/L
BLANK	Y AXIAL	1.00079641	0.455846433	mg/L
BLANK	Cu 327.393	-3.58E-03	17.11846274	mg/L
BLANK	Cr 267.716	-1.03E-03	83.05210881	mg/L
BLANK	As 188.979	-7.58E-03	65.29412661	mg/L
BLANK	As AXIAL	-1.08E-03	40.6263902	mg/L
BLANK	Cu AXIAL	-2.22E-03	3.207848607	mg/L
BLANK	Cr AXIAL	-8.30E-04	12.55656793	mg/L
1.00 PPM HP	Y 371.029	1.03056789	0.248341969	mg/L
1.00 PPM HP	Y AXIAL	1.02832551	0.683917681	mg/L
1.00 PPM HP	Cu 327.393	1.05126747	0.265043741	mg/L
1.00 PPM HP	Cr 267.716	1.01505429	0.164540262	mg/L
1.00 PPM HP	As 188.979	1.02784239	0.732214393	mg/L
1.00 PPM HP	As AXIAL	1.01319313	0.923076688	mg/L
1.00 PPM HP	Cu AXIAL	0.98463103	0.707995778	mg/L
1.00 PPM HP	Cr AXIAL	0.97563206	0.442476408	mg/L
5.00 PPM HP	Y 371.029	1.03204257	0.572160969	mg/L
5.00 PPM HP	Y AXIAL	1.0168626	0.192183674	mg/L
5.00 PPM HP	Cu 327.393	5.14467373	0.118902518	mg/L
5.00 PPM HP	Cr 267.716	5.04904278	0.156425168	mg/L
5.00 PPM HP	As 188.979	5.18402094	0.242090398	mg/L
5.00 PPM HP	As AXIAL	5.0218699	0.801505214	mg/L
5.00 PPM HP	Cu AXIAL	4.89319367	0.593312885	mg/L
5.00 PPM HP	Cr AXIAL	4.79777996	0.529086473	mg/L
10.00 PPM HP	Y 371.029	1.00279623	0.201664685	mg/L
10.00 PPM HP	Y AXIAL	0.98064035	0.680414993	mg/L
10.00 PPM HP	Cu 327.393	10.3590171	0.178982341	mg/L
10.00 PPM HP	Cr 267.716	10.253178	0.155252339	mg/L
10.00 PPM HP	As 188.979	10.4883232	0.551561407	mg/L
10.00 PPM HP	As AXIAL	10.1102285	0.421185666	mg/L
10.00 PPM HP	Cu AXIAL	9.96832557	0.361024619	mg/L
10.00 PPM HP	Cr AXIAL	9.67297393	4.16E-02	mg/L
20.00 PPM HP	Y 371.029	0.98705492	0.387431074	mg/L
20.00 PPM HP	Y AXIAL	0.94057986	0.517633341	mg/L
20.00 PPM HP	Cu 327.393	20.8717963	0.363799081	mg/L
20.00 PPM HP	Cr 267.716	20.6949626	0.327961206	mg/L
20.00 PPM HP	As 188.979	21.2291126	0.497757542	mg/L
20.00 PPM HP	As AXIAL	19.9647447	0.142018569	mg/L
20.00 PPM HP	Cu AXIAL	19.8266707	0.400840057	mg/L
20.00 PPM HP	Cr AXIAL	18.942691	0.109757144	mg/L

0.500 PPM HP	Y 371.029	1.03430462	0.207831576	mg/L
0.500 PPM HP	Y AXIAL	1.03219808	0.822710194	mg/L
0.500 PPM HP	Cu 327.393	0.52998996	0.451184612	mg/L
0.500 PPM HP	Cr 267.716	0.50783911	0.184235291	mg/L
0.500 PPM HP	As 188.979	0.52221142	0.835375747	mg/L
0.500 PPM HP	As AXIAL	0.50786358	0.398760859	mg/L
0.500 PPM HP	Cu AXIAL	0.49676741	1.026461465	mg/L
0.500 PPM HP	Cr AXIAL	0.48795685	0.734580178	mg/L
0.250 PPM HP	Y 371.029	1.02807829	0.347807939	mg/L
0.250 PPM HP	Y AXIAL	1.02772368	0.34633772	mg/L
0.250 PPM HP	Cu 327.393	0.26375293	0.163832632	mg/L
0.250 PPM HP	Cr 267.716	0.25282856	0.525742923	mg/L
0.250 PPM HP	As 188.979	0.24980841	2.099874182	mg/L
0.250 PPM HP	As AXIAL	0.25225977	0.921218425	mg/L
0.250 PPM HP	Cu AXIAL	0.24710535	0.492691018	mg/L
0.250 PPM HP	Cr AXIAL	0.24259169	0.379342016	mg/L
0.050 PPM HP	Y 371.029	1.01604854	0.512283128	mg/L
0.050 PPM HP	Y AXIAL	1.0135613	0.219470925	mg/L
0.050 PPM HP	Cu 327.393	0.12903241	0.412779249	mg/L
0.050 PPM HP	Cr 267.716	0.12696434	1.58599448	mg/L
0.050 PPM HP	As 188.979	0.12723013	4.965811759	mg/L
0.050 PPM HP	As AXIAL	0.12584448	1.645635403	mg/L
0.050 PPM HP	Cu AXIAL	0.12245361	0.608360506	mg/L
0.050 PPM HP	Cr AXIAL	0.12151398	0.607333151	mg/L
6-6-02 1 DF2	Y 371.029	1.27999378	0.208493548	mg/L
6-6-02 1 DF2	Y AXIAL	1.27838043	0.230868942	mg/L
6-6-02 1 DF2	Cu 327.393	8.78E-03	7.862965329	mg/L
6-6-02 1 DF2	Cr 267.716	1.91E-02	2.909029977	mg/L
6-6-02 1 DF2	As 188.979	-6.21E-03	27.10256539	mg/L
6-6-02 1 DF2	As AXIAL	9.74E-03	13.0491975	mg/L
6-6-02 1 DF2	Cu AXIAL	9.06E-03	0.559549568	mg/L
6-6-02 1 DF2	Cr AXIAL	1.81E-02	0.509701396	mg/L
0.050 PPM HP	Y 371.029	1.02206937	0.176879808	mg/L
0.050 PPM HP	Y AXIAL	1.02143599	0.245650321	mg/L
0.050 PPM HP	Cu 327.393	4.73E-02	1.868271196	mg/L
0.050 PPM HP	Cr 267.716	4.91E-02	1.354116129	mg/L
0.050 PPM HP	As 188.979	4.51E-02	7.813218353	mg/L
0.050 PPM HP	As AXIAL	4.79E-02	0.797563741	mg/L
0.050 PPM HP	Cu AXIAL	4.56E-02	0.223926761	mg/L
0.050 PPM HP	Cr AXIAL	4.67E-02	0.62700818	mg/L
6-6-02 2 DF2	Y 371.029	1.32216098	0.356966249	mg/L
6-6-02 2 DF2	Y AXIAL	1.31220295	0.174334714	mg/L
6-6-02 2 DF2	Cu 327.393	5.43E-03	8.655200573	mg/L

6-6-02 2 DF2	Cr 267.716	1.56E-02	1.328333959	mg/L
6-6-02 2 DF2	As 188.979	-2.29E-03	149.4887841	mg/L
6-6-02 2 DF2	As AXIAL	8.64E-03	15.90031437	mg/L
6-6-02 2 DF2	Cu AXIAL	6.28E-03	1.420528178	mg/L
6-6-02 2 DF2	Cr AXIAL	1.47E-02	0.514238966	mg/L
6-6-02 3 DF2	Y 371.029	1.0632244	0.102042905	mg/L
6-6-02 3 DF2	Y AXIAL	1.05605995	0.427221653	mg/L
6-6-02 3 DF2	Cu 327.393	0.1355152	0.361075782	mg/L
6-6-02 3 DF2	Cr 267.716	14.6371798	0.570060358	mg/L
6-6-02 3 DF2	As 188.979	10.2234909	0.225522692	mg/L
6-6-02 3 DF2	As AXIAL	9.56842733	0.574087398	mg/L
6-6-02 3 DF2	Cu AXIAL	0.13122315	1.139292935	mg/L
6-6-02 3 DF2	Cr AXIAL	13.8835765	0.268371602	mg/L
6-6-02 4 DF2	Y 371.029	1.06527217	0.276344811	mg/L
6-6-02 4 DF2	Y AXIAL	1.0555877	0.399073588	mg/L
6-6-02 4 DF2	Cu 327.393	0.28678978	0.120939917	mg/L
6-6-02 4 DF2	Cr 267.716	14.737671	0.348471869	mg/L
6-6-02 4 DF2	As 188.979	10.3563059	0.126359664	mg/L
6-6-02 4 DF2	As AXIAL	9.69610613	0.646369567	mg/L
6-6-02 4 DF2	Cu AXIAL	0.27580618	0.803943111	mg/L
6-6-02 4 DF2	Cr AXIAL	13.9706689	0.426703739	mg/L
6-6-02 5 DF2	Y 371.029	4.81457395	0.348443677	mg/L
6-6-02 5 DF2	Y AXIAL	4.58536765	0.334067997	mg/L
6-6-02 5 DF2	Cu 327.393	11.2634309	0.743320093	mg/L
6-6-02 5 DF2	Cr 267.716	3.3342159	4.07E-02	mg/L
6-6-02 5 DF2	As 188.979	15.6989546	6.23E-02	mg/L
6-6-02 5 DF2	As AXIAL	14.2330624	0.602539705	mg/L
6-6-02 5 DF2	Cu AXIAL	10.806844	0.460340638	mg/L
6-6-02 5 DF2	Cr AXIAL	3.0591969	0.491779652	mg/L
6-6-02 6 DF2	Y 371.029	4.77224082	1.17866151	mg/L
6-6-02 6 DF2	Y AXIAL	4.54439182	0.256903484	mg/L
6-6-02 6 DF2	Cu 327.393	11.0310864	1.349184498	mg/L
6-6-02 6 DF2	Cr 267.716	3.23855315	0.324055863	mg/L
6-6-02 6 DF2	As 188.979	15.6124518	0.527530745	mg/L
6-6-02 6 DF2	As AXIAL	14.1591009	1.183915916	mg/L
6-6-02 6 DF2	Cu AXIAL	10.5939618	1.261010644	mg/L
6-6-02 6 DF2	Cr AXIAL	2.97039571	1.183793001	mg/L
6-6-02 7 DF2	Y 371.029	1.01247179	0.426560796	mg/L
6-6-02 7 DF2	Y AXIAL	0.98243072	0.457107797	mg/L
6-6-02 7 DF2	Cu 327.393	0.1093564	0.366075798	mg/L
6-6-02 7 DF2	Cr 267.716	3.73397083	0.237702048	mg/L
6-6-02 7 DF2	As 188.979	0.11520607	7.443928498	mg/L
6-6-02 7 DF2	As AXIAL	9.52E-02	1.794640692	mg/L

6-6-02 7 DF2	Cu AXIAL	0.10968107	0.86082518	mg/L
6-6-02 7 DF2	Cr AXIAL	3.47824231	0.740410049	mg/L
6-6-02 8 DF2	Y 371.029	0.96016012	0.150822614	mg/L
6-6-02 8 DF2	Y AXIAL	0.93274414	0.637304034	mg/L
6-6-02 8 DF2	Cu 327.393	9.47E-02	0.327684092	mg/L
6-6-02 8 DF2	Cr 267.716	4.41756732	0.278897121	mg/L
6-6-02 8 DF2	As 188.979	6.46E-02	9.820955422	mg/L
6-6-02 8 DF2	As AXIAL	5.19E-02	2.411281922	mg/L
6-6-02 8 DF2	Cu AXIAL	9.55E-02	1.110380045	mg/L
6-6-02 8 DF2	Cr AXIAL	4.13716631	0.428934717	mg/L
6-6-02 9 DF2	Y 371.029	4.05641301	0.120568312	mg/L
6-6-02 9 DF2	Y AXIAL	3.92760263	0.210068127	mg/L
6-6-02 9 DF2	Cu 327.393	11.9584824	0.465715237	mg/L
6-6-02 9 DF2	Cr 267.716	2.43435145	0.461132701	mg/L
6-6-02 9 DF2	As 188.979	0.3968904	0.779899941	mg/L
6-6-02 9 DF2	As AXIAL	0.40437302	0.861081922	mg/L
6-6-02 9 DF2	Cu AXIAL	11.4946033	0.452661591	mg/L
6-6-02 9 DF2	Cr AXIAL	2.25942845	0.158075333	mg/L
BLANK	Y 371.029	1.00685699	0.142261007	mg/L
BLANK	Y AXIAL	1.01526884	0.362722675	mg/L
BLANK	Cu 327.393	5.32E-03	12.60508885	mg/L
BLANK	Cr 267.716	2.17E-03	43.12312713	mg/L
BLANK	As 188.979	9.63E-03	28.8949644	mg/L
BLANK	As AXIAL	7.96E-03	26.88357253	mg/L
BLANK	Cu AXIAL	4.85E-03	12.37233224	mg/L
BLANK	Cr AXIAL	1.93E-03	11.31142991	mg/L
1.00 PPM HP	Y 371.029	1.03460047	0.302527387	mg/L
1.00 PPM HP	Y AXIAL	1.02847438	0.403815763	mg/L
1.00 PPM HP	Cu 327.393	1.0511184	0.590799846	mg/L
1.00 PPM HP	Cr 267.716	1.01295266	0.31920386	mg/L
1.00 PPM HP	As 188.979	1.04156793	1.064194961	mg/L
1.00 PPM HP	As AXIAL	1.01248505	0.175224811	mg/L
1.00 PPM HP	Cu AXIAL	0.98595784	1.138499336	mg/L
1.00 PPM HP	Cr AXIAL	0.97112352	0.388524809	mg/L
5.00 PPM HP	Y 371.029	1.03244181	0.14257628	mg/L
5.00 PPM HP	Y AXIAL	1.01450197	0.433909152	mg/L
5.00 PPM HP	Cu 327.393	5.09532942	0.447013412	mg/L
5.00 PPM HP	Cr 267.716	5.05351353	0.15323458	mg/L
5.00 PPM HP	As 188.979	5.20605021	0.328179061	mg/L
5.00 PPM HP	As AXIAL	4.98951478	0.276524536	mg/L
5.00 PPM HP	Cu AXIAL	4.88399513	0.720687908	mg/L
5.00 PPM HP	Cr AXIAL	4.79567422	0.254136015	mg/L
10.00 PPM HP	Y 371.029	1.01391049	0.59286187	mg/L

10.00 PPM HP	Y AXIAL	0.98799019	0.327641726	mg/L
10.00 PPM HP	Cu 327.393	10.2820689	0.690004864	mg/L
10.00 PPM HP	Cr 267.716	10.2067831	0.707870792	mg/L
10.00 PPM HP	As 188.979	10.5347748	1.481954213	mg/L
10.00 PPM HP	As AXIAL	10.038701	0.644996774	mg/L
10.00 PPM HP	Cu AXIAL	9.89886436	0.674457722	mg/L
10.00 PPM HP	Cr AXIAL	9.62831282	0.647446077	mg/L
20.00 PPM HP	Y 371.029	0.99958071	0.967912907	mg/L
20.00 PPM HP	Y AXIAL	0.95084006	7.15E-02	mg/L
20.00 PPM HP	Cu 327.393	20.6570977	1.183523584	mg/L
20.00 PPM HP	Cr 267.716	20.5395093	1.232882949	mg/L
20.00 PPM HP	As 188.979	21.2230644	0.650407497	mg/L
20.00 PPM HP	As AXIAL	19.9164365	1.025038067	mg/L
20.00 PPM HP	Cu AXIAL	19.7819716	0.660965158	mg/L
20.00 PPM HP	Cr AXIAL	18.8713142	0.746737924	mg/L
0.500 PPM HP	Y 371.029	1.04382427	8.71E-02	mg/L
0.500 PPM HP	Y AXIAL	1.04356609	0.383687796	mg/L
0.500 PPM HP	Cu 327.393	0.53141291	0.381778518	mg/L
0.500 PPM HP	Cr 267.716	0.5081777	0.33996877	mg/L
0.500 PPM HP	As 188.979	0.52864244	1.635401529	mg/L
0.500 PPM HP	As AXIAL	0.50450999	0.309434513	mg/L
0.500 PPM HP	Cu AXIAL	0.49982432	0.385280366	mg/L
0.500 PPM HP	Cr AXIAL	0.48594502	0.13897196	mg/L
0.250 PPM HP	Y 371.029	1.04026054	0.472885089	mg/L
0.250 PPM HP	Y AXIAL	1.03803824	0.347720376	mg/L
0.250 PPM HP	Cu 327.393	0.26393876	0.194997464	mg/L
0.250 PPM HP	Cr 267.716	0.25376995	0.236892415	mg/L
0.250 PPM HP	As 188.979	0.25763627	1.64435654	mg/L
0.250 PPM HP	As AXIAL	0.25483452	0.168757628	mg/L
0.250 PPM HP	Cu AXIAL	0.24810876	0.46196465	mg/L
0.250 PPM HP	Cr AXIAL	0.24191937	0.42998614	mg/L
0.050 PPM HP	Y 371.029	1.02704077	0.29447965	mg/L
0.050 PPM HP	Y AXIAL	1.02210068	0.72108845	mg/L
0.050 PPM HP	Cu 327.393	5.13E-02	1.633987476	mg/L
0.050 PPM HP	Cr 267.716	5.11E-02	0.62120043	mg/L
0.050 PPM HP	As 188.979	4.72E-02	6.325996841	mg/L
0.050 PPM HP	As AXIAL	5.02E-02	2.479610171	mg/L
0.050 PPM HP	Cu AXIAL	4.88E-02	1.145659837	mg/L
0.050 PPM HP	Cr AXIAL	4.80E-02	0.561732097	mg/L
6-6-02 10 DF2	Y 371.029	4.04993654	0.214278847	mg/L
6-6-02 10 DF2	Y AXIAL	3.90462659	0.33358496	mg/L
6-6-02 10 DF2	Cu 327.393	11.6440214	0.436386539	mg/L
6-6-02 10 DF2	Cr 267.716	2.43470529	0.501485854	mg/L

6-6-02	10 DF2	As 188.979	0.47346739	0.3207965	mg/L
6-6-02	10 DF2	As AXIAL	0.48168935	0.886537765	mg/L
6-6-02	10 DF2	Cu AXIAL	11.0955497	0.227722784	mg/L
6-6-02	10 DF2	Cr AXIAL	2.24456284	4.26E-02	mg/L
6-6-02	11 DF2	Y 371.029	1.00112139	0.678567005	mg/L
6-6-02	11 DF2	Y AXIAL	0.96564664	0.325159124	mg/L
6-6-02	11 DF2	Cu 327.393	5.96E-02	2.499326125	mg/L
6-6-02	11 DF2	Cr 267.716	5.07486102	0.123626933	mg/L
6-6-02	11 DF2	As 188.979	5.27E-02	8.541628737	mg/L
6-6-02	11 DF2	As AXIAL	4.49E-02	1.314701818	mg/L
6-6-02	11 DF2	Cu AXIAL	5.96E-02	2.143376589	mg/L
6-6-02	11 DF2	Cr AXIAL	4.70757383	0.995764994	mg/L
6-6-02	12 DF2	Y 371.029	1.0374761	0.373008462	mg/L
6-6-02	12 DF2	Y AXIAL	0.99723117	0.65111612	mg/L
6-6-02	12 DF2	Cu 327.393	5.25E-02	1.825837191	mg/L
6-6-02	12 DF2	Cr 267.716	5.49643642	7.04E-02	mg/L
6-6-02	12 DF2	As 188.979	5.13E-02	15.43008681	mg/L
6-6-02	12 DF2	As AXIAL	4.88E-02	5.055529212	mg/L
6-6-02	12 DF2	Cu AXIAL	5.31E-02	0.961853418	mg/L
6-6-02	12 DF2	Cr AXIAL	5.09138031	0.643303555	mg/L
6-6-02	13 DF2	Y 371.029	1.00956157	0.247786413	mg/L
6-6-02	13 DF2	Y AXIAL	0.9885403	0.560547288	mg/L
6-6-02	13 DF2	Cu 327.393	0.14149859	0.256857114	mg/L
6-6-02	13 DF2	Cr 267.716	2.84506466	0.12511685	mg/L
6-6-02	13 DF2	As 188.979	3.48E-02	14.99504161	mg/L
6-6-02	13 DF2	As AXIAL	2.72E-02	2.363830485	mg/L
6-6-02	13 DF2	Cu AXIAL	0.14242367	0.622029484	mg/L
6-6-02	13 DF2	Cr AXIAL	2.66145571	0.626044705	mg/L
6-6-02	14 DF2	Y 371.029	1.01070043	0.607815752	mg/L
6-6-02	14 DF2	Y AXIAL	0.98760719	0.823325687	mg/L
6-6-02	14 DF2	Cu 327.393	0.16125348	0.411146145	mg/L
6-6-02	14 DF2	Cr 267.716	2.88659779	0.331849287	mg/L
6-6-02	14 DF2	As 188.979	7.27E-02	4.133160661	mg/L
6-6-02	14 DF2	As AXIAL	7.16E-02	2.040708558	mg/L
6-6-02	14 DF2	Cu AXIAL	0.16167351	1.018576915	mg/L
6-6-02	14 DF2	Cr AXIAL	2.71413612	0.700338033	mg/L
6-6-02	BLANK	Y 371.029	1.00922779	0.41331193	mg/L
6-6-02	BLANK	Y AXIAL	1.02367794	0.753302093	mg/L
6-6-02	BLANK	Cu 327.393	2.43E-03	37.67940986	mg/L
6-6-02	BLANK	Cr 267.716	-6.00E-04	31.42729967	mg/L
6-6-02	BLANK	As 188.979	-4.36E-03	40.98877742	mg/L
6-6-02	BLANK	As AXIAL	-6.09E-03	15.91820584	mg/L
6-6-02	BLANK	Cu AXIAL	2.80E-03	7.853202659	mg/L

