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)

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Housekeeping

- Please mute your phone lines, Do NOT put this call on hold
- Q&A
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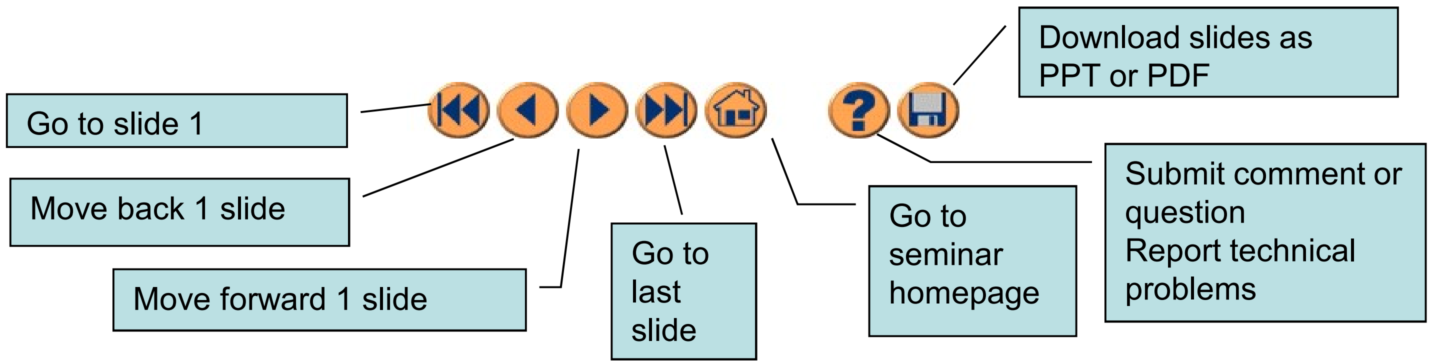
- Move through slides using # links on left or buttons



- This event is being recorded
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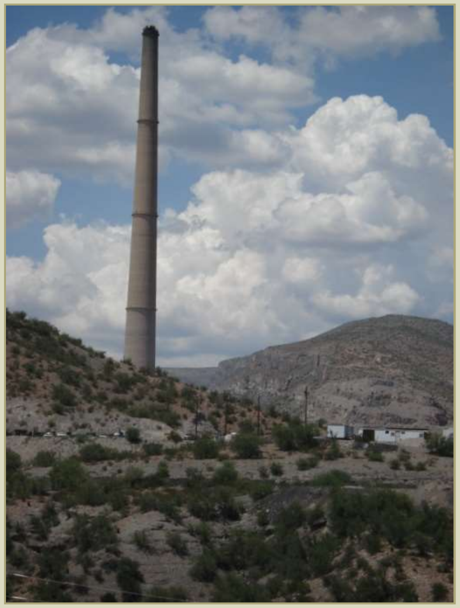
Atmospheric Aerosols from Mining Operations in Hayden and Dewey-Humboldt, AZ

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

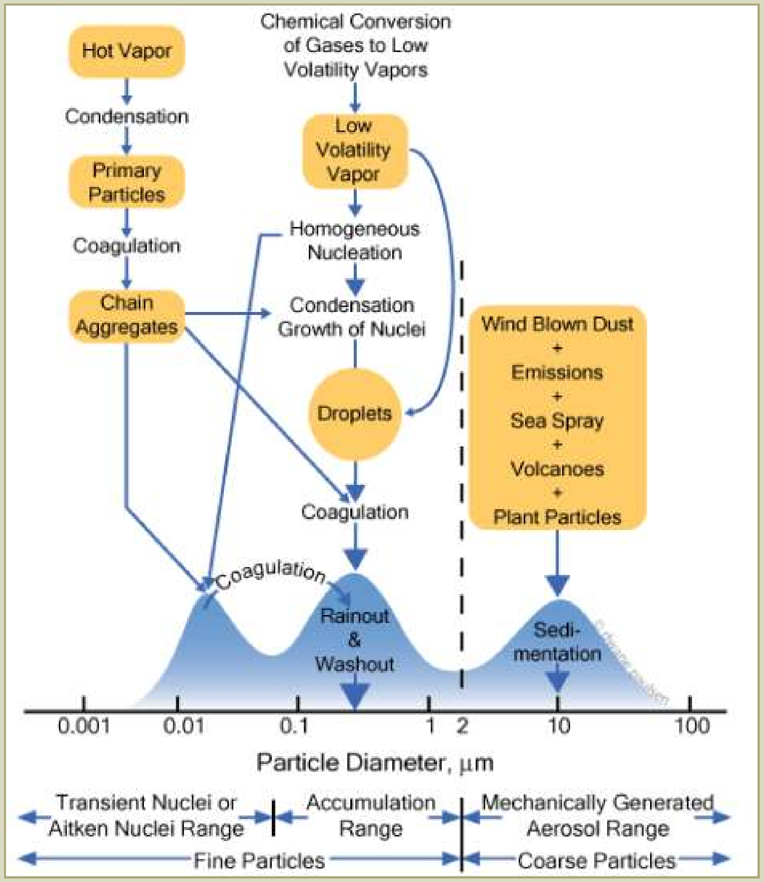
I-10 between PHX and TUS October 4, 2011. Wind gusts 30 to 50+ mph

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

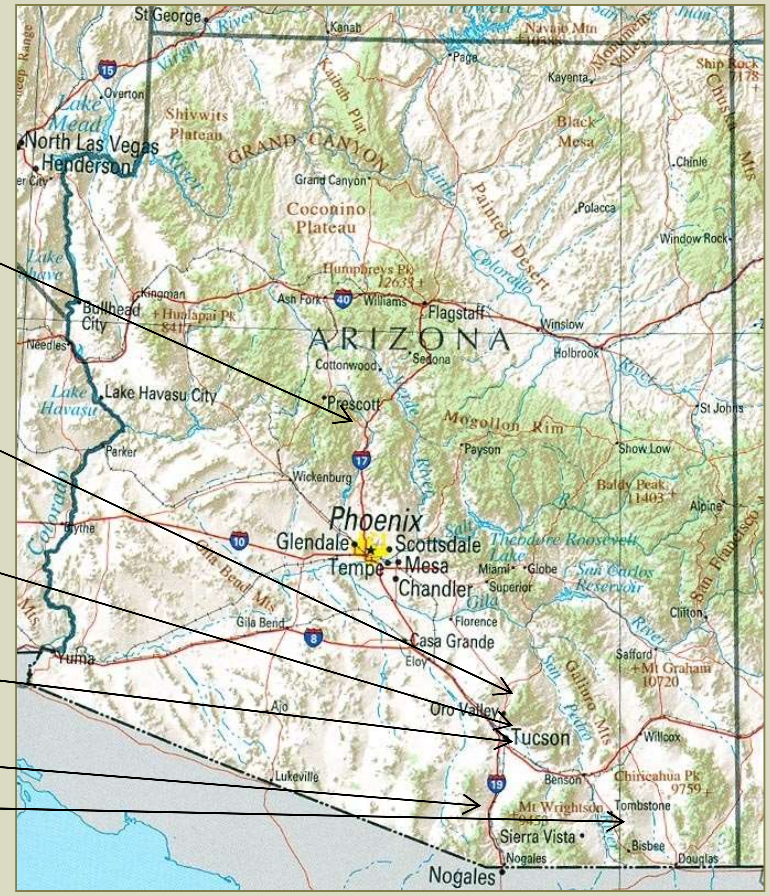
- Crushing, Grinding, Mine Tailings Management
  - Coarse >2.5 µm *(mechanical action)*
- Smelting, Refining
  - Ultra-fine <0.1 µm *(gas to particle conversion)*
  - Accumulation 0.1-2.5 µm *(coagulation of ultrafine and condensation growth)*



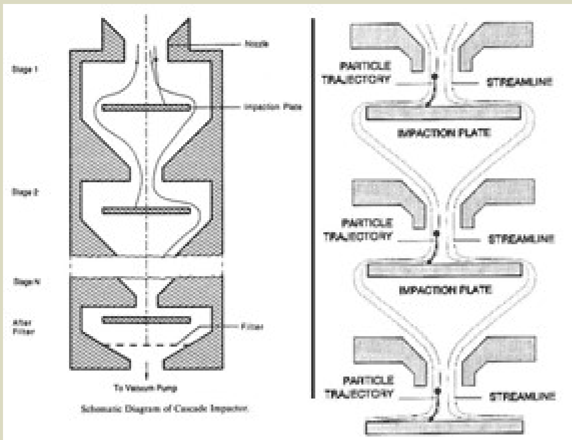
(Seinfeld and Pandis 1998)

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

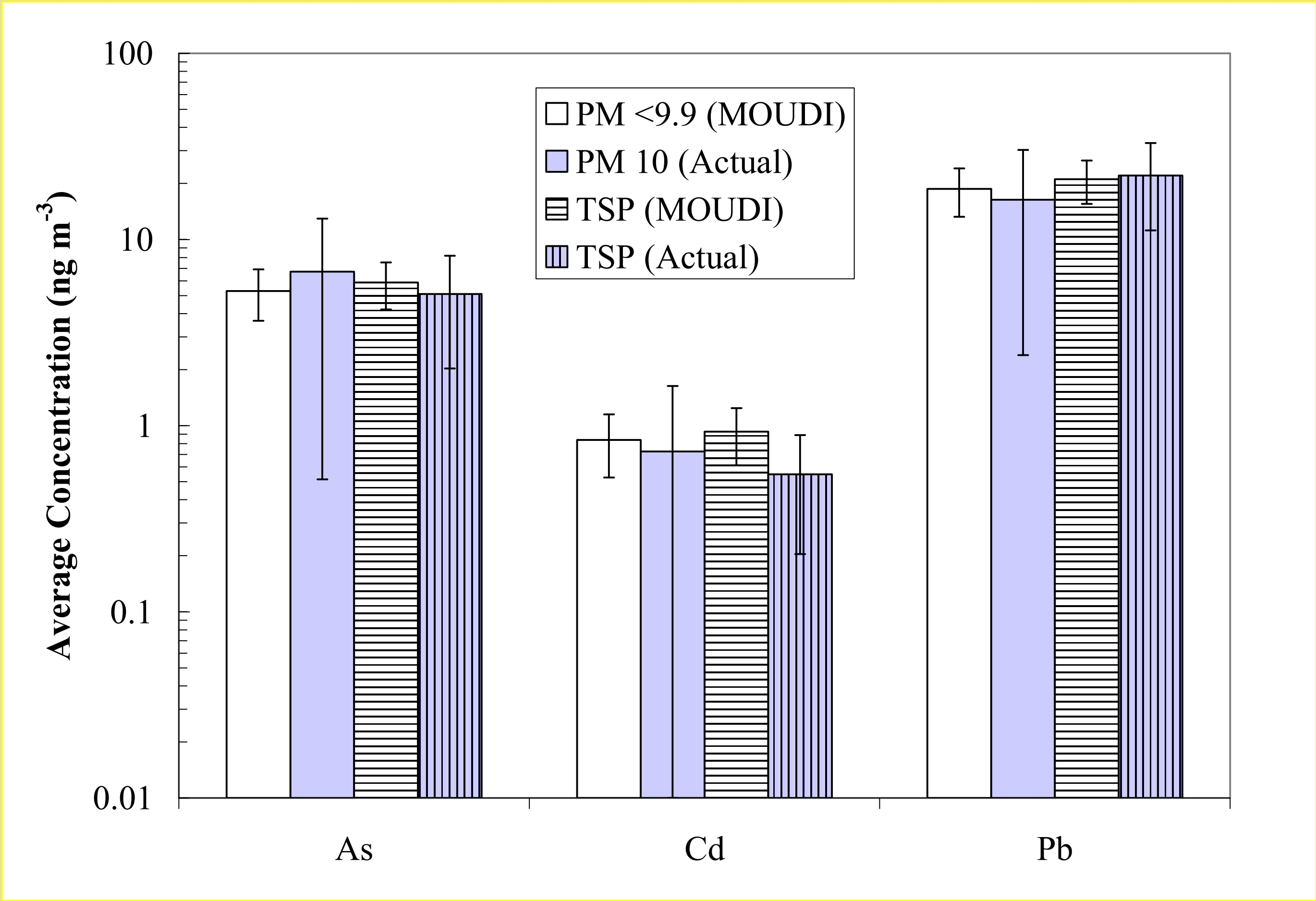


Sampling Techniques



- **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

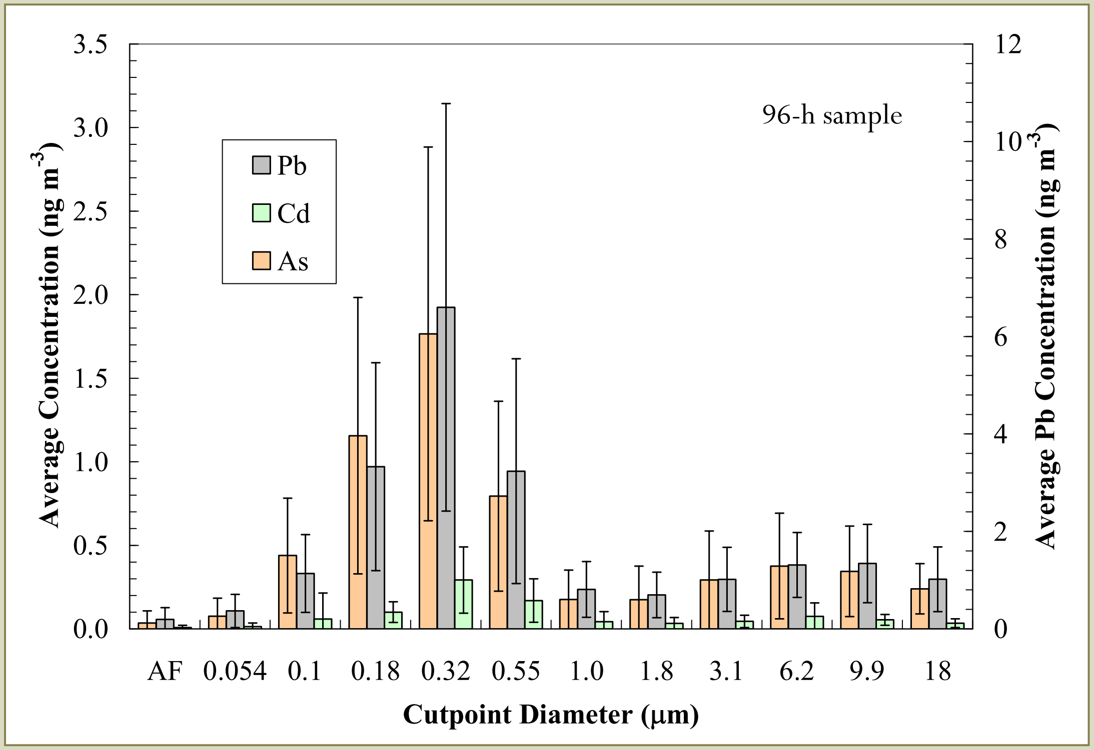
Hayden MOUDI Measurement Verification (ng m^{-3})



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

Hayden smelter building

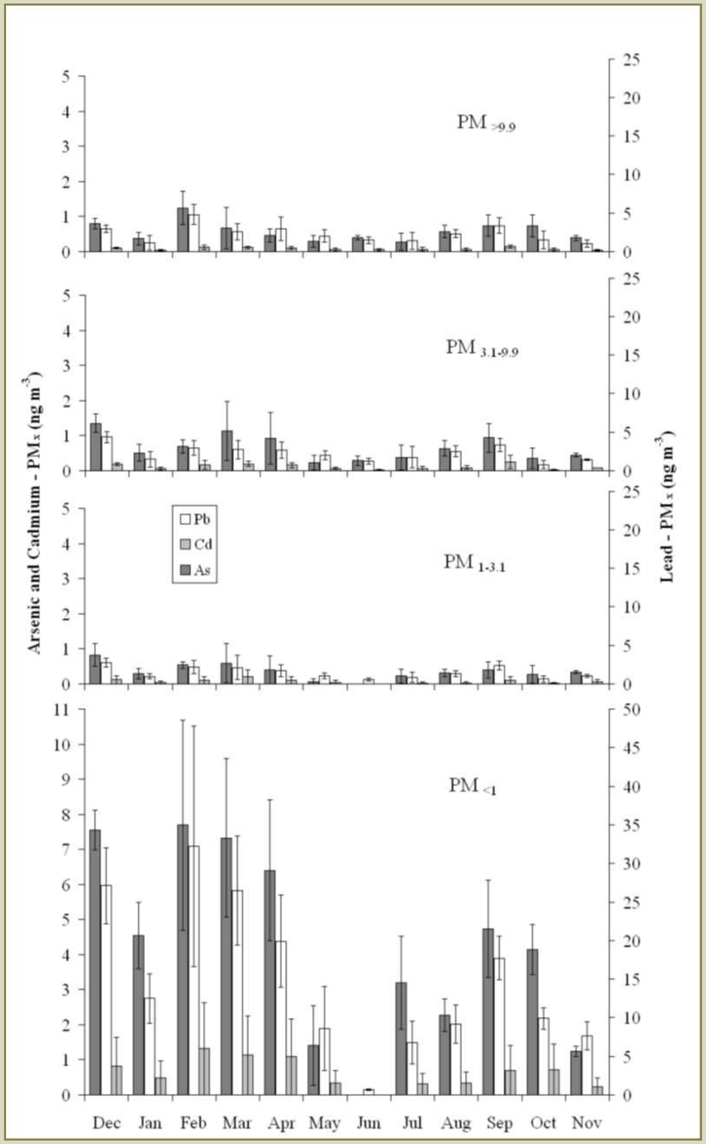
Hayden slag pour



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”

