## Why EPA and Biochar?

#### **Multiple problems**

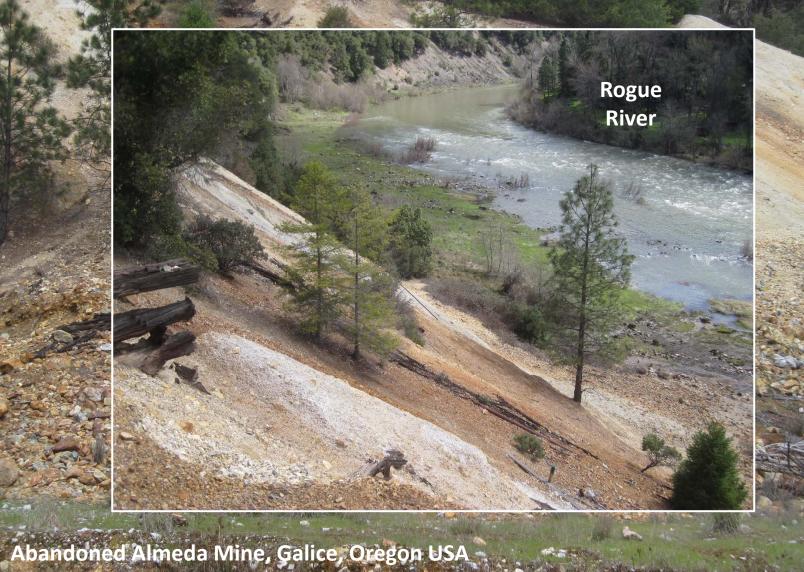
- There are approximately 500,000 abandoned mines across the U.S. that pose a considerable and pervasive risk to human health
  - World-wide the problem is even greater
- Contaminated soils and sediments require remediation
- Globally there are hundreds of thousands of hectares of degraded soils that limit food security and in some countries continued overfertilization and overuse threatens air and water quality New and advanced materials are needed that can be engineered to address these specific problems!

## Why EPA and Biochar?

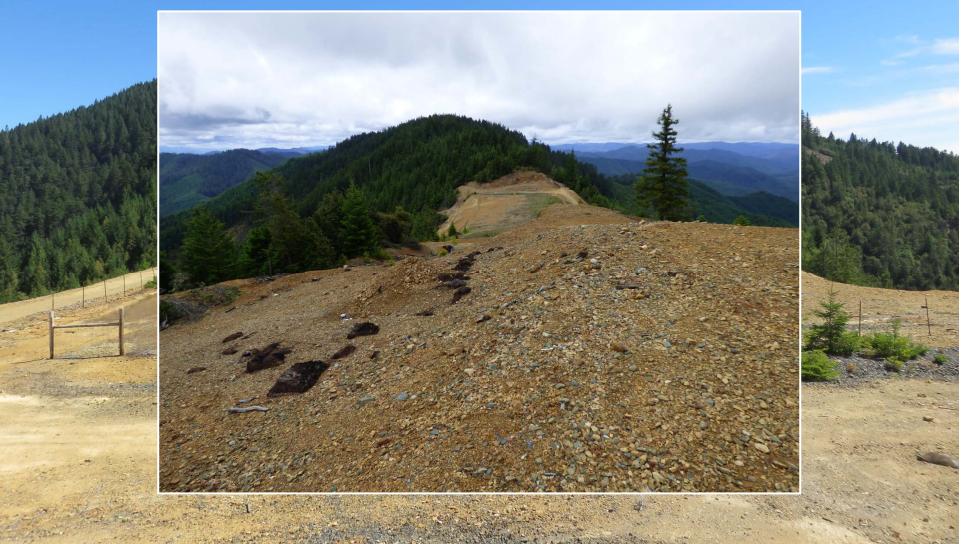
#### **Multiple problems**

- There are approximately 500,000 abandoned mines across the U.S. that pose a considerable and pervasive risk to human health
  - World-wide the problem is even greater
- Contaminated soils and sediments require remediation
- Globally there are hundreds of thousands of hectares of degraded soils that limit food security and in some countries continued overfertilization and overuse threatens air and water quality Biochar when used as a soil amendment
- Has beneficial and tunable remedial properties
- Biochar can reduce contaminant exposure by limiting the exposure pathways and immobilizing contaminants
- Biochar can help to restore soil quality and health of degraded soils
- Biochar can enable site in situ remediation, re-vegetation and revitalization, and reuse
- Biochar is a carbon negative material (i.e., removes CO<sub>2</sub> from the atmosphere)