6-6-02 BLANK	Cr AXIAL	3.23E-04	35.35628135	mg/L
3-14-12-5	Y 371.029	6.92844545	0.928248915	mg/L
3-14-12-5	Y AXIAL	6.5466695	0.335691153	mg/L
3-14-12-5	Cu 327.393	9.81441683	0.93739168	mg/L
3-14-12-5	Cr 267.716	2.74141319	0.229677828	mg/L
3-14-12-5	As 188.979	12.5066725	0.230894503	mg/L
3-14-12-5	As AXIAL	11.1946166	0.862304817	mg/L
3-14-12-5	Cu AXIAL	9.30022068	1.563264573	mg/L
3-14-12-5	Cr AXIAL	2.47752557	0.947049174	mg/L
3-14-02-7	Y 371.029	5.54215102	0.748593274	mg/L
3-14-02-7	Y AXIAL	5.33625669	0.355300809	mg/L
3-14-02-7	Cu 327.393	9.16896965	5.40E-02	mg/L
3-14-02-7	Cr 267.716	0.76091639	0.260980905	mg/L
3-14-02-7	As 188.979	2.84E-02	5.150632543	mg/L
3-14-02-7	As AXIAL	6.47E-02	0.79569794	mg/L
3-14-02-7	Cu AXIAL	8.73992078	0.273902018	mg/L
3-14-02-7	Cr AXIAL	0.70493356	0.598103008	mg/L
D1-1 DF2	Y 371.029	0.99001846	0.539968671	mg/L
D1-1 DF2	Y AXIAL	0.96133581	0.2621997	mg/L
D1-1 DF2	Cu 327.393	2.13E-02	8.914762004	mg/L
D1-1 DF2	Cr 267.716	123.610342	0.891052554	mg/L
D1-1 DF2	As 188.979	2.06278036	0.670877347	mg/L
D1-1 DF2	As AXIAL	1.77135346	0.606242172	mg/L
D1-1 DF2	Cu AXIAL	2.14E-02	1.685495263	mg/L
D1-1 DF2	Cr AXIAL	107.480492	0.513143763	mg/L
D2-1 DF2	Y 371.029	0.98886913	0.936317031	mg/L
D2-1 DF2	Y AXIAL	0.98829501	0.680422931	mg/L
D2-1 DF2	Cu 327.393	1.71E-02	3.242184562	mg/L
D2-1 DF2	Cr 267.716	95.6654783	0.621418596	mg/L
D2-1 DF2	As 188.979	2.29491762	0.982084437	mg/L
D2-1 DF2	As AXIAL	2.02200304	0.748991519	mg/L
D2-1 DF2	Cu AXIAL	1.76E-02	0.408683849	mg/L
D2-1 DF2	Cr AXIAL	83.9317045	1.193818156	mg/L
BLANK	Y 371.029	1.00086911	0.707834722	mg/L
BLANK	Y AXIAL	1.0089305	0.330501804	mg/L
BLANK	Cu 327.393	2.91E-03	43.41002382	mg/L
BLANK	Cr 267.716	4.39E-02	11.57646485	mg/L
BLANK	As 188.979	7.76E-04	500.3737567	mg/L
BLANK	As AXIAL	5.04E-03	22.7200776	mg/L
BLANK	Cu AXIAL	3.56E-03	8.607653693	mg/L
BLANK	Cr AXIAL	3.48E-02	6.086096099	mg/L
1.00 PPM HP	Y 371.029	1.03278938	0.467348969	mg/L
1.00 PPM HP	Y AXIAL	1.0222209	0.415390717	mg/L

1.00 PPM HP	Cu 327.393	1.05560551	0.577965948	mg/L
1.00 PPM HP	Cr 267.716	1.03691356	7.44E-02	mg/L
1.00 PPM HP	As 188.979	1.04374507	0.328251897	mg/L
1.00 PPM HP	As AXIAL	1.00409224	0.822566475	mg/L
1.00 PPM HP	Cu AXIAL	0.99122504	0.94586871	mg/L
1.00 PPM HP	Cr AXIAL	0.99469424	0.602542897	mg/L
5.00 PPM HP	Y 371.029	1.03507269	0.260017445	mg/L
5.00 PPM HP	Y AXIAL	1.01334272	0.19714189	mg/L
5.00 PPM HP	Cu 327.393	5.12561936	0.367943095	mg/L
5.00 PPM HP	Cr 267.716	5.05056841	0.343336646	mg/L
5.00 PPM HP	As 188.979	5.18639799	0.30691982	mg/L
5.00 PPM HP	As AXIAL	4.94822406	0.234975826	mg/L
5.00 PPM HP	Cu AXIAL	4.87063295	0.818479078	mg/L
5.00 PPM HP	Cr AXIAL	4.77916135	0.517355356	mg/L
10.00 PPM HP	Y 371.029	1.01344521	0.85821683	mg/L
10.00 PPM HP	Y AXIAL	0.98567356	0.381068617	mg/L
10.00 PPM HP	Cu 327.393	10.2760767	0.255440614	mg/L
10.00 PPM HP	Cr 267.716	10.2264794	0.36391385	mg/L
10.00 PPM HP	As 188.979	10.5081253	0.318765402	mg/L
10.00 PPM HP	As AXIAL	9.99441374	1.055297113	mg/L
10.00 PPM HP	Cu AXIAL	9.83670882	0.804358089	mg/L
10.00 PPM HP	Cr AXIAL	9.57778734	0.757930625	mg/L
20.00 PPM HP	Y 371.029	0.99696701	0.804204682	mg/L
20.00 PPM HP	Y AXIAL	0.94213797	0.574123518	mg/L
20.00 PPM HP	Cu 327.393	20.5321299	0.498656198	mg/L
20.00 PPM HP	Cr 267.716	20.4756552	0.594187242	mg/L
20.00 PPM HP	As 188.979	21.1156239	0.224920002	mg/L
20.00 PPM HP	As AXIAL	19.7355351	1.196987156	mg/L
20.00 PPM HP	Cu AXIAL	19.6470752	0.909413949	mg/L
20.00 PPM HP	Cr AXIAL	18.7945368	0.907213019	mg/L
0.500 PPM HP	Y 371.029	1.02786782	0.433690084	mg/L
0.500 PPM HP	Y AXIAL	1.02778722	0.182754926	mg/L
0.500 PPM HP	Cu 327.393	0.5340605	0.597727496	mg/L
0.500 PPM HP	Cr 267.716	0.51811382	1.040306413	mg/L
0.500 PPM HP	As 188.979	0.52551233	0.869986829	mg/L
0.500 PPM HP	As AXIAL	0.50763223	0.558779533	mg/L
0.500 PPM HP	Cu AXIAL	0.50060809	0.237289906	mg/L
0.500 PPM HP	Cr AXIAL	0.497324	0.486517961	mg/L
0.250 PPM HP	Y 371.029	1.02857888	0.329926406	mg/L
0.250 PPM HP	Y AXIAL	1.02335014	6.92E-02	mg/L
0.250 PPM HP	Cu 327.393	0.26529236	0.551045569	mg/L
0.250 PPM HP	Cr 267.716	0.25941825	0.539253731	mg/L
0.250 PPM HP	As 188.979	0.26204413	2.509391809	mg/L

0.250 PPM HP	As AXIAL	0.25221726	0.348879097	mg/L
0.250 PPM HP	Cu AXIAL	0.24824657	0.337663791	mg/L
0.250 PPM HP	Cr AXIAL	0.24738592	0.200454774	mg/L
0.050 PPM HP	Y 371.029	1.01320506	0.294322272	mg/L
0.050 PPM HP	Y AXIAL	1.01511802	0.105589155	mg/L
0.050 PPM HP	Cu 327.393	5.12E-02	1.317416521	mg/L
0.050 PPM HP	Cr 267.716	5.53E-02	0.617514978	mg/L
0.050 PPM HP	As 188.979	4.39E-02	10.85828603	mg/L
0.050 PPM HP	As AXIAL	5.11E-02	0.597130616	mg/L
0.050 PPM HP	Cu AXIAL	4.88E-02	0.240298272	mg/L
0.050 PPM HP	Cr AXIAL	5.24E-02	0.217510209	mg/L
D3-1 DF2	Y 371.029	0.92927726	1.447133925	mg/L
D3-1 DF2	Y AXIAL	0.96451971	2.17371353	mg/L
D3-1 DF2	Cu 327.393	1.79E-02	7.544737221	mg/L
D3-1 DF2	Cr 267.716	122.852674	1.484802757	mg/L
D3-1 DF2	As 188.979	2.07973245	2.192812658	mg/L
D3-1 DF2	As AXIAL	1.76059244	1.001031915	mg/L
D3-1 DF2	Cu AXIAL	1.73E-02	2.022963528	mg/L
D3-1 DF2	Cr AXIAL	104.970064	1.776102146	mg/L
D4-1 DF2	Y 371.029	0.99993297	0.472722992	mg/L
D4-1 DF2	Y AXIAL	0.97433401	0.311686743	mg/L
D4-1 DF2	Cu 327.393	1.42E-02	3.376882054	mg/L
D4-1 DF2	Cr 267.716	112.476554	0.650538116	mg/L
D4-1 DF2	As 188.979	1.61288572	0.339729971	mg/L
D4-1 DF2	As AXIAL	1.39287767	0.630407103	mg/L
D4-1 DF2	Cu AXIAL	1.55E-02	0.915895092	mg/L
D4-1 DF2	Cr AXIAL	98.164477	0.428759932	mg/L
D5-1 DF2	Y 371.029	1.6837156	0.185314314	mg/L
D5-1 DF2	Y AXIAL	1.6197987	0.510640811	mg/L
D5-1 DF2	Cu 327.393	1.43464168	0.429787446	mg/L
D5-1 DF2	Cr 267.716	17.0733728	0.344862071	mg/L
D5-1 DF2	As 188.979	1.28678554	0.555878343	mg/L
D5-1 DF2	As AXIAL	1.20300743	0.573010606	mg/L
D5-1 DF2	Cu AXIAL	1.38574184	0.435972474	mg/L
D5-1 DF2	Cr AXIAL	15.6160203	0.277224235	mg/L
D6-1 DF2	Y 371.029	1.59754373	0.149263845	mg/L
D6-1 DF2	Y AXIAL	1.55319391	0.221656262	mg/L
D6-1 DF2	Cu 327.393	1.36562631	0.276553129	mg/L
D6-1 DF2	Cr 267.716	16.2832812	0.224299481	mg/L
D6-1 DF2	As 188.979	1.26788274	0.266407537	mg/L
D6-1 DF2	As AXIAL	1.17685646	0.847140824	mg/L
D6-1 DF2	Cu AXIAL	1.3312018	0.632219302	mg/L
D6-1 DF2	Cr AXIAL	15.1605466	0.388547337	mg/L

D7-1 DF2	Y 371.029	13.2168626	0.748774533	mg/L
D7-1 DF2	Y AXIAL	12.187424	0.130955202	mg/L
D7-1 DF2	Cu 327.393	17.5739055	1.49223158	mg/L
D7-1 DF2	Cr 267.716	4.48522257	0.122723234	mg/L
D7-1 DF2	As 188.979	40.7714684	0.124432577	mg/L
D7-1 DF2	As AXIAL	27.8523767	0.742933818	mg/L
D7-1 DF2	Cu AXIAL	15.7344888	1.216158011	mg/L
D7-1 DF2	Cr AXIAL	3.86961058	0.816635602	mg/L
D8-1 DF2	Y 371.029	14.6088928	8.37E-02	mg/L
D8-1 DF2	Y AXIAL	13.1056544	0.263451009	mg/L
D8-1 DF2	Cu 327.393	19.1369237	0.201524005	mg/L
D8-1 DF2	Cr 267.716	5.1514244	0.109571057	mg/L
D8-1 DF2	As 188.979	49.0097142	0.125909561	mg/L
D8-1 DF2	As AXIAL	29.5039581	3.46E-02	mg/L
D8-1 DF2	Cu AXIAL	17.0433507	0.215144301	mg/L
D8-1 DF2	Cr AXIAL	4.26290142	7.35E-02	mg/L
D9-1 DF2	Y 371.029	3.34919691	0.140071676	mg/L
D9-1 DF2	Y AXIAL	3.05498964	0.168458173	mg/L
D9-1 DF2	Cu 327.393	20.4857685	0.638457171	mg/L
D9-1 DF2	Cr 267.716	6.36425546	0.177987683	mg/L
D9-1 DF2	As 188.979	51.4659499	0.152403	mg/L
D9-1 DF2	As AXIAL	43.1571286	0.264465459	mg/L
D9-1 DF2	Cu AXIAL	20.1488958	0.179265	mg/L
D9-1 DF2	Cr AXIAL	5.61631334	0.274082362	mg/L
D10-1 DF2	Y 371.029	6.65803697	0.604131782	mg/L
D10-1 DF2	Y AXIAL	5.74507995	0.19418342	mg/L
D10-1 DF2	Cu 327.393	32.6080238	0.642621724	mg/L
D10-1 DF2	Cr 267.716	8.2013309	0.245916528	mg/L
D10-1 DF2	As 188.979	73.6537786	0.295276588	mg/L
D10-1 DF2	As AXIAL	48.9947354	0.650311914	mg/L
D10-1 DF2	Cu AXIAL	30.1164739	0.604022502	mg/L
D10-1 DF2	Cr AXIAL	6.73343531	0.601313919	mg/L
D13-1 DF2	Y 371.029	1.41538218	0.341776132	mg/L
D13-1 DF2	Y AXIAL	1.3628532	0.137285747	mg/L
D13-1 DF2	Cu 327.393	1.23264134	0.260186917	mg/L
D13-1 DF2	Cr 267.716	24.5844218	0.299692187	mg/L
D13-1 DF2	As 188.979	1.52422785	1.228903639	mg/L
D13-1 DF2	As AXIAL	1.34729203	0.671018129	mg/L
D13-1 DF2	Cu AXIAL	1.19943136	0.479614235	mg/L
D13-1 DF2	Cr AXIAL	22.3925214	0.372253163	mg/L
D14-1 DF2	Y 371.029	1.47682549	0.228663085	mg/L
D14-1 DF2	Y AXIAL	1.4181847	0.805962039	mg/L
D14-1 DF2	Cu 327.393	1.29312683	1.67E-02	mg/L

D14-1 DF2	Cr 267.716	28.037783	0.656621003	mg/L
D14-1 DF2	As 188.979	1.67230013	0.452014846	mg/L
D14-1 DF2	As AXIAL	1.50378448	0.353961121	mg/L
D14-1 DF2	Cu AXIAL	1.2620031	0.416837428	mg/L
D14-1 DF2	Cr AXIAL	25.3945544	0.270140876	mg/L
BLANK	Y 371.029	1.03874134	0.369838647	mg/L
BLANK	Y AXIAL	1.02790723	0.444854724	mg/L
BLANK	Cu 327.393	3.70E-02	5.943830443	mg/L
BLANK	Cr 267.716	2.94E-02	1.059012639	mg/L
BLANK	As 188.979	0.2477034	3.369292288	mg/L
BLANK	As AXIAL	0.19850535	4.148895914	mg/L
BLANK	Cu AXIAL	3.09E-02	13.28568678	mg/L
BLANK	Cr AXIAL	2.48E-02	5.393473393	mg/L
1.00 PPM HP	Y 371.029	1.05383299	0.21730282	mg/L
1.00 PPM HP	Y AXIAL	1.04610611	0.662213711	mg/L
1.00 PPM HP	Cu 327.393	1.06871893	6.35E-02	mg/L
1.00 PPM HP	Cr 267.716	1.02670533	0.290450107	mg/L
1.00 PPM HP	As 188.979	1.23939227	0.984644564	mg/L
1.00 PPM HP	As AXIAL	1.15451559	4.73E-02	mg/L
1.00 PPM HP	Cu AXIAL	1.00647832	0.642988355	mg/L
1.00 PPM HP	Cr AXIAL	0.97627926	0.308374971	mg/L
5.00 PPM HP	Y 371.029	1.05466455	0.308655593	mg/L
5.00 PPM HP	Y AXIAL	1.02588442	7.68E-02	mg/L
5.00 PPM HP	Cu 327.393	5.12324589	0.234812866	mg/L
5.00 PPM HP	Cr 267.716	5.02544546	0.202943439	mg/L
5.00 PPM HP	As 188.979	5.35898053	0.346609517	mg/L
5.00 PPM HP	As AXIAL	5.03663644	0.28803237	mg/L
5.00 PPM HP	Cu AXIAL	4.85104332	0.254816804	mg/L
5.00 PPM HP	Cr AXIAL	4.71493778	0.312509047	mg/L
10.00 PPM HP	Y 371.029	1.03565664	5.87E-02	mg/L
10.00 PPM HP	Y AXIAL	1.00037704	0.339865707	mg/L
10.00 PPM HP	Cu 327.393	10.2337149	0.301362619	mg/L
10.00 PPM HP	Cr 267.716	10.131505	0.142953934	mg/L
10.00 PPM HP	As 188.979	10.5954912	0.354193599	mg/L
10.00 PPM HP	As AXIAL	9.97028882	0.250022613	mg/L
10.00 PPM HP	Cu AXIAL	9.74807828	0.590182206	mg/L
10.00 PPM HP	Cr AXIAL	9.39888102	0.217584548	mg/L
20.00 PPM HP	Y 371.029	1.0244005	0.885349183	mg/L
20.00 PPM HP	Y AXIAL	0.95767398	0.176629936	mg/L
20.00 PPM HP	Cu 327.393	20.4167437	0.621485469	mg/L
20.00 PPM HP	Cr 267.716	20.2739732	0.708738488	mg/L
20.00 PPM HP	As 188.979	21.1243601	0.143088822	mg/L
20.00 PPM HP	As AXIAL	19.4670018	0.930434287	mg/L

20.00 PPM HP	Cu AXIAL	19.3815635	1.166588737	mg/L
20.00 PPM HP	Cr AXIAL	18.3277757	0.911318172	mg/L
0.500 PPM HP	Y 371.029	1.05332058	0.489496232	mg/L
0.500 PPM HP	Y AXIAL	1.04407233	0.161323292	mg/L
0.500 PPM HP	Cu 327.393	0.54054047	0.181513527	mg/L
0.500 PPM HP	Cr 267.716	0.51118572	0.40593072	mg/L
0.500 PPM HP	As 188.979	0.6486768	1.023381775	mg/L
0.500 PPM HP	As AXIAL	0.59527933	0.562610883	mg/L
0.500 PPM HP	Cu AXIAL	0.50562601	0.174065847	mg/L
0.500 PPM HP	Cr AXIAL	0.48678168	0.312621179	mg/L
0.250 PPM HP	Y 371.029	1.04737869	0.449992438	mg/L
0.250 PPM HP	Y AXIAL	1.03599853	0.453141705	mg/L
0.250 PPM HP	Cu 327.393	0.2715931	0.191928686	mg/L
0.250 PPM HP	Cr 267.716	0.25736123	0.532201857	mg/L
0.250 PPM HP	As 188.979	0.36071983	0.631751369	mg/L
0.250 PPM HP	As AXIAL	0.33147665	0.631626077	mg/L
0.250 PPM HP	Cu AXIAL	0.2516321	0.793119552	mg/L
0.250 PPM HP	Cr AXIAL	0.24466512	0.197217291	mg/L
0.050 PPM HP	Y 371.029	1.03758205	0.157354459	mg/L
0.050 PPM HP	Y AXIAL	1.03348841	0.594567102	mg/L
0.050 PPM HP	Cu 327.393	5.61E-02	1.639466392	mg/L
0.050 PPM HP	Cr 267.716	5.48E-02	1.484215441	mg/L
0.050 PPM HP	As 188.979	0.12635902	4.113014932	mg/L
0.050 PPM HP	As AXIAL	0.1150736	1.74114175	mg/L
0.050 PPM HP	Cu AXIAL	5.27E-02	1.957171295	mg/L
0.050 PPM HP	Cr AXIAL	5.16E-02	0.731298662	mg/L
D15-1 DF2	Y 371.029	4.19290525	0.429258571	mg/L
D15-1 DF2	Y AXIAL	3.75522225	0.536616444	mg/L
D15-1 DF2	Cu 327.393	29.2087848	0.779077178	mg/L
D15-1 DF2	Cr 267.716	7.42224843	0.236438396	mg/L
D15-1 DF2	As 188.979	67.6477812	0.262374865	mg/L
D15-1 DF2	As AXIAL	52.6827712	0.641469059	mg/L
D15-1 DF2	Cu AXIAL	28.0646799	0.327195086	mg/L
D15-1 DF2	Cr AXIAL	6.397753	0.585749897	mg/L
D16-1 DF2	Y 371.029	3.41183294	0.540215208	mg/L
D16-1 DF2	Y AXIAL	3.07287759	0.329470532	mg/L
D16-1 DF2	Cu 327.393	28.0541561	0.450016541	mg/L
D16-1 DF2	Cr 267.716	7.24364386	5.98E-02	mg/L
D16-1 DF2	As 188.979	67.5102177	8.65E-02	mg/L
D16-1 DF2	As AXIAL	54.5030121	0.446789785	mg/L
D16-1 DF2	Cu AXIAL	27.1221203	0.314304584	mg/L
D16-1 DF2	Cr AXIAL	6.31367211	0.488930453	mg/L
D1-5 DF2	Y 371.029	1.04377127	2.80E-02	mg/L

