Ecotoxic Metal Retention in Ecologically Engineered Passive Treatment Systems: An *Engineering With Nature* Application in Small Mid-Continent Watersheds

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THE UNIVERSITY OF OKLAHOMA
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SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE
The UNIVERSITY of OKLAHOMA

CREW
Center for Restoration of Ecosystems and Watersheds
University of Oklahoma

Natural Infrastructure

- Natural capital
- Green infrastructure
- Nature’s services
- Ecosystem services

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- Green infrastructure
- Nature's services
- Ecosystem services

PROVISIONING SERVICES

Products obtained from ecosystems

- Energy
- Seafood
- Biomedial
- Transportation
- National defense

REGULATING SERVICES

Benefits obtained from the regulation of ecosystem processes

- Flood prevention
- Climate regulation
- Erosion control
- Control of pests and pathogens

CULTURAL SERVICES

Nonmaterial benefits obtained from ecosystems

- Educational
- Recreational
- Heritage
- Spiritual

SUPPORTING SERVICES

Services necessary for the production of all other ecosystem services

- Biological diversity maintenance
- Nutrient recycling
- Primary productivity

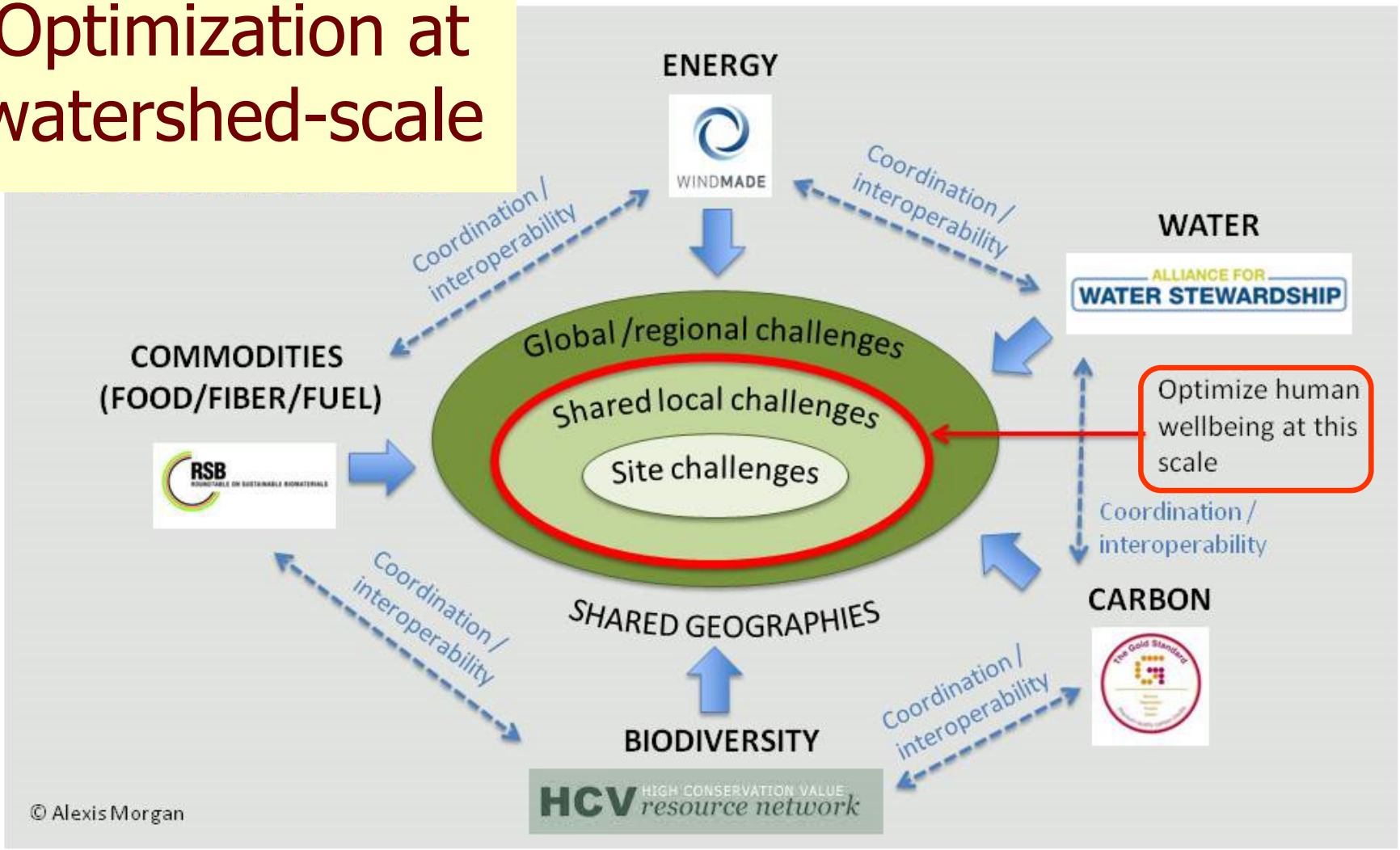
source: *Final Recommendations of the Interagency Ocean Policy Taskforce, 2010*

Natural Infrastructure and Ecosystem Services

- **Conservation of intact natural ecosystems**
  - Taxa richness and diversity
  - Biogeochemical functions
- **Creation and restoration of ecologically engineered ecosystems**
  - Often specific to solving anthropocentric problems

North Texas Municipal Water District
East Fork Raw Water Supply Project and
John Bunker Sands Wetlands Center

Optimization at watershed-scale



https://www.2degreesnetwork.com

Center for Restoration of Ecosystems and Watersheds

- Watershed biogeochemistry
  - Drainage-basin scale evaluations
  - Materials and energy transport and fate
- Ecological engineering
  - Ecosystem remediation, restoration and creation
  - Passive treatment systems
  - Low impact development
  - Water and land reclamation

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Watershed Biogeochemistry

- Watershed management and restoration
  - Complex land use/land cover impacts
  - Reservoir water and ecological quality
  - Indirect potable water reuse
  - Industrial and agricultural water quality
  - Urban stormwater management
  - Novel data collection technologies (sUAS)
  - Wetland creation and restoration

Ecological Engineering

- Sustainable ecosystem design for water and land remediation and restoration
- Passive treatment technologies
  - Tri-State Lead-Zinc Mining District (OK, KS, MO) – Tar Creek Superfund Site
  - Arkoma Basin Coal Fields (OK, AR)
  - Altiplano and Eastern Cordillera (Bolivian Andes)
  - Urban stormwater LID BMPs (OK)

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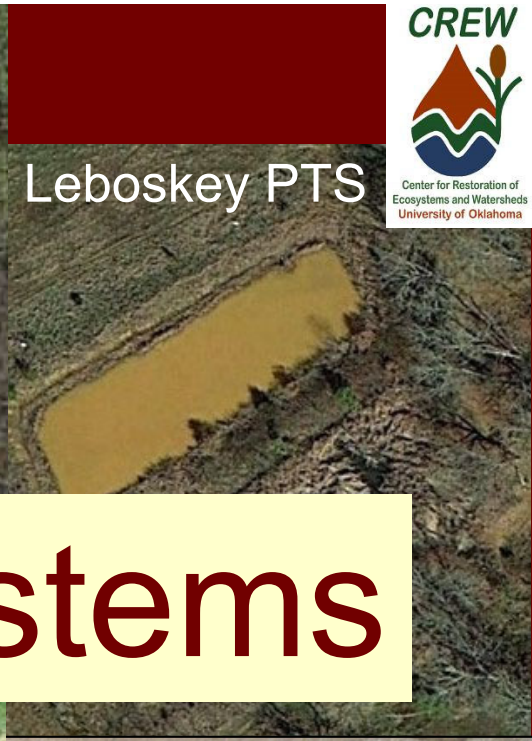
Slide 9

NRW2 Nairn, Robert W., 11/6/2018



CREW builds ecosystems

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Slide 10

NRW2 Nairn, Robert W., 11/6/2018

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Ecological Engineering

The design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both

- Mitsch and Jorgenson (2004)

Ecological Engineering

The design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both

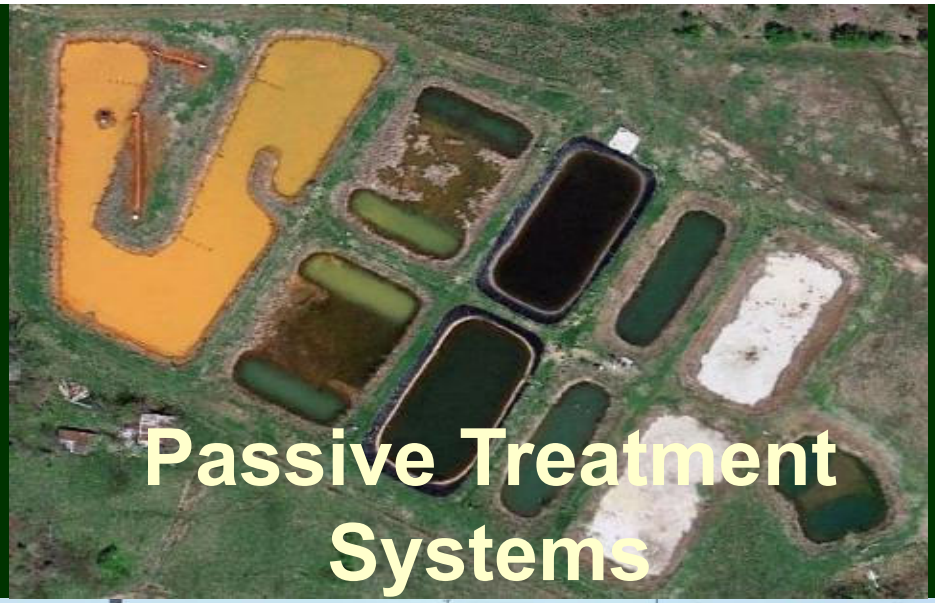
- Mitsch and Jorgenson (2004)

Engineering With Nature

The intentional alignment of natural and engineering processes to efficiently and sustainably deliver economic, environmental, and societal benefits through collaboration

- Bridges (2019)

Problems/Challenges


Passive Treatment Systems

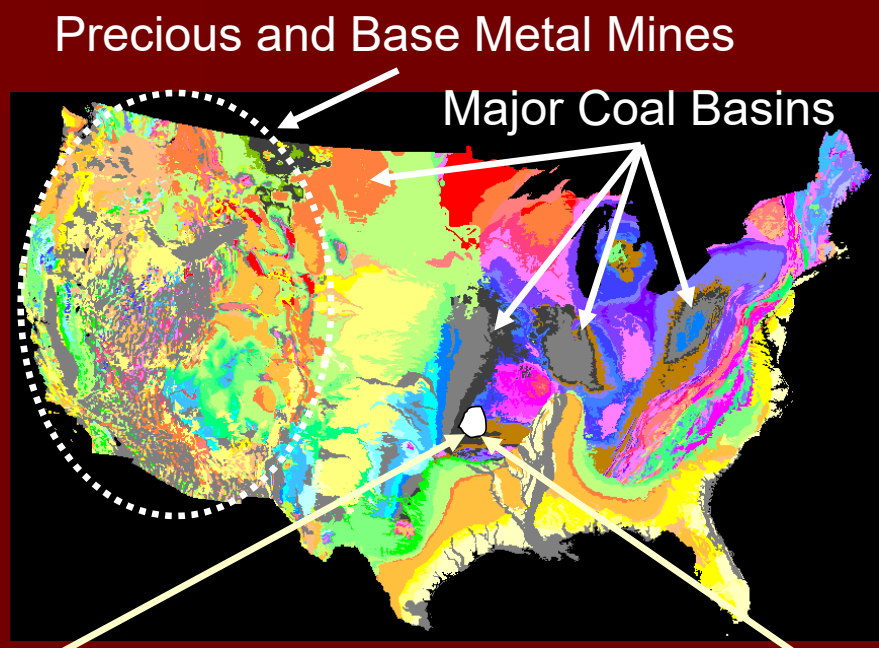
Receiving Stream Recovery

Conclusions

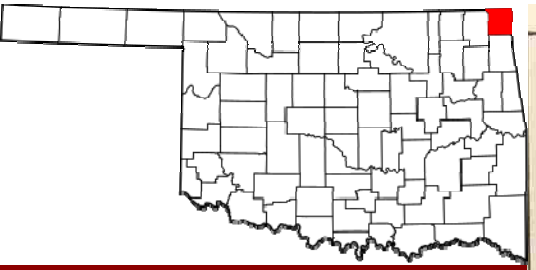
Problem/Challenges

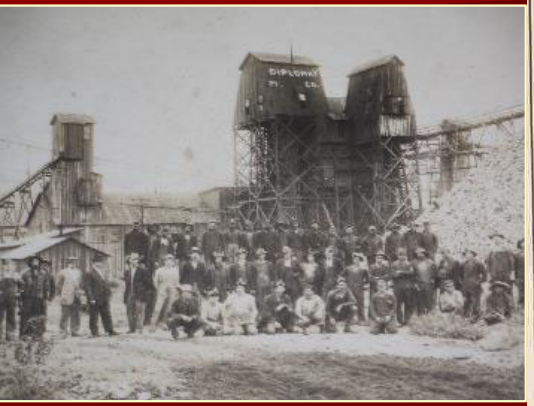
Tri-State Lead-Zinc Mining District

- >3000 km^2 mined ~1838-1971
- Mississippian sulfides
  - Galena (PbS)
  - Sphalerite (ZnS)
- Extensive underground workings
- Massive surface processing operations



Tri-State Lead-Zinc Mining District
- Joplin Field, Missouri
- Galena Field, Kansas
- Picher Field, Oklahoma





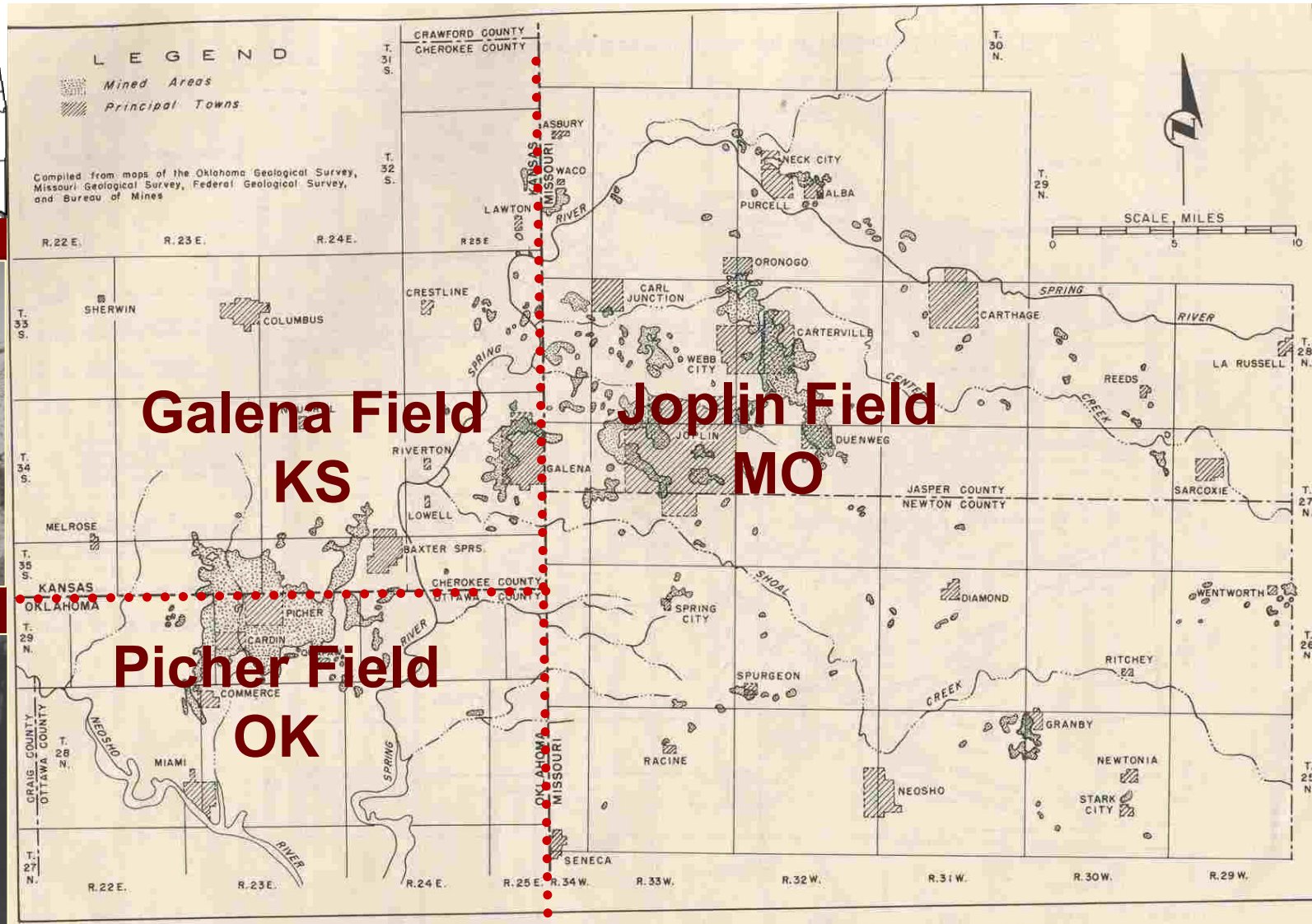
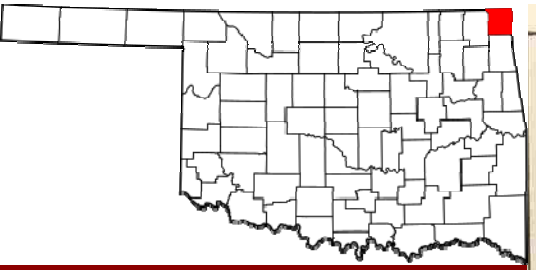
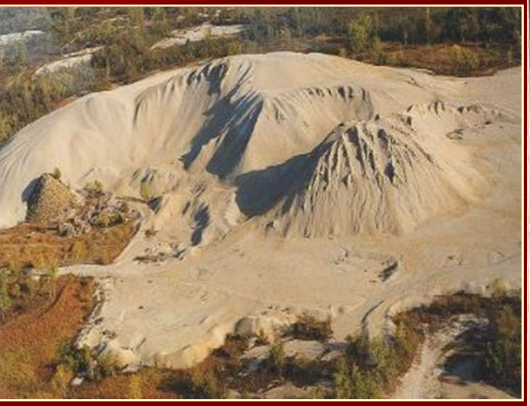
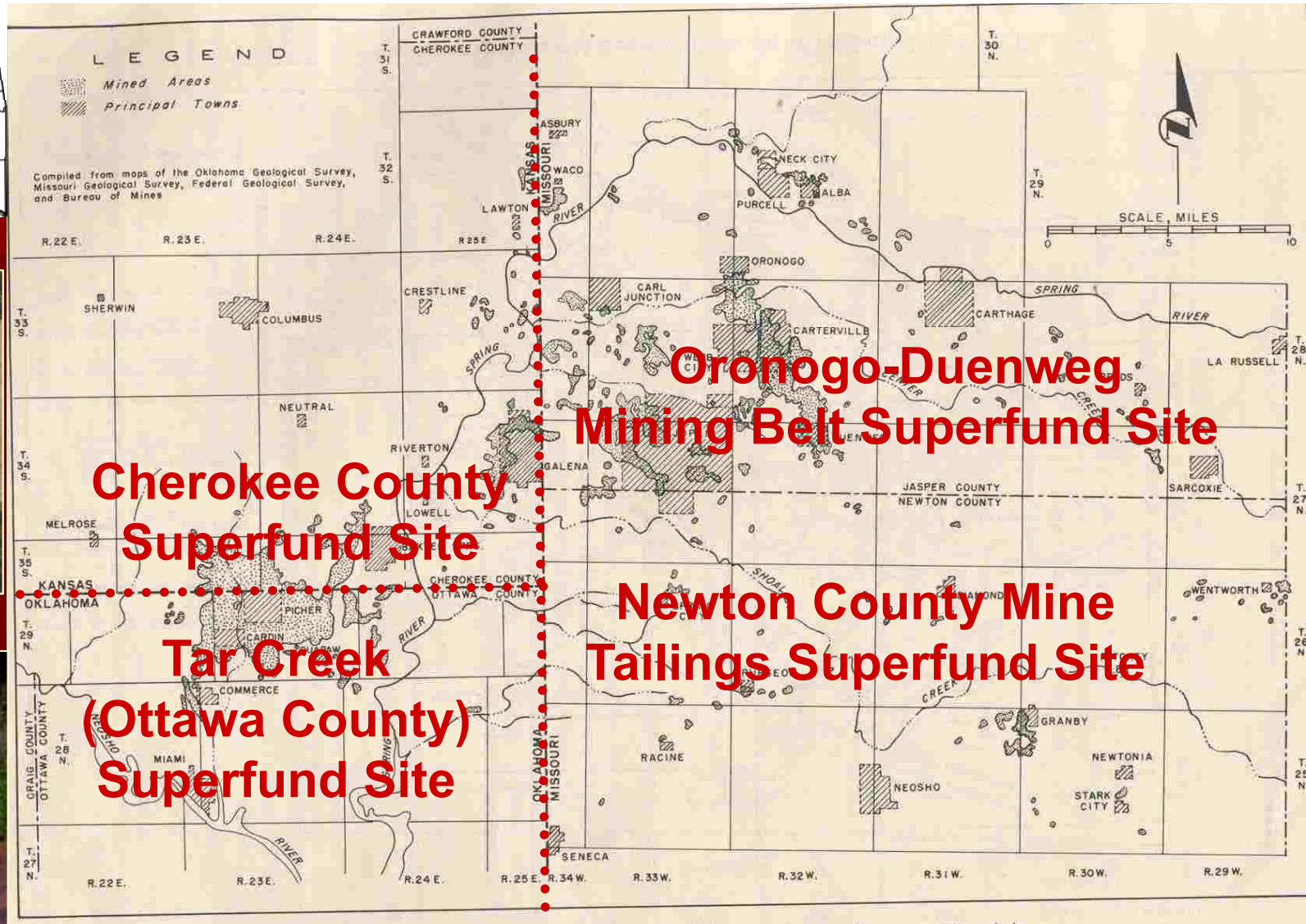


FIGURE 1. - Principal Part of Tri-State Zinc-Lead District, Showing Mined Areas.