# **Mining Impacted Soils**



## **Mining Impacted Soils**



Abandoned Formosa Mine, Riddle, Oregon USA

## **Mining Impacted Soils**

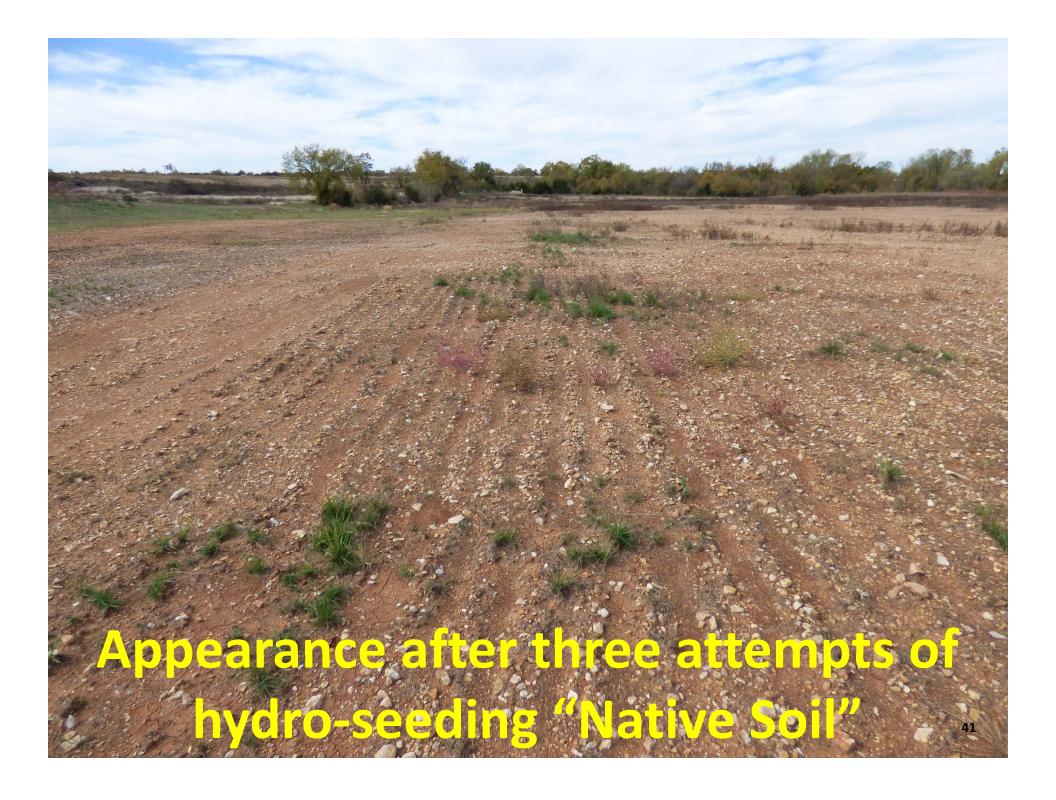


Oronogo-Duenweg Mining Belt Mine and Smelting Residue Site, Jasper County, Missouri USA 39



# "Native Sub-Soil" Surface After Removal of

Mine Spoil Overburden



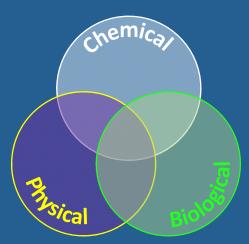
# Common Limitations of Mining Impacted Soils

#### Chemical

- Metal toxicity
- Low: pH, Organic Matter, Nutrients
- Physical
  - Compacted
  - Coarse fragments
  - Poor structure
  - Poor water infiltration or holding properties
  - Depth of spoil material
  - Proximity to water table

#### • Biological

- Low activity (e.g., plants, microbes, higher organisms)
- Low diversity
- Wrong kinds of organisms



# Solving the Problem: Start with the End in Mind

**Before Amendments and Revitalization** 

**After Amendments and Revitalization** 



#### Formosa Mine Superfund Site, Riddle Oregon

# **Strategic Intervention**

Acidic, Metal Contaminated & Barren

Re-vegetated, Revitalized & Stabilized



Soil Revitalization Using Biochar and Other Soil Amendments and Native Plant Re-establishment

### **Biochar and Contaminated Site Remediation:** The Literature...

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	538	face area and this specific structure has been proved to have the capability in increasing water and nutrient retention of soil (-1).	Effect of temperature and material Preparation tem
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## **Biochar and Contaminated Sites**

- Biochar has been shown to be effective at sorbing inorganic (i.e., heavy metals) and organic contaminants
- Biochar can be used to either raise or lower soil pH
- Biochar can increase and manage soil nutrient supply
- Biochar can improve soil water holding and infiltration properties
- Biochar can have a role in soil rejuvenation
  - Soil carbon addition/carbon sequestration
  - Refugia for microbes
- Biochar, particularly high temperature biochars, are very stable and can be useful for carbon sequestration
  - Unlike other organic materials commonly used in remediation, biochar can have residence times of hundreds to thousands of years

