Removal of Excess Gaseous and Aqueous Sulfide from Vertical Flow Bioreactor Effluent Using Activated Carbon and Solar-Powered Blowers

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1890

GALLOGLY COLLEGE OF ENGINEERING
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE
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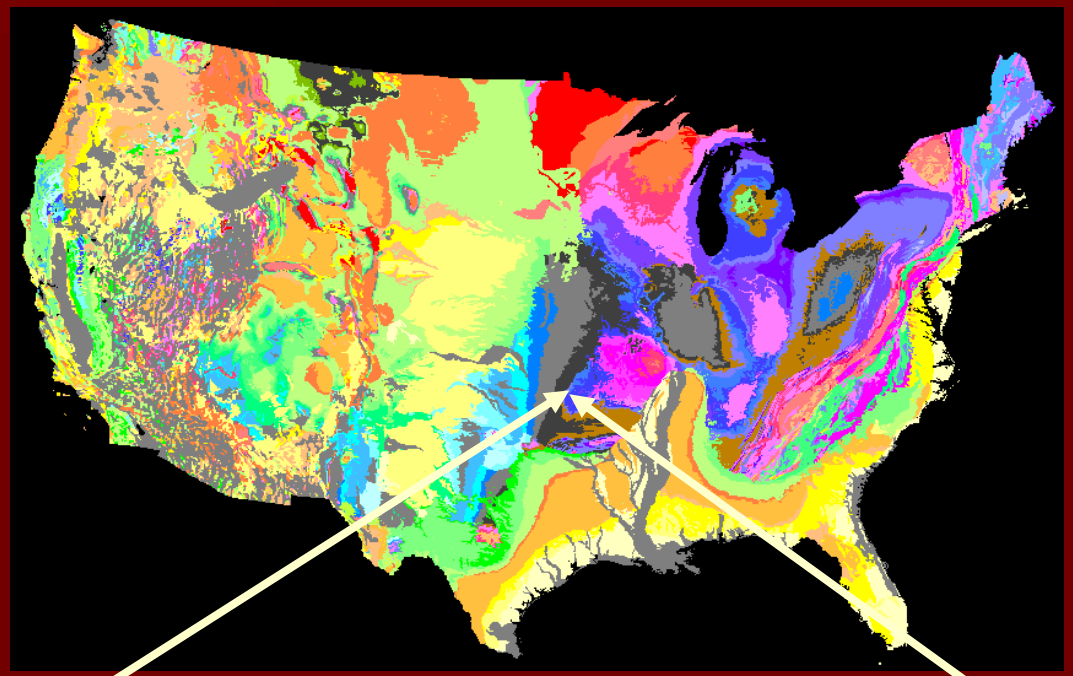
CREW
Center for Restoration of Ecosystems and Watersheds
University of Oklahoma

Thank you to

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
- Picher Field, OK from 1891-1971
  - $3x10^6$ tons Pb and $9x10^6$ tons Zn concentrates
  - 26% of U.S. production



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

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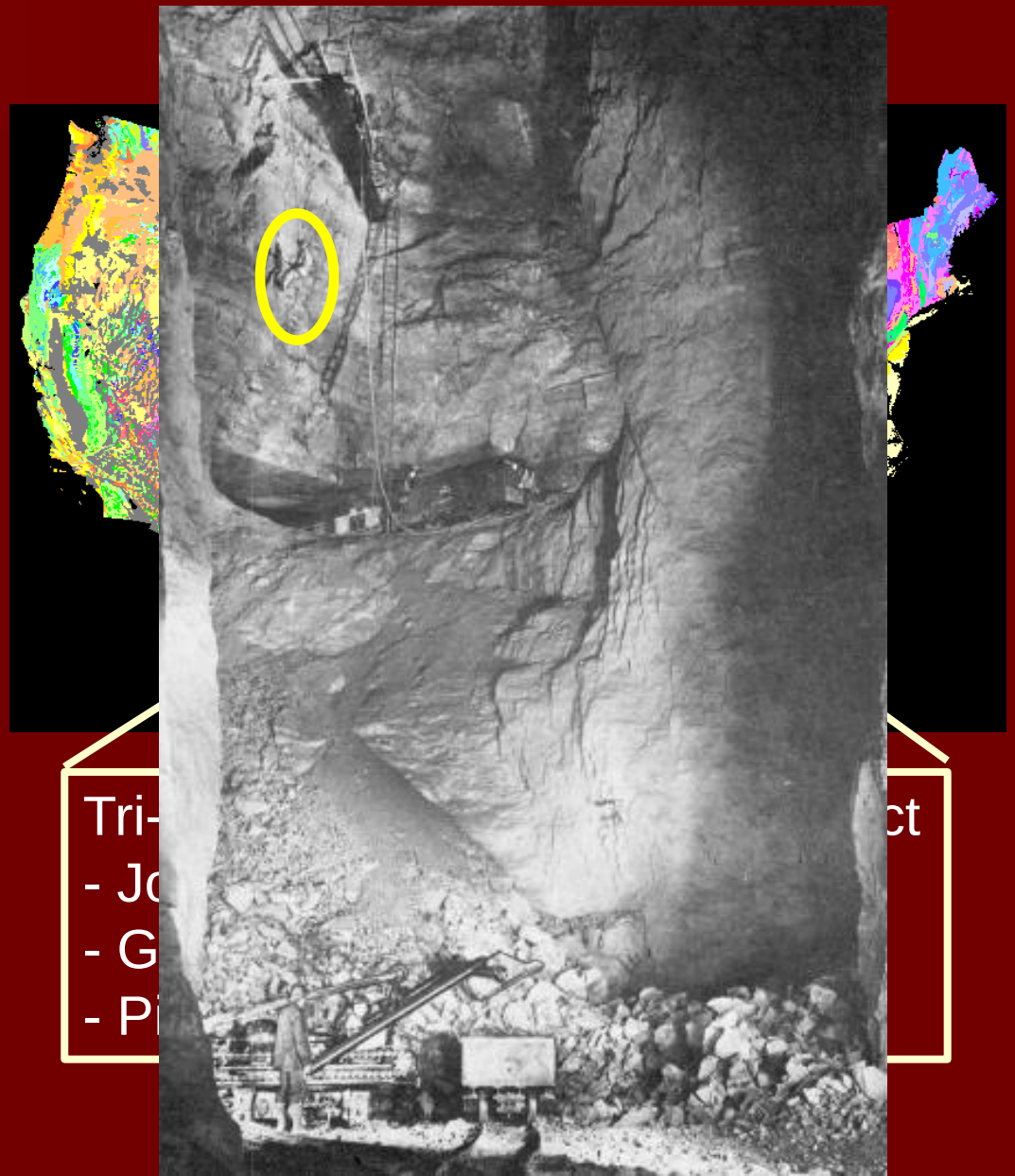
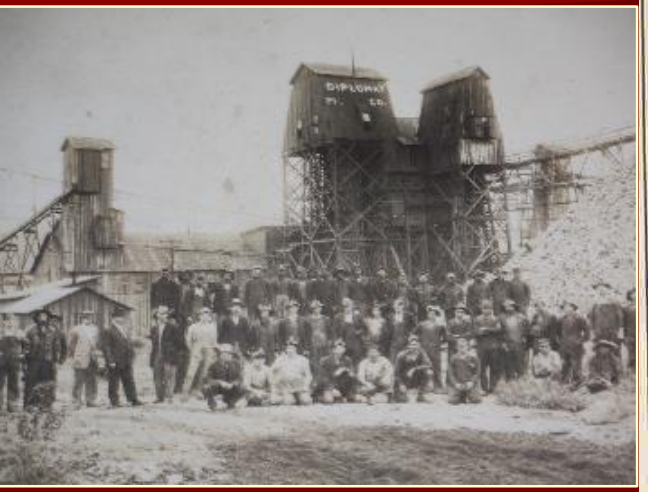