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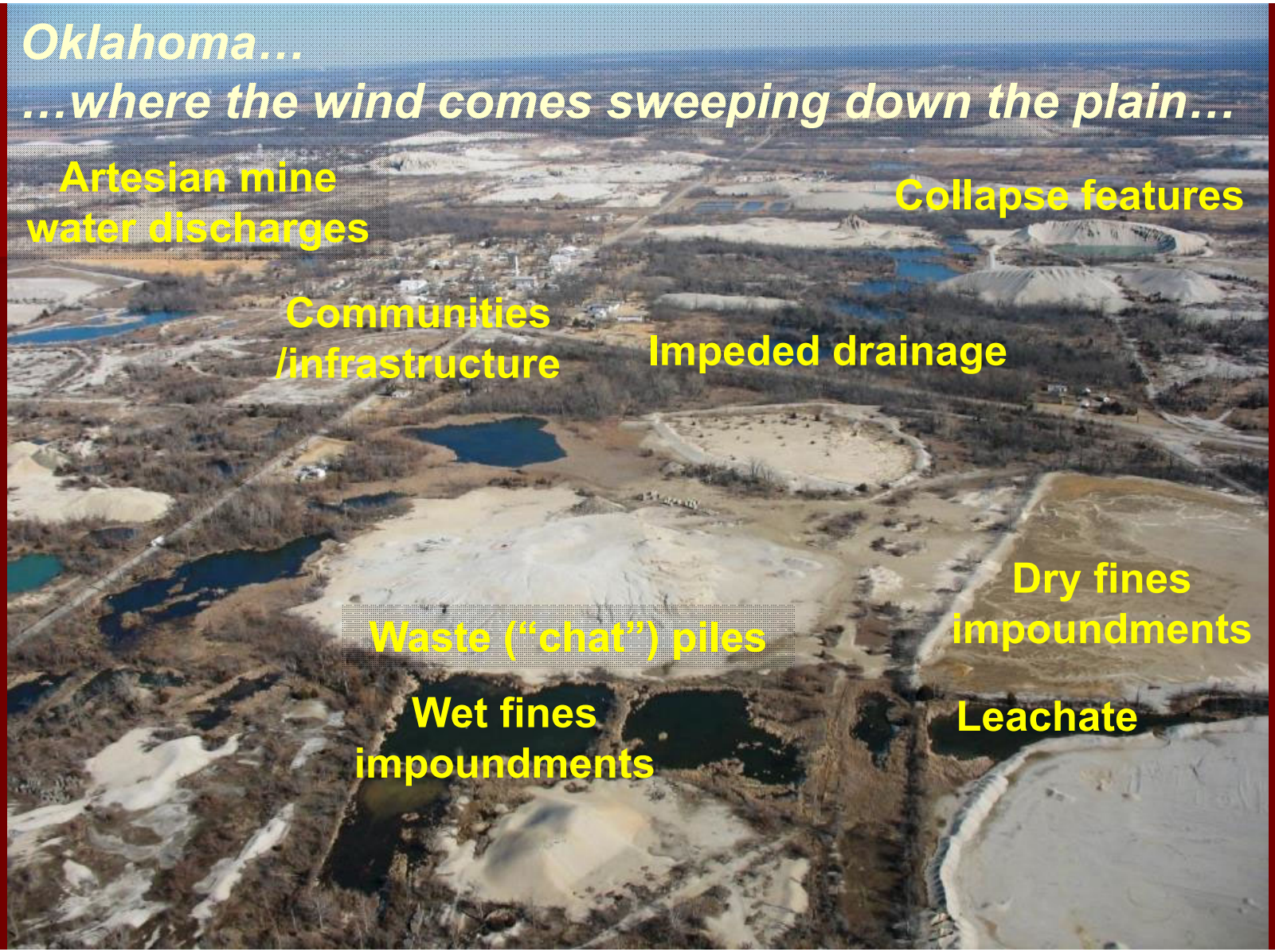
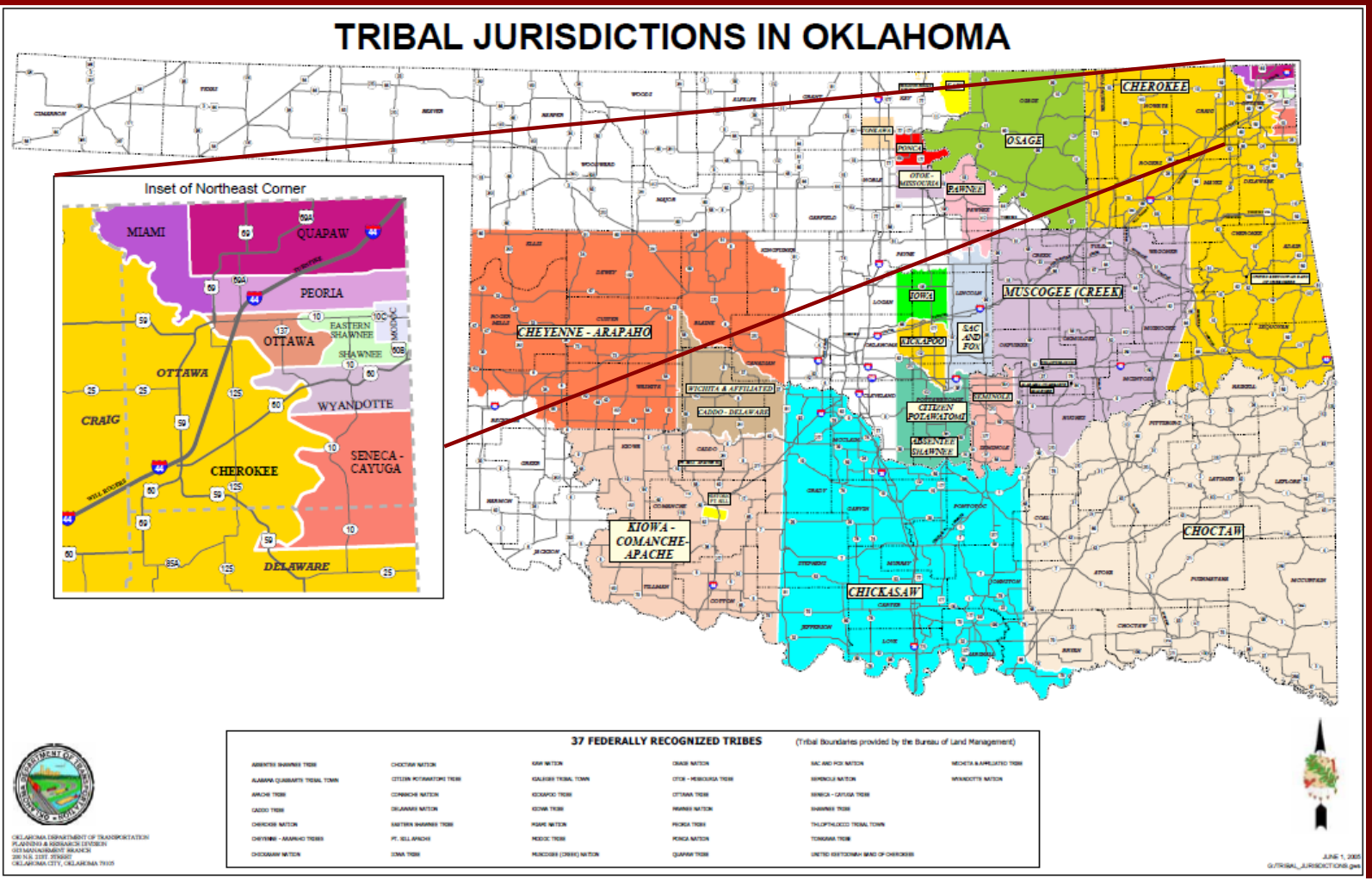
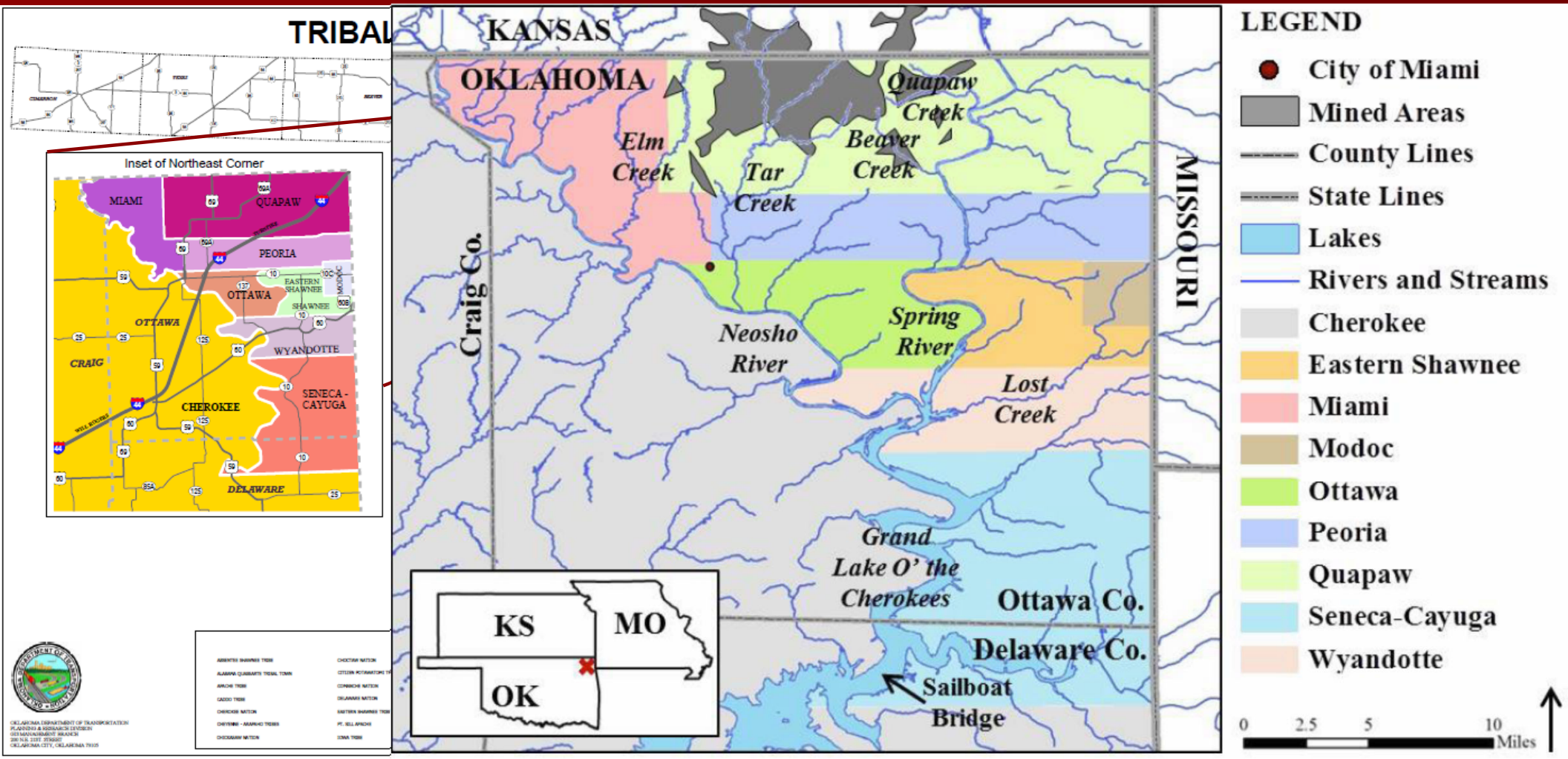

Oklahoma…
…where the wind comes sweeping down the plain…
Artesian mine water discharges
Collapse features
Communities /infrastructure
Impeded drainage
Dry fines impoundments
Waste ("chat") piles
Wet fines impoundments
Leachate

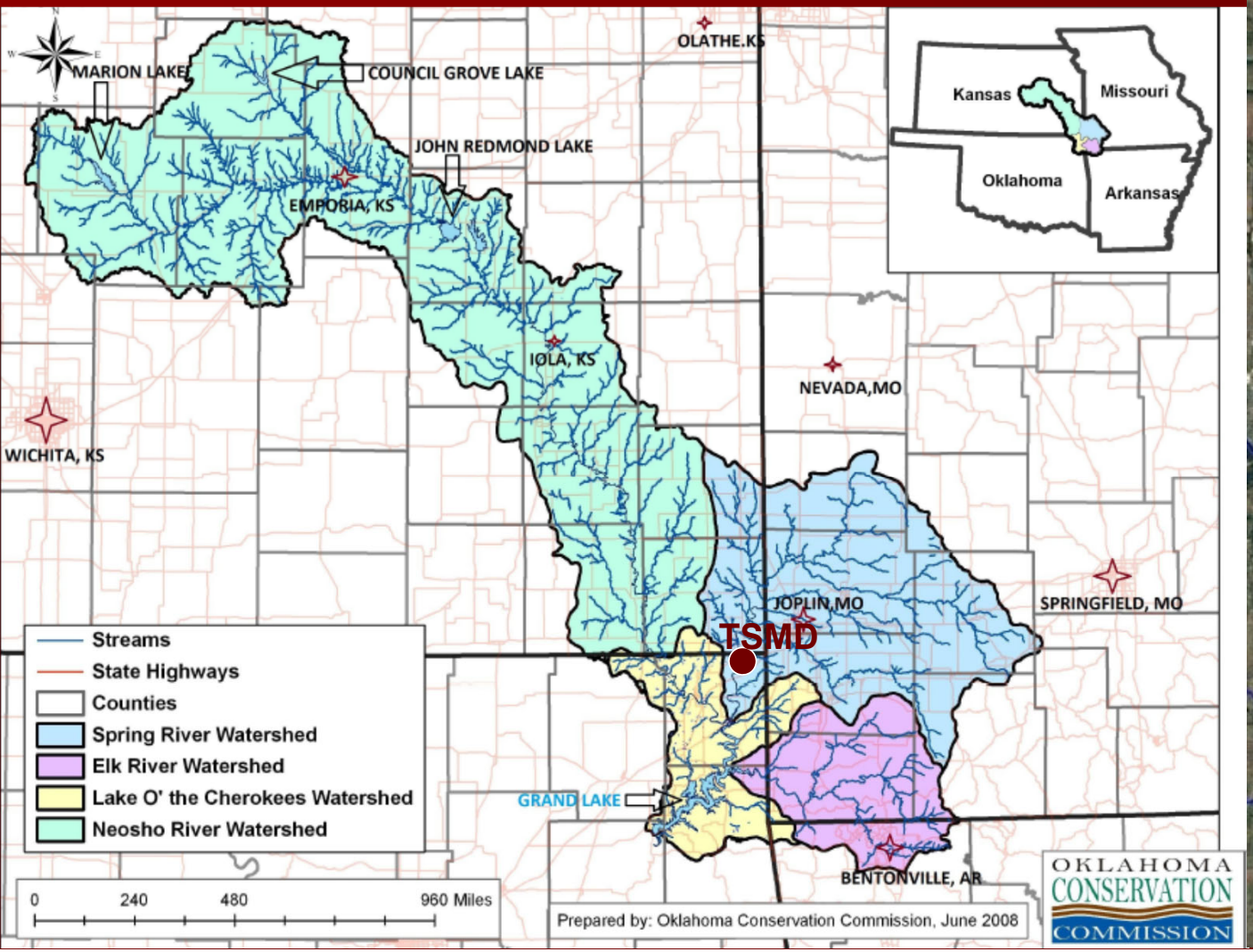
Oklahoma: *Native America*

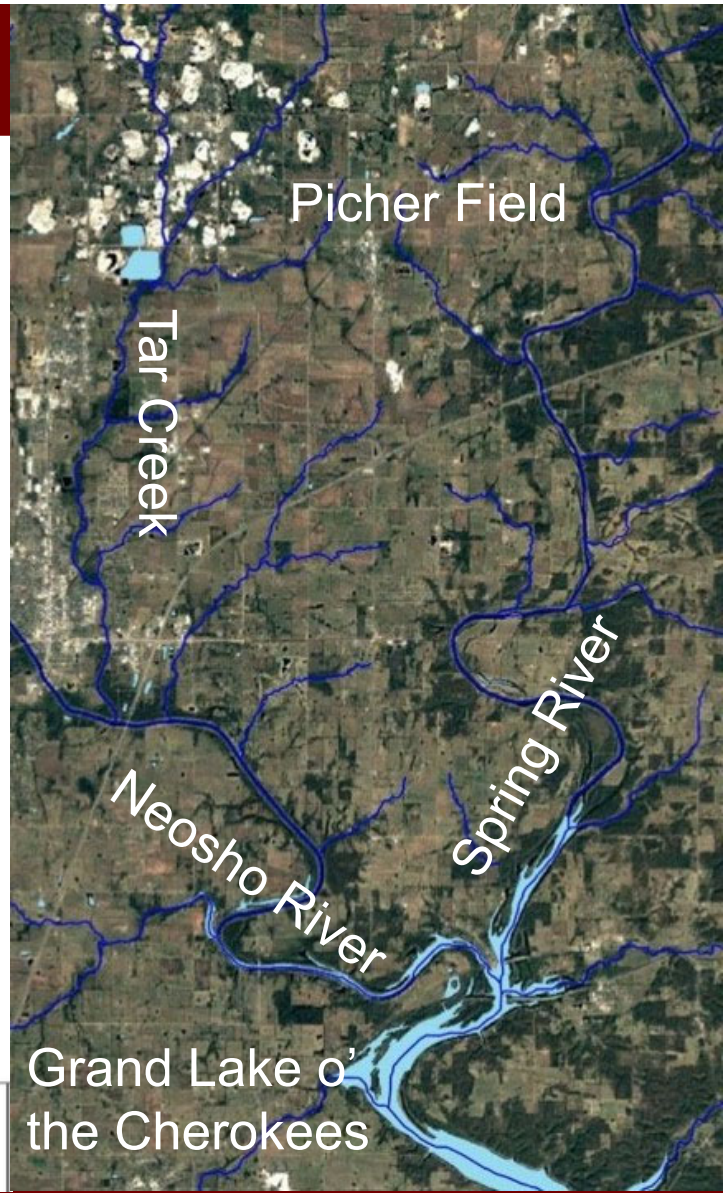


Oklahoma: *Native America*



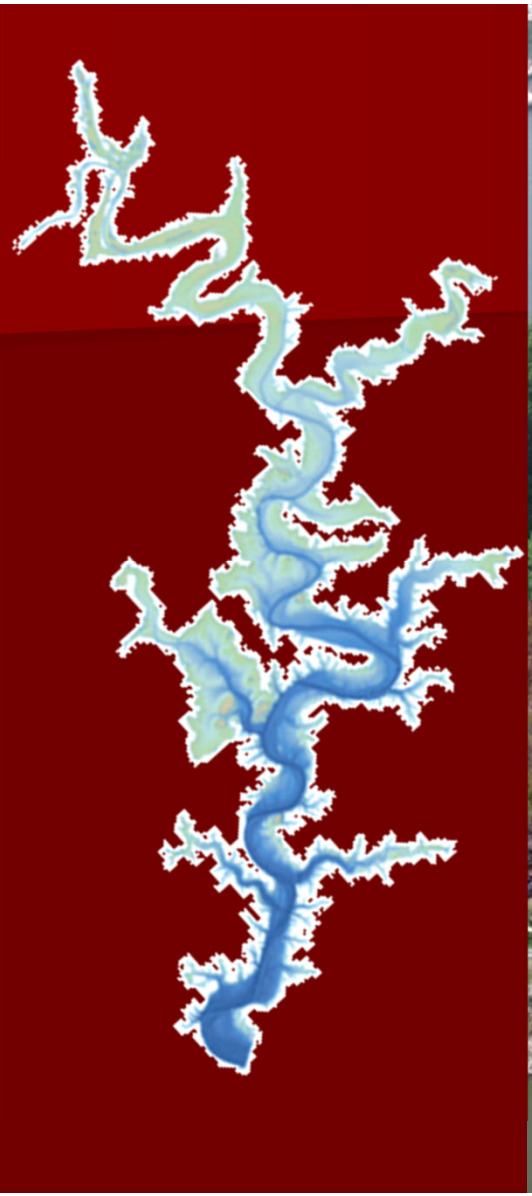
Grand Lake O' the Cherokees Watershed





Grand Lake O' the Cherokees

- Pensacola Dam
  - Longest multiple arch dam in world
- Third largest reservoir in Oklahoma
  - 10,298 mi^2 watershed
  - 46,500 surface acres
  - 1,300 shoreline miles
- Operated by GRDA
- Beneficial uses
  - Hydroelectric power
  - Flood control
  - Water supply
  - Recreation
  - Fish and wildlife propagation



