Long-Term Performance of Biochemical Reactors for **Passive Treatment of Mine-Impacted Water**

Robert ("B.T.") Thomas
Jim Bays

April 23 2019

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Health and Safety Moment

Biological Hazards

Can you spot the copperhead?

Found in much of **North America**

Pit viper, typically **2 to 4 feet in length**

Hemolytic venom (destroys red corpuscles)

Bite is not usually fatal to humans, but **long and painful recovery is common**.

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Health and Safety Moment
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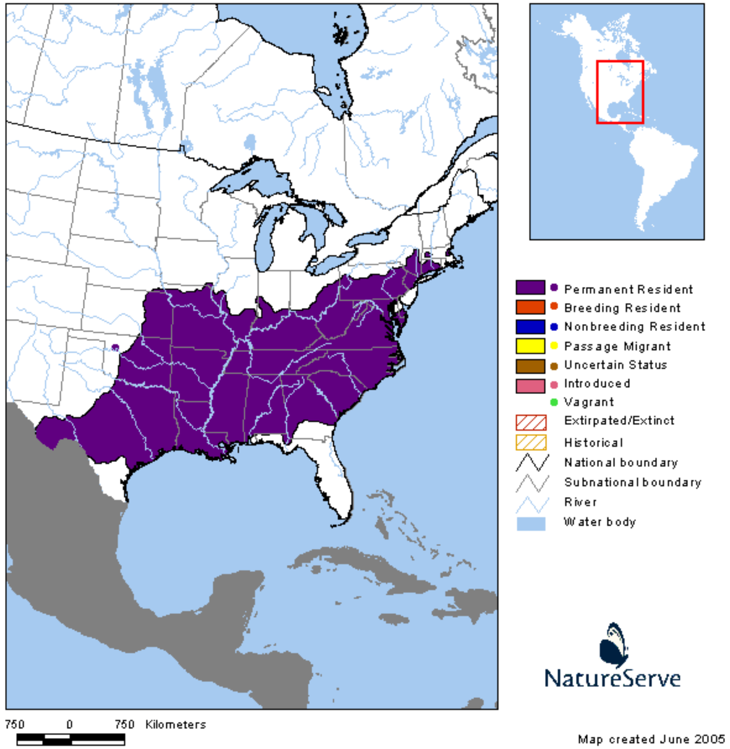

www.tnwatchablewildlife.org

Today's
Outline

What is Passive Treatment

What are Biochemical Reactors

Coal Mac System

Mayer Ranch System

Conclusion

What is
Natural Treatment

Any low maintenance mine impacted water (MIW) treatment method that does not require continual chemical addition and monitoring.

Based upon historic observations of natural polishing of mine impacted waters in natural wetlands.

Advantages

- Substantially **lower construction & operating cost**
- **Low maintenance**
- **No** or limited use of **power and chemicals**
- **Limited** health & safety **risks**
- Can be **installed in remote locations**

Natural Treatment approaches are applied at mine sites through the design and construction of engineered Passive Treatment Systems

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Sustainability in Industry

Multiple Forms and Benefits

- Triple bottom line driver
- Many forms
  - Water use reduction
  - Energy reduction
  - Carbon capture/emission reduction
  - Resource recovery
  - Residuals reduction and recycling
  - Land conservation and restoration
  - Community benefits
- Can be quantified for rating/ranking

