CHARACTERIZATION AND APPLICATION OF IRON-ENRICHED COMPOST FOR REDUCING LEAD AND ARSENIC AVAILABILITY IN CONTAMINATED SOIL

Patrick M. Freeze[1], James B. Harsh[1], Ravi Kukkadapu[2], and Zhenqing Shi[3]

(1) Crop and Soil Sciences, Washington State University, Pullman, WA, (2) Pacific Northwest National Laboratory, Richland, WA,

(3) School of Environment & Energy Guangzhou, South China University of Technology, Guangdong, China,

Abstract

- ~1900 – 1947: apple and pear orchards across the United States were repeatedly applied with lead-arsenate pesticides to treat codling moths.
- Today: ~400 to 2000 mg/kg lead (Pb) and ~50 to 650 mg/kg arsenic (As) in residential and agricultural soils.
- Increased Pb and As exposure to humans, facilitated through dust inhalation, soil ingestion, and plant uptake.
- Previous research: high Fe-biosolids can reduce bioavailable soil Pb and As by providing sorption sites that include carbon functional groups, Fe-(hydr)oxide particles, and ternary complexes with organic FeOH functional groups [1][2][3][4].

Overall Objective: To prepare, characterize, and test a stable iron amended compost with a high capacity to decrease arsenic and lead availability in water and soil.

H1: Fe-gluconate amendments will result in a stable compost product (low DOC) with more Fe bound to organic matter and less inorganic Fe-containing precipitates, compared to the Fe-sulfate compost amendments.

H2: The highest Fe-gluconate treatment will have the greatest capacity to adsorb both As and Pb from solution, and subsequently lower NH_4AOc extractable As and Pb in contaminated soil incubations.

Methods

SAMPLE PREPARATION:

Two Fe-salts: Fe (II)-gluconate (FG)
$Fe(II)SO_4$ (FS)

1. Compost development

2. Composting with treatment bags

Feedstock: sawdust, straw, lawn clippings, woody biomass, and animal bedding.

Thermophilic composting method:
4 x 4 x 4 ft positively aerated bins located at WSU Composting Facility (Pullman, WA). Bins housed separate treatment mesh bags with 1 kg of compost mixed with either Fe-sulfate or Fe-gluconate, producing a range of Fe-concentrations for each salt. Compost initial C:N ratio was 35/40:1, moisture content of approximately 65%, and composted for several months.

CHEMICAL METHODS

Ammonium Oxalate/Citrate Dithionite/Sodium Pyrophosphate Iron Extractions:
Per SSSA Chemical Methods. Extracts were filtered and analyzed with a Microwave Plasma Atomic Emission Spectrometer (Agilent MP-AES 4200).

Mossbauer Spectroscopy:
Spectra were collected on two milled samples, FG8 and FS50, at room temperature (RT), 77K, 10K (FG8), and 25K (FS50), and modeled with Recoil software using a Voigt-based structural fitting routine.

Pb and As Adsorption Isotherm:
0.1 g compost samples suspended in 20 mL 10 mM $NaNO_3$ and spiked with Pb (0.02 mM to 2 mM) or As (0.01 mM to 0.5 mM) stock solution. Total Pb or As in the solutions were analyzed via Agilent MP-AES 4200.

Soil Incubation and Plant Available Index Assessment:
10 g of soil (contaminated and controls) was mixed with 1 g of compost treatment, adjusted to pH 5, incubated in 60 x 15 mm Petri dishes, and kept at field capacity. At each time point, 4 g subsamples were extracted with 1 M NH_4AOc @ pH 4.8 and analyzed for Pb and As.

Results

***FG:** Ferrous Gluconate, **FS:** Ferrous Sulfate. Numerical value represents approximate final Fe concentration in compost treatment in mg/g*

Final compost composition

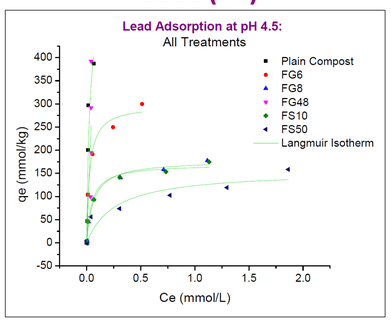
SAMPLE ID	Fe mg/g	C:N	pH
Plain Compost	3.1 ± 0.11	36.7:1	8.4 ± 0.16
FG6	5.6 ± 0.78	25.2:1	7.6 ± 0.12
FG8	7.9 ± 0.20	30.6:1	7.4 ± 0.13
FG48	48 ± 1.1	22.4:1	4.9 ± 0.050
FS10	10 ± 0.56	35.1:1	7.2 ± 0.10
FS50	51 ± 3.9	36.9:1	4.2 ± 0.17

