Retardance of Rainwater-Leached Metals in Amended Soil Systems: A Case Study

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Presentation Overview

- Goal and Scope of Research
- Background
- Ash and Soil Classification
- Batch Studies
- Column Studies
- Conclusions
- Future Work

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Research Goal

Identify a readily available agricultural soil amendment to reduce the mobility of metals at Chromated Copper Arsenate (CCA)-treated wood burn sites.

Iron sulfate, agricultural lime, and gypsum were studied. The results for gypsum ($CaSO_4 \cdot 2H_2O$) are presented.

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Scope of Research

- What are the potential environmental effects on soil and water resulting from the burning of CCA-wood?
  - What is the composition of the ash?
  - What is the fate of the ash in soil?
  - How effectively are metals leached from the soil/ash by rainwater?
- Can the leaching rates be reduced by the addition of soil amendments?

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Background
What is CCA?

- Chromated Copper Arsenate (CCA) wood preservative
- Designed for the humid Southeastern U.S. where wood is prone to insect and fungal attack
  - **Cu** - serves as a fungicide
  - **As** - serves as an insecticide
  - **Cr** - a fixing agent for bonding Cu & As to wood
- Used in residential-use wood until 2004
- Very large amounts of wood were treated

Pictures: www.google.com/search?q=pictures+of+CCA+wood

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Statistics on CCA Production

- ~1lb CCA preservative/3 ft^3 treated wood
- 1997: 450 x 10^6 ft^3 of CCA-wood products
- Service life of CCA-wood 20-50 years
- CCA-treated wood waste will increase from 5 to 32 x 10^6 ft^3/yr by 2015
- **As** in CCA-wood waste: 31,000 metric tons introduced into Florida environment over the past 30 years
- Burning of waste/old CCA-treated wood has been common practice

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Metal Species in CCA-Wood/Ash

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**

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Investigations to Quantify Metals and Evaluate Mobility

- Produce ash & Quantify metals in CCA-ash
- How mobile are the metals?
  - Batch Leaching Experiments
    - Accelerated leach studies
    - Regulatory classification of CCA-ash
    - Leaching of CCA-ash & a soil/CCA-ash mixture
    - Potential contamination of water by CCA-metals
- Effect of $CaSO_4$ on metals mobility
  - Optimization Study
- Column Leaching Experiments
    - Evaluate $CaSO_4$ performance versus natural soil
    - Measure the pH range of the leach events

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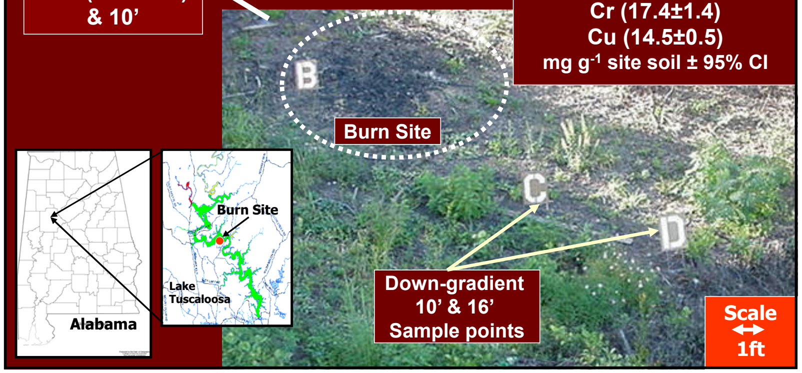
Sampling Points & CCA-metals Concentration at Burn Site



Soil & CCA-ash

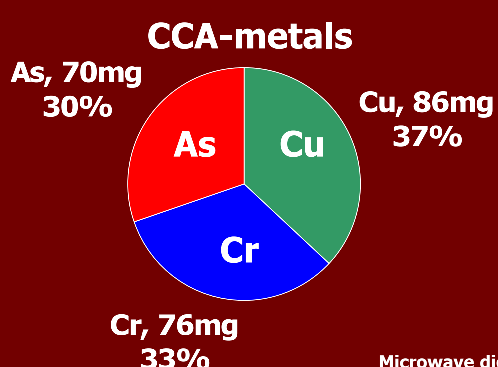
Soils in US & Proportions of Major Adsorbed Cations on Surface Layers

Soil Order	Typical location	H^+ and Al^{+3}	Ca^{+2}	Mg^{+2}	K^+	Na^+
Oxisols	Hawaii	85	10	3	2	trace
Spodosols	New England	80	15	3	2	trace
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.	[illegible]	65	20	10	5

Adapted from Brady, 1990

Total CCA-metals in 1g CCA-ash

1000mg CCA-ash contains 232mg (23%) CCA-metals

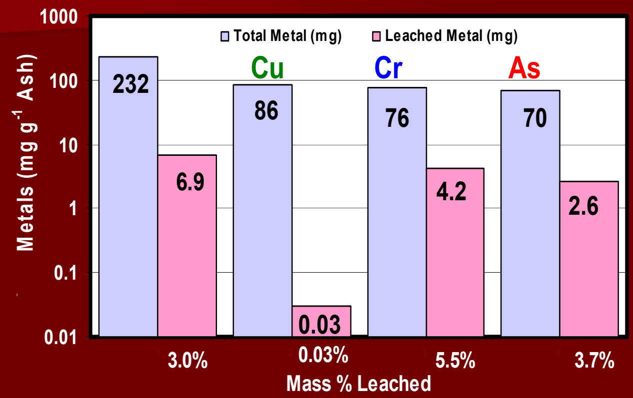


Microwave digestion & ICP

Batch Leaching

Establish preliminary leaching trends for column design

Metals Present and Leached from Soil/Ash Mixture (mg g^{-1} & %)