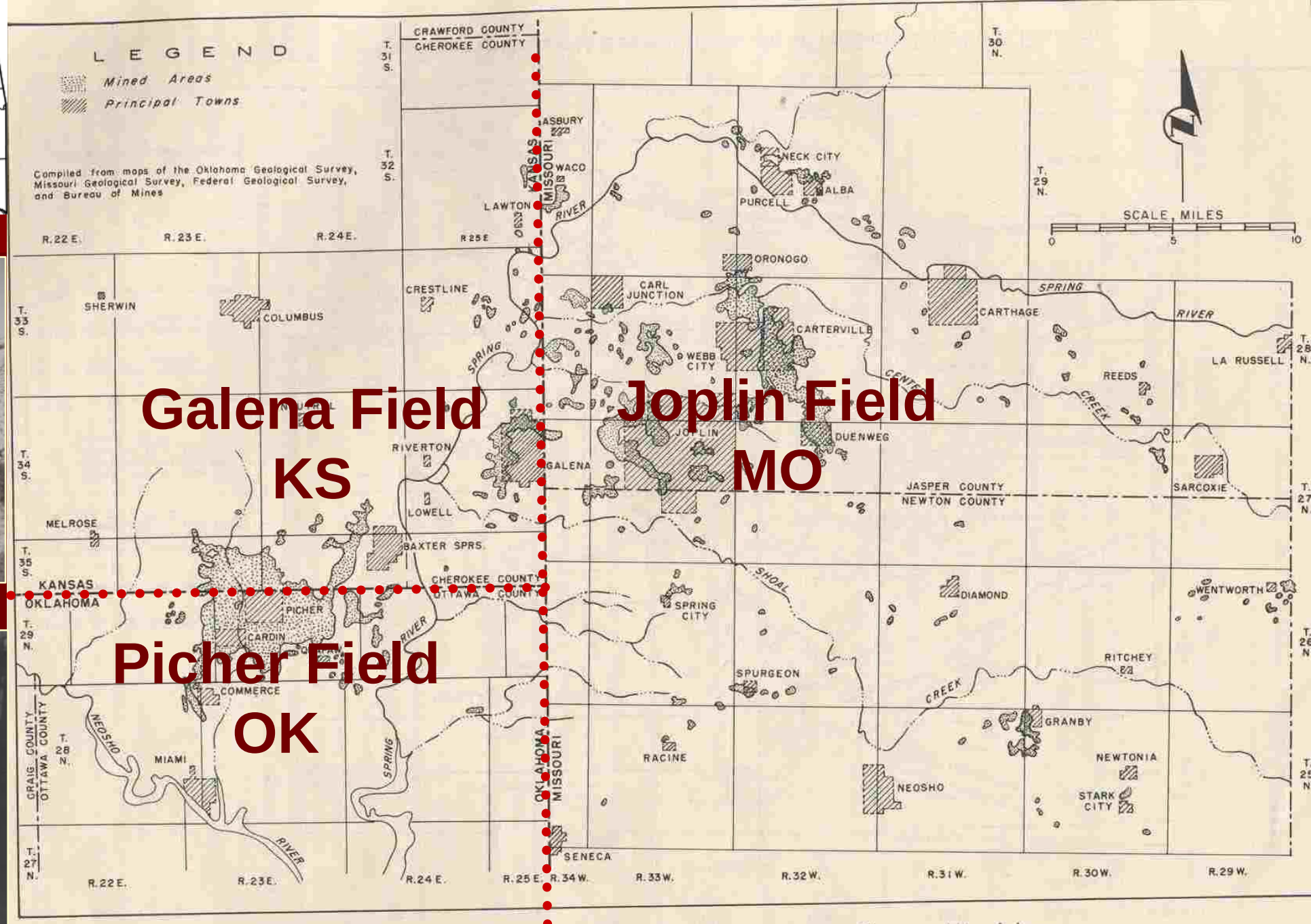
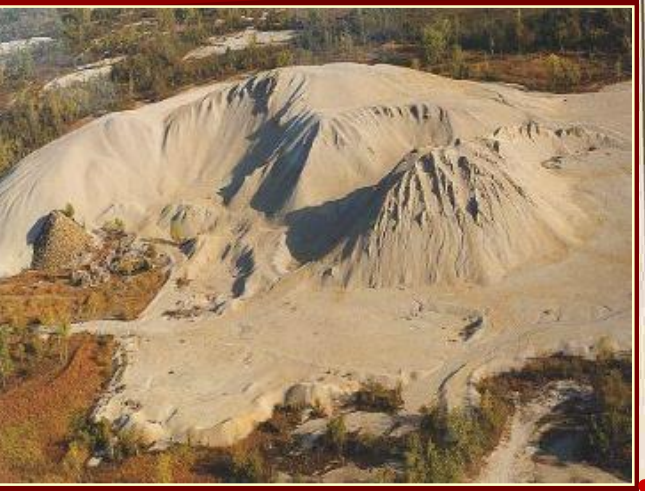
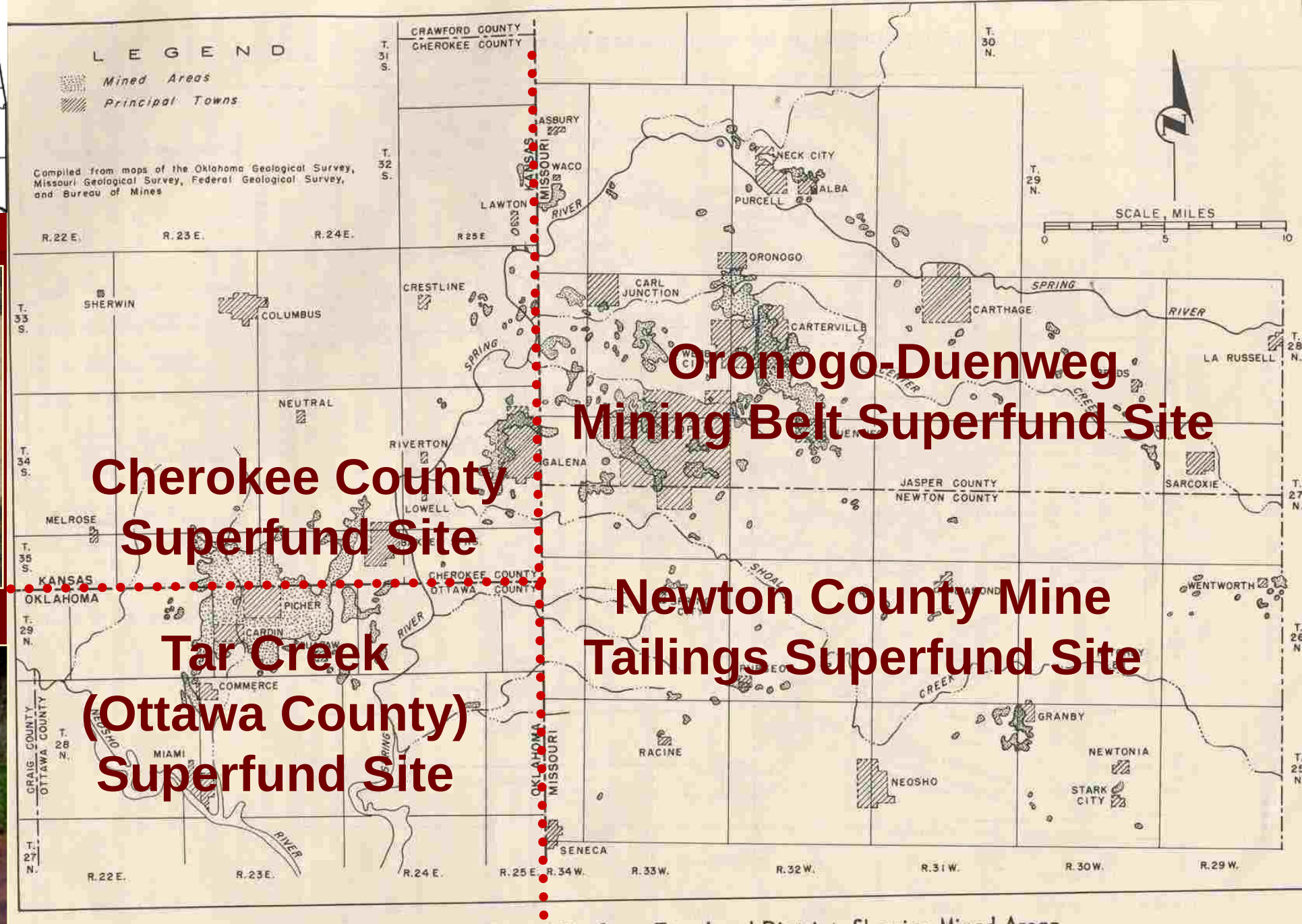


FIGURE 1. - Principal Part of Tri-State Zinc-Lead District, Showing Mined Areas.





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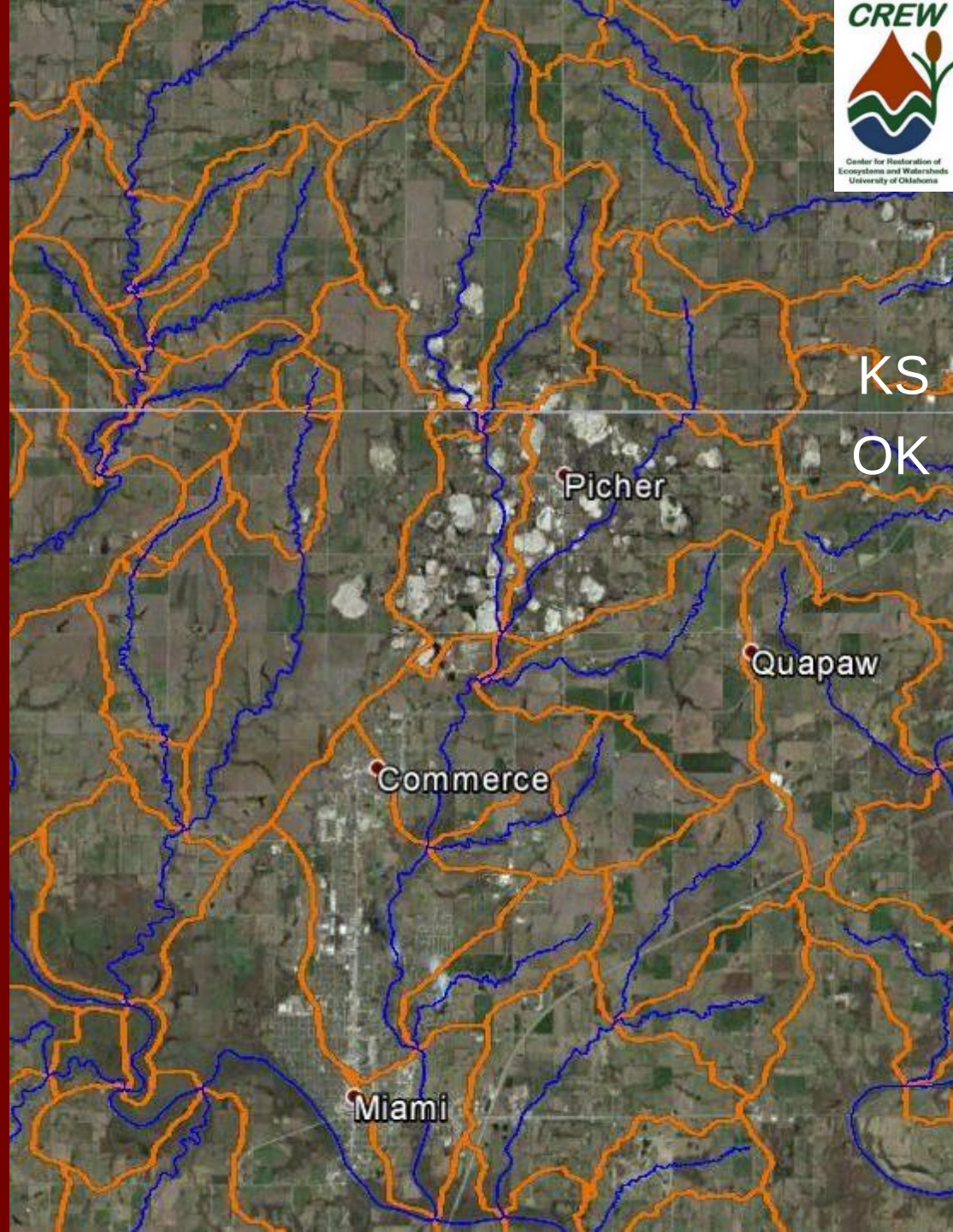
Tar Creek Superfund Site