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2005 11 10

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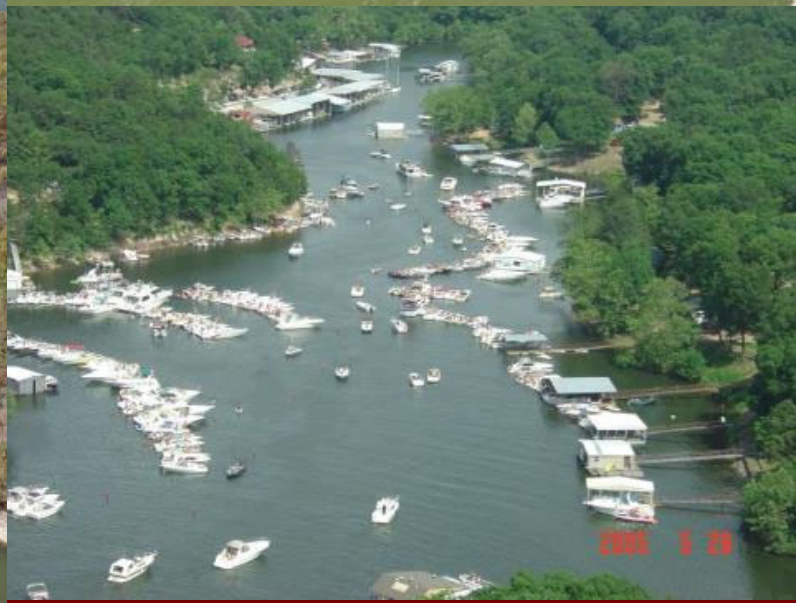
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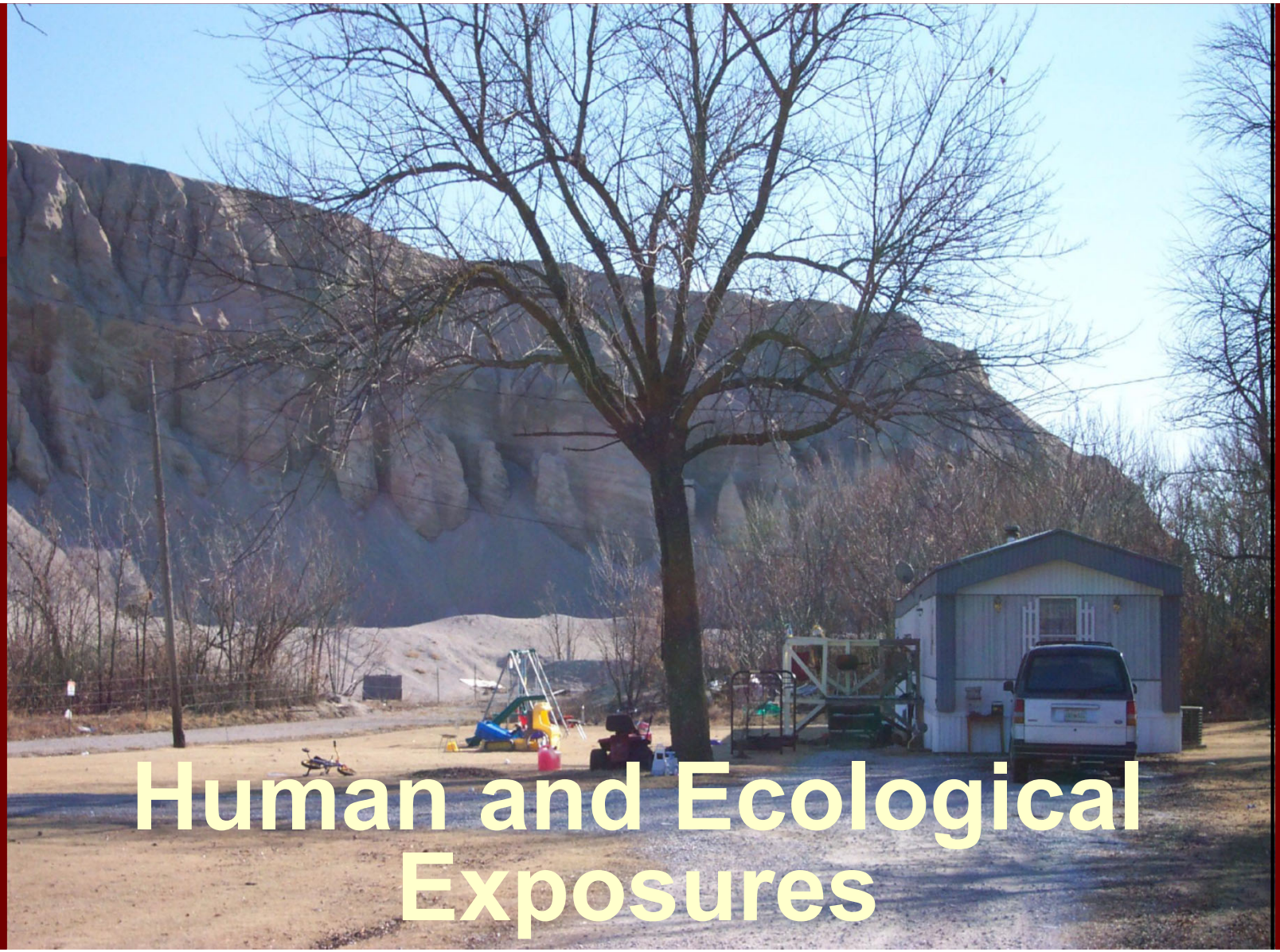
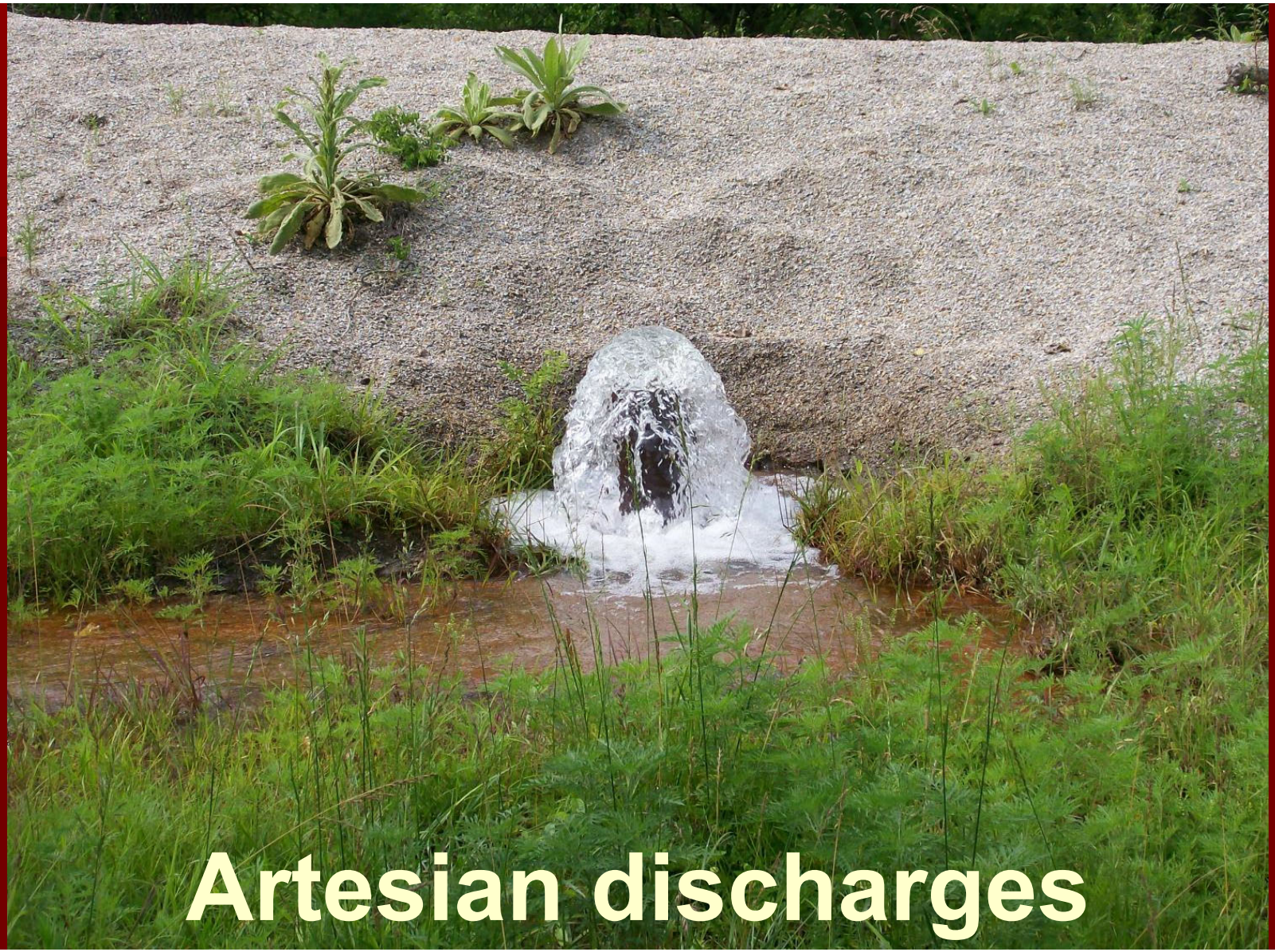
Grand River Dam Authority

ECOSYSTEMS & EDUCATION CENTER

PARTNERS IN CONSERVATION AND RESTORATION



Human and Ecological Exposures



Artesian discharges

Runoff and leachate

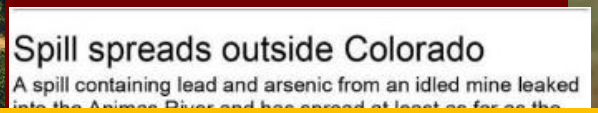
Tar Creek Surface and Ground Water Decision

- Initial artesian discharges (1979)
- USEPA concluded that (1984):

  *"impacts to (surface waters) are due to **irreversible man-made damages** resulting from past mining operations at the site"*
- Fund-balancing waiver used
  - Costs prohibitively high to address surface water contamination
- Unabated flows for nearly 40 years

Gold King Mine Disaster, Silverton, CO
August 6, 2015

Gold King Mine Disaster, Silverton, CO
August 6, 2015



3 million gallons of mine water

Tar Creek Mine Disaster, Ottawa County, OK, November 1979 - ?

Tar Creek Mine Disaster, Ottawa County, OK, November 1979 - ?

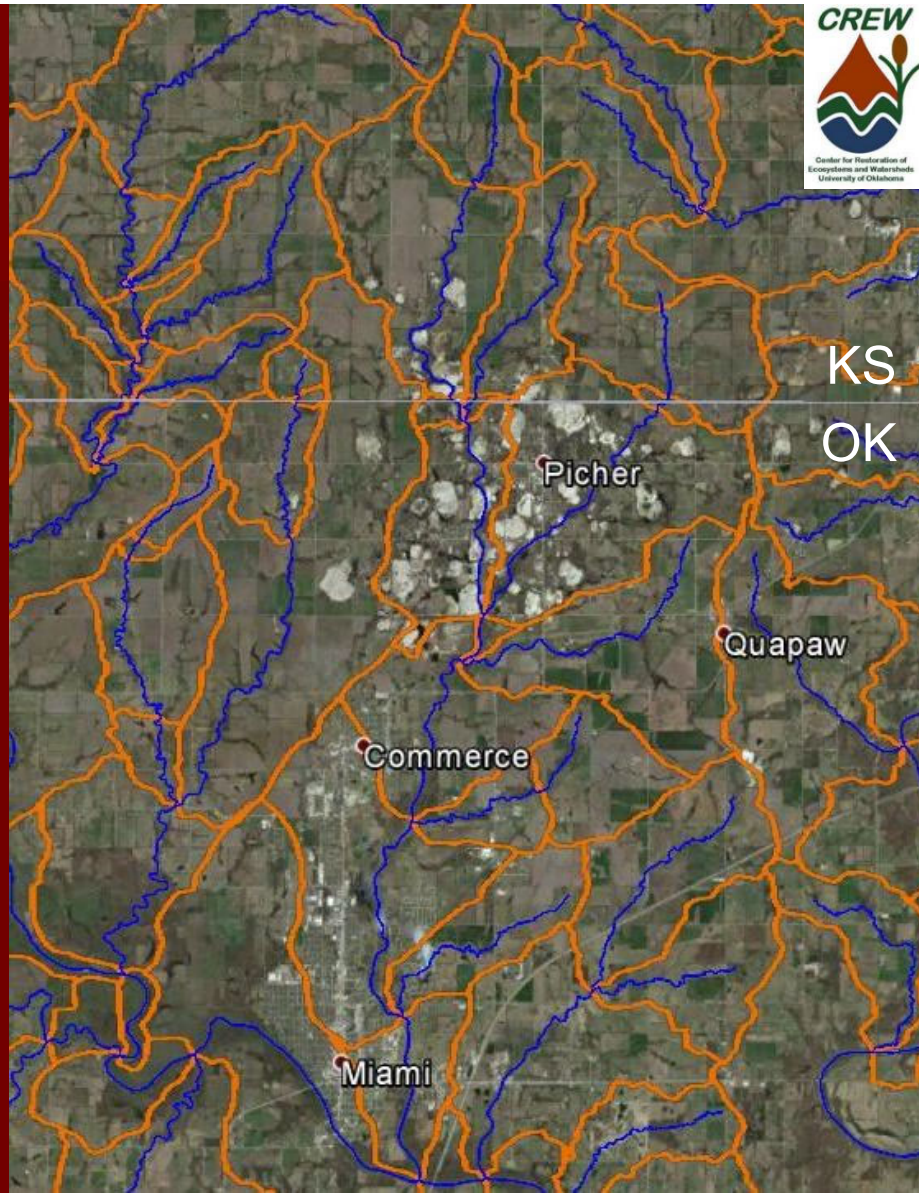
3 million gallons of mine water...
~ every 3 days, 24 hours a day,
7 days a week, 52 weeks a year,
for 39 years and counting...

Tar Creek Superfund Site

- National Priorities List (1983)
- Elevated Fe, Zn, Cd, Pb, As in water, chat, soils and biota
- Mining "mega-site"
- Ten Native American Tribes

OU CREW comprehensive watershed monitoring

- 1997 - 2019
- Streams, point (artesian discharges), nonpoint (waste pile runoff / leachate) sources



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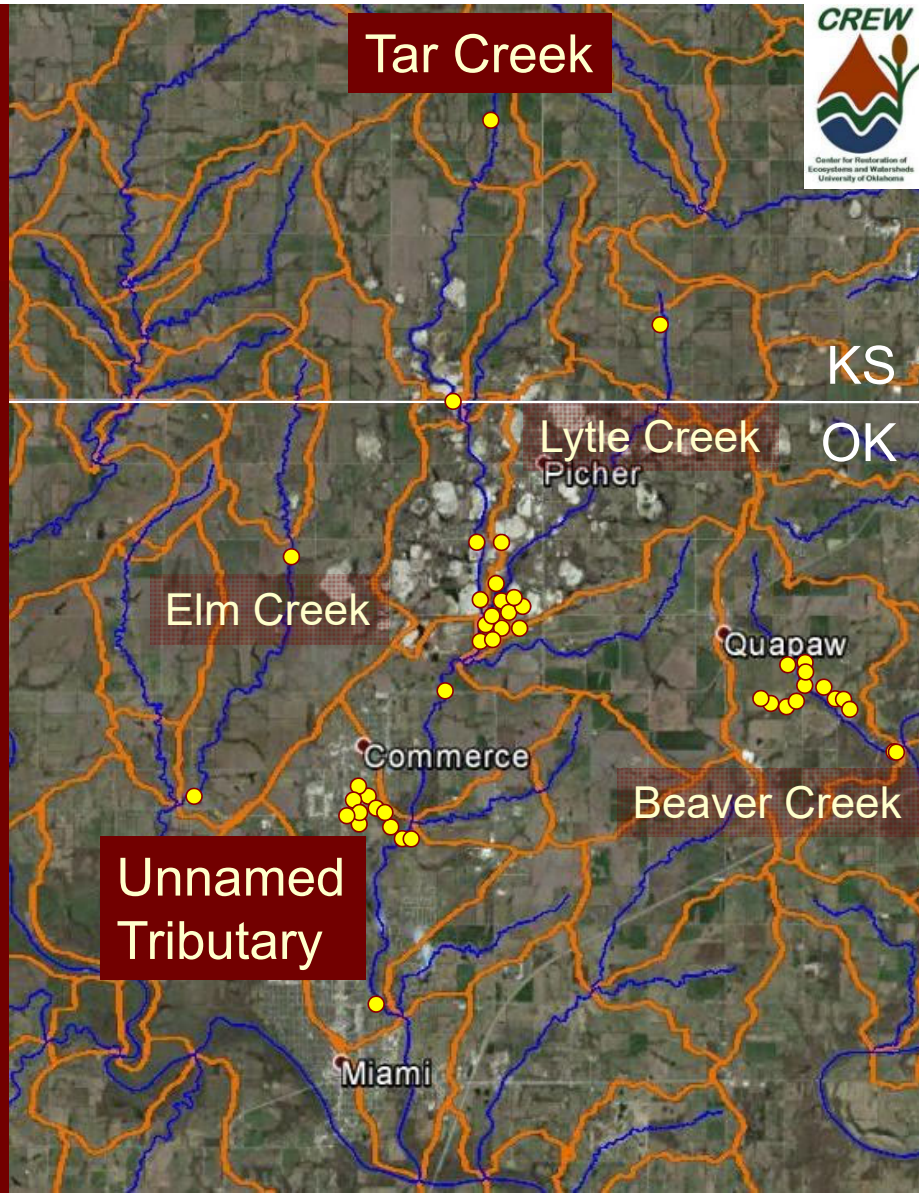
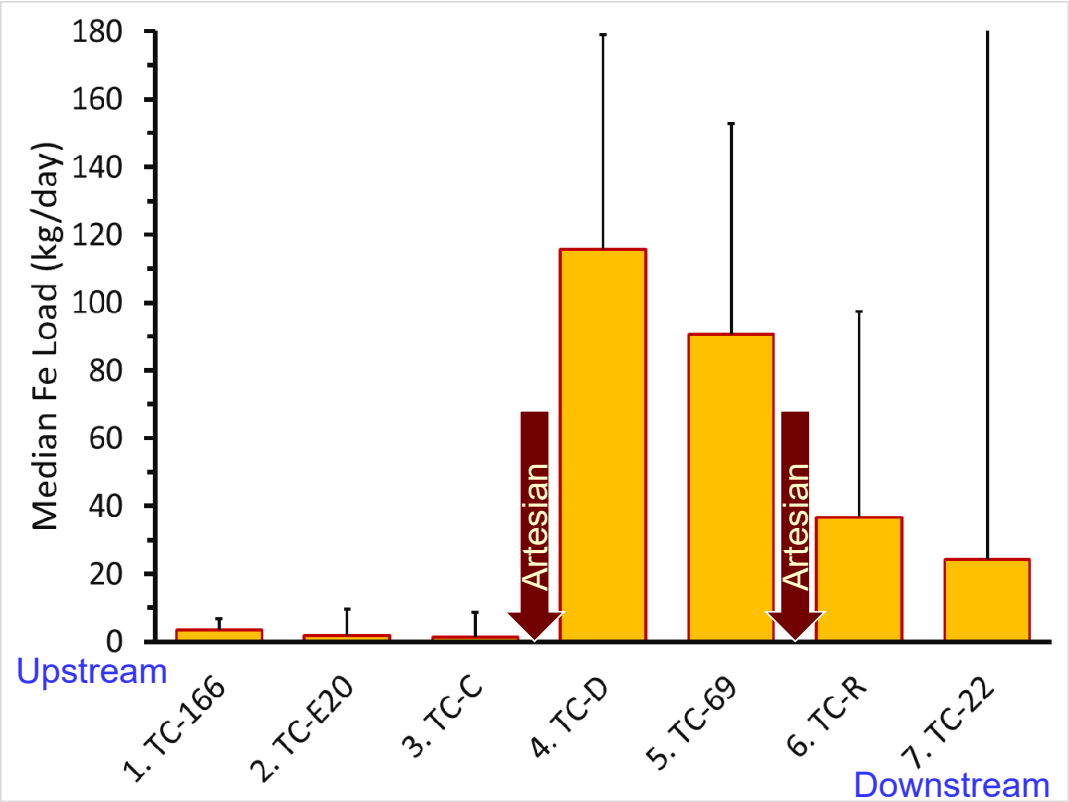