Leaching Trend : Cr>As>Cu

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Regulatory Classification of CCA-ash by RCRA-TCLP

- As - Regulated Haz. Waste (RCRA)
  - TCLP Limit: 5.0 mg L^{-1}
  - CCA-ash by TCLP: 578±44.7 mg L^{-1}
- Cr - Regulated Haz. Waste (RCRA)
  - TCLP Limit Cr(VI): 5.0 mg L^{-1}
  - CCA-ash Cr(VI+III) by TCLP: 0.719±0.057 mg L^{-1}
- Cu - Not regulated under RCRA
  - CCA-ash Cu by TCLP: 6.72±0.713 mg L^{-1}

Results reported in mg L^{-1} ± 95% CI

Therefore CCA-ash is classified as a regulated RCRA Haz. Waste due to As

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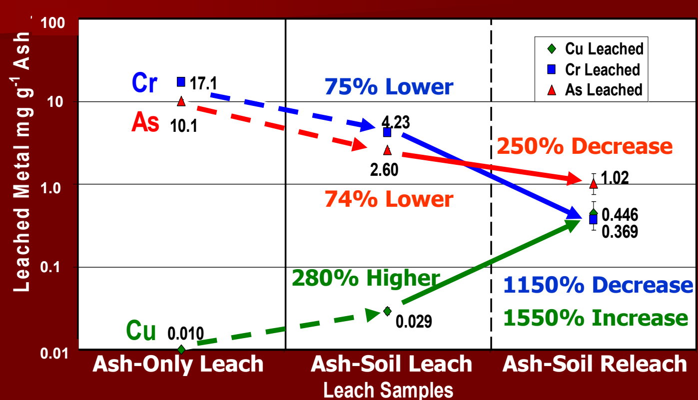
Batch Leaching of CCA-ash & Soil/CCA-ash Mixture



Therefore natural soil retards Cr & As mobility

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Potential Contamination of Water by CCA-metals

Batch Leach (5 Leachings)
1.45 g CCA-ash, 8.25 g Test Soil, 465 mL Total Rainwater

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

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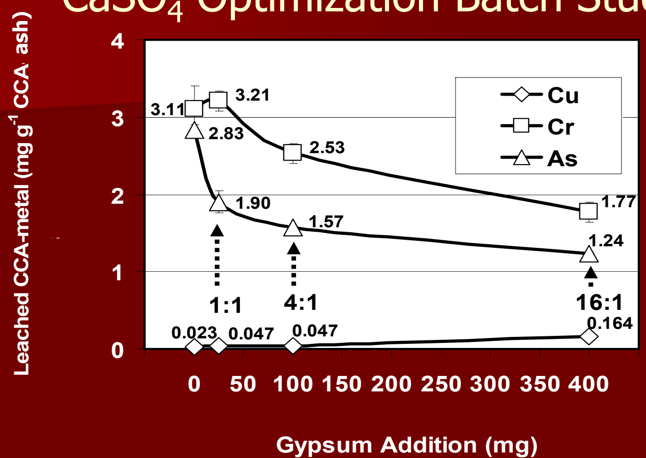
$CaSO_4$ Optimization Batch Study



A 1:1 to 3:1 ratio of $CaSO_4$:CCA-ash was acceptable

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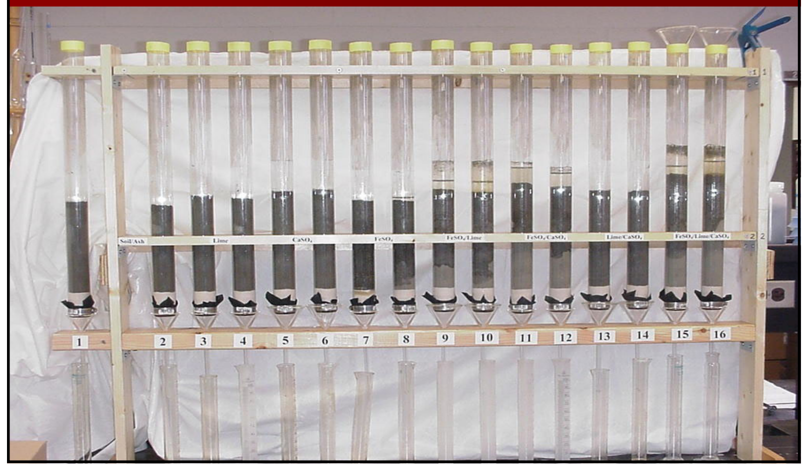
Column Leaching Objectives