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



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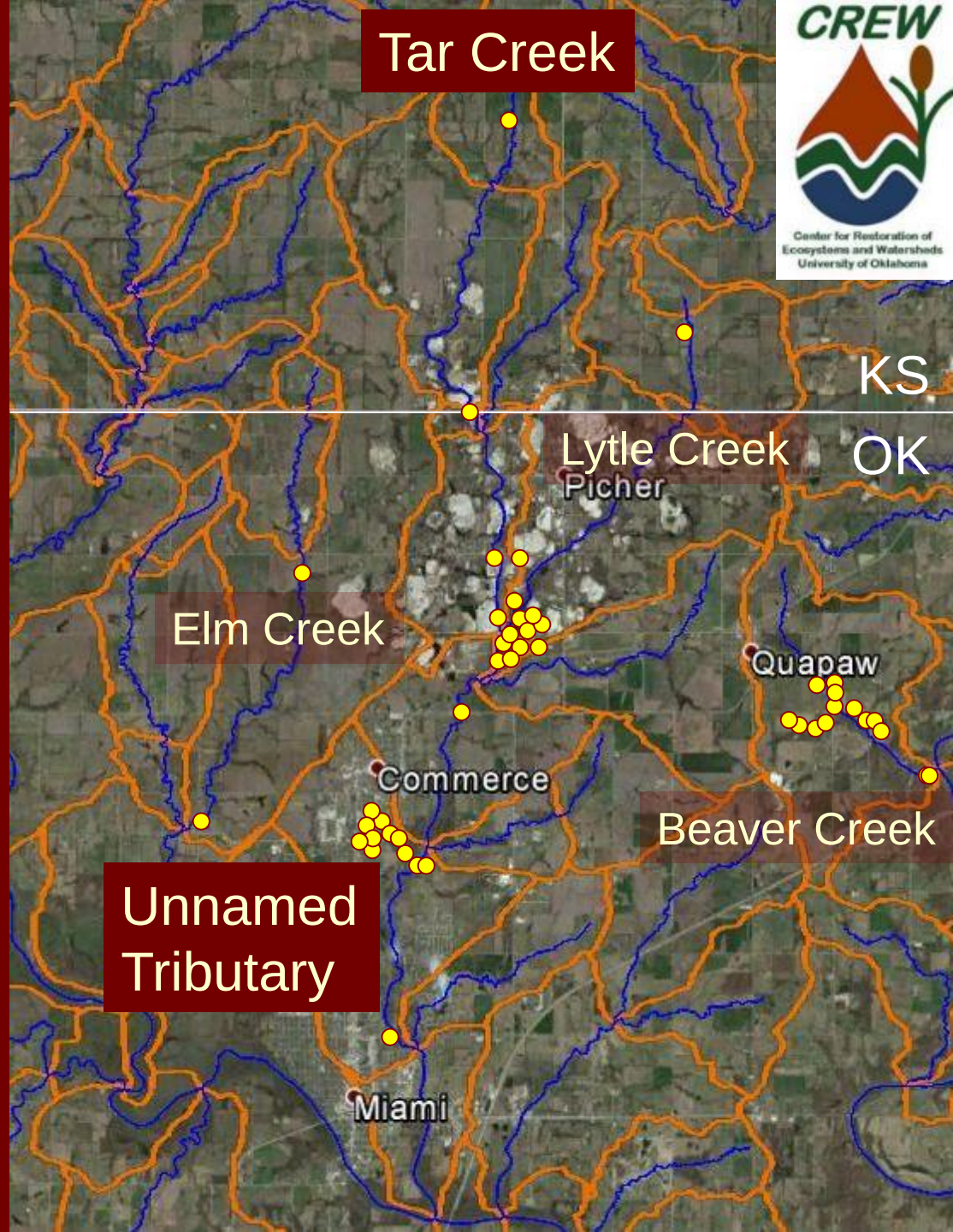

Tar Creek Operable Unit 1
Surface and Ground Water Decision

- 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

Problems/Challenges

System Design

System Performance

Conclusions

Problems/Challenges

Bacterial sulfate reduction in Vertical Flow Bioreactors (VFBRs)

Bacterial sulfate reduction in Vertical Flow Bioreactors (VFBRs)

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$

$$H_2S + Zn^{2+} + 2HCO_3^- \rightarrow ZnS(s) + 2H_2O + 2CO_2$$

Bacterial sulfate reduction in Vertical Flow Bioreactors (VFBRs)

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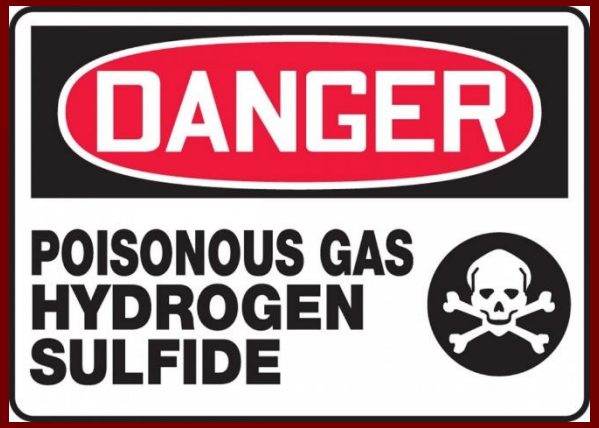
Design for ~20 year lifetime

Potential excess sulfide production

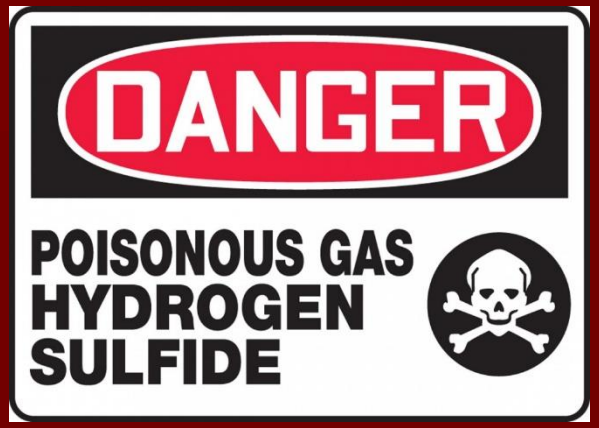
Excess Sulfide Concerns



- Corrosive, poisonous and flammable
- Aqueous sulfide
  - Potential nuisance constituent
  - Toxic to aquatic life > 0.002 mg/L (USEPA 1986)
- Gaseous sulfide
  - Nuisance odor problems
  - Substantial human health effects

Excess Sulfide Concerns

Gaseous H_2S (ppmv)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odor threshold
2-5	Nausea, headache, loss of sleep
20	Fatigue, loss of appetite, headache, irritability, poor memory, dizziness
50-100	Conjunctivitis, respiratory tract irritation, digestive upset, loss of appetite
100-150	Olfactory fatigue and paralysis (loss of sense of smell)
200-300	Pulmonary edema from prolonged exposure
500-700	Staggering, collapse in 5 minutes, damage to eyes in 30 minutes
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes
1000-2000	Nearly instant death



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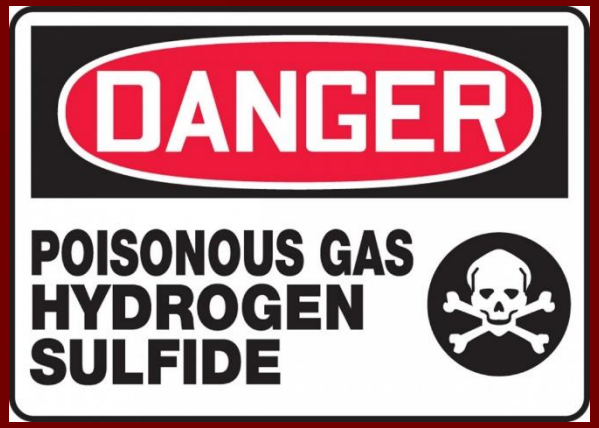
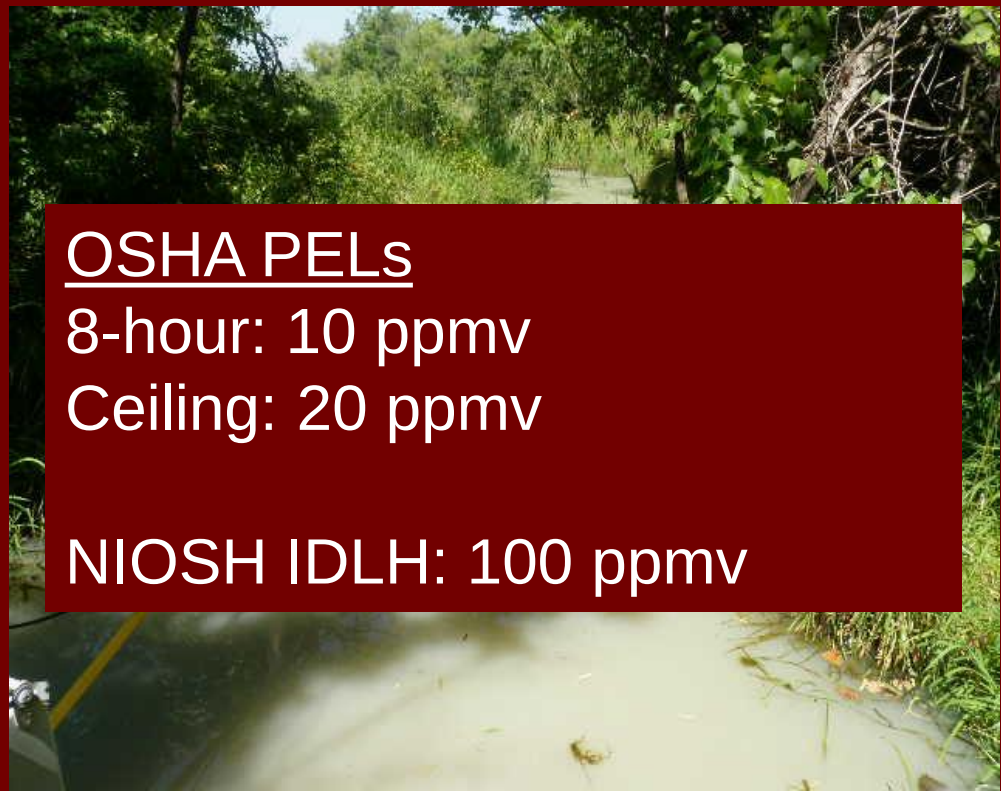