D1-5 DF2	Y AXIAL	1.02428084	8.74E-02	mg/L
D1-5 DF2	Cu 327.393	3.57E-02	1.810154518	mg/L
D1-5 DF2	Cr 267.716	2.82465859	9.59E-02	mg/L
D1-5 DF2	As 188.979	12.5105379	3.14E-02	mg/L
D1-5 DF2	As AXIAL	11.4940719	6.88E-02	mg/L
D1-5 DF2	Cu AXIAL	3.47E-02	4.716480066	mg/L
D1-5 DF2	Cr AXIAL	2.66266284	8.24E-02	mg/L
D2-5 DF2	Y 371.029	1.06045679	0.384322838	mg/L
D2-5 DF2	Y AXIAL	1.04040257	0.356098576	mg/L
D2-5 DF2	Cu 327.393	3.36E-02	4.086274654	mg/L
D2-5 DF2	Cr 267.716	2.53568781	0.200784192	mg/L
D2-5 DF2	As 188.979	12.3028071	0.335814714	mg/L
D2-5 DF2	As AXIAL	11.2726592	0.570905396	mg/L
D2-5 DF2	Cu AXIAL	3.21E-02	3.270714298	mg/L
D2-5 DF2	Cr AXIAL	2.40060761	0.646074876	mg/L
D3-5 DF2	Y 371.029	1.04603647	0.126444588	mg/L
D3-5 DF2	Y AXIAL	1.03703872	0.550139515	mg/L
D3-5 DF2	Cu 327.393	4.19E-02	1.349136558	mg/L
D3-5 DF2	Cr 267.716	2.3371602	0.231916517	mg/L
D3-5 DF2	As 188.979	11.4849127	0.164736473	mg/L
D3-5 DF2	As AXIAL	10.6719761	0.459809572	mg/L
D3-5 DF2	Cu AXIAL	3.96E-02	1.102712265	mg/L
D3-5 DF2	Cr AXIAL	2.21559227	0.343846479	mg/L
D4-5 DF2	Y 371.029	1.05393341	0.218135336	mg/L
D4-5 DF2	Y AXIAL	1.04840775	0.665339168	mg/L
D4-5 DF2	Cu 327.393	4.46E-02	0.634433769	mg/L
D4-5 DF2	Cr 267.716	2.18316003	0.18716964	mg/L
D4-5 DF2	As 188.979	11.881501	0.193907744	mg/L
D4-5 DF2	As AXIAL	11.0625088	0.431466998	mg/L
D4-5 DF2	Cu AXIAL	4.33E-02	0.246613417	mg/L
D4-5 DF2	Cr AXIAL	2.0720814	0.249530287	mg/L
D5-5 DF2	Y 371.029	1.05678248	0.425782596	mg/L
D5-5 DF2	Y AXIAL	1.03663892	0.379744455	mg/L
D5-5 DF2	Cu 327.393	6.56E-02	0.511946677	mg/L
D5-5 DF2	Cr 267.716	2.13245968	0.441950068	mg/L
D5-5 DF2	As 188.979	1.46673995	0.261136074	mg/L
D5-5 DF2	As AXIAL	1.35972913	0.490611457	mg/L
D5-5 DF2	Cu AXIAL	6.45E-02	3.314919431	mg/L
D5-5 DF2	Cr AXIAL	1.99905565	0.376810452	mg/L
D6-5 DF2	Y 371.029	1.0515715	0.435410344	mg/L
D6-5 DF2	Y AXIAL	1.02495094	0.35048876	mg/L
D6-5 DF2	Cu 327.393	7.13E-02	1.118715767	mg/L
D6-5 DF2	Cr 267.716	2.08724317	0.487042605	mg/L

D6-5 DF2	As 188.979	1.56015777	0.361127479	mg/L
D6-5 DF2	As AXIAL	1.44092781	0.408501862	mg/L
D6-5 DF2	Cu AXIAL	6.84E-02	0.903012605	mg/L
D6-5 DF2	Cr AXIAL	1.95888831	0.629253808	mg/L
D7-5 DF2	Y 371.029	2.12675037	0.403917485	mg/L
D7-5 DF2	Y AXIAL	2.05733517	0.560913968	mg/L
D7-5 DF2	Cu 327.393	7.9416189	0.373596386	mg/L
D7-5 DF2	Cr 267.716	2.26493641	0.136156902	mg/L
D7-5 DF2	As 188.979	17.8824338	0.229985661	mg/L
D7-5 DF2	As AXIAL	16.4617235	0.517091925	mg/L
D7-5 DF2	Cu AXIAL	7.62988558	0.665395096	mg/L
D7-5 DF2	Cr AXIAL	2.10829452	0.501292723	mg/L
D8-5 DF2	Y 371.029	2.33154493	0.58171028	mg/L
D8-5 DF2	Y AXIAL	2.25006382	0.633402344	mg/L
D8-5 DF2	Cu 327.393	8.01457524	0.816934478	mg/L
D8-5 DF2	Cr 267.716	2.33305399	0.225003534	mg/L
D8-5 DF2	As 188.979	18.6758148	0.202125146	mg/L
D8-5 DF2	As AXIAL	17.1600091	0.257556941	mg/L
D8-5 DF2	Cu AXIAL	7.6492955	0.299340529	mg/L
D8-5 DF2	Cr AXIAL	2.1684239	0.243736245	mg/L
BLANK	Y 371.029	1.03547379	0.619930827	mg/L
BLANK	Y AXIAL	1.02729917	0.405243832	mg/L
BLANK	Cu 327.393	2.09E-03	28.75955735	mg/L
BLANK	Cr 267.716	2.94E-03	25.75618712	mg/L
BLANK	As 188.979	7.29E-02	5.347347396	mg/L
BLANK	As AXIAL	5.96E-02	2.841135805	mg/L
BLANK	Cu AXIAL	1.67E-03	14.11970656	mg/L
BLANK	Cr AXIAL	2.79E-03	2.4233198	mg/L
1.00 PPM HP	Y 371.029	1.04987074	0.71240989	mg/L
1.00 PPM HP	Y AXIAL	1.03908231	0.349392887	mg/L
1.00 PPM HP	Cu 327.393	1.04132957	0.371331888	mg/L
1.00 PPM HP	Cr 267.716	1.00721201	0.267881179	mg/L
1.00 PPM HP	As 188.979	1.08852467	1.416400631	mg/L
1.00 PPM HP	As AXIAL	1.03863084	0.810257151	mg/L
1.00 PPM HP	Cu AXIAL	0.98291765	0.742607496	mg/L
1.00 PPM HP	Cr AXIAL	0.96055957	0.640112447	mg/L
5.00 PPM HP	Y 371.029	1.05688993	0.518660116	mg/L
5.00 PPM HP	Y AXIAL	1.02755509	0.234182351	mg/L
5.00 PPM HP	Cu 327.393	5.07638426	1.195837397	mg/L
5.00 PPM HP	Cr 267.716	4.99758367	0.342770595	mg/L
5.00 PPM HP	As 188.979	5.21027667	0.38710524	mg/L
5.00 PPM HP	As AXIAL	4.92789609	0.428477416	mg/L
5.00 PPM HP	Cu AXIAL	4.80294122	0.295011701	mg/L

5.00 PPM HP	Cr AXIAL	4.68308986	0.353699187	mg/L
10.00 PPM HP	Y 371.029	1.03793859	0.168180252	mg/L
10.00 PPM HP	Y AXIAL	0.99975769	0.344213408	mg/L
10.00 PPM HP	Cu 327.393	10.181857	0.29990448	mg/L
10.00 PPM HP	Cr 267.716	10.1032296	0.218810278	mg/L
10.00 PPM HP	As 188.979	10.4814552	0.205983032	mg/L
10.00 PPM HP	As AXIAL	9.83785194	0.18063192	mg/L
10.00 PPM HP	Cu AXIAL	9.71458656	0.317524127	mg/L
10.00 PPM HP	Cr AXIAL	9.37557095	4.15E-02	mg/L
20.00 PPM HP	Y 371.029	1.02366205	0.717659026	mg/L
20.00 PPM HP	Y AXIAL	0.95892988	0.246527019	mg/L
20.00 PPM HP	Cu 327.393	20.4096866	1.202062089	mg/L
20.00 PPM HP	Cr 267.716	20.2155093	0.995104838	mg/L
20.00 PPM HP	As 188.979	21.0236773	0.313833005	mg/L
20.00 PPM HP	As AXIAL	19.398057	0.70953526	mg/L
20.00 PPM HP	Cu AXIAL	19.4214704	0.682185141	mg/L
20.00 PPM HP	Cr AXIAL	18.2939711	0.700565638	mg/L
0.500 PPM HP	Y 371.029	1.05632986	0.360699631	mg/L
0.500 PPM HP	Y AXIAL	1.04645397	0.599261789	mg/L
0.500 PPM HP	Cu 327.393	0.52808878	0.261200899	mg/L
0.500 PPM HP	Cr 267.716	0.50451541	0.423259009	mg/L
0.500 PPM HP	As 188.979	0.56417997	7.01E-02	mg/L
0.500 PPM HP	As AXIAL	0.53295631	0.307644689	mg/L
0.500 PPM HP	Cu AXIAL	0.49415595	1.158601882	mg/L
0.500 PPM HP	Cr AXIAL	0.48051314	0.714151416	mg/L
0.250 PPM HP	Y 371.029	1.05873059	0.340648654	mg/L
0.250 PPM HP	Y AXIAL	1.04711658	0.170567827	mg/L
0.250 PPM HP	Cu 327.393	0.26470362	0.333201202	mg/L
0.250 PPM HP	Cr 267.716	0.25167145	0.576328526	mg/L
0.250 PPM HP	As 188.979	0.29844523	0.536611074	mg/L
0.250 PPM HP	As AXIAL	0.27799195	0.190861144	mg/L
0.250 PPM HP	Cu AXIAL	0.24662523	0.654724178	mg/L
0.250 PPM HP	Cr AXIAL	0.23800215	0.284157377	mg/L
0.050 PPM HP	Y 371.029	1.05018694	0.216723983	mg/L
0.050 PPM HP	Y AXIAL	1.04265402	0.384406658	mg/L
0.050 PPM HP	Cu 327.393	5.06E-02	0.639125671	mg/L
0.050 PPM HP	Cr 267.716	5.02E-02	1.321851343	mg/L
0.050 PPM HP	As 188.979	8.19E-02	7.377775977	mg/L
0.050 PPM HP	As AXIAL	7.60E-02	1.602845361	mg/L
0.050 PPM HP	Cu AXIAL	4.99E-02	0.857085591	mg/L
0.050 PPM HP	Cr AXIAL	4.76E-02	8.23E-02	mg/L
D13-5 DF2	Y 371.029	1.07315883	0.658990559	mg/L
D13-5 DF2	Y AXIAL	1.04259067	0.393620448	mg/L

D13-5 DF2	Cu 327.393	7.83E-02	0.900073726	mg/L
D13-5 DF2	Cr 267.716	3.02539659	0.406492899	mg/L
D13-5 DF2	As 188.979	1.72974361	0.382220321	mg/L
D13-5 DF2	As AXIAL	1.60225766	1.115639867	mg/L
D13-5 DF2	Cu AXIAL	7.54E-02	0.651321283	mg/L
D13-5 DF2	Cr AXIAL	2.82312004	0.924575493	mg/L
D14-5 DF2	Y 371.029	1.05426541	0.715865009	mg/L
D14-5 DF2	Y AXIAL	1.03259067	0.50485907	mg/L
D14-5 DF2	Cu 327.393	7.41E-02	1.01369931	mg/L
D14-5 DF2	Cr 267.716	2.69390682	0.551417625	mg/L
D14-5 DF2	As 188.979	2.03531684	0.692389728	mg/L
D14-5 DF2	As AXIAL	1.90342145	0.611966758	mg/L
D14-5 DF2	Cu AXIAL	7.19E-02	1.162218834	mg/L
D14-5 DF2	Cr AXIAL	2.54125475	1.111260374	mg/L
D1-9 DF2	Y 371.029	1.06743424	8.68E-02	mg/L
D1-9 DF2	Y AXIAL	1.04352987	7.22E-02	mg/L
D1-9 DF2	Cu 327.393	3.50E-02	2.939771173	mg/L
D1-9 DF2	Cr 267.716	5.38197132	8.45E-02	mg/L
D1-9 DF2	As 188.979	41.8650147	5.68E-02	mg/L
D1-9 DF2	As AXIAL	38.1463363	6.50E-02	mg/L
D1-9 DF2	Cu AXIAL	3.41E-02	1.508326896	mg/L
D1-9 DF2	Cr AXIAL	5.06157032	0.295847569	mg/L
D2-9 DF2	Y 371.029	1.07404963	0.161330717	mg/L
D2-9 DF2	Y AXIAL	1.05275962	0.254394104	mg/L
D2-9 DF2	Cu 327.393	6.39E-02	0.488536083	mg/L
D2-9 DF2	Cr 267.716	3.65902226	0.130510028	mg/L
D2-9 DF2	As 188.979	39.7408343	0.101363063	mg/L
D2-9 DF2	As AXIAL	36.3608674	0.302123073	mg/L
D2-9 DF2	Cu AXIAL	6.17E-02	0.642759389	mg/L
D2-9 DF2	Cr AXIAL	3.44905556	0.264595115	mg/L
D3-9 DF2	Y 371.029	1.04128198	0.521456836	mg/L
D3-9 DF2	Y AXIAL	1.02323524	0.225821848	mg/L
D3-9 DF2	Cu 327.393	5.79E-02	1.434269596	mg/L
D3-9 DF2	Cr 267.716	4.03014216	0.144287083	mg/L
D3-9 DF2	As 188.979	40.4048179	0.184339776	mg/L
D3-9 DF2	As AXIAL	37.0162161	0.47959326	mg/L
D3-9 DF2	Cu AXIAL	5.66E-02	0.850738511	mg/L
D3-9 DF2	Cr AXIAL	3.80985713	0.559164501	mg/L
D4-9 DF2	Y 371.029	1.07312632	0.488083597	mg/L
D4-9 DF2	Y AXIAL	1.05383447	0.305250371	mg/L
D4-9 DF2	Cu 327.393	6.47E-02	0.298688391	mg/L
D4-9 DF2	Cr 267.716	3.01818873	0.304636824	mg/L
D4-9 DF2	As 188.979	38.2080202	0.397061555	mg/L

D4-9 DF2	As AXIAL	35.0832484	0.49550737	mg/L
D4-9 DF2	Cu AXIAL	6.33E-02	0.94660564	mg/L
D4-9 DF2	Cr AXIAL	2.84890092	0.652543104	mg/L
D5-9 DF2	Y 371.029	1.0325958	0.172353095	mg/L
D5-9 DF2	Y AXIAL	0.97928905	0.434059737	mg/L
D5-9 DF2	Cu 327.393	0.1318766	0.376428132	mg/L
D5-9 DF2	Cr 267.716	3.08603338	0.172645135	mg/L
D5-9 DF2	As 188.979	6.81977814	0.145575691	mg/L
D5-9 DF2	As AXIAL	6.32395985	0.94312422	mg/L
D5-9 DF2	Cu AXIAL	0.12737808	0.504771072	mg/L
D5-9 DF2	Cr AXIAL	2.83358615	0.970758479	mg/L
D6-9 DF2	Y 371.029	1.00780294	0.410714349	mg/L
D6-9 DF2	Y AXIAL	0.97828523	0.464567618	mg/L
D6-9 DF2	Cu 327.393	0.13247432	0.500062072	mg/L
D6-9 DF2	Cr 267.716	3.03266467	0.154549408	mg/L
D6-9 DF2	As 188.979	7.08069642	0.321780141	mg/L
D6-9 DF2	As AXIAL	6.69503835	0.649376973	mg/L
D6-9 DF2	Cu AXIAL	0.13197734	0.434829679	mg/L
D6-9 DF2	Cr AXIAL	2.83680689	0.674407537	mg/L
D7-9 DF2	Y 371.029	2.30333437	0.486823129	mg/L
D7-9 DF2	Y AXIAL	2.24339371	0.709412701	mg/L
D7-9 DF2	Cu 327.393	2.19182721	0.817636591	mg/L
D7-9 DF2	Cr 267.716	0.36532129	0.144436686	mg/L
D7-9 DF2	As 188.979	0.39161718	0.217000448	mg/L
D7-9 DF2	As AXIAL	0.39868859	1.090583986	mg/L
D7-9 DF2	Cu AXIAL	2.12825533	0.357789081	mg/L
D7-9 DF2	Cr AXIAL	0.34800601	0.315071525	mg/L
D8-9 DF2	Y 371.029	2.21914608	2.507136691	mg/L
D8-9 DF2	Y AXIAL	2.25106625	0.758279511	mg/L
D8-9 DF2	Cu 327.393	2.05254373	1.140849732	mg/L
D8-9 DF2	Cr 267.716	0.3651253	0.152588953	mg/L
D8-9 DF2	As 188.979	0.51323107	4.94E-02	mg/L
D8-9 DF2	As AXIAL	0.52866298	1.744809679	mg/L
D8-9 DF2	Cu AXIAL	2.10305236	1.920500022	mg/L
D8-9 DF2	Cr AXIAL	0.35810655	2.392746008	mg/L
BLANK	Y 371.029	0.99367225	1.666124255	mg/L
BLANK	Y AXIAL	1.01027476	0.907851865	mg/L
BLANK	Cu 327.393	-3.35E-03	1.906906941	mg/L
BLANK	Cr 267.716	1.18E-03	17.53507598	mg/L
BLANK	As 188.979	3.44E-02	6.170617324	mg/L
BLANK	As AXIAL	2.40E-02	3.632722431	mg/L
BLANK	Cu AXIAL	-1.25E-03	88.66912026	mg/L
BLANK	Cr AXIAL	1.01E-03	9.230952944	mg/L