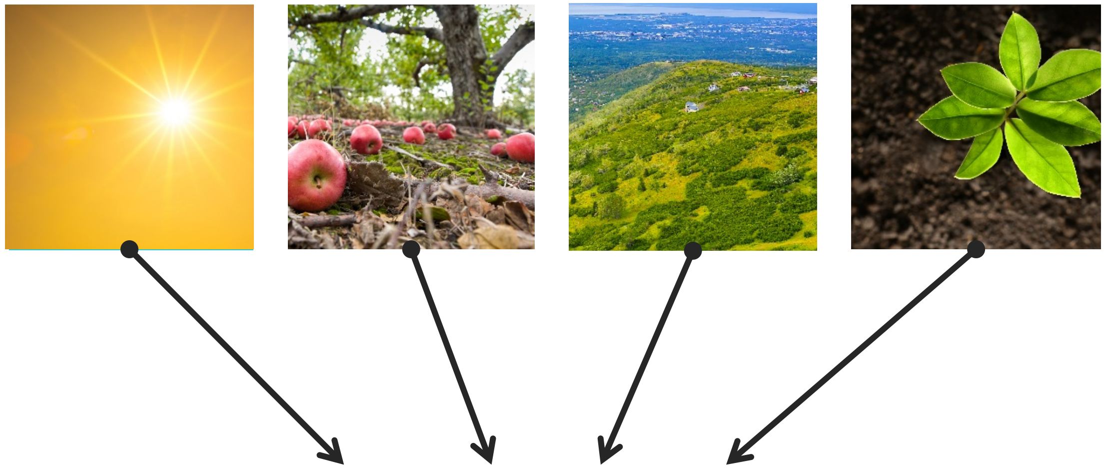
Jacobs and Envision Lead the Way in Sustainability

Envision Categories of Evaluation

Natural Treatment **Where Feasible**

Can Show Greater Sustainability Than Conventional

Natural Systems



Sun

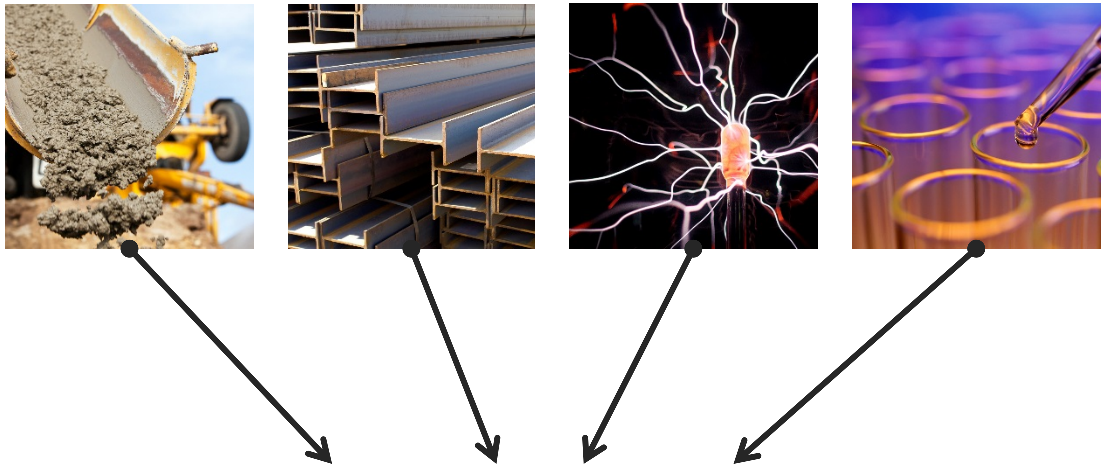
Gravity

Land

Biomass

$ Water Treatment

Conventional Systems



Concrete

Steel

Electricity

Chemicals

Water Treatment $ $ $

Passive Capital and Operations & Maintenance (O&M)
Costs Are Lower Than Active Treatment