## Addressing Specific Soil Limitations with Biochar

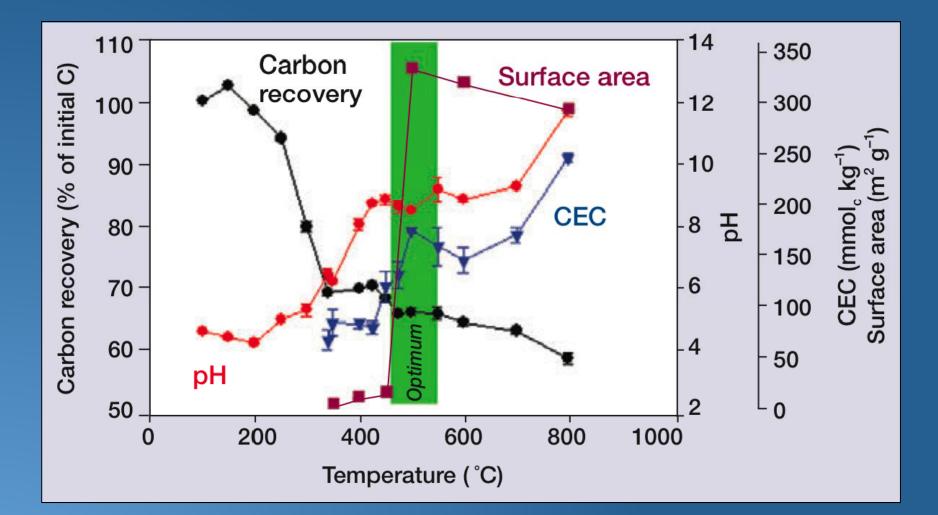
Limiting Factor	Variable	Problem	Role of Biochar Amendment
Physical	Soil Structure	Soil too compact	<ul> <li>Decreased soil bulk density, increased infiltration, and decreased erodibility.</li> </ul>
	Soil Erosion	High erodibility	<ul> <li>Increased water retention due to surface area, pore size distribution and charge</li> </ul>
	Soil Moisture	Too wet	characteristics.
		Too dry	
Nutritional	Macronutrients	Too Low	<ul><li>Slow nutrient release.</li><li>Soil organic matter stabilization.</li></ul>
	Micronutrients	Other Deficiencies	<ul> <li>Soil organic matter addition.</li> <li>Soil organic matter addition.</li> <li>Retention of released nutrients.</li> <li>Increased microbial activity.</li> <li>Habitat for mycorrhizal fungi.</li> <li>Increases plant productivity.</li> </ul>
Toxicity	рН	Acid soils (< 4.5)	<ul> <li>Designed to function as lime</li> </ul>
	рН	Alkaline soils (>7.8)	<ul> <li>Low pH biochar and reduce soil alkalinity.</li> <li>High CEC for Na retention.</li> </ul>
	Heavy metals	High concentrations	<ul> <li>High surface area and cation exchange capacity and pores to sorb metals</li> </ul>

#### Adapted from Shrestha and Lal, 2006

# **Designer Biochar Concept**

- It's possible to design and make biochar with its own set of characteristics that can selectively improve soil properties.
- Biochars can be engineered from strategic permutations of feedstocks, blends of feedstocks, and a few key pyrolysis parameters to create "designer biochars" to address specific soil limitations.
- Static biochar properties provide a predictor of its ability to modify a specific soil property.
- Testing of biochar effectiveness in real world situations is needed to prove efficacy.

### **Biochar Properties**



Properties of pyrolyzed Robinia pseudacacia. From Lehmann 2007

### **Biochar characterization: Nutrients**

Feedstock	Pyrolysis (°C)	Fertilizer eq	uivalent ratio (I	Source	
		Ν	Р	К	
Swine manure	350	37	39	18	Cantrell & Martin, 2011
	700	26	59	26	
Cow manure	400	14	4	26	Singh et al. 2010
	550	11	5	23	
Poultry litter	350	50	30	60	Novak et al. 2009
	700	30	40	90	
Pine chips	350	5	0.2	2	Novak et al. 2012
	500	4	0.3	3	
Switchgrass	250	4	1	5	Novak et al. 2012
	500	11	2	12	

Biochars made from manures have higher fertilizer equivalent N P K ratios, and as pyrolysis temperature increases (> 500°C) N declines, P & K increase. Slide - J.M. Novak

# **Designer Biochar Approach**

- ARS-scientists (Novak et al.) are engineering biochars to improve specific soil chemical, physical issues, and sorb P from manures.
- Accomplished by selecting/manipulating feedstocks and pyrolysis conditions:

Single Feedstock or Feedstock Blend*	Pyrolysis (°C)	Biochar Particle Size	Soil impact
Switchgrass	250 to 500	Dust	↑ water storage
Hardwood Chips	350 to 700	Dust	个 water storage
Pecan Shells	700	Dust	↑ nutrients/lime
Pine Chips	350 to 700	Dust, Pellets	C sequestration
Pine chips + Swine Solids	350 to 700	Dust, Pellets	C sequestration & balance soil [P]
Switchgrass + Poultry Litter	350 to 700	Dust, Pellets	Water storage & balance soil [P]
Pine Chips + Hardwood Chips + Poultry Litter	350 to 500	Dust, Pellets	Water infiltration & root growth
Plant Biomass + Manure + Fe	>600	Variable	Microbial processes & P sorption <sup>†</sup>

\*Novak et al., 2014

<sup>†</sup>Spokas et al., & Bolan et al.,

## **Other Soil Amendments can Include:**

- Biosolids
- Manures/litters
- Sugar beet lime
- Wood ash
- Coal combustion products
- Log yard wastes
- Wastes from bioenergy production
- pH neutralizing lime products
- Some metal oxides

- Composted biosolids
- Composted agricultural byproducts
- Composted yard wastes
- Mineral material
  - Foundry sands
  - Steel slag
  - Dredged sediments
  - Water treatment residuals
- Traditional agricultural fertilizers