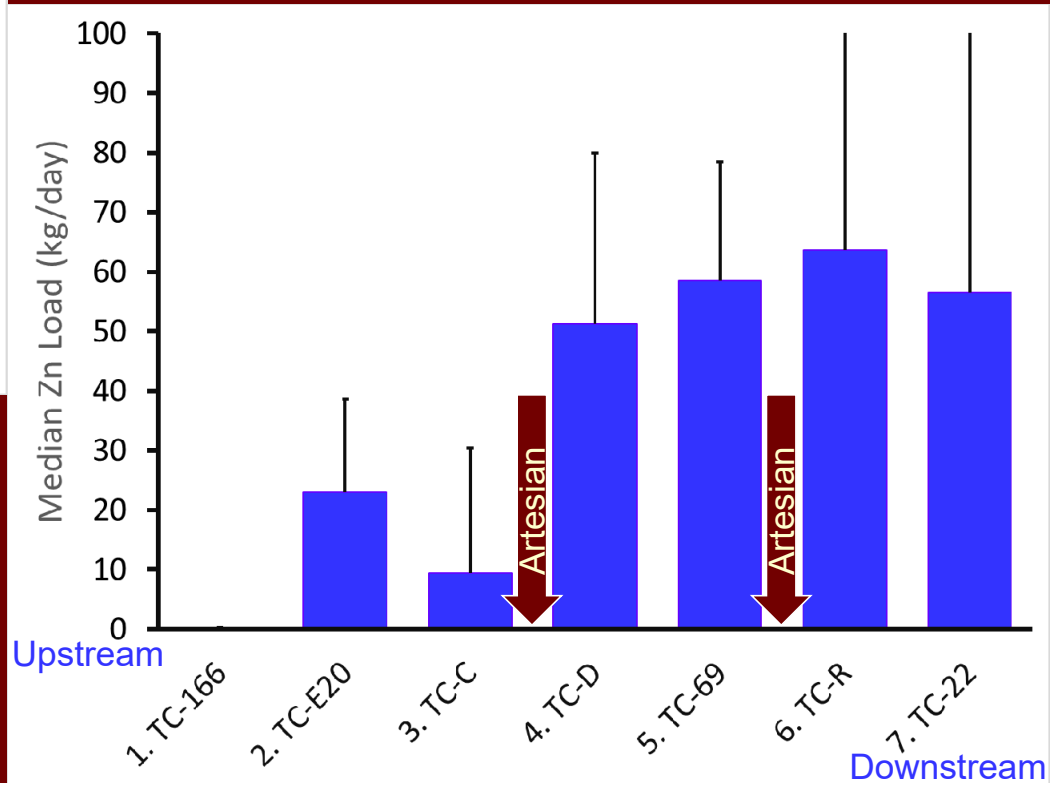
Tar Creek (main stem) locations

1. TC-166
   - Upstream of mining influence
2. TC-E20
   - Chat influence
3. TC-C
   - Major chat influence
4. TC-D
   - Major chat influence
   - Substantial artesian upwellings
5. TC-69
   - Downstream major impacts
6. TC-R
   - Substantial artesian upwellings
   - Minor chat influence
7. TC-22
   - Downstream of all mining influences



Iron mass loads

- Obvious artesian influences
- Considerable in-stream oxidation, hydrolysis and settling
- $[Fe_{artesian}] > [Fe_{leachate}]$

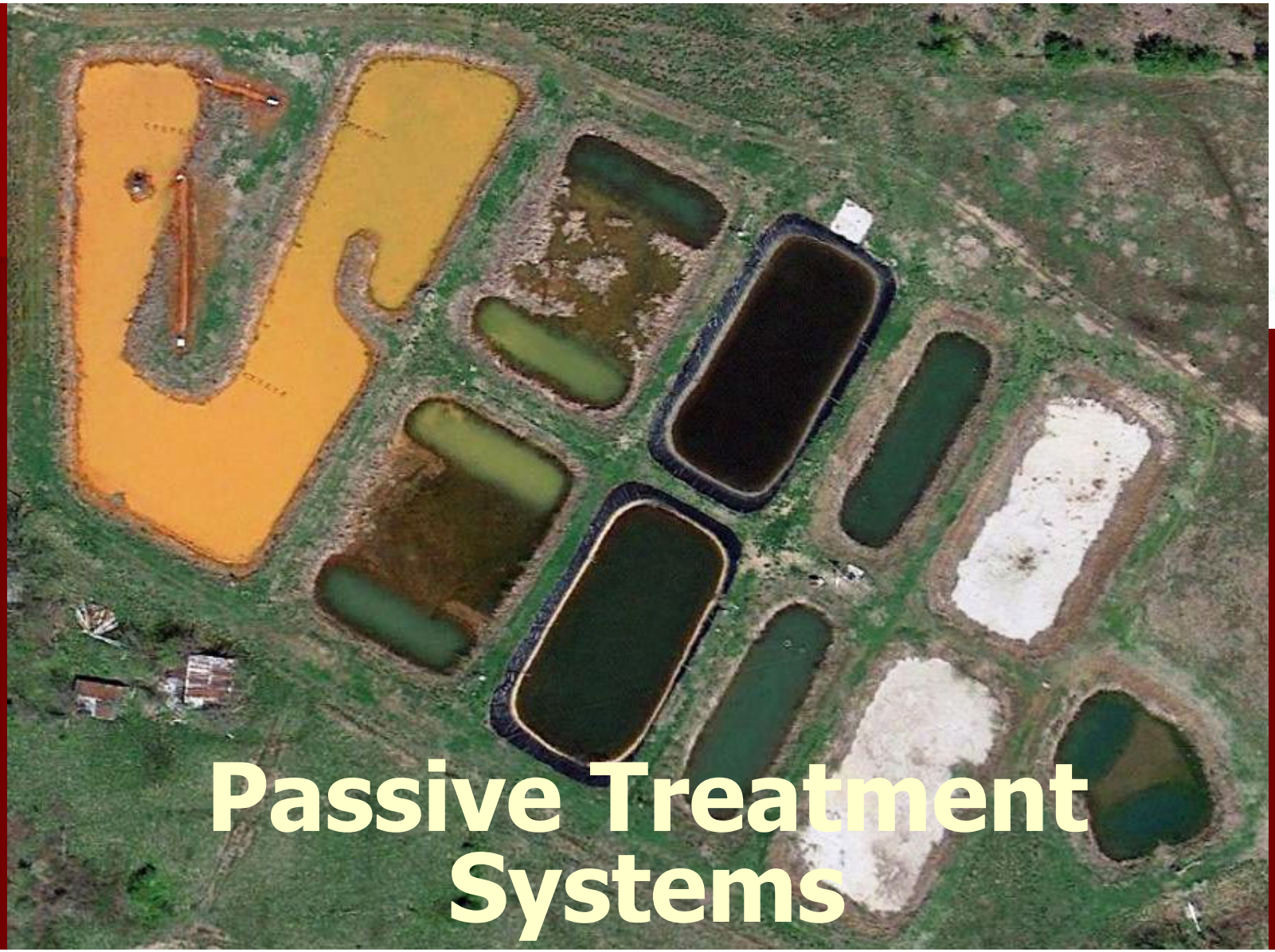


Zn mass loads

- Chat leachate influences
- Obvious artesian influences
- Little in-stream retention
- Transport of $Zn_{particulate}$

Is it true?

"impacts to (surface waters) are due to <u>irreversible man-made damages</u> resulting from past mining operations at the site"



Passive Treatment Systems

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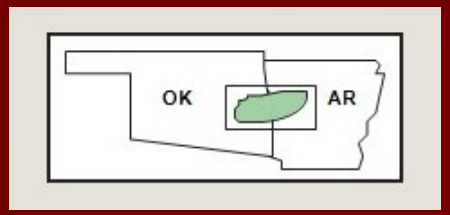
Passive Treatment Systems: An Ecological Engineering Solution

- Promote naturally-occurring biogeochemical, microbiological and ecological processes
- Driven by renewable energies
- Using only natural unprocessed materials
- Lower O&M costs but larger land areas
- 30+ years experience

Arkoma Basin Coal Mines



CREW PTS

Applicable technology to hard rock mine drainage in the Tri-State Mining District and Tar Creek Superfund Site?

Conceptual Design

- Based on > decade of research
- Targeted contaminant removal
  - Oxidation reactions
  - Reduction reactions
  - Sorption
  - Precipitation
- Sequential process units

Create Conditions for Biogeochemical Solutions

Designed redox coupling

- <u>Oxidative</u> iron removal in net alkaline mine waters

$$Fe^{2+} + \mathbf{\frac{1}{4}O_2} + 2HCO_3^- \rightarrow \mathbf{FeOOH(s)} + 2CO_2 + \frac{1}{2}H_2O$$

- <u>Reductive</u> trace metal removal via bacterial sulfate reduction

$$Zn^{2+} + SO_4^{2-} + \mathbf{2CH_2O} \rightarrow \mathbf{ZnS(s)} + 2CO_2 + 2H_2O$$

- Sorption, exchange, carbonate precipitation

Ecological Engineered Passive Treatment Systems at Tar Creek

- Target artesian discharges of net alkaline mine waters
- Multiple process units for sequential treatment
- Focus on Unnamed Tributary watershed (340 ha)
- Two study sites
  - Mayer Ranch
  - Southeast Commerce
  - $Q_{total} \approx 2000\ m^3/day$

Oxidative Processes

- Oxidize, hydrolyze, precipitate Fe
- Utilize off-grid aeration
- Trace metal sorption
- Potential resource recovery

MRPTS oxidation cell under construction, fall 2008

MRPTS oxidation cell during managed drawdown, winter 2017

SECPTS oxidation cell directional baffle curtains, early 2017

SECPTS oxidation cell solar-powered aerators, early 2017

Reductive Processes

- Promote bacterial sulfate reduction
- Provide exogenous substrate
- Retention of metal sulfides

MRPTS vertical flow bioreactor, under construction, fall 2008

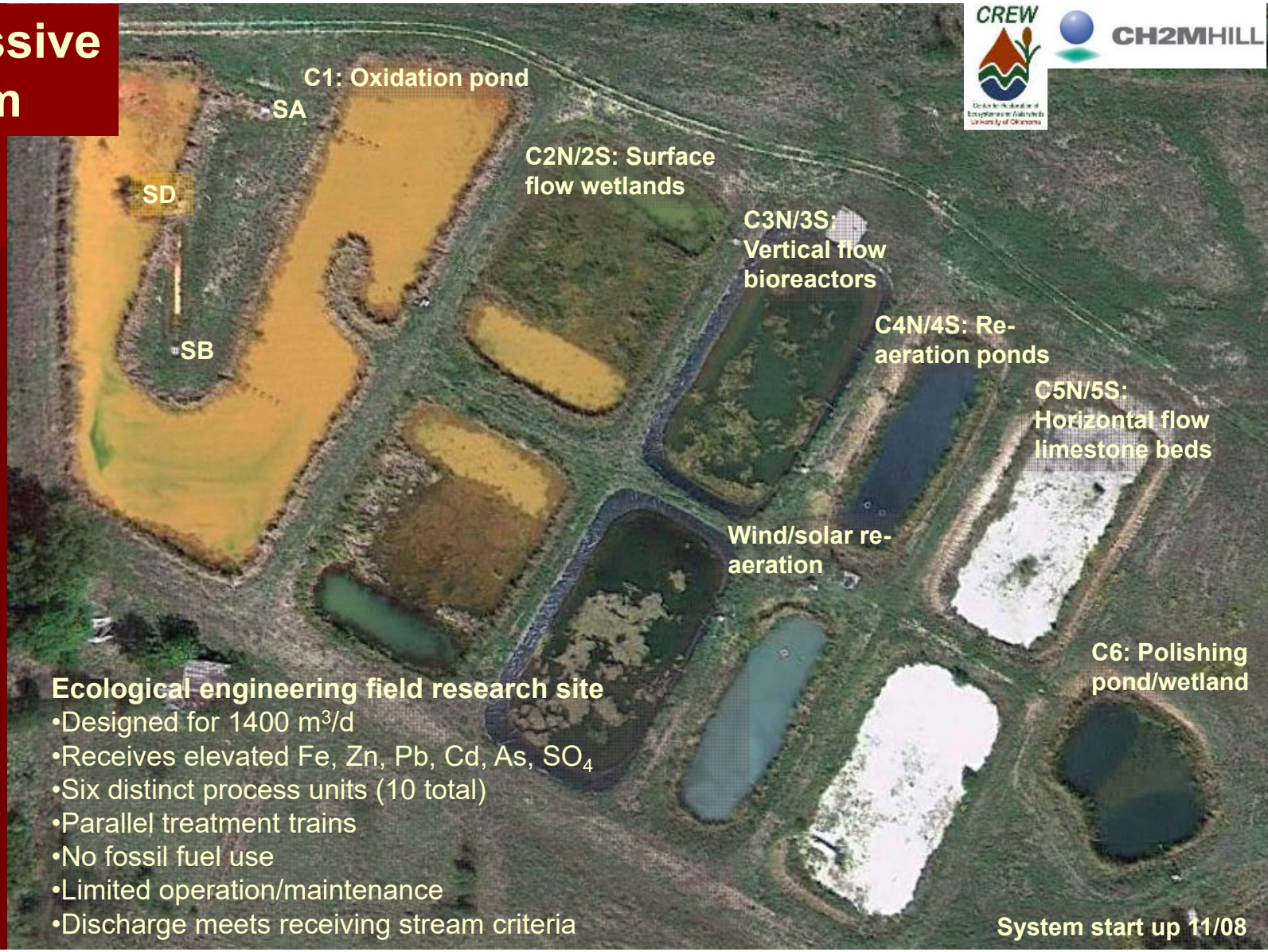
MRPTS vertical flow bioreactor, before flooding, fall 2008

SECPTS vertical flow bioreactor, under construction, fall 2016

SECPTS vertical flow bioreactor, before flooding, early 2017

Mayer Ranch Passive Treatment System

- USEPA funding 2004-10
- 10 process units
  - 8 in parallel
- First PTS in entire Tri-State Mining District
- Continuous operation since 11/2008

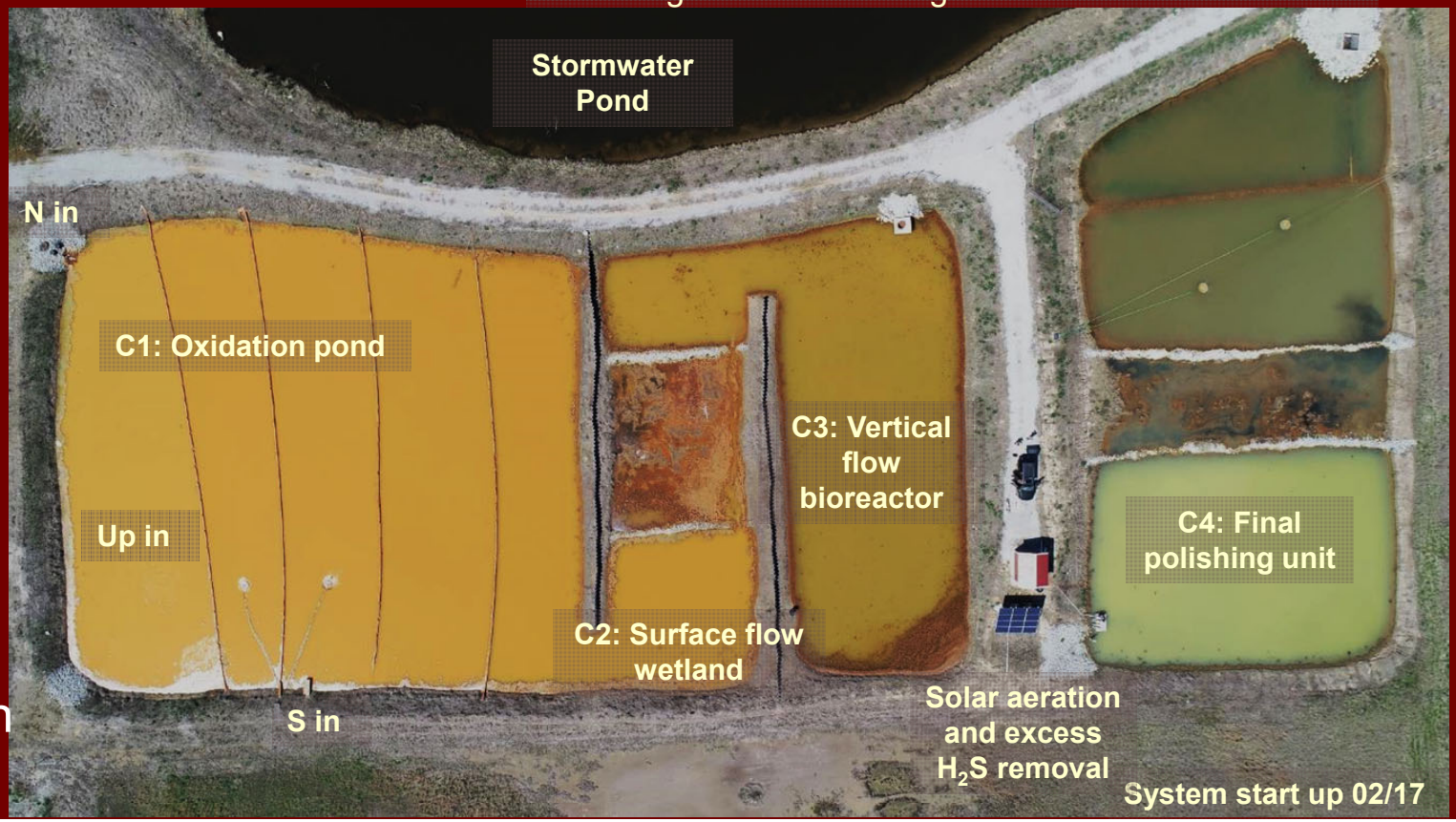


Southeast Commerce Passive Treatment System

- Oklahoma DEQ funding 2015-present
- 4 process units
  - Directional baffle curtains and z-piling
  - Innovative solar-powered air-lift aerators
  - Unique GAC S^{2-} capture system
- Second PTS in Tri-State Mining District
- Continuous operation since 02/2017

Ecological engineering field research site

- Designed for 550 m^3/d
- Receives elevated Fe, Zn, Pb, Cd, As, SO_4
- Four total process units
- Shared water surfaces/baffles/z-piling
- Solar-powered aeration/reaeration
- Limited operation/maintenance
- Discharge meets receiving stream criteria



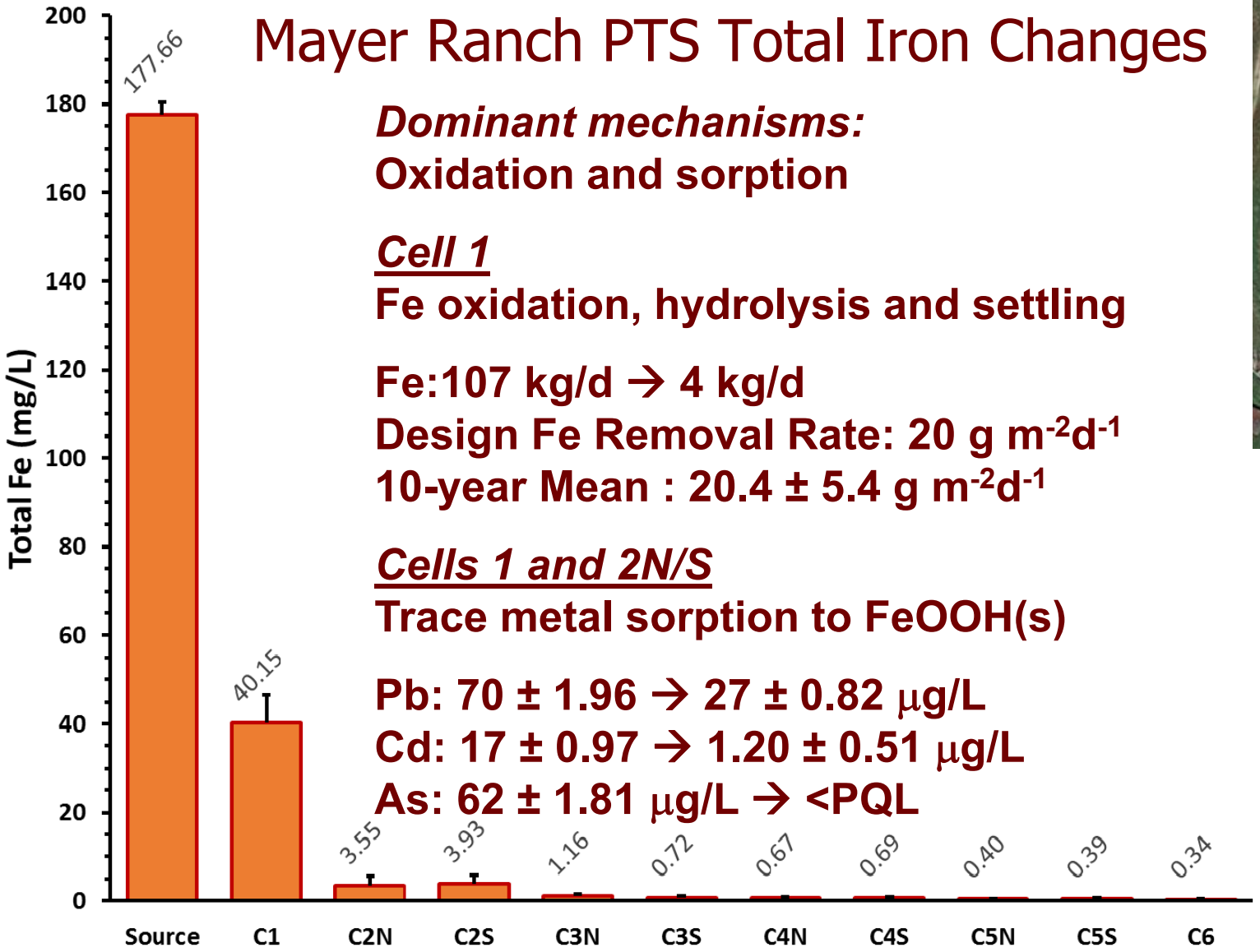
Water Quality Changes

Mayer Ranch		
	In (n=82)	Out (n=43)
pH	5.95	7.02
Alk_T (mg/L)	393	224
Fe_T (mg/L)	192	0.13
Zn_T (mg/L)	11	0.25
Ni_T (mg/L)	0.97	0.15
Cd_T (μg/L)	17	<PQL
Pb_T (μg/L)	60	<PQL
As_T (μg/L)	64	<PQL
SO_4^{-2} (mg/L)	2239	2057