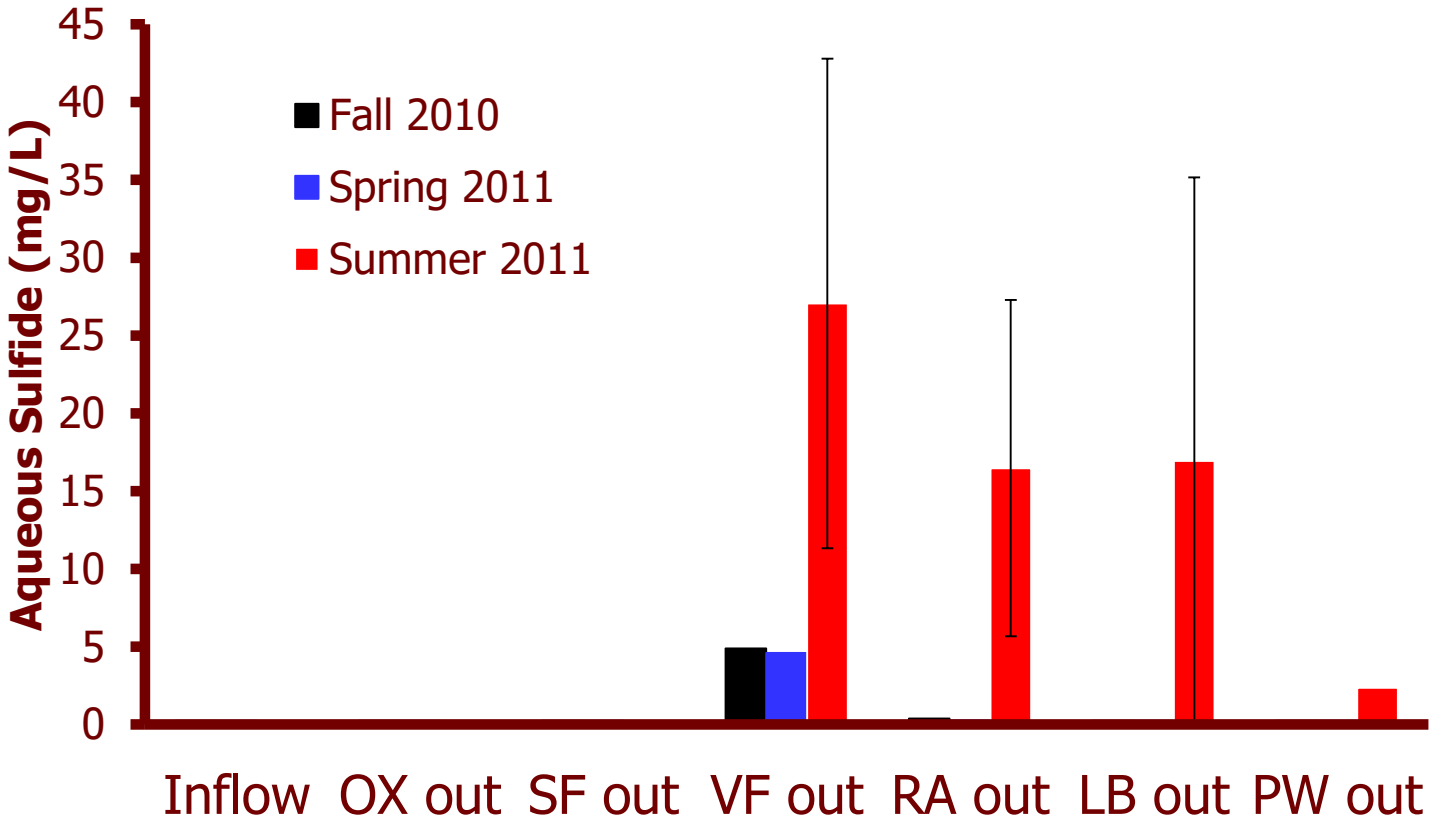
OSHA PELs
8-hour: 10 ppmv
Ceiling: 20 ppmv

NIOSH IDLH: 100 ppmv

Excess Sulfide Production – Mayer Ranch PTS

- Continuous operation since 2008
- First PTS in TSMD

Excess aqueous sulfide



System Design

Southeast Commerce Site

Southeast Commerce

- "Red Hole" and "Green Hole" collapse features
- Water discharges into Unnamed Tributary to Tar Creek
- Collapses filled and surface reclaimed 2006

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- Water discharges into Unnamed Tributary to Tar Creek
- Collapses filled and surface reclaimed 2006
- Mine water collected in French Drain and directed to UT

Southeast Commerce

- "Red Hole" and
  collapse featur
- Water discharg
  Unnamed Tribu
  Creek
- Collapses filled
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- Mine water col
  Drain and direc

Untreated SEC Waters

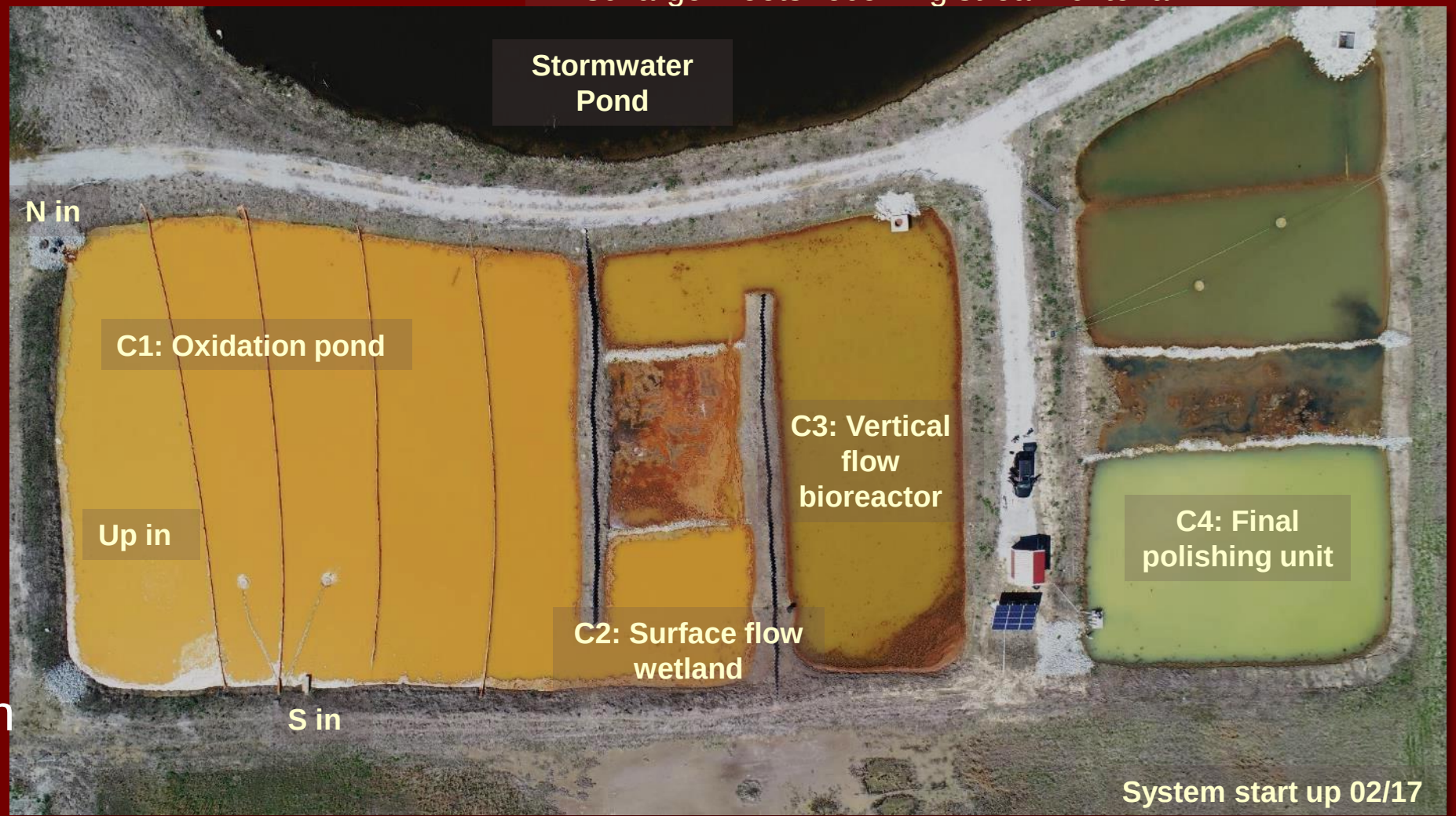
pH	6.06
T. Alk.	350 mg/L $CaCO_3$
Fe	138 mg/L
Zn	6.2 mg/L
Ni	0.52 mg/L
Cd	20 μg/L
Pb	80 μg/L
As	38 μg/L
SO_4^{2-}	2100 mg/L
Q	100 gpm

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

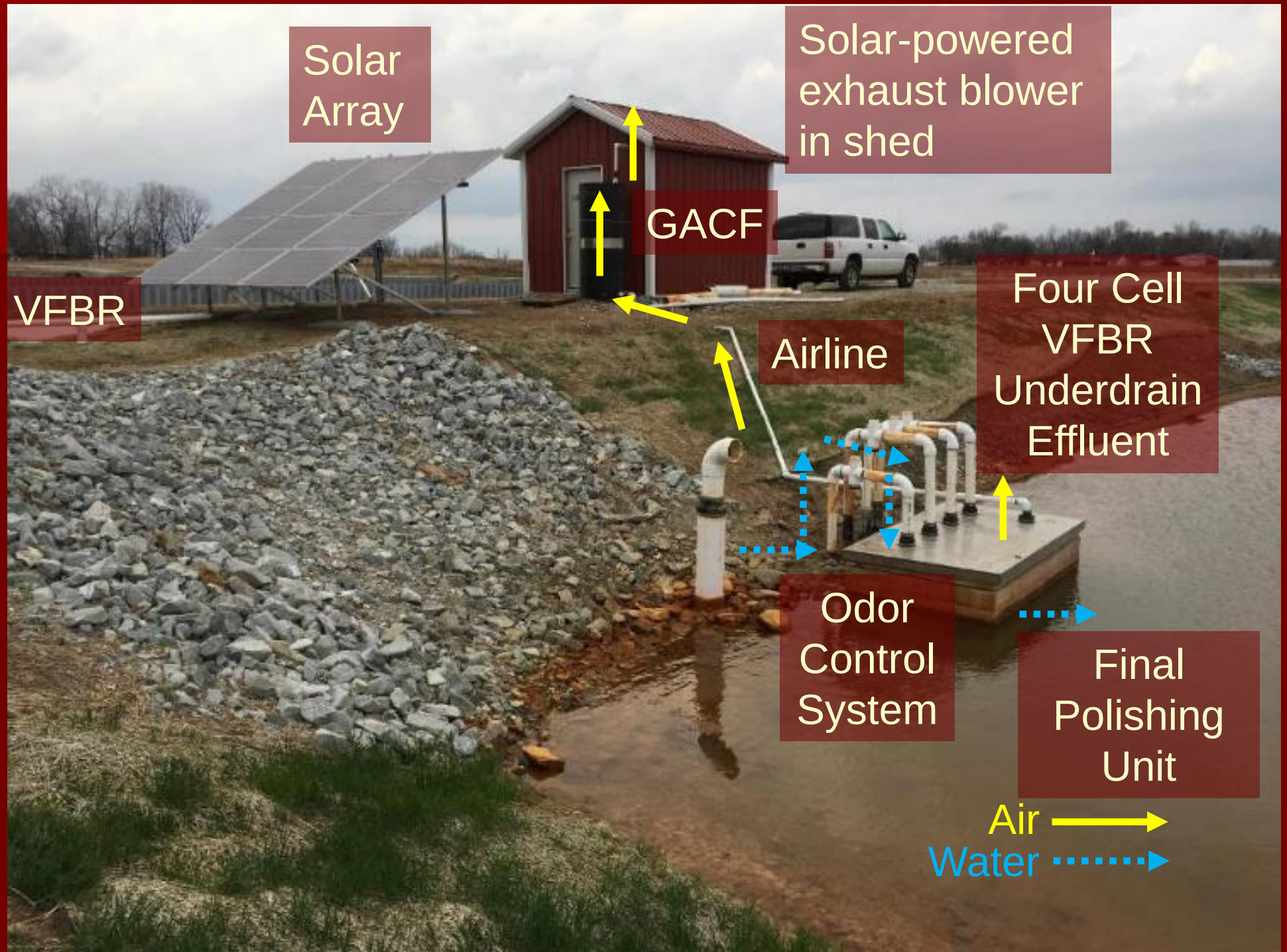
Ecological engineering field research site