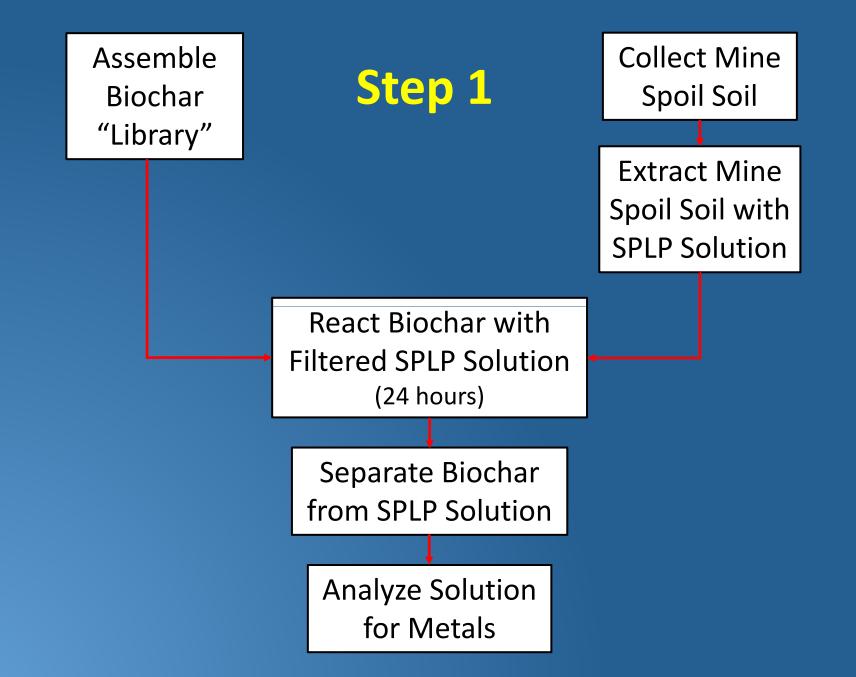
## Goals for Using Biochar and Other Soil Amendments on Metal Contaminated Sites:

- To immobilize metal contaminants through <u>adsorption</u>, <u>precipitation</u>, and <u>complexation</u> reactions which result in the redistribution of the contaminants from solution phase to solid phase, thereby reducing their bioavailability and transport in the environment.
  - Reduce hazards
  - Reduce exposure
  - Restore soil function & ecosystem services
- To establish a sustainable native plant cover

## **Screening Biochars**

### **Three step laboratory process:**

- Challenge candidate biochars (we use biochars from our "Biochar Library") with SPLP<sup>†</sup> extract of metal contaminated soil
- 2. Determine metal binding characteristics of tested biochars
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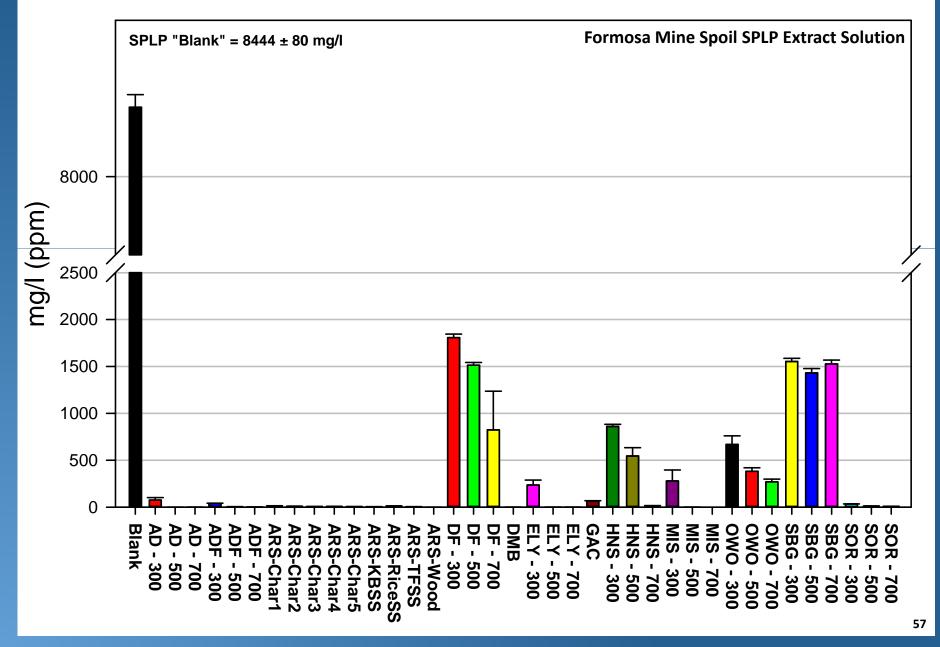