Water Quality Changes

	Mayer Ranch		Southeast Commerce	
	In (n=82)	Out (n=43)	In (n=80)	Out (n=22)
pH	5.95	7.02	6.06	7.02
Alk_T (mg/L)	393	224	350	117
Fe_T (mg/L)	192	0.13	127	0.79
Zn_T (mg/L)	11	0.25	6.15	0.69
Ni_T (mg/L)	0.97	0.15	0.52	0.06
Cd_T (μg/L)	17	<PQL	18	<PQL
Pb_T (μg/L)	60	<PQL	80	26
As_T (μg/L)	64	<PQL	38	<PQL
SO_4^{-2} (mg/L)	2239	2057	2102	1956

Mayer Ranch PTS Total Iron Changes



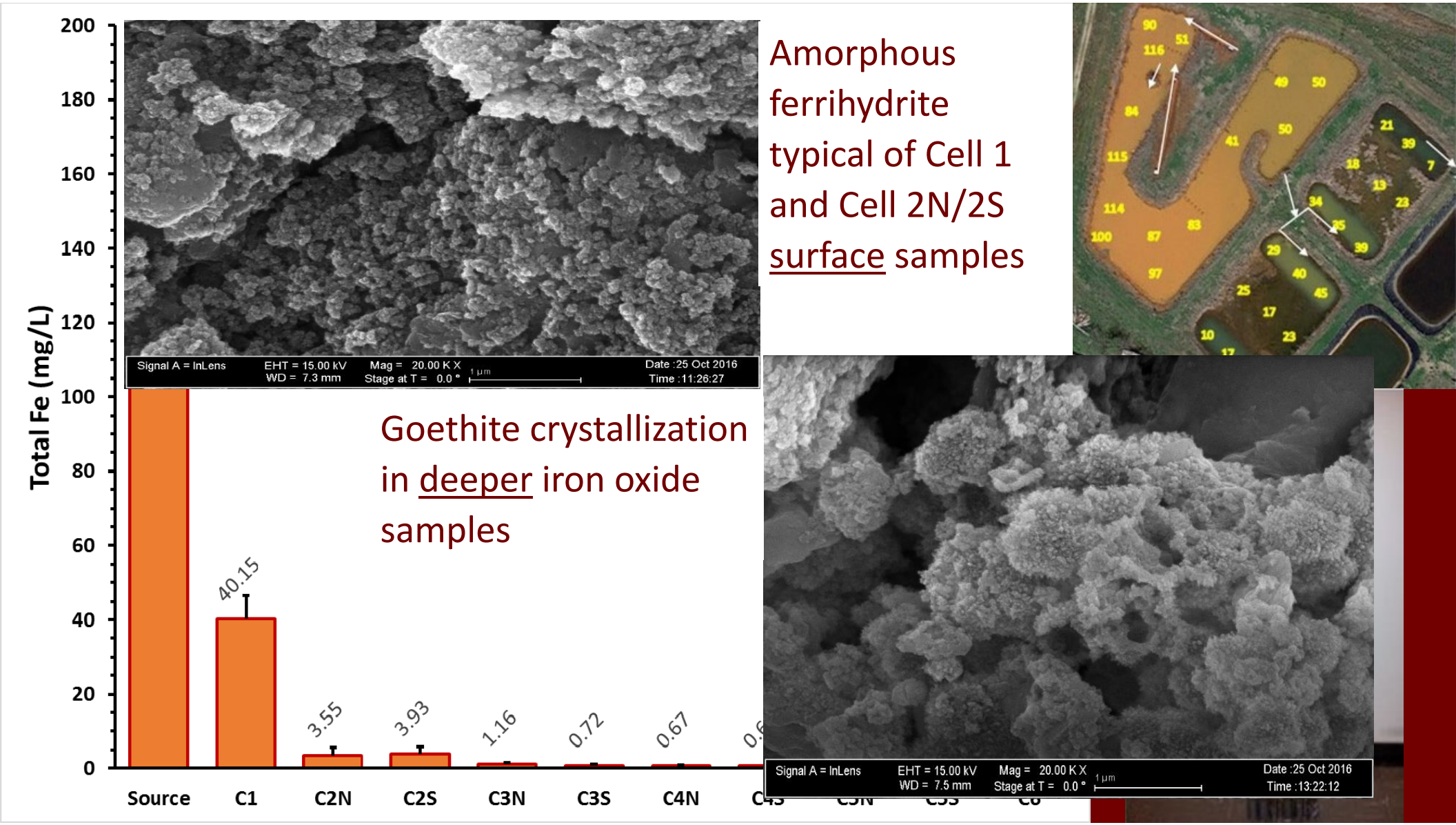
Dominant mechanisms:
Oxidation and sorption

Cell 1
Fe oxidation, hydrolysis and settling

Fe:107 kg/d → 4 kg/d
Design Fe Removal Rate: 20 g $m^{-2}d^{-1}$
10-year Mean : 20.4 ± 5.4 g $m^{-2}d^{-1}$

Cells 1 and 2N/S
Trace metal sorption to FeOOH(s)

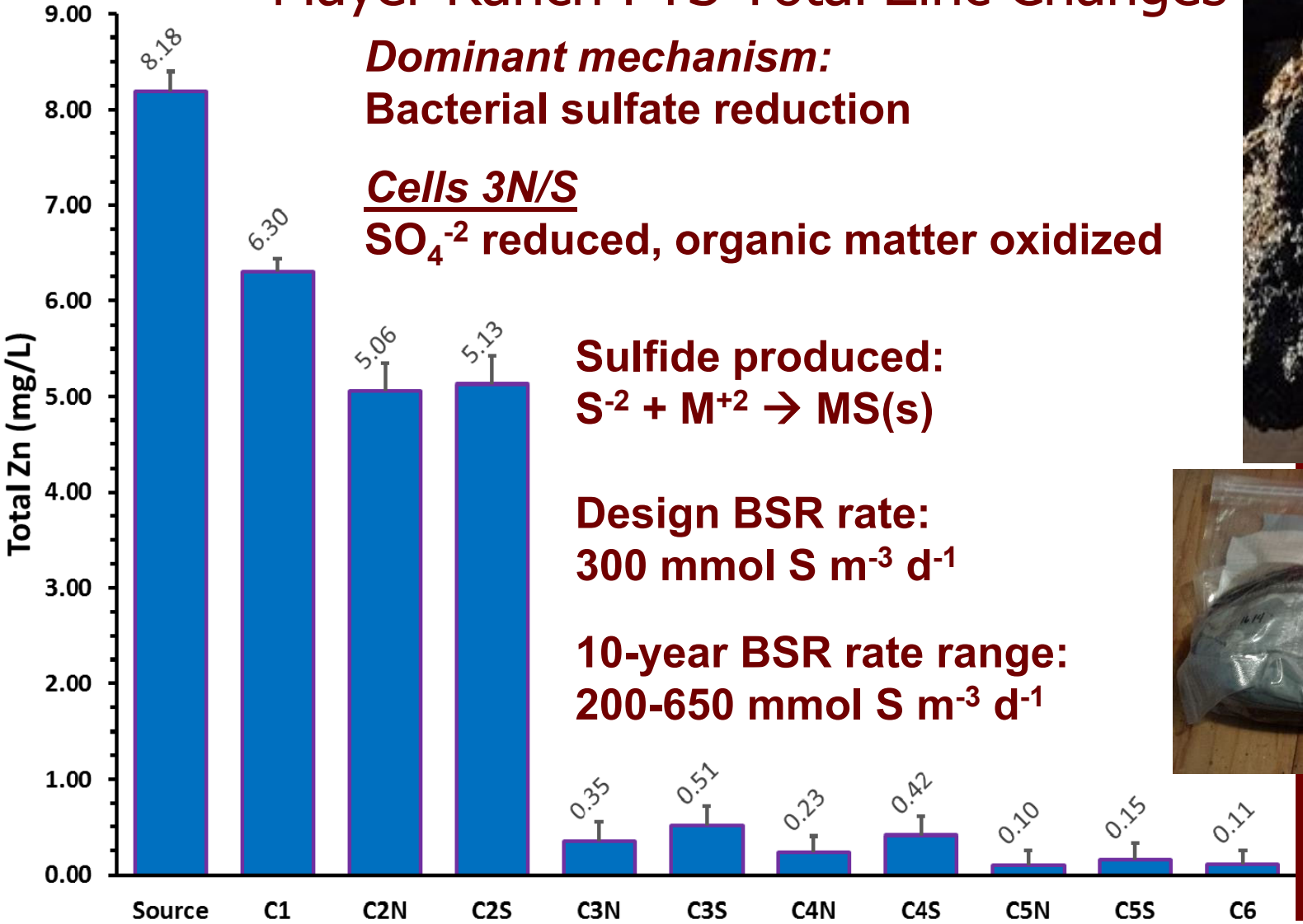
Pb: 70 ± 1.96 → 27 ± 0.82 μg/L
Cd: 17 ± 0.97 → 1.20 ± 0.51 μg/L
As: 62 ± 1.81 μg/L → <PQL



Amorphous ferrihydrite typical of Cell 1 and Cell 2N/2S surface samples

Goethite crystallization in deeper iron oxide samples

Mayer Ranch PTS Total Zinc Changes



Dominant mechanism:
Bacterial sulfate reduction

Cells 3N/S
SO_4^{-2} reduced, organic matter oxidized

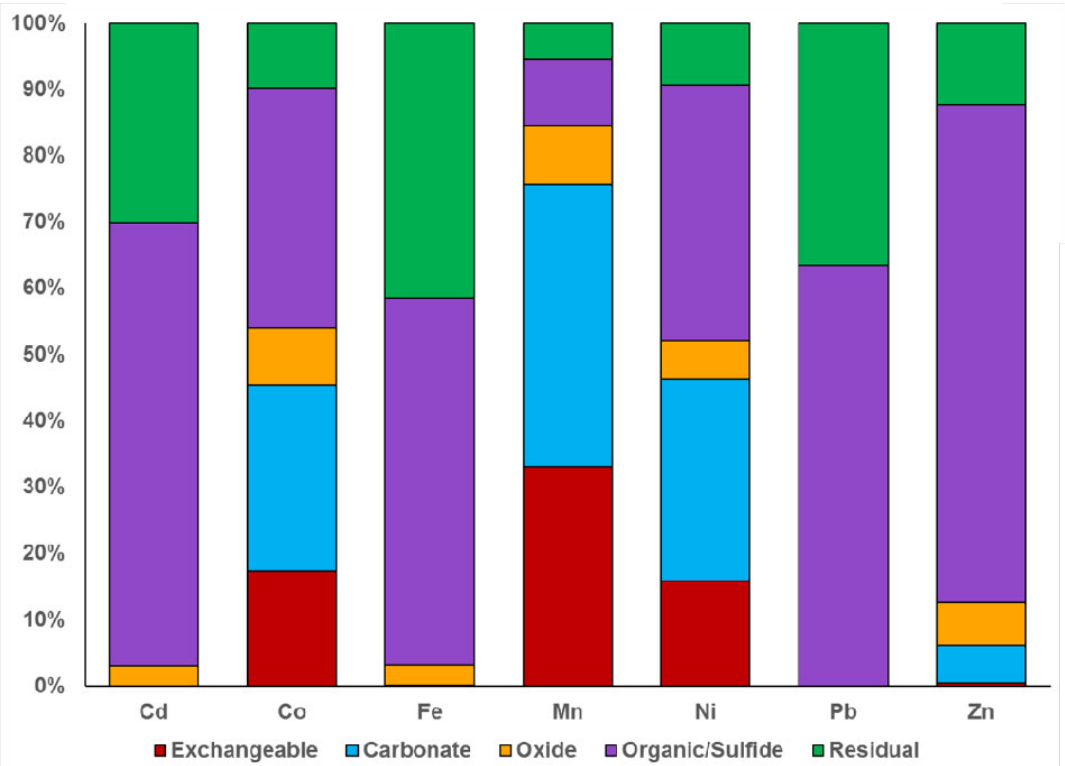
Sulfide produced:
$S^{-2} + M^{+2} \rightarrow MS(s)$

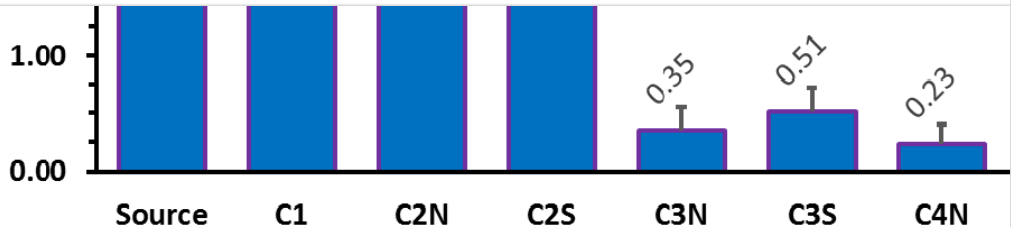
Design BSR rate:
300 mmol S m^{-3} d^{-1}

10-year BSR rate range:
200-650 mmol S m^{-3} d^{-1}

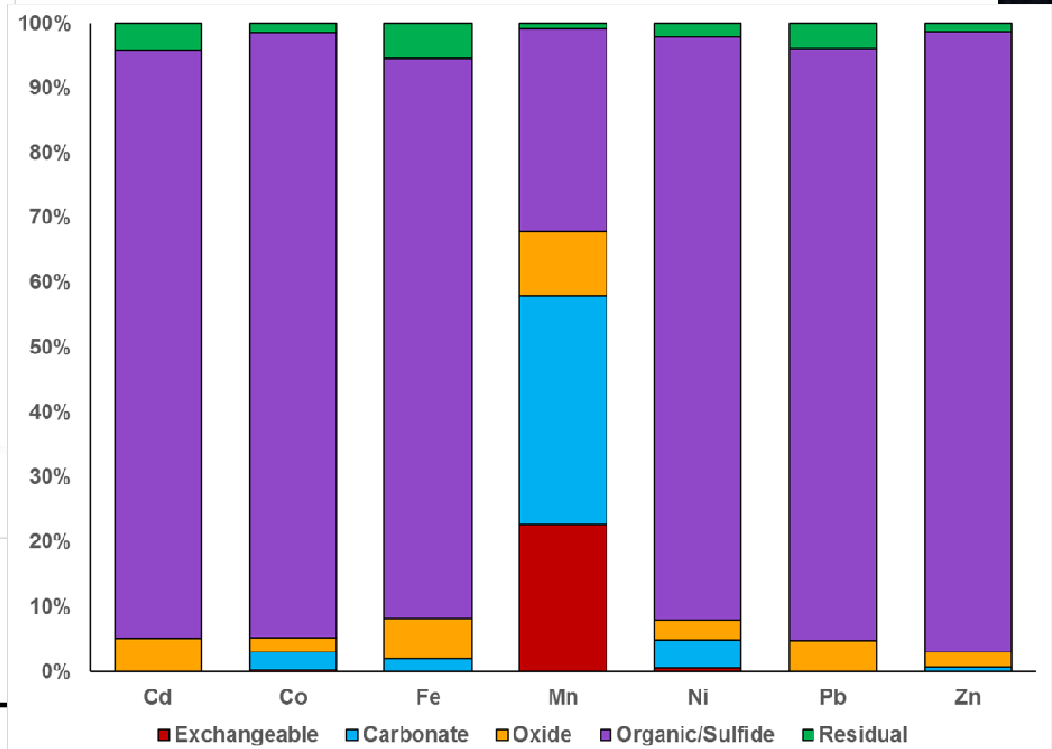
Mayer Ranch PTS Total Zinc Changes

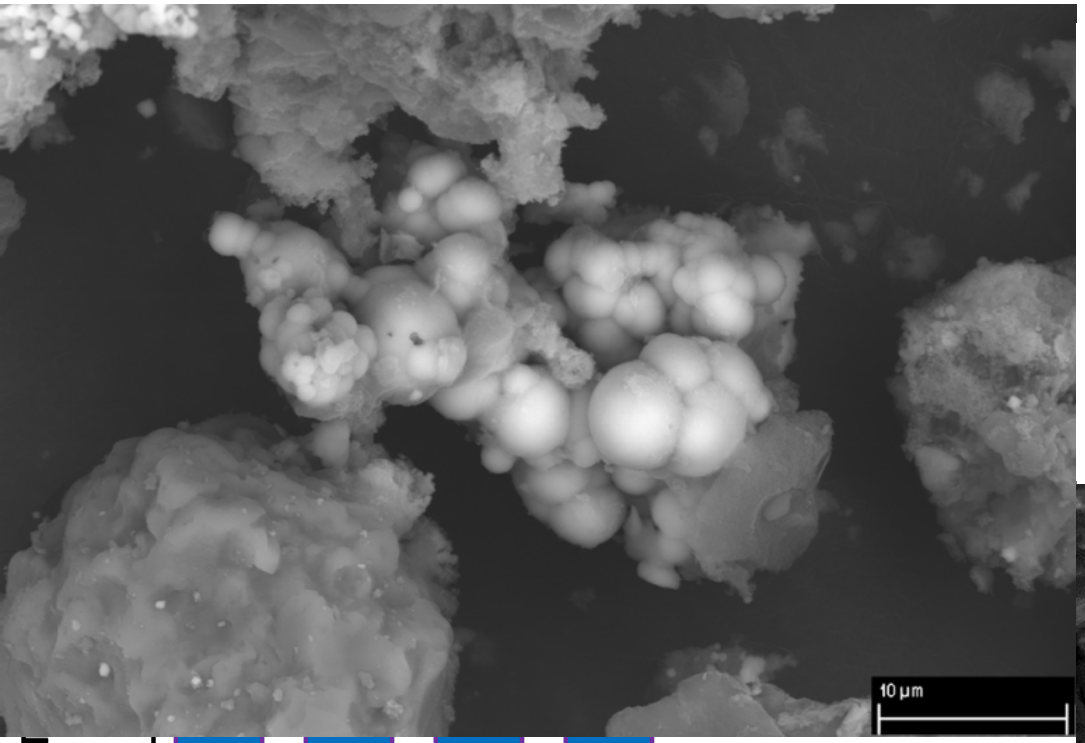
2010 VFBR Sequential Extractions



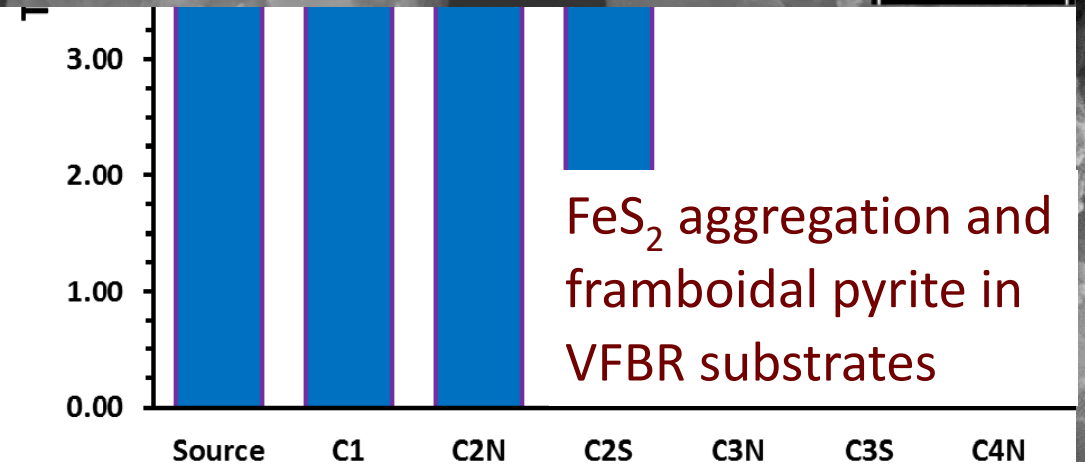


2014 VFBR Sequential Extractions

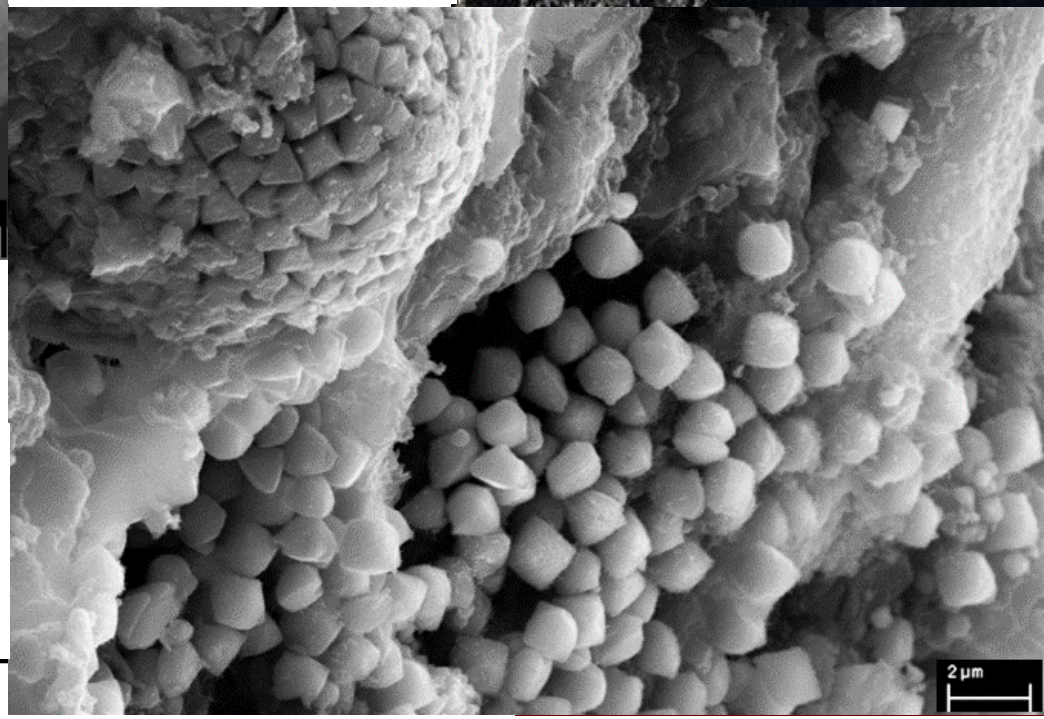




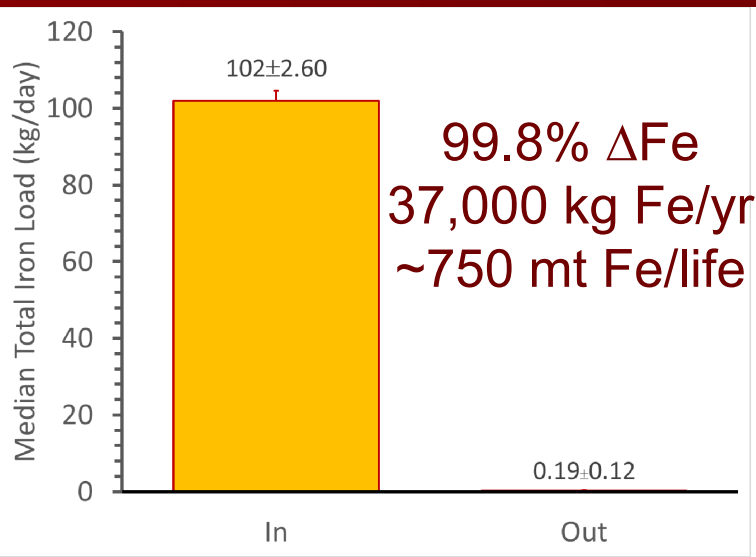
Well-developed ZnS colloidal aggregates on humic materials in VFBR substrates