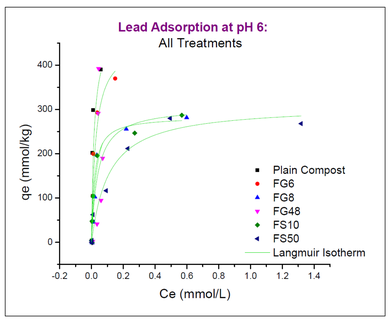
Leachate composition

DOC mg/g	TP mg/kg	TN mg/g
8.6 ± 0.094	48 ± 1.6	1.7 ± 0.061
9.0 ± 0.29	20 ± 0.78	0.48 ± 0.046
10 ± 0.023	20 ± 2.0	0.51 ± 0.023
44 ± 1.8	57 ± 1.1	7.6 ± 0.28
8.8 ± 0.27	5.7 ± 0.58	0.43 ± 0.010
2.4 ± 0.23	3.0 ± 0.23	0.57 ± 0.013

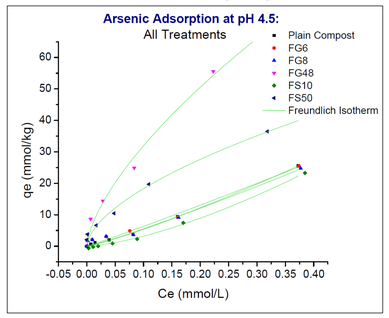
Adsorption Isotherms: Langmuir (Pb) and Freundlich (As)

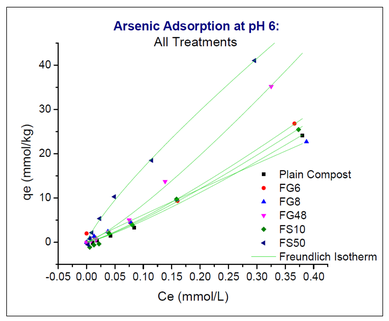
Lead (Pb)





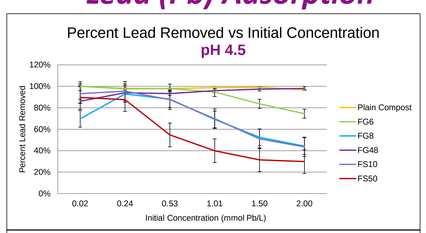
Arsenic (As)

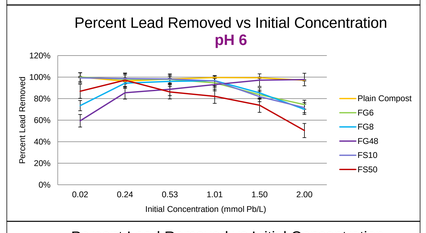


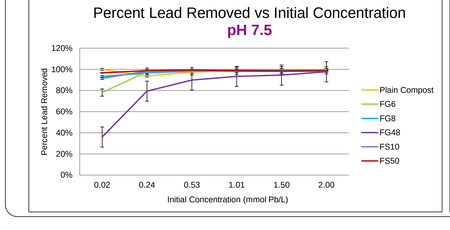


***qe:** amount sorbed at equilibrium (mmol/kg); **Ce:** final solution concentration at equilibrium (mmol/L)*

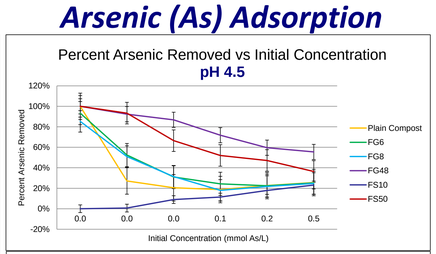
Lead (Pb) Adsorption

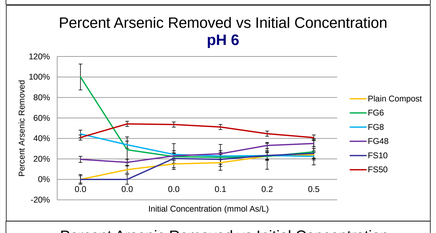


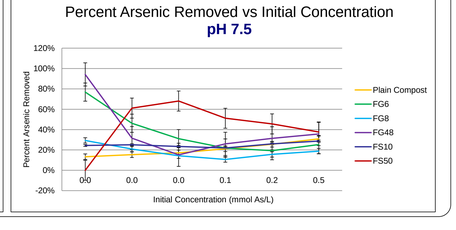




Arsenic (As) Adsorption







Adsorption Modeling: Langmuir (La) and Freundlich (Fr)

