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 over-fertilization 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?

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    - 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 over-fertilization 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_2 from the atmosphere)

Mining Impacted Soils

Abandoned Almeda Mine, Galice, Oregon USA

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

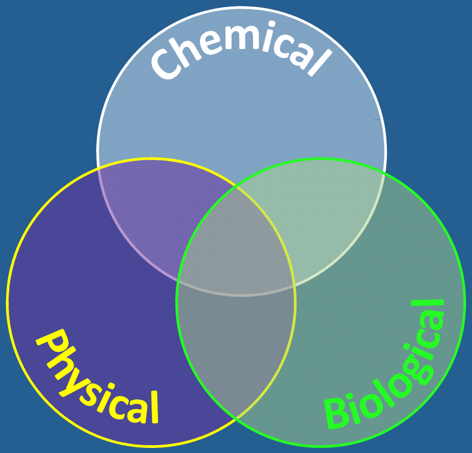
Mining Impacted Soils

“Native Sub-Soil” Surface After Removal of Mine Spoil Overburden

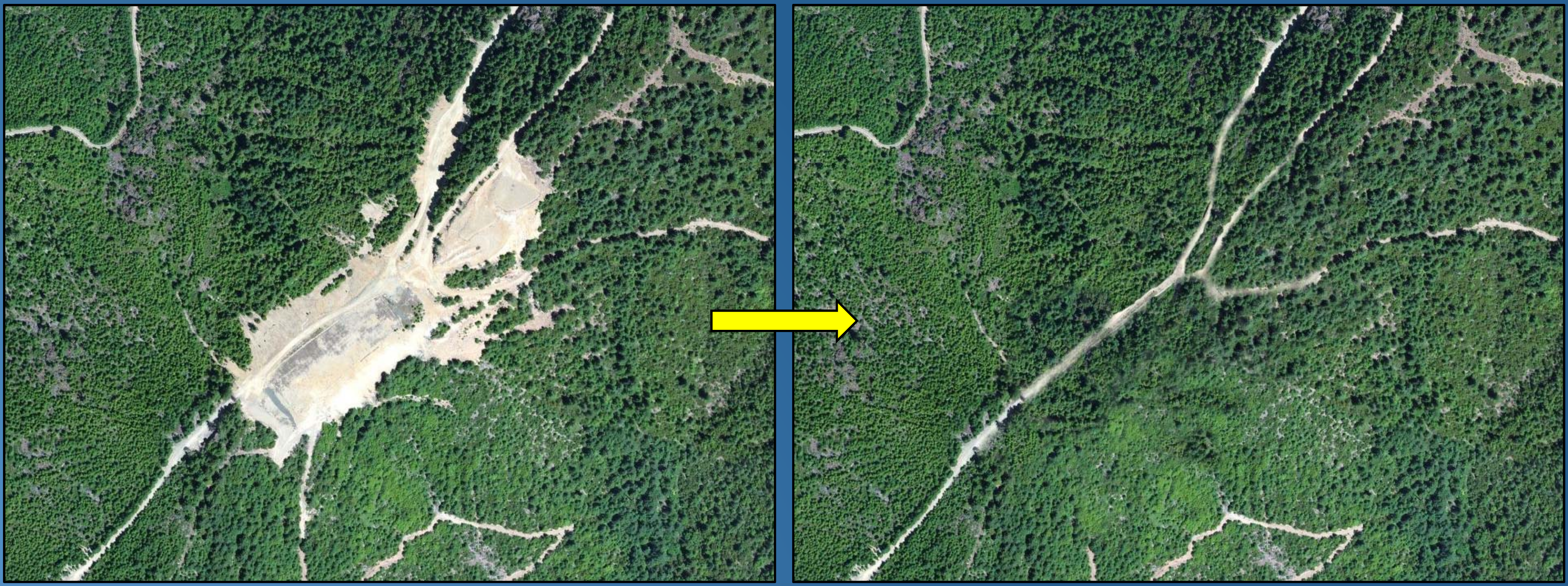
Appearance after three attempts of hydro-seeding "Native Soil"

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…

European Journal of Soil Science

Suitability of biochars (pyro- and hydrochars) for metal immobilization on former sewage-field soils

Journal of Hazardous Materials

Screening biochars for heavy metal retention in soil: Role of oxygen functional groups

Journal of Environmental Quality SPECIAL SECTION
ENVIRONMENTAL BENEFITS OF BIOCHAR

Biochar Reduces Copper Toxicity in *Chenopodium quinoa* Willd. in a Sandy Soil

Bioresource Technology

Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution

Environmental Science & Technology

Evaluation of Biochars and Activated Carbons for In Situ Remediation Of Sediments Impacted With Organics, Mercury, And Methylmercury

Environmental Science & Technology

Influence of Molecular Structure and Adsorbent Properties on Sorption of Organic Compounds to a Temperature Series of Wood Chars

Published March 2012

Journal of Environmental Quality SPECIAL SECTION
ENVIRONMENTAL BENEFITS OF BIOCHAR

Retention of Heavy Metals in a Typic Kandiudult Amended with Different Manure-based Biochars

Journal of Bioscience and Bioengineering
VOL. 116 No. 6, 653–659, 2013

REVIEW

Characteristics of biochar and its application in remediation of contaminated soil

Jingchun Tang, Wenying Zhu, Rai Kookana, and Arata Katayama

ACS Sustainable Chemistry & Engineering

Stabilizing Chromium from Leather Waste in Biochar

Bioresource Technology

Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review

Environmental Pollution

Review

A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils

Luke Beesley, Eduardo Moreno-Jiménez, Jose L. Gomez-Eyles, Eva Harris, Brett Robinson, Tom Sizmur

Journal of Environmental Quality SPECIAL SECTION
ENVIRONMENTAL BENEFITS OF BIOCHAR

Biochar Produced from Anaerobically Digested Fiber Reduces Phosphorus in Dairy Lagoons