# Biochar Library - Formosa Mine Spoil Screening

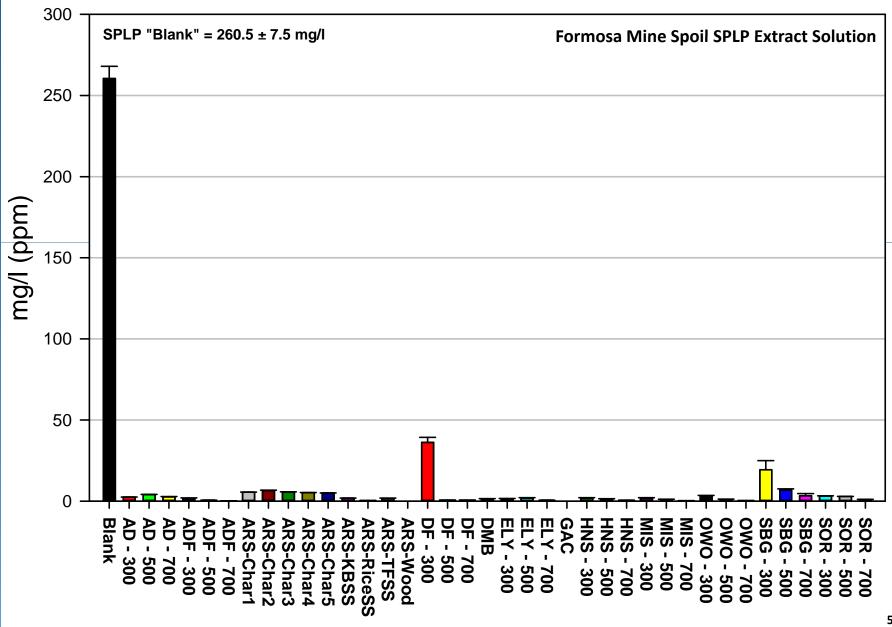
Sample Code	Feedstock	HTT (°C) <sup>†</sup>	Sample Code	Feedstock	HTT (°C) <sup>†</sup>
AD - 300	Arundo donax	300	ELY - 300	Elymus glaucus	300
AD - 500	Arundo donax	500	ELY - 500	Elymus glaucus	500
AD - 700	Arundo donax	700	ELY - 700	Elymus glaucus	700
ADF - 300	Anaerobically Digested Fiber	300	GAC	Granulated Activated	2
ADF - 500	<b>Anaerobically Digested Fiber</b>	500	GAC	Charcoal	?
ADF - 700	Anaerobically Digested Fiber	700	HNS - 300	Hazelnut shells	300
ARS-Char1	ARS Char 1	?	HNS - 500	Hazelnut shells	500
ARS-Char2	ARS Char 2	?	HNS - 700	Hazelnut shells	700
ARS-Char3	ARS Char 3	?	MIS - 300	Miscanthus	300
ARS-Char4	ARS Char 4	?	MIS - 500	Miscanthus	500
ARS-Char5	ARS Char 5	?	MIS - 700	Miscanthus	700
	ARS Kentucky Bluegrass	?	OWO - 300	Oregon White Oak	300
ARS-KBSS	Seed Screenings	r	OWO - 500	Oregon White Oak	500
ARS-RiceSS	ARS Rice Seed Screenings	?	OWO - 700	Oregon White Oak	700
ARS-TFSS	ARS Tall Fescue Seed	?	SBG - 300	Spent Brewer's Grain	300
ANJ-1155	Screenings	r	SBG - 500	Spent Brewer's Grain	500
ARS-Wood	ARS Wood (tree tops)	?	SBG - 700	Spent Brewer's Grain	700
DF - 300	Douglas fir	300	SOR - 300	Sorghum	300
DF - 500	Douglas fir	500	SOR - 500	Sorghum	500
DF - 700	Douglas fir	700	SOR - 700	Sorghum	700
DMB	Dairy Manure (Enchar)	?			

<sup>+</sup>HTT = Highest Temperature Treatment

#### Solution Zn Concentration



#### Solution Cu Concentration



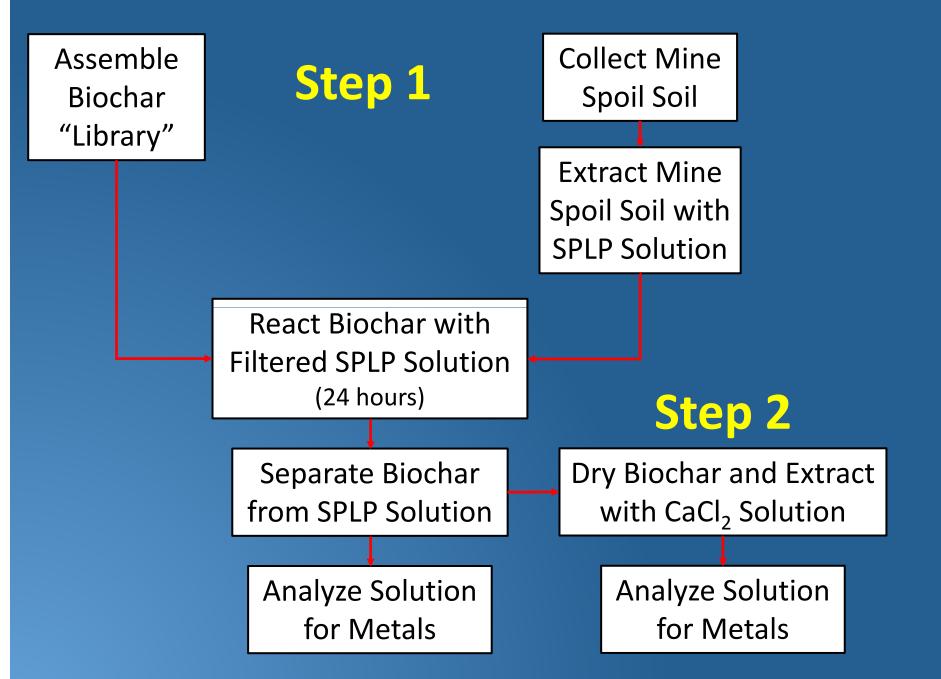
#### % Removal of Initial Metal Concentrations in SPLP<sup>+</sup> Extract of Formosa Mine Soil After 24 Hour Contact with Biochar