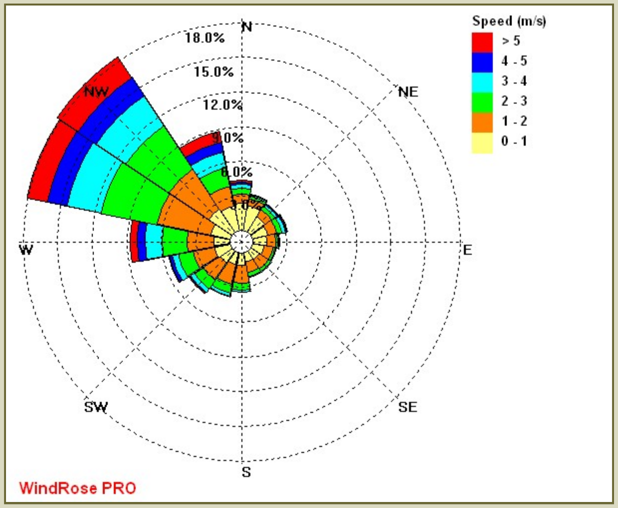
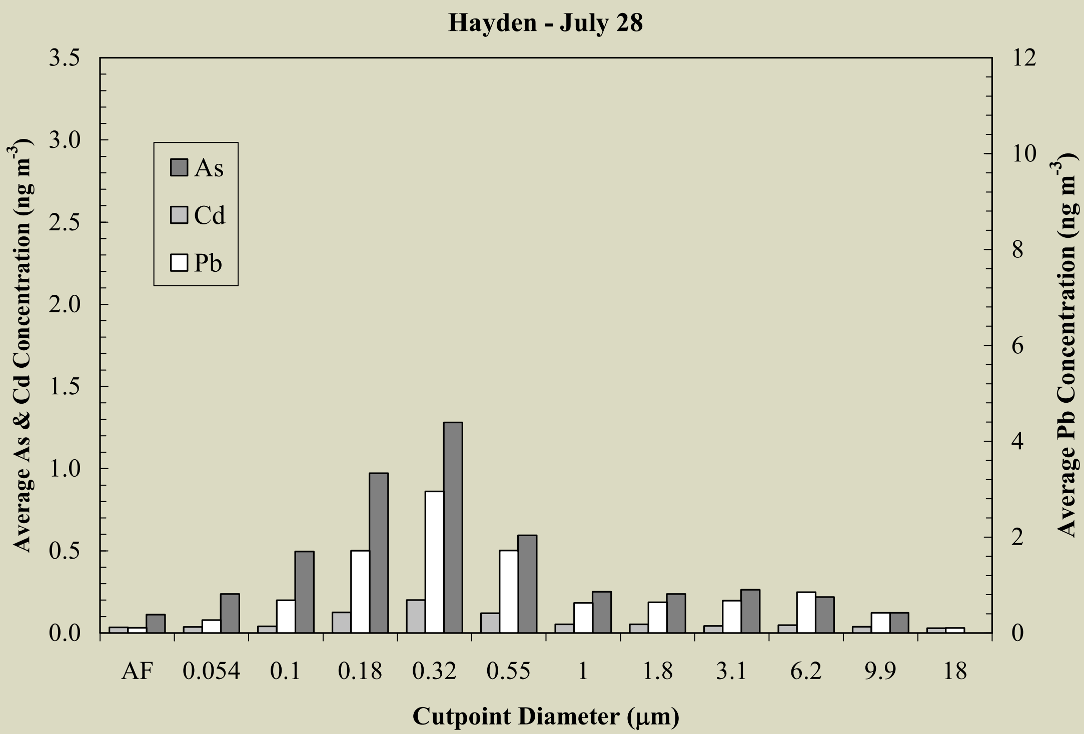


Figure 1. July 28, 2010 MOUDI ON (Programmed 300° -360°)



Hayden – NE “background”

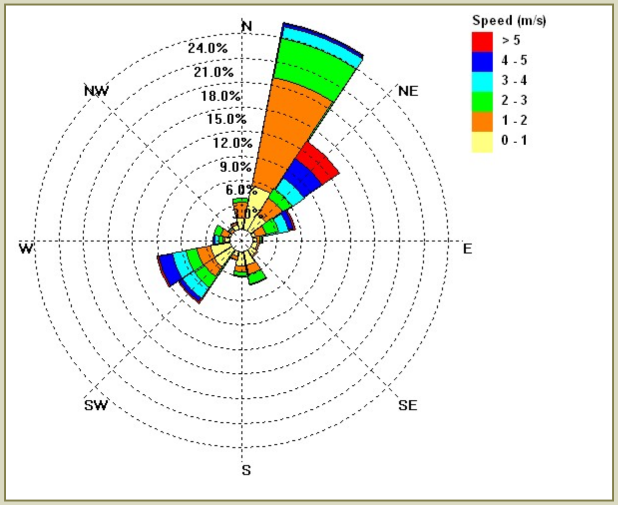
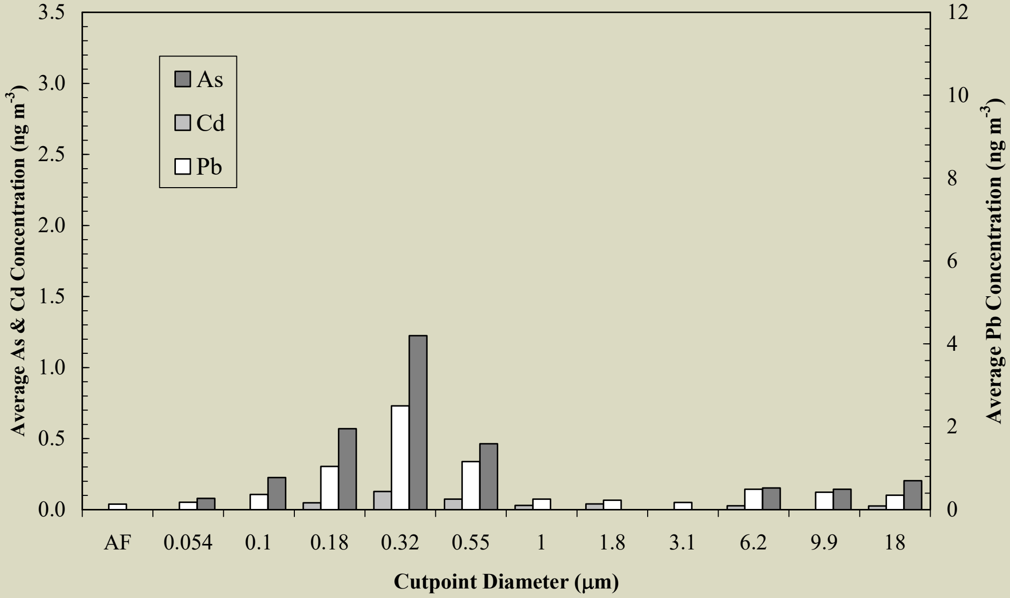
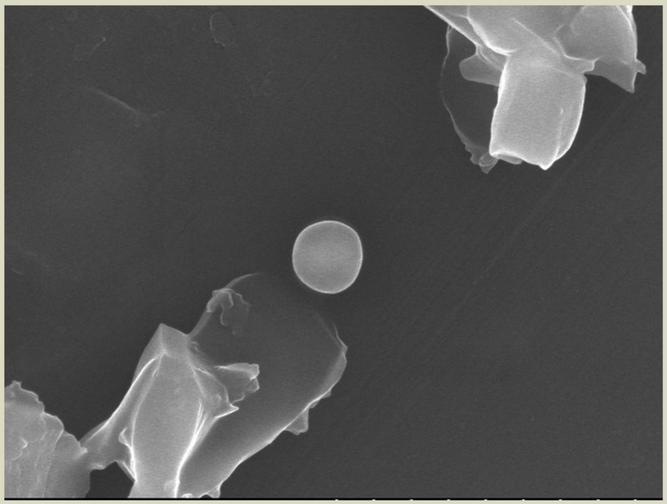
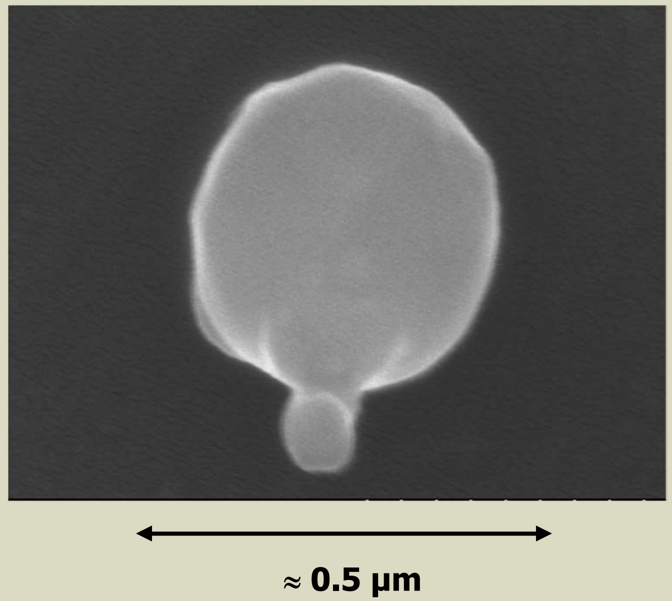


Figure 1. November 16, 2010 MOUDI ON (Programmed 30° - 160°)



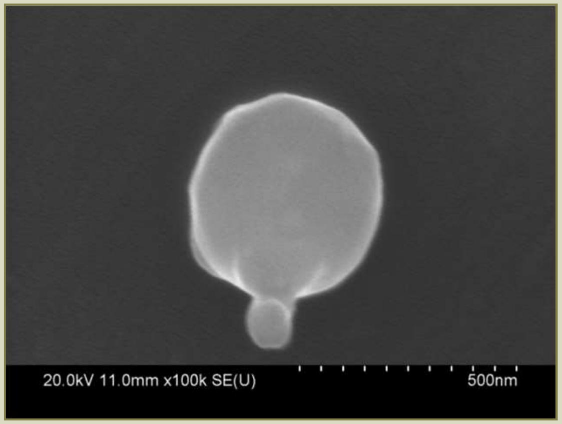
Scanning Electron Microscopy (fine fraction)





•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

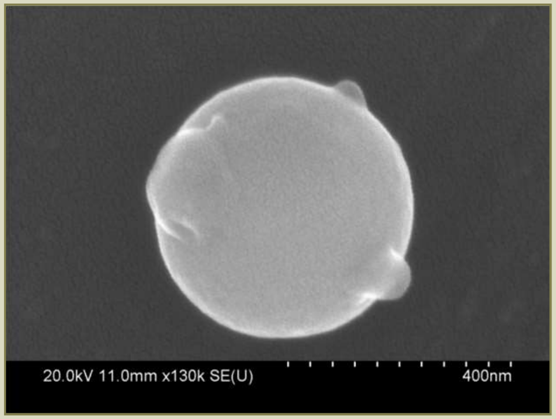


Weight %

	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)

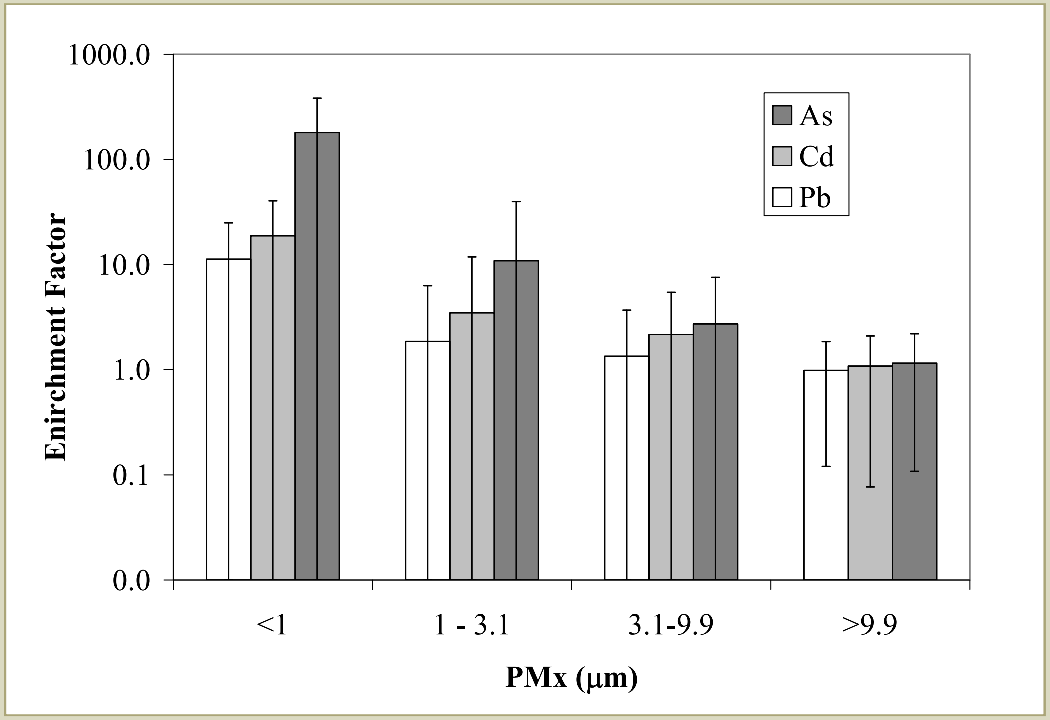
	C-K	O-K	Al-K	Si-K	S-K	Cl-K	Fe-K	Cu-K	As-K	Pt-L
Base(11)_pt1	+/-1.02	+/-0.29	+/-0.18	+/-0.10	+/-0.06	+/-0.02	+/-0.03	+/-0.18	+/-0.31	+/-0.25

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

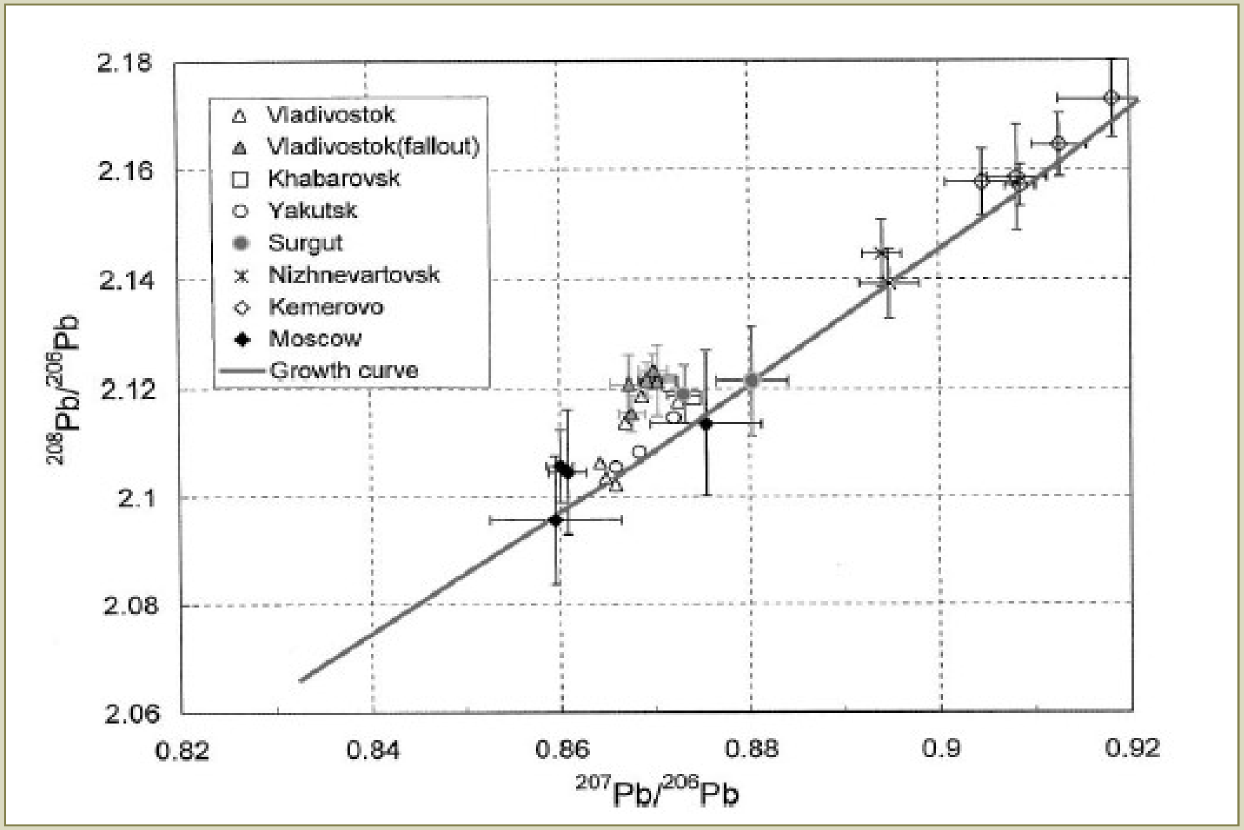
$$\textbf{EF} = [C_{n(SmelterON)}/C_{ref(SmelterON)}]/[B_{n(SmelterOFF)}/B_{ref(SmelterOFF)}]$$

