Contaminated Site Clean-Up Information

Welcome to the CLU-IN Internet Seminar

Mine Tailings: Enumeration and Remediation

Delivered: January 11, 2012, 1:00 PM - 3:00 PM, EST (18:00-20:00 GMT)

Presenters:

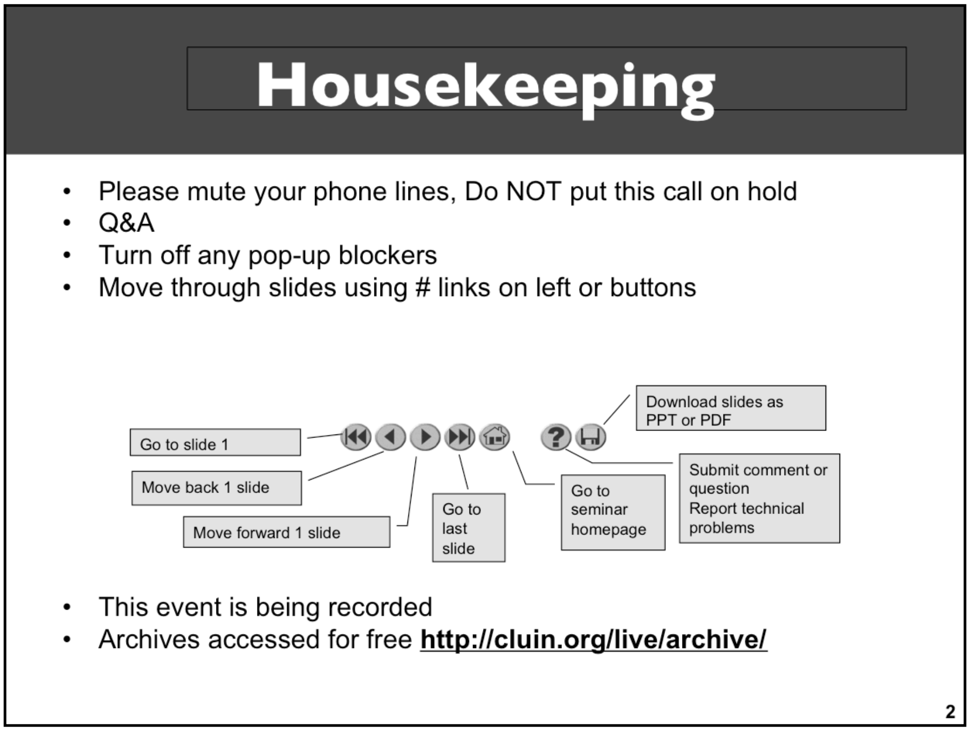
Dr. Eric Betterton, Department of Atmospheric Sciences/Institute of Atmospheric Physics, University of Arizona (better@atmo.arizona.edu)

Dr. Raina Maier, Department of Soil, Water and Environmental Science, University of Arizona (rmaier@ag.arizona.edu)

Moderator:

Sarah T. Wilkinson, Superfund Research Program, University of Arizona (wilkinso@pharmacy.arizona.edu)

Visit the Clean Up Information Network online at www.cluin.org



Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

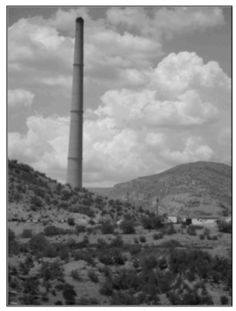
With that, please move to slide 3.

Atmospheric Aerosols from Mining Operations in Hayden and Dewey-Humboldt, AZ

Eric A. Betterton[1,2]; Janae L. Csavina[1]; Jason P. Field[3]; Andrea C. Landázuri[1]; Omar Felix Villar[1]; Kyle P. Rine[2]; A. Eduardo Sáez[1]; Jana Pence[2]; Homa Shayan[1]; Mike Stovern[1] ; MacKenzie Russell[1]

Supported by NIEHS Superfund Research Program

Hayden slag pour



Hayden smelter stack

Dewey-Humboldt tailings

Poisoned Places

Toxic Air, Neglected Communities

NPR News Investigations – November 17, 2011

EPA Takes Action Against Toxic Arizona Copper Plant

"The Environmental Protection Agency has taken tough enforcement action against a copper smelter in Arizona that has drawn complaints about toxic pollution for years.

The unpublicized "finding of violation" issued against the Asarco copper smelter in Hayden, Ariz., claims the company has been continuously emitting illegal amounts of lead, arsenic and eight other dangerous compounds for six years."

"A haze can be seen at night hovering over the Asarco copper smelter, which turns copper ore into nearly pure copper bars."

Effects of dust/aerosols

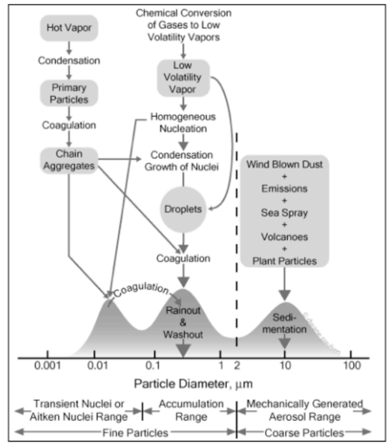
I-10 between PHX and TUS October 4, 2011. Wind gusts 30 to 50+ mph

View of dust storm from Kitt peak, looking north, 3pm

- Public health
- Public safety
  - Role of Particle Diameter
    - Global vs. regional transport
    - Respiratory deposition
    - Associated contaminants
    - Visibility

Mining Operations & Particle Size

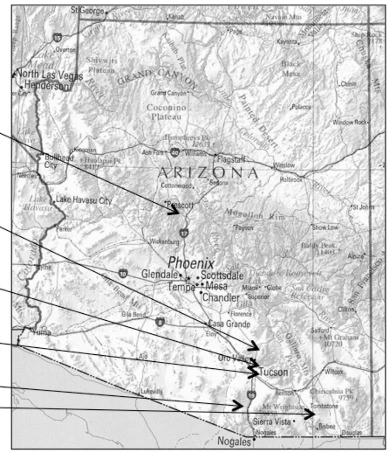
- Crushing, Grinding, Mine Tailings Management
  - Coarse >2.5 μm *(mechanical action)*
- Smelting, Refining
  - Ultra-fine <0.1 μm *(gas to particle conversion)*
  - Accumulation 0.1-2.5 μm *(coagulation of ultrafine and condensation growth)*



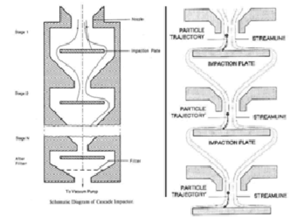
(Seinfeld and Pandis 1998)

Arizona Field Sites

- **Contaminated Sites**
  - **Iron King (Humboldt-Dewey)** - Inactive smelter; now a Superfund site (arsenic, lead contaminated tailings)
  - **Hayden & Winkelman (ASARCO)** - active copper mine with smelter (arsenic, lead contaminated soil; airborne lead)
- **Comparison Sites**
  - **Mount Lemmon** - Remote background
  - **Tucson** - Urban
  - **Green Valley** - Active copper mine; “clean” tailings
  - **Wilcox Playa** - Natural dust source

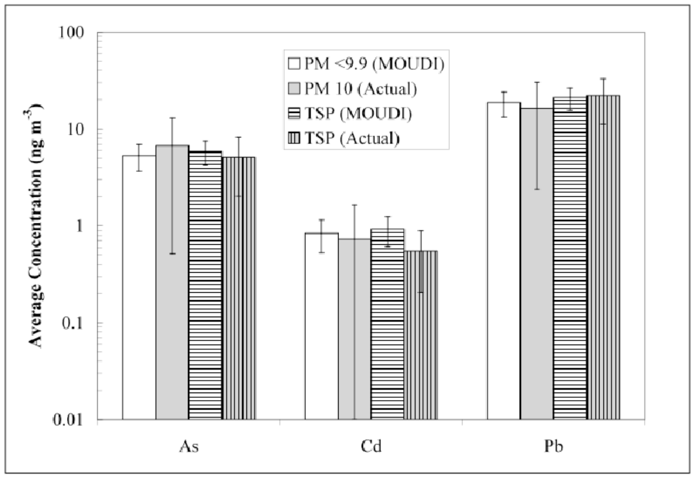


Sampling Techniques



- **MOUDI (Micro-Orifice Uniform Deposit Impactor)**
  - 10 aerosol size fractions on separate stages
  - Cut-point diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18 µm, 0.1 and 0.056 µm
  - 30 L/min flow rate
- **SMPS (Scanning Mobility Particle Sizer™)**
  - Number concentration from 1 to 10^8 particles/cm^3
  - Dp from 2.5 nm to 1.0 µm
- **TSP (Total Suspended Particulate)**
  - High volume sampler (14 ft^3/min)
  - Mass concentration for ambient particulate
  - 24 hour sampling period
- **Weather Station**
  - Wind speed/direction, temperature, relative humidity
- **Dust Flux Monitors**
  - Optical PM-10 measurements

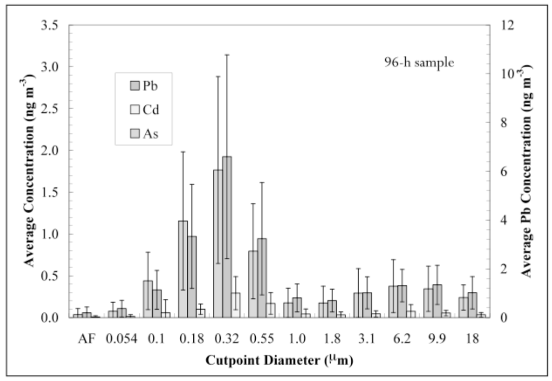
Hayden MOUDI Measurement Verification (ng m^{-3})