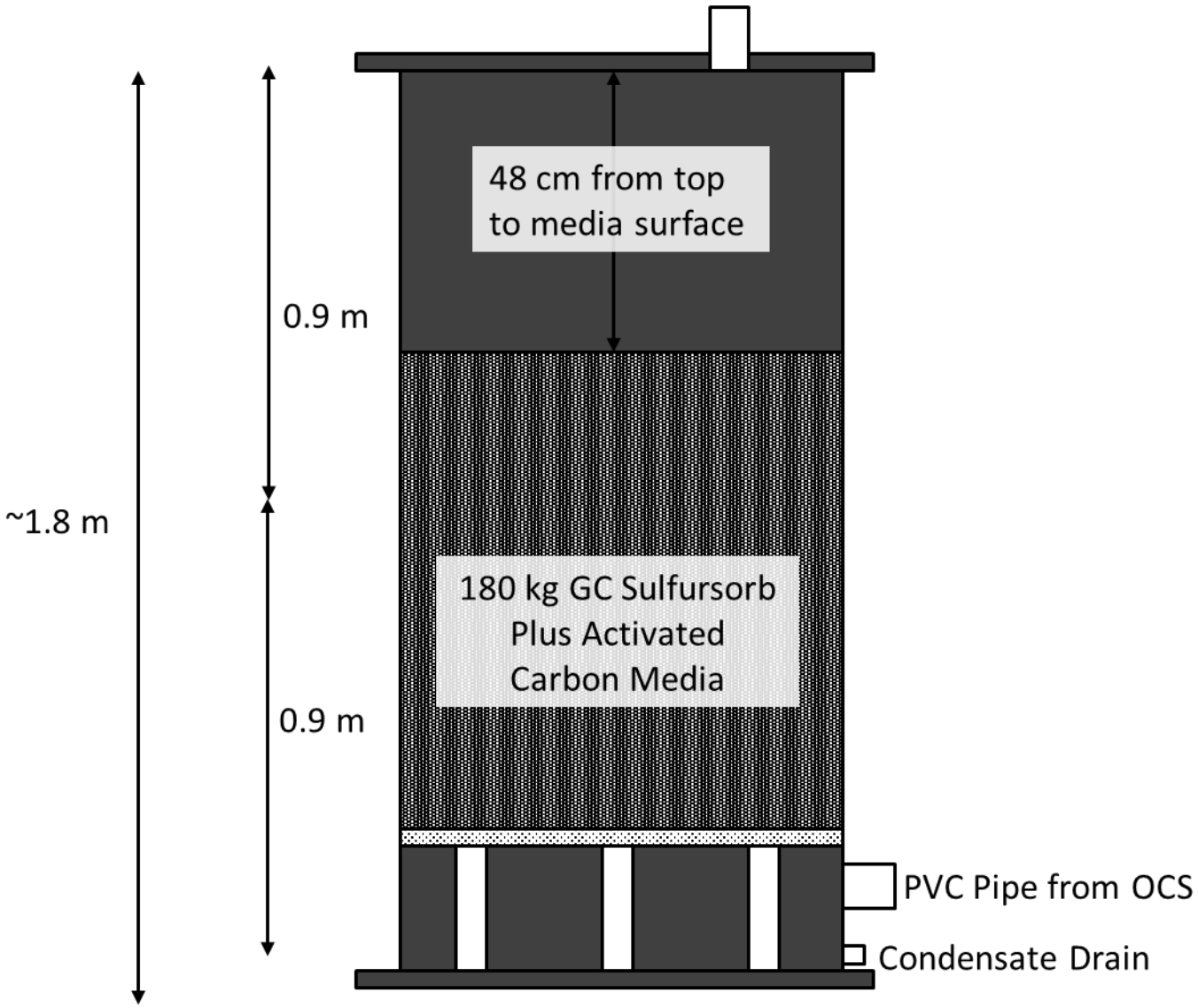
- Designed for 550 m^3/d
- Receives elevated Fe, Zn, Pb, Cd, As, SO_4
- Four total process units
- Shared water surfaces/baffles/z-piling
- Solar-powered aeration/reaeration
- Limited operation/maintenance
- Discharge meets receiving stream criteria



VFBR Substrate

- 1,000 yd^3 single-shredded wood chips
- 132 tons (~240 yd^3) spent mushroom compost
- ~3.0 ft thickness
- Underdrain 616 tons non-calcareous AASHTO #57 aggregate (~2.0 ft thickness)

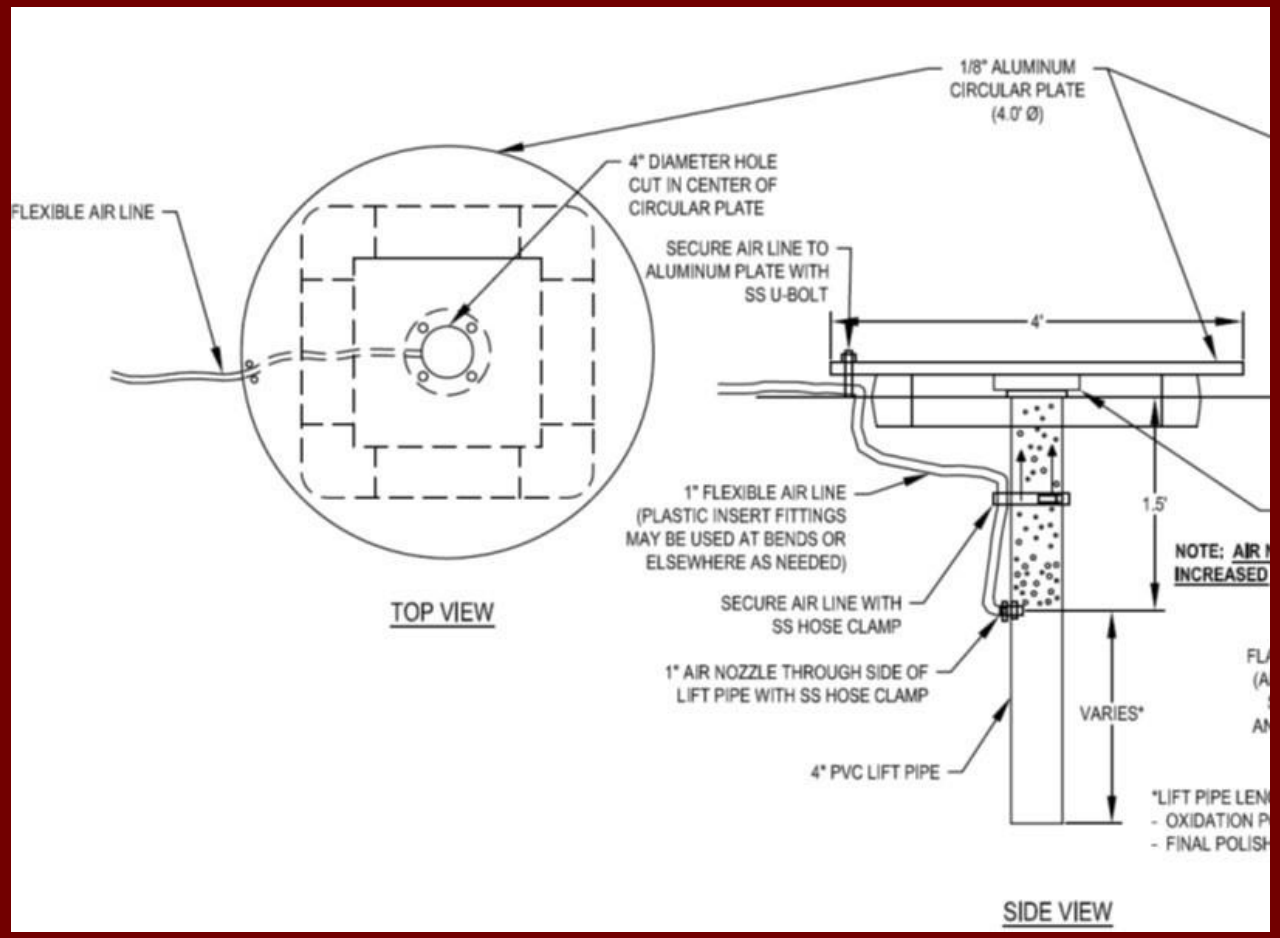

Solar Array
Solar-powered exhaust blower in shed
GACF
VFBR
Airline
Four Cell VFBR Underdrain Effluent
Odor Control System
Final Polishing Unit
Air
Water