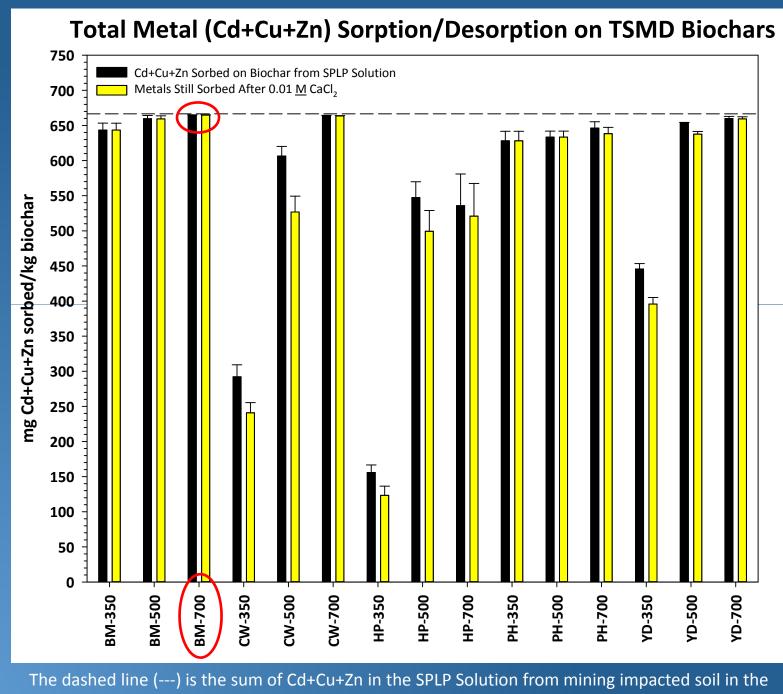
	Formosa	SPLP Solution	Mean Metal	Concentratio	ons (ppm)	
	Zn	Mn	Cu	Cd	Ni	
	8444.62	630.23	260.46	59.00	16.42	
Biochar Code	% Zn Removal	% Mn Removal	% Cu Removal	% Cd Removal	% Ni Removal	Sum of Removal Percentages
ARS-Wood	100.00	100.00	100.00	100.00	100.00	500.00
MIS - 700	100.00	99.98	99.91	100.00	99.99	499.88
ELY - 700	99.99	99.99	99.77	100.00	99.76	499.50
DMB	99.99	99.98	99.48	100.00	99.97	499.42
ADF - 700	99.98	99.59	99.94	99.96	99.52	498.98
SOR - 700	99.92	99.94	99.60	99.89	98.93	498.28
ELY - 500	99.99	99.65	99.32	100.00	99.12	498.08
AD - 700	99.99	99.93	98.98	99.98	99.01	497.89
ADF - 500	99.96	98.36	99.77	99.93	99.38	497.39
ARS-TFSS	99.96	99.91	99.35	100.00	97.83	497.06
ARS-KBSS	99.94	99.72	99.30	99.89	98.12	496.98
MIS - 500	99.99	97.96	99.64	100.00	99.33	496.92
ARS-RiceSS	99.88	98.81	99.86	99.58	98.67	496.81
SOR - 500	99.88	99.88	98.88	99.82	97.85	496.30
AD - 500	100.00	99.73	98.46	99.89	98.10	496.18
SOR - 300	99.60	98.27	98.83	99.75	98.48	494.93
ARS-Char4	99.90	99.88	98.00	99.87	96.43	494.09
ARS-Char5	99.92	99.92	98.09	99.91	96.23	494.07
ARS-Char3	99.91	99.88	97.86	99.87	96.26	493.78
ARS-Char1	99.85	99.82	97.88	99.89	95.50	492.95
GAC	99.22	95.16	100.00	99.33	98.98	492.69
ARS-Char2	99.88	99.79	97.51	99.78	94.80	491.75
HNS - 700	99.85	91.53	99.78	99.77	98.30	489.23
AD - 300	99.11	94.32	99.05	99.74	96.56	488.77
ADF - 300	99.52	89.79	99.38	99.64	98.03	486.36
ELY - 300	97.22	91.25	99.49	98.96	95.01	481.92
OWO - 500	95.47	90.48	99.69	99.85	92.06	477.54
OWO - 700	96.81	86.88	99.88	99.70	91.63	474.91
MIS - 300	96.70	87.43	99.35	98.25	92.57	474.29
HNS - 500	93.54	84.61	99.48	96.26	90.62	464.51
OWO - 300	92.09	88.01	98.95	93.94	89.73	462.72
DF - 700	90.25	85.61	99.86	91.84	92.63	460.19
HNS - 300	89.81	83.18	99.30	94.88	89.68	456.86
DF - 500	82.08	79.48	99.78	84.58	84.06	429.98
SBG - 700	81.92	79.90	98.75	85.00	82.41	427.99
SBG - 500	83.07	80.69	97.42	84.76	80.12	426.06
SBG - 300	81.61	79.21	92.58	82.03	79.57	415.00
DF - 300	78.61	78.31	86.11	79.04	79.13	401.20
	<sup>†</sup> SPLP = Svnt	hetic Precipitat	ion Leaching P	rotocol (EPA M	lethod 1312)	