1.00 PPM HP	Y 371.029	1.02218884	0.194088999	mg/L
1.00 PPM HP	Y AXIAL	1.02030196	0.206279465	mg/L
1.00 PPM HP	Cu 327.393	1.03619955	0.299309236	mg/L
1.00 PPM HP	Cr 267.716	1.00880273	0.230195418	mg/L
1.00 PPM HP	As 188.979	1.06624829	0.587512559	mg/L
1.00 PPM HP	As AXIAL	1.02178315	0.546570492	mg/L
1.00 PPM HP	Cu AXIAL	0.98409756	0.564202681	mg/L
1.00 PPM HP	Cr AXIAL	0.97558373	0.227361156	mg/L
5.00 PPM HP	Y 371.029	1.01415411	0.314811529	mg/L
5.00 PPM HP	Y AXIAL	0.99994376	0.690248903	mg/L
5.00 PPM HP	Cu 327.393	5.08001551	0.131671718	mg/L
5.00 PPM HP	Cr 267.716	5.0280045	0.149586005	mg/L
5.00 PPM HP	As 188.979	5.22114811	0.34923057	mg/L
5.00 PPM HP	As AXIAL	4.9940407	0.56701942	mg/L
5.00 PPM HP	Cu AXIAL	4.8505127	0.729069586	mg/L
5.00 PPM HP	Cr AXIAL	4.78022288	0.561642604	mg/L
10.00 PPM HP	Y 371.029	0.99686842	1.069001382	mg/L
10.00 PPM HP	Y AXIAL	0.97617875	0.36864518	mg/L
10.00 PPM HP	Cu 327.393	10.1669183	0.80984772	mg/L
10.00 PPM HP	Cr 267.716	10.137415	0.863266334	mg/L
10.00 PPM HP	As 188.979	10.4980872	0.85635999	mg/L
10.00 PPM HP	As AXIAL	10.0145747	1.214826049	mg/L
10.00 PPM HP	Cu AXIAL	9.76856561	0.651058526	mg/L
10.00 PPM HP	Cr AXIAL	9.58044314	0.926256553	mg/L
20.00 PPM HP	Y 371.029	0.98218921	0.403650532	mg/L
20.00 PPM HP	Y AXIAL	0.93129217	0.270782188	mg/L
20.00 PPM HP	Cu 327.393	20.3640225	0.637996679	mg/L
20.00 PPM HP	Cr 267.716	20.368174	0.590052826	mg/L
20.00 PPM HP	As 188.979	21.1470679	0.256519884	mg/L
20.00 PPM HP	As AXIAL	19.7501664	0.614271987	mg/L
20.00 PPM HP	Cu AXIAL	19.6835991	0.413978461	mg/L
20.00 PPM HP	Cr AXIAL	18.8843807	0.47777612	mg/L
0.500 PPM HP	Y 371.029	1.01287719	0.201936478	mg/L
0.500 PPM HP	Y AXIAL	1.01401939	0.474017219	mg/L
0.500 PPM HP	Cu 327.393	0.52717424	0.539048431	mg/L
0.500 PPM HP	Cr 267.716	0.5077968	0.275659174	mg/L
0.500 PPM HP	As 188.979	0.54646597	0.358084895	mg/L
0.500 PPM HP	As AXIAL	0.52386408	0.55989579	mg/L
0.500 PPM HP	Cu AXIAL	0.4959259	0.737625347	mg/L
0.500 PPM HP	Cr AXIAL	0.49087353	0.419561799	mg/L
0.250 PPM HP	Y 371.029	1.00619353	0.758816436	mg/L
0.250 PPM HP	Y AXIAL	1.00710606	0.317497374	mg/L
0.250 PPM HP	Cu 327.393	0.26435893	1.003881268	mg/L

0.250 PPM HP	Cr 267.716	0.25349666	0.707714253	mg/L
0.250 PPM HP	As 188.979	0.28145071	3.312945341	mg/L
0.250 PPM HP	As AXIAL	0.26723391	0.841880661	mg/L
0.250 PPM HP	Cu AXIAL	0.24764009	0.476378888	mg/L
0.250 PPM HP	Cr AXIAL	0.24461332	0.951508996	mg/L
0.050 PPM HP	Y 371.029	1.00640489	0.449773576	mg/L
0.050 PPM HP	Y AXIAL	1.00739643	0.506241295	mg/L
0.050 PPM HP	Cu 327.393	5.16E-02	2.260890827	mg/L
0.050 PPM HP	Cr 267.716	5.07E-02	0.830060548	mg/L
0.050 PPM HP	As 188.979	6.71E-02	6.896028358	mg/L
0.050 PPM HP	As AXIAL	6.27E-02	1.703604136	mg/L
0.050 PPM HP	Cu AXIAL	4.93E-02	1.303242885	mg/L
0.050 PPM HP	Cr AXIAL	4.87E-02	0.471953644	mg/L
D13-9 DF2	Y 371.029	0.95463021	1.094603378	mg/L
D13-9 DF2	Y AXIAL	0.93181323	0.2413475	mg/L
D13-9 DF2	Cu 327.393	0.1595291	0.810133824	mg/L
D13-9 DF2	Cr 267.716	3.21145385	0.296674268	mg/L
D13-9 DF2	As 188.979	8.90524097	0.445315206	mg/L
D13-9 DF2	As AXIAL	8.50210326	0.827719753	mg/L
D13-9 DF2	Cu AXIAL	0.15767711	0.791273963	mg/L
D13-9 DF2	Cr AXIAL	3.04604121	0.865139343	mg/L
D14-9 DF2	Y 371.029	0.9610131	0.479962056	mg/L
D14-9 DF2	Y AXIAL	0.95995881	0.463140436	mg/L
D14-9 DF2	Cu 327.393	0.13498883	0.661375491	mg/L
D14-9 DF2	Cr 267.716	3.3412398	0.256105569	mg/L
D14-9 DF2	As 188.979	9.94019978	0.341858119	mg/L
D14-9 DF2	As AXIAL	9.54913052	1.272527846	mg/L
D14-9 DF2	Cu AXIAL	0.13759975	0.84178418	mg/L
D14-9 DF2	Cr AXIAL	3.19943254	1.205212725	mg/L
6-28-D9 DF2	Y 371.029	0.94532444	0.379369131	mg/L
6-28-D9 DF2	Y AXIAL	0.92855669	0.334151119	mg/L
6-28-D9 DF2	Cu 327.393	0.15506101	0.937149896	mg/L
6-28-D9 DF2	Cr 267.716	1.32897708	0.438556229	mg/L
6-28-D9 DF2	As 188.979	5.90E-02	11.50392279	mg/L
6-28-D9 DF2	As AXIAL	4.93E-02	1.747524116	mg/L
6-28-D9 DF2	Cu AXIAL	0.15619311	0.490186359	mg/L
6-28-D9 DF2	Cr AXIAL	1.25353927	1.452258352	mg/L
6-28-D10 DF2	Y 371.029	0.93706126	0.884858536	mg/L
6-28-D10 DF2	Y AXIAL	0.92835997	0.663835037	mg/L
6-28-D10 DF2	Cu 327.393	0.15879979	1.877247784	mg/L
6-28-D10 DF2	Cr 267.716	1.27206272	0.297380839	mg/L
6-28-D10 DF2	As 188.979	5.93E-02	10.2376114	mg/L
6-28-D10 DF2	As AXIAL	6.21E-02	2.361596672	mg/L

6-28-D10 DF2	Cu AXIAL	0.15833879	0.819768719	mg/L
6-28-D10 DF2	Cr AXIAL	1.22020176	1.641780942	mg/L
6-28-D11 DF2	Y 371.029	5.21177958	0.155475172	mg/L
6-28-D11 DF2	Y AXIAL	5.00555327	0.553175351	mg/L
6-28-D11 DF2	Cu 327.393	12.7248623	0.322533256	mg/L
6-28-D11 DF2	Cr 267.716	3.23486106	0.160720125	mg/L
6-28-D11 DF2	As 188.979	6.70750067	0.410849421	mg/L
6-28-D11 DF2	As AXIAL	6.25806264	0.484369447	mg/L
6-28-D11 DF2	Cu AXIAL	12.1545786	0.509519402	mg/L
6-28-D11 DF2	Cr AXIAL	2.98675821	0.377898467	mg/L
6-28-D12 DF2	Y 371.029	5.10193146	0.551197665	mg/L
6-28-D12 DF2	Y AXIAL	4.92406674	0.24175494	mg/L
6-28-D12 DF2	Cu 327.393	12.0024181	0.412342531	mg/L
6-28-D12 DF2	Cr 267.716	3.23549696	0.30302854	mg/L
6-28-D12 DF2	As 188.979	7.29540898	0.189607534	mg/L
6-28-D12 DF2	As AXIAL	6.80624276	0.733271673	mg/L
6-28-D12 DF2	Cu AXIAL	11.5581489	0.49365346	mg/L
6-28-D12 DF2	Cr AXIAL	3.00649317	0.735662583	mg/L
6-28-D13 DF2	Y 371.029	0.98623422	0.472982388	mg/L
6-28-D13 DF2	Y AXIAL	0.97488475	0.638206344	mg/L
6-28-D13 DF2	Cu 327.393	0.12369043	0.424718971	mg/L
6-28-D13 DF2	Cr 267.716	11.0618155	0.513926692	mg/L
6-28-D13 DF2	As 188.979	6.35171297	0.78269223	mg/L
6-28-D13 DF2	As AXIAL	6.11252143	0.930311541	mg/L
6-28-D13 DF2	Cu AXIAL	0.12320254	0.356699988	mg/L
6-28-D13 DF2	Cr AXIAL	10.6021202	0.943832109	mg/L
6-28-D14 DF2	Y 371.029	1.00254256	1.034282895	mg/L
6-28-D14 DF2	Y AXIAL	0.98103826	0.115503501	mg/L
6-28-D14 DF2	Cu 327.393	0.11628693	0.985473286	mg/L
6-28-D14 DF2	Cr 267.716	11.5711091	0.958870552	mg/L
6-28-D14 DF2	As 188.979	6.58208577	0.713135293	mg/L
6-28-D14 DF2	As AXIAL	6.23598306	1.036787622	mg/L
6-28-D14 DF2	Cu AXIAL	0.11467729	1.490127662	mg/L
6-28-D14 DF2	Cr AXIAL	10.8659921	1.351414063	mg/L
6-28-D15 DF2	Y 371.029	0.96712961	1.626351692	mg/L
6-28-D15 DF2	Y AXIAL	0.96367788	2.963974764	mg/L
6-28-D15 DF2	Cu 327.393	0.12004306	2.088923647	mg/L
6-28-D15 DF2	Cr 267.716	2.00E-02	5.635150538	mg/L
6-28-D15 DF2	As 188.979	7.30E-02	6.467192019	mg/L
6-28-D15 DF2	As AXIAL	7.52E-02	2.347530244	mg/L
6-28-D15 DF2	Cu AXIAL	0.12370838	1.97044468	mg/L
6-28-D15 DF2	Cr AXIAL	1.78E-02	2.749560682	mg/L
6-28-D16 DF2	Y 371.029	1.01546585	1.452385834	mg/L

6-28-D16 DF2	Y AXIAL	0.97903477	0.354575785	mg/L
6-28-D16 DF2	Cu 327.393	0.10924921	2.262642207	mg/L
6-28-D16 DF2	Cr 267.716	2.21E-02	5.437768022	mg/L
6-28-D16 DF2	As 188.979	6.33E-02	5.604043914	mg/L
6-28-D16 DF2	As AXIAL	5.68E-02	3.150273865	mg/L
6-28-D16 DF2	Cu AXIAL	0.10936623	3.092804482	mg/L
6-28-D16 DF2	Cr AXIAL	2.03E-02	3.049269983	mg/L
BLANK	Y 371.029	0.93054574	0.330809582	mg/L
BLANK	Y AXIAL	0.95554671	0.745569123	mg/L
BLANK	Cu 327.393	-2.09E-03	26.01739765	mg/L
BLANK	Cr 267.716	2.26E-03	42.99259626	mg/L
BLANK	As 188.979	1.50E-02	45.74028498	mg/L
BLANK	As AXIAL	1.07E-02	13.16761189	mg/L
BLANK	Cu AXIAL	-6.08E-05	756.2723489	mg/L
BLANK	Cr AXIAL	2.77E-03	7.33481997	mg/L
1.00 PPM HP	Y 371.029	0.98420393	5.79E-02	mg/L
1.00 PPM HP	Y AXIAL	0.98821683	0.226689657	mg/L
1.00 PPM HP	Cu 327.393	1.03425065	0.771950225	mg/L
1.00 PPM HP	Cr 267.716	1.01293145	0.127794421	mg/L
1.00 PPM HP	As 188.979	1.05781622	0.981829743	mg/L
1.00 PPM HP	As AXIAL	1.02026342	0.244950364	mg/L
1.00 PPM HP	Cu AXIAL	0.98237974	0.631256063	mg/L
1.00 PPM HP	Cr AXIAL	0.98421617	0.368843914	mg/L
5.00 PPM HP	Y 371.029	0.98407274	0.422771129	mg/L
5.00 PPM HP	Y AXIAL	0.97208379	0.347948921	mg/L
5.00 PPM HP	Cu 327.393	5.08358577	0.235823479	mg/L
5.00 PPM HP	Cr 267.716	5.03321774	0.247268358	mg/L
5.00 PPM HP	As 188.979	5.19385478	0.268353311	mg/L
5.00 PPM HP	As AXIAL	4.99341375	0.393426403	mg/L
5.00 PPM HP	Cu AXIAL	4.84456497	0.963000089	mg/L
5.00 PPM HP	Cr AXIAL	4.82414522	0.658877092	mg/L
10.00 PPM HP	Y 371.029	0.95945981	0.937546877	mg/L
10.00 PPM HP	Y AXIAL	0.94300938	0.13887598	mg/L
10.00 PPM HP	Cu 327.393	10.1768731	0.88015619	mg/L
10.00 PPM HP	Cr 267.716	10.2041211	0.971229354	mg/L
10.00 PPM HP	As 188.979	10.5202364	0.613124012	mg/L
10.00 PPM HP	As AXIAL	10.089759	0.992887156	mg/L
10.00 PPM HP	Cu AXIAL	9.8232482	1.821988449	mg/L
10.00 PPM HP	Cr AXIAL	9.74906621	1.410338742	mg/L
20.00 PPM HP	Y 371.029	0.95421413	0.474840224	mg/L
20.00 PPM HP	Y AXIAL	0.91917294	0.678866662	mg/L
20.00 PPM HP	Cu 327.393	20.5137644	0.932995046	mg/L
20.00 PPM HP	Cr 267.716	20.5654684	0.755356238	mg/L

20.00 PPM HP	As 188.979	21.2512885	0.711970738	mg/L
20.00 PPM HP	As AXIAL	20.0559789	0.699318214	mg/L
20.00 PPM HP	Cu AXIAL	19.7565554	0.747724695	mg/L
20.00 PPM HP	Cr AXIAL	19.1198035	0.660162709	mg/L
0.500 PPM HP	Y 371.029	0.98662581	0.697521947	mg/L
0.500 PPM HP	Y AXIAL	0.99648767	0.233567661	mg/L
0.500 PPM HP	Cu 327.393	0.53026648	0.179386536	mg/L
0.500 PPM HP	Cr 267.716	0.50903049	0.692533522	mg/L
0.500 PPM HP	As 188.979	0.53819495	0.286330949	mg/L
0.500 PPM HP	As AXIAL	0.52044269	0.641132268	mg/L
0.500 PPM HP	Cu AXIAL	0.50128733	0.714405391	mg/L
0.500 PPM HP	Cr AXIAL	0.49613042	0.691037228	mg/L
0.250 PPM HP	Y 371.029	0.98988999	8.13E-02	mg/L
0.250 PPM HP	Y AXIAL	0.99478792	0.572457511	mg/L
0.250 PPM HP	Cu 327.393	0.26594722	0.294272396	mg/L
0.250 PPM HP	Cr 267.716	0.25447674	0.353193042	mg/L
0.250 PPM HP	As 188.979	0.26565331	1.85585668	mg/L
0.250 PPM HP	As AXIAL	0.26221102	0.462432827	mg/L
0.250 PPM HP	Cu AXIAL	0.24935417	0.602508338	mg/L
0.250 PPM HP	Cr AXIAL	0.24520972	0.263011321	mg/L
0.050 PPM HP	Y 371.029	0.97952284	0.223453419	mg/L
0.050 PPM HP	Y AXIAL	0.98989306	0.716419049	mg/L
0.050 PPM HP	Cu 327.393	5.27E-02	1.092026989	mg/L
0.050 PPM HP	Cr 267.716	5.06E-02	1.431763996	mg/L
0.050 PPM HP	As 188.979	6.11E-02	12.21005758	mg/L
0.050 PPM HP	As AXIAL	5.88E-02	2.096024657	mg/L
0.050 PPM HP	Cu AXIAL	5.09E-02	0.243822998	mg/L
0.050 PPM HP	Cr AXIAL	4.96E-02	0.332762818	mg/L

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			radial	axial	radial	axial	radial	axial
	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
0.050 PPM HP	1.14	1.11	0.054	0.051	0.05	0.05	0.02	0.052
	1.109	1.076	0.055	0.051	0.048	0.047	0.019	0.052
AVERAGE	1.124	1.093	0.055	0.051	0.049	0.049	0.019	0.052
STDEV	0.022	0.024	0	0	0.001	0.002	0	0
%RSD	1.955	2.172	0.371	0.877	2.192	4.226	2.396	0.88
%DIFFERENCE	12.423	9.284	9.064	2.27	-2.335	-2.884	-61.342	3.68
ACTUAL	1	1	0.05	0.05	0.05	0.05	0.05	0.05

			radial	axial	radial	axial	radial	axial

	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
0.250 PPM HP	1.206	1.187	0.269	0.254	0.251	0.251	0.234	0.263
	1.148	1.111	0.272	0.256	0.236	0.233	0.21	0.24
AVERAGE	1.177	1.149	0.271	0.255	0.244	0.242	0.222	0.252
STDEV	0.041	0.054	0.002	0.001	0.01	0.012	0.016	0.016
%RSD	3.473	4.678	0.665	0.495	4.118	5.129	7.398	6.434
%DIFFERENCE	17.663	14.942	8.301	1.935	-2.576	-3.213	-11.194	0.641
ACTUAL	1	1	0.25	0.25	0.25	0.25	0.25	0.25

			radial	axial	radial	axial	radial	axial
	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
0.500 PPM HP	1.188	1.157	0.551	0.511	0.492	0.485	0.492	0.518
	1.142	1.107	0.553	0.514	0.476	0.47	0.48	0.506
AVERAGE	1.165	1.132	0.552	0.512	0.484	0.478	0.486	0.512
STDEV	0.032	0.035	0.002	0.002	0.011	0.011	0.008	0.008
%RSD	2.787	3.114	0.284	0.439	2.367	2.248	1.66	1.554
%DIFFERENCE	16.461	13.175	10.333	2.456	-3.173	-4.427	-2.762	2.393
ACTUAL	1	1	0.5	0.5	0.5	0.5	0.5	0.5

			radial	axial	radial	axial	radial	axial
	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
1.00 PPM HP	1.164	1.132	1.09	1.014	0.956	0.942	0.976	0.995
	1.14	1.107	1.095	1.02	0.955	0.93	0.959	0.978
AVERAGE	1.152	1.12	1.093	1.017	0.956	0.936	0.968	0.986
STDEV	0.017	0.018	0.003	0.004	0.001	0.008	0.012	0.012
%RSD	1.472	1.567	0.308	0.405	0.075	0.887	1.234	1.193
%DIFFERENCE	15.153	11.979	9.26	1.673	-4.418	-6.435	-3.243	-1.36
ACTUAL	1	1	1	1	1	1	1	1

			radial	axial	radial	axial	radial	axial
	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
5.00 PPM HP	1.151	1.128	5.289	4.943	4.709	4.702	4.959	4.92
	1.121	1.101	5.309	4.968	4.688	4.677	4.939	4.901
AVERAGE	1.136	1.114	5.299	4.955	4.699	4.69	4.949	4.91
STDEV	0.021	0.019	0.014	0.018	0.015	0.018	0.014	0.013
%RSD	1.879	1.671	0.263	0.36	0.312	0.375	0.277	0.275
%DIFFERENCE	13.629	11.435	5.978	-0.893	-6.023	-6.204	-1.022	-1.793
ACTUAL	1	1	5	5	5	5	5	5

			radial	axial	radial	axial	radial	axial

	Y 371.029	Y	Cu 327.393	Cu	Cr 267.716	Cr	As 188.979	As
10.00 PPM HP	1.121	1.083	10.578	9.741	9.339	9.214	9.911	9.801
	1.122	1.088	10.442	9.69	9.289	9.161	9.927	9.817
AVERAGE	1.121	1.085	10.51	9.716	9.314	9.187	9.919	9.809
STDEV	0.001	0.004	0.096	0.037	0.035	0.038	0.011	0.011
%RSD	0.087	0.324	0.912	0.376	0.379	0.41	0.115	0.114
%DIFFERENCE	12.127	8.514	5.098	-2.844	-6.858	-8.127	-0.808	-1.911
ACTUAL	1	1	10	10	10	10	10	10

	Y 371.029	Y	radial Cu 327.393	axial Cu	radial Cr 267.716	axial Cr	radial As 188.979	axial As
20.00 PPM HP	1.111	1.134	20.882	19.997	18.687	20.54	20.306	20.046
	1.083	1.06	21.202	19.592	18.85	18.714	20.26	20.001
AVERAGE	1.097	1.097	21.042	19.794	18.768	19.627	20.283	20.024
STDEV	0.02	0.052	0.226	0.286	0.115	1.291	0.033	0.032
%RSD	1.819	4.767	1.076	1.447	0.614	6.576	0.161	0.16
%DIFFERENCE	9.693	9.654	5.211	-1.029	-6.158	-1.865	1.416	0.118
ACTUAL	1	1	20	20	20	20	20	20