Hayden MOUDI
2009 Annual Average (ng m^{-3})

Hayden smelter building

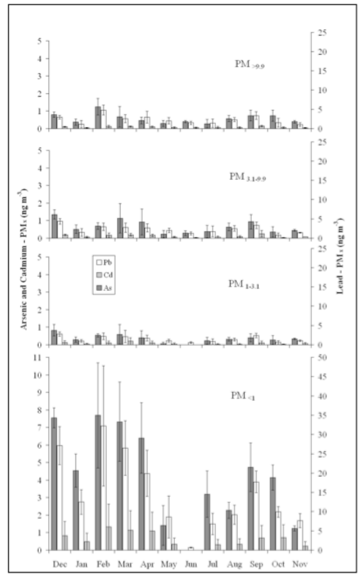
Hayden slag pour



Bimodal size distribution

Hayden MOUDI 2009 Seasonal Average (ng m^{-3})

- MOUDI results for Pb, Cd, and As with monthly averages.
- Majority of metals in fine size fraction.
- Higher mixing height occurs in summer months.
- Smelter shutdown periods apparent



Hayden – NW “smelter”

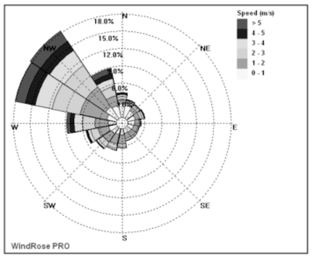
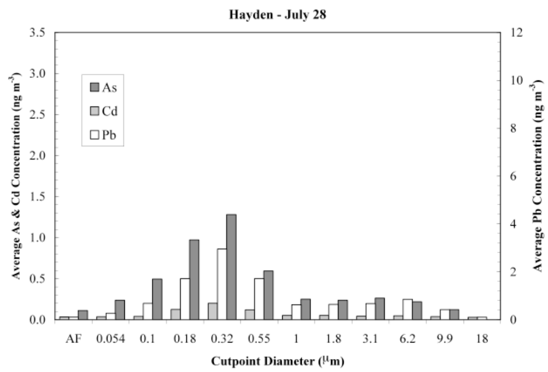


Figure 1. July 28, 2010 MOUDI ON (Programmed 300°-360°)



Hayden – NE "background"

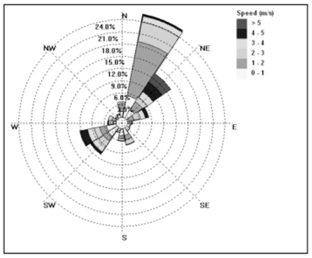
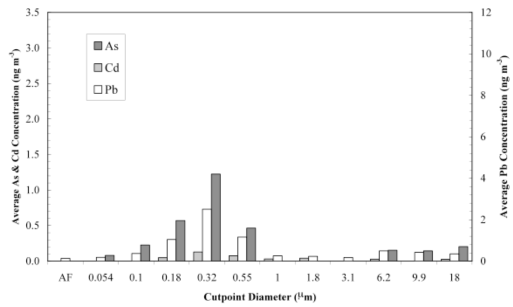
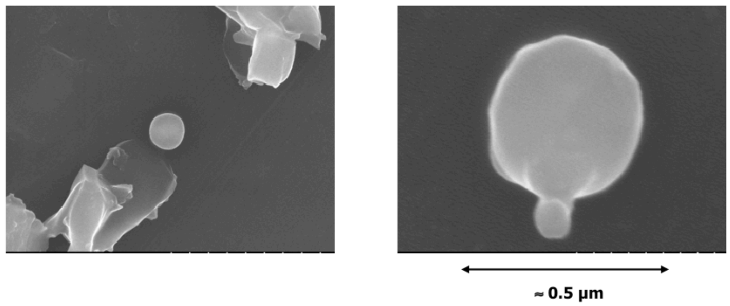


Figure 1. November 16, 2010 MOUDI ON (Programmed 30°- 160°)

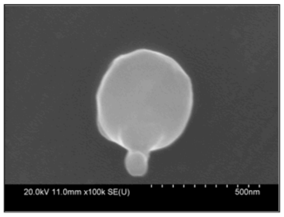


Scanning Electron Microscopy (fine fraction)



•Spherical nature of the arsenic- and lead-containing particles.
•Lead particle shows direct evidence of coagulation with a smaller spherical particle.
•Angular nature of the arsenic-free particles.

Hayden Source Apportionment
SEM with EDS
Particles Containing Lead and Arsenic

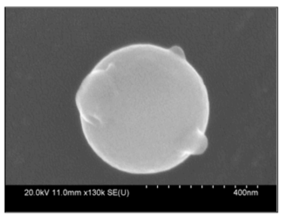


Weight %

	C-K	O-K	Al-K	S-K	Fe-K	Zn-K	Zr-L	Pb-L
Base(13)_pt1	7.47	20.72	54.87	2.06	0.54	1.53	1.93	10.88

Weight % Error (+/- 1 Sigma)

	C-K	O-K	Al-K	S-K	Fe-K	Zn-K	Zr-L	Pb-L
Base(13)_pt1	+/-1.85	+/-0.52	+/-0.19	+/-0.29	+/-0.10	+/-0.22	+/-0.22	+/-1.00



	C-K	O-K	Al-K	Si-K	S-K	Cl-K	Fe-K	Cu-K	As-K	Pt-L
Base(11)_pt1	10.83	22.27	52.12	1.12	0.56	0.24	0.24	9.31	2.32	0.99

Weight % Error (+/- 1 Sigma)

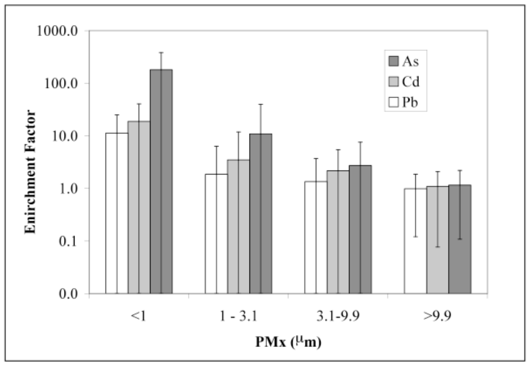
	C-K	O-K	Al-K	Si-K	S-K	Cl-K	Fe-K	Cu-K	As-K	Pt-L
Base(11)_pt1	+/-1.02	+/-0.29	+/-0.18	+/-0.10	+/-0.06	+/-0.02	+/-0.03	+/-0.18	+/-0.31	+/-0.25

Energy-dispersive X-ray microanalysis imagery with SEM of MOUDI samples collected at Hayden showing the existence of arsenic- and lead-containing particles. The elemental analysis is for the areas targeted with a square on each particle.

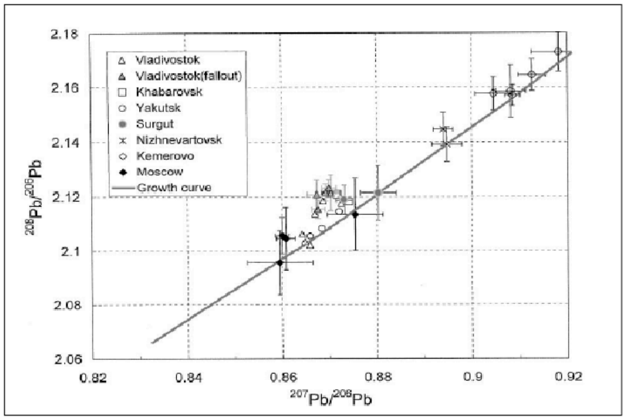
Hayden Enrichment Factors
Smelter Off as Baseline

$$\mathbf{EF} = [C_{n(SmelterON)}/C_{ref(SmelterON)}]/[B_{n(SmelterOFF)}/B_{ref(SmelterOFF)}]$$

n = As, Pb, Cd. **ref** = Sc

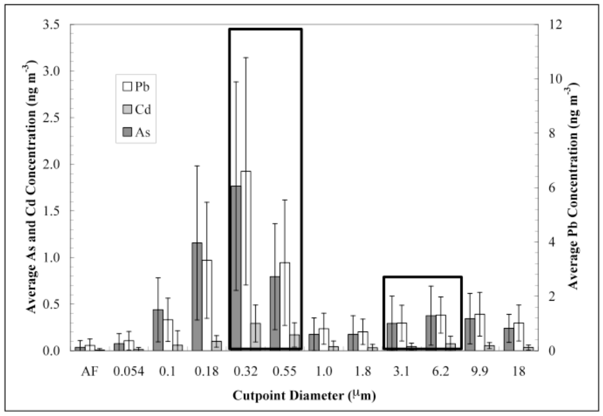


Lead stable isotopes in atmospheric aerosols



Mukai et al., 2001

Fractions for Pb Isotope Analysis



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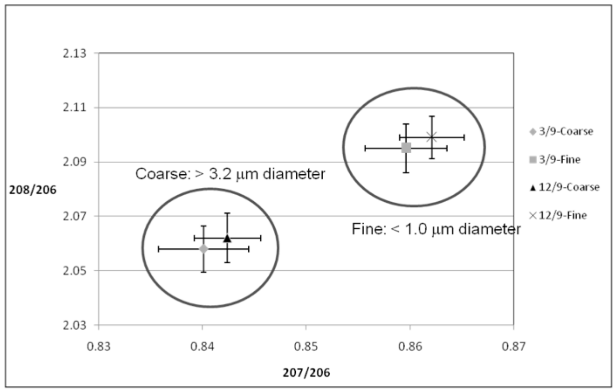
Lead Isotopes in Coarse and Fine Fractions

Ratios between the three stable Pb isotopes are often ore specific.