Lower **Structural Requirements**

Lower **Power Cost**

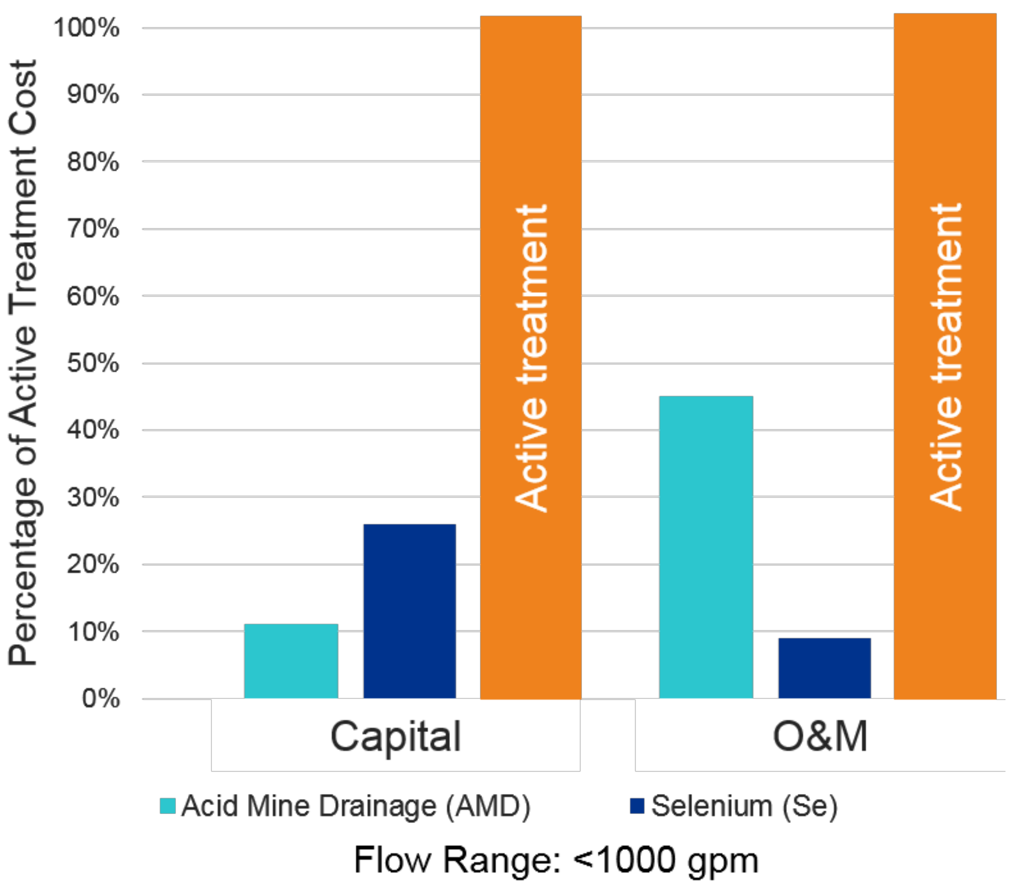
Lower **Labor**

Lower **Monitoring**

Lower **Chemical Cost**

Lower **Residuals Cost**

Locally **Available Media**



The “Natural Treatment Toolbox” Spans the Spectrum of Upland to Wetland Ecosystems

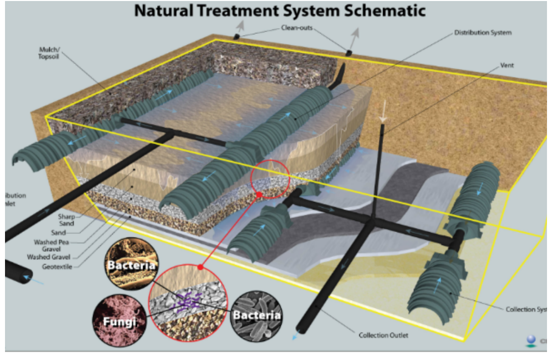
Upland Systems

Land Application

Engineered Plant Systems
(Phytoremediation)

Wetland Systems

Surface Flow



Subsurface Flow

Passive Media Beds

Biochemical Reactors

Limestone Beds

Ponds & Aquatics

Ponds & Floating Wetland Islands

Aeration

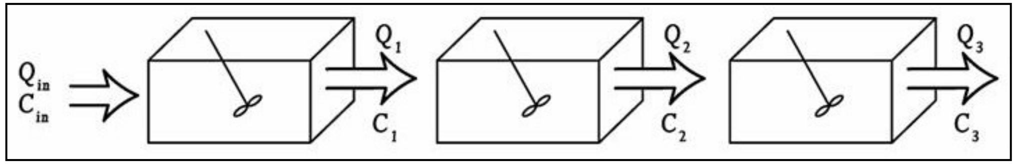
Integrating Passive Treatment Systems

The Rationale and Benefits of a “Treatment Train”