Jason D. Streubel, Harold P. Collins, Julie M. Tarara, and Rebecca L. Cochran

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

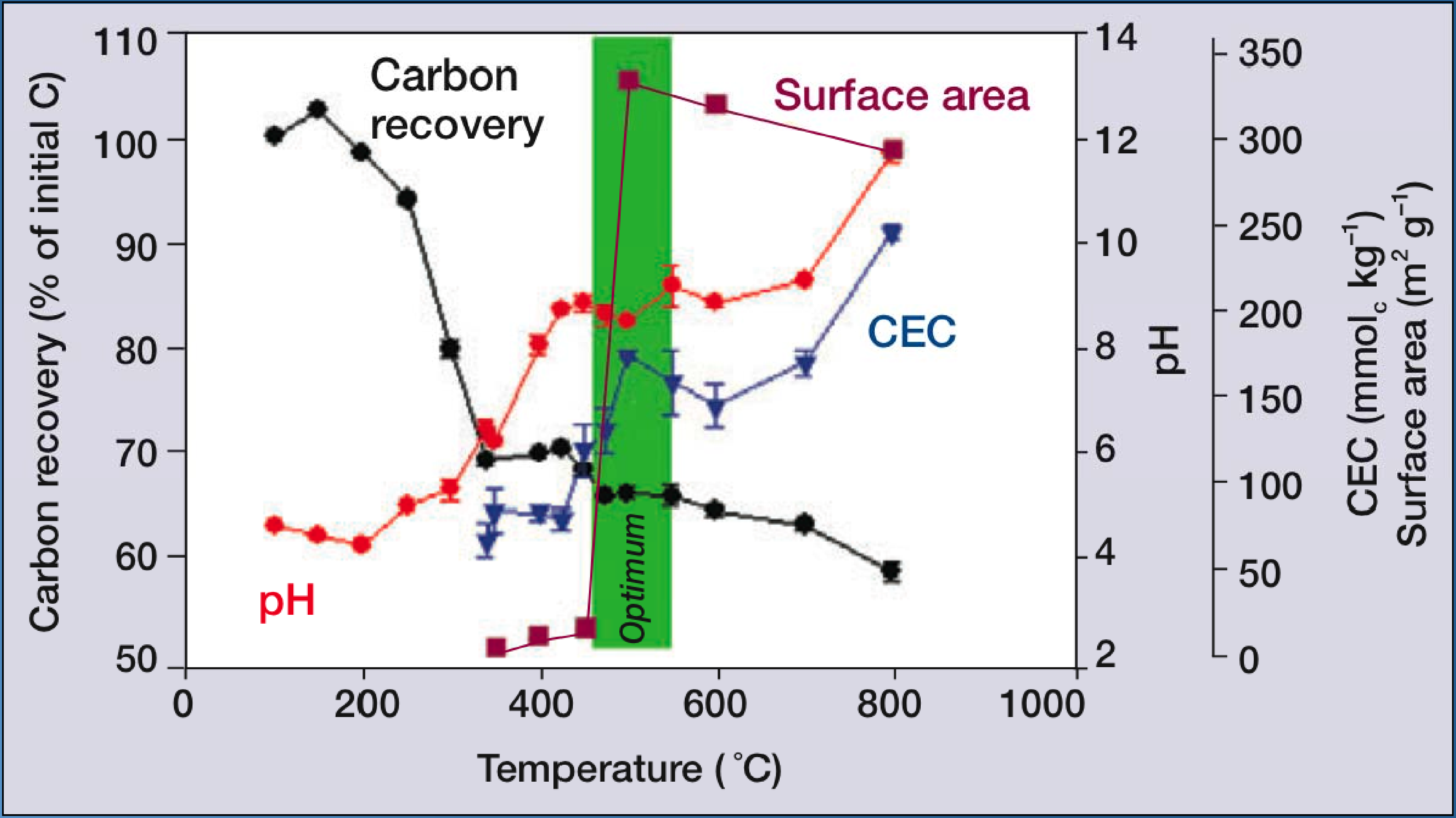
Adapted from Shrestha and Lal, 2006

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.

Slide - J.M. Novak

Biochar Properties



Properties of pyrolyzed Robinia pseudacacia.
From Lehmann 2007

Biochar characterization: Nutrients

Feedstock	Pyrolysis (°C)	Fertilizer equivalent ratio (kg/t biochar)			Source
		N	P	K	
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	↑ 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†

**Novak et al., 2014*

†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 adsorption, precipitation, and complexation 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

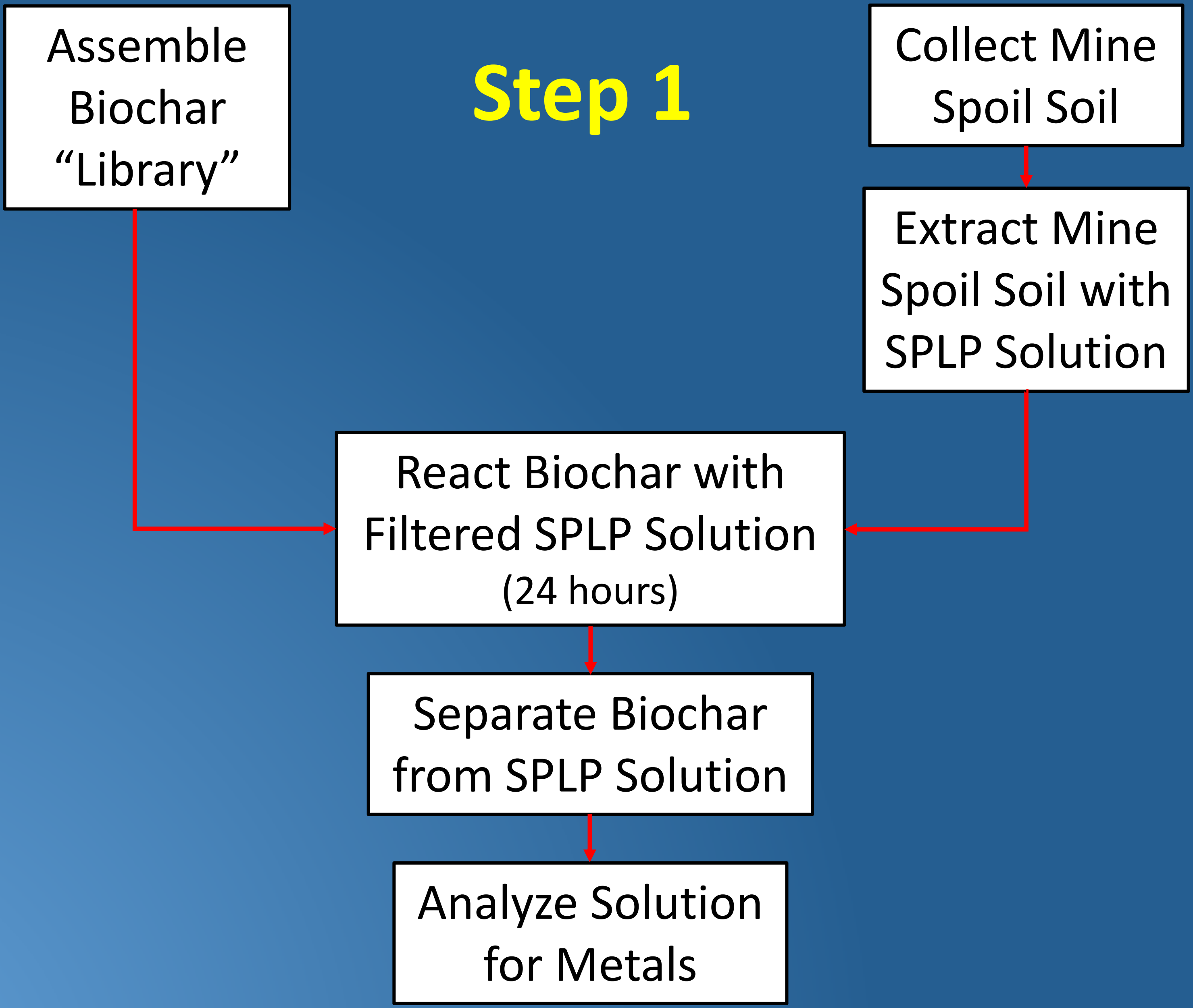
Screening Biochars

Three step laboratory process:

1. Challenge candidate biochars (we use biochars from our "Biochar Library") with SPLP[†] extract of metal contaminated soil
2. Determine metal binding characteristics of tested biochars
3. 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

[†] **Synthetic Precipitation Leaching Protocol (EPA SW-846 Test Method 1312)**
http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf

Step 1



Assemble Biochar "Library"

Collect Mine Spoil Soil

Extract Mine Spoil Soil with SPLP Solution

React Biochar with Filtered SPLP Solution (24 hours)

Separate Biochar from SPLP Solution

Analyze Solution for Metals

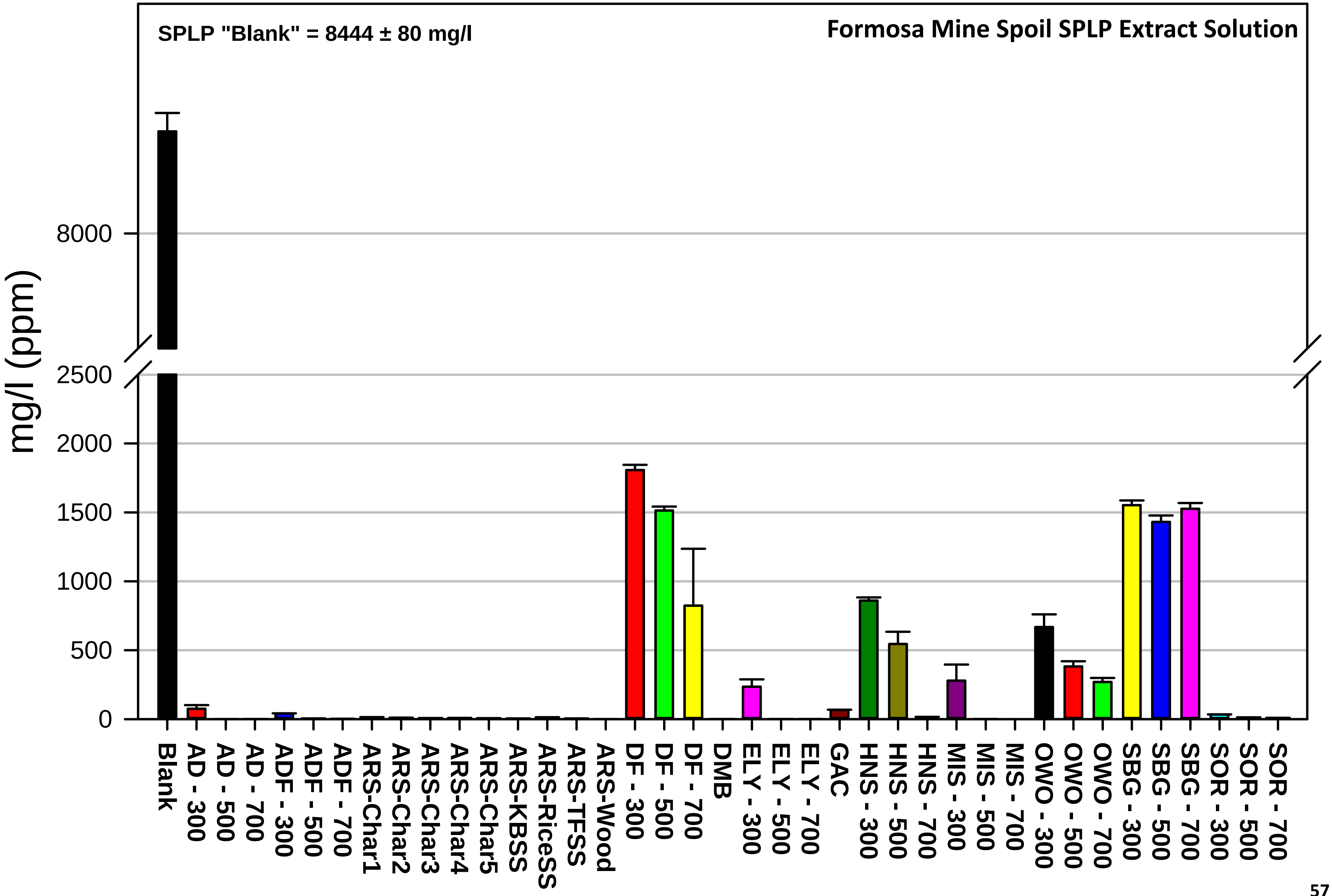
Biochar Library - Formosa Mine Spoil Screening

Sample Code	Feedstock	HTT (°C)[†]
AD - 300	Arundo donax	300
AD - 500	Arundo donax	500
AD - 700	Arundo donax	700
ADF - 300	Anaerobically Digested Fiber	300
ADF - 500	Anaerobically Digested Fiber	500
ADF - 700	Anaerobically Digested Fiber	700
ARS-Char1	ARS Char 1	?
ARS-Char2	ARS Char 2	?
ARS-Char3	ARS Char 3	?
ARS-Char4	ARS Char 4	?
ARS-Char5	ARS Char 5	?
ARS-KBSS	ARS Kentucky Bluegrass Seed Screenings	?
ARS-RiceSS	ARS Rice Seed Screenings	?
ARS-TFSS	ARS Tall Fescue Seed Screenings	?
ARS-Wood	ARS Wood (tree tops)	?
DF - 300	Douglas fir	300
DF - 500	Douglas fir	500
DF - 700	Douglas fir	700
DMB	Dairy Manure (Enchar)	?