Note: Structure inner diameter: 71.2 cm

Float-Mix Aerators

- Two each in Oxidation Pond and Final Polishing Unit

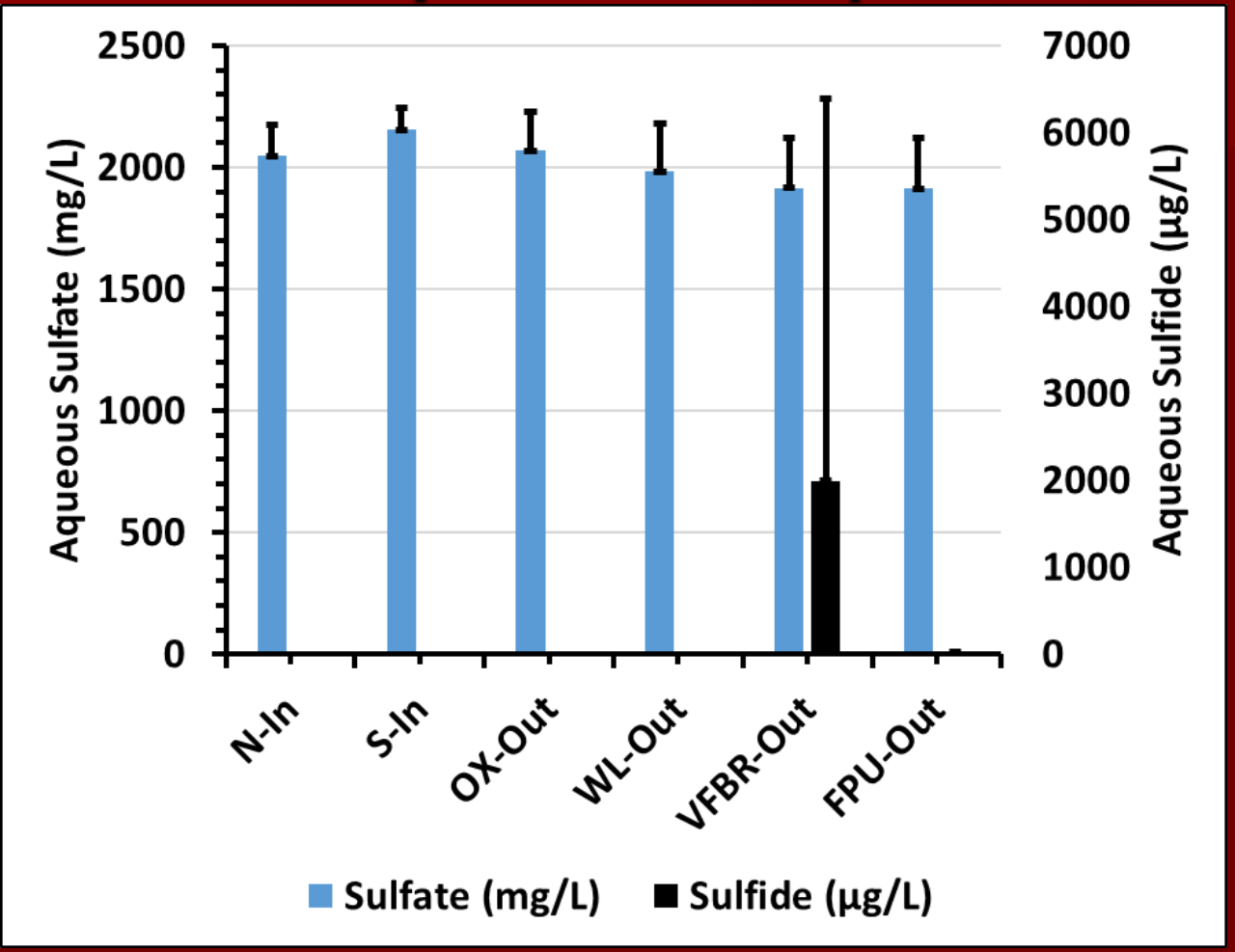


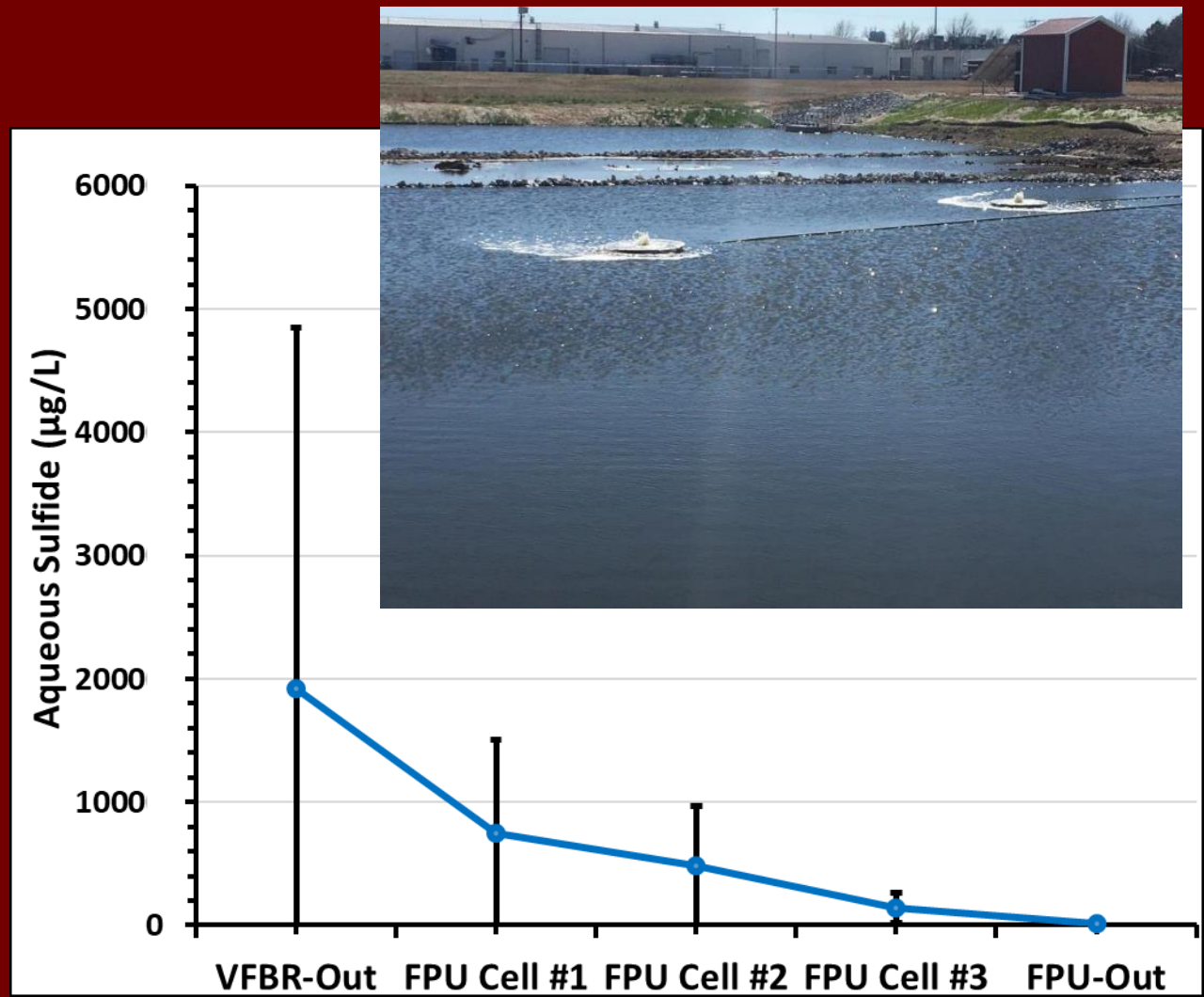
System Performance

Water Quality Changes

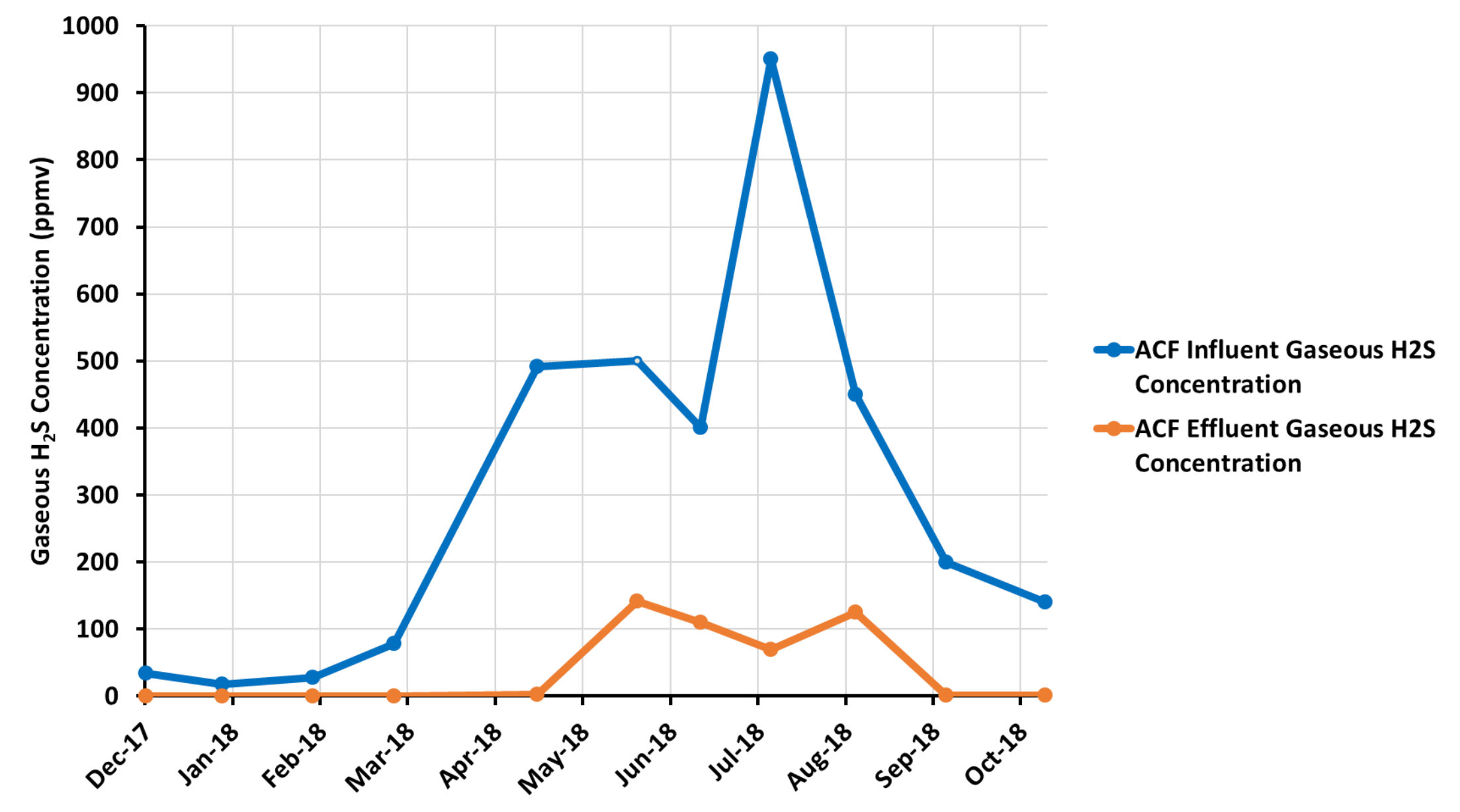
	Mayer Ranch		Southeast Commerce	
	In (n=82)	Out (n=43)	In (n=80)	Out (n=22)
pH	5.95	7.02	6.06	7.02
Alk_T (mg/L)	393	224	350	117
Fe_T (mg/L)	192	0.13	138	0.79
Zn_T (mg/L)	11	0.25	6.15	0.69
Ni_T (mg/L)	0.97	0.15	0.52	0.06
Cd_T (μg/L)	17	<PQL	20	<PQL
Pb_T (μg/L)	60	<PQL	80	26
As_T (μg/L)	64	<PQL	38	<PQL
SO_4^{-2} (mg/L)	2239	2057	2100	1956