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



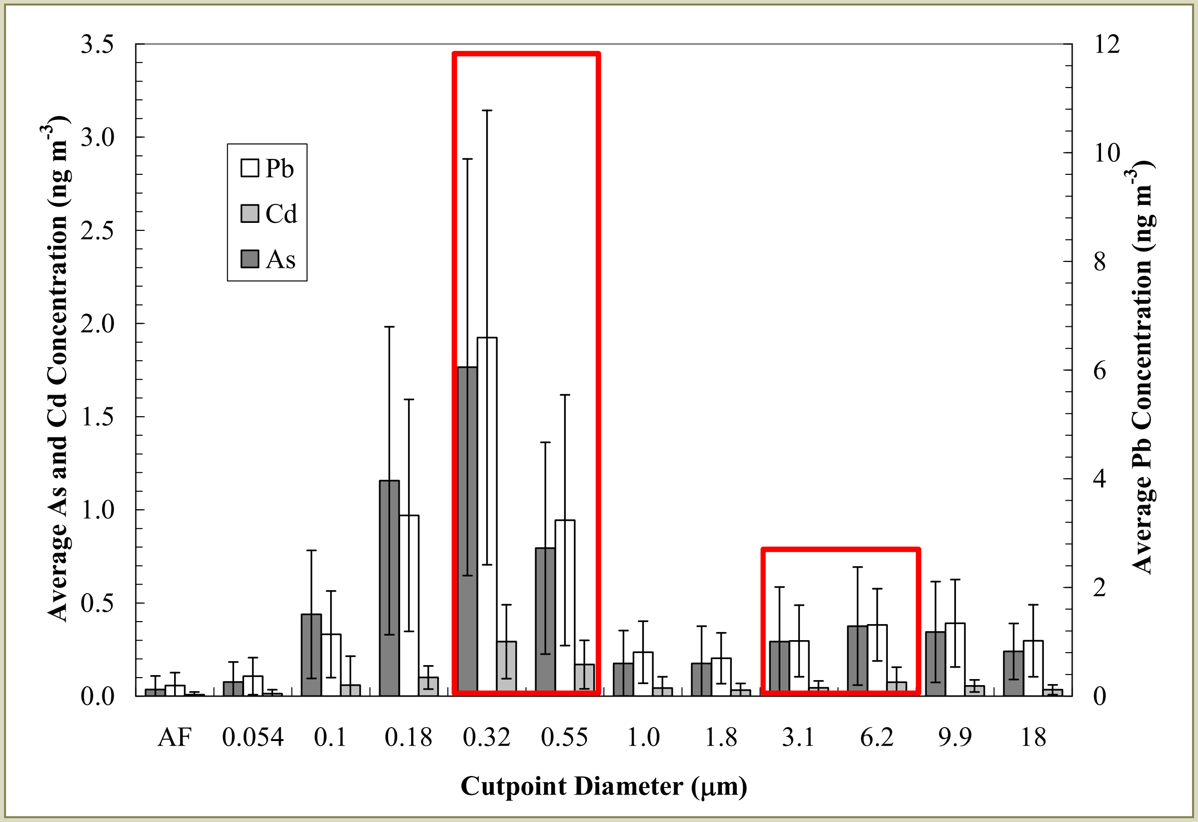
Betterton, January 11, 2012

Lead stable isotopes in atmospheric aerosols



Mukai et al., 2001

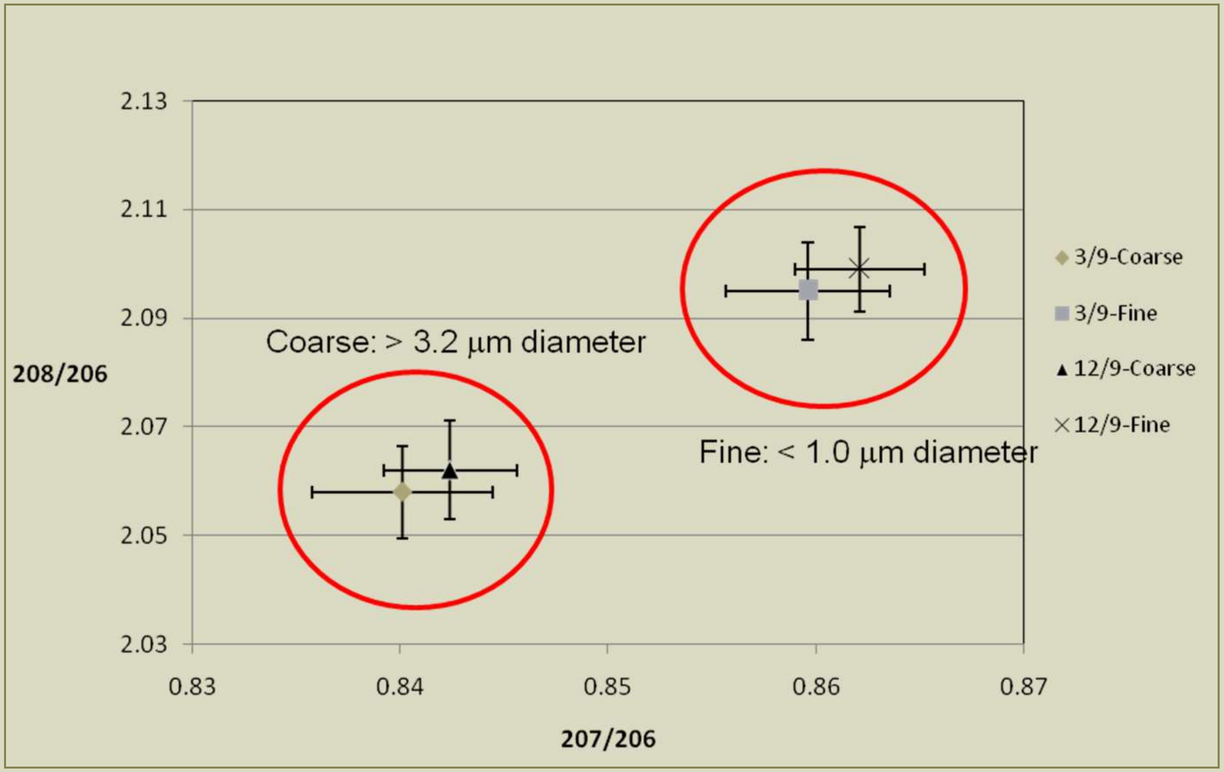
Fractions for Pb Isotope Analysis



Lead Isotopes in Coarse and Fine Fractions

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

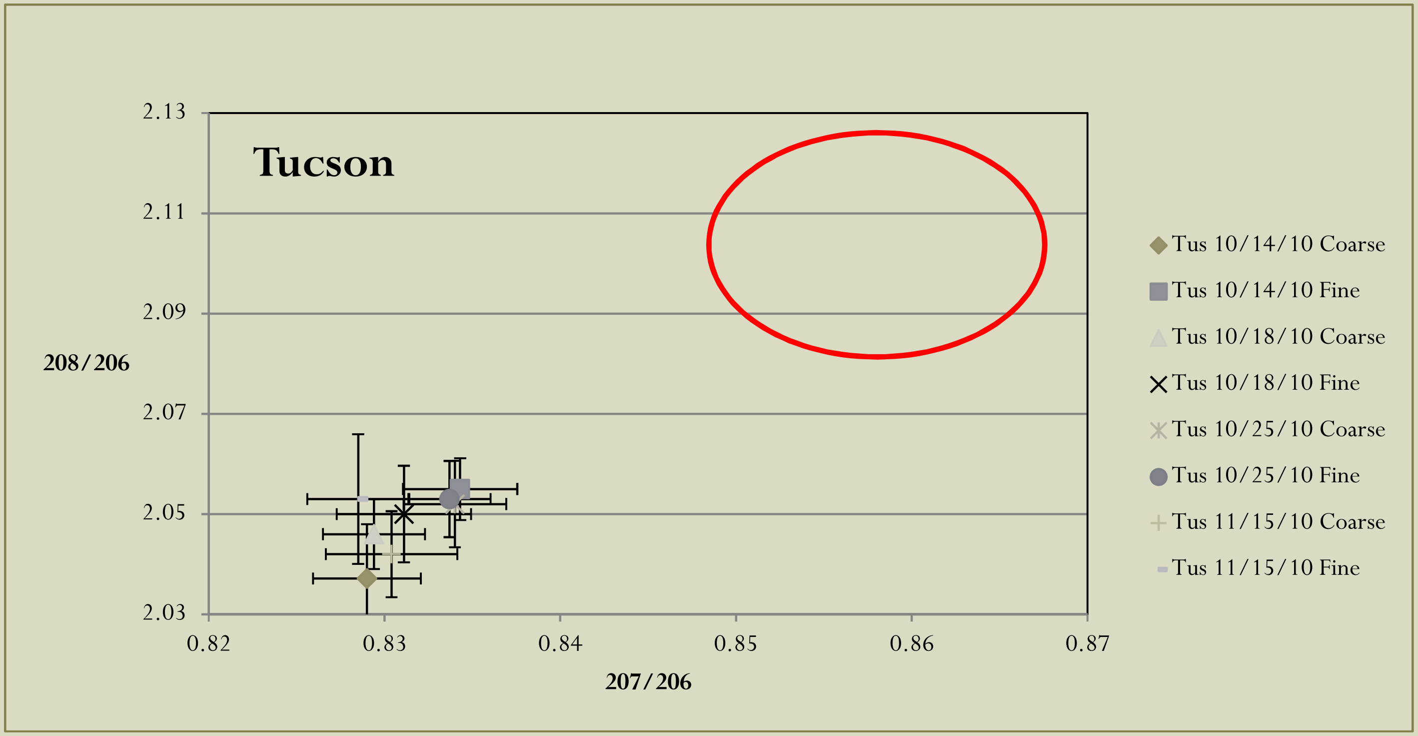
- Used to date ore formation
- Fingerprint anthropogenic Pb



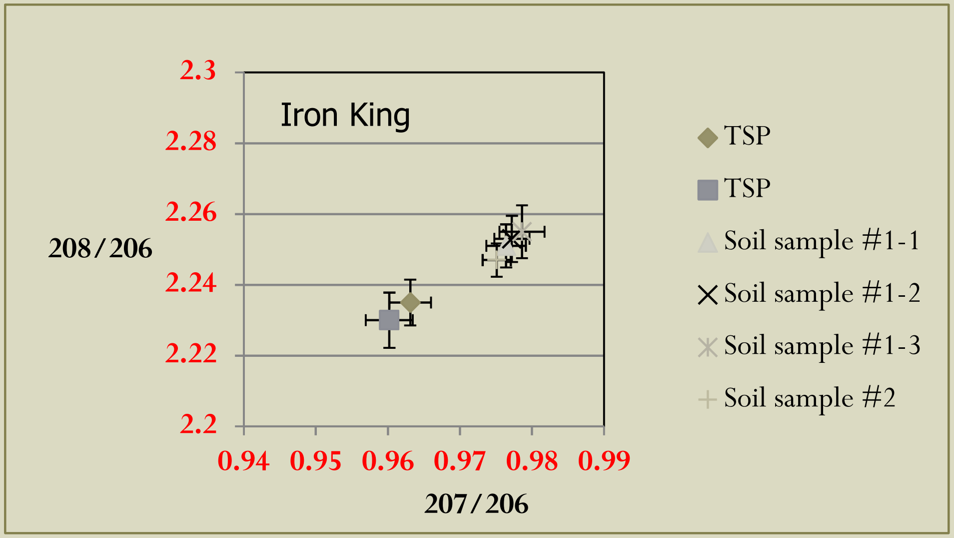
Lead isotope ratios for two sampling periods at Hayden (MOUDI not programmed)