Sample Code	Feedstock	HTT (°C)[†]
ELY - 300	Elymus glaucus	300
ELY - 500	Elymus glaucus	500
ELY - 700	Elymus glaucus	700
GAC	Granulated Activated Charcoal	?
HNS - 300	Hazelnut shells	300
HNS - 500	Hazelnut shells	500
HNS - 700	Hazelnut shells	700
MIS - 300	Miscanthus	300
MIS - 500	Miscanthus	500
MIS - 700	Miscanthus	700
OWO - 300	Oregon White Oak	300
OWO - 500	Oregon White Oak	500
OWO - 700	Oregon White Oak	700
SBG - 300	Spent Brewer's Grain	300
SBG - 500	Spent Brewer's Grain	500
SBG - 700	Spent Brewer's Grain	700
SOR - 300	Sorghum	300
SOR - 500	Sorghum	500
SOR - 700	Sorghum	700

[†] HTT = Highest Temperature Treatment

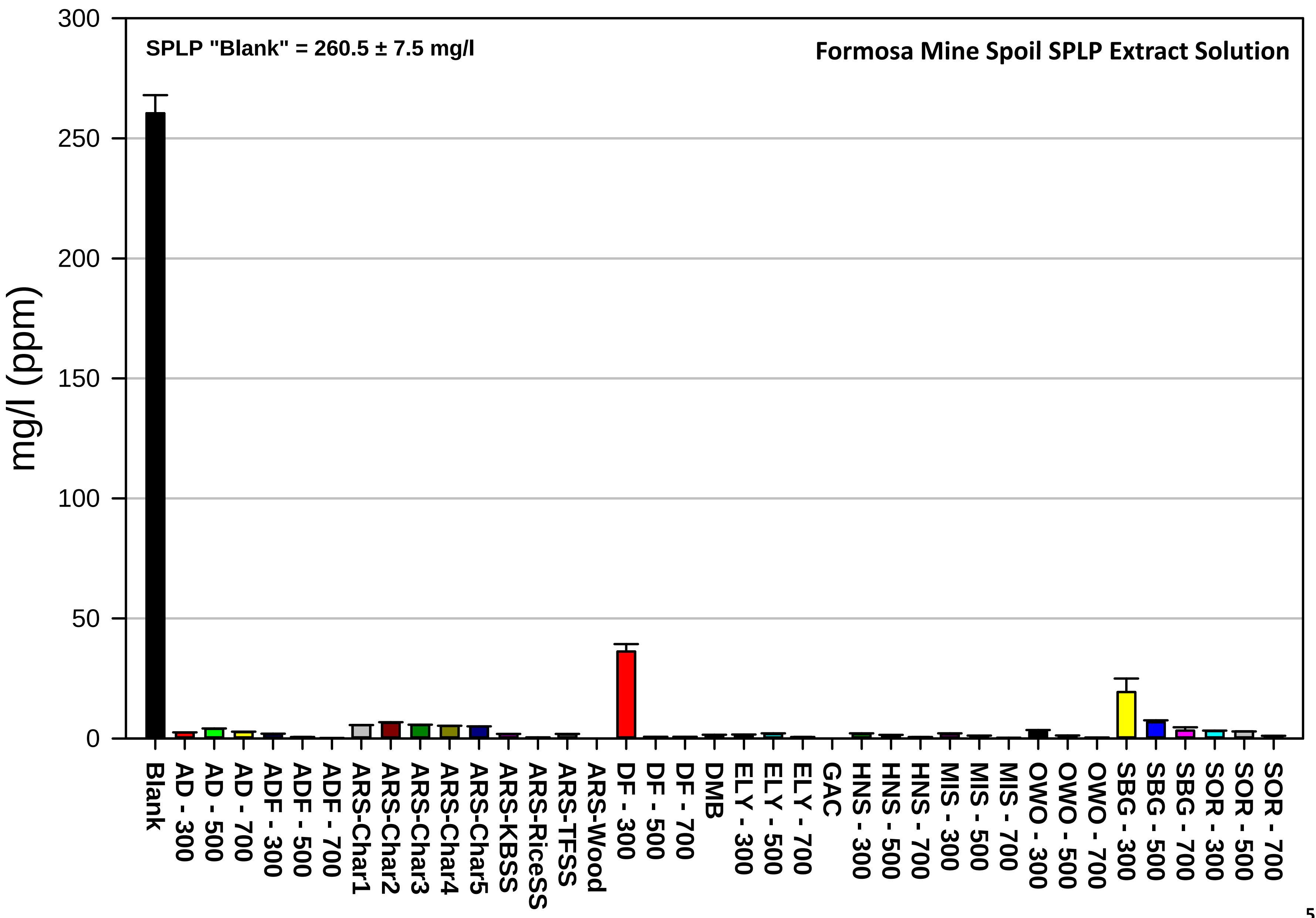
Solution Zn Concentration



SPLP "Blank" = 8444 ± 80 mg/l

Formosa Mine Spoil SPLP Extract Solution

Solution Cu Concentration



% Removal of Initial Metal Concentrations in SPLP[†] Extract of Formosa Mine Soil After 24 Hour Contact with Biochar

Formosa SPLP Solution Mean Metal Concentrations (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

[†] SPLP = Synthetic Precipitation Leaching Protocol (EPA Method 1312)

Screening Biochars

Three step laboratory process:

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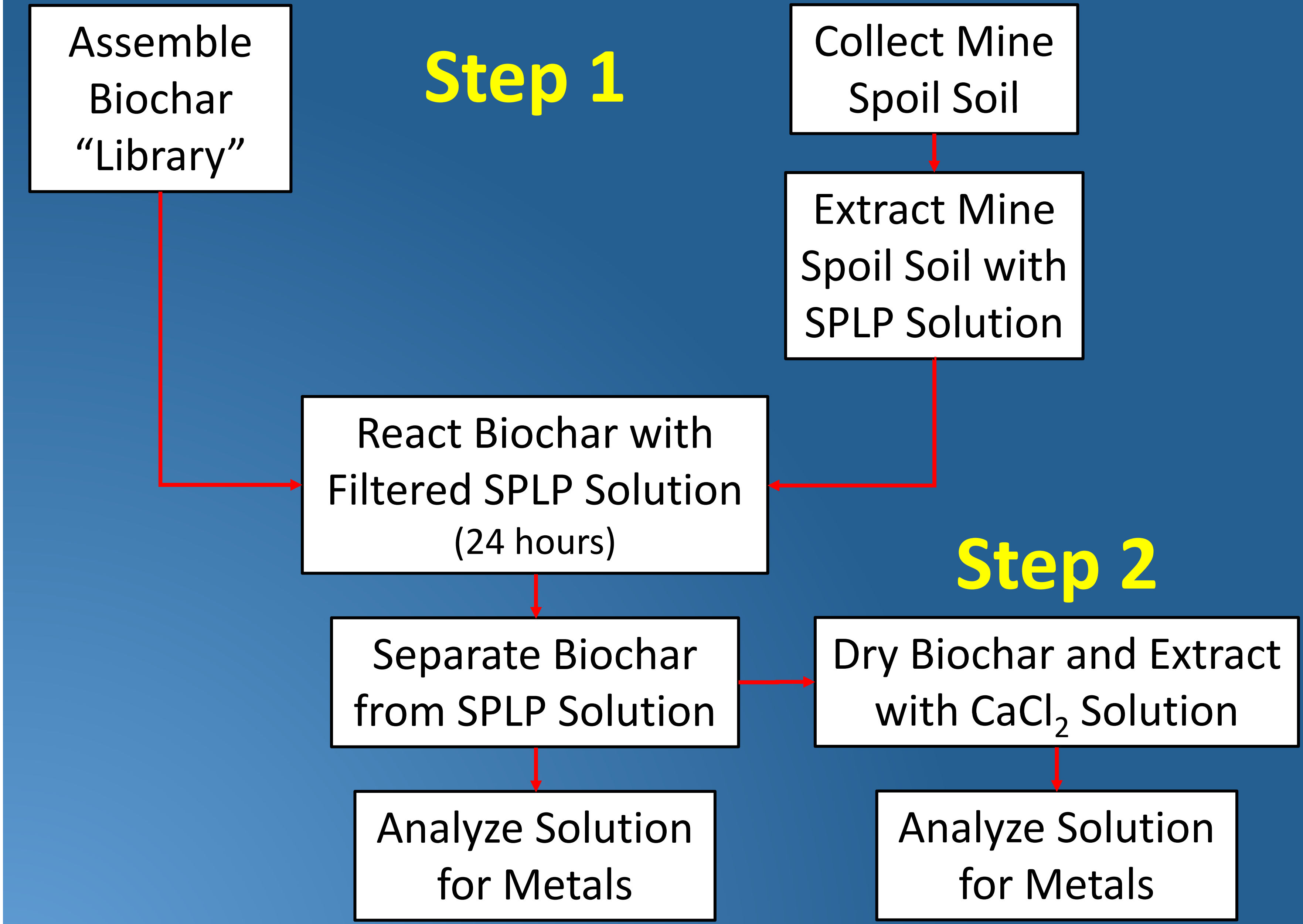