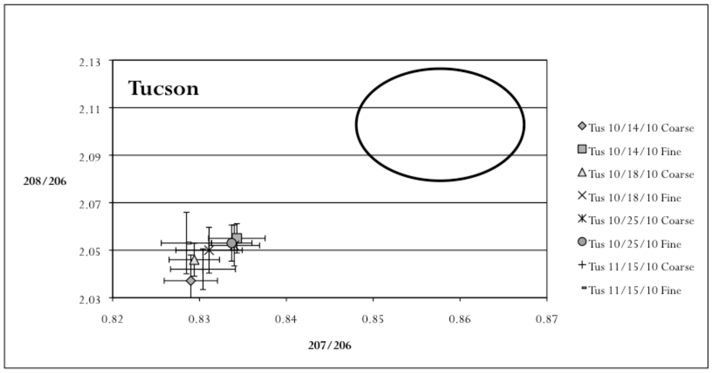
- Used to date ore formation
- Fingerprint anthropogenic Pb



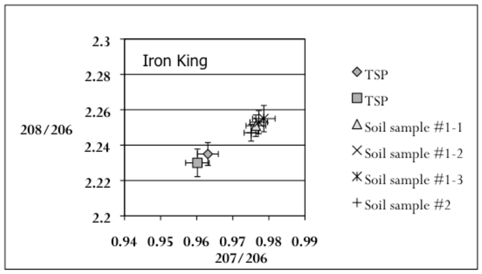
Lead isotope ratios for two sampling periods at Hayden (MOUDI not programmed)

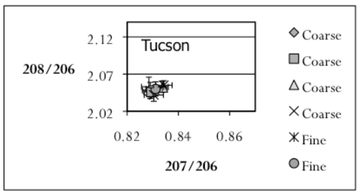
Tucson Pb Isotopes

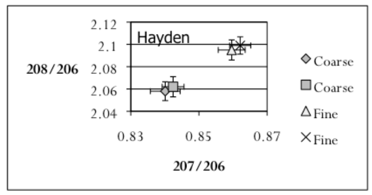
MOUDI not programmed



Iron King TSP and Soil







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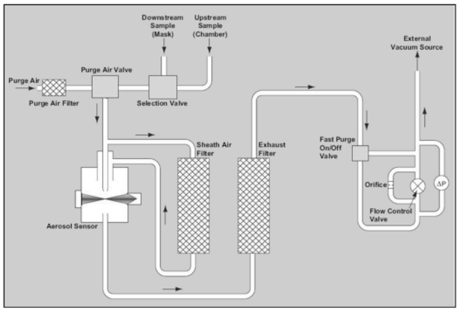
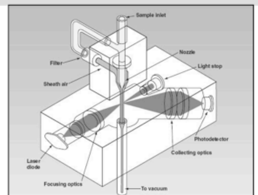
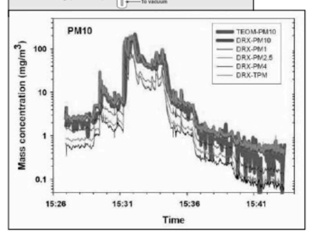
DustTrack Optical Particle Monitor



TSI DustTrak Aerosol Monitor
•Particle concentrations corresponding to PM10, PM2.5, PM1.0
•Rapid response, portable, battery-operated

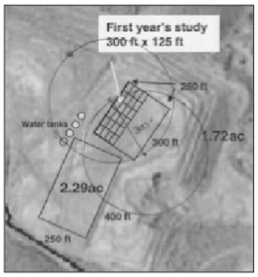


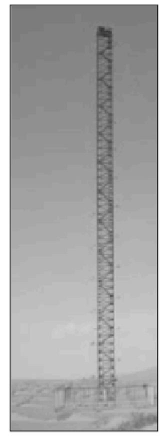


Comparison of Arizona Road Dust (A1) mass concentration measured by the DUSTTRAK DRX and the TEOM with a PM10 impactor.

Iron King
Dust Flux and Winds

- Dust Flux towers installed at Iron King
  - Support model development
  - Track effects of phytoremediation.
- Passive samplers also installed - help characterize horizontal flux.

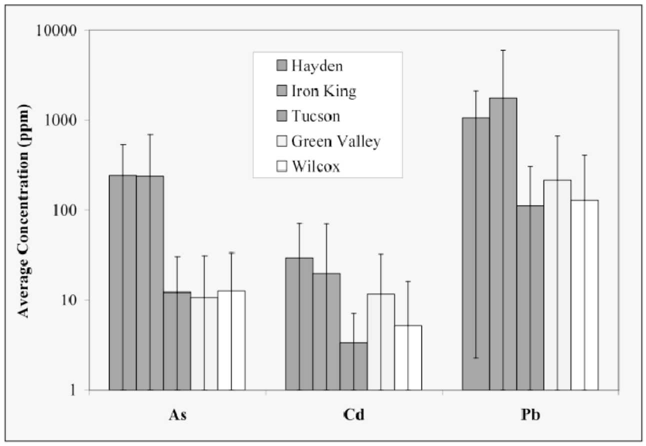




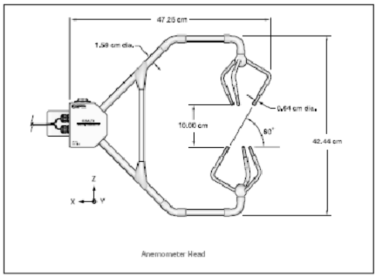
Iron King
Dust Flux Monitors

- Two 10-m dust flux towers
- PM10, PM2.5, PM1.0
- Passive dust samplers
- Meteorological stations
- 3-D winds

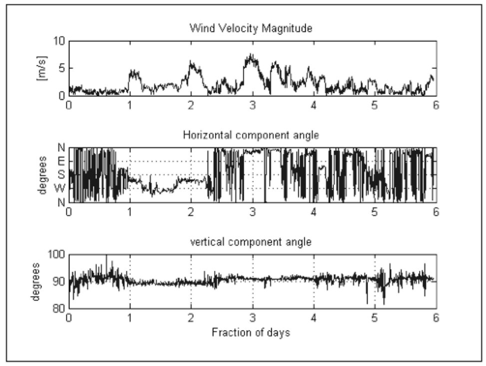
Iron King TSP



Iron King
3-D Winds

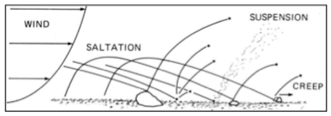


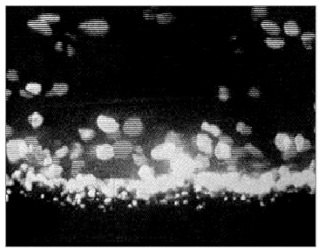
3-D Ultrasonic anemometer



Sample 3-D winds from Iron King tailings November, 2011

Wind Erosion Modeling



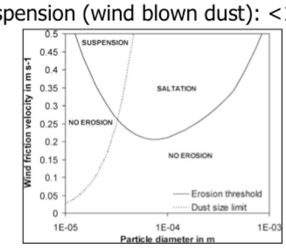


Saltating sand dune particles in wind tunnel

Kansas State University http://www.weru.ksu.edu/new_weru/multimedia/movies/dust003.mpg

Mass flux:

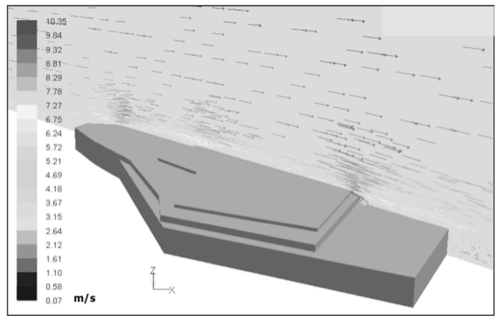
- Creep (rolling): 800-2000 μm D_p
- Saltation (hopping): 100-800 μm D_p
- Suspension (wind blown dust): <100 μm D_p



Greeley-Iversen erosion threshold curve

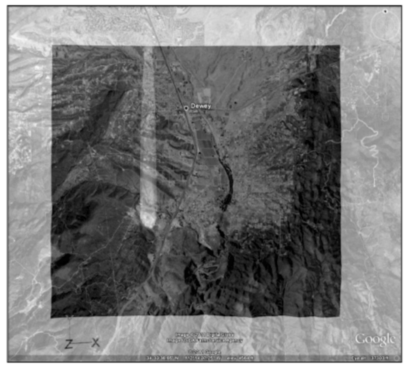
Kon *et al., Int. J. Min. Reclamation & Env.* **21**, 198 (2007)

Wind Vectors - IK tailings
FLUENT



Iron King

Arbitrary concentration (0 - 100 scale), 30 min after surface ejection from IK tailing w/ Google earth overlay



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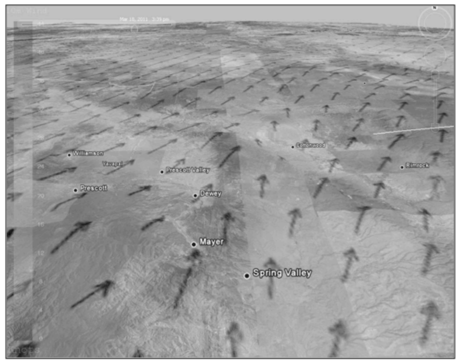
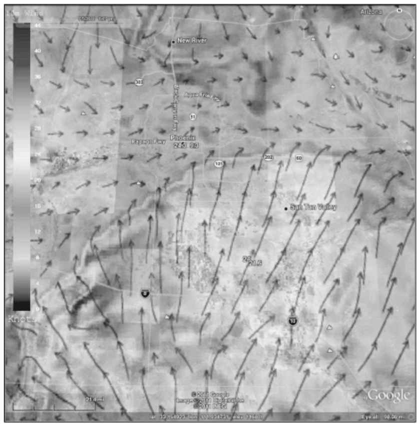
Weather Research and Forecast Model (WRF)