$$\frac{Ce}{q} = \frac{Ce}{qmax1} + \frac{1}{K * qmax} \qquad \log qe = \log kf + \frac{1}{nf}\log Ce$$

Lead (Pb)

	pH	K	qmax	R2	Model
Plain	3	3.5	301	0.97	La.
	4.5	35	579	0.84	La.
	6	59	493	0.62	La.
	7.5	*Could not model*			
	9	*Could not model*			
FG6	4.5	36	298	0.98	La.
	6	37	456	0.89	La.
	9	7.1	2E+03	0.96	La.
FG8	4.5	16	178	0.98	La.
	6	25	307	0.91	La.
FG48	6	29	336	0.24	La.
	7.5	*Could not model*			
	9	73	214	0.24	La.
FS10	4.5	21	170	0.98	La.
	6	52	284	0.96	La.
FS50	3	8E+03	1E+08	0.58	La.
	4.5	3.8	156	0.88	La.

	pH	K	qmax	R2	Model
FS50	6	9.1	309	0.96	La.
	7.5	8.2	2E+03	0.98	La.

	pH	K	β (1/n)	R2	Model
FG6	3	84	0.39	0.98	Fr.
	7.5	7E+05	1.9	0.88	Fr.
FG8	3	52	0.55	0.99	Fr.
	7.5	6E+04	1.2	0.51	Fr.
	9	6E+04	1.6	0.91	Fr.
FG48	3	9E+03	1.8	0.62	Fr.
	* 4.5	4.5	0.64	0.95	Fr.
FS10	3	50	0.5	0.99	Fr.
	7.5	1E+04	1.0	0.98	Fr.
	9	5E+04	1.3	0.94	Fr.
FS50	9	1E+05	1.4	0.94	Fr.

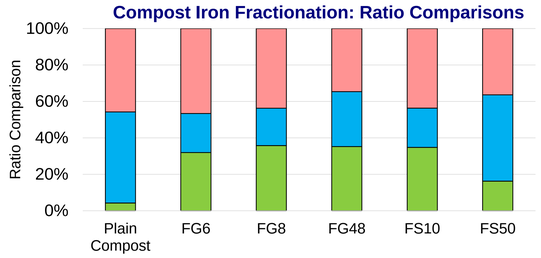
* Langmuir model on graph for comparison

Arsenic (As)

	pH	K	β (1/n)	R2	Model
Plain	3	114	0.95	0.99	Fr.
	4.5	82.3	1.2	1.00	Fr.
	6	77.2	1.2	1.00	Fr.
	7.5	130	1.3	1.00	Fr.
	9	56.5	0.91	0.99	Fr.
FG6	3	80.3	1.3	1.00	Fr.
	4.5	70.5	1.0	0.98	Fr.
	6	89.9	1.2	0.99	Fr.
	7.5	80.7	1.2	0.97	Fr.
	9	112	1.2	1.00	Fr.
FG8	3	56.6	0.82	0.99	Fr.
	4.5	73.4	1.1	0.98	Fr.
	6	56.2	0.96	1.00	Fr.
	7.5	59.9	1.3	1.00	Fr.
	9	82.4	1.6	1.00	Fr.

	pH	K	β (1/n)	R2	Model
FG48	3	32.7	0.72	0.92	Fr.
	4.5	147	0.66	0.98	Fr.
	6	137	1.2	1.00	Fr.
	7.5	154	1.3	0.99	Fr.
	9	122	0.94	1.00	Fr.
FS10	3	68.2	1.1	1.00	Fr.
	4.5	95.1	1.5	1.00	Fr.
	6	83.8	1.2	0.99	Fr.
	7.5	96.8	1.2	1.00	Fr.
	9	74.6	1.1	0.98	Fr.
FS50	3	51.8	0.53	0.99	Fr.
	4.5	71.6	0.59	0.99	Fr.
	6	111	0.82	1.00	Fr.
	7.5	92.2	0.75	0.96	Fr.
	9	85.4	0.99	0.99	Fr.