Step 1

Assemble Biochar "Library"

Collect Mine Spoil Soil

Extract Mine Spoil Soil with SPLP Solution

React Biochar with Filtered SPLP Solution (24 hours)

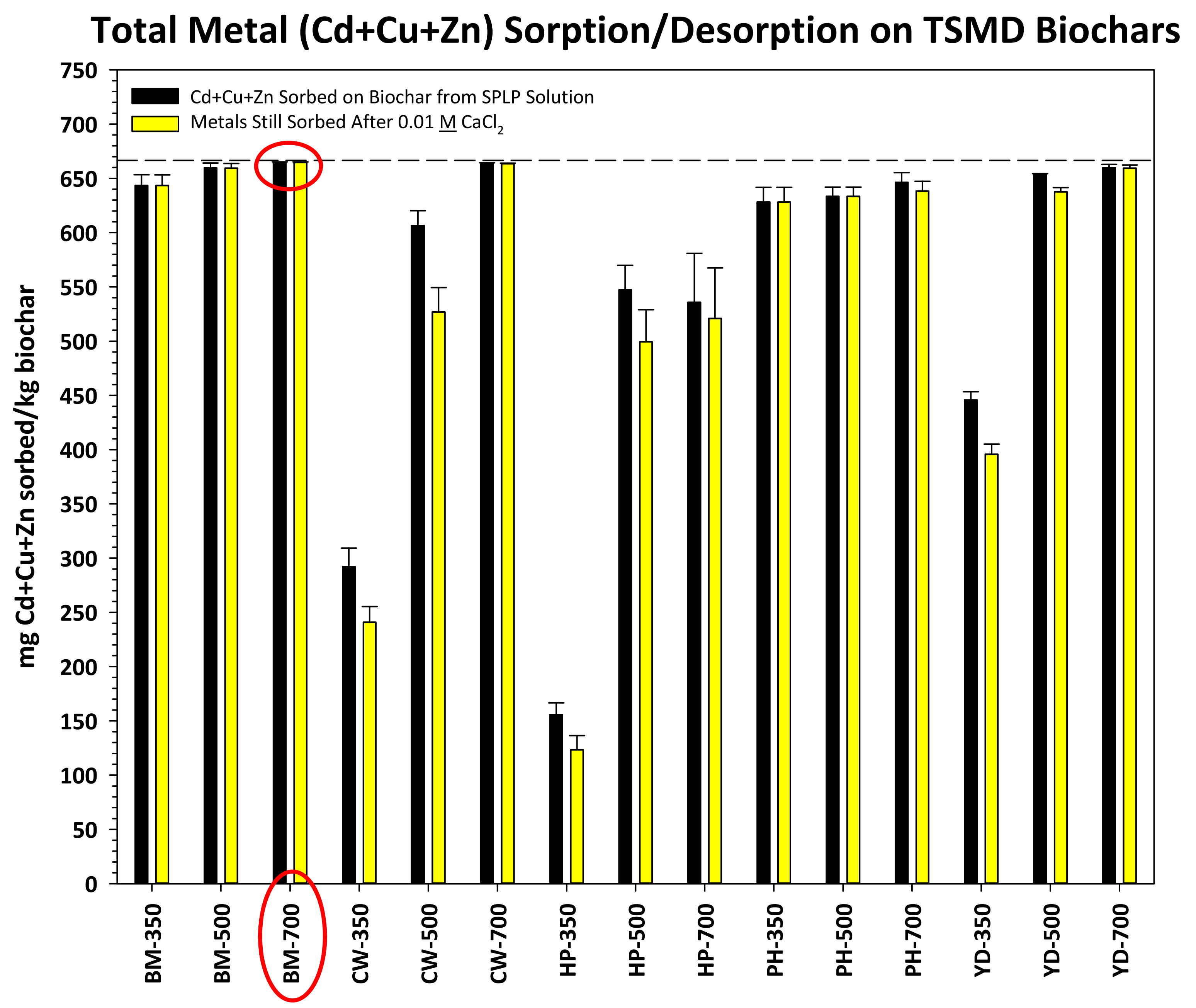
Separate Biochar from SPLP Solution

Analyze Solution for Metals

Step 2

Dry Biochar and Extract with $CaCl_2$ Solution

Analyze Solution for Metals



The dashed line (---) is the sum of Cd+Cu+Zn in the SPLP Solution from mining impacted soil in the Tri-State Mining District site near Webb City, MO