10-meter wind forecast on Google Earth

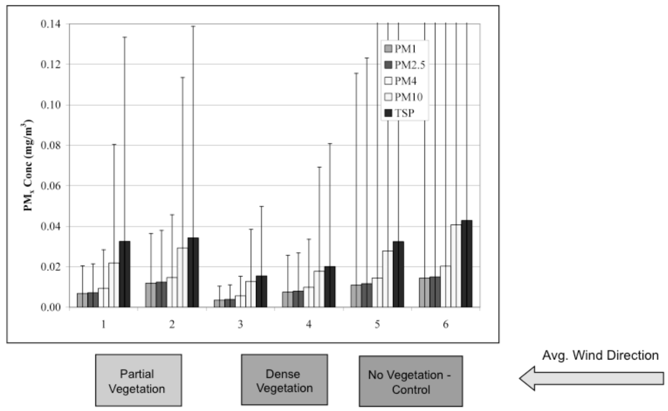
Weather Research and Forecast Model (WRF)



WRF 10-meter wind forecast for Phoenix area: 6 pm, July 5, 2011 (initialized 5 am)

Phoenix dust storm: 8 pm, July 5, 2011

Iron King Dust Track



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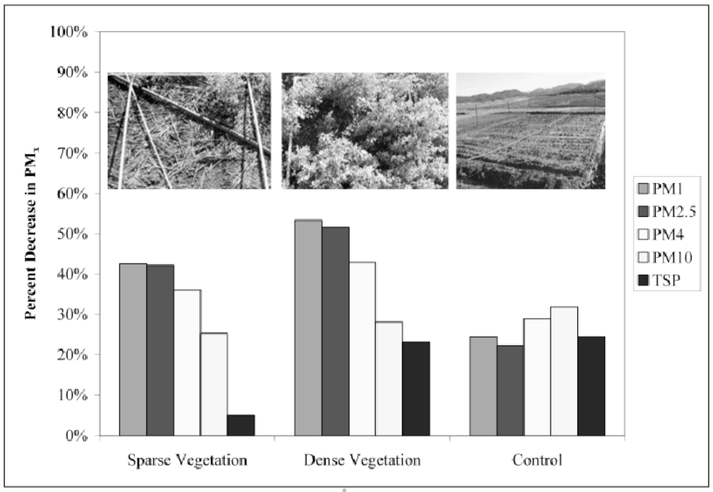
Iron King Phytoremediation



Questions?

Phoenix, Arizona, July 6, 2011

2009-2011

Janae Csavina, Jason Field, Mark P. Taylor, Song Gao, Andrea Landazuri, Eric A. Betterton, A. Eduardo Sáez , A Review on the Importance of Metals and Metalloids in Atmospheric Dust and Aerosol from Mining Operations, ready for submission to *Sci. Total Environ.* (2011).

Eric A. Betterton, Janae Csavina, Jason Field, Omar Ignacio Felix Villar, Andrea Landázuri, Kyle Rine, A. Eduardo Sáez, Jana Pence, Homa Shayan, MacKenzie Russell, Metal and Metalloid Contaminants in Airborne Dust Associated with Mining Operations, accepted AGU Fall Meeting, 5-9 December, San Francisco (2011).

Csavina, J., A. Landázuri, A. Wonaschütz, K. Rine, P. Rheinheimer, B. Barbaris, W. Conant, A.E. Sáez and E.A. Betterton, Metal and Metalloid Contaminants in Atmospheric Aerosols from Mining Operations, Water, Air, and Soil Pollution, 221, 145-157 (2011).

A MINE TAILINGS PHYTOSTABILIZATION CASE STUDY:

THE IRON KING MINE HUMBOLDT SMELTER SUPERFUND SITE

Raina M. Maier
Department Soil, Water and Environmental Science
The University of Arizona, Tucson, AZ

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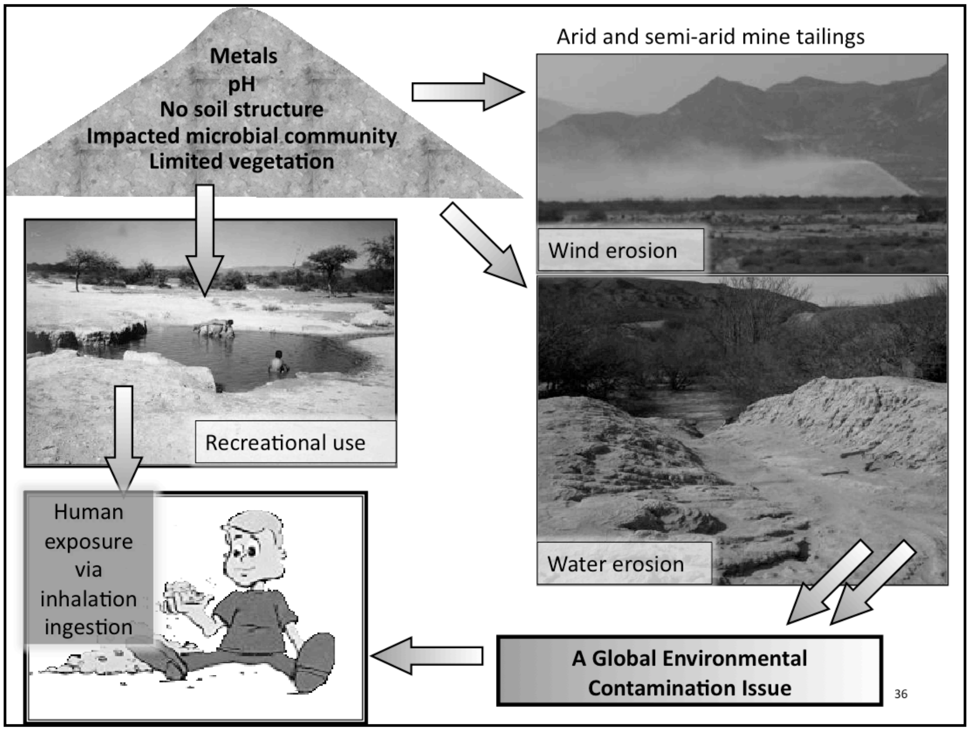
Metals
pH
No soil structure
Impacted microbial community
Limited vegetation
Arid and semi-arid mine tailings
Wind erosion
Recreational use
Water erosion
Human
exposure
via
inhalation
ingestion
A Global Environmental
Contamination Issue
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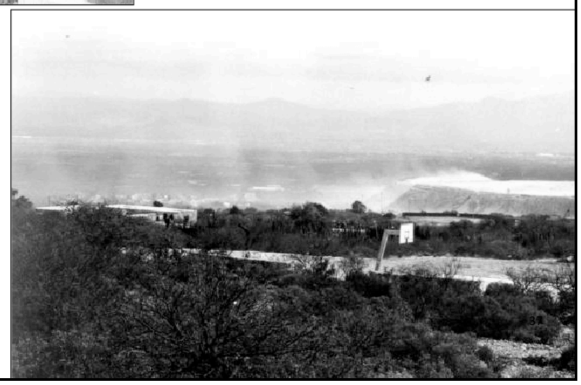
On a still day….

On a windy day….

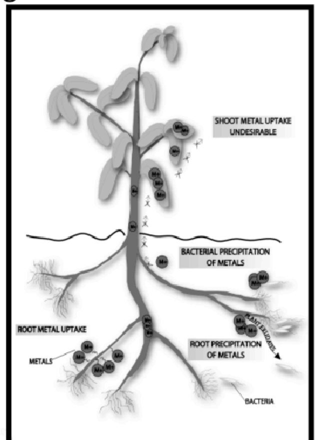


Research Goals

To examine whether mine tailings can be stabilized against wind and water erosion by a vegetative cap to effectively reduce the risk of human exposure to tailings contaminants.

Important parameters to evaluate:

- identify suitable native plants
- establish minimum inputs required for plant growth and survival
- longevity and succession of vegetative cap
- metal speciation during revegetation
- evaluate reduction in erosion processes



Mendez and Maier, 2008. Environ. Health Perspec.