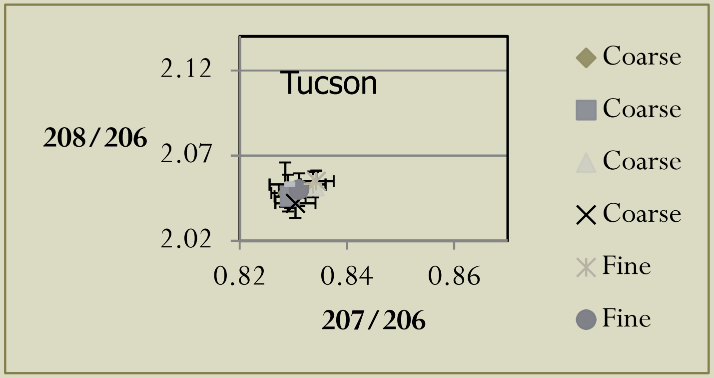
Tucson Pb Isotopes

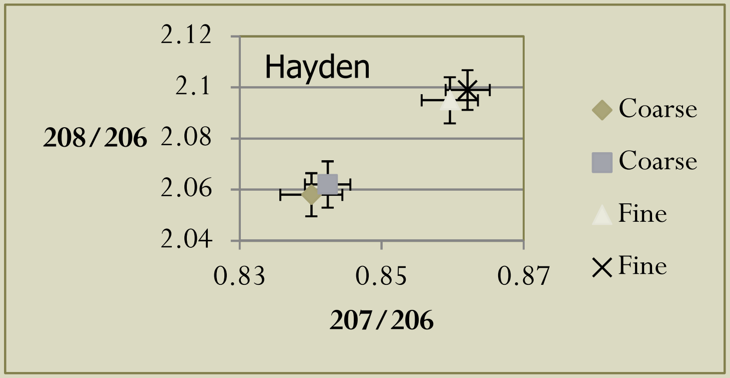
MOUDI not programmed



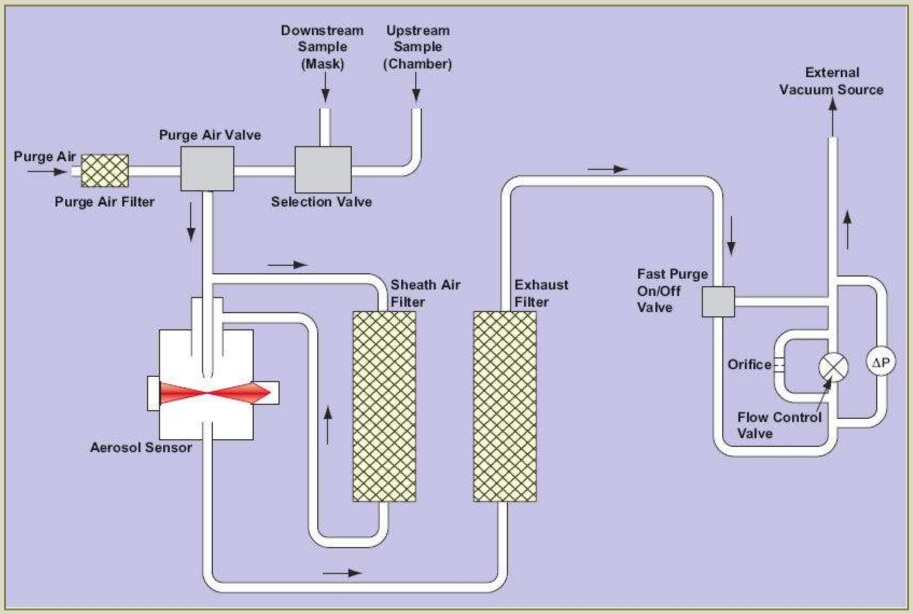
Iron King TSP and Soil

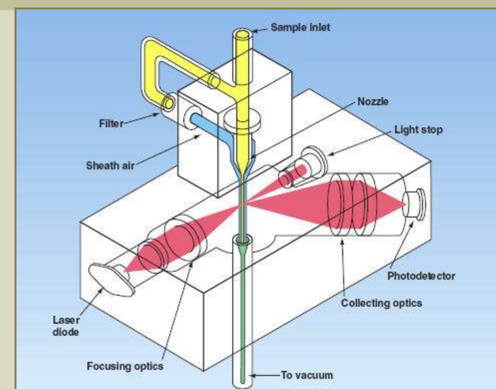


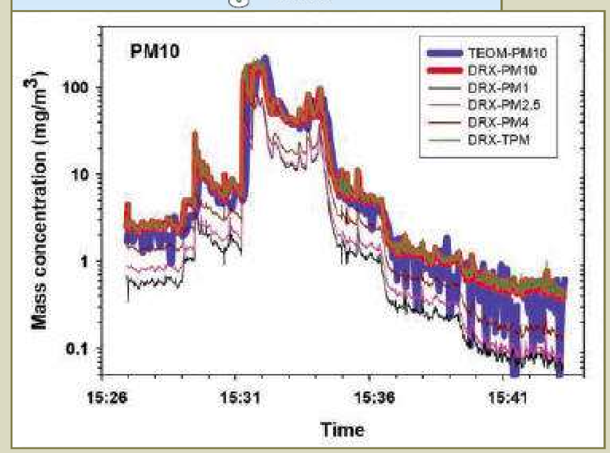




DustTrack Optical Particle Monitor







TSI DustTrak Aerosol Monitor

•Particle concentrations corresponding to PM10, PM2.5, PM1.0

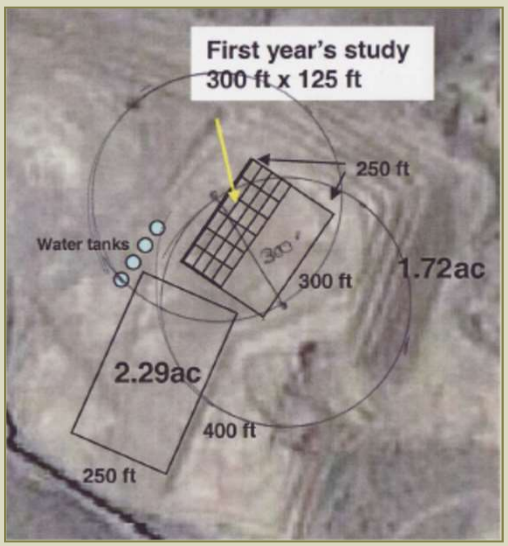
•Rapid response, portable, battery-operated

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.

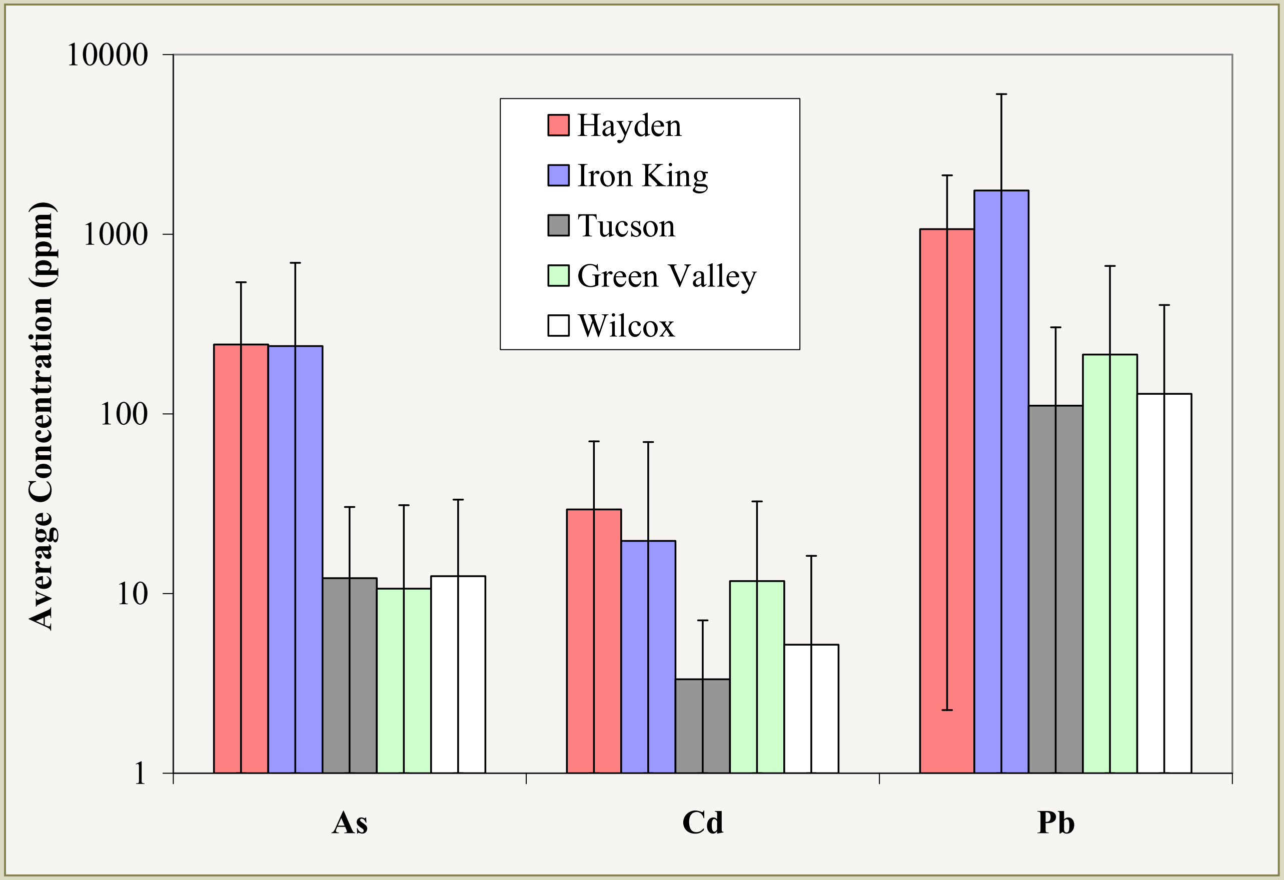


Iron King

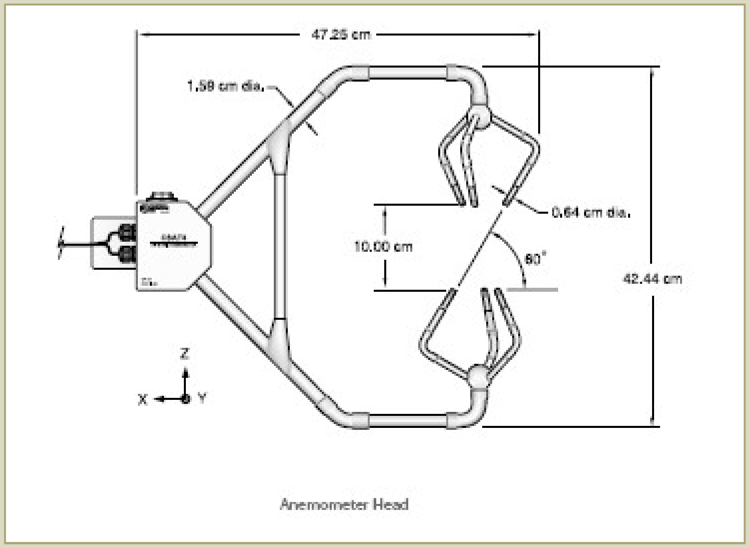
Dust Flux Monitors

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

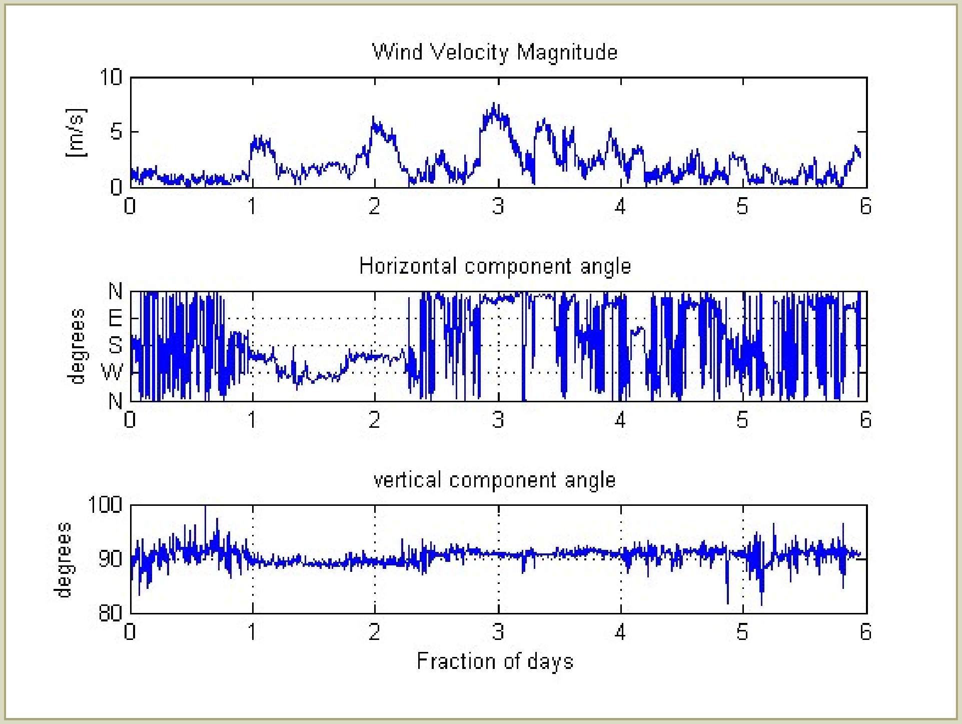
Iron King TSP



Iron King
3-D Winds

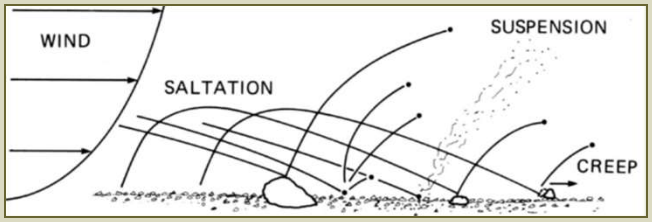


3-D Ultrasonic anemometer



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

Wind Erosion Modeling

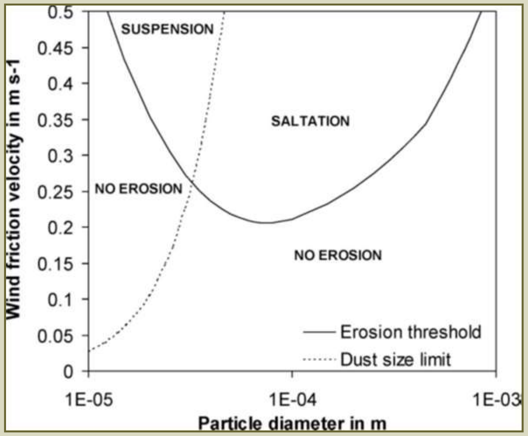


Saltating sand dune particles in wind tunnel

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

Mass flux:

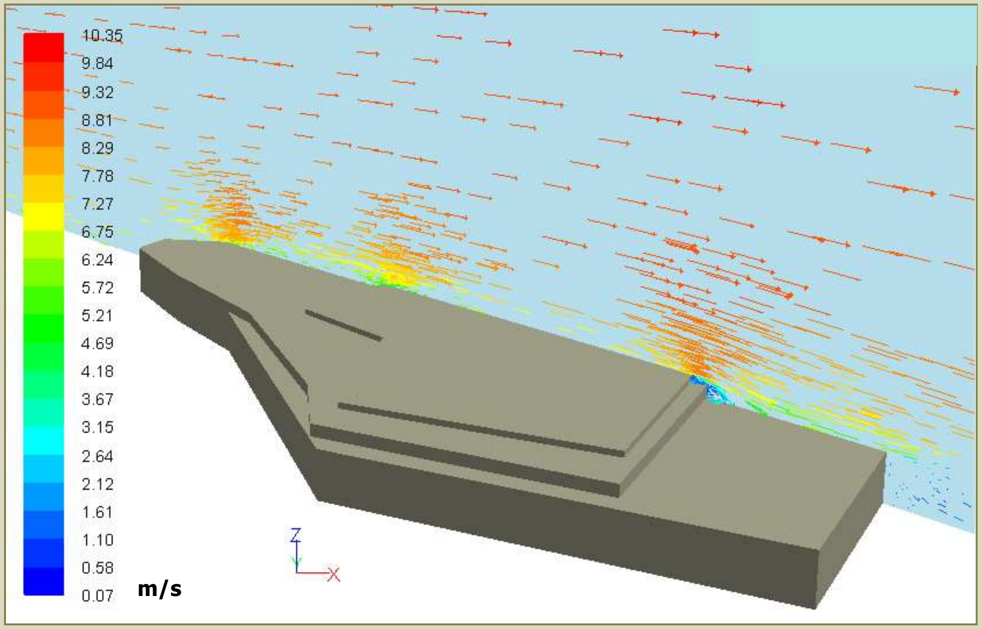
- Creep (rolling): 800-2000 μm D_p
- Saltation (hopping): 100-800 μm D_p
- Suspension (wind blown dust): <100 μm D_p



Greeley-Iversen erosion threshold curve

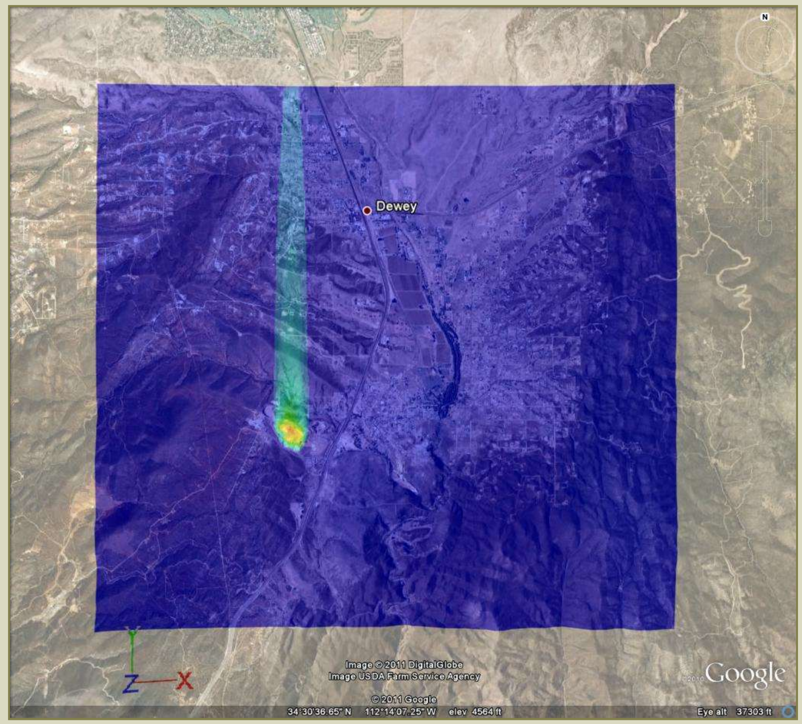
Kon *et al.*, *Int. J. Min. Reclamation & Env.* **21**, 198 (2007)