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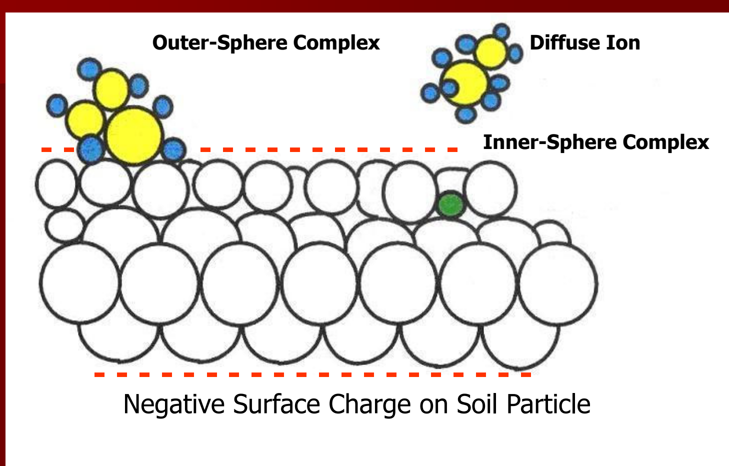
Mobility Reducing Mechanisms



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Soil/CCA-ash/$CaSO_4$ System

- Ultisol Soil
  - Low Cation Exchange Capacity (CEC), 35% efficiency
  - Low to moderate Anion Exchange Capacity (AEC)
- CCA-ash
  - XO => $X(OH)_2$ => XCO_3, where X = Ca, Mg, Cu, Cr, As
- General Mechanisms from $CaSO_4$ Amendment
  - Ca^{+2} replaces Al^{+3}, increases CEC efficiency
  - Increased $Al(OH)_3$ and $Cr(OH)_3$ precipitation
  - Increased Ca^{+2} concentration and negative surface charge produces greater adsorption and coprecipitation of As and Cr. Increased Cu mobility due to competition with Ca^{+2} for adsorption sites and increased mobility of Cu-bound organic compounds

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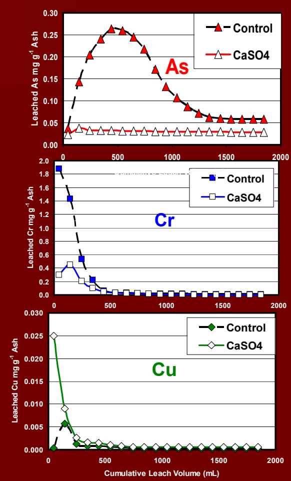
Accelerated One-Year Mass Leach of Metals

Accelerated One-Year Mass Leach Control vs $CaSO_4$

Metal	Combination	Mass (mg g^{-1})	± %
As	Control	2.53	-77%
	$CaSO_4$	0.578	
Cr	Control	4.31	-72%
	$CaSO_4$	1.20	
Cu	Control	0.012	400%
	$CaSO_4$	0.048	

- $CaSO_4$ reduces mobility of As by a further 77% and Cr by 72% over soil alone
- Cu mobility increases by a small mass compared to the large reduction in As and Cr mobility



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Conclusions

- Unamended soil retards leaching of As & Cr from CCA-ash while increasing Cu mobility
- $CaSO_4$ amendment of soil further reduces mobility of As by 77% and Cr by 72%
- Optimization study revealed 3:1 ratio of $CaSO_4$ to CCA-ash mass is recommended
- A higher ratio of $CaSO_4$ to CCA-ash mass would serve as a continued source of Ca^{+2} cations for long-term stabilization of As & Cr
- $CaSO_4$/Soil/CCA-ash system: 7.3 to 8.0 pH

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Ongoing Work & Future Potential

- *Soil and Sediment Contamination* journal has published two articles from this research on CCA- metals adsorption/desorption mechanisms in amended soil systems and a third article is under review in another journal
- The future of metals immobilization in soil by the use of common soil amendments could involve the manufacture of "enhanced" soil amendments to improve the performance of immobilization mechanisms

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Presentations

Parts of the research results have been presented at the following:

- EWRI-World Environmental & Water Resources Congress 2008
  Honolulu, HI
- American Water Resources Association 2010 Annual Conference
  Philadelphia, PA

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Questions ?

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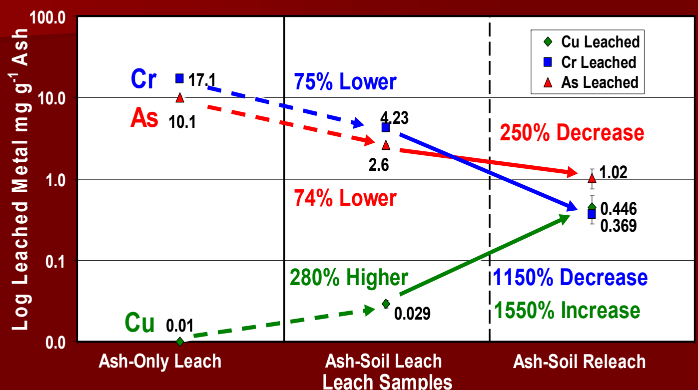
Batch Leaching of CCA-Ash & Soil/CCA-Ash Mixture



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