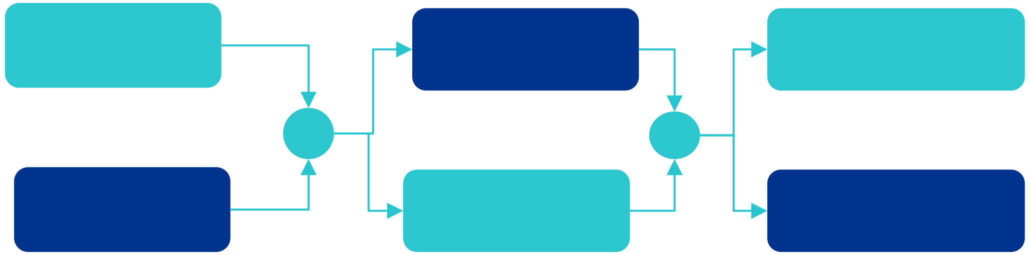
- Unit Process Approach

Sedimentation → **Bio transformation** → **Conditioning**

- Compartmentalization

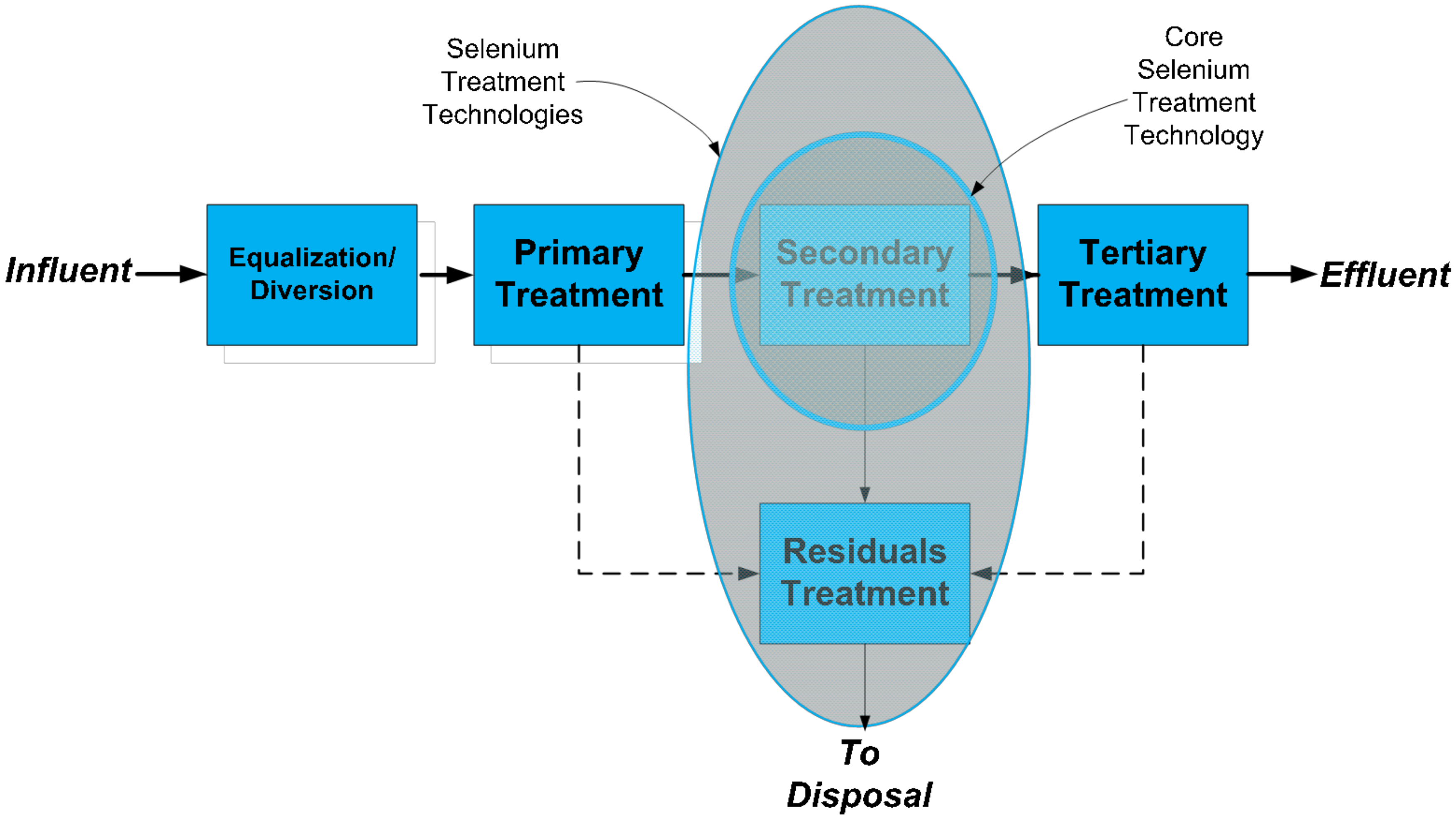


- Manageability



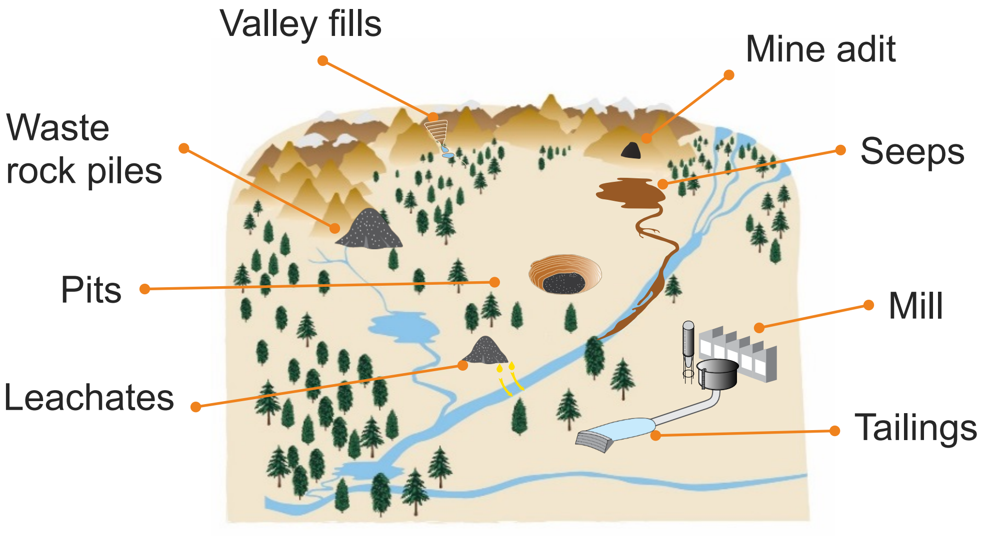
Biochemical Reactor Plans

Require Systems Approach



Mine Impacted Waters

Range Widely in Source and Composition



Mining

- Surface water: oxidized metals, solids (suspended and dissolved)
- Groundwater: leachate (reduced metals (Fe, Mn), hydrocarbons, nutrients

Manufacturing

- Process WW: nutrients, metals, organics, inorganic
- Concentrate: inorganic ions, metals
- Stormwater: solids, metals, nutrients, organics

Power

- FGD: metals (Se, Hg), salts, inorganics (S, Ca), hydrocarbons
- Concentrate: inorganics, metals
- Stormwater: solids, metals
- Cooling water: temperature, algal solids, antiscalants