Wind Vectors - IK tailings
FLUENT

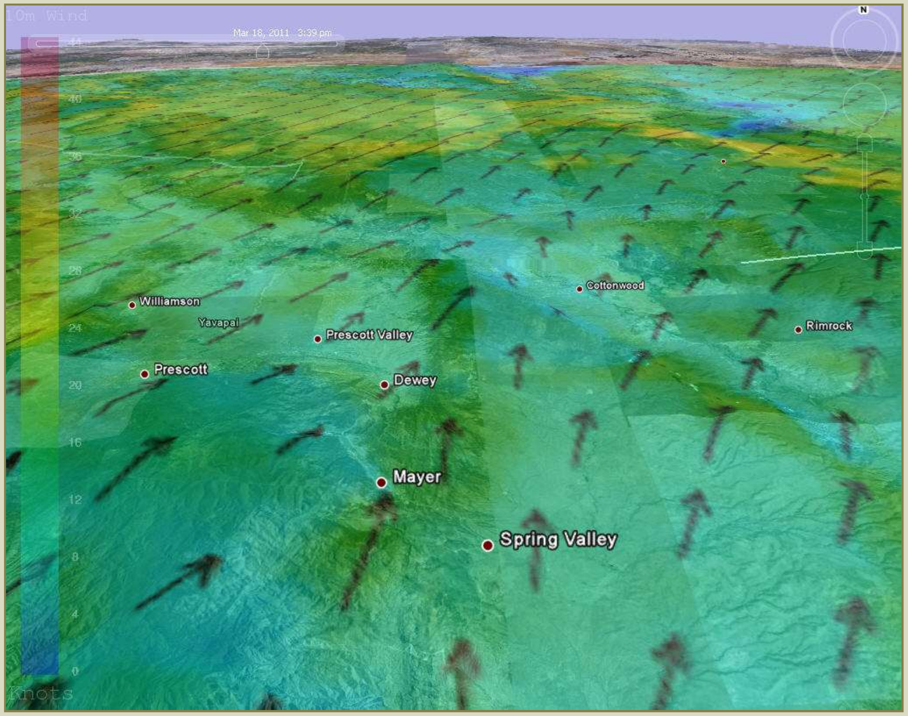


Iron King

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

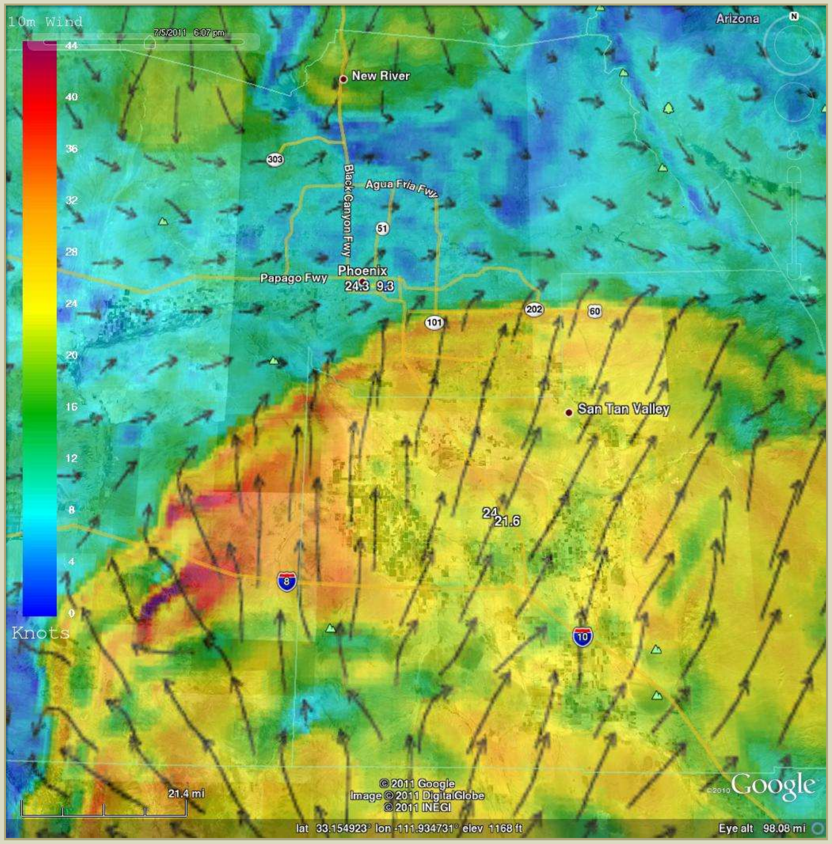


Weather Research and Forecast Model (WRF)



10-meter wind forecast on Google Earth

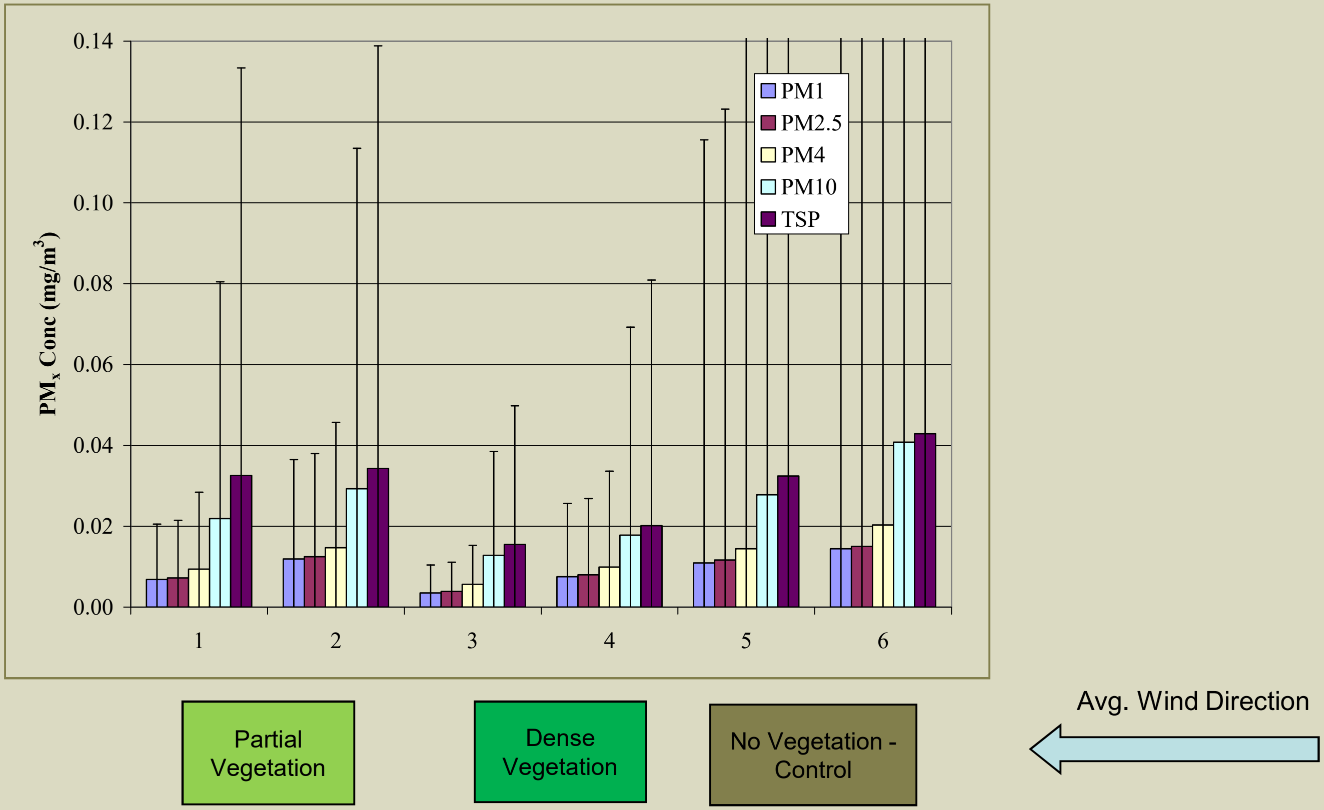
Weather Research and Forecast Model (WRF)



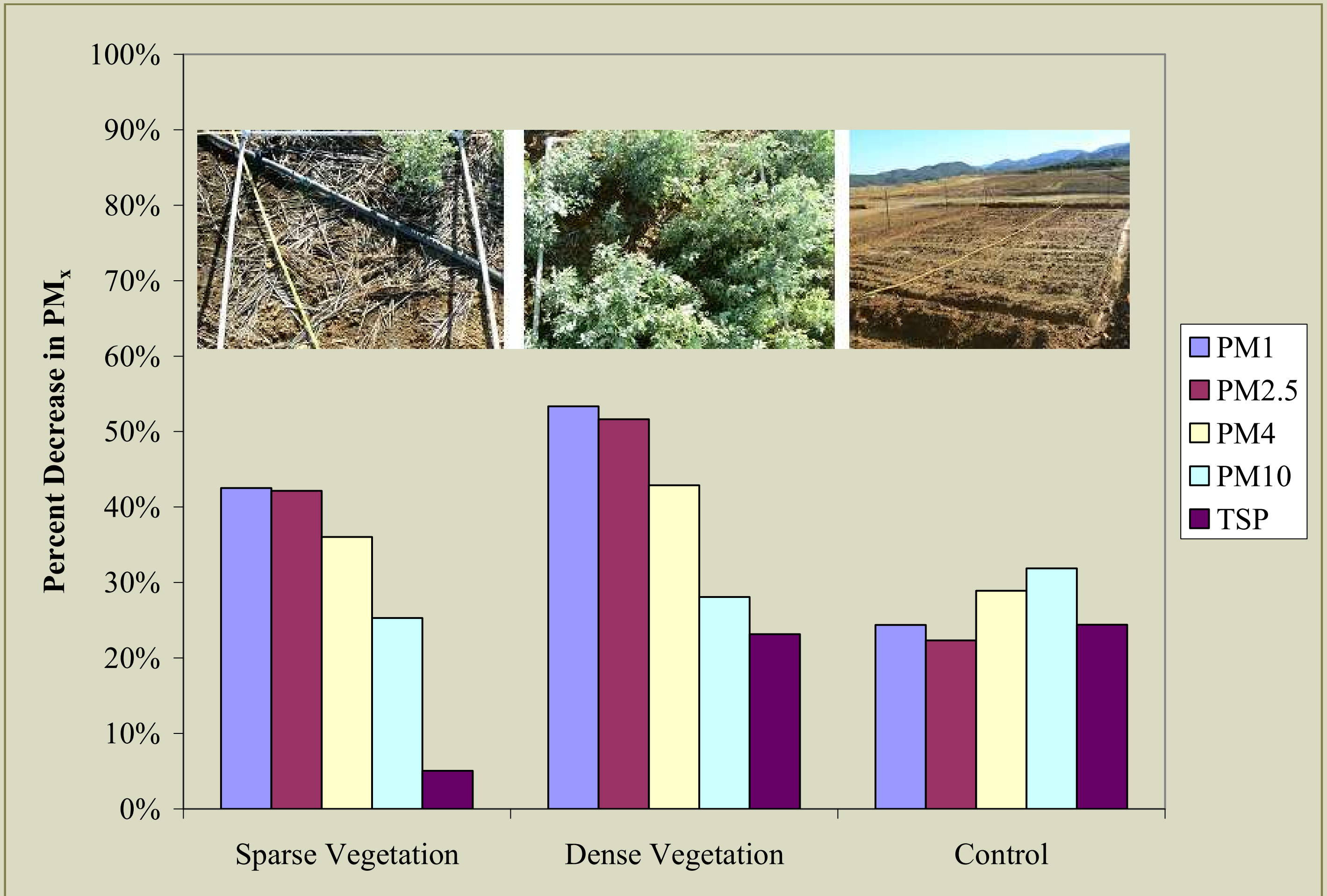
WRF 10-meter wind forecast for Phoenix area: 6 pm, July 5, 2011 (initialized 5 am)

Phoenix dust storm: 8 pm, July 5, 2011

Iron King Dust Track



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
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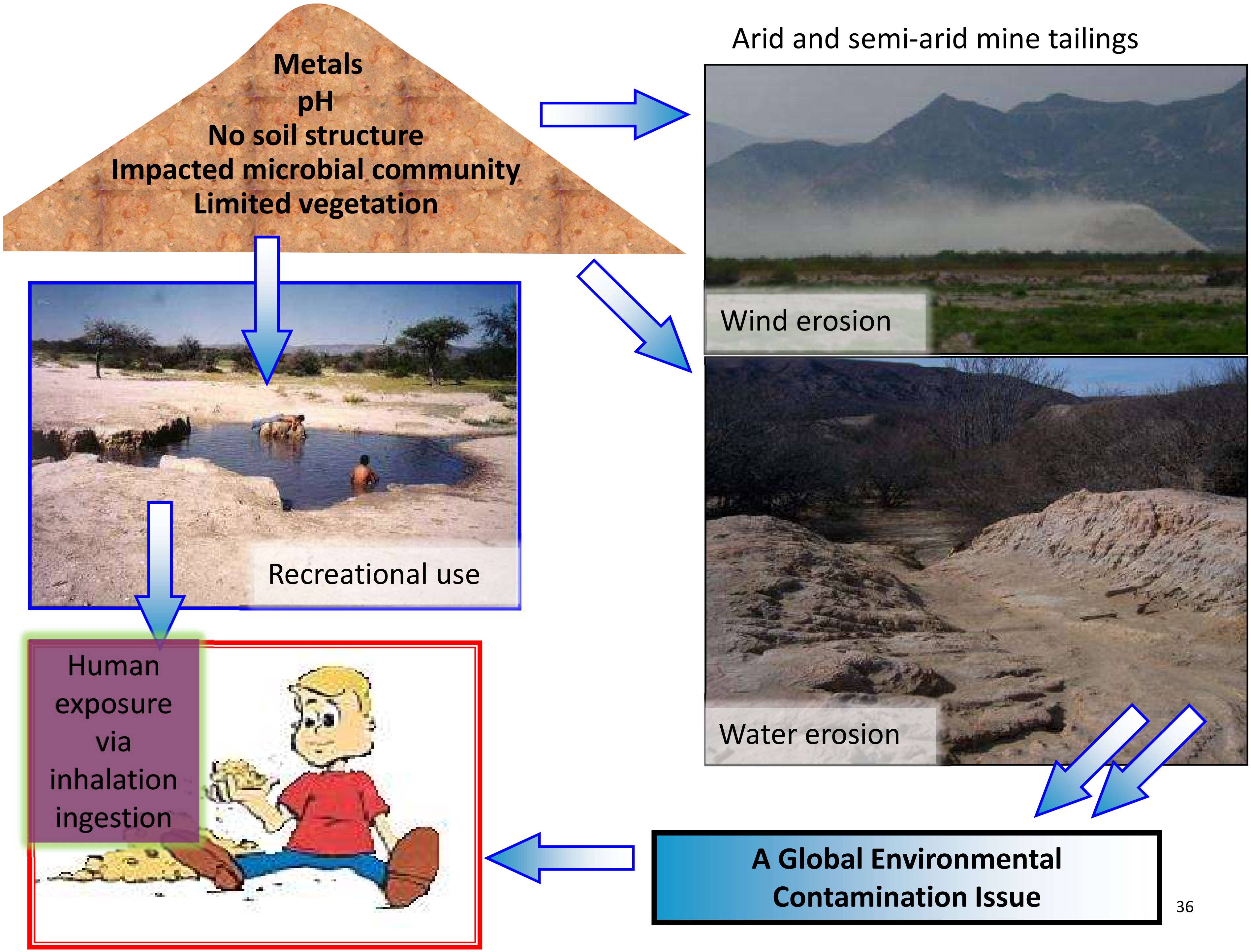
The University of Arizona, Tucson, AZ



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

On a still day….

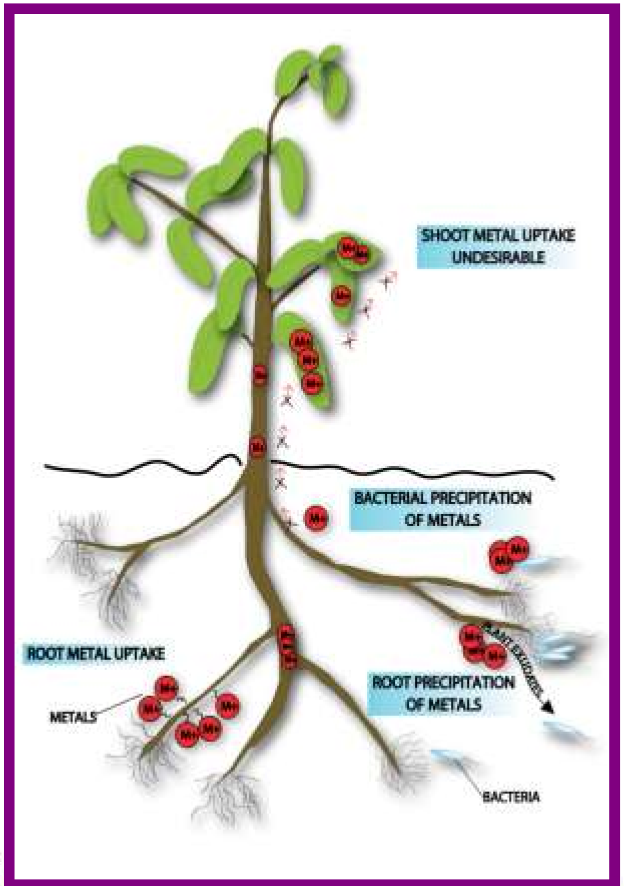
On a windy day….