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Iron King Mine-Humboldt Smelter Site (IKMHSS)

- Operated 1904-1969
- Lead, gold, silver, zinc, and copper mined
- Ore processing left behind heavy metals in soil and water
- Tailings pH = 2 to 4

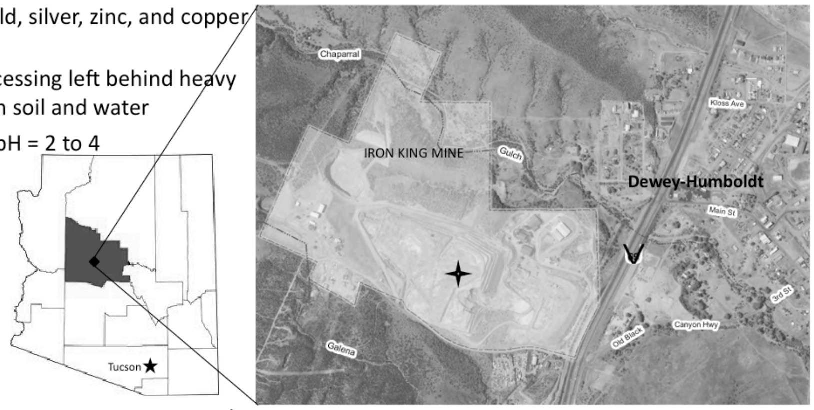

Photo modified from: http://www.azdeq.gov/environ/waste/sps/

- Tailings contains up to 4000 mg/kg arsenic, 4000 mg/kg lead
- Listed as an NPL site in Sept. 2008

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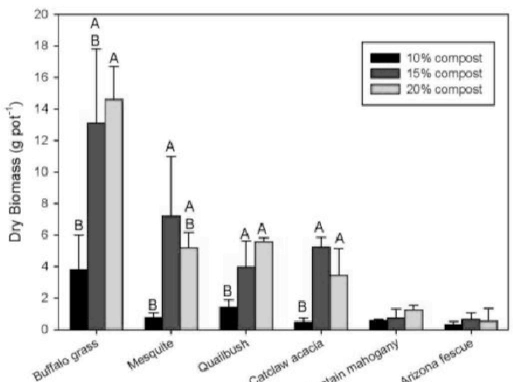
Preliminary greenhouse studies showed:

- 7/15 native species survived
- minimum 15% (w/w) compost amendment needed



Buffalo grass

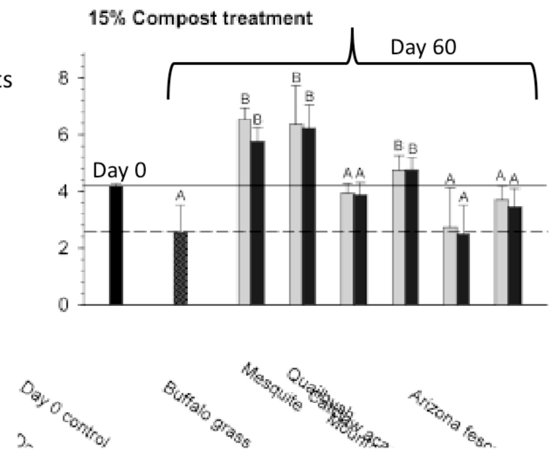
0% compost (w/w)

10% 15% 20%

40

Greenhouse studies showed:

- Effect of compost was to immediately:
  - ⬇ aqueous metal solubility
  - ⬆ pH
  - ⬆ heterotrophic bacterial counts



- Effect of plants was to:
  - Prevent pH from decreasing

41

Greenhouse studies showed:

- Effect of compost was to immediately:

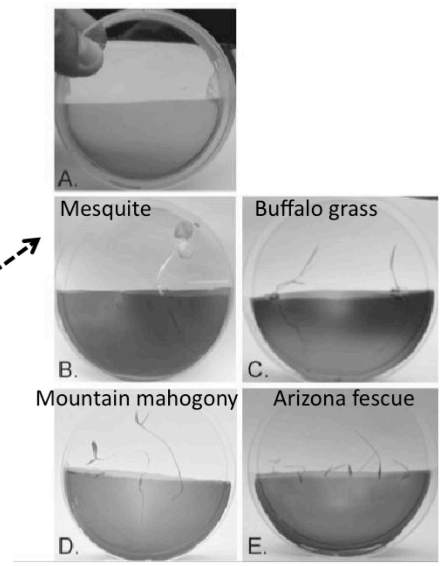
⇩ aqueous metal solubility

⇧ pH

⇧ heterotrophic bacterial counts

- Effect of plants was to:

  Prevent pH from decreasing



Greenhouse studies showed:

- Effect of compost was to immediately:

↓ aqueous metal solubility

↑ pH

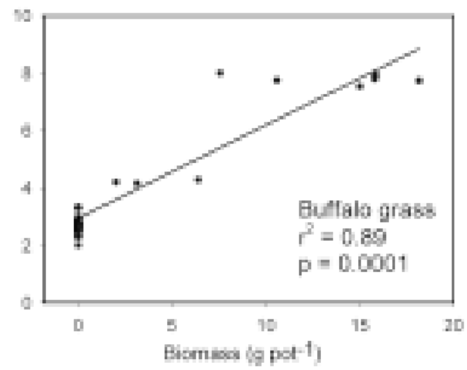
↑ heterotrophic bacterial counts

- Effect of plants was to:

Prevent pH from decreasing

Maintain high heterotrophic counts

Shoot metal accumulation < DATLs



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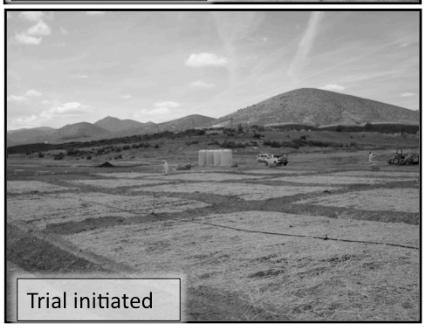
Field trial – initiated May 2010



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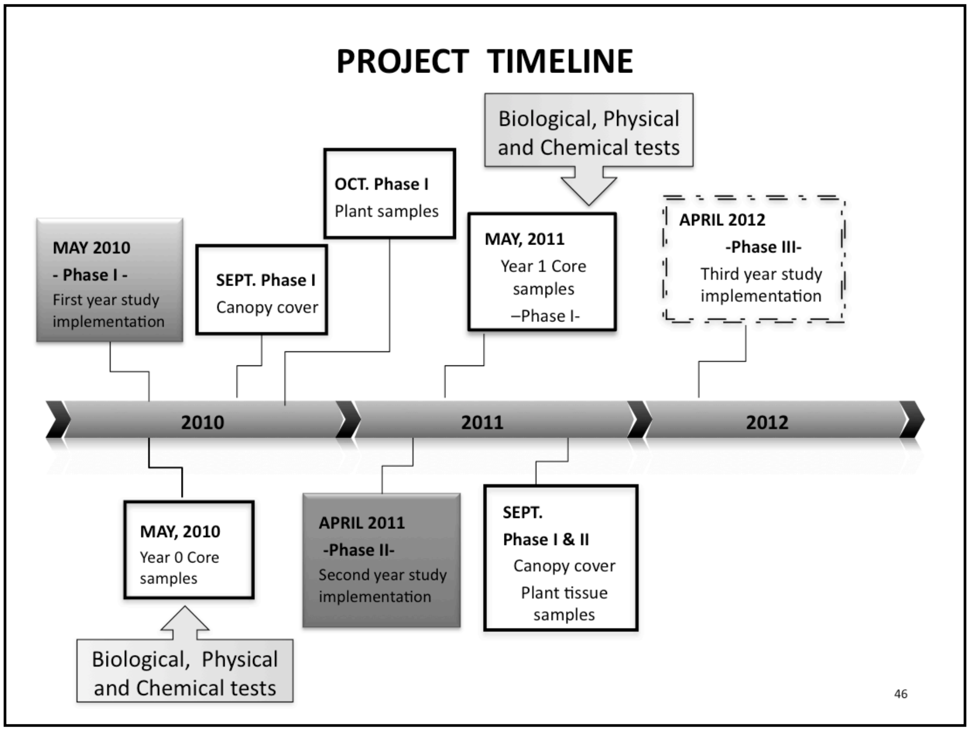
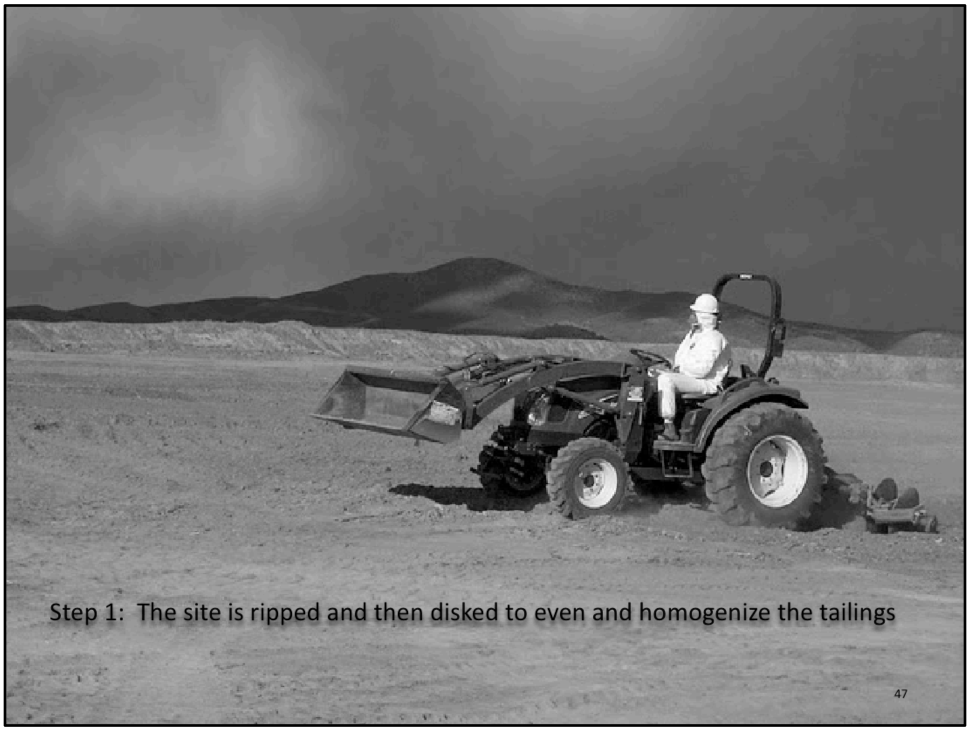
OBJECTIVE

To determine whether successful results from greenhouse studies can be translated to the field, and also, to identify the parameters that indicate successful phytostabilization at IKMHSS.