Two Main Water Chemistry Types with Respect to BCR Design

Oxyhydroxide-bearing Water

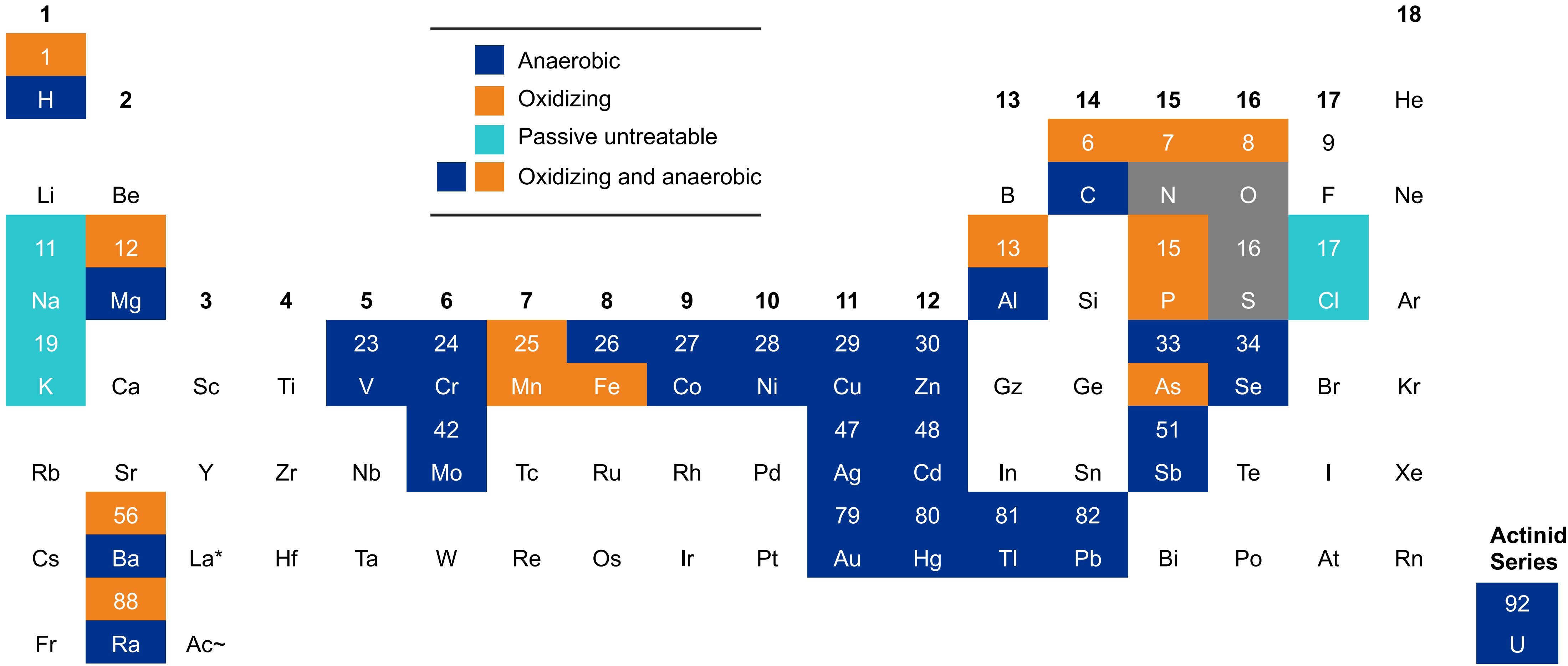
- Water with iron (Fe^{2+} or Fe^{3+}) and/or aluminum.
- Fe/Al-oxyhydroxide precipitates can clog porosity and greatly reduce longevity
- Requires (mainly abiotic) pretreatment units to remove before BCR
- Mn-bearing water passes through BCR units and is typically treated in post-treatment units