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.

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

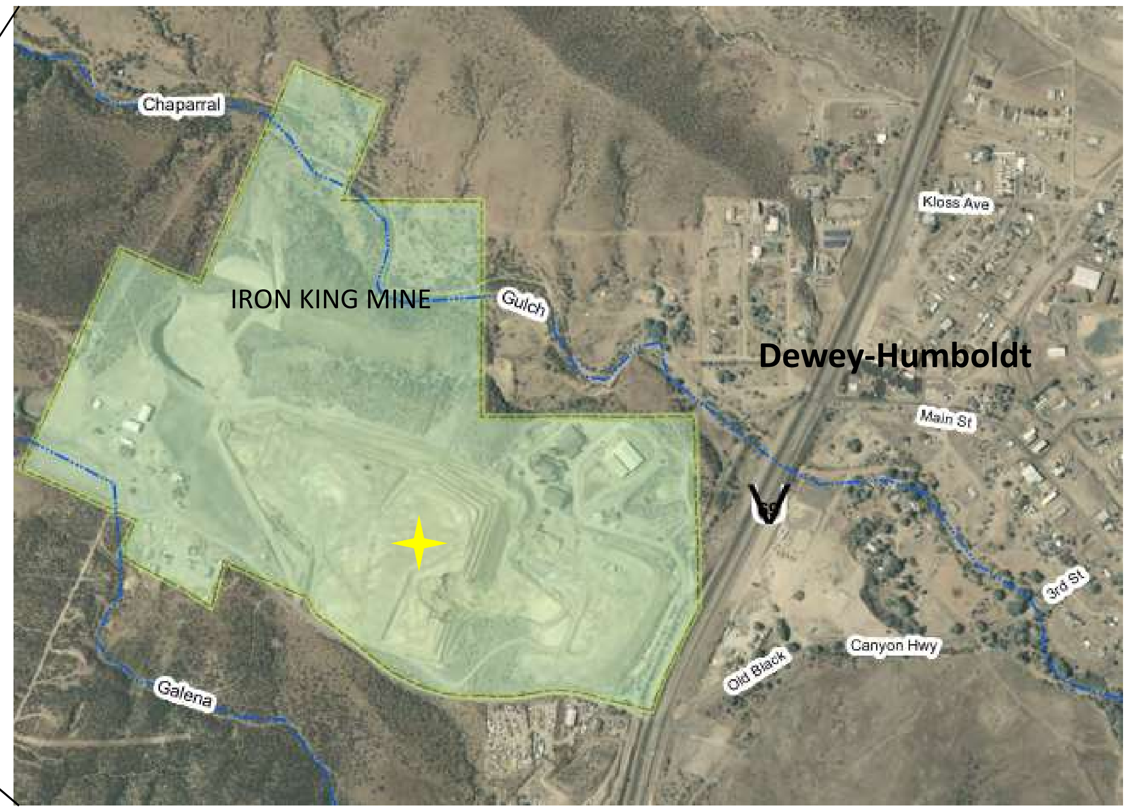
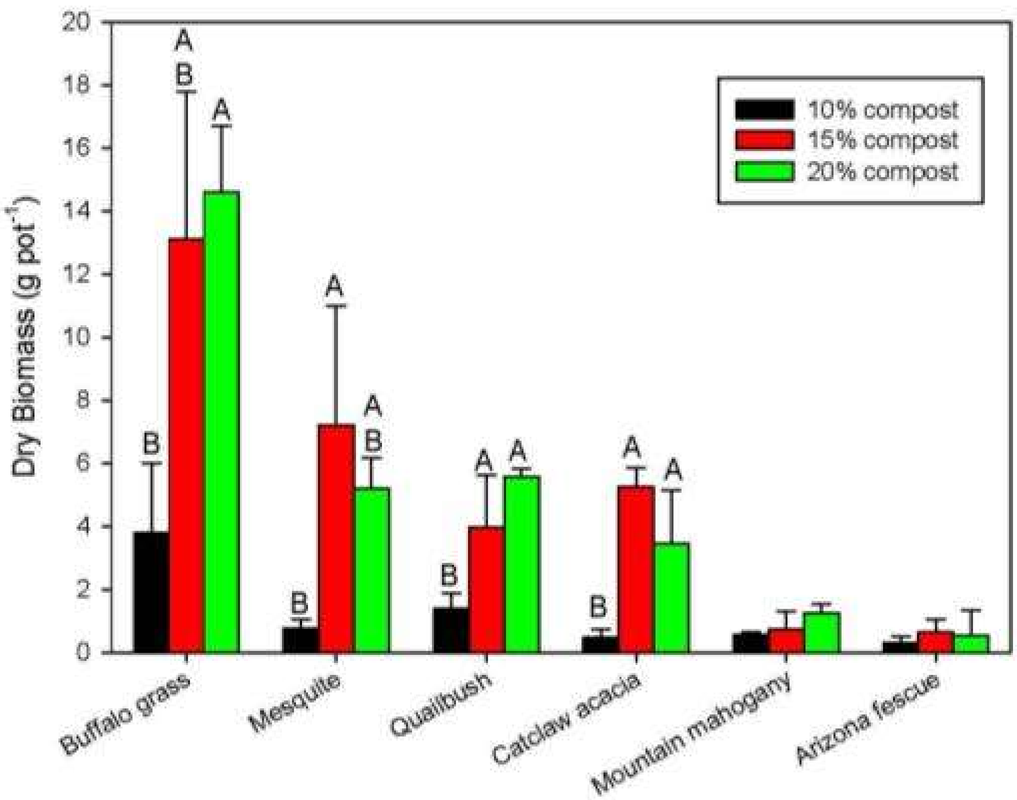


Photo modified from: http://www.azdeq.gov/environ/waste/sps/

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

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%

Greenhouse studies showed:

- Effect of compost was to immediately:

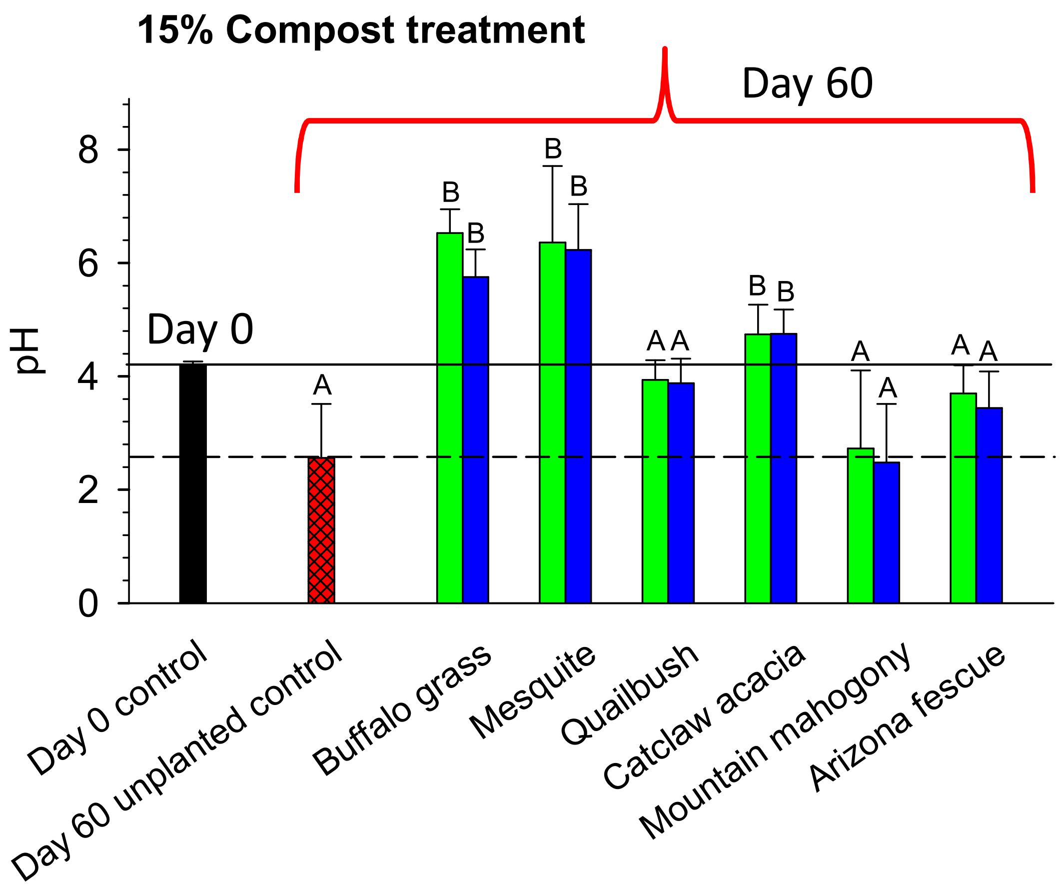
⬇ aqueous metal solubility

⬆ pH

⬆ heterotrophic bacterial counts

- Effect of plants was to:

  Prevent pH from decreasing



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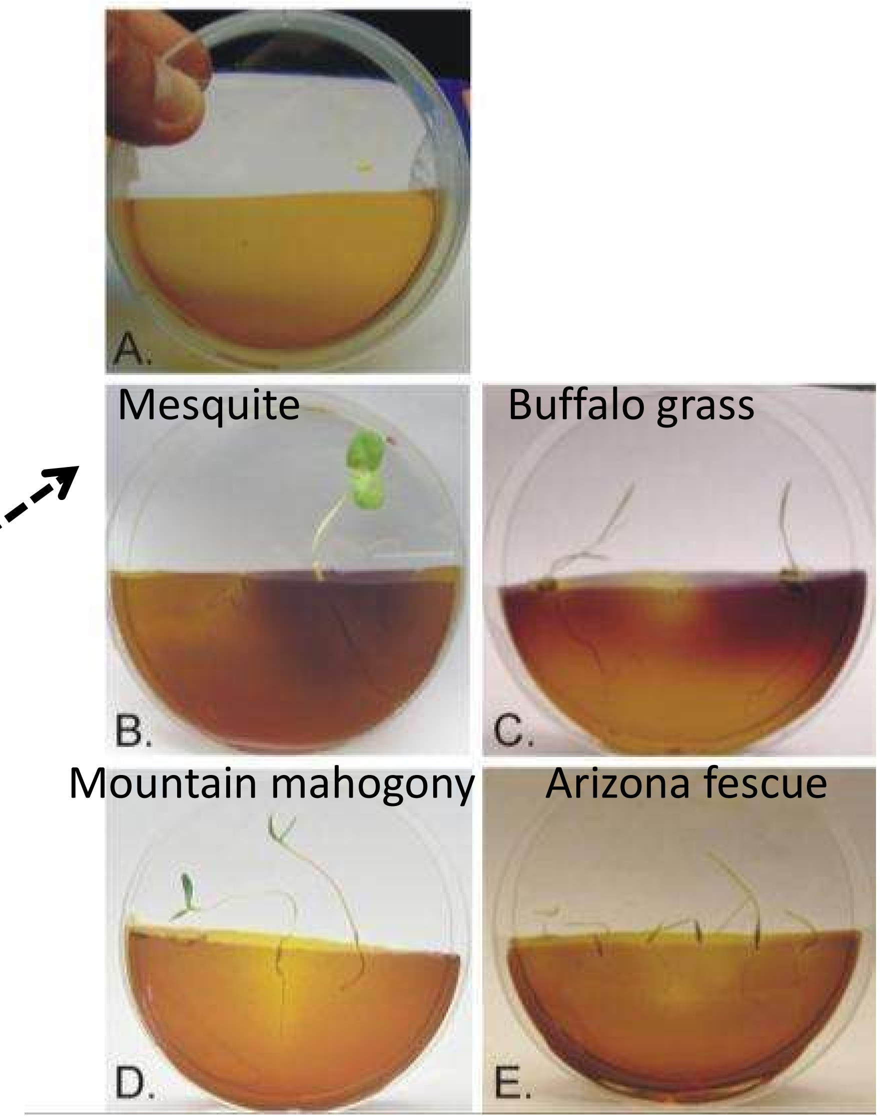


Greenhouse studies showed:

- Effect of compost was to immediately:

↓ aqueous metal solubility

↑ pH

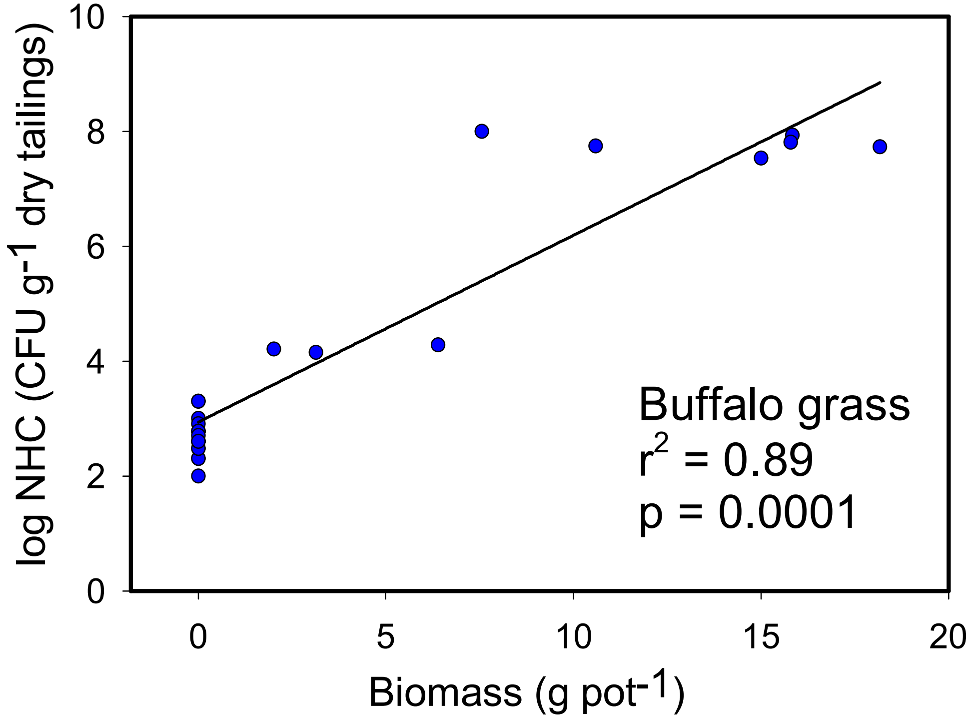
↑ heterotrophic bacterial counts

- Effect of plants was to:

  Prevent pH from decreasing

  Maintain high heterotrophic counts

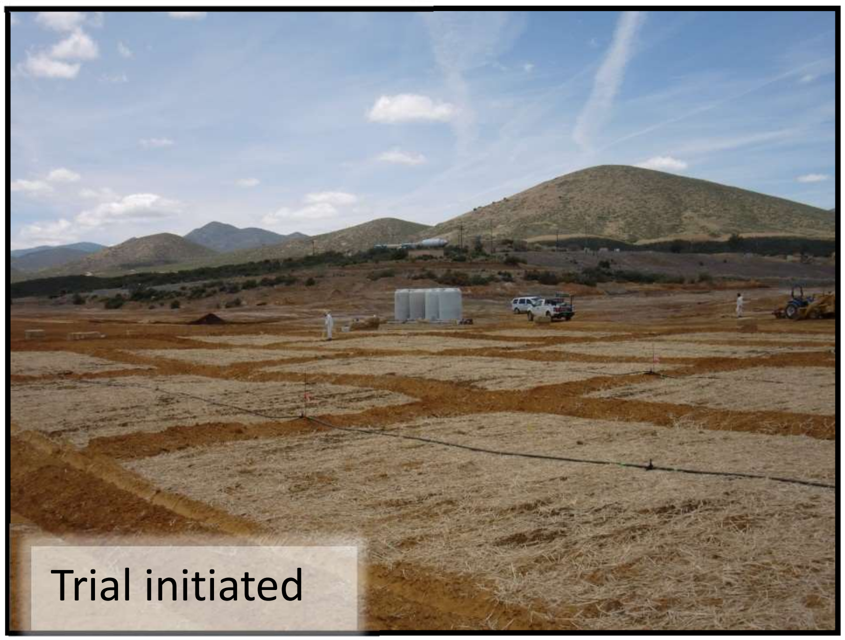
  Shoot metal accumulation < DATLs



Field trial – initiated May 2010


Site preparation


OSHA-trained workers

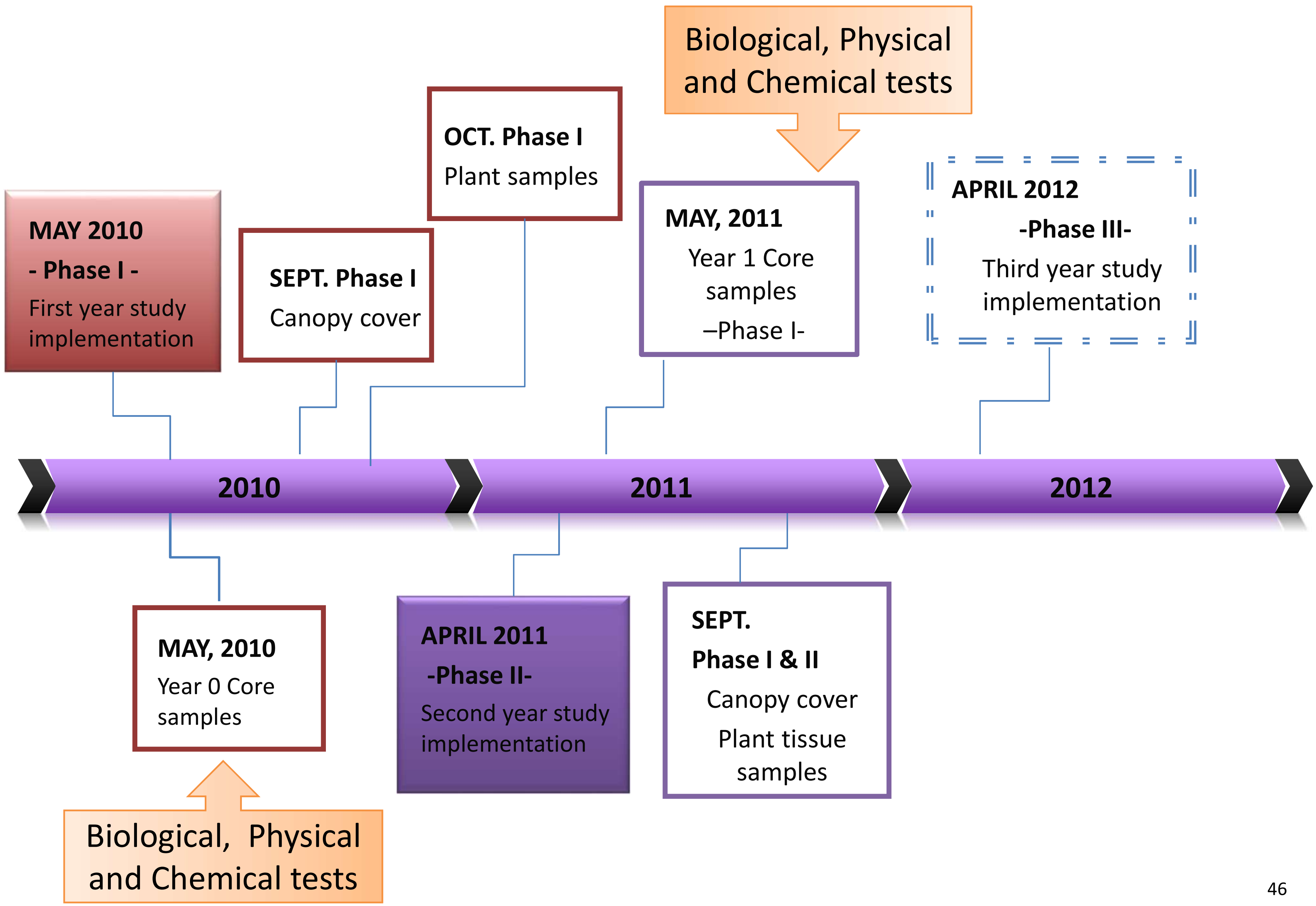

Trial initiated


A windy day

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.

PROJECT TIMELINE



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

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


Step 3: Compost is delivered

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

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

Mixing the compost into the tailings


Compost amendment is complete!!

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

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!

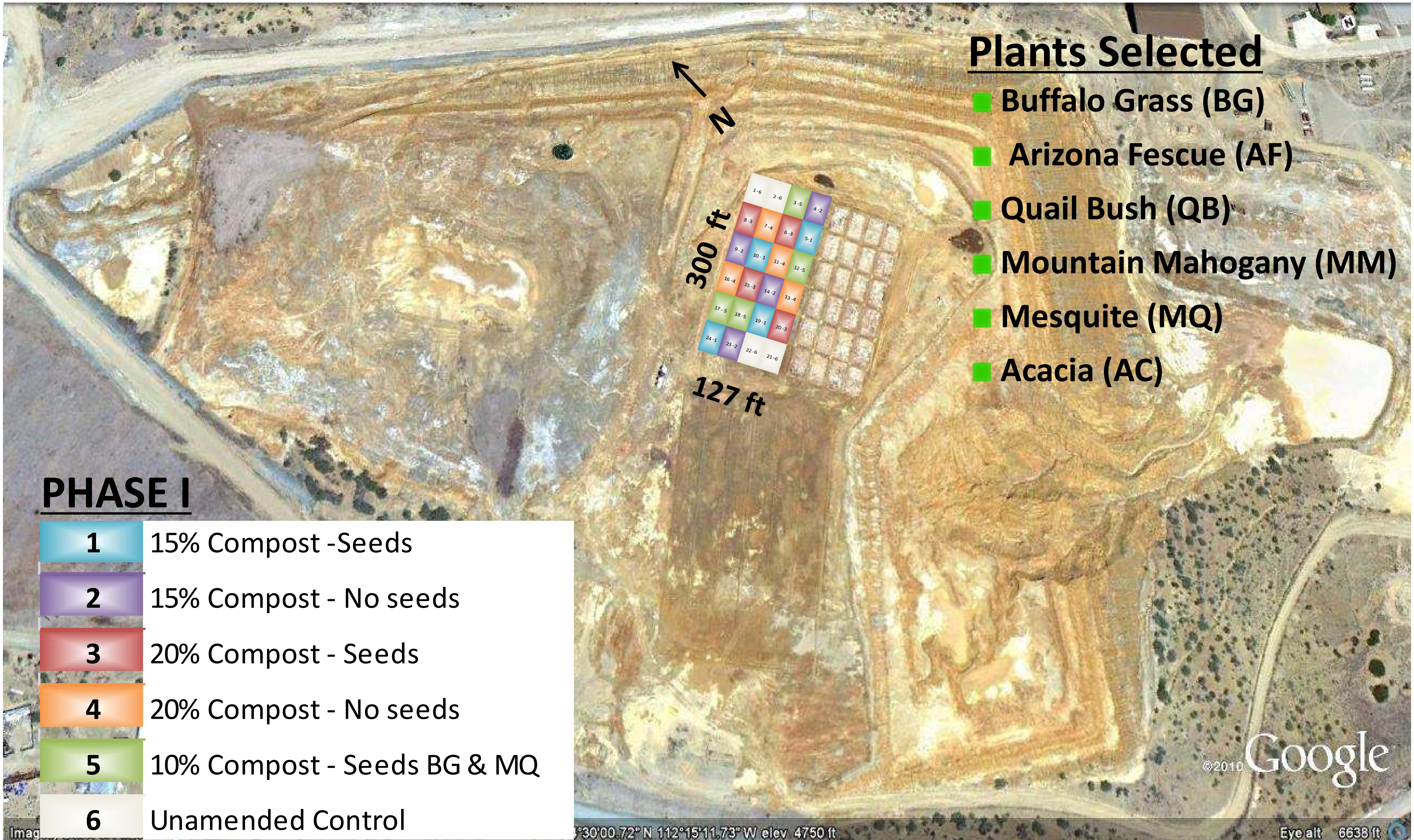
Step 7: Setting up the irrigation


Some finishing touches

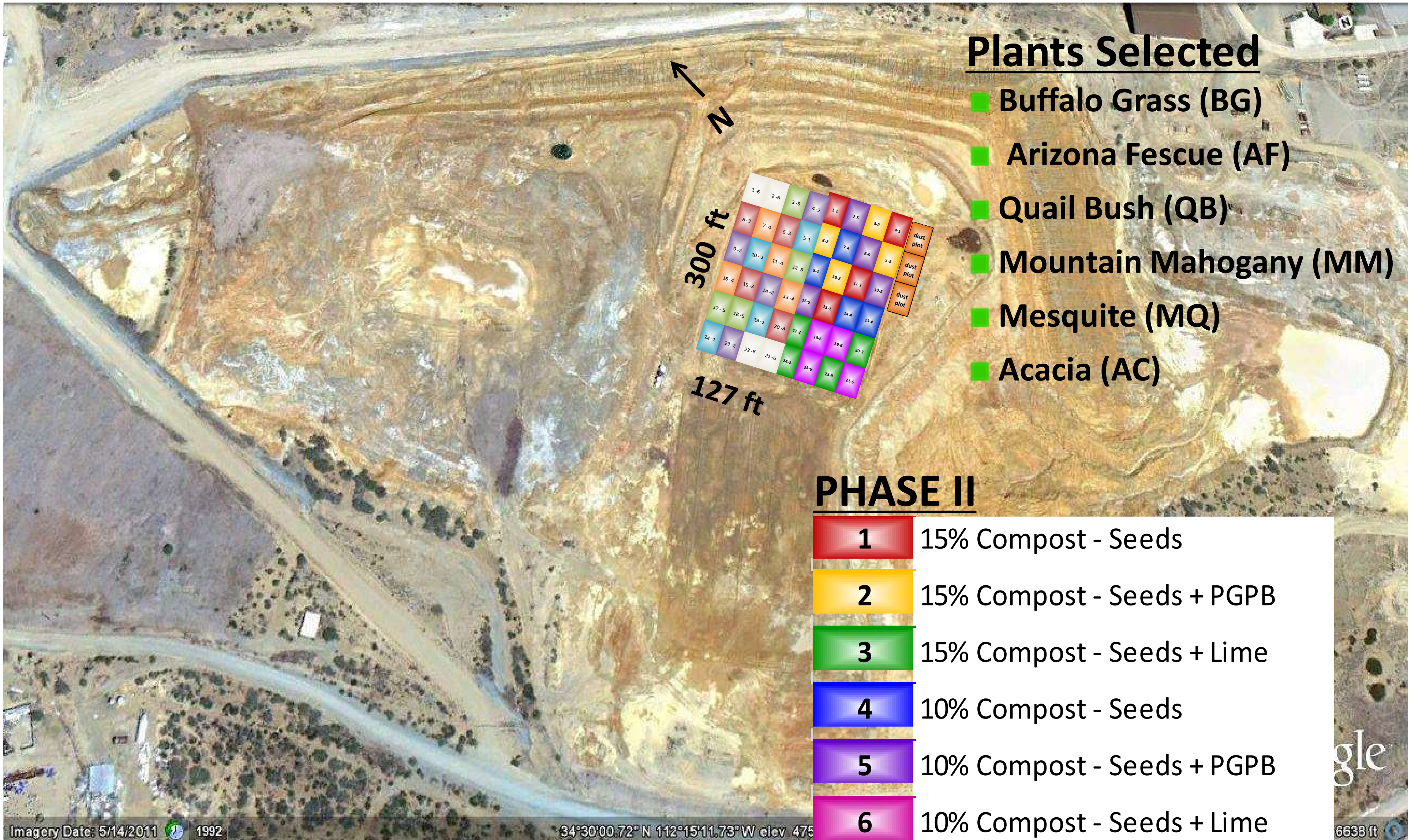

Field trial begins – May 18, 2010

METHODOLOGY -Field plots and treatments-

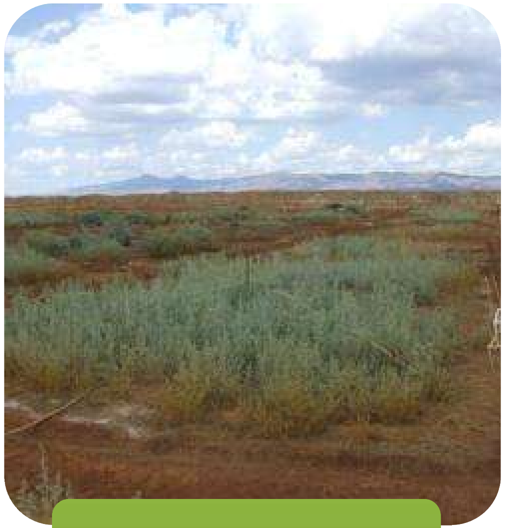
METHODOLOGY -Field plots and treatments-



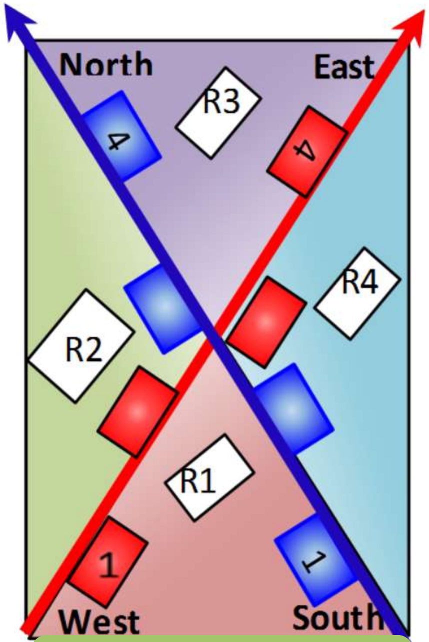
METHODOLOGY -Field plots and treatments-