	Y 371.029	Y	radial Cu 327.393	axial Cu	radial Cr 267.716	axial Cr	radial As 188.979	axial As
BLANK	1.15	1.083	-0.001	-0.001	0.001	0.001	-0.032	0.001
	1.123	1.09	-0.001	-0.002	0.001	0.002	-0.035	-0.002
	1.106	1.067	-0.001	-0.001	0.001	0.002	-0.036	-0.003
	1.306	1.264	0.015	0.013	0.015	0.016	-0.016	0.017
	1.349	1.325	0.015	0.015	0.017	0.019	-0.009	0.024
	1.379	1.353	0.016	0.015	0.016	0.015	-0.016	0.017
	1.211	1.177	-0.104	-0.001	0.039	-0.001	-0.005	0
AVERAGE	1.232	1.194	-0.009	0.006	0.013	0.008	-0.021	0.008
STDEV	0.112	0.12	0.043	0.008	0.014	0.009	0.013	0.011
lod	0.337	0.361	0.128	0.025	0.041	0.026	0.039	0.034
loq	1.124	1.204	0.426	0.084	0.138	0.086	0.13	0.112

	Y 371.029	Y	radial Cu 327.393	axial Cu	radial Cr 267.716	axial Cr	radial As 188.979	axial As
BLANK DF2	1.124	1.101	<lod	<lod	<lod	<lod	<lod	<lod
BLANK			<lod	<lod	<lod	<lod	<lod	<lod
CCA ASH 1 112601 DF100	1.145	1.121	2.743	2.586	2.543	2.536	1.979	1.983
CCA ASH 1 112601			274.265	258.613	254.326	253.617	197.859	198.284

CCA ASH 2 112601 DF100	1.154	1.113	3.093	2.868	2.526	2.461	2.72	2.713
CCA ASH 2 112601			309.286	286.849	252.646	246.101	271.961	271.317
CCA ASH 3 112601 DF100	1.145	1.12	2.001	1.875	1.38	1.387	2.42	2.418
CCA ASH 3 112601			200.098	187.546	138.001	138.738	241.969	241.758
CCA ASH 8 112601 DF100	1.148	1.11	4.216	3.913	3.553	3.463	3.193	3.179
CCA ASH 8 112601			421.611	391.342	355.294	346.313	319.264	317.939
TEST SOIL 4 112601 DF10	1.238	1.219	<lod	<lod	<lod	<lod	<lod	<lod
			<lod	<lod	<lod	<lod	<lod	<lod
TEST SOIL 4 112601 DF2	1.659	1.621	<lod	<lod	<lod	<lod	<lod	<lod
			<lod	<lod	<lod	<lod	<lod	<lod
TEST SOIL 5 112601 DF10	1.296	1.249	<lod	<lod	<lod	<lod	<lod	<lod
			<lod	<lod	<lod	<lod	<lod	<lod
TEST SOIL 5 112601 DF2	1.773	1.745	<lod	<lod	<lod	0.028	<lod	<lod
			<lod	<lod	<lod	0.055	<lod	<lod
TEST SOIL 6 112601 DF10	1.229	1.224	<lod	<lod	<lod	<lod	<lod	<lod
			<lod	<lod	<lod	<lod	<lod	<lod
TEST SOIL 6 112601 DF2	1.75	1.711	<lod	<lod	<lod	<lod	<lod	<lod
			<lod	<lod	<lod	<lod	<lod	<lod

JH092802R

Sample ID	Analyte Name	Conc (Calib)	RSD (Conc)	Calib Units
Calib Blank 1	Y 371.029		1.57173467	mg/L
Calib Blank 1	Y AXIAL		0.77555199	mg/L
Calib Blank 1	Cu 327.393		0	mg/L
Calib Blank 1	Cr 267.716		0	mg/L
Calib Blank 1	As 188.979		0	mg/L
Calib Blank 1	As AXIAL		0	mg/L
Calib Blank 1	Cu AXIAL		0	mg/L
Calib Blank 1	Cr AXIAL		0	mg/L
Calib Std 1	Y 371.029		0.87884247	mg/L
Calib Std 1	Y AXIAL		0.41731799	mg/L
Calib Std 1	As AXIAL		1.32E-06	mg/L
Calib Std 1	Cu AXIAL		1.32E-06	mg/L
Calib Std 1	Cr AXIAL		1.32E-06	mg/L
Calib Std 2	Y 371.029		0.83855798	mg/L

Calib Std 2	Y AXIAL		0.52818321	mg/L
Calib Std 2	As AXIAL		0	mg/L
Calib Std 2	Cu AXIAL		0	mg/L
Calib Std 2	Cr AXIAL		0	mg/L
Calib Std 3	Y 371.029		0.23522343	mg/L
Calib Std 3	Y AXIAL		1.16491693	mg/L
Calib Std 3	As AXIAL		0	mg/L
Calib Std 3	Cu AXIAL		0	mg/L
Calib Std 3	Cr AXIAL		0	mg/L
Calib Std 4	Y 371.029		6.93E-02	mg/L
Calib Std 4	Y AXIAL		0.33211422	mg/L
Calib Std 4	Cu 327.393		0	mg/L
Calib Std 4	Cr 267.716		0	mg/L
Calib Std 4	As 188.979		0	mg/L
Calib Std 4	As AXIAL		0	mg/L
Calib Std 4	Cu AXIAL		0	mg/L
Calib Std 4	Cr AXIAL		0	mg/L
Calib Std 5	Y 371.029		0.41225394	mg/L
Calib Std 5	Y AXIAL		1.6329993	mg/L
Calib Std 5	Cu 327.393		0	mg/L
Calib Std 5	Cr 267.716		0	mg/L
Calib Std 5	As 188.979		0	mg/L
Calib Std 6	Y 371.029		1.00373374	mg/L
Calib Std 6	Y AXIAL		0.5609166	mg/L
Calib Std 6	Cu 327.393		0	mg/L
Calib Std 6	Cr 267.716		0	mg/L
Calib Std 6	As 188.979		0	mg/L
Calib Std 7	Y 371.029		1.15061174	mg/L
Calib Std 7	Y AXIAL		0.93583219	mg/L
Calib Std 7	Cu 327.393		0	mg/L
Calib Std 7	Cr 267.716		0	mg/L
Calib Std 7	As 188.979		0	mg/L
Reagent Blank 1	Y 371.029	1.00059266	1.27891261	mg/L
Reagent Blank 1	Y AXIAL	0.98547857	0.35441843	mg/L
Reagent Blank 1	Cu 327.393	-5.26E-02	14.2619787	mg/L
Reagent Blank 1	Cr 267.716	-4.64E-02	15.5175972	mg/L
Reagent Blank 1	As 188.979	1.38E-02	67.9882512	mg/L
Reagent Blank 1	As AXIAL	1.51E-02	18.6282224	mg/L
Reagent Blank 1	Cu AXIAL	2.68E-02	16.422468	mg/L
BLANK	Y 371.029	1.00051581	0.97158726	mg/L
BLANK	Y AXIAL	0.97968443	0.73306238	mg/L
BLANK	Cu 327.393	-2.94E-02	5.8446023	mg/L
BLANK	Cr 267.716	-1.02E-02	28.5866603	mg/L

BLANK	As 188.979	-3.41E-02	23.841369	mg/L
BLANK	As AXIAL	-1.01E-02	35.1435215	mg/L
BLANK	Cu AXIAL	-1.77E-02	9.5348082	mg/L
BLANK	Cr AXIAL	2.08E-03	38.0003287	mg/L
1.00 PPM HP	Y 371.029	1.00984603	0.15814501	mg/L
1.00 PPM HP	Y AXIAL	0.97899348	0.66940987	mg/L
1.00 PPM HP	Cu 327.393	1.05425162	0.5876386	mg/L
1.00 PPM HP	Cr 267.716	1.04941688	0.61787297	mg/L
1.00 PPM HP	As 188.979	1.05341502	1.67733022	mg/L
1.00 PPM HP	As AXIAL	1.06337607	0.55889946	mg/L
1.00 PPM HP	Cu AXIAL	1.04291855	0.38206029	mg/L
1.00 PPM HP	Cr AXIAL	1.0540084	0.37173247	mg/L
5.00 PPM HP	Y 371.029	0.99229416	0.23393713	mg/L
5.00 PPM HP	Y AXIAL	0.95382287	0.35083962	mg/L
5.00 PPM HP	Cu 327.393	5.48723175	1.45100051	mg/L
5.00 PPM HP	Cr 267.716	5.42375842	1.39074148	mg/L
5.00 PPM HP	As 188.979	5.43952242	0.17368168	mg/L
5.00 PPM HP	As AXIAL	5.42230517	0.44008051	mg/L
5.00 PPM HP	Cu AXIAL	5.41660237	0.99764893	mg/L
5.00 PPM HP	Cr AXIAL	5.26531618	0.81403222	mg/L
10.00 PPM HP	Y 371.029	1.00431906	0.55628373	mg/L
10.00 PPM HP	Y AXIAL	0.98227353	1.3712552	mg/L
10.00 PPM HP	Cu 327.393	0.51528842	0.55990628	mg/L
10.00 PPM HP	Cr 267.716	0.5243686	0.80736023	mg/L
10.00 PPM HP	As 188.979	0.52433992	3.64671234	mg/L
10.00 PPM HP	As AXIAL	0.53251426	0.88256085	mg/L
10.00 PPM HP	Cu AXIAL	0.50951384	1.24955769	mg/L
10.00 PPM HP	Cr AXIAL	0.52838772	0.92687831	mg/L
20.00 PPM HP	Y 371.029	0.95622915	1.44159753	mg/L
20.00 PPM HP	Y AXIAL	0.89187899	1.88761905	mg/L
20.00 PPM HP	Cu 327.393	22.0604539	1.57124441	mg/L
20.00 PPM HP	Cr 267.716	22.1278647	1.70592313	mg/L
20.00 PPM HP	As 188.979	22.3307292	0.16042833	mg/L
20.00 PPM HP	As AXIAL	21.6695038	1.64915873	mg/L
20.00 PPM HP	Cu AXIAL	22.1220828	1.25848058	mg/L
20.00 PPM HP	Cr AXIAL	21.0064062	1.09525432	mg/L
0.500 PPM HP	Y 371.029	1.02436169	0.96320257	mg/L
0.500 PPM HP	Y AXIAL	0.99621422	0.25009284	mg/L
0.500 PPM HP	Cu 327.393	0.27119275	3.06868302	mg/L
0.500 PPM HP	Cr 267.716	0.26845543	1.85218262	mg/L
0.500 PPM HP	As 188.979	0.27108869	2.45822405	mg/L
0.500 PPM HP	As AXIAL	0.26399765	1.26762187	mg/L
0.500 PPM HP	Cu AXIAL	0.26018871	1.20455614	mg/L

0.500 PPM HP	Cr AXIAL	0.2673113	0.4793125	mg/L
0.250 PPM HP	Y 371.029	1.02895146	1.00335784	mg/L
0.250 PPM HP	Y AXIAL	0.98426301	1.06981774	mg/L
0.250 PPM HP	Cu 327.393	10.2247968	0.91911768	mg/L
0.250 PPM HP	Cr 267.716	10.1557528	0.81450116	mg/L
0.250 PPM HP	As 188.979	10.5199312	0.72341729	mg/L
0.250 PPM HP	As AXIAL	10.4584657	1.86410121	mg/L
0.250 PPM HP	Cu AXIAL	10.4757773	0.99435305	mg/L
0.250 PPM HP	Cr AXIAL	10.0789588	1.75784216	mg/L
0.050 PPM HP	Y 371.029	1.01684349	0.45325914	mg/L
0.050 PPM HP	Y AXIAL	0.99185449	0.60880776	mg/L
0.050 PPM HP	Cu 327.393	2.99E-02	13.5548554	mg/L
0.050 PPM HP	Cr 267.716	4.53E-02	8.92753285	mg/L
0.050 PPM HP	As 188.979	3.81E-02	39.4167616	mg/L
0.050 PPM HP	As AXIAL	5.00E-02	4.38520241	mg/L
0.050 PPM HP	Cu AXIAL	3.67E-02	5.51262701	mg/L
0.050 PPM HP	Cr AXIAL	5.34E-02	2.7368313	mg/L
DR5-9 25 DF2	Y 371.029	1.02511903	0.67893193	mg/L
DR5-9 25 DF2	Y AXIAL	0.97565275	0.75252893	mg/L
DR5-9 25 DF2	Cu 327.393	-2.58E-02	9.28557793	mg/L
DR5-9 25 DF2	Cr 267.716	8.24E-03	36.9750821	mg/L
DR5-9 25 DF2	As 188.979	4.60E-02	30.7911601	mg/L
DR5-9 25 DF2	As AXIAL	4.99E-02	20.3175101	mg/L
DR5-9 25 DF2	Cu AXIAL	-1.27E-02	33.3361012	mg/L
DR5-9 25 DF2	Cr AXIAL	2.04E-02	16.0081884	mg/L
DR5-10 25 DF2	Y 371.029	0.9747571	1.41686509	mg/L
DR5-10 25 DF2	Y AXIAL	0.92565543	0.60987831	mg/L
DR5-10 25 DF2	Cu 327.393	-4.28E-02	2.54662302	mg/L
DR5-10 25 DF2	Cr 267.716	2.86E-02	9.95086137	mg/L
DR5-10 25 DF2	As 188.979	5.11E-02	43.2501933	mg/L
DR5-10 25 DF2	As AXIAL	5.24E-02	8.62105056	mg/L
DR5-10 25 DF2	Cu AXIAL	-2.55E-02	2.33545988	mg/L
DR5-10 25 DF2	Cr AXIAL	4.46E-02	2.29663027	mg/L
DR1-11 5 DF2	Y 371.029	28.5466082	2.30922761	mg/L
DR1-11 5 DF2	Y AXIAL	23.8076972	1.21637957	mg/L
DR1-11 5 DF2	Cu 327.393	28.2510931	2.2864345	mg/L
DR1-11 5 DF2	Cr 267.716	7.6701639	0.35731765	mg/L
DR1-11 5 DF2	As 188.979	26.2522885	0.37669585	mg/L
DR1-11 5 DF2	As AXIAL	18.599413	2.57195203	mg/L
DR1-11 5 DF2	Cu AXIAL	23.3692358	2.44366117	mg/L
DR1-11 5 DF2	Cr AXIAL	6.31607337	2.67722018	mg/L
DR2-11 5 DF2	Y 371.029	9.33680464	0.99922839	mg/L
DR2-11 5 DF2	Y AXIAL	8.54375207	0.67382612	mg/L

DR2-11 5 DF2	Cu 327.393	24.346736	1.91741121	mg/L
DR2-11 5 DF2	Cr 267.716	6.37227433	0.25181884	mg/L
DR2-11 5 DF2	As 188.979	51.7393182	0.2750914	mg/L
DR2-11 5 DF2	As AXIAL	42.2706512	1.06457177	mg/L
DR2-11 5 DF2	Cu AXIAL	24.1048036	2.36772443	mg/L
DR2-11 5 DF2	Cr AXIAL	5.9080792	1.01517795	mg/L
DR5-11 25 DF2	Y 371.029	2.43318194	0.85477794	mg/L
DR5-11 25 DF2	Y AXIAL	2.31281376	0.81509864	mg/L
DR5-11 25 DF2	Cu 327.393	3.49840699	3.45314581	mg/L
DR5-11 25 DF2	Cr 267.716	0.29176573	13.5879346	mg/L
DR5-11 25 DF2	As 188.979	0.54301777	32.0573773	mg/L
DR5-11 25 DF2	As AXIAL	0.40762878	6.48503353	mg/L
DR5-11 25 DF2	Cu AXIAL	3.41683073	1.60163061	mg/L
DR5-11 25 DF2	Cr AXIAL	0.25865335	3.50408877	mg/L
DR9-11 25 DF2	Y 371.029	1.68921603	1.10115108	mg/L
DR9-11 25 DF2	Y AXIAL	1.68616821	0.84329325	mg/L
DR9-11 25 DF2	Cu 327.393	2.16574329	6.40717223	mg/L
DR9-11 25 DF2	Cr 267.716	0.17457792	21.5370331	mg/L
DR9-11 25 DF2	As 188.979	0.43936138	31.7143744	mg/L
DR9-11 25 DF2	As AXIAL	0.32414137	4.03494805	mg/L
DR9-11 25 DF2	Cu AXIAL	2.18329788	0.68745658	mg/L
DR9-11 25 DF2	Cr AXIAL	0.14870914	2.75946076	mg/L
DR5-12 25 DF2	Y 371.029	2.49921898	0.80169287	mg/L
DR5-12 25 DF2	Y AXIAL	2.42984912	1.63988911	mg/L
DR5-12 25 DF2	Cu 327.393	2.99195651	2.13917324	mg/L
DR5-12 25 DF2	Cr 267.716	0.36305389	4.12693401	mg/L
DR5-12 25 DF2	As 188.979	0.26942953	20.0143937	mg/L
DR5-12 25 DF2	As AXIAL	0.27843974	1.69068704	mg/L
DR5-12 25 DF2	Cu AXIAL	3.10449143	0.95725894	mg/L
DR5-12 25 DF2	Cr AXIAL	0.3585919	0.54539883	mg/L
DR9-12 25 DF2	Y 371.029	1.48931286	1.28138687	mg/L
DR9-12 25 DF2	Y AXIAL	1.41299654	0.85170372	mg/L
DR9-12 25 DF2	Cu 327.393	0.40495384	13.4052626	mg/L
DR9-12 25 DF2	Cr 267.716	1.89E-02	44.0239989	mg/L
DR9-12 25 DF2	As 188.979	9.01E-02	39.9492753	mg/L
DR9-12 25 DF2	As AXIAL	8.17E-02	2.40836712	mg/L
DR9-12 25 DF2	Cu AXIAL	0.39000598	1.51906367	mg/L
DR9-12 25 DF2	Cr AXIAL	2.18E-02	2.312259	mg/L
BLANK	Y 371.029	1.08976363	0.31559807	mg/L
BLANK	Y AXIAL	1.06133891	0.82513506	mg/L
BLANK	Cu 327.393	1.69E-02	43.4046149	mg/L
BLANK	Cr 267.716	1.47E-04	1985.52078	mg/L
BLANK	As 188.979	8.75E-02	20.5506051	mg/L

BLANK	As AXIAL	9.81E-02	7.17142044	mg/L
BLANK	Cu AXIAL	4.08E-02	20.7162081	mg/L
BLANK	Cr AXIAL	1.86E-02	14.6889366	mg/L
1.00 PPM HP	Y 371.029	1.08492613	1.24496694	mg/L
1.00 PPM HP	Y AXIAL	1.04587439	0.37005494	mg/L
1.00 PPM HP	Cu 327.393	1.07626849	2.09078932	mg/L
1.00 PPM HP	Cr 267.716	1.04721383	6.61E-02	mg/L
1.00 PPM HP	As 188.979	1.11112301	1.46123424	mg/L
1.00 PPM HP	As AXIAL	1.11199226	1.52801539	mg/L
1.00 PPM HP	Cu AXIAL	1.07998727	2.41307821	mg/L
1.00 PPM HP	Cr AXIAL	1.0513781	1.73683904	mg/L
5.00 PPM HP	Y 371.029	1.0483996	0.83440175	mg/L
5.00 PPM HP	Y AXIAL	1.02817721	0.63614576	mg/L
5.00 PPM HP	Cu 327.393	5.40852874	0.70623295	mg/L
5.00 PPM HP	Cr 267.716	5.30163492	0.6051879	mg/L
5.00 PPM HP	As 188.979	5.44699234	0.76901564	mg/L
5.00 PPM HP	As AXIAL	5.57024316	0.64578999	mg/L
5.00 PPM HP	Cu AXIAL	5.49406502	0.98931477	mg/L
5.00 PPM HP	Cr AXIAL	5.24334067	0.90806485	mg/L
10.00 PPM HP	Y 371.029	1.0484746	1.78615379	mg/L
10.00 PPM HP	Y AXIAL	1.06236033	0.91050383	mg/L
10.00 PPM HP	Cu 327.393	0.52849482	1.73923497	mg/L
10.00 PPM HP	Cr 267.716	0.52251327	0.84963547	mg/L
10.00 PPM HP	As 188.979	0.55928716	3.20180558	mg/L
10.00 PPM HP	As AXIAL	0.58614972	1.15177102	mg/L
10.00 PPM HP	Cu AXIAL	0.54952838	1.43944159	mg/L
10.00 PPM HP	Cr AXIAL	0.54538711	1.37362835	mg/L
20.00 PPM HP	Y 371.029	1.02148011	0.17172707	mg/L
20.00 PPM HP	Y AXIAL	0.96107541	0.11340959	mg/L
20.00 PPM HP	Cu 327.393	21.1939689	2.09437306	mg/L
20.00 PPM HP	Cr 267.716	21.2118324	2.22954031	mg/L
20.00 PPM HP	As 188.979	21.9182637	0.23847338	mg/L
20.00 PPM HP	As AXIAL	21.7524432	0.35539117	mg/L
20.00 PPM HP	Cu AXIAL	21.7759009	1.66866597	mg/L
20.00 PPM HP	Cr AXIAL	20.4817832	1.18899361	mg/L
0.500 PPM HP	Y 371.029	1.07143276	0.54932893	mg/L
0.500 PPM HP	Y AXIAL	1.05962813	0.57313997	mg/L
0.500 PPM HP	Cu 327.393	0.275983	3.57955683	mg/L
0.500 PPM HP	Cr 267.716	0.27329433	2.8117018	mg/L
0.500 PPM HP	As 188.979	0.29316884	1.64276919	mg/L
0.500 PPM HP	As AXIAL	0.29202184	0.52864711	mg/L
0.500 PPM HP	Cu AXIAL	0.27757036	4.07495067	mg/L
0.500 PPM HP	Cr AXIAL	0.27158345	1.13116089	mg/L