Non-oxyhydroxide bearing water

- Water that does not require chemical pretreatment prior to BCR (no oxyhydroxide-bearing metals)
- May require sedimentation unit to remove TSS (i.e., wetland or settling basin)

Periodic Table of

Passive Treatment



Anaerobic

Oxidizing

Passive untreatable

Oxidizing and anaerobic

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	He
Li	Be											B	6 C	7 N	8 O	9 F	Ne
11 Na	12 Mg											13 Al	Si	15 P	16 S	17 Cl	Ar
19 K	Ca	Sc	Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	Gz	Ge	33 As	34 Se	Br	Kr
Rb	Sr	Y	Zr	Nb	42 Mo	Tc	Ru	Rh	Pd	47 Ag	48 Cd	In	Sn	51 Sb	Te	I	Xe
Cs	56 Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	79 Au	80 Hg	81 Tl	82 Pb	Bi	Po	At	Rn
Fr	88 Ra	Ac~															

Actinide Series

92 U

Gusek, 2009

Types of

Passive Treatment Operational Units

Abiotic/geochemical-based units

- Commonly limestone-based
- Based on abiotic design parameters
- Raise pH, add alkalinity, and/or neutralize/reduce mineral acidity
- Precipitation/removal of iron and aluminum
- Often used as pretreatment units to biological-based units

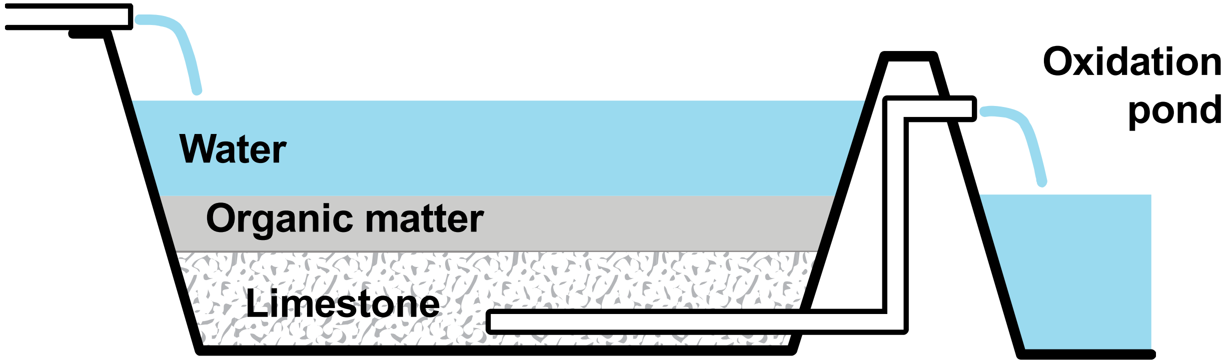
Biological-based units

- Engineered to promote biological activity
- Anaerobic units for trace metal removal (BCRs)
- Aerobic units for polishing 2nd parameters
- Cold climate operation
- Largest unit(s) in a passive treatment design

What is

Biochemical Reactor

- Biochemical reactor (BCR) units are common in PTS design, especially where sulfate reduction is desired as the removal mechanism for trace metals
- The BCR media is designed to support high levels of anaerobic microbial activity over an extended timeframe (>10 years)
- Metal removal is through both biological and abiotic removal mechanisms (mainly sulfide precipitation)
- Downstream APC units are typically installed to re-oxidize the BCR effluent and remove any excess sulfide before discharge to the environment



Biochemical Reactors are

Constructed Anaerobic Substrates

- Wood
  - Chips, sawdust
- Grass
  - Hay
- Peat
- Limestone Sand
- Manure and Soil
- Natural Power
  - Gravity
  - Solar

ITRC 2013

How do

Biochemical Reactors (BCR) Work?