Screening Biochars

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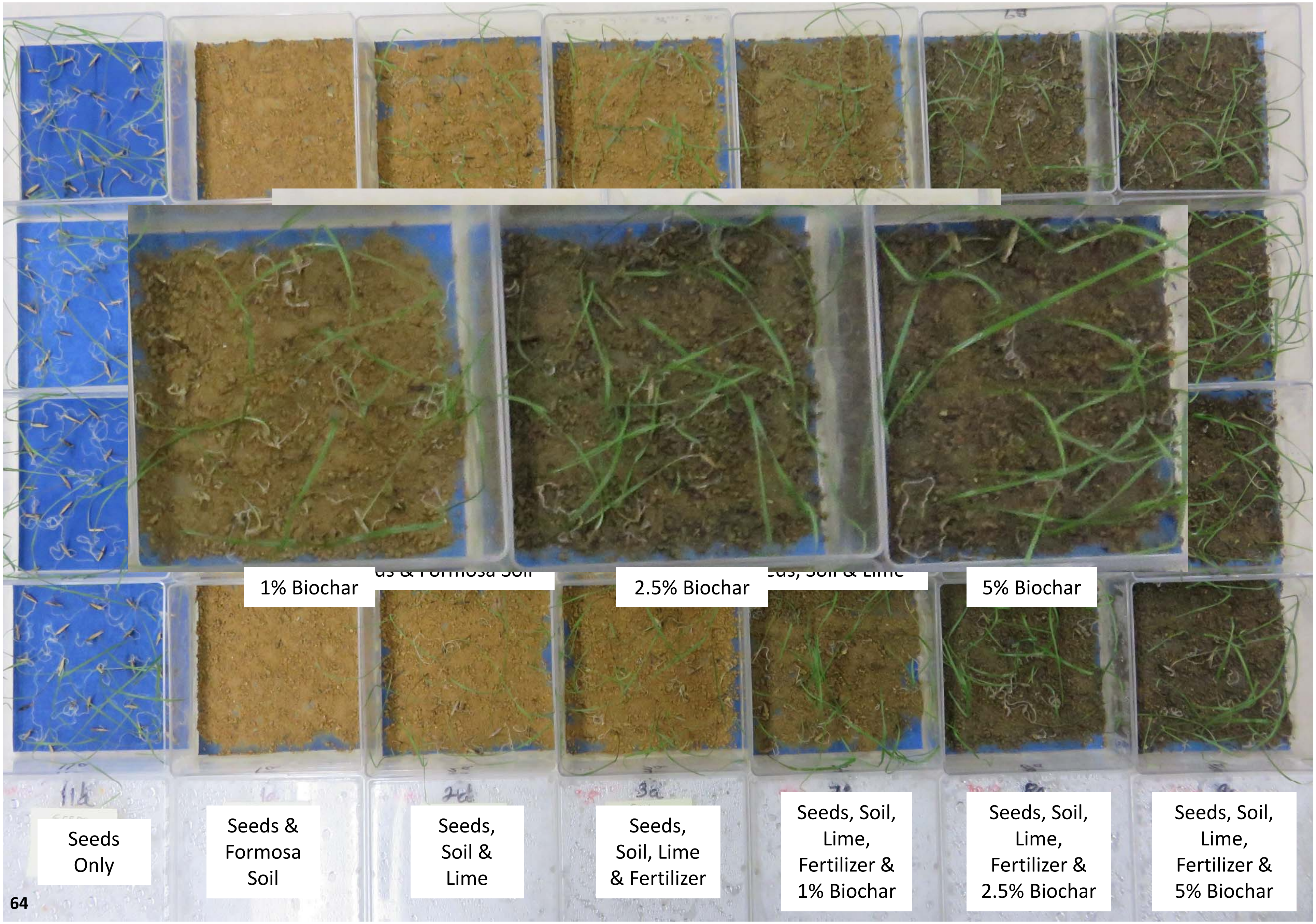
Seed Germination Study: Formosa Mine Spoil Soil, Amendments and Miscanthus Biochar



1% Biochar

2.5% Biochar

5% Biochar

Seeds Only

Seeds & Formosa Soil

Seeds, Soil & Lime

Seeds, Soil, Lime & Fertilizer

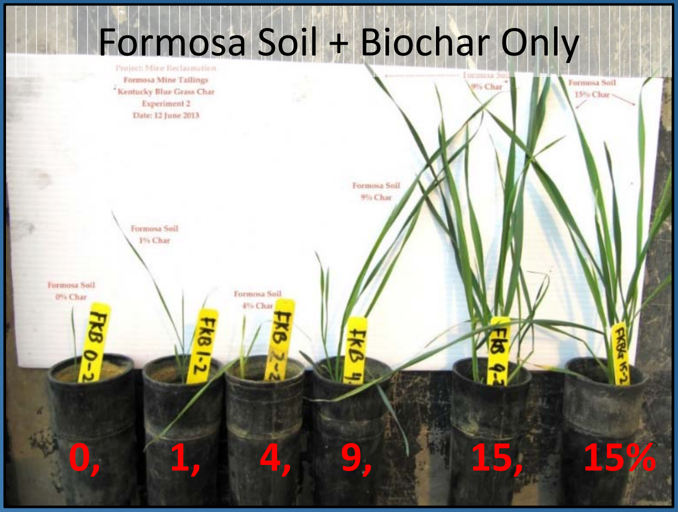
Seeds, Soil, Lime, Fertilizer & 1% Biochar