45


PROJECT TIMELINE
Biological, Physical and Chemical tests
OCT. Phase I
Plant samples
MAY 2010
- Phase I -
First year study implementation
SEPT. Phase I
Canopy cover
MAY, 2011
Year 1 Core samples
–Phase I-
APRIL 2012
-Phase III-
Third year study implementation
2010
2011
2012
MAY, 2010
Year 0 Core samples
APRIL 2011
-Phase II-
Second year study implementation
SEPT.
Phase I & II
Canopy cover
Plant tissue samples
Biological, Physical and Chemical tests
46


Step 1: The site is ripped and then disked to even and homogenize the tailings
47

Step 2: Twenty four plots (6 treatments in quadruplicate) are laid out and flagged

48


Step 3: Compost is delivered
49


DEERE
Step 4: Compost is added to selected plots depending on the treatment
50

A truck scale is used to weigh the compost added to each treatment

52

Mixing the compost into the tailings

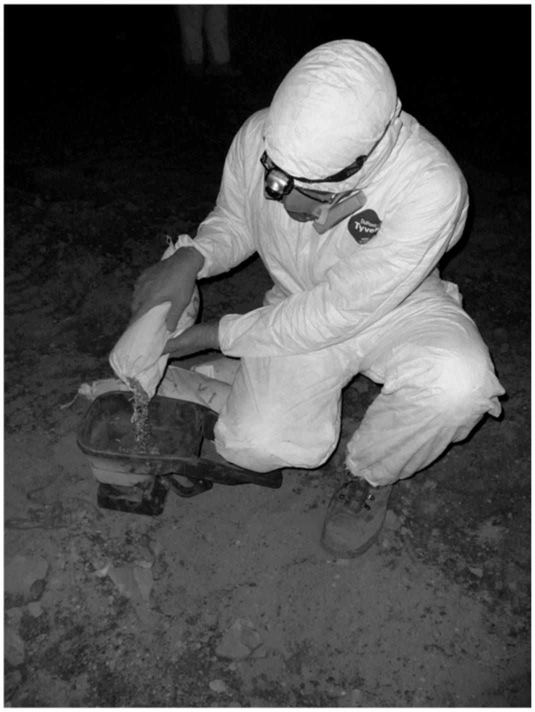
53


Compost amendment is complete!!
54

Step 5: Triplicate cores are taken from each plot for biological and chemical analysis

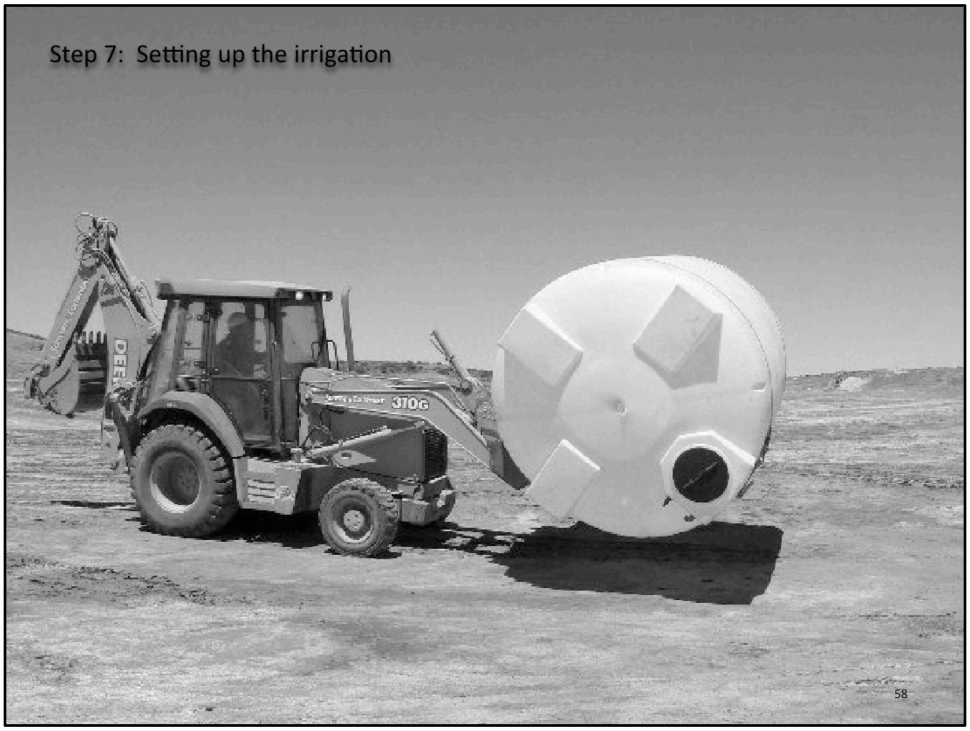
55

56



Step 6: A mix of grass and shrub seeds is broadcast on selected treatments and the plots are covered with straw. This is done at night to avoid the stronger winds that occur during the daytime and to stay cool!

57


Step 7: Setting up the irrigation
310G
58


59


Some finishing touches
61


Field trial begins – May 18, 2010
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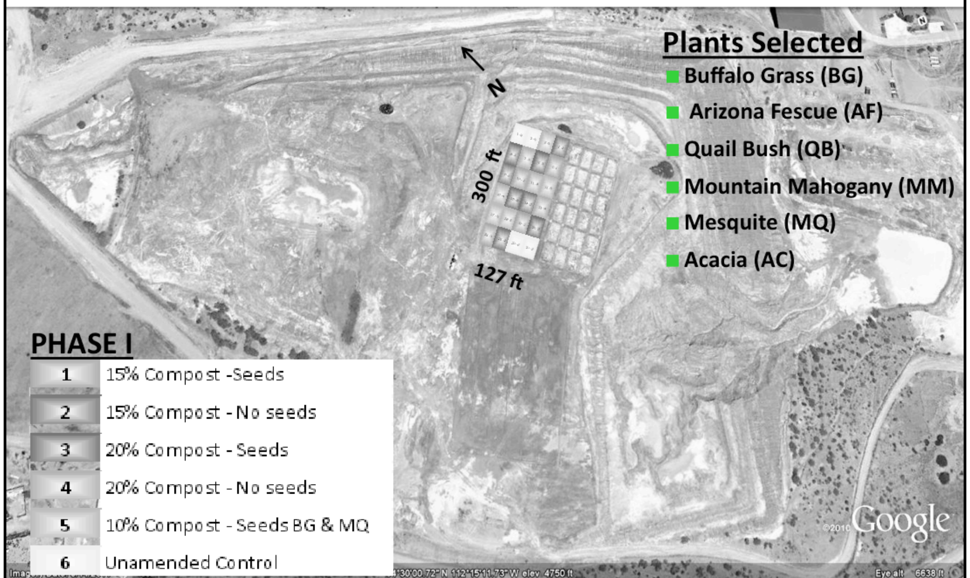
METHODOLOGY -Field plots and treatments-

METHODOLOGY -Field plots and treatments-



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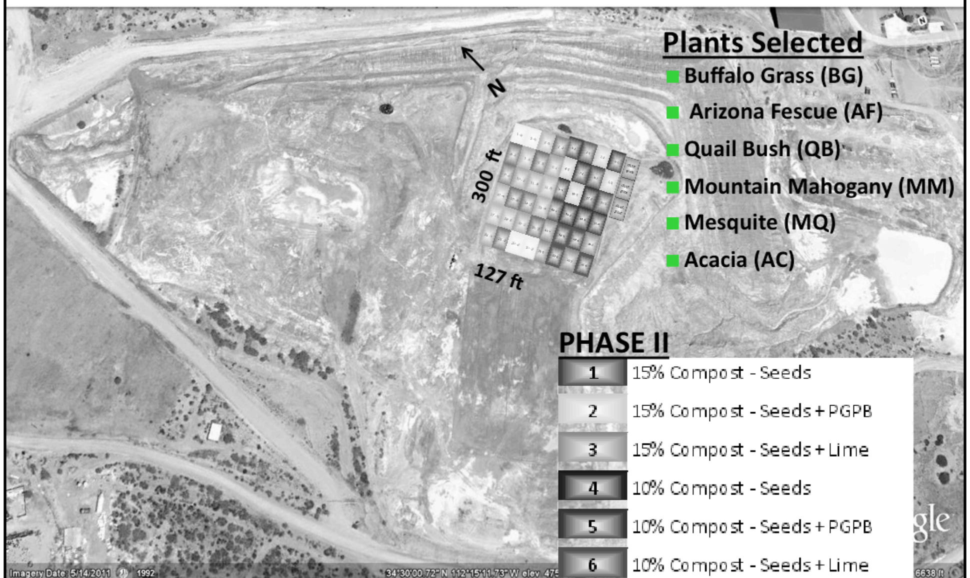
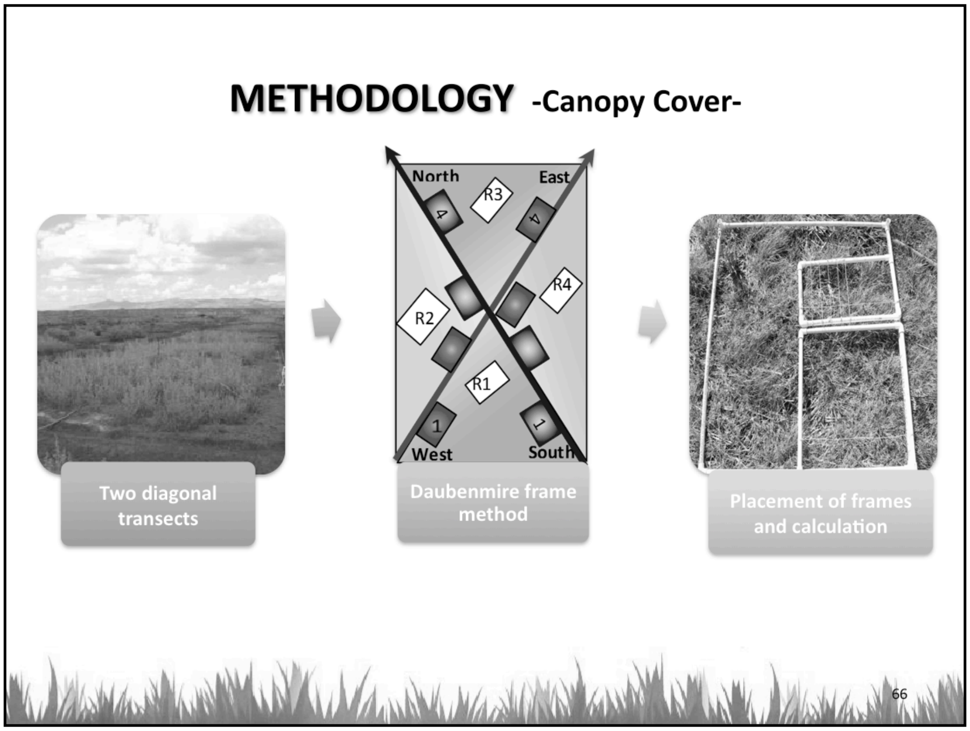
METHODOLOGY -Field plots and treatments-