0.250 PPM HP	Y 371.029	1.07604427	0.99876985	mg/L
0.250 PPM HP	Y AXIAL	1.02574915	0.95977516	mg/L
0.250 PPM HP	Cu 327.393	10.2121231	1.91282893	mg/L
0.250 PPM HP	Cr 267.716	10.0897469	1.75589444	mg/L
0.250 PPM HP	As 188.979	10.405657	0.17621197	mg/L
0.250 PPM HP	As AXIAL	10.4104201	0.31444793	mg/L
0.250 PPM HP	Cu AXIAL	10.5084719	0.78076701	mg/L
0.250 PPM HP	Cr AXIAL	9.92538046	0.38596479	mg/L
0.050 PPM HP	Y 371.029	1.06199689	1.26771841	mg/L
0.050 PPM HP	Y AXIAL	1.04804747	0.95366819	mg/L
0.050 PPM HP	Cu 327.393	4.72E-02	12.637483	mg/L
0.050 PPM HP	Cr 267.716	5.39E-02	8.17536328	mg/L
0.050 PPM HP	As 188.979	7.26E-02	10.9314608	mg/L
0.050 PPM HP	As AXIAL	6.58E-02	6.6864056	mg/L
0.050 PPM HP	Cu AXIAL	5.36E-02	6.99080327	mg/L
0.050 PPM HP	Cr AXIAL	5.88E-02	6.21716262	mg/L
DR1-15 5 DF2	Y 371.029	2.87320541	1.70409349	mg/L
DR1-15 5 DF2	Y AXIAL	2.66891486	0.95274955	mg/L
DR1-15 5 DF2	Cu 327.393	26.4285119	1.35734105	mg/L
DR1-15 5 DF2	Cr 267.716	6.72405087	0.18698206	mg/L
DR1-15 5 DF2	As 188.979	58.6531966	0.12252096	mg/L
DR1-15 5 DF2	As AXIAL	54.9016238	2.00607799	mg/L
DR1-15 5 DF2	Cu AXIAL	27.8500371	0.92775599	mg/L
DR1-15 5 DF2	Cr AXIAL	6.43743783	2.05658056	mg/L
DR2-15 5 DF2	Y 371.029	1.13239939	0.70188674	mg/L
DR2-15 5 DF2	Y AXIAL	1.08961011	0.82201819	mg/L
DR2-15 5 DF2	Cu 327.393	1.92782504	2.49808991	mg/L
DR2-15 5 DF2	Cr 267.716	0.45055946	2.65640482	mg/L
DR2-15 5 DF2	As 188.979	3.33482405	2.77166157	mg/L
DR2-15 5 DF2	As AXIAL	3.20501539	0.58513423	mg/L
DR2-15 5 DF2	Cu AXIAL	1.94718947	1.37609188	mg/L
DR2-15 5 DF2	Cr AXIAL	0.44065071	1.07202351	mg/L
DR5-15 25 DF2	Y 371.029	1.06417895	1.37043486	mg/L
DR5-15 25 DF2	Y AXIAL	1.01208201	0.41431815	mg/L
DR5-15 25 DF2	Cu 327.393	6.22E-02	11.5982666	mg/L
DR5-15 25 DF2	Cr 267.716	-1.38E-02	11.2066548	mg/L
DR5-15 25 DF2	As 188.979	0.19499916	5.26340721	mg/L
DR5-15 25 DF2	As AXIAL	0.20786111	8.1546777	mg/L
DR5-15 25 DF2	Cu AXIAL	8.47E-02	6.06803215	mg/L
DR5-15 25 DF2	Cr AXIAL	4.70E-03	29.6089278	mg/L
Reagent Blank 1	Y 371.029	1.06720233	0.22389601	mg/L
Reagent Blank 1	Y AXIAL	1.05450808	0.87016545	mg/L
Reagent Blank 1	Cu 327.393	-8.98E-02	2.75223887	mg/L

Reagent Blank 1	Cr 267.716	-6.40E-02	3.09257793	mg/L
Reagent Blank 1	As 188.979	2.42E-04	2483.40039	mg/L
Reagent Blank 1	As AXIAL	2.33E-02	3.70908756	mg/L
Reagent Blank 1	Cu AXIAL	9.00E-03	28.1517075	mg/L
DR1-16 5 DF2	Y 371.029	2.31223165	1.78557475	mg/L
DR1-16 5 DF2	Y AXIAL	2.18503396	0.8201236	mg/L
DR1-16 5 DF2	Cu 327.393	22.8169434	1.73694638	mg/L
DR1-16 5 DF2	Cr 267.716	5.42589617	0.13884197	mg/L
DR1-16 5 DF2	As 188.979	42.3551909	0.14540311	mg/L
DR1-16 5 DF2	As AXIAL	40.9227925	1.47443565	mg/L
DR1-16 5 DF2	Cu AXIAL	24.1818951	2.06836007	mg/L
DR1-16 5 DF2	Cr AXIAL	5.23475182	1.46123662	mg/L
DR2-16 5 DF2	Y 371.029	1.04628843	1.17793385	mg/L
DR2-16 5 DF2	Y AXIAL	1.02274024	0.59006144	mg/L
DR2-16 5 DF2	Cu 327.393	0.21769391	20.4735846	mg/L
DR2-16 5 DF2	Cr 267.716	3.83E-02	30.1606471	mg/L
DR2-16 5 DF2	As 188.979	0.30509318	29.6393827	mg/L
DR2-16 5 DF2	As AXIAL	8.18E-02	37.5889826	mg/L
DR2-16 5 DF2	Cu AXIAL	0.1224851	18.9180521	mg/L
DR2-16 5 DF2	Cr AXIAL	9.08E-03	39.9148929	mg/L
DR5-16 25 DF2	Y 371.029	1.06093587	0.47324477	mg/L
DR5-16 25 DF2	Y AXIAL	1.0250547	0.5923094	mg/L
DR5-16 25 DF2	Cu 327.393	7.71E-02	10.756102	mg/L
DR5-16 25 DF2	Cr 267.716	2.55E-03	81.7056761	mg/L
DR5-16 25 DF2	As 188.979	0.35067071	6.13475807	mg/L
DR5-16 25 DF2	As AXIAL	0.32858011	1.46006977	mg/L
DR5-16 25 DF2	Cu AXIAL	7.06E-02	3.04655983	mg/L
DR5-16 25 DF2	Cr AXIAL	-1.24E-03	46.3446016	mg/L
D5-2 5 DF2	Y 371.029	1.13416854	1.10373941	mg/L
D5-2 5 DF2	Y AXIAL	1.10042299	0.41921764	mg/L
D5-2 5 DF2	Cu 327.393	0.22359835	1.68508147	mg/L
D5-2 5 DF2	Cr 267.716	13.5782314	0.507795	mg/L
D5-2 5 DF2	As 188.979	0.90869079	0.8432491	mg/L
D5-2 5 DF2	As AXIAL	0.86617588	0.80178133	mg/L
D5-2 5 DF2	Cu AXIAL	0.22210292	1.43419669	mg/L
D5-2 5 DF2	Cr AXIAL	13.4244141	1.4562828	mg/L
D6-2 5 DF2	Y 371.029	1.11906702	0.23152141	mg/L
D6-2 5 DF2	Y AXIAL	1.10494151	0.57569847	mg/L
D6-2 5 DF2	Cu 327.393	0.22255359	0.63895732	mg/L
D6-2 5 DF2	Cr 267.716	13.6578242	2.1801005	mg/L
D6-2 5 DF2	As 188.979	0.95280702	1.37404889	mg/L
D6-2 5 DF2	As AXIAL	0.9375427	0.65136516	mg/L
D6-2 5 DF2	Cu AXIAL	0.22877168	0.49553946	mg/L

D6-2 5 DF2	Cr AXIAL	13.323556	1.19830289	mg/L
D13-2 5 DF2	Y 371.029	1.12017151	1.47439351	mg/L
D13-2 5 DF2	Y AXIAL	1.09775631	0.23966345	mg/L
D13-2 5 DF2	Cu 327.393	0.29841895	0.56751286	mg/L
D13-2 5 DF2	Cr 267.716	13.3238226	0.30384024	mg/L
D13-2 5 DF2	As 188.979	1.05457236	2.18802969	mg/L
D13-2 5 DF2	As AXIAL	1.04365815	1.24924982	mg/L
D13-2 5 DF2	Cu AXIAL	0.30611235	1.11347886	mg/L
D13-2 5 DF2	Cr AXIAL	13.1255788	1.01550653	mg/L
D14-2 5 DF2	Y 371.029	1.1359936	0.25189305	mg/L
D14-2 5 DF2	Y AXIAL	1.10837144	0.4233496	mg/L
D14-2 5 DF2	Cu 327.393	0.2902975	0.49802687	mg/L
D14-2 5 DF2	Cr 267.716	13.9235517	1.61664749	mg/L
D14-2 5 DF2	As 188.979	1.24832272	1.13700998	mg/L
D14-2 5 DF2	As AXIAL	1.23437398	0.91625316	mg/L
D14-2 5 DF2	Cu AXIAL	0.29407222	0.89443675	mg/L
D14-2 5 DF2	Cr AXIAL	13.8236554	1.76014738	mg/L
BLANK	Y 371.029	1.03634736	0.79615722	mg/L
BLANK	Y AXIAL	1.04143095	0.75876177	mg/L
BLANK	Cu 327.393	-7.13E-03	24.4122331	mg/L
BLANK	Cr 267.716	4.06E-02	16.0104641	mg/L
BLANK	As 188.979	-8.81E-03	39.8466511	mg/L
BLANK	As AXIAL	-1.10E-02	31.8545211	mg/L
BLANK	Cu AXIAL	-9.17E-03	12.7157706	mg/L
BLANK	Cr AXIAL	2.31E-02	17.8594859	mg/L
1.00 PPM HP	Y 371.029	1.04579482	0.10295851	mg/L
1.00 PPM HP	Y AXIAL	1.02321823	0.2915934	mg/L
1.00 PPM HP	Cu 327.393	1.07720925	0.91894313	mg/L
1.00 PPM HP	Cr 267.716	1.05851844	0.19826599	mg/L
1.00 PPM HP	As 188.979	1.0627777	0.41700041	mg/L
1.00 PPM HP	As AXIAL	1.05842625	0.5749038	mg/L
1.00 PPM HP	Cu AXIAL	1.05781379	1.41343577	mg/L
1.00 PPM HP	Cr AXIAL	1.04845977	1.41753947	mg/L
5.00 PPM HP	Y 371.029	1.01642417	1.4316645	mg/L
5.00 PPM HP	Y AXIAL	0.983296	2.48779541	mg/L
5.00 PPM HP	Cu 327.393	5.44463958	0.77741847	mg/L
5.00 PPM HP	Cr 267.716	5.31262202	0.91313545	mg/L
5.00 PPM HP	As 188.979	5.33161736	0.58148695	mg/L
5.00 PPM HP	As AXIAL	5.44250724	2.84066471	mg/L
5.00 PPM HP	Cu AXIAL	5.32937192	5.51807677	mg/L
5.00 PPM HP	Cr AXIAL	5.16433732	4.46386183	mg/L
10.00 PPM HP	Y 371.029	1.02662146	1.41565682	mg/L
10.00 PPM HP	Y AXIAL	1.02978142	0.84605325	mg/L

10.00 PPM HP	Cu 327.393	0.55066112	0.59453298	mg/L
10.00 PPM HP	Cr 267.716	0.53634189	0.41594151	mg/L
10.00 PPM HP	As 188.979	0.53031097	4.70177282	mg/L
10.00 PPM HP	As AXIAL	0.53362581	0.88155096	mg/L
10.00 PPM HP	Cu AXIAL	0.54236136	2.5824347	mg/L
10.00 PPM HP	Cr AXIAL	0.53843065	2.15424435	mg/L
20.00 PPM HP	Y 371.029	0.98294321	0.17367807	mg/L
20.00 PPM HP	Y AXIAL	0.94168134	1.16130873	mg/L
20.00 PPM HP	Cu 327.393	21.4676305	1.27624454	mg/L
20.00 PPM HP	Cr 267.716	21.3063794	1.28504632	mg/L
20.00 PPM HP	As 188.979	21.8712961	0.17528321	mg/L
20.00 PPM HP	As AXIAL	21.9964723	0.88381497	mg/L
20.00 PPM HP	Cu AXIAL	22.2413456	1.13444456	mg/L
20.00 PPM HP	Cr AXIAL	20.8977738	0.89906622	mg/L
0.500 PPM HP	Y 371.029	1.0386261	0.20073898	mg/L
0.500 PPM HP	Y AXIAL	1.03647339	0.85138455	mg/L
0.500 PPM HP	Cu 327.393	0.31443932	2.78006382	mg/L
0.500 PPM HP	Cr 267.716	0.2951694	3.21838408	mg/L
0.500 PPM HP	As 188.979	0.28693876	2.32463204	mg/L
0.500 PPM HP	As AXIAL	0.2824566	2.4310569	mg/L
0.500 PPM HP	Cu AXIAL	0.29340095	0.30151753	mg/L
0.500 PPM HP	Cr AXIAL	0.2801681	8.09E-02	mg/L
0.250 PPM HP	Y 371.029	1.05285133	1.22541912	mg/L
0.250 PPM HP	Y AXIAL	1.00228612	1.19601296	mg/L
0.250 PPM HP	Cu 327.393	10.4676585	0.60276929	mg/L
0.250 PPM HP	Cr 267.716	10.1738013	0.58721541	mg/L
0.250 PPM HP	As 188.979	10.3233739	0.44725937	mg/L
0.250 PPM HP	As AXIAL	10.3283592	1.86168881	mg/L
0.250 PPM HP	Cu AXIAL	10.6244413	1.42787502	mg/L
0.250 PPM HP	Cr AXIAL	10.0718413	1.33608043	mg/L
0.050 PPM HP	Y 371.029	1.0301934	0.92993022	mg/L
0.050 PPM HP	Y AXIAL	1.03100129	0.42079604	mg/L
0.050 PPM HP	Cu 327.393	7.13E-02	2.67560156	mg/L
0.050 PPM HP	Cr 267.716	6.21E-02	4.57293476	mg/L
0.050 PPM HP	As 188.979	5.06E-02	21.8754366	mg/L
0.050 PPM HP	As AXIAL	4.30E-02	3.79314015	mg/L
0.050 PPM HP	Cu AXIAL	6.11E-02	4.05143291	mg/L
0.050 PPM HP	Cr AXIAL	5.32E-02	4.19436982	mg/L
D5-19 25 DF2	Y 371.029	1.04768295	0.46608363	mg/L
D5-19 25 DF2	Y AXIAL	1.02310215	0.33285977	mg/L
D5-19 25 DF2	Cu 327.393	8.21E-02	3.78378622	mg/L
D5-19 25 DF2	Cr 267.716	4.38E-02	2.68044226	mg/L
D5-19 25 DF2	As 188.979	6.40225902	0.59983463	mg/L

D5-19 25 DF2	As AXIAL	6.54981054	0.57358363	mg/L
D5-19 25 DF2	Cu AXIAL	8.44E-02	4.1920188	mg/L
D5-19 25 DF2	Cr AXIAL	4.06E-02	1.51983314	mg/L
D6-19 25 DF2	Y 371.029	1.05681159	1.12770237	mg/L
D6-19 25 DF2	Y AXIAL	1.01722416	1.1142378	mg/L
D6-19 25 DF2	Cu 327.393	7.09E-02	3.42118822	mg/L
D6-19 25 DF2	Cr 267.716	6.32E-02	2.50069612	mg/L
D6-19 25 DF2	As 188.979	6.65222287	0.8197417	mg/L
D6-19 25 DF2	As AXIAL	6.68018656	0.51632812	mg/L
D6-19 25 DF2	Cu AXIAL	7.22E-02	1.59963483	mg/L
D6-19 25 DF2	Cr AXIAL	6.06E-02	7.32E-02	mg/L
D13-19 25 DF2	Y 371.029	1.0363026	0.82372766	mg/L
D13-19 25 DF2	Y AXIAL	0.99644306	1.72086805	mg/L
D13-19 25 DF2	Cu 327.393	6.04E-02	1.81973553	mg/L
D13-19 25 DF2	Cr 267.716	3.95E-02	4.87185537	mg/L
D13-19 25 DF2	As 188.979	6.99095587	0.4017741	mg/L
D13-19 25 DF2	As AXIAL	7.0444539	1.49638271	mg/L
D13-19 25 DF2	Cu AXIAL	6.11E-02	2.16616749	mg/L
D13-19 25 DF2	Cr AXIAL	3.70E-02	2.1813884	mg/L
D14-19 25 DF2	Y 371.029	1.04449859	0.13039206	mg/L
D14-19 25 DF2	Y AXIAL	1.017403	0.93619484	mg/L
D14-19 25 DF2	Cu 327.393	5.30E-02	2.73183568	mg/L
D14-19 25 DF2	Cr 267.716	5.85E-02	2.12334628	mg/L
D14-19 25 DF2	As 188.979	7.13148327	0.66993286	mg/L
D14-19 25 DF2	As AXIAL	7.24179328	1.17362203	mg/L
D14-19 25 DF2	Cu AXIAL	5.62E-02	1.88323142	mg/L
D14-19 25 DF2	Cr AXIAL	5.47E-02	0.68997373	mg/L
6-28-D1 25 DF2	Y 371.029	1.06612314	0.88113405	mg/L
6-28-D1 25 DF2	Y AXIAL	1.04246302	1.27087668	mg/L
6-28-D1 25 DF2	Cu 327.393	0.11155427	1.4041101	mg/L
6-28-D1 25 DF2	Cr 267.716	15.7671206	0.12337013	mg/L
6-28-D1 25 DF2	As 188.979	11.1244418	0.12395508	mg/L
6-28-D1 25 DF2	As AXIAL	11.0837922	2.06530373	mg/L
6-28-D1 25 DF2	Cu AXIAL	0.11159987	3.42309414	mg/L
6-28-D1 25 DF2	Cr AXIAL	15.9239223	2.22558651	mg/L
6-28-D2 25 DF2	Y 371.029	1.07840128	1.64462995	mg/L
6-28-D2 25 DF2	Y AXIAL	1.05618036	1.76260659	mg/L
6-28-D2 25 DF2	Cu 327.393	0.16379275	0.63761022	mg/L
6-28-D2 25 DF2	Cr 267.716	15.7265022	0.70075273	mg/L
6-28-D2 25 DF2	As 188.979	11.1734895	0.62768053	mg/L
6-28-D2 25 DF2	As AXIAL	11.2098484	1.35543212	mg/L
6-28-D2 25 DF2	Cu AXIAL	0.16689233	3.11507895	mg/L
6-28-D2 25 DF2	Cr AXIAL	15.8495238	2.52260577	mg/L