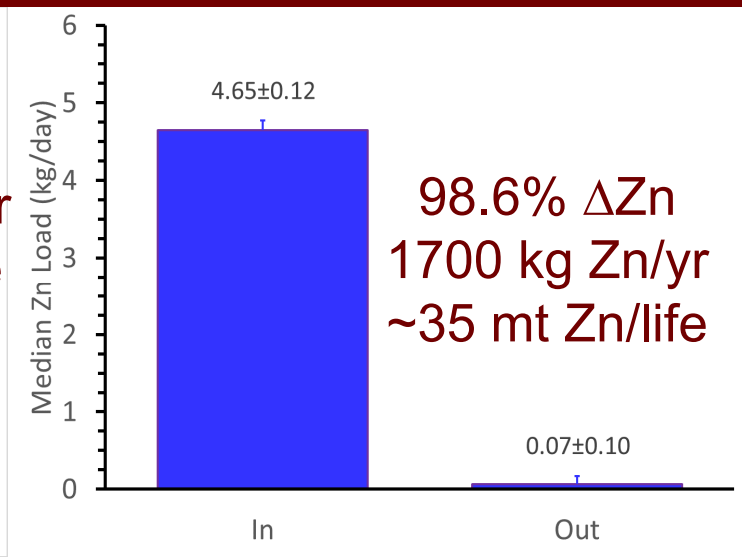
FeS_2 aggregation and framboidal pyrite in VFBR substrates



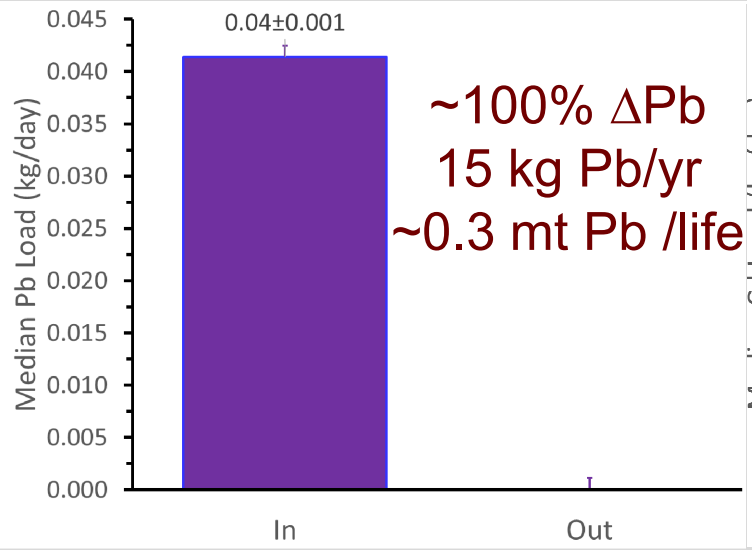
Mayer Ranch PTS – Contaminants of Concern



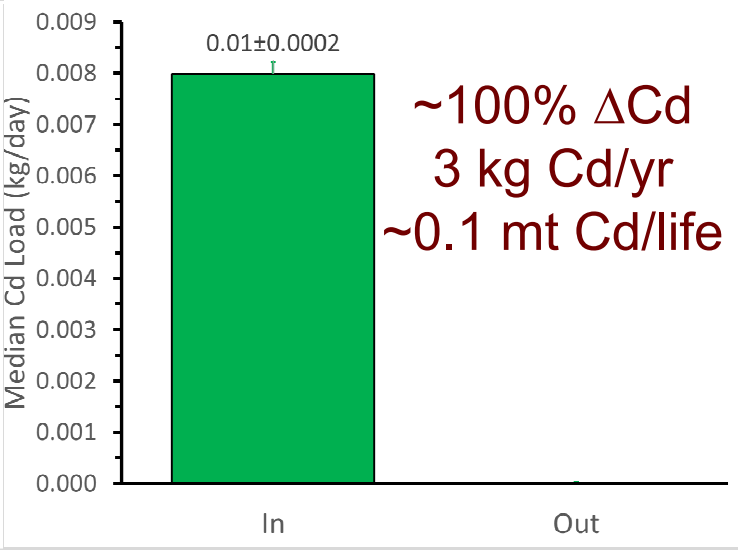
99.8% ΔFe
37,000 kg Fe/yr
~750 mt Fe/life