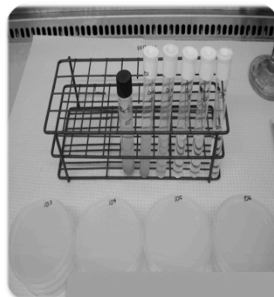


65

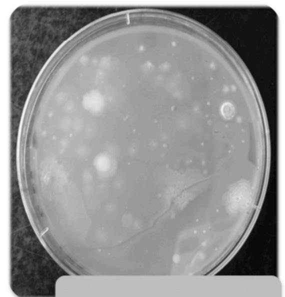

METHODOLOGY -Canopy Cover-
North
East
West
South
R1
R2
R3
R4
4
4
1
1
Two diagonal transects
Daubenmire frame method
Placement of frames and calculation
66

METHODOLOGY -Neutrophilic Heterotrophic Count (NHC)-

Top 20 cm from core samples each plot



Serial dilutions and plate counts



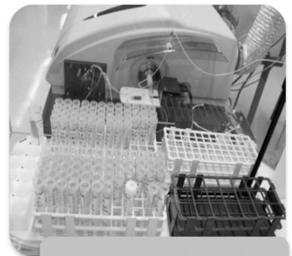
Counting after 5 days

67

METHODOLOGY -Shoot uptake of metals-

Plant tissue samples BG and QB

Washing and drying



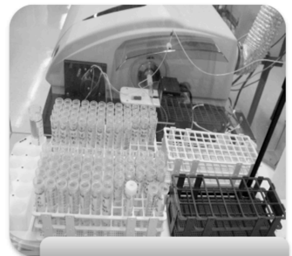
Microwave digestion and ICP-MS analysis

68

METHODOLOGY – 1:1 paste measurement of EC and pH

Samples from 3, 6, and 9” of each core

1:1 paste



pH meter, EC probe

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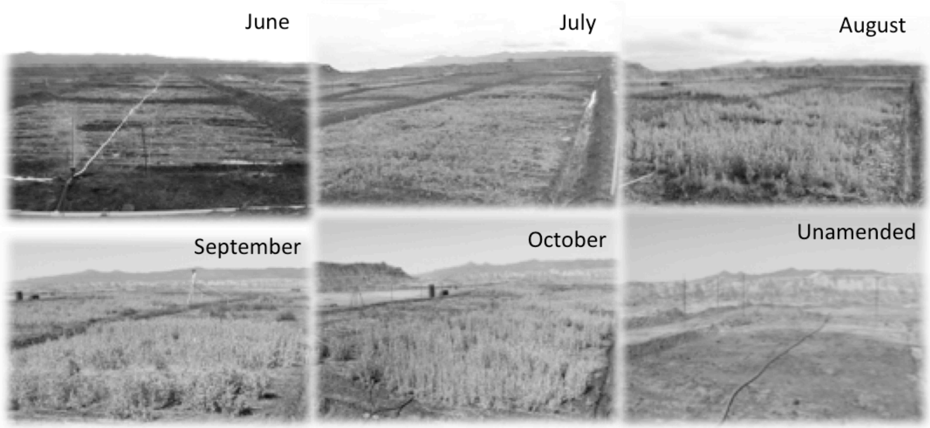
RESULTS

1. Canopy Cover
2. Neutrophilic Heterotrophic Counts
3. Shoot Metal Uptake
4. pH and EC

After 17 months of phytostabilization

70

Results – Canopy Cover



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RESULTS -CANOPY COVER PHASE I -

Canopy cover: Percentage of the ground area covered by vegetation.

Treatments	% Canopy Cover[a]		
	5 Months[b]	17 Months[b]	[c]T-test
20% - Seeds	33.8 ± 5.4 a	26.3 ± 1.9 a	S*
20% - No Seeds	4.2 ± 2.2 b	16.1 ± 5.9 ab	S*
15% - Seeds	38.7 ± 6.6 a	18.6 ± 11.4 ab	S*
15% - No Seeds	6 ± 2.3 b	7.15 ± 6.5 bc	NS
10% - BG/MQ	29.9 ± 10.0 a	23.8 ± 6.7 a	NS
Unamended control	0 b	0 b	NS

[a] Values are mean ± standard deviation (n=4). [b] Values with different letters are significantly different at $p<0.05$ (one way ANOVA, Tukey's test) for each column.
[c] T-test $p<0.05$ for each row; NS = no significant difference, S* = significant difference.

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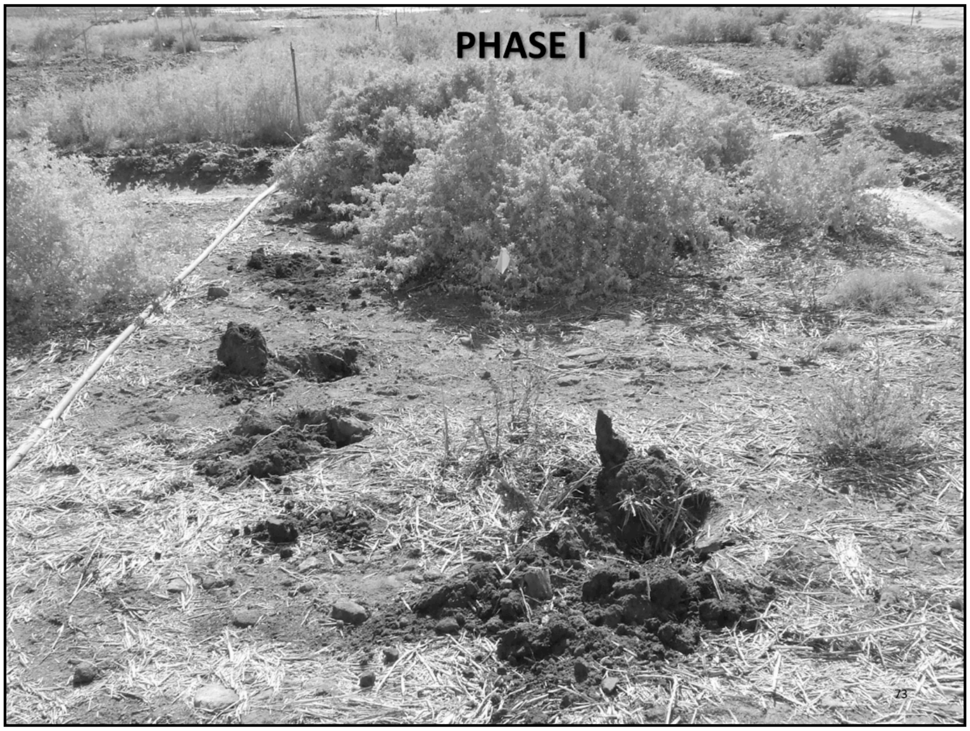
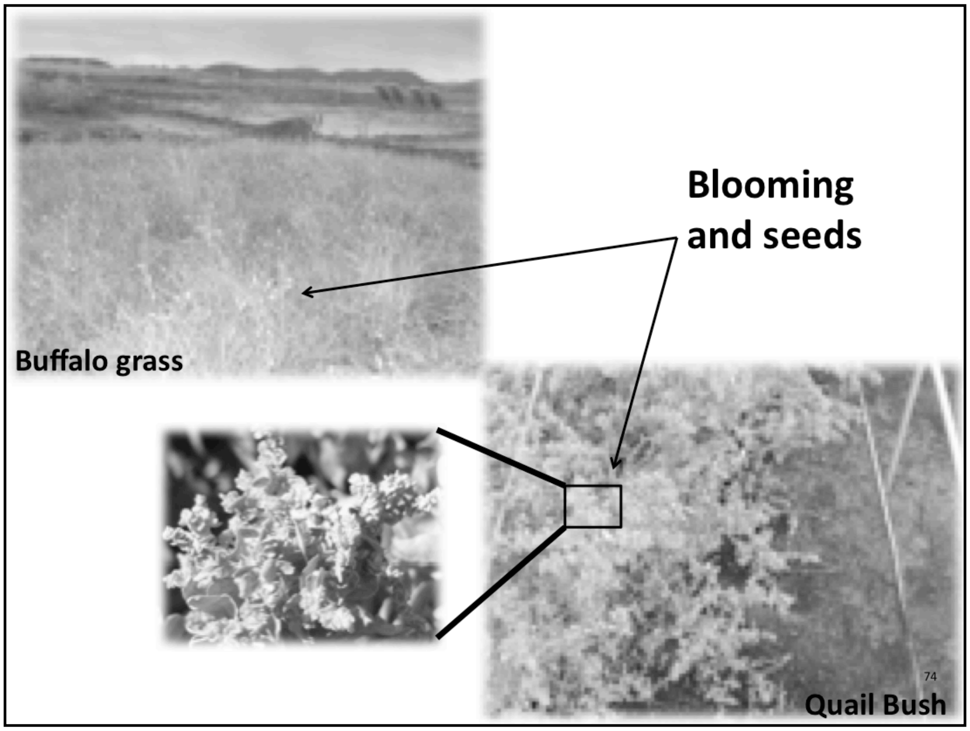