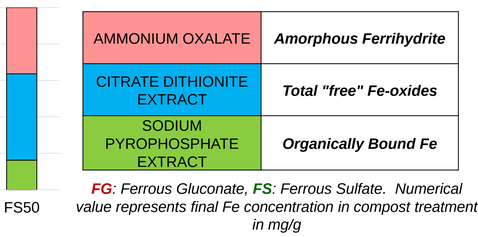
Iron Speciation: Fractionation and Mossbauer Spectroscopy



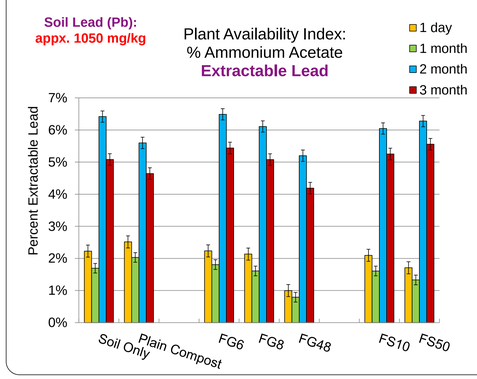
AMMONIUM OXALATE	*Amorphous Ferrihydrite*
CITRATE DITHIONITE EXTRACT	*Total "free" Fe-oxides*
SODIUM PYROPHOSPHATE EXTRACT	*Organically Bound Fe*

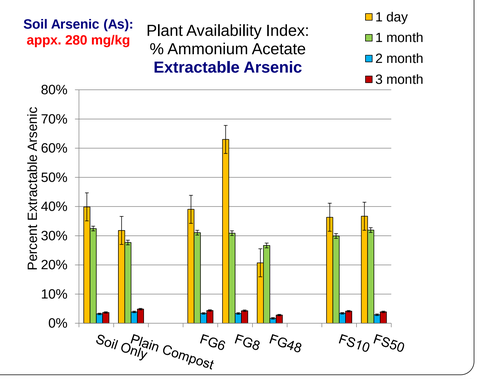
***FG**: Ferrous Gluconate, **FS**: Ferrous Sulfate. Numerical value represents final Fe concentration in compost treatment in mg/g*

Mossbauer Spectroscopy Iron Species	FG8	FS50
Species 1: Fe(II) in compost (?)	5%	17%
Species 2: Fe(III) in organic matter (?)	30%	18%
Species 3: Amorphous ferrihydrite	41%	27%
Species 4: Nanogoethite	22%	
Species 5: Fe(III)SO_4/Jarosite		38%



Soil Incubation: Ammonium Acetate Extractable Pb and As





Conclusions

H1: Fe-amendments in compost:
Fe-gluconate amendments resulted in higher Fe-OM associations compared to highest Fe-sulfate amendments (Fe-precipitates), supported by chemical extracts and compared with Mossbauer spectroscopy. Both contained a large fraction of reactive ferrihydrite.
Fe-gluconate amendments resulted in lower C:N ratios in the compost, but higher DOC and P in leachate compared to FS treatments.

H2: Adsorption:
FG treatments showed higher As adsorption but only at pH<6. Highest FS treatments adsorbed highest amounts of As at pH > 4.5
FG treatments showed higher Pb adsorption but not more so than the controls.
FG: lower extractable As from contaminated soil; minor differences with Pb.
pH drop from >pH 5 to ~4.5 resulted in decreasing extractable As but increasing extractable Pb.

Bibliography

[1] Jang, A., Seo, Y., & Bishop, P. L. (2005) Environmental Pollution, 133, 117-127.
[2] Gu, B., & Schmitt, J. (1994) Environmental Science & Technology, 28.
[3] Brown, S. L., Clausen, I., Chappell, M. A., Scheckel, K. G., Newville, M., & Hettiarachchi, G. M. (2012) Journal of Environmental Quality, 41, 1612-1622.
[4] Mikutta, C., & Kretzschmar, R. (2011) Environmental Science & Technology, 45, 9550-9557.
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https://www.hcn.org/issues/42.21/farmings-toxic-legacy