6-28-D3 25 DF2	Y 371.029	1.06925287	0.90357557	mg/L
6-28-D3 25 DF2	Y AXIAL	1.04241166	0.89230848	mg/L
6-28-D3 25 DF2	Cu 327.393	9.14E-02	1.04543499	mg/L
6-28-D3 25 DF2	Cr 267.716	16.207317	1.93203384	mg/L
6-28-D3 25 DF2	As 188.979	10.5597361	0.91910179	mg/L
6-28-D3 25 DF2	As AXIAL	10.5164954	0.96235074	mg/L
6-28-D3 25 DF2	Cu AXIAL	9.02E-02	0.80716323	mg/L
6-28-D3 25 DF2	Cr AXIAL	16.1629989	1.51891281	mg/L
6-28-D4 25 DF2	Y 371.029	1.07435201	1.02053954	mg/L
6-28-D4 25 DF2	Y AXIAL	1.05995667	0.10423717	mg/L
6-28-D4 25 DF2	Cu 327.393	0.10708068	1.5038322	mg/L
6-28-D4 25 DF2	Cr 267.716	15.8202603	0.91009235	mg/L
6-28-D4 25 DF2	As 188.979	10.2070718	0.49484478	mg/L
6-28-D4 25 DF2	As AXIAL	10.2671627	1.0267281	mg/L
6-28-D4 25 DF2	Cu AXIAL	0.10726386	0.61482472	mg/L
6-28-D4 25 DF2	Cr AXIAL	15.8438048	0.34535278	mg/L
6-28-D5 25 DF2	Y 371.029	1.03113485	1.26849277	mg/L
6-28-D5 25 DF2	Y AXIAL	0.97051873	2.09877245	mg/L
6-28-D5 25 DF2	Cu 327.393	0.11531294	0.67875385	mg/L
6-28-D5 25 DF2	Cr 267.716	11.0875583	1.08608609	mg/L
6-28-D5 25 DF2	As 188.979	6.13674498	0.71638697	mg/L
6-28-D5 25 DF2	As AXIAL	6.05044822	1.58302102	mg/L
6-28-D5 25 DF2	Cu AXIAL	0.11622936	2.55652122	mg/L
6-28-D5 25 DF2	Cr AXIAL	10.8886837	0.41533751	mg/L
BLANK	Y 371.029	1.05016542	1.21715977	mg/L
BLANK	Y AXIAL	1.03097075	0.29143496	mg/L
BLANK	Cu 327.393	-7.10E-03	13.7555194	mg/L
BLANK	Cr 267.716	2.36E-02	4.23647764	mg/L
BLANK	As 188.979	3.05E-03	344.925721	mg/L
BLANK	As AXIAL	-8.13E-03	26.9703111	mg/L
BLANK	Cu AXIAL	-7.13E-03	19.8750825	mg/L
BLANK	Cr AXIAL	1.09E-02	9.29912557	mg/L
1.00 PPM HP	Y 371.029	1.04741829	1.56063079	mg/L
1.00 PPM HP	Y AXIAL	1.03027068	0.80895264	mg/L
1.00 PPM HP	Cu 327.393	1.05781795	2.92656021	mg/L
1.00 PPM HP	Cr 267.716	1.04367712	0.61860582	mg/L
1.00 PPM HP	As 188.979	1.04328884	2.3982193	mg/L
1.00 PPM HP	As AXIAL	1.07044604	1.92215762	mg/L
1.00 PPM HP	Cu AXIAL	1.07422119	0.28401731	mg/L
1.00 PPM HP	Cr AXIAL	1.05189933	0.41080264	mg/L
5.00 PPM HP	Y 371.029	1.03450076	1.00207804	mg/L
5.00 PPM HP	Y AXIAL	0.99636854	0.34797542	mg/L
5.00 PPM HP	Cu 327.393	5.33509848	0.76073293	mg/L

5.00 PPM HP	Cr 267.716	5.1952085	0.7123511	mg/L
5.00 PPM HP	As 188.979	5.35353344	0.75644567	mg/L
5.00 PPM HP	As AXIAL	5.39591837	0.76869593	mg/L
5.00 PPM HP	Cu AXIAL	5.44755572	0.80106284	mg/L
5.00 PPM HP	Cr AXIAL	5.21509573	1.1485041	mg/L
10.00 PPM HP	Y 371.029	1.04555731	1.01551789	mg/L
10.00 PPM HP	Y AXIAL	1.02842293	0.29110294	mg/L
10.00 PPM HP	Cu 327.393	0.54549655	0.39878132	mg/L
10.00 PPM HP	Cr 267.716	0.52483216	0.3316697	mg/L
10.00 PPM HP	As 188.979	0.52122495	1.40155513	mg/L
10.00 PPM HP	As AXIAL	0.52572765	0.8401976	mg/L
10.00 PPM HP	Cu AXIAL	0.53008956	0.86118548	mg/L
10.00 PPM HP	Cr AXIAL	0.52068761	1.14923734	mg/L
20.00 PPM HP	Y 371.029	0.99262938	0.74295481	mg/L
20.00 PPM HP	Y AXIAL	0.94651135	2.02E-02	mg/L
20.00 PPM HP	Cu 327.393	21.6362592	2.49340003	mg/L
20.00 PPM HP	Cr 267.716	21.3918609	2.49689427	mg/L
20.00 PPM HP	As 188.979	21.7270537	0.63732821	mg/L
20.00 PPM HP	As AXIAL	21.9426758	0.78583819	mg/L
20.00 PPM HP	Cu AXIAL	22.1347449	2.13864012	mg/L
20.00 PPM HP	Cr AXIAL	20.7311481	1.77180006	mg/L
0.500 PPM HP	Y 371.029	1.05362861	0.8370967	mg/L
0.500 PPM HP	Y AXIAL	1.04913031	0.45913472	mg/L
0.500 PPM HP	Cu 327.393	0.31072576	2.49662042	mg/L
0.500 PPM HP	Cr 267.716	0.28880979	1.95412698	mg/L
0.500 PPM HP	As 188.979	0.29213989	5.69346875	mg/L
0.500 PPM HP	As AXIAL	0.27326257	1.36475303	mg/L
0.500 PPM HP	Cu AXIAL	0.29630603	2.21858718	mg/L
0.500 PPM HP	Cr AXIAL	0.27591822	1.74754984	mg/L
0.250 PPM HP	Y 371.029	1.06131133	0.89107418	mg/L
0.250 PPM HP	Y AXIAL	1.01534297	1.10173616	mg/L
0.250 PPM HP	Cu 327.393	10.3485126	0.60071642	mg/L
0.250 PPM HP	Cr 267.716	10.1162445	0.4656171	mg/L
0.250 PPM HP	As 188.979	10.2582658	0.10544459	mg/L
0.250 PPM HP	As AXIAL	10.4087853	1.51496589	mg/L
0.250 PPM HP	Cu AXIAL	10.3856077	1.13595456	mg/L
0.250 PPM HP	Cr AXIAL	9.91754224	1.45474863	mg/L
0.050 PPM HP	Y 371.029	1.05154771	1.24985468	mg/L
0.050 PPM HP	Y AXIAL	1.03728116	0.42461441	mg/L
0.050 PPM HP	Cu 327.393	8.01E-02	8.02788683	mg/L
0.050 PPM HP	Cr 267.716	6.85E-02	9.6109188	mg/L
0.050 PPM HP	As 188.979	5.64E-02	6.82203873	mg/L
0.050 PPM HP	As AXIAL	4.84E-02	7.37800996	mg/L

0.050 PPM HP	Cu AXIAL	6.77E-02	7.43558932	mg/L
0.050 PPM HP	Cr AXIAL	5.73E-02	6.26633987	mg/L
6-28-D6 25 DF2	Y 371.029	1.05886543	1.05409762	mg/L
6-28-D6 25 DF2	Y AXIAL	1.03041598	1.1506626	mg/L
6-28-D6 25 DF2	Cu 327.393	0.13687517	1.5641	mg/L
6-28-D6 25 DF2	Cr 267.716	10.6360242	1.76224256	mg/L
6-28-D6 25 DF2	As 188.979	6.05165966	0.29288935	mg/L
6-28-D6 25 DF2	As AXIAL	6.21524165	0.43475343	mg/L
6-28-D6 25 DF2	Cu AXIAL	0.14286792	0.88145701	mg/L
6-28-D6 25 DF2	Cr AXIAL	10.3056326	1.71201367	mg/L
6-28-D7 25 DF2	Y 371.029	5.66915385	1.31391364	mg/L
6-28-D7 25 DF2	Y AXIAL	5.41079451	1.0568585	mg/L
6-28-D7 25 DF2	Cu 327.393	12.6668686	3.6571451	mg/L
6-28-D7 25 DF2	Cr 267.716	3.14763483	0.16898784	mg/L
6-28-D7 25 DF2	As 188.979	12.6648098	0.36138624	mg/L
6-28-D7 25 DF2	As AXIAL	12.6019288	2.11066408	mg/L
6-28-D7 25 DF2	Cu AXIAL	13.1870057	0.45319776	mg/L
6-28-D7 25 DF2	Cr AXIAL	3.05059166	2.02419689	mg/L
6-28-D8 25 DF2	Y 371.029	5.79365421	2.01452887	mg/L
6-28-D8 25 DF2	Y AXIAL	5.52453232	0.3787145	mg/L
6-28-D8 25 DF2	Cu 327.393	12.3685681	1.30056447	mg/L
6-28-D8 25 DF2	Cr 267.716	3.24248639	0.24282614	mg/L
6-28-D8 25 DF2	As 188.979	13.5111038	0.31343716	mg/L
6-28-D8 25 DF2	As AXIAL	13.348805	1.82084196	mg/L
6-28-D8 25 DF2	Cu AXIAL	12.7534811	2.4362584	mg/L
6-28-D8 25 DF2	Cr AXIAL	3.13505842	1.93327751	mg/L
6-29-D1 25 DF2	Y 371.029	1.32394245	1.02772208	mg/L
6-29-D1 25 DF2	Y AXIAL	1.28707688	1.25233491	mg/L
6-29-D1 25 DF2	Cu 327.393	2.46678936	4.55648294	mg/L
6-29-D1 25 DF2	Cr 267.716	3.33510423	5.88645059	mg/L
6-29-D1 25 DF2	As 188.979	7.68721107	0.39457523	mg/L
6-29-D1 25 DF2	As AXIAL	7.70837229	2.34199443	mg/L
6-29-D1 25 DF2	Cu AXIAL	2.39662205	0.93361958	mg/L
6-29-D1 25 DF2	Cr AXIAL	3.16681187	2.3837511	mg/L
6-29-D2 25 DF2	Y 371.029	1.32486371	1.37894246	mg/L
6-29-D2 25 DF2	Y AXIAL	1.27640474	0.94667252	mg/L
6-29-D2 25 DF2	Cu 327.393	1.86479276	0.43856101	mg/L
6-29-D2 25 DF2	Cr 267.716	2.26417836	0.46715274	mg/L
6-29-D2 25 DF2	As 188.979	7.25106875	0.64358029	mg/L
6-29-D2 25 DF2	As AXIAL	7.24543626	2.13283567	mg/L
6-29-D2 25 DF2	Cu AXIAL	1.87599614	0.37698697	mg/L
6-29-D2 25 DF2	Cr AXIAL	2.22919049	2.29211537	mg/L
6-29-D5 25 DF2	Y 371.029	1.06493299	1.5413942	mg/L

6-29-D5 25 DF2	Y AXIAL	1.02543359	1.15050102	mg/L
6-29-D5 25 DF2	Cu 327.393	5.54E-02	1.01239797	mg/L
6-29-D5 25 DF2	Cr 267.716	2.33876178	0.28511035	mg/L
6-29-D5 25 DF2	As 188.979	3.3174196	0.71604801	mg/L
6-29-D5 25 DF2	As AXIAL	3.34811372	1.65512007	mg/L
6-29-D5 25 DF2	Cu AXIAL	5.68E-02	3.06804977	mg/L
6-29-D5 25 DF2	Cr AXIAL	2.26224335	0.57043824	mg/L
6-29-D6 25 DF2	Y 371.029	1.04432761	1.57851759	mg/L
6-29-D6 25 DF2	Y AXIAL	1.01916031	0.35172845	mg/L
6-29-D6 25 DF2	Cu 327.393	4.17E-02	1.00499147	mg/L
6-29-D6 25 DF2	Cr 267.716	2.26749292	0.57463864	mg/L
6-29-D6 25 DF2	As 188.979	3.44796706	0.56581959	mg/L
6-29-D6 25 DF2	As AXIAL	3.54152476	1.88504622	mg/L
6-29-D6 25 DF2	Cu AXIAL	4.54E-02	2.46433633	mg/L
6-29-D6 25 DF2	Cr AXIAL	2.24459879	0.89873366	mg/L
6-29-D13 25 DF2	Y 371.029	1.04454927	0.86521014	mg/L
6-29-D13 25 DF2	Y AXIAL	0.9931743	1.24934818	mg/L
6-29-D13 25 DF2	Cu 327.393	3.90E-02	0.71300713	mg/L
6-29-D13 25 DF2	Cr 267.716	2.30767351	9.22E-02	mg/L
6-29-D13 25 DF2	As 188.979	3.23510244	0.56060537	mg/L
6-29-D13 25 DF2	As AXIAL	3.23319888	1.20114377	mg/L
6-29-D13 25 DF2	Cu AXIAL	3.96E-02	3.51617713	mg/L
6-29-D13 25 DF2	Cr AXIAL	2.27360399	0.65388212	mg/L
6-29-D14 25 DF2	Y 371.029	1.04722811	1.68064091	mg/L
6-29-D14 25 DF2	Y AXIAL	1.00180181	0.28411925	mg/L
6-29-D14 25 DF2	Cu 327.393	3.75E-02	5.35706118	mg/L
6-29-D14 25 DF2	Cr 267.716	2.44407715	0.46221775	mg/L
6-29-D14 25 DF2	As 188.979	3.42861182	0.50211868	mg/L
6-29-D14 25 DF2	As AXIAL	3.4393661	1.65857249	mg/L
6-29-D14 25 DF2	Cu AXIAL	3.80E-02	2.73839875	mg/L
6-29-D14 25 DF2	Cr AXIAL	2.38418627	1.8934401	mg/L
6-29-D15 25 DF2	Y 371.029	1.05972049	1.49125785	mg/L
6-29-D15 25 DF2	Y AXIAL	1.03071849	0.80553665	mg/L
6-29-D15 25 DF2	Cu 327.393	2.72E-02	3.30056442	mg/L
6-29-D15 25 DF2	Cr 267.716	1.52E-02	8.48623632	mg/L
6-29-D15 25 DF2	As 188.979	4.11E-02	21.5488382	mg/L
6-29-D15 25 DF2	As AXIAL	2.50E-02	9.77914509	mg/L
6-29-D15 25 DF2	Cu AXIAL	2.91E-02	2.35696649	mg/L
6-29-D15 25 DF2	Cr AXIAL	8.30E-03	19.8467472	mg/L
BLANK	Y 371.029	1.07664512	0.25608662	mg/L
BLANK	Y AXIAL	1.03533439	0.70396225	mg/L
BLANK	Cu 327.393	-7.55E-03	6.79125458	mg/L
BLANK	Cr 267.716	-2.42E-04	403.679785	mg/L

BLANK	As 188.979	-4.80E-03	163.229511	mg/L
BLANK	As AXIAL	-1.32E-02	12.5477792	mg/L
BLANK	Cu AXIAL	-8.56E-03	4.07919288	mg/L
BLANK	Cr AXIAL	-2.06E-03	11.4765258	mg/L
1.00 PPM HP	Y 371.029	1.04266427	0.17485764	mg/L
1.00 PPM HP	Y AXIAL	1.01306157	0.78513063	mg/L
1.00 PPM HP	Cu 327.393	1.05490987	0.84302751	mg/L
1.00 PPM HP	Cr 267.716	1.03909724	0.15934887	mg/L
1.00 PPM HP	As 188.979	1.03802068	0.33499905	mg/L
1.00 PPM HP	As AXIAL	1.05456691	0.25903994	mg/L
1.00 PPM HP	Cu AXIAL	1.03787264	0.44431693	mg/L
1.00 PPM HP	Cr AXIAL	1.0209913	0.22416608	mg/L
5.00 PPM HP	Y 371.029	1.0083961	0.47664474	mg/L
5.00 PPM HP	Y AXIAL	0.98194326	0.64989144	mg/L
5.00 PPM HP	Cu 327.393	5.34754835	2.84098909	mg/L
5.00 PPM HP	Cr 267.716	5.21660955	2.73118285	mg/L
5.00 PPM HP	As 188.979	5.35087832	0.21014016	mg/L
5.00 PPM HP	As AXIAL	5.46065655	0.69295569	mg/L
5.00 PPM HP	Cu AXIAL	5.46645815	1.65765535	mg/L
5.00 PPM HP	Cr AXIAL	5.2598056	1.4999318	mg/L
10.00 PPM HP	Y 371.029	1.04631701	1.69985349	mg/L
10.00 PPM HP	Y AXIAL	1.02751747	1.96239997	mg/L
10.00 PPM HP	Cu 327.393	0.67645618	18.6882378	mg/L
10.00 PPM HP	Cr 267.716	0.57143141	10.4769509	mg/L
10.00 PPM HP	As 188.979	0.60923715	22.0670714	mg/L
10.00 PPM HP	As AXIAL	0.52524215	1.0557286	mg/L
10.00 PPM HP	Cu AXIAL	0.53074797	3.59409231	mg/L
10.00 PPM HP	Cr AXIAL	0.51901781	2.94168312	mg/L
20.00 PPM HP	Y 371.029	0.996698	1.59854719	mg/L
20.00 PPM HP	Y AXIAL	0.93674643	0.71385435	mg/L
20.00 PPM HP	Cu 327.393	21.385346	1.6541572	mg/L
20.00 PPM HP	Cr 267.716	21.142373	1.57540729	mg/L
20.00 PPM HP	As 188.979	21.6187331	0.18201103	mg/L
20.00 PPM HP	As AXIAL	21.7658663	2.2021337	mg/L
20.00 PPM HP	Cu AXIAL	22.288422	1.31289141	mg/L
20.00 PPM HP	Cr AXIAL	20.7389567	1.31000472	mg/L
0.500 PPM HP	Y 371.029	1.05162876	1.64009884	mg/L
0.500 PPM HP	Y AXIAL	1.03264463	0.5309248	mg/L
0.500 PPM HP	Cu 327.393	0.31637034	3.62090337	mg/L
0.500 PPM HP	Cr 267.716	0.29149458	3.62961805	mg/L
0.500 PPM HP	As 188.979	0.27999276	6.17811817	mg/L
0.500 PPM HP	As AXIAL	0.26902927	3.80532289	mg/L
0.500 PPM HP	Cu AXIAL	0.2914406	4.34966985	mg/L

0.500 PPM HP	Cr AXIAL	0.27176481	3.66468842	mg/L
0.250 PPM HP	Y 371.029	1.05772967	0.65298659	mg/L
0.250 PPM HP	Y AXIAL	1.01252095	1.16558128	mg/L
0.250 PPM HP	Cu 327.393	10.2227461	0.34999272	mg/L
0.250 PPM HP	Cr 267.716	9.98717813	0.33923586	mg/L
0.250 PPM HP	As 188.979	10.2689822	5.36E-02	mg/L
0.250 PPM HP	As AXIAL	10.3988681	1.17739473	mg/L
0.250 PPM HP	Cu AXIAL	10.5319919	1.25972536	mg/L
0.250 PPM HP	Cr AXIAL	9.94311686	0.91602311	mg/L
0.050 PPM HP	Y 371.029	1.0416063	1.14636305	mg/L
0.050 PPM HP	Y AXIAL	1.03015126	0.65790824	mg/L
0.050 PPM HP	Cu 327.393	8.21E-02	7.09173727	mg/L
0.050 PPM HP	Cr 267.716	7.04E-02	5.47489227	mg/L
0.050 PPM HP	As 188.979	6.16E-02	26.5375691	mg/L
0.050 PPM HP	As AXIAL	4.64E-02	6.8132761	mg/L
0.050 PPM HP	Cu AXIAL	6.82E-02	6.428547	mg/L
0.050 PPM HP	Cr AXIAL	5.71E-02	5.95287929	mg/L
6-29-D16 25 DF2	Y 371.029	1.05351117	0.73090286	mg/L
6-29-D16 25 DF2	Y AXIAL	1.01372361	0.47540254	mg/L
6-29-D16 25 DF2	Cu 327.393	6.64E-02	3.28833256	mg/L
6-29-D16 25 DF2	Cr 267.716	1.25E-02	9.3765725	mg/L
6-29-D16 25 DF2	As 188.979	1.73E-02	36.1127837	mg/L
6-29-D16 25 DF2	As AXIAL	1.01E-02	9.52700954	mg/L
6-29-D16 25 DF2	Cu AXIAL	6.35E-02	3.87400056	mg/L
6-29-D16 25 DF2	Cr AXIAL	8.39E-03	2.08503803	mg/L
7-15-D1 25 DF2	Y 371.029	1.17029337	0.51696075	mg/L
7-15-D1 25 DF2	Y AXIAL	1.14600251	0.87348341	mg/L
7-15-D1 25 DF2	Cu 327.393	1.36197791	0.85555907	mg/L
7-15-D1 25 DF2	Cr 267.716	2.13534989	0.27720653	mg/L
7-15-D1 25 DF2	As 188.979	4.51003318	0.29487145	mg/L
7-15-D1 25 DF2	As AXIAL	4.54195016	0.19003309	mg/L
7-15-D1 25 DF2	Cu AXIAL	1.37199692	0.46195741	mg/L
7-15-D1 25 DF2	Cr AXIAL	2.11713991	0.41144311	mg/L
7-15-D2 25 DF2	Y 371.029	1.16382862	0.9788277	mg/L
7-15-D2 25 DF2	Y AXIAL	1.1408204	0.41571106	mg/L
7-15-D2 25 DF2	Cu 327.393	1.49041968	3.35239455	mg/L
7-15-D2 25 DF2	Cr 267.716	2.31158566	1.01106976	mg/L
7-15-D2 25 DF2	As 188.979	4.72809848	0.86063665	mg/L
7-15-D2 25 DF2	As AXIAL	4.70325573	1.47564308	mg/L
7-15-D2 25 DF2	Cu AXIAL	1.44789201	1.20783347	mg/L
7-15-D2 25 DF2	Cr AXIAL	2.26516739	1.20245573	mg/L
7-15-D5 25 DF2	Y 371.029	1.04490784	1.08399483	mg/L
7-15-D5 25 DF2	Y AXIAL	1.01960376	0.47244928	mg/L