98.6% ΔZn
1700 kg Zn/yr
~35 mt Zn/life

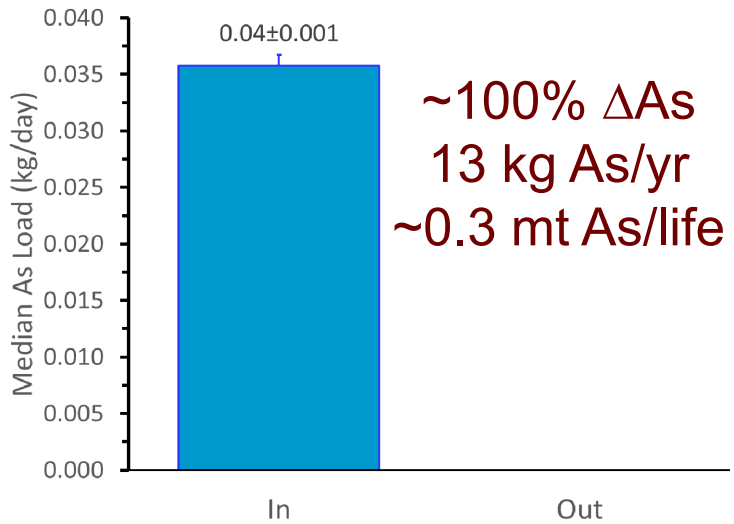


~100% ΔPb
15 kg Pb/yr
~0.3 mt Pb /life

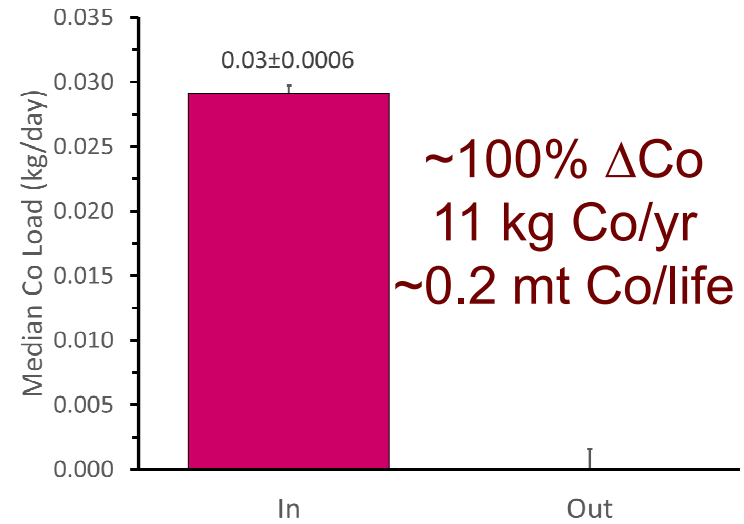


~100% ΔCd
3 kg Cd/yr
~0.1 mt Cd/life

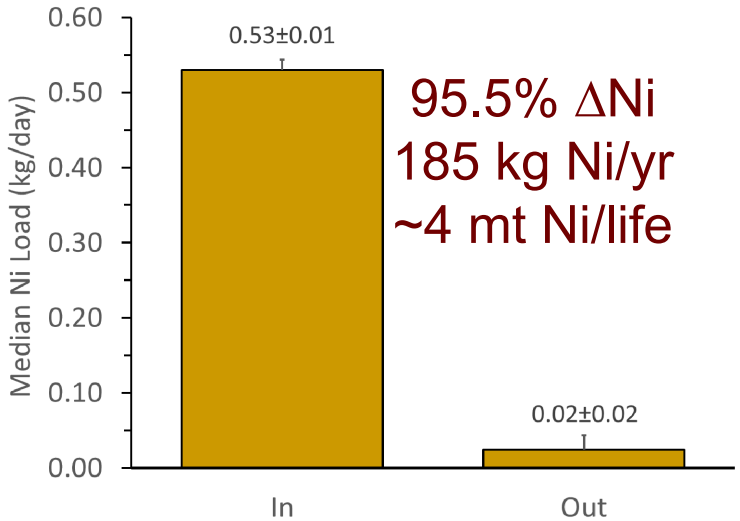
Mayer Ranch PTS – Other Metals



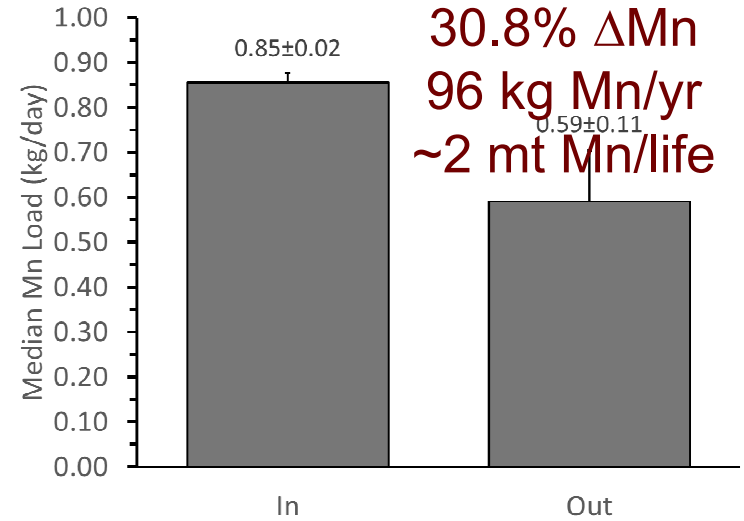
~100% ΔAs
13 kg As/yr
~0.3 mt As/life



~100% ΔCo
11 kg Co/yr
~0.2 mt Co/life

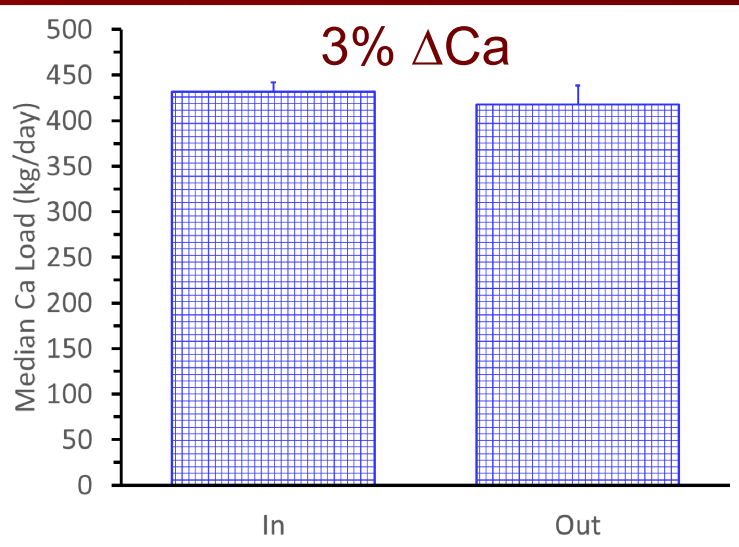


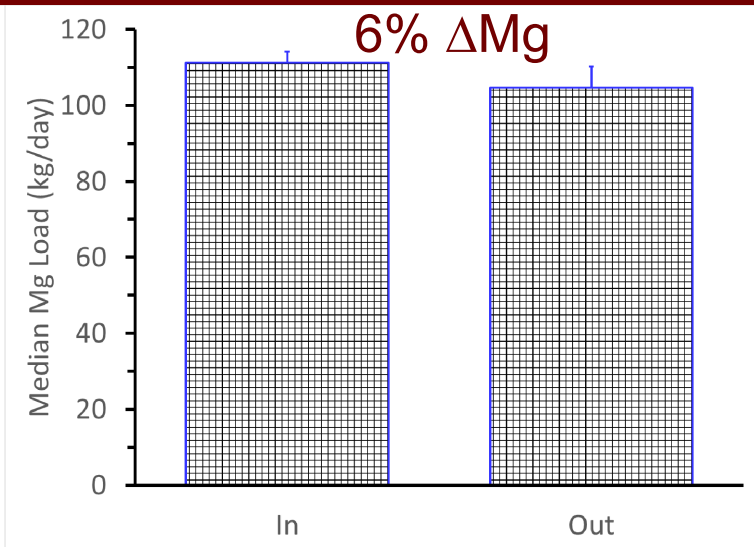
95.5% ΔNi
185 kg Ni/yr
~4 mt Ni/life

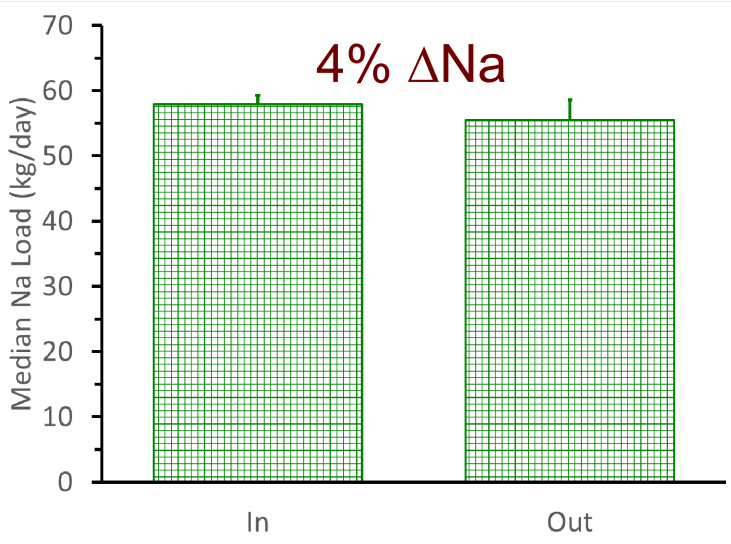


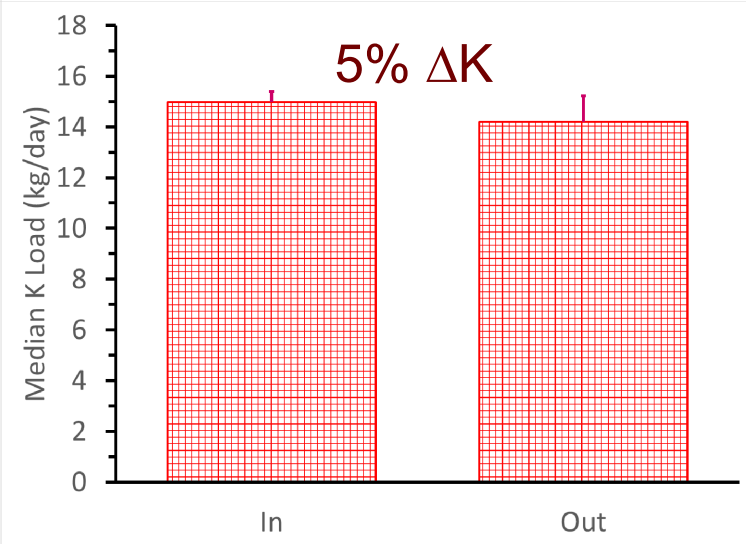
30.8% ΔMn
96 kg Mn/yr
~2 mt Mn/life

Mayer Ranch PTS – Base Cations

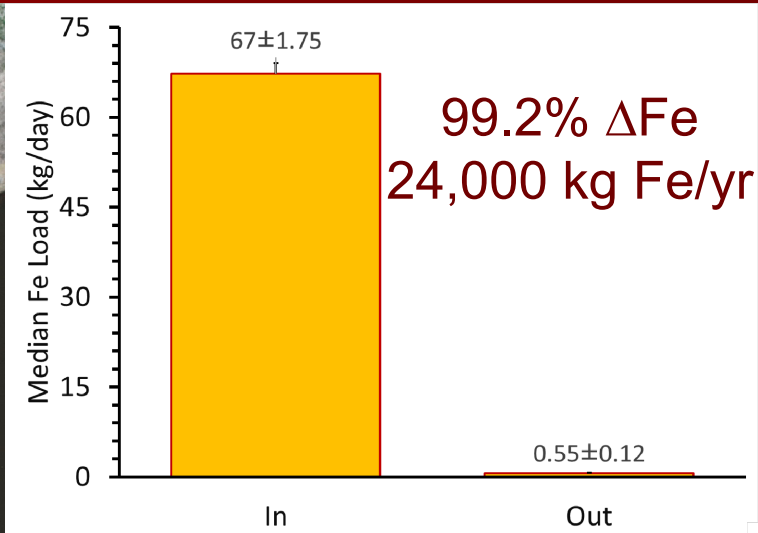


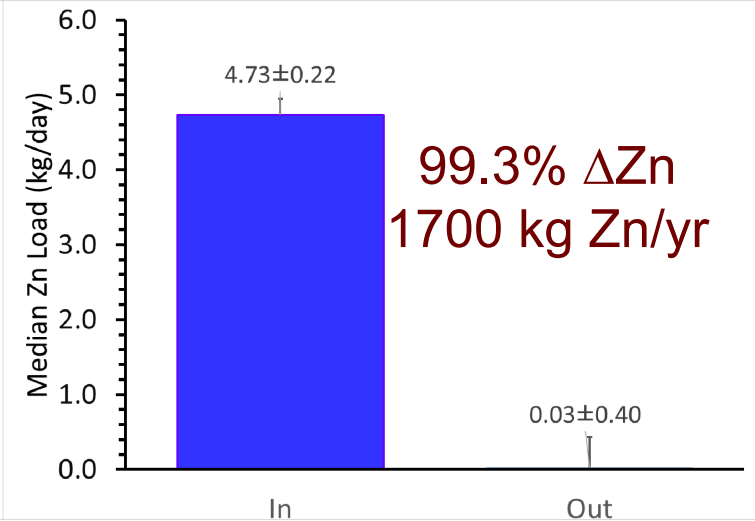


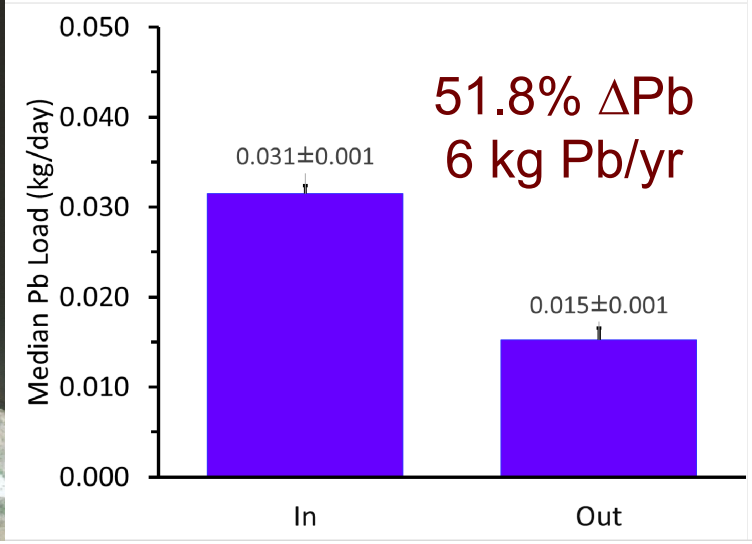


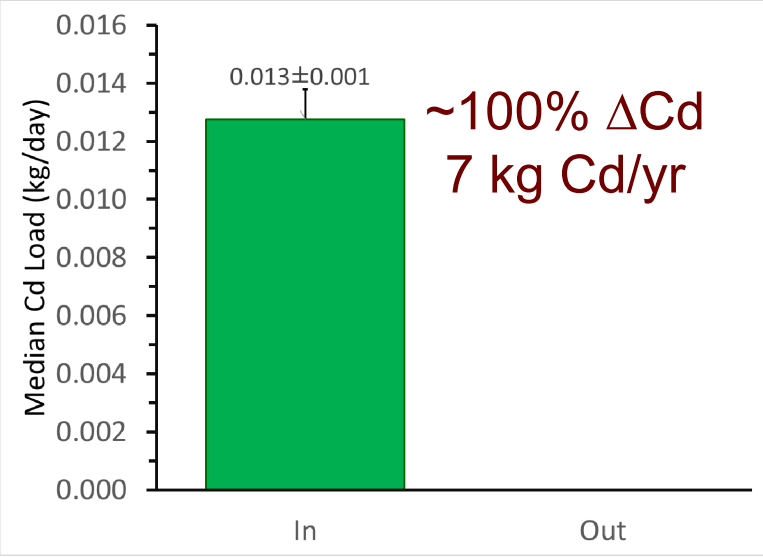


Southeast Commerce PTS - COCs

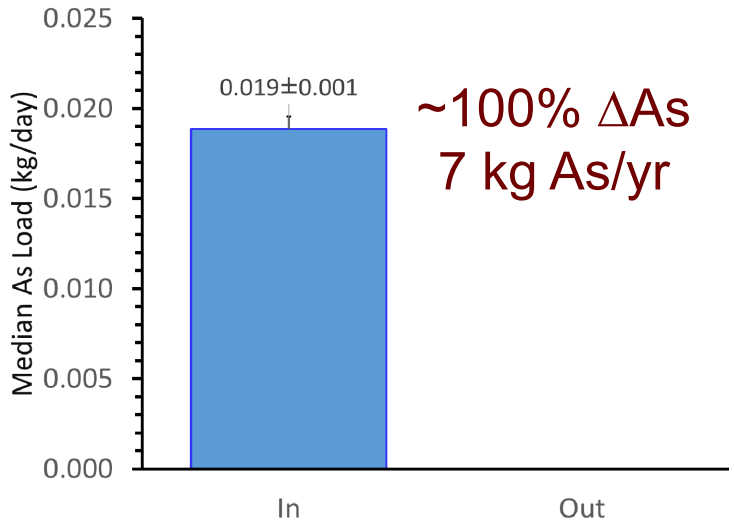


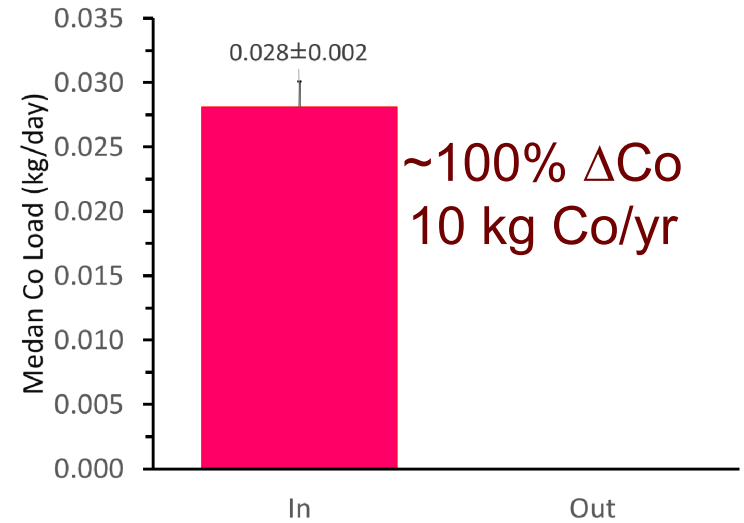


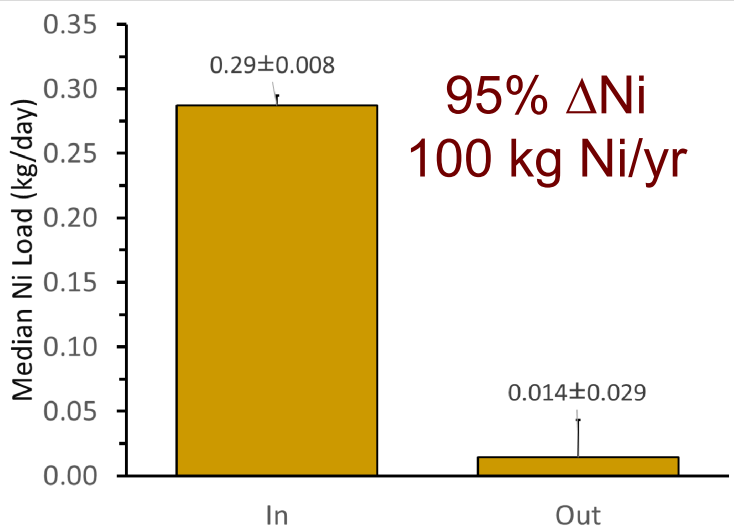


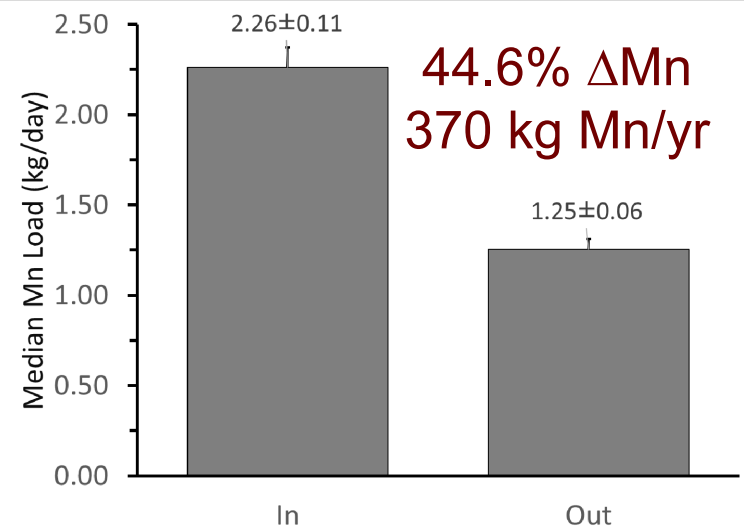


Southeast Commerce PTS – Other Metals

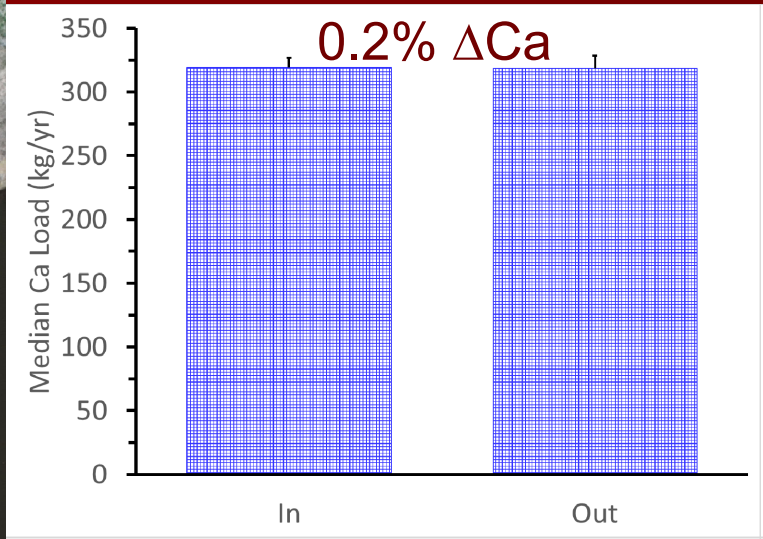


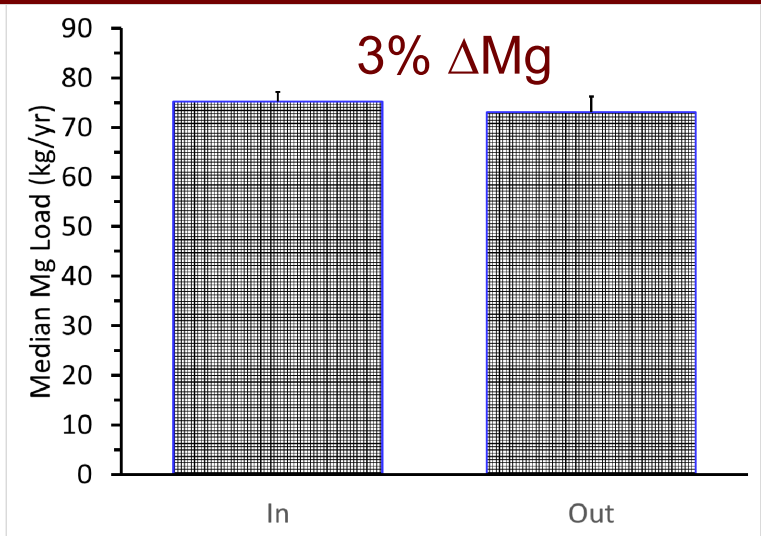


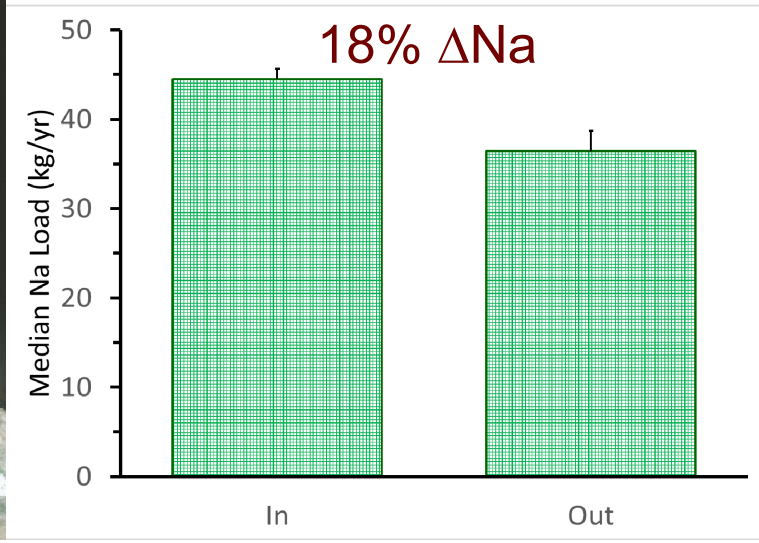


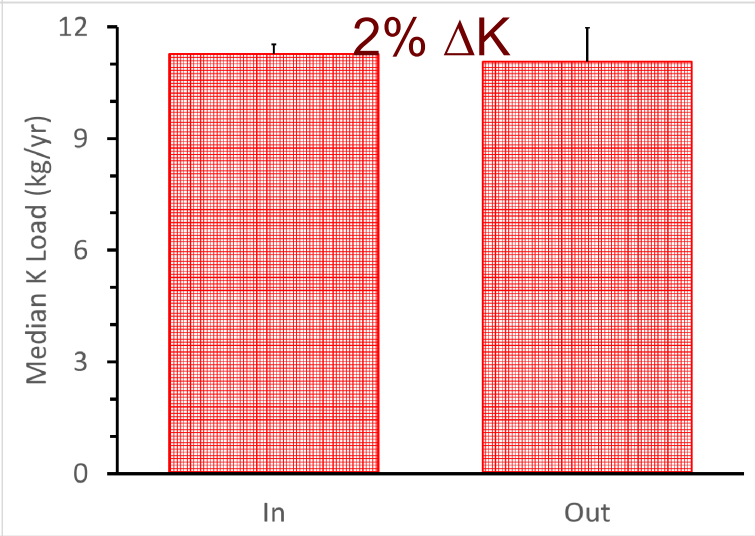


Southeast Commerce PTS – Base Cations





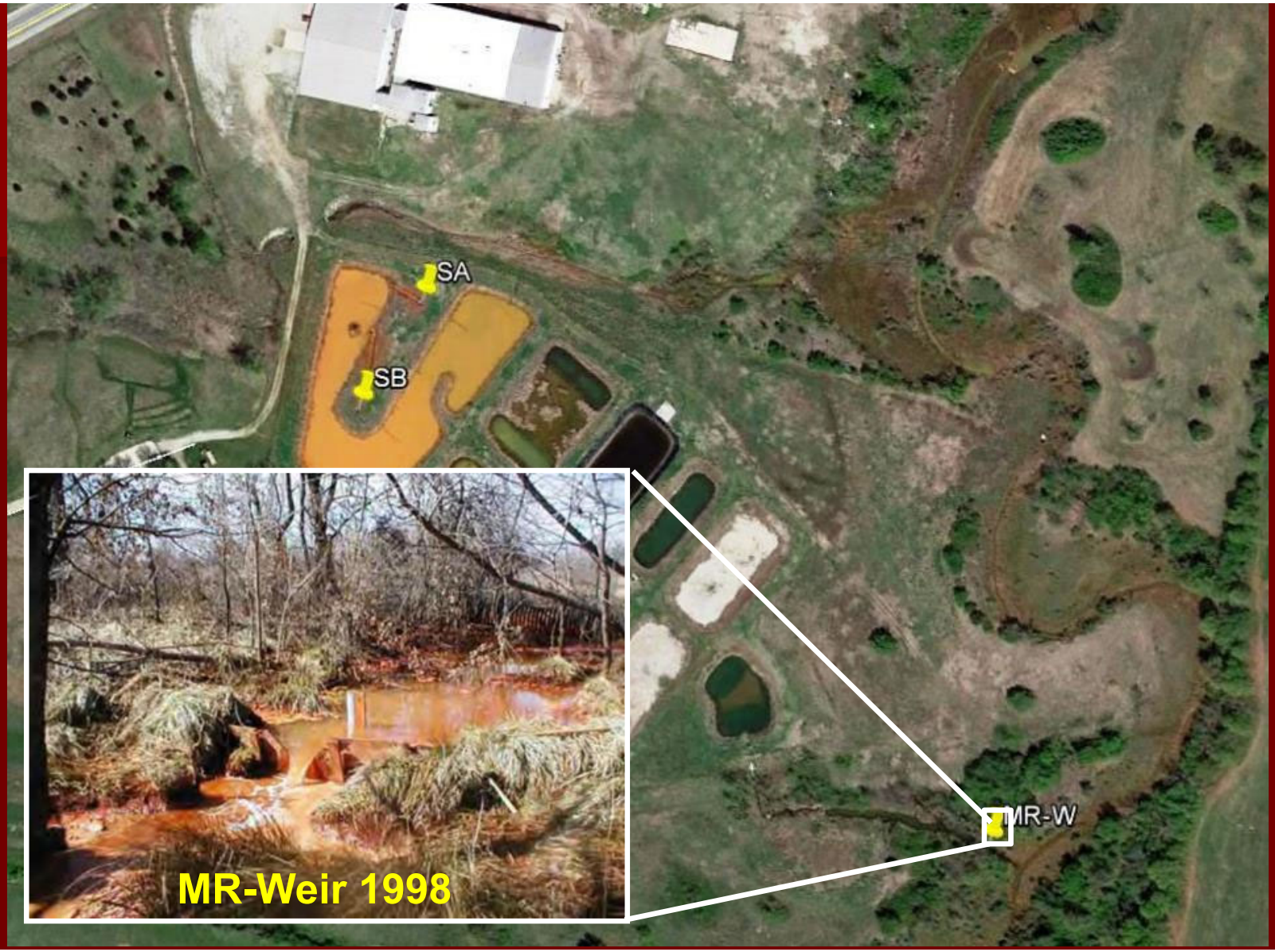


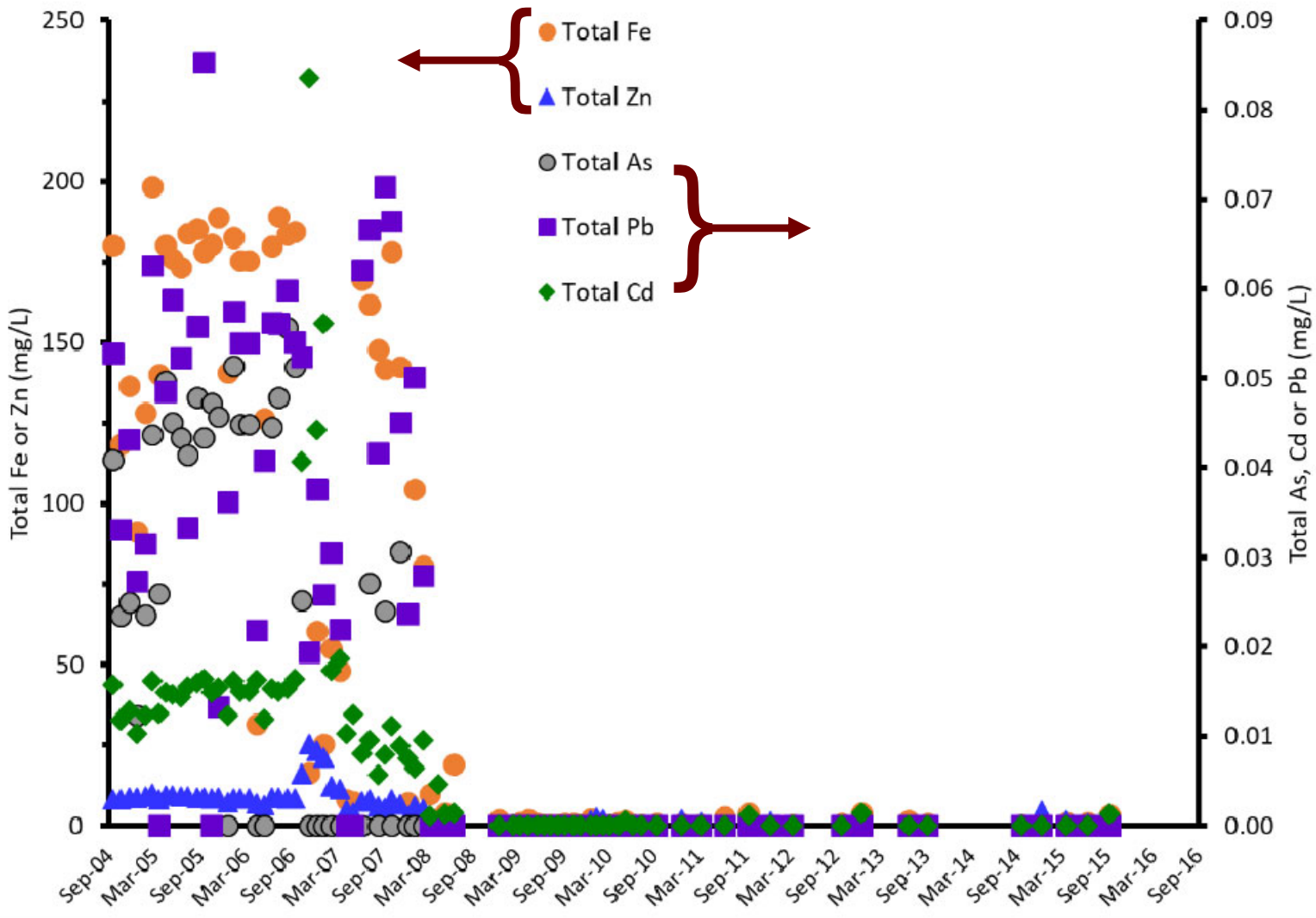


Irreversibly Damaged?