METHODOLOGY -Canopy Cover-



Two diagonal transects



Daubenmire frame method

Placement of frames and calculation

METHODOLOGY -Neutrophilic Heterotrophic Count (NHC)-

Top 20 cm from core samples each plot

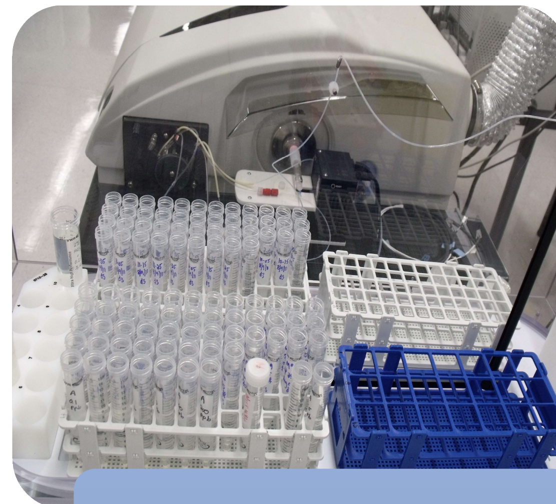
Serial dilutions and plate counts

Counting after 5 days

METHODOLOGY -Shoot uptake of metals-

Plant tissue samples BG and QB

Washing and drying

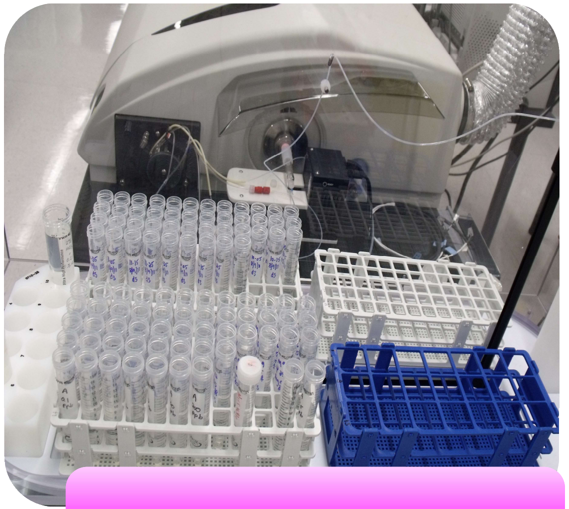


Microwave digestion and ICP-MS analysis

METHODOLOGY – 1:1 paste measurement of EC and pH

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

1:1 paste



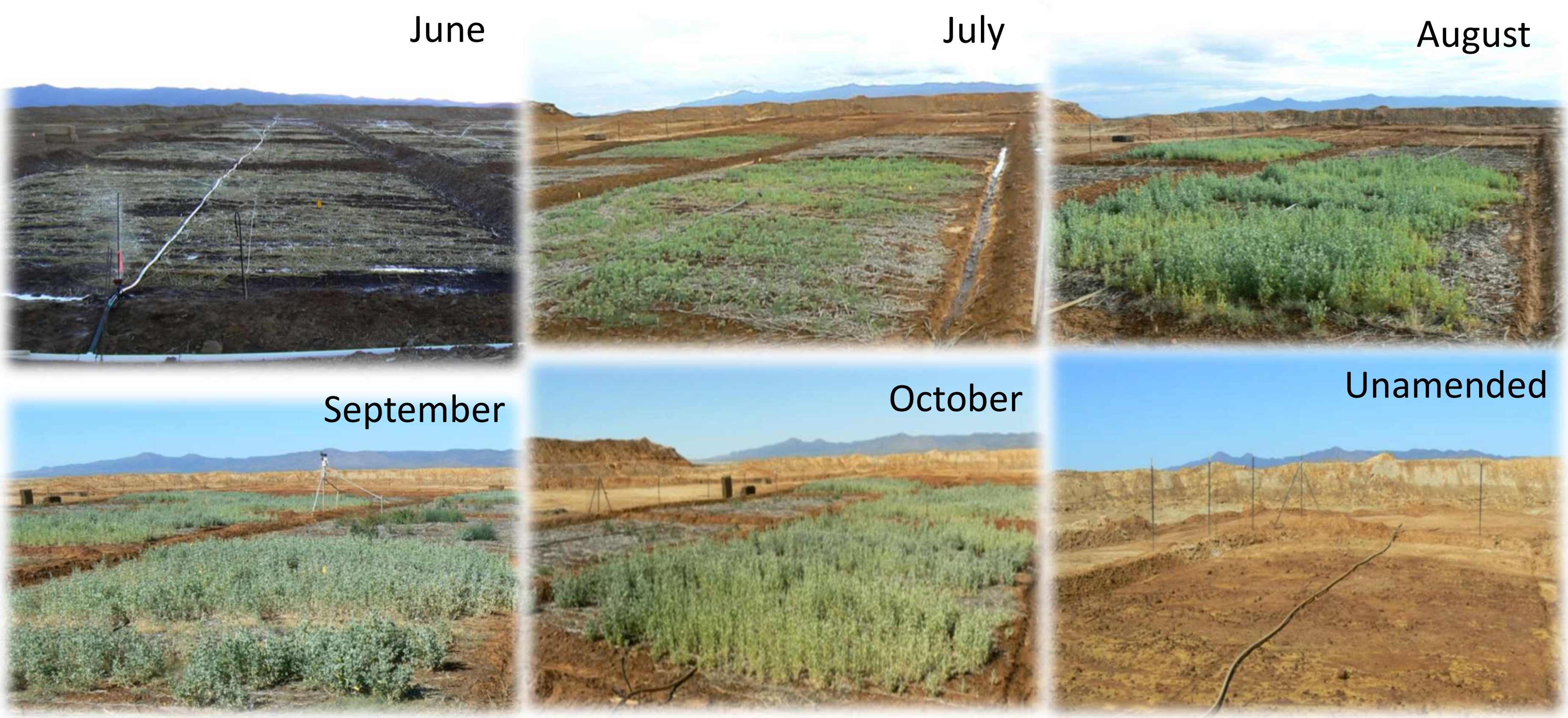
pH meter, EC probe

RESULTS

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

After 17 months of phytostabilization

Results – Canopy Cover



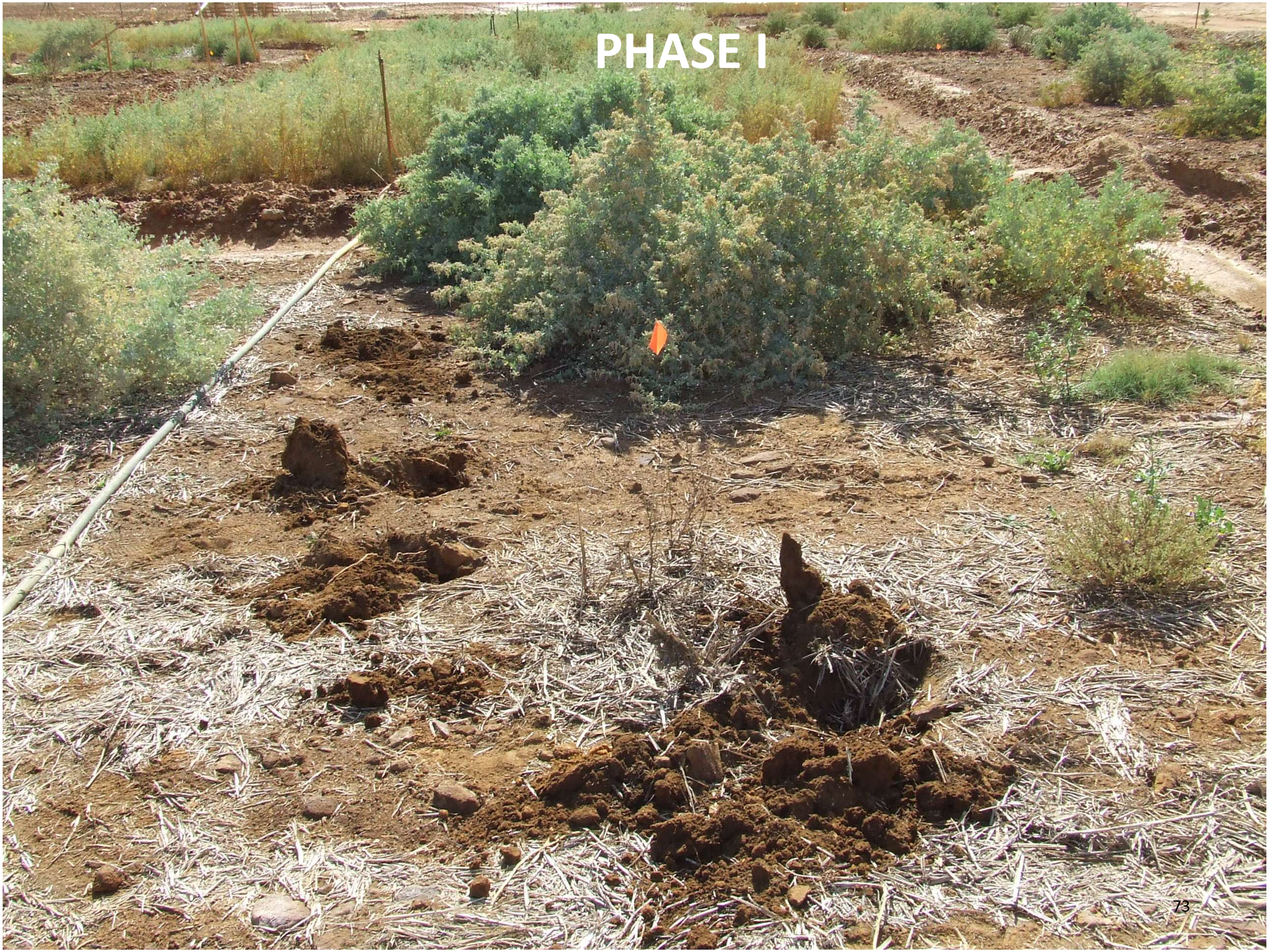
RESULTS -CANOPY COVER PHASE I -

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

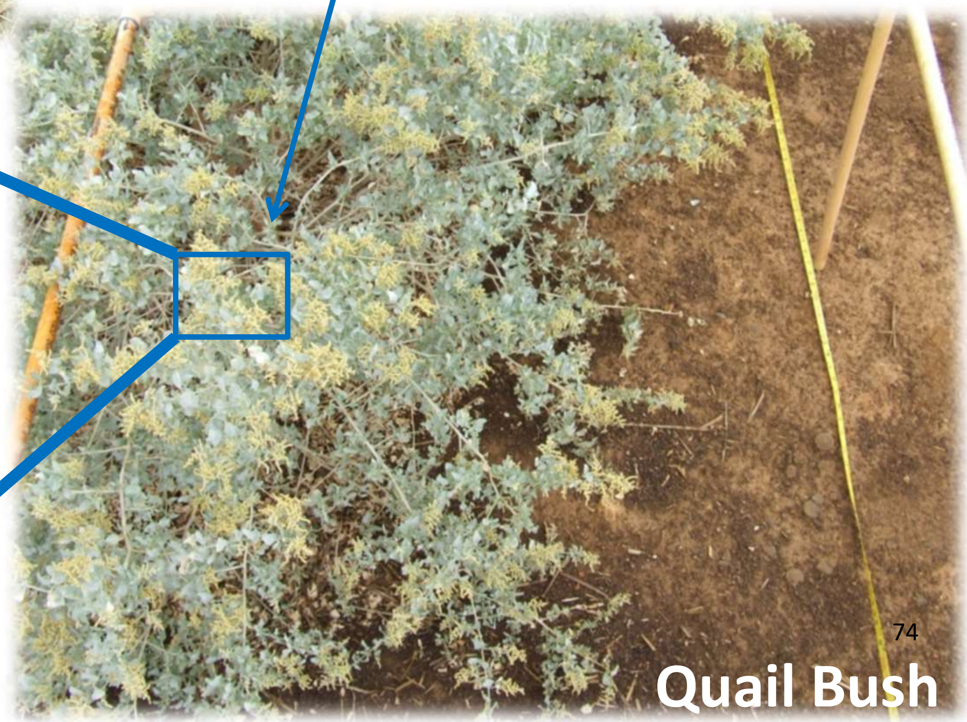
Treatments	% Canopy Cover[a]		
	5 Months[b]	17 Months[b]	[c]T-test
20% - Seeds	33.8 ± 5.4 a	26.3 ± 1.9 a	S*
20% - No Seeds	4.2 ± 2.2 b	16.1 ± 5.9 ab	S*
15% - Seeds	38.7 ± 6.6 a	18.6 ± 11.4 ab	S*
15% - No Seeds	6 ± 2.3 b	7.15 ± 6.5 bc	NS
10% - BG/MQ	29.9 ± 10.0 a	23.8 ± 6.7 a	NS
Unamended control	0 b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

PHASE I



Blooming and seeds



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)

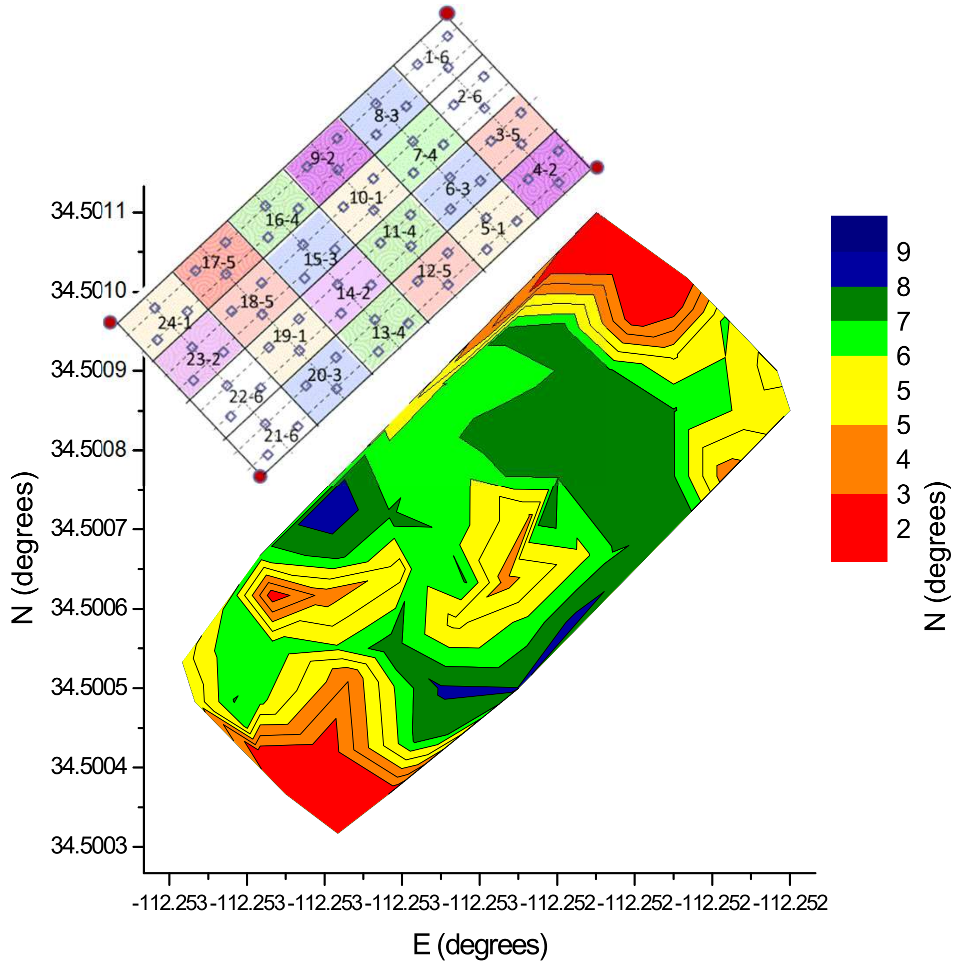
RESULTS -SHOOT UPTAKE OF METALS-

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	

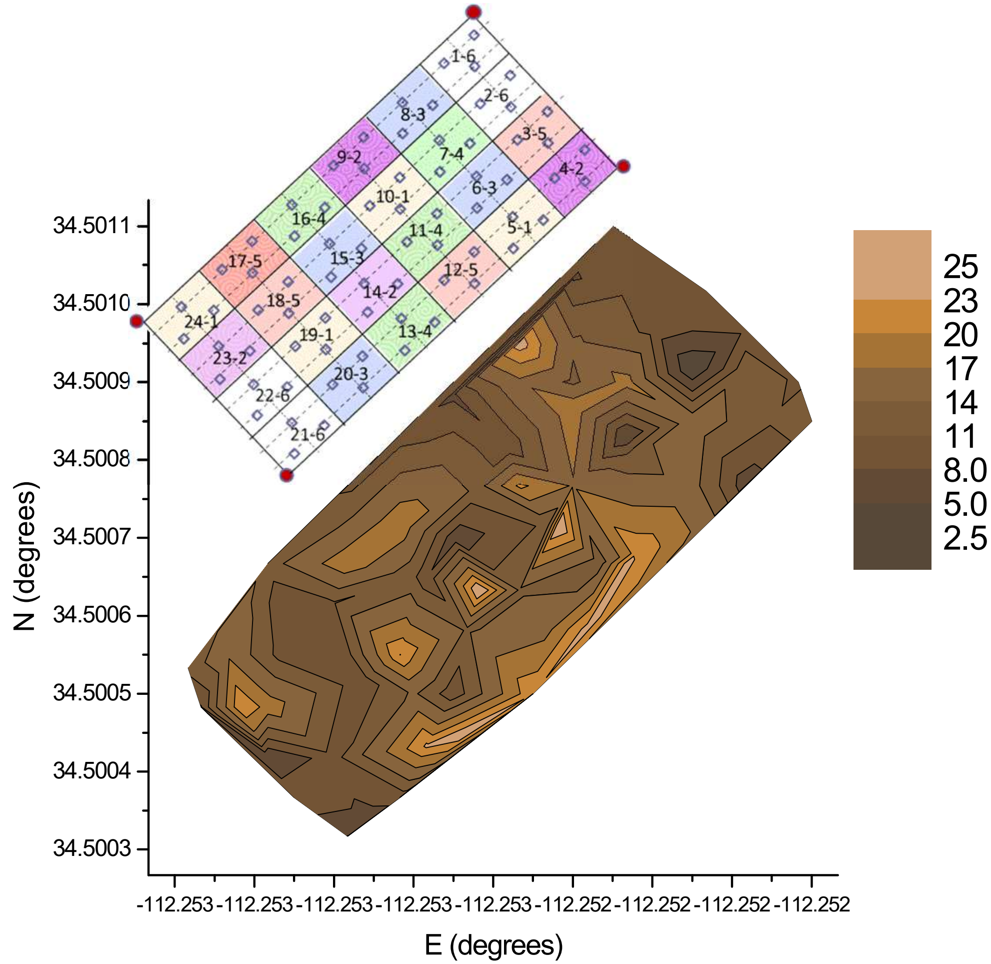
[a] DATL= domestic animal toxicity limit. [b] Values are mean ± standard deviation (n= 4).
[c] t-Test p<0.05 for each row (NS = no significant difference; S* = significant difference).

Initial Surface Characterization of Year 1 Plots

pH



EC (mS cm^{-1})



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

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-

15% Seeds

10% Seeds

15% Seeds+pgpb

10% Seeds+pgpb

15% Seeds+Lime

10% Seeds+Lime

15% Seed +Lime


15% Seed +Lime

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.

THANKS TO…

supported by: **NIEHS SRP**

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<u>Region 9 EPA:</u>
Leah Butler
Monika O'Sullivan
<u>Site owner:</u>
Stephen Schuchardt

Superfund Research Program

NIEHS
National Institute of Environmental Health Sciences


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

Superfund Research Program
The University of Arizona

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.

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