System Aqueous Sulfate and Sulfide

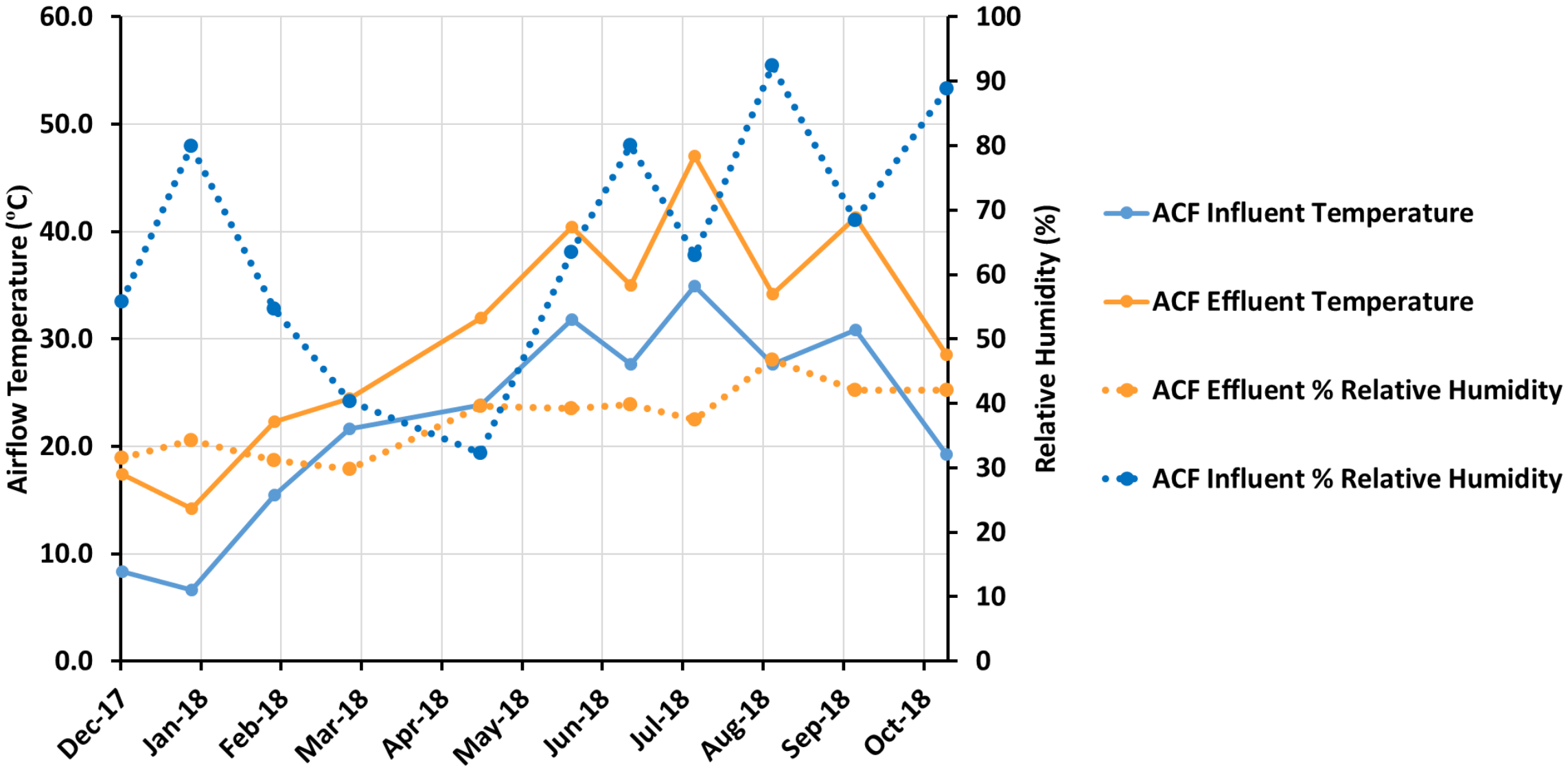




ACF Gaseous Sulfide



ACF Temperature and Relative Humidity



	Air Flow (L/sec)	Temperature (°C)	Relative Humidity (%)
ACF Influent	14±0.2	23±2.7	65±5.5
ACF Effluent	15±0.1	31±9.1	38±1.5

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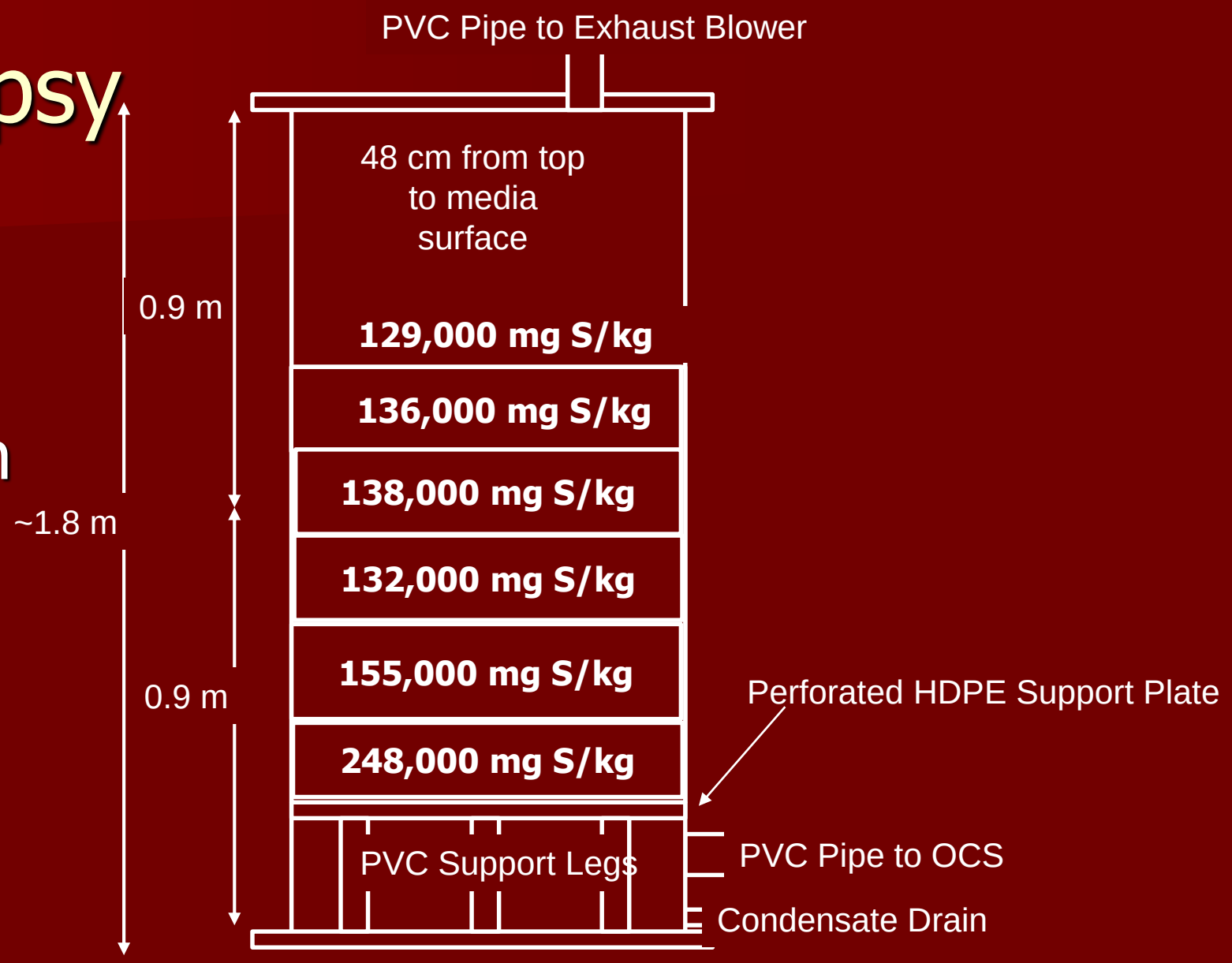
$$2H_2S + 4O_2 \rightarrow 2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4$$

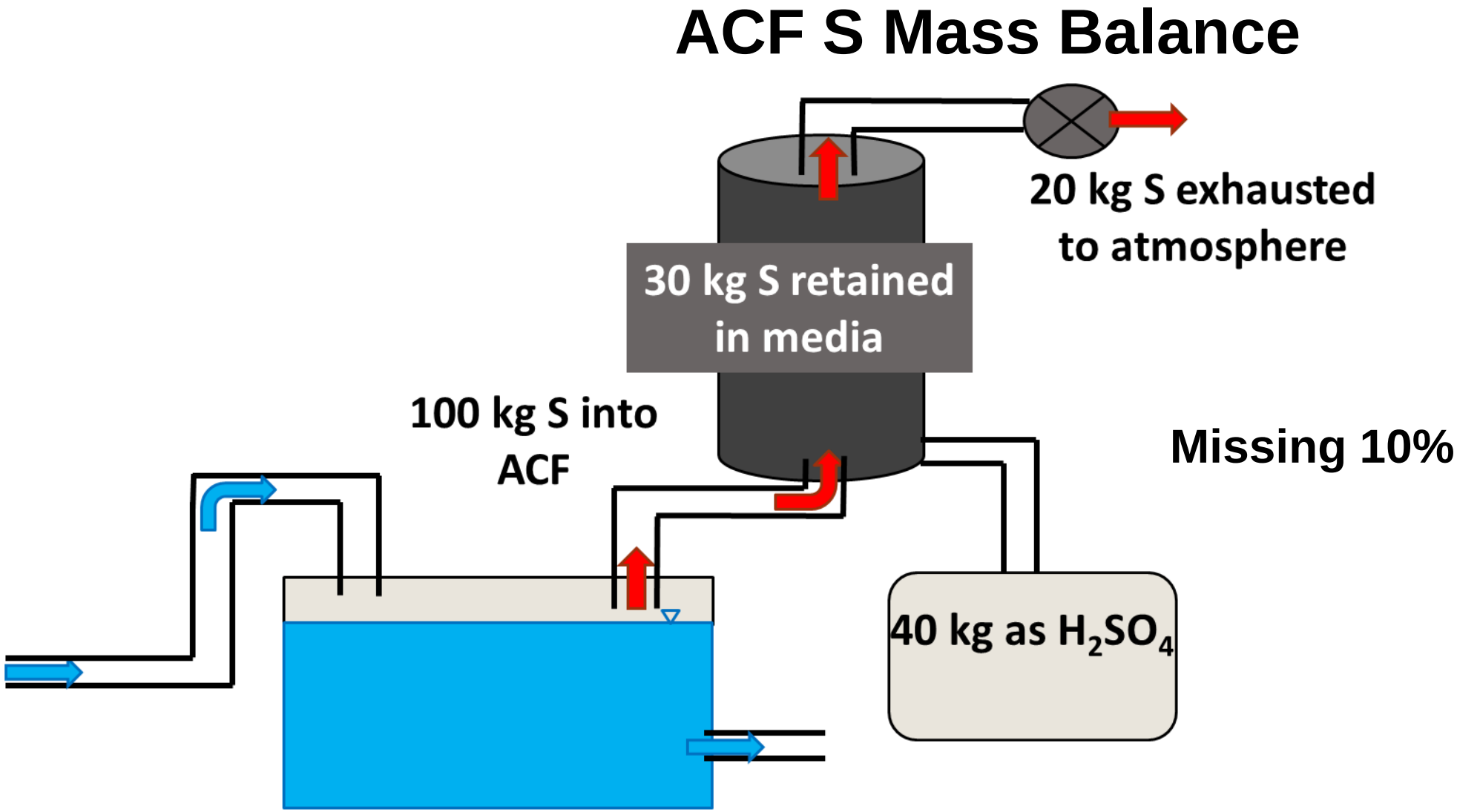
Elevated gaseous sulfide under moist aerobic conditions forms sulfuric acid