# **Screening Biochars**

### **Three step laboratory process:**

- Challenge candidate biochars (we use biochars from our "Biochar Library") with SPLP<sup>+</sup> extract of metal contaminated soil
- 2. Determine metal binding characteristics of tested biochars
- Select "best" biochars, as indicated from #1 and #2 above, and conduct a direct Soil:Biochar incubations, greenhouse studies, etc. to determine best performing biochar and the possible need for other amendments





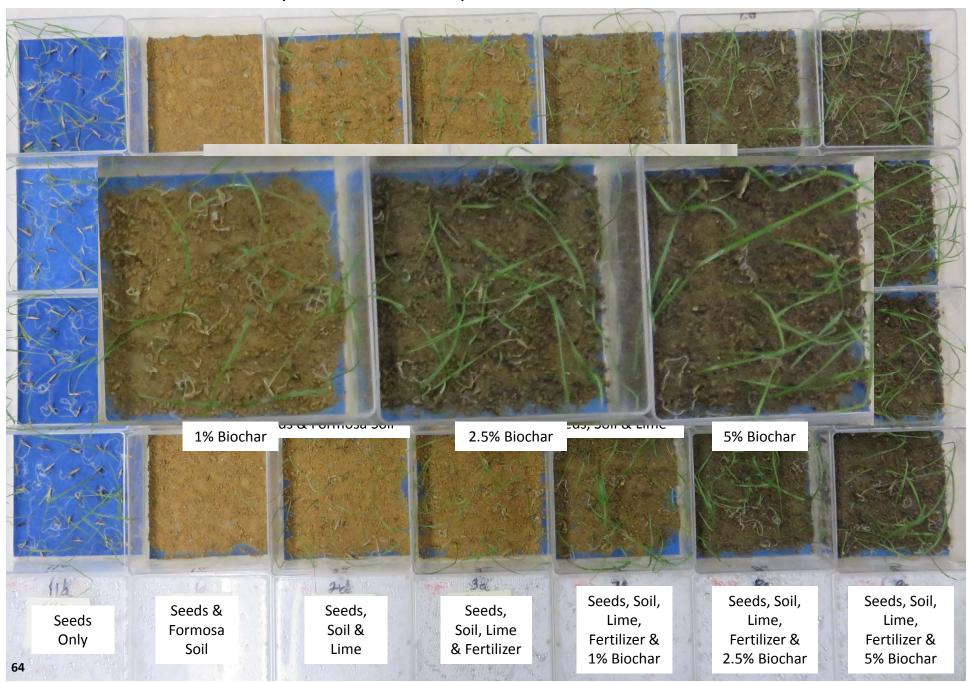
Tri-State Mining District site near Webb City, MO

# **Screening Biochars**

### **Three step laboratory process:**

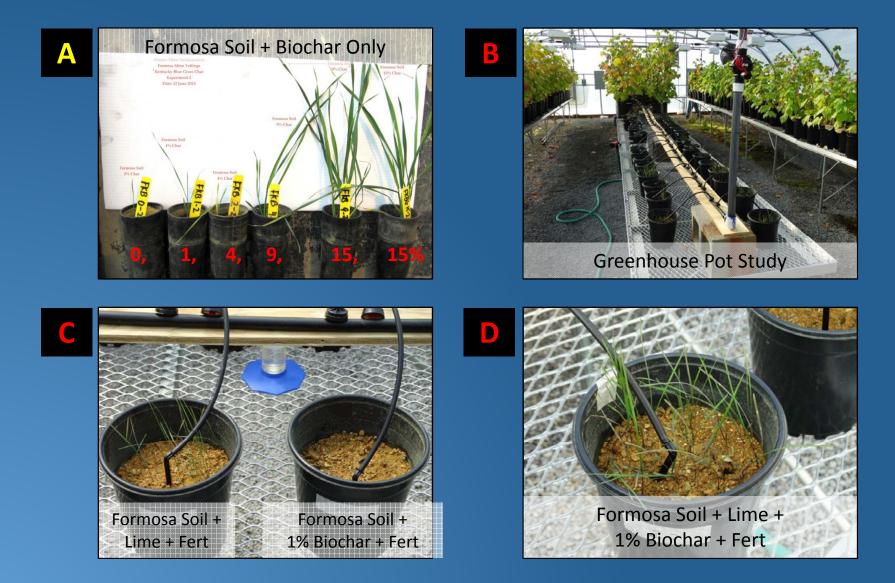
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<sup>+</sup>Synthetic Precipitation Leaching Protocol (EPA SW-846 Test Method 1312) http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf



#### Seed Germination Study: Formosa Mine Spoil Soil, Amendments and Miscanthus Biochar

### **Greenhouse Treatability Studies**



#### Formosa III GH Study – 8 17 17 – Blue Wildrye 104 Days After Planting



Soil Only



Soil + Lime



Soil + Biosolids



Soil + Lime + Biosolids



Soil + Lime + Biosolids + 1% Biochar



Soil + Lime + Biosolids + 2.5% Biochar

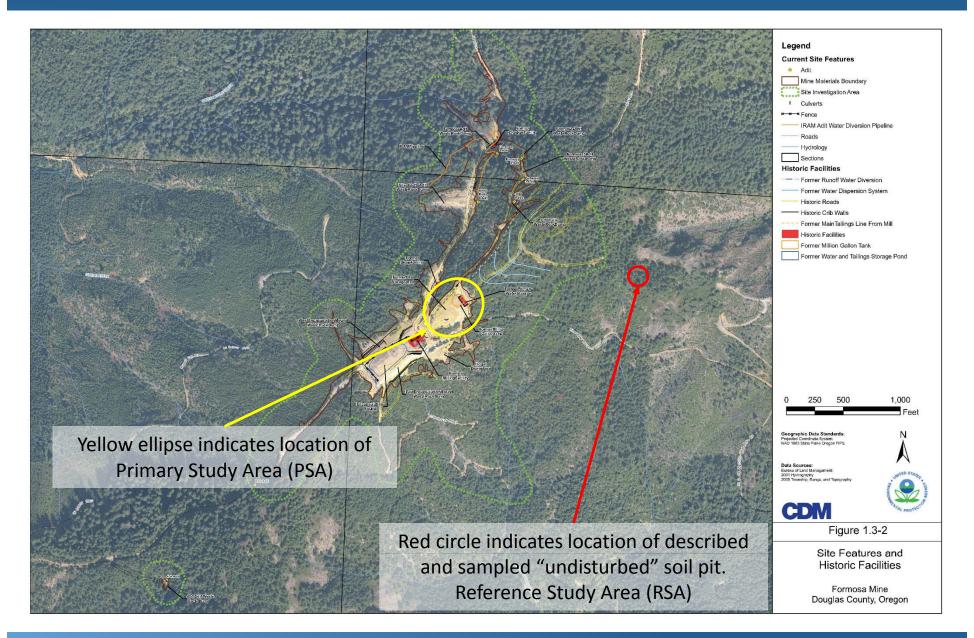


Soil + Lime + Biosolids + 5% Biochar

## **Establishing Remediation Targets**

- Once you know what the problems are at your site, you need to determine the extent of adjustment required to provide sufficient site remediation to establish a sustainable native plant community
- Compare the properties of your site to that of proximal "undisturbed" site
  - How different are they?
  - What needs to be adjusted?
- Develop soil remediation/amendment plan
   Prioritizing remediation activities

#### Formosa Mine Site Example

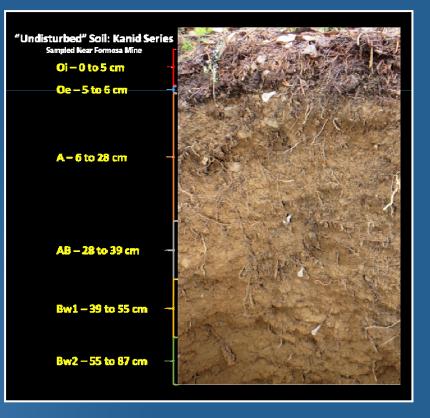


## **Formosa Mine Remediation - Target Soil**

#### "Spoil Soil"



#### **Target Soil**



### **Setting Goals and Tracking Progress**

#### • Target Soil

- Has properties that approximates soil conditions prior to alteration or disturbance
- May be difficult to locate
- May set unrealistic expectations
- What parameters are important to the remediation?
- Setting Goals
  - What is achievable?
- Remediation priorities
  - Most important
  - Next important...

#### Formosa Mine Example

Count	Parameter	Units	Range	Target Soil	Actual
1	рН	рН	2.0 - 7.5	5.5	2.6
2	Σtoxic metals <sup>-1</sup>	ppm <sup>-1</sup>	0 - 50	50	0.0001
3	Base Saturation	%	0 - 75	55	5
4	тос	%	0.1 - 3.5	2.9	0.3
5	TN	%	0.01 - 0.35	0.3	0.03
6	Bulk Density	gcm <sup>-3</sup>	1.0 - 1.5	1.2	1.5
7	Ksat	µmsec <sup>-1</sup>	0 - 100	100	15
8	Microbes (Total PFLA)	nmole/g soil	0 - 500	450	85

## Radar Plots: Setting Goals and Tracking Progress