PHASE I
23


Blooming
and seeds
Buffalo grass
Quail Bush
74

RESULTS -NEUTROPHILIC HETEROTROPHIC COUNT (NHC)-

Treatments	CFU/g dry soil		[b]T-Test
	0 Months[a]	14 Months[a]	
20% - Seeds	$1.4 \pm 1.0 \times 10^5$	$2.6 \pm 1.6 \times 10^6$	S*
20% - No Seeds	$3.1 \pm 3.1 \times 10^5$	$2.1 \pm 0.80 \times 10^7$	S*
15% - Seeds	$2.7 \pm 4.6 \times 10^5$	$1.2 \pm 0.22 \times 10^6$	S*
15% - No Seeds	$1.5 \pm 1.7 \times 10^4$	$6.6 \pm 4.1 \times 10^5$	S*
10% - BG/MQ	$2.0 \pm 1.7 \times 10^4$	$3.5 \pm 1.7 \times 10^5$	S*
Unamended Control	$1.7 \pm 1.3 \times 10^2$	$3.6 \pm 4.2 \times 10^2$	NS

[a] Values are mean ± standard deviation (n=4). [b] T-test $p<0.05$ for each row; (NS = no significant difference, S* = significant difference)

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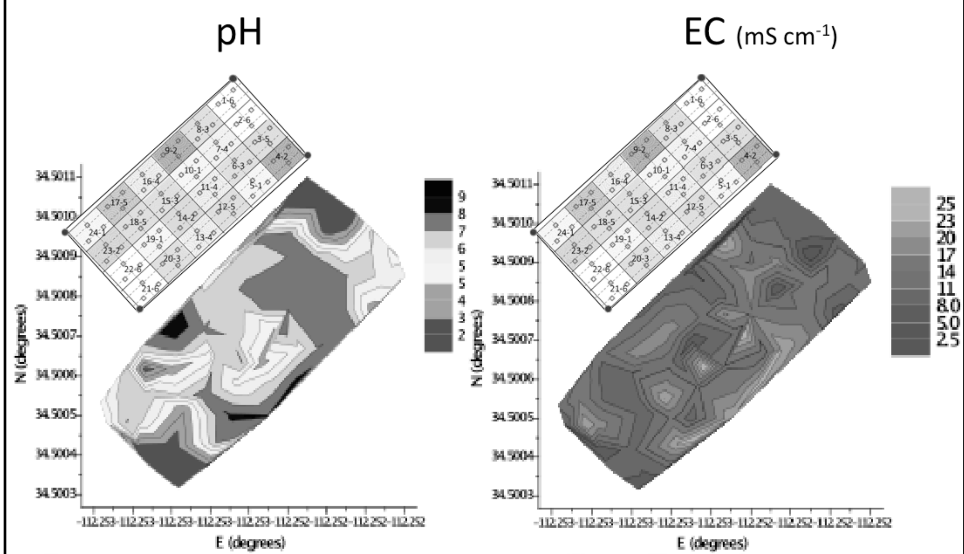
RESULTS -SHOOT UPTAKE OF METALS-

Element	Total mg mg kg^{-1}	[a]DATL mg kg^{-1}	Plant Species	[b]15% - Seeds mg kg^{-1}	[b]20% - Seeds mg kg^{-1}	[c]t Test
As	2593	≤ 30	Buffalo grass	24.8 ± 18.2	14.8 ± 1.4	NS
			Quailbush	19.7 ± 5.5	11.8 ± 3.3	
Pb	2197	≤ 100	Buffalo grass	11.9 ± 8.6	8.1 ± 1.8	NS
			Quailbush	12.3 ± 5.0	6.4 ± 2.2	
Zn	2003	≤ 500	Buffalo grass	207.5 ± 155.8	147.2 ± 78.4	NS
			Quailbush	655.0 ± 228.9	506.1 ± 253.4	

[a] DATL= domestic animal toxicity limit. [b] Values are mean ± standard deviation (n= 4).
[c] t-Test p<0.05 for each row (NS = no significant difference; S* = significant difference).

Initial Surface Characterization of Year 1 Plots



17 Month Surface Characterization of Year 1 Plots

Treatments	pH	
	3 inches	9 inches
20% Compost	6.6	2.9
15% - Compost	4.8	2.9
10% - Compost	3.6	2.6
Unamended Control	2.5	2.6

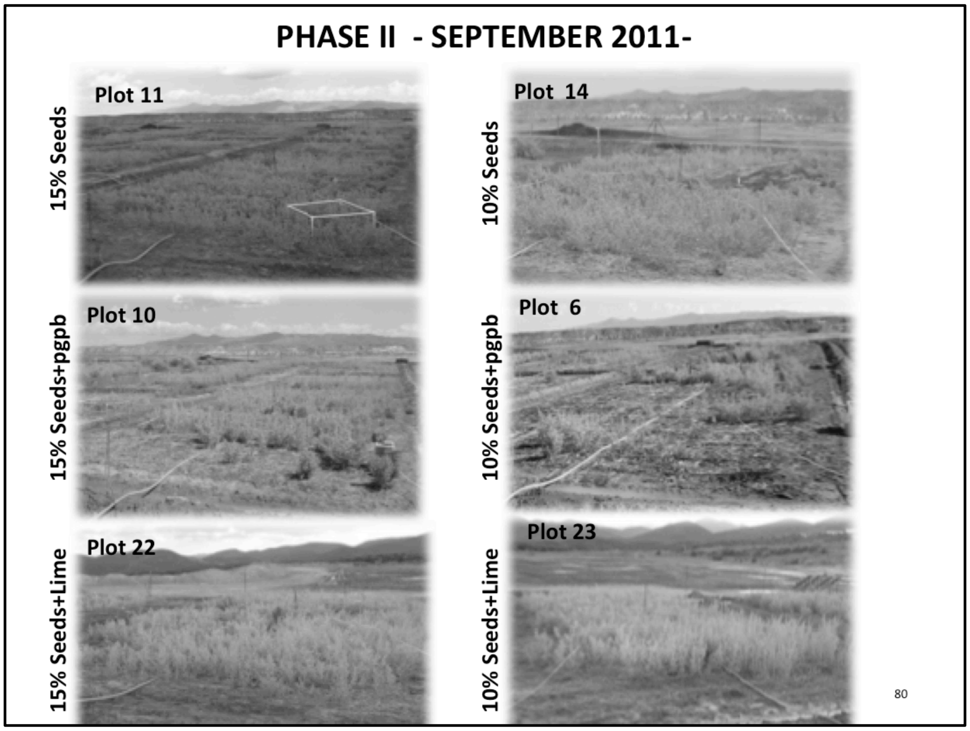
EC = 6 to 7 mS cm^{-1} for all treatments

78

RESULTS -CANOPY COVER PHASE II -

Treatments*	% Canopy Cover 5 Months
15% - Seeds	17.1 ± 4.5 bc
15% - Seeds + PGPB	17.1 ± 5.7 bc
15% - Seeds + Lime	29.4 ± 0.9 a
10% - Seeds	7.9 ± 4.5 c
10% - Seeds + PGPB	9.2 ± 2.9 bc
10% - Seeds + Lime	18.2 ± 6.3 c

* Percentage number indicates rate of compost.. Values are Mean ± Standard deviation (n=4). Values with different letters are significantly different at $p<0.05$ (One-way ANOVA, Tukey's test).


PHASE II - SEPTEMBER 2011-
Plot 11
15% Seeds
Plot 14
10% Seeds
Plot 10
15% Seeds+pgpb
Plot 6
10% Seeds+pgpb
Plot 22
15% Seeds+Lime
Plot 23
10% Seeds+Lime
80

81


15% Seed +Lime
82

CONCLUSIONS

- Greenhouse results translate well to the field.
- Percent canopy cover increases with the rate of compost.
- The establishment of a vegetative cap **increases** neutrophilic heterotrophic bacteria.
- Neutrophilic heterotrophic bacteria, percent canopy cover, and shoot uptake of metal(oids) are promising criteria to use in evaluating phytostabilization success.

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THANKS TO…

supported by: **NIEHS SRP Grant**
P42 ESO4940

Region 9 EPA:
- Leah Butler
- Monika O'Sullivan

Site owner:
- Stephen Schuchardt

Superfund Research Program

NIEHS
National Institute of Environmental Health Sciences

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Photos were taken by Alexis Valentin, Corin Hammond, Karis Neilson, Robert Root and Scott White . THANK YOU !!!!

You can follow the field study:

http://cals.arizona.edu/crops/irrigation/azdrip/BostonMill/IK/photolog.htm

Questions ?

Selected References:

Solís-Dominguez, F., S.A. White, T. Borrillo Hutter, M.K. Amistadi, R.A. Root, J. Chorover and R.M. Maier. Response of key soil parameters during phytostabilization in extremely acidic tailings: effect of plant species, Environ. Sci. Technol. DOI: 10.1021/es202846n.

Mendez, M.O., and R.M. Maier. 2008. Phytostabilization of mine tailings in arid and semiarid environments – an emerging remediation technology. Environ. Health Perspec. 116:278-283.

Superfund Research Program
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