ACF media autopsy

- October 2018
- 20 months operation
- Core samples in lifts



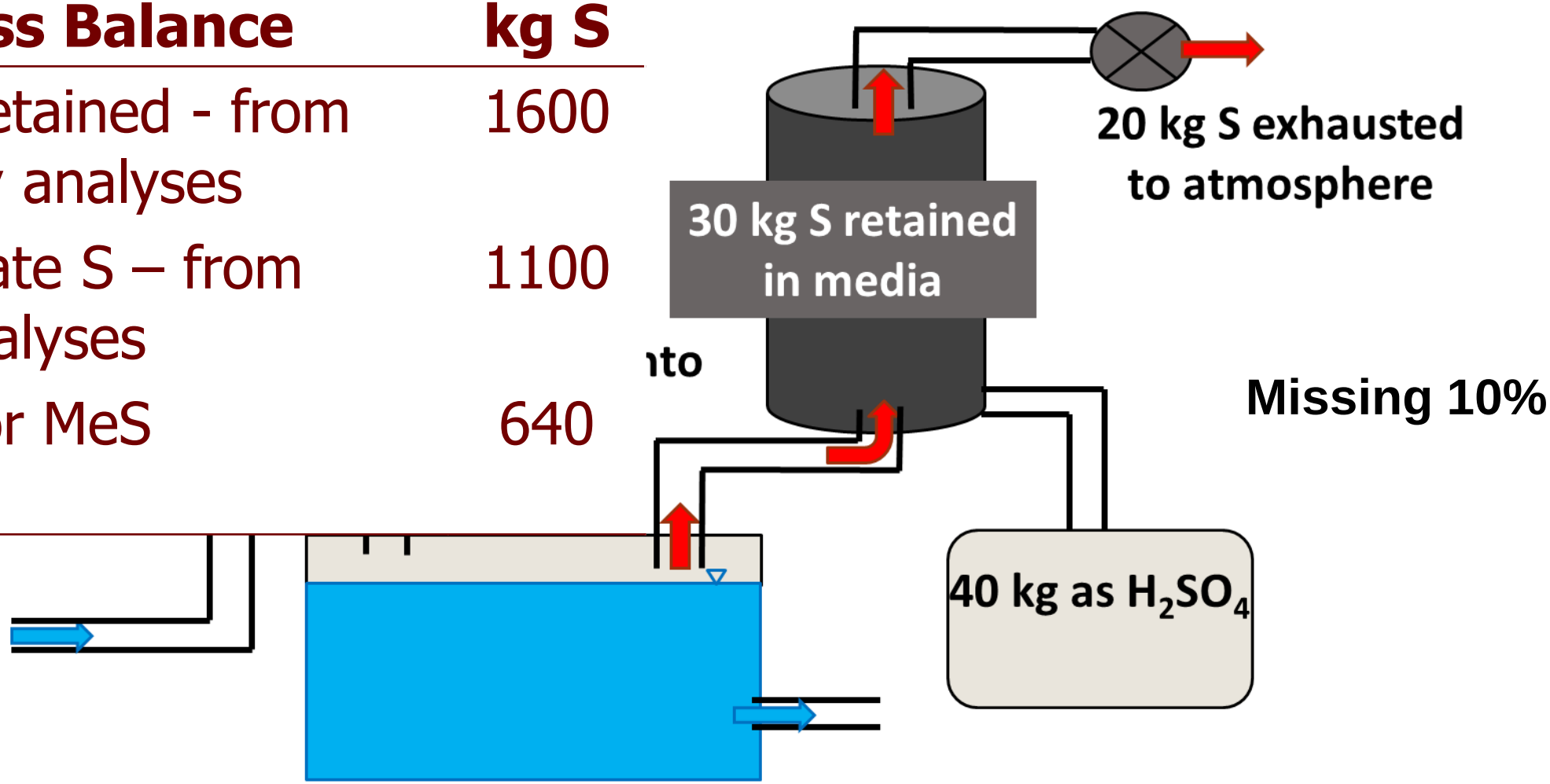
Sulfur mass balances



Sulfur mass balances

VFBR S Mass Balance	kg S
Aqueous S retained - from water quality analyses	1600
VFBR substrate S – from substrate analyses	1100
S required for MeS precipitation	640

ACF S Mass Balance

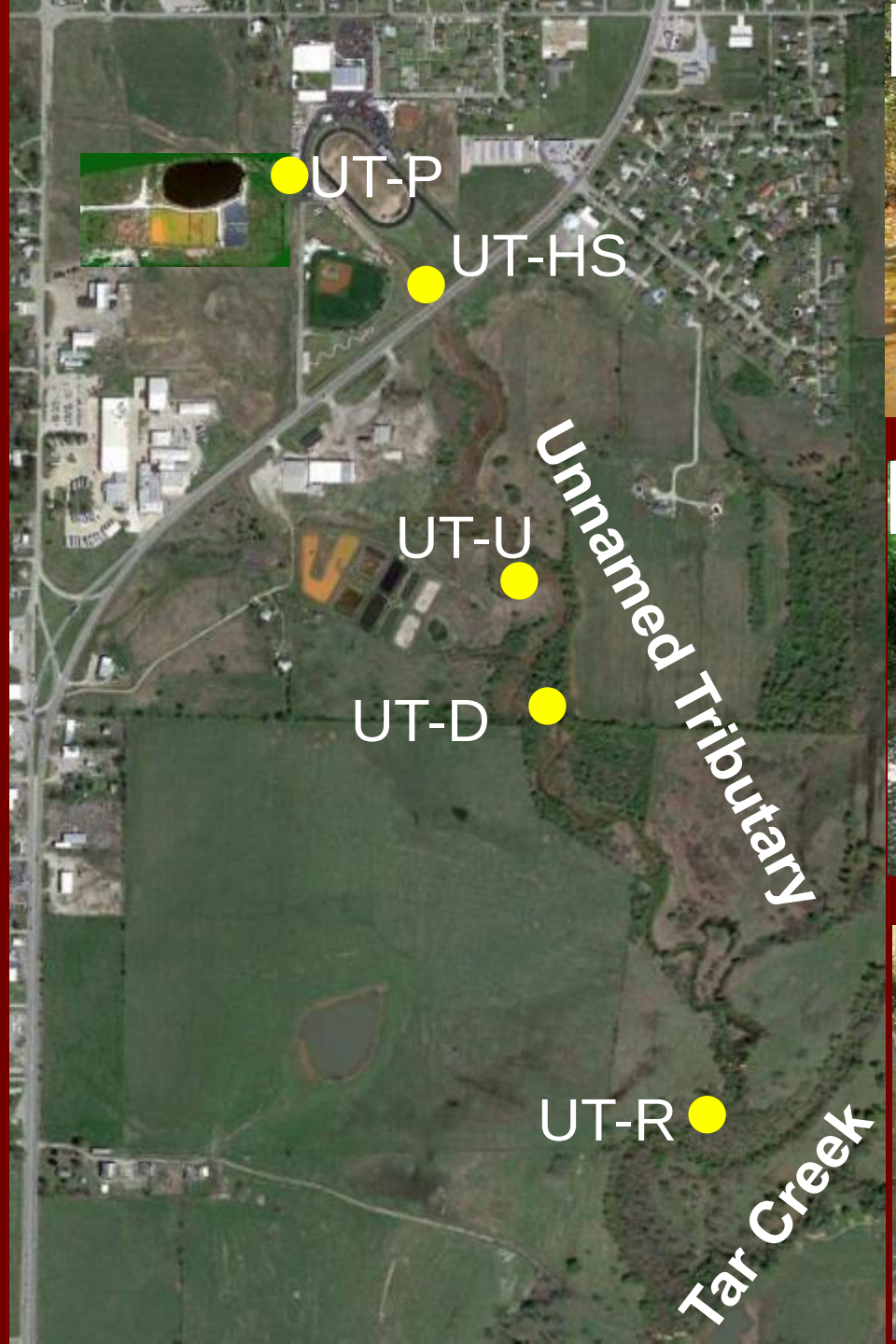


Irreversibly Damaged?

Receiving Stream Recovery

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	2009-16
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

Conclusions

Study Conclusions

1. VFBR bacterial sulfate reduction produced excess sulfide beyond that needed for trace metal precipitation
2. Capture and removal of gaseous sulfide helped to decrease aqueous sulfide concentrations
3. Solar-driven blowers and an activated carbon filter (ACF) effectively removed gaseous sulfide
4. Solar-driven float mix aerators (FMAs) effectively removed aqueous sulfide in the final polishing unit (FPU)
5. Estimates of sulfur species in aqueous, gaseous and solid phases accounted for reasonable mass balance of sulfur

Big Picture 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

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
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  - LEAD Agency
- CREW past and present

CREW

Center for Restoration of Ecosystems and Watersheds
University of Oklahoma

The CREW

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Questions?

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