7-15-D5 25 DF2	Cu 327.393	7.34E-02	0.99711907	mg/L
7-15-D5 25 DF2	Cr 267.716	0.36904383	0.42968029	mg/L
7-15-D5 25 DF2	As 188.979	2.91519714	0.38225447	mg/L
7-15-D5 25 DF2	As AXIAL	2.91831247	1.12776828	mg/L
7-15-D5 25 DF2	Cu AXIAL	7.08E-02	2.06857669	mg/L
7-15-D5 25 DF2	Cr AXIAL	0.36290743	1.81930038	mg/L
7-15-D6 25 DF2	Y 371.029	1.05773824	1.19973688	mg/L
7-15-D6 25 DF2	Y AXIAL	1.02309352	1.67955974	mg/L
7-15-D6 25 DF2	Cu 327.393	6.36E-02	1.96382923	mg/L
7-15-D6 25 DF2	Cr 267.716	0.28535387	0.75680643	mg/L
7-15-D6 25 DF2	As 188.979	2.96967526	0.65998817	mg/L
7-15-D6 25 DF2	As AXIAL	2.95415175	1.29155194	mg/L
7-15-D6 25 DF2	Cu AXIAL	6.20E-02	1.50224221	mg/L
7-15-D6 25 DF2	Cr AXIAL	0.27962389	1.19839039	mg/L
7-15-D13 25 DF2	Y 371.029	1.04439313	1.8842309	mg/L
7-15-D13 25 DF2	Y AXIAL	1.02826194	1.56219311	mg/L
7-15-D13 25 DF2	Cu 327.393	6.59E-02	1.51343443	mg/L
7-15-D13 25 DF2	Cr 267.716	0.35709023	0.55795776	mg/L
7-15-D13 25 DF2	As 188.979	2.86281512	0.10653888	mg/L
7-15-D13 25 DF2	As AXIAL	2.90639577	3.4298866	mg/L
7-15-D13 25 DF2	Cu AXIAL	6.48E-02	5.16881338	mg/L
7-15-D13 25 DF2	Cr AXIAL	0.35564992	3.15994769	mg/L
7-15-D14 25 DF2	Y 371.029	1.05319152	1.76844889	mg/L
7-15-D14 25 DF2	Y AXIAL	1.05343126	0.34272427	mg/L
7-15-D14 25 DF2	Cu 327.393	4.87E-02	0.21674541	mg/L
7-15-D14 25 DF2	Cr 267.716	0.32310749	0.66416922	mg/L
7-15-D14 25 DF2	As 188.979	2.77183203	1.29531961	mg/L
7-15-D14 25 DF2	As AXIAL	2.84332321	1.5399441	mg/L
7-15-D14 25 DF2	Cu AXIAL	5.10E-02	1.57294823	mg/L
7-15-D14 25 DF2	Cr AXIAL	0.32644095	1.52316688	mg/L
7-15-D15 25 DF2	Y 371.029	1.03012139	1.28595252	mg/L
7-15-D15 25 DF2	Y AXIAL	0.99971132	0.55458599	mg/L
7-15-D15 25 DF2	Cu 327.393	1.71E-02	9.07618588	mg/L
7-15-D15 25 DF2	Cr 267.716	3.15E-02	3.43276595	mg/L
7-15-D15 25 DF2	As 188.979	4.53E-02	12.4766047	mg/L
7-15-D15 25 DF2	As AXIAL	3.33E-02	10.4537326	mg/L
7-15-D15 25 DF2	Cu AXIAL	1.78E-02	4.52999898	mg/L
7-15-D15 25 DF2	Cr AXIAL	2.68E-02	0.77819986	mg/L
7-15-D16 25 DF2	Y 371.029	1.02780621	0.57416986	mg/L
7-15-D16 25 DF2	Y AXIAL	0.99285427	0.16395879	mg/L
7-15-D16 25 DF2	Cu 327.393	1.48E-02	6.86611932	mg/L
7-15-D16 25 DF2	Cr 267.716	3.91E-02	4.17971284	mg/L
7-15-D16 25 DF2	As 188.979	2.55E-02	57.5719392	mg/L

7-15-D16 25 DF2	As AXIAL	2.35E-02	15.7884458	mg/L
7-15-D16 25 DF2	Cu AXIAL	1.60E-02	2.12191722	mg/L
7-15-D16 25 DF2	Cr AXIAL	3.51E-02	2.05544231	mg/L
9-15-01-2 5	Y 371.029	1.04493897	1.74909998	mg/L
9-15-01-2 5	Y AXIAL	1.03543212	0.60966637	mg/L
9-15-01-2 5	Cu 327.393	1.12E-02	9.34075665	mg/L
9-15-01-2 5	Cr 267.716	1.19983067	0.16580544	mg/L
9-15-01-2 5	As 188.979	1.1619852	1.86989014	mg/L
9-15-01-2 5	As AXIAL	1.19112153	1.39647548	mg/L
9-15-01-2 5	Cu AXIAL	9.47E-03	4.95135228	mg/L
9-15-01-2 5	Cr AXIAL	1.20657612	2.53607608	mg/L
BLANK	Y 371.029	1.03846648	1.82883744	mg/L
BLANK	Y AXIAL	1.03150111	1.43834684	mg/L
BLANK	Cu 327.393	-7.65E-03	9.29340341	mg/L
BLANK	Cr 267.716	1.16E-03	136.368717	mg/L
BLANK	As 188.979	-9.80E-03	133.08182	mg/L
BLANK	As AXIAL	-2.04E-02	10.7827885	mg/L
BLANK	Cu AXIAL	-9.31E-03	0.3395559	mg/L
BLANK	Cr AXIAL	-2.40E-03	11.1869833	mg/L
1.00 PPM HP	Y 371.029	1.03918024	0.18472874	mg/L
1.00 PPM HP	Y AXIAL	1.0199089	0.8507845	mg/L
1.00 PPM HP	Cu 327.393	1.06309279	1.69719748	mg/L
1.00 PPM HP	Cr 267.716	1.03629982	0.1765943	mg/L
1.00 PPM HP	As 188.979	1.03271946	1.74830834	mg/L
1.00 PPM HP	As AXIAL	1.06307852	0.79957269	mg/L
1.00 PPM HP	Cu AXIAL	1.0539228	1.48513093	mg/L
1.00 PPM HP	Cr AXIAL	1.03042516	1.48614827	mg/L
5.00 PPM HP	Y 371.029	1.01615035	0.7861109	mg/L
5.00 PPM HP	Y AXIAL	0.98646984	0.53011297	mg/L
5.00 PPM HP	Cu 327.393	5.36940573	0.69425187	mg/L
5.00 PPM HP	Cr 267.716	5.21211521	0.78284657	mg/L
5.00 PPM HP	As 188.979	5.33143243	9.84E-02	mg/L
5.00 PPM HP	As AXIAL	5.44654283	1.11280282	mg/L
5.00 PPM HP	Cu AXIAL	5.45537478	0.79310831	mg/L
5.00 PPM HP	Cr AXIAL	5.22565153	0.63471019	mg/L
10.00 PPM HP	Y 371.029	1.02438019	0.96984978	mg/L
10.00 PPM HP	Y AXIAL	1.01138963	1.1310839	mg/L
10.00 PPM HP	Cu 327.393	0.55028219	0.16603595	mg/L
10.00 PPM HP	Cr 267.716	0.52750582	0.46523467	mg/L
10.00 PPM HP	As 188.979	0.52016796	0.56503954	mg/L
10.00 PPM HP	As AXIAL	0.5374647	2.13210986	mg/L
10.00 PPM HP	Cu AXIAL	0.53559232	2.70919055	mg/L
10.00 PPM HP	Cr AXIAL	0.52721227	2.30139753	mg/L

20.00 PPM HP	Y 371.029	0.97742248	9.64E-02	mg/L
20.00 PPM HP	Y AXIAL	0.92663494	1.06774871	mg/L
20.00 PPM HP	Cu 327.393	21.6254993	2.135948	mg/L
20.00 PPM HP	Cr 267.716	21.2994222	1.90977238	mg/L
20.00 PPM HP	As 188.979	21.6630193	0.53525797	mg/L
20.00 PPM HP	As AXIAL	21.8927519	1.00599839	mg/L
20.00 PPM HP	Cu AXIAL	22.5870077	0.87780582	mg/L
20.00 PPM HP	Cr AXIAL	21.0326684	0.57891055	mg/L
0.500 PPM HP	Y 371.029	1.03416618	0.45295784	mg/L
0.500 PPM HP	Y AXIAL	1.03295299	0.38684669	mg/L
0.500 PPM HP	Cu 327.393	0.31307364	2.62908977	mg/L
0.500 PPM HP	Cr 267.716	0.28818653	2.133742	mg/L
0.500 PPM HP	As 188.979	0.28054215	7.44491552	mg/L
0.500 PPM HP	As AXIAL	0.27495776	3.34839364	mg/L
0.500 PPM HP	Cu AXIAL	0.29843751	1.52871727	mg/L
0.500 PPM HP	Cr AXIAL	0.27670178	3.07620996	mg/L
0.250 PPM HP	Y 371.029	1.049616	0.74799001	mg/L
0.250 PPM HP	Y AXIAL	1.01738192	1.11243038	mg/L
0.250 PPM HP	Cu 327.393	10.4750588	1.59588799	mg/L
0.250 PPM HP	Cr 267.716	10.2335102	1.63278393	mg/L
0.250 PPM HP	As 188.979	10.2525311	0.21349277	mg/L
0.250 PPM HP	As AXIAL	10.5811148	1.56249782	mg/L
0.250 PPM HP	Cu AXIAL	10.5564373	0.60376473	mg/L
0.250 PPM HP	Cr AXIAL	10.0482253	1.53800348	mg/L
0.050 PPM HP	Y 371.029	1.0370196	1.54563985	mg/L
0.050 PPM HP	Y AXIAL	1.02719118	0.29012742	mg/L
0.050 PPM HP	Cu 327.393	8.11E-02	7.07161457	mg/L
0.050 PPM HP	Cr 267.716	6.77E-02	6.96258837	mg/L
0.050 PPM HP	As 188.979	6.05E-02	10.4536627	mg/L
0.050 PPM HP	As AXIAL	4.62E-02	10.1649339	mg/L
0.050 PPM HP	Cu AXIAL	6.69E-02	9.51846025	mg/L
0.050 PPM HP	Cr AXIAL	5.62E-02	9.64721911	mg/L
9-15-02-2 5	Y 371.029	1.05506075	2.26653624	mg/L
9-15-02-2 5	Y AXIAL	1.06112058	0.11336334	mg/L
9-15-02-2 5	Cu 327.393	1.25E-02	11.128937	mg/L
9-15-02-2 5	Cr 267.716	1.4442638	0.47208167	mg/L
9-15-02-2 5	As 188.979	1.18269905	0.56314625	mg/L
9-15-02-2 5	As AXIAL	1.22972379	2.18629942	mg/L
9-15-02-2 5	Cu AXIAL	1.17E-02	2.8862408	mg/L
9-15-02-2 5	Cr AXIAL	1.4508324	2.55296596	mg/L
9-15-02-3 5	Y 371.029	1.0731689	1.80155598	mg/L
9-15-02-3 5	Y AXIAL	1.04858376	0.50020102	mg/L
9-15-02-3 5	Cu 327.393	9.60E-03	14.4409687	mg/L

9-15-02-3	5	Cr 267.716	1.31902822	0.12096793	mg/L
9-15-02-3	5	As 188.979	0.73944442	2.36039438	mg/L
9-15-02-3	5	As AXIAL	0.75844475	2.37194055	mg/L
9-15-02-3	5	Cu AXIAL	8.51E-03	4.84512164	mg/L
9-15-02-3	5	Cr AXIAL	1.30958777	1.91774973	mg/L
9-15-02-4	5	Y 371.029	1.06453892	0.90602694	mg/L
9-15-02-4	5	Y AXIAL	1.05833599	0.32175999	mg/L
9-15-02-4	5	Cu 327.393	2.91E-02	4.74260537	mg/L
9-15-02-4	5	Cr 267.716	1.4148617	0.14895435	mg/L
9-15-02-4	5	As 188.979	0.85560521	1.19131341	mg/L
9-15-02-4	5	As AXIAL	0.88778413	0.9709749	mg/L
9-15-02-4	5	Cu AXIAL	2.78E-02	1.97797191	mg/L
9-15-02-4	5	Cr AXIAL	1.42610772	1.24549448	mg/L
9-15-02-5	5	Y 371.029	1.07842734	0.89585443	mg/L
9-15-02-5	5	Y AXIAL	1.05016166	1.21106436	mg/L
9-15-02-5	5	Cu 327.393	4.15E-02	65.1990432	mg/L
9-15-02-5	5	Cr 267.716	1.14656863	0.70662114	mg/L
9-15-02-5	5	As 188.979	0.6724571	4.00738814	mg/L
9-15-02-5	5	As AXIAL	0.65276017	0.94494827	mg/L
9-15-02-5	5	Cu AXIAL	1.60E-02	2.87250099	mg/L
9-15-02-5	5	Cr AXIAL	1.12418257	2.03459602	mg/L
9-15-02-6	5	Y 371.029	1.09203017	1.16080272	mg/L
9-15-02-6	5	Y AXIAL	1.07301134	1.27243088	mg/L
9-15-02-6	5	Cu 327.393	6.51E-03	10.3345668	mg/L
9-15-02-6	5	Cr 267.716	1.03245006	0.36721295	mg/L
9-15-02-6	5	As 188.979	0.66405463	0.92746005	mg/L
9-15-02-6	5	As AXIAL	0.68146478	1.67489641	mg/L
9-15-02-6	5	Cu AXIAL	7.21E-03	3.9567063	mg/L
9-15-02-6	5	Cr AXIAL	1.0301927	2.24731988	mg/L
9-15-02-7	5	Y 371.029	1.09287251	0.40492766	mg/L
9-15-02-7	5	Y AXIAL	1.07552027	0.15764122	mg/L
9-15-02-7	5	Cu 327.393	6.97E-02	0.68228237	mg/L
9-15-02-7	5	Cr 267.716	0.70033424	0.10492561	mg/L
9-15-02-7	5	As 188.979	0.5098134	0.94114549	mg/L
9-15-02-7	5	As AXIAL	0.53480805	1.20840358	mg/L
9-15-02-7	5	Cu AXIAL	7.12E-02	2.73903308	mg/L
9-15-02-7	5	Cr AXIAL	0.69607871	0.45655358	mg/L
9-15-02-8	5	Y 371.029	1.08859571	0.68324904	mg/L
9-15-02-8	5	Y AXIAL	1.07050123	0.47041397	mg/L
9-15-02-8	5	Cu 327.393	7.37E-02	0.43520904	mg/L
9-15-02-8	5	Cr 267.716	0.80993088	0.19147625	mg/L
9-15-02-8	5	As 188.979	0.51977308	2.96420207	mg/L
9-15-02-8	5	As AXIAL	0.54591501	0.59402971	mg/L

9-15-02-8 5	Cu AXIAL	7.50E-02	0.23123828	mg/L
9-15-02-8 5	Cr AXIAL	0.80741728	1.01498001	mg/L
BLANK	Y 371.029	1.06643979	0.9859729	mg/L
BLANK	Y AXIAL	1.04139186	0.27636107	mg/L
BLANK	Cu 327.393	-5.91E-03	2.72098338	mg/L
BLANK	Cr 267.716	7.14E-04	44.4908996	mg/L
BLANK	As 188.979	-1.97E-02	99.8844335	mg/L
BLANK	As AXIAL	-1.83E-02	15.1367392	mg/L
BLANK	Cu AXIAL	-6.02E-03	0.70499762	mg/L
BLANK	Cr AXIAL	-2.92E-03	9.80244233	mg/L
1.00 PPM HP	Y 371.029	1.04946502	0.38141877	mg/L
1.00 PPM HP	Y AXIAL	1.04101204	0.49411661	mg/L
1.00 PPM HP	Cu 327.393	1.08369432	1.14841	mg/L
1.00 PPM HP	Cr 267.716	1.03273541	3.09E-02	mg/L
1.00 PPM HP	As 188.979	1.04081728	0.79408436	mg/L
1.00 PPM HP	As AXIAL	1.06914261	0.79374615	mg/L
1.00 PPM HP	Cu AXIAL	1.06257131	1.18170634	mg/L
1.00 PPM HP	Cr AXIAL	1.03089812	0.85730792	mg/L
5.00 PPM HP	Y 371.029	1.02114928	1.36696705	mg/L
5.00 PPM HP	Y AXIAL	0.98370207	2.27614773	mg/L
5.00 PPM HP	Cu 327.393	5.43779293	0.59021025	mg/L
5.00 PPM HP	Cr 267.716	5.2688585	0.62830152	mg/L
5.00 PPM HP	As 188.979	5.3325067	0.24336476	mg/L
5.00 PPM HP	As AXIAL	5.39985575	1.85516489	mg/L
5.00 PPM HP	Cu AXIAL	5.48000358	2.35281764	mg/L
5.00 PPM HP	Cr AXIAL	5.23844161	2.11909033	mg/L
10.00 PPM HP	Y 371.029	1.04400332	1.92618002	mg/L
10.00 PPM HP	Y AXIAL	1.03287404	1.52243844	mg/L
10.00 PPM HP	Cu 327.393	0.55329686	0.61497319	mg/L
10.00 PPM HP	Cr 267.716	0.52593375	0.96751133	mg/L
10.00 PPM HP	As 188.979	0.52600823	1.5235449	mg/L
10.00 PPM HP	As AXIAL	0.52848389	1.99268252	mg/L
10.00 PPM HP	Cu AXIAL	0.54196954	4.25870461	mg/L
10.00 PPM HP	Cr AXIAL	0.52489249	3.46910223	mg/L
20.00 PPM HP	Y 371.029	0.99460491	0.34889399	mg/L
20.00 PPM HP	Y AXIAL	0.94300812	1.70631936	mg/L
20.00 PPM HP	Cu 327.393	21.324094	2.5513095	mg/L
20.00 PPM HP	Cr 267.716	20.9601121	2.35190749	mg/L
20.00 PPM HP	As 188.979	21.6362184	0.1440225	mg/L
20.00 PPM HP	As AXIAL	21.8505285	1.37356005	mg/L
20.00 PPM HP	Cu AXIAL	22.0682489	0.39528333	mg/L
20.00 PPM HP	Cr AXIAL	20.6004526	0.38920306	mg/L
0.500 PPM HP	Y 371.029	1.03866896	0.74525001	mg/L

0.500 PPM HP	Y AXIAL	1.04344694	0.10965384	mg/L
0.500 PPM HP	Cu 327.393	0.31673233	1.95658033	mg/L
0.500 PPM HP	Cr 267.716	0.2888784	0.32470242	mg/L
0.500 PPM HP	As 188.979	0.28709722	2.86199684	mg/L
0.500 PPM HP	As AXIAL	0.27532009	4.87968199	mg/L
0.500 PPM HP	Cu AXIAL	0.30250825	3.64365381	mg/L
0.500 PPM HP	Cr AXIAL	0.27717415	3.77854776	mg/L
0.250 PPM HP	Y 371.029	1.06507214	0.43030965	mg/L
0.250 PPM HP	Y AXIAL	1.00338518	1.63628928	mg/L
0.250 PPM HP	Cu 327.393	10.2694272	0.31087429	mg/L
0.250 PPM HP	Cr 267.716	10.007908	0.17804799	mg/L
0.250 PPM HP	As 188.979	10.2856083	0.28445482	mg/L
0.250 PPM HP	As AXIAL	10.2754073	1.71118933	mg/L
0.250 PPM HP	Cu AXIAL	10.4070763	1.43950951	mg/L
0.250 PPM HP	Cr AXIAL	9.77134862	1.70939804	mg/L
0.050 PPM HP	Y 371.029	1.04539031	1.48754261	mg/L
0.050 PPM HP	Y AXIAL	1.04134949	0.78795462	mg/L
0.050 PPM HP	Cu 327.393	8.06E-02	4.92452988	mg/L
0.050 PPM HP	Cr 267.716	6.55E-02	4.67616356	mg/L
0.050 PPM HP	As 188.979	4.83E-02	17.1075205	mg/L
0.050 PPM HP	As AXIAL	4.19E-02	8.16455256	mg/L
0.050 PPM HP	Cu AXIAL	6.95E-02	7.61727677	mg/L
0.050 PPM HP	Cr AXIAL	5.60E-02	8.40317729	mg/L