Seeds, Soil, Lime, Fertilizer & 2.5% Biochar

Seeds, Soil, Lime, Fertilizer & 5% Biochar

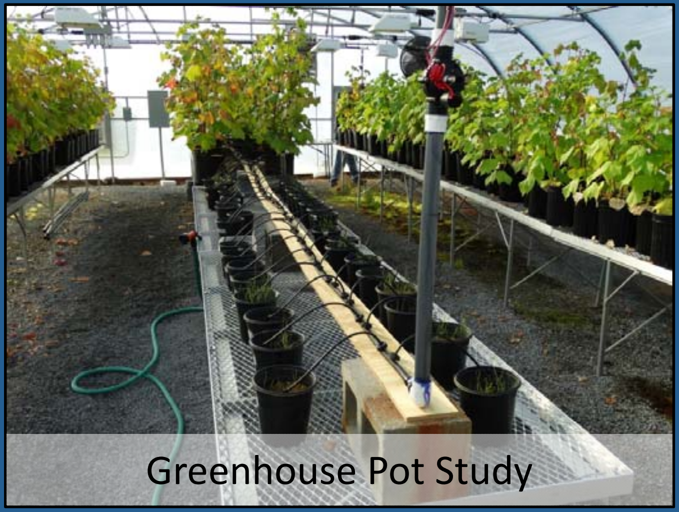
Greenhouse Treatability Studies

A



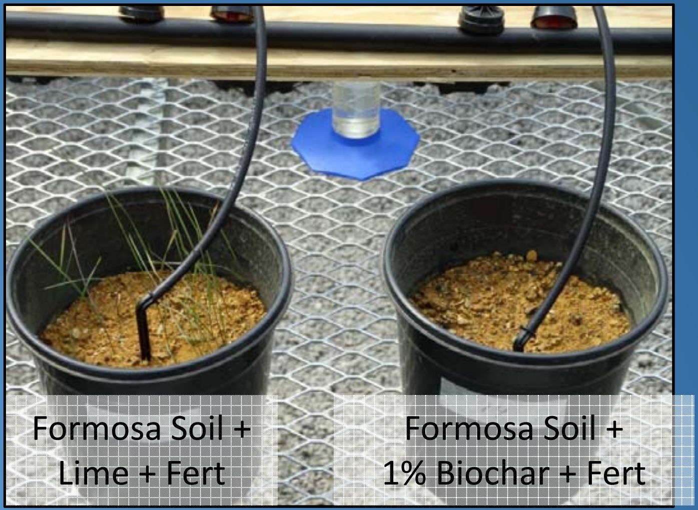
Formosa Soil + Biochar Only

B



Greenhouse Pot Study

C



Formosa Soil + Lime + Fert

Formosa Soil + 1% Biochar + Fert

D

Formosa Soil + Lime + 1% Biochar + Fert

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

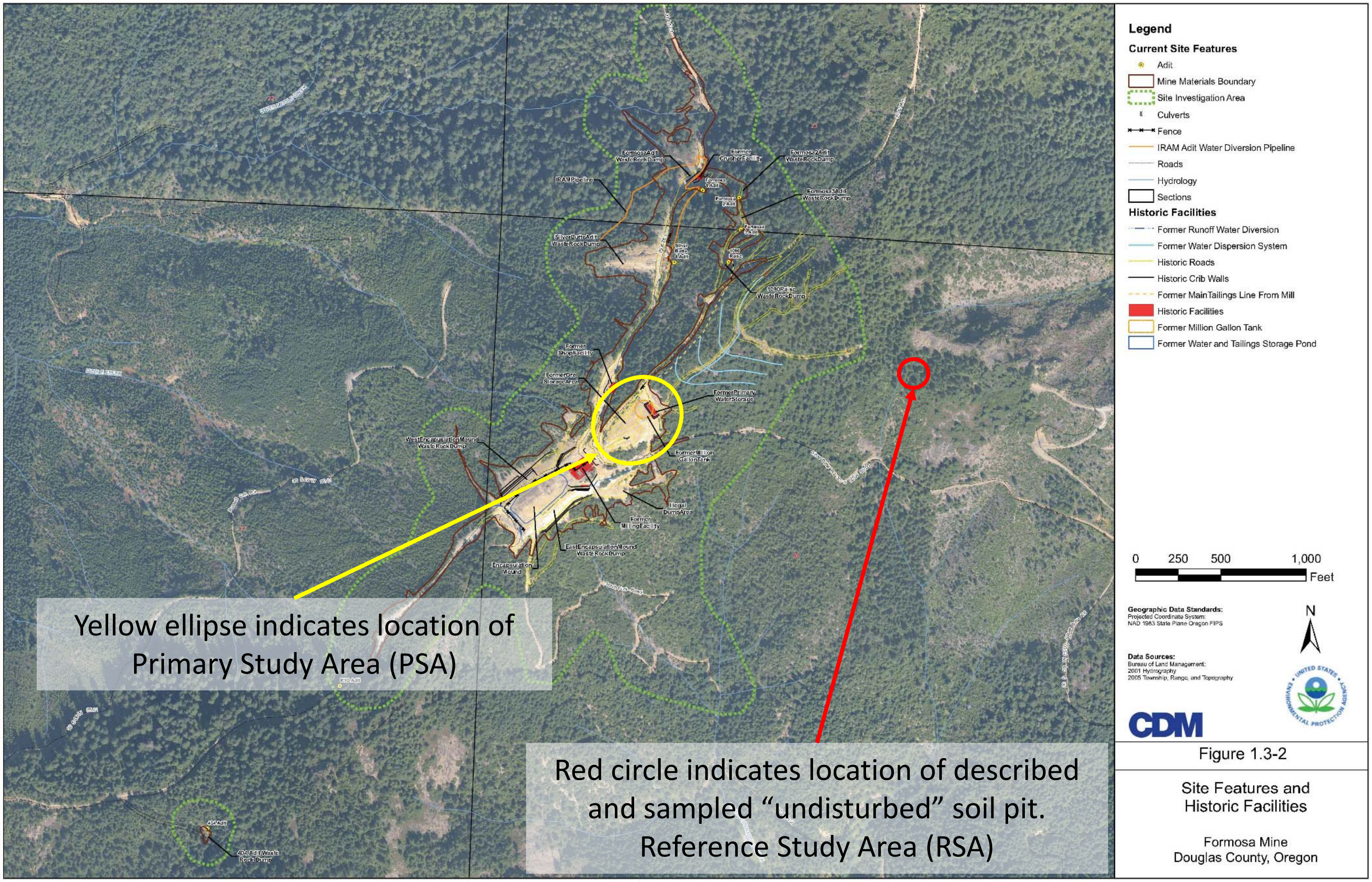
Soil + Lime + Biosolids +
2.5% Biochar

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



Geographic Data Standards:
Projected Coordinate System:
NAD 1983 State Plane Oregon FIPS

Data Sources:
Bureau of Land Management:
2001 Hydrography
2005 Township, Range, and Topography

CDM

Figure 1.3-2

Site Features and
Historic Facilities

Formosa Mine
Douglas County, Oregon

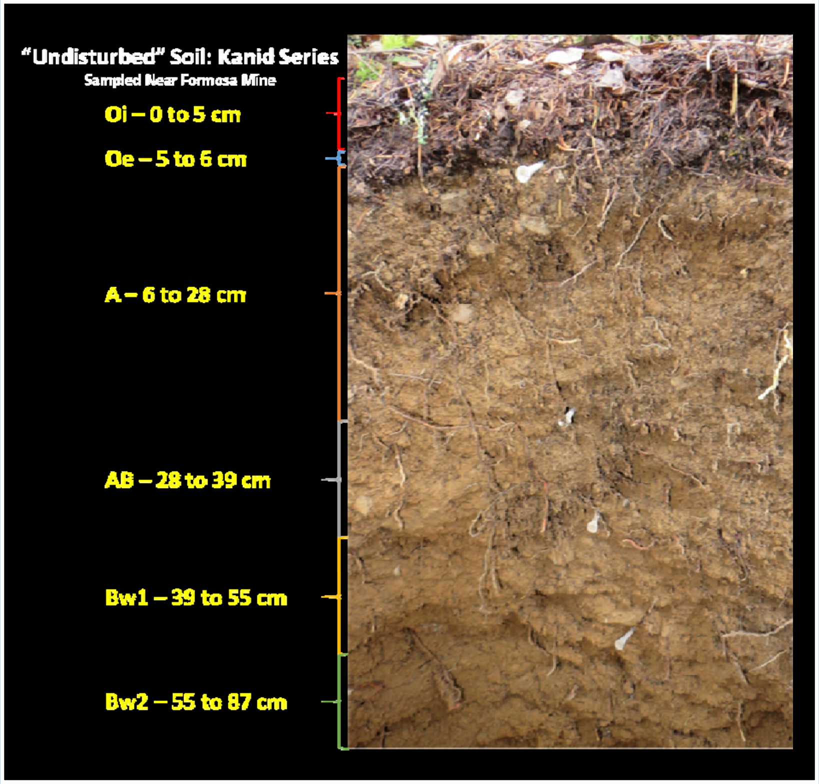
Yellow ellipse indicates location of Primary Study Area (PSA)

Red circle indicates location of described and sampled “undisturbed” soil pit. Reference Study Area (RSA)

Formosa Mine Remediation - Target Soil

“Spoil Soil”