Receiving Stream Recovery

SA
SB
MR-W


SA
SB
MR-W
MR-Weir 1998


Total Fe
Total Zn
Total As
Total Pb
Total Cd
Total Fe or Zn (mg/L)
Total As, Cd or Pb (mg/L)
250
200
150
100
50
0
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Sep-04
Mar-05
Sep-05
Mar-06
Sep-06
Mar-07
Sep-07
Mar-08
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Mar-09
Sep-09
Mar-10
Sep-10
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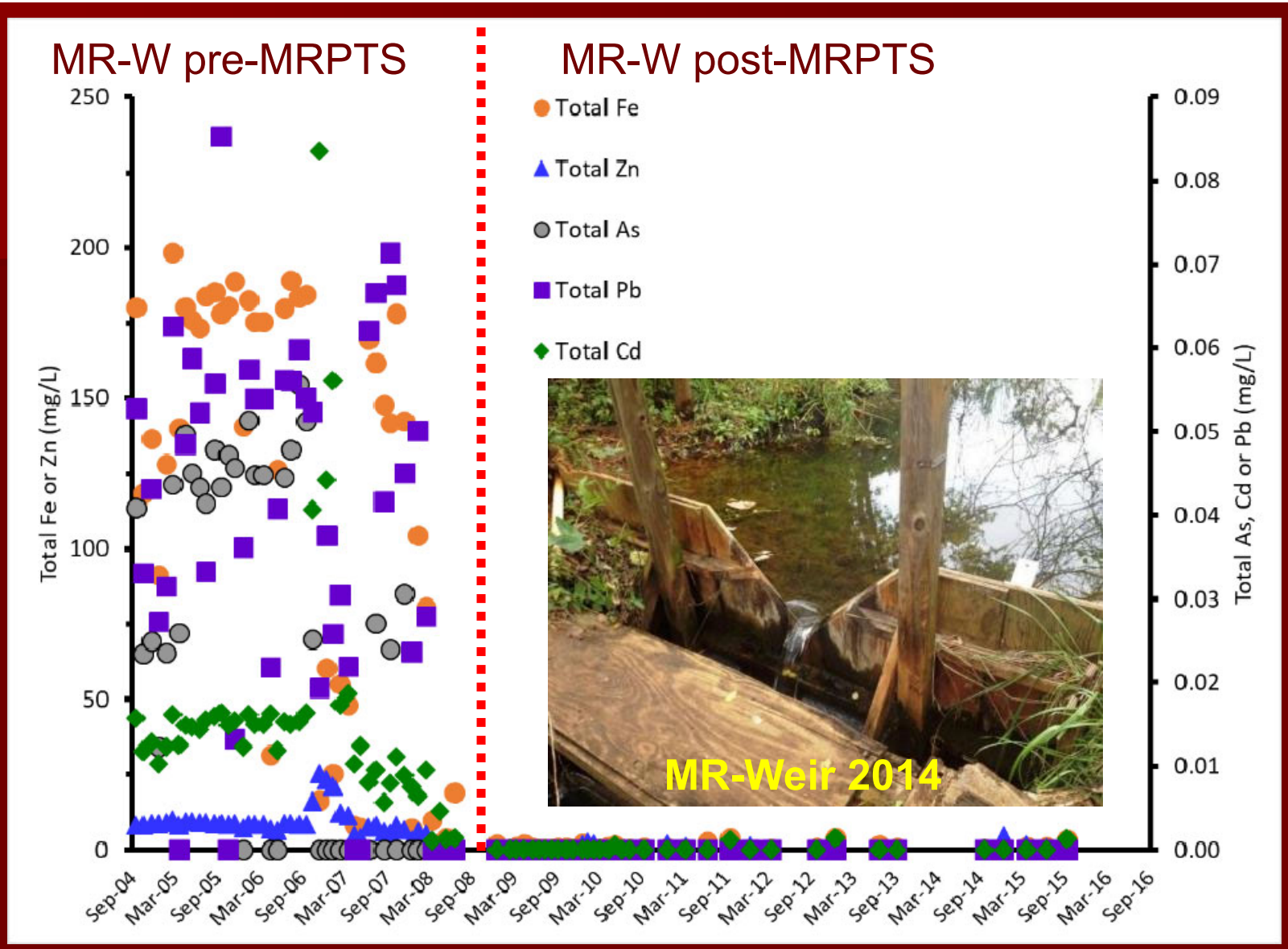
Mar-15
Sep-15
Mar-16
Sep-16


MR-W pre-MRPTS
MR-W post-MRPTS
Total Fe
Total Zn
Total As
Total Pb
Total Cd
MR-Weir 2014
Total Fe or Zn (mg/L)
Total As, Cd or Pb (mg/L)
250
200
150
100
50
0
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
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Mar-11
Sep-11
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Sep-12
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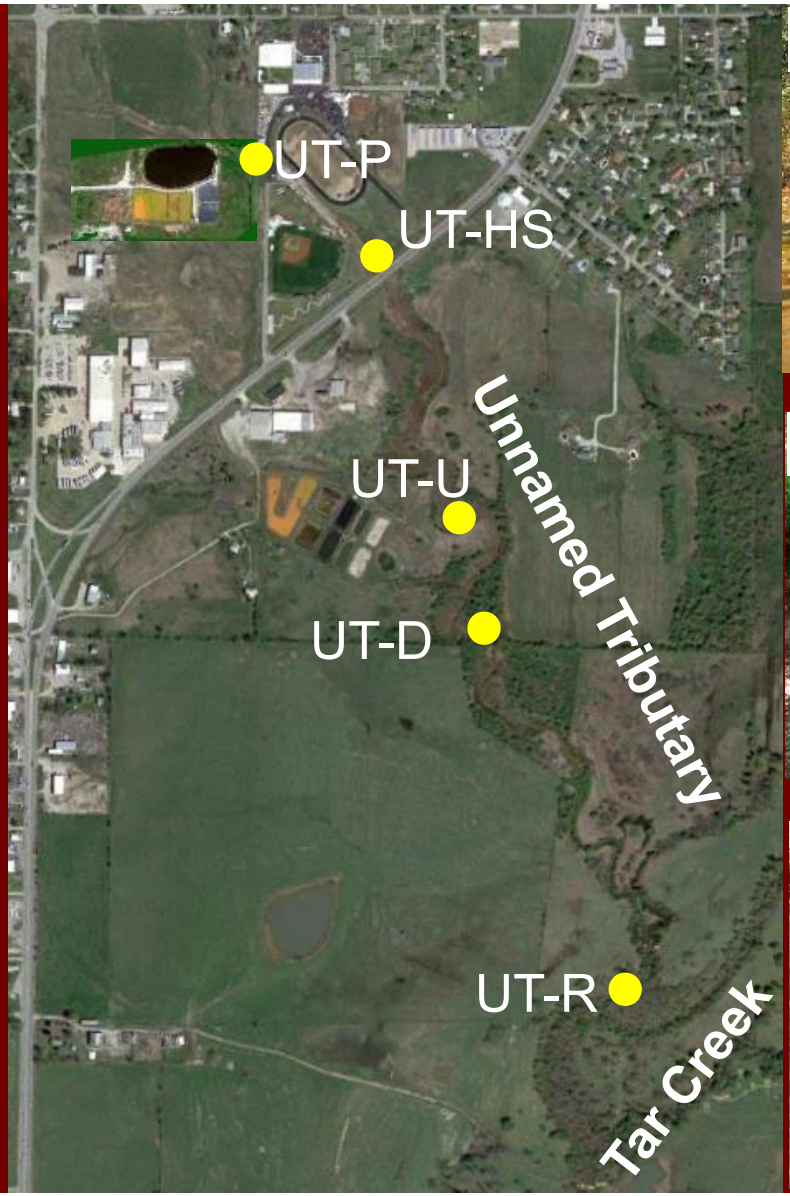
Sep-15
Mar-16
Sep-16

Receiving Stream Recovery

- Long-term water quality data collection (15+ years)
- Long-term fish community analysis (12+ years)
- Documented changes in water quality and ecological community

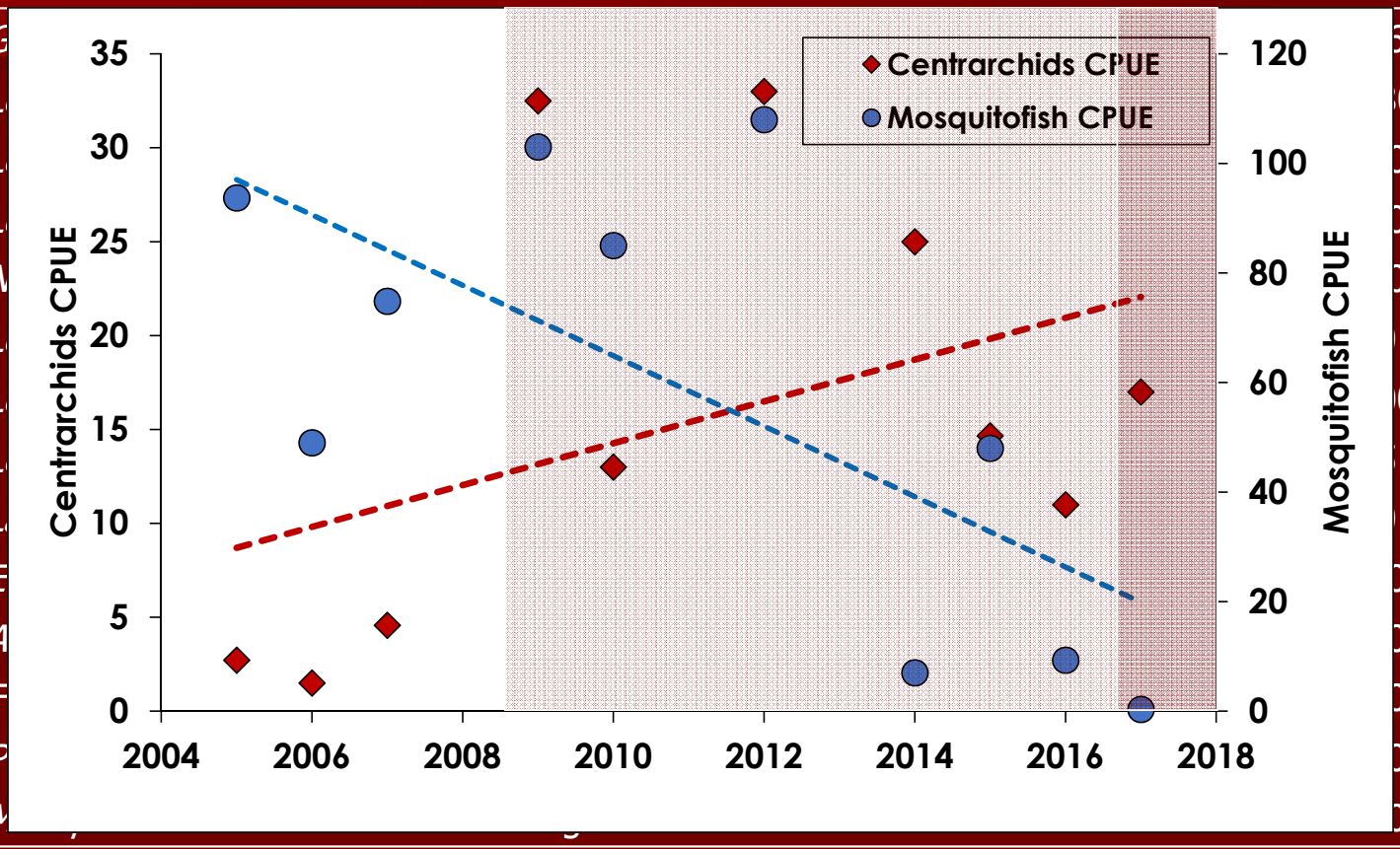


Unnamed Tributary fish data

		Catch per unit effort (CPUE)	
Scientific name	Common name	2005-07	2009-18
Gambusia affinis	Western mosquitofish	39.24	187.60
Lepomis cyanellus	Green sunfish	0.81	16.80
Lepomis macrochirus	Bluegill	1.00	3.00
Lepomis megalotis	Longear sunfish	0.02	6.80
Notemigonus crysoleucas	Golden shiner	0.17	0.60
Lepomis gulosus	Warmouth	0.07	1.0
Lepomis microlophus	Redear sunfish	0	18.00
Lepomis sp.	Sunfish hybrid	0	2.5
Labidesthes sicculus	Brook silversides	0	2.0
Etheostoma gracile	Slough darter	0	0.80
Ameiurus melas	Black bullhead	0	0.40
Fundulus notatus	Blackstriped topminnow	0	0.40
Pomoxis annularis	White crappie	0	0.30
Micropterus salmoides	Largemouth bass	0	0.20
	Species richness	6	14

Unnamed Tributary fish data

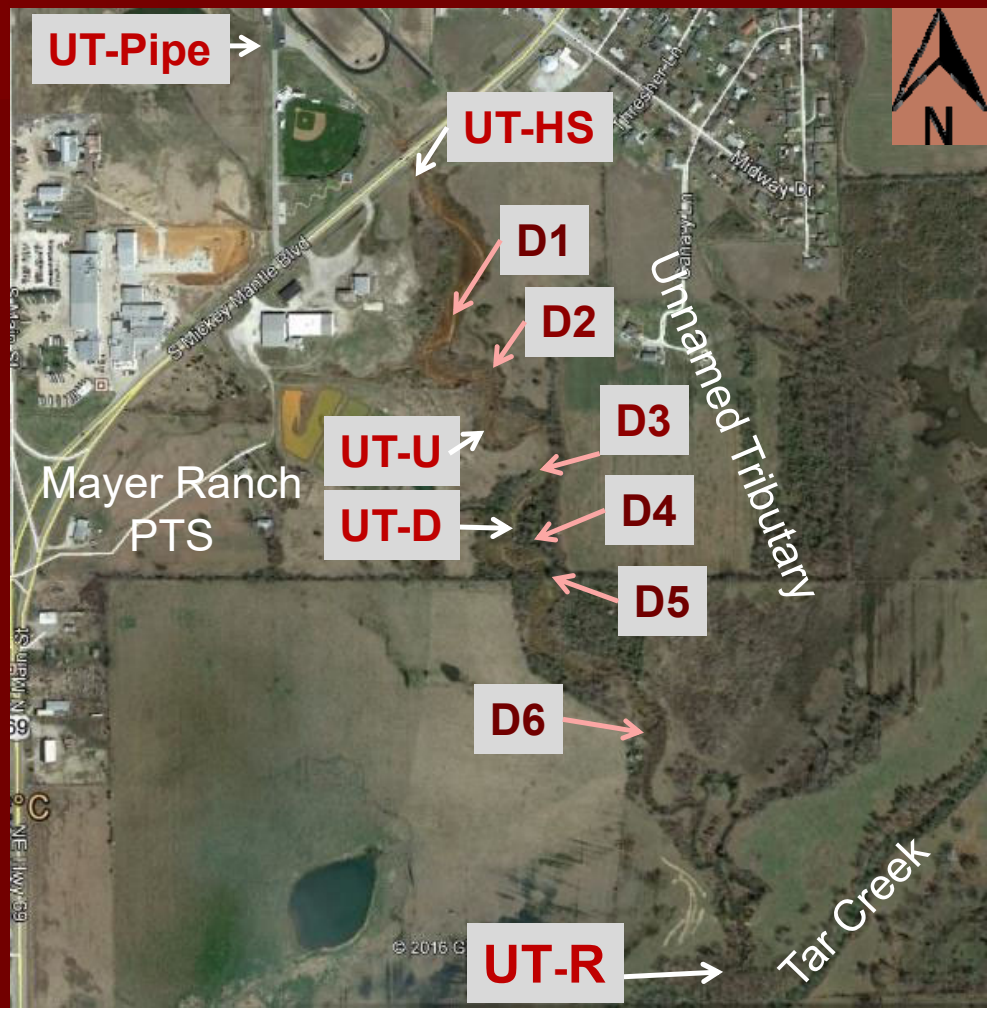
		Catch per unit effort (CPUE)	
Scientific name	Common name	2005-07	2009-18
G			60
L			0
L			0
L			0
N			0
L			
L			0
L			
L			
E			0
A			0
F			0
P			0
M			0
	Species richness	6	14



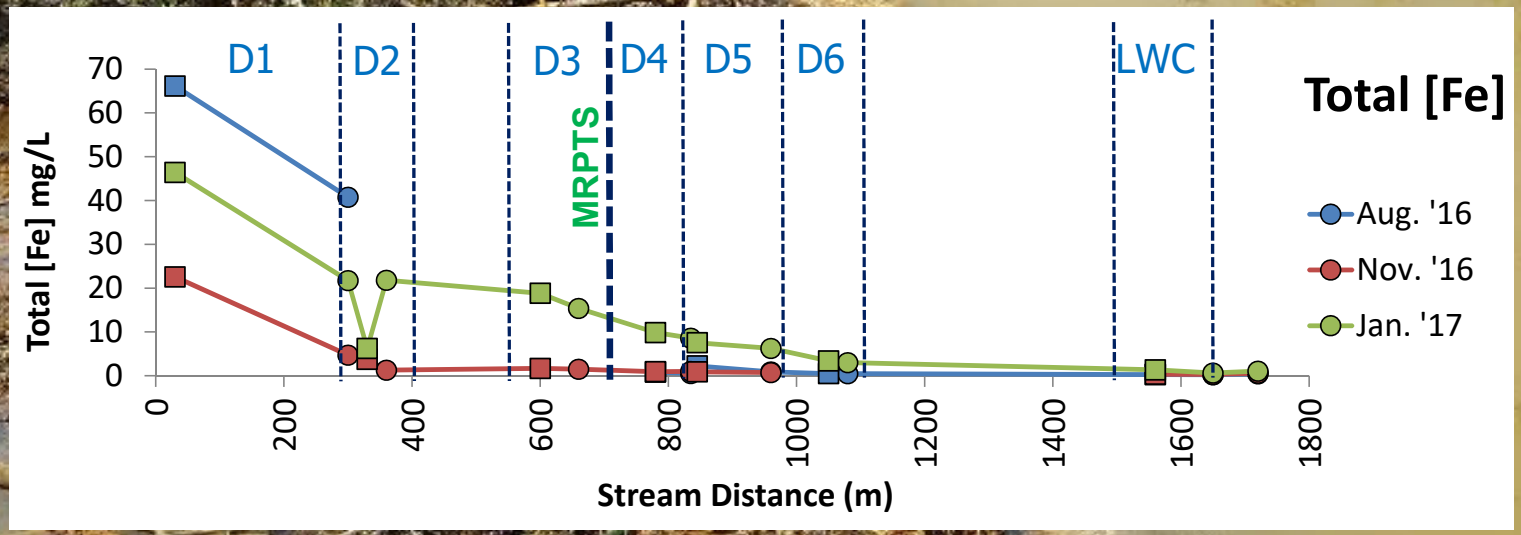
- Single seine haul at UT-HS in October 2018, where no fish were found until late 2017
- No in-stream habitat restoration, just improvement of source water quality

Beaver in Unnamed Tributary

- 340 ha watershed, ~1.6 km stream length
- Water quality monitoring since 2004
- MRPTS implemented 2008
- Beaver recolonization first noted 2013
- Evaluation conducted before SECPTS (online 2017)



- Presence of beaver dams decreased [Fe], [Cd], and [Zn] in a mine drainage impacted stream



Beaver pond Fe removal rate: 4.6 g $m^{-2}d^{-1}$

Beaver maintenance of v-notch weir

Conclusions

Conclusions

- Passive treatment is a demonstrated ecological engineering technology to improve mine water quality
- Water quality improvement has direct influence on ecological metrics in stream and riparian areas
- Widespread applicability requires revisiting and revising administrative and regulatory constraints

2000 USEPA Five-Year Review Statement

- *"…the massive costs associated with any engineering remedy for surface water contamination in the Tar Creek Basin are still prohibitively high, and expenditures to meet those costs would drain the (Super)Fund. In short, there is no reason to revisit the fund-balancing waiver that was made in the 1984 OU1 ROD"*

2015 USEPA Five-Year Review Statement

- *"…Treating mine water discharge via passive treatment appears to be economically feasible… passive treatment would be evaluated to determine its effectiveness at reducing the risks posed by mine water discharge… the fund balancing applicable or relevant and appropriate requirements waiver… may no longer be valid and should be reevaluated…"*

2019 USEPA Strategic Plan

- Major Site Milestones
  - *2008: Mayer Ranch passive treatment system construction completed*
  - *2017: Southeast Commerce passive treatment system construction completed*
- Strategic plan priorities
  - *Expand use of passive treatment systems*

Big Picture Conclusions

- Ecological engineering technologies using *natural infrastructure* may address other water quality problems
  - Urban stormwater
  - Agricultural runoff
  - Municipal wastewater reuse
  - Produced waters
  - Industrial process waters

Ecologically engineered technologies can play an essential role in solving our Nation's suite of water challenges

Ecological Engineering

The design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both

- Mitsch and Jorgenson (2004)

Engineering With Nature

The intentional alignment of natural and engineering processes to efficiently and sustainably deliver economic, environmental, and societal benefits through collaboration

- Bridges (2019)

Acknowledgements

- Our private landowners
  - Mayer, Pritchard, Martin and Corbus families
- Our funding sources
  - ODEQ Land Protection Division
  - Grand River Dam Authority Ecosystems Management
  - USEPA Water Division
  - USGS Toxic Substances Hydrology Program
- Our partners
  - OU CREW, CEES and Biology
  - Quapaw Nation of Oklahoma
  - City of Commerce
  - Northeastern Oklahoma A&M College
  - CH2M-Hill team and subcontractors
  - BioMost Inc. and Riverman Engineering
  - LEAD Agency
- CREW past and present

CREW

Center for Restoration of Ecosystems and Watersheds
University of Oklahoma

The CREW

R Knox, K Strevett, W Matthews, E Bergey, J Basara, J LaBar, C Kellogg, A O'Sullivan, B Holzbauer-Schweitzer, D Nguyen, B Page, A Sikora, Z Tang, T Wall, E Fielding, E Thornton, K Steele, S Yepez, A Smith, J McAllister, W Andrews, A Brewer, B Santamaria, C Neely, A Garrido, W Strosnider, D Lutes, M Roberts, D Hensley, R White, C Gause, T Traw, J Coffey, C Porter, D Athay, B Winter, N Iverson, V Arvidson, R Garrett, C DuBois, E Breetzke, M Mercer, J Arango Calderon, N Berg-Mattson, J Brumley, B Furneaux, M Rice, R Dutnell, L Oxenford, A Strevett, Z Sansom, L Mignogna, W Runyon, K Ryan, P Eger, J Clifton, A Donaldson, H Bragg, A Danielson, A Oberst, D Tepo, K Swanson, D Miller, E Spargo, K Wahnee, J Fowler, S Guzman, N Shepherd, V Nadiq, A Marsh, S Zawrotny, T Bisanar, B. Winfrey, I Gray, M Cogburn, K Walker, D Morris, D Ertegrul, P Baczynski, B Johnson, A Sutter, K Kauk, C Turley, E Shaw, J Ingendorf, T Verlander, C Robb, H Stanfield, K Markley, D Bruer, M Dorman, S Hobson, J Ingendorf, T Pipher, H Stanfield, D Wright, E Wu. **et al.**

Questions?

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