Target Soil



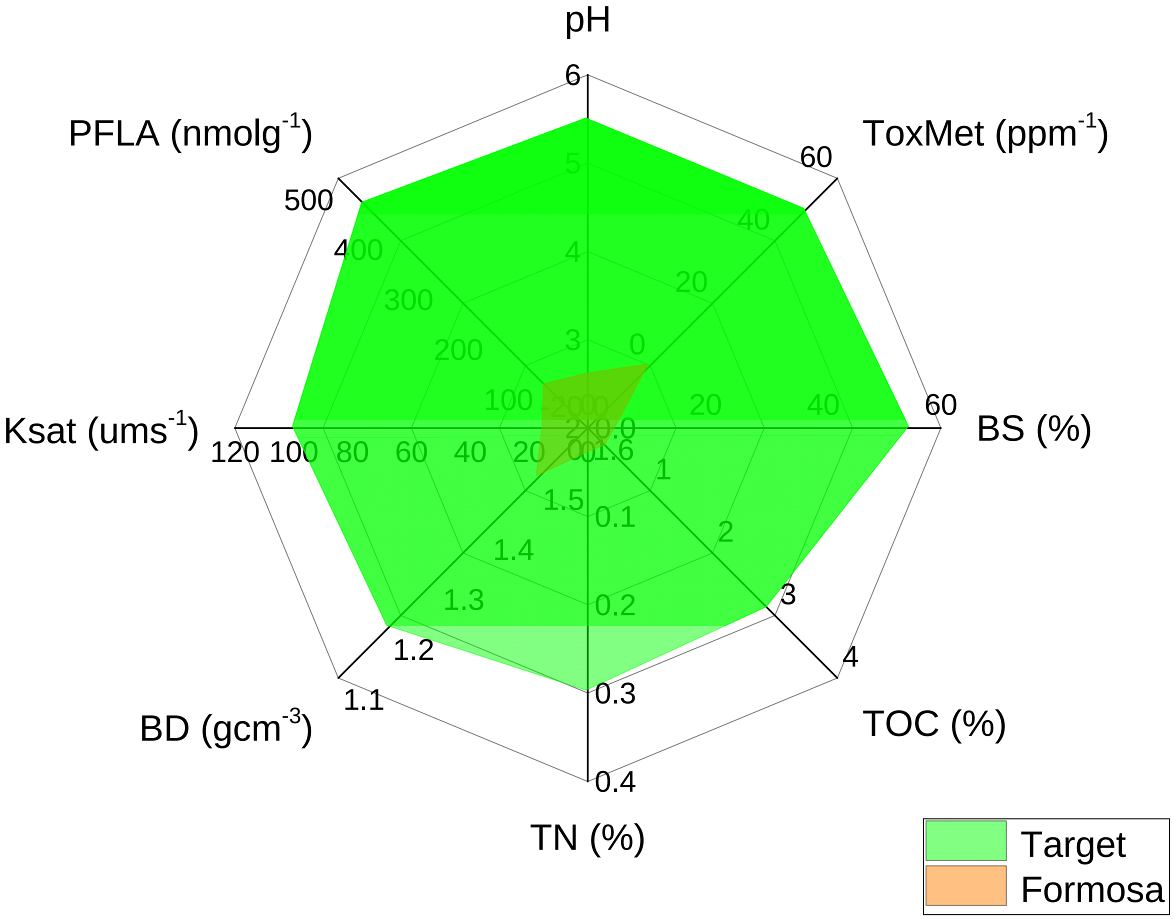
Setting Goals and Tracking Progress

- 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

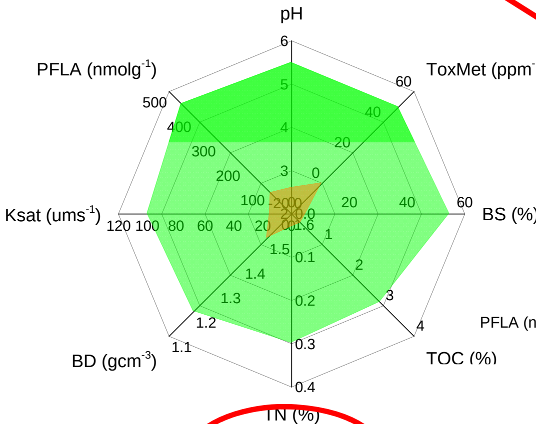
Count	Parameter	Units	Range	Target Soil	Actual
1	pH	pH	2.0 - 7.5	5.5	2.6
2	Σtoxic metals^{-1}	ppm^{-1}	0 - 50	50	0.0001
3	Base Saturation	%	0 - 75	55	5
4	TOC	%	0.1 - 3.5	2.9	0.3
5	TN	%	0.01 - 0.35	0.3	0.03
6	Bulk Density	gcm^{-3}	1.0 - 1.5	1.2	1.5
7	Ksat	μmsec^{-1}	0 - 100	100	15
8	Microbes (Total PFLA)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

Radar Plots: Setting Goals and Tracking Progress



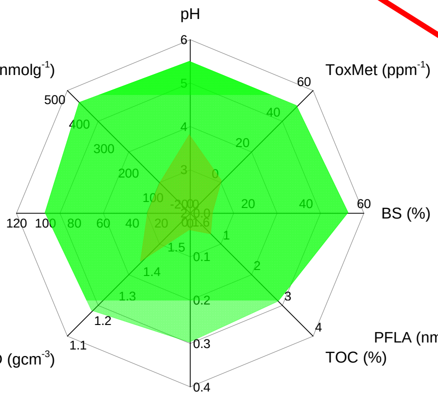
Radar Plots: Setting Goals and Tracking Progress

Time 0



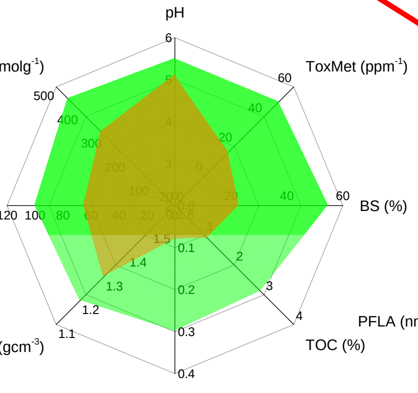
RI = 17.3

Time 1



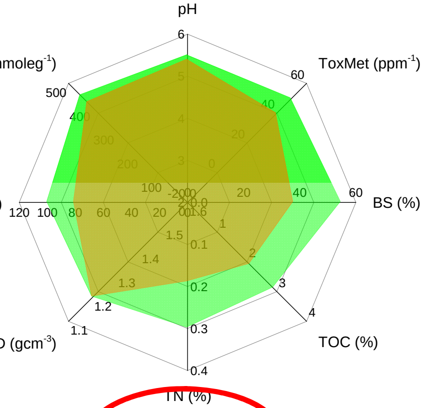
RI = 24.1

Time 2



RI = 50.5

Time 3



RI = 79.9

Time

Remediation Index (RI)

$$RI = \left(\frac{\text{Space of Metrics Covered by Treated Site}}{\text{Space of Metrics Covered by Target Site}} \right) \times 100$$