- Anaerobic trace metal removal units
- Designed to promote “elemental reducing” microorganisms (Fe, Se, SO4)
- Removal of trace metals as either sulfide or elemental precipitates
- Designed using empirically-based loading models
- Typically 1 – 4 day hydraulic residence time (load based)
- Removal of hydrolysable metals (Fe, Al) in pretreatment units

$$H^+ + HS^- \rightarrow H_2S$$

$$H_2S + M^{2+} \rightarrow MS_{(s)} + 2H^+$$

e.g. $H_2S + Pb^{2+} \rightarrow PbS + 2H^+$

Competitive Exclusion:

Electron Tower Theory

Aerobic respiration	$\frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O$
Denitrification	$2NO_3^- + 12 H^+ + 10e^- \rightarrow N_2 + 6H_2O$
Manganese reduction	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$
Iron reduction	$Fe(OH)_3 + 3 H^+ + 2e^- \rightarrow Fe^{2+} + 2H_2O$
Sulfate reduction	$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$
Methane production	$CO_2 + 8 H^+ + 8e^- \rightarrow CH_4 + 2 H_2O$

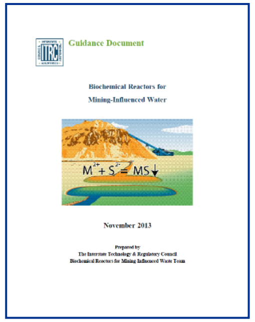
Process	Eh (mV)
Aerobic respiration	+330
Denitrification	+220
Manganese reduction	+200
Ferric to ferrous reduction	+120
Sulfate reduction	-150
Methanogenesis	-250

Organic carbon substrate provides electrons via microbial process

History of

Bioreactors

- Tuttle et al., 1969, “Microbial Sulfate Reduction and Its Potential Utility as an Acid Mine Water Pollution Abatement Procedure”. Applied Microbiology; 17(2): 297–302
  - “A mixed culture of microorganisms degraded wood dust cellulose, and the degradation products served as carbon and energy sources for sulfate-reducing bacteria.”
- Agricultural denitrifcation bioreactors
- Wildeman et al, 1993, Wetlands Design for Mining Operations – example from Big Five
- ITRC (Interstate Technology & Regulatory Council). 2012. Biochemical Reactors for Mining Influenced Waste. BCR-1. Washington, D.C.: Interstate Technology & Regulatory Council, Biochemical Reactors for Mining-Influenced Waste Team



Guidance Document

Biochemical Reactors for
Mining-Influenced Water

November 2013

Prepared by
The Interstate Technology & Regulatory Council
Biochemical Reactors for Mining Influenced Waste Team

BCRs Commonly Used for
Nitrate Reduction

- Applied throughout Midwest
- Long track-record
- Wood chips
- Removal Range: 2-18 g NO3-N/m3 media per day
- HRT~<<1 day

www.sdcornblog.com

Warnecke et al 2011
Schipper 2012

BCR Longevity

Factors Affecting Lifespan

Carbon Depletion

- Possible cause:
  - Sizing – too small?
  - Carbon source
- Has it happened?
  - No record for denitrifying BCRs
  - Pilot projects exhausted C source
- Low potential based on half-life
  - Anaerobic media 36.6 yrs
  - Aerobic media 4.5 yrs
    - Moorman et al 2008
- Ultimately depends on contaminant load

Hydraulic Conductivity Decline

- Excess inorganic solids
  - Pre-treatment for solids reduction
- Media consolidation
  - Include heterogeneous mix of media. Some use gravel
  - Consider maintenance “fluffing”
- Precipitation of metals
  - Create intermediate process units for settling

BCR Longevity

Two Case Studies

- Case Study 1: Coal Mac Se Treatment System
  - ~8 years of continuous, compliant operation
  - ~$5K in annual Operation and Maintenance
- Case Study 2: Mayer Ranch PTS
  - ~10.5 years of continuous, effective operation
  - ~$10K in annual Operation and Maintenance
  - One maintenance “event” after 8 years to rejuvenate BCR substrate hydraulics ($4K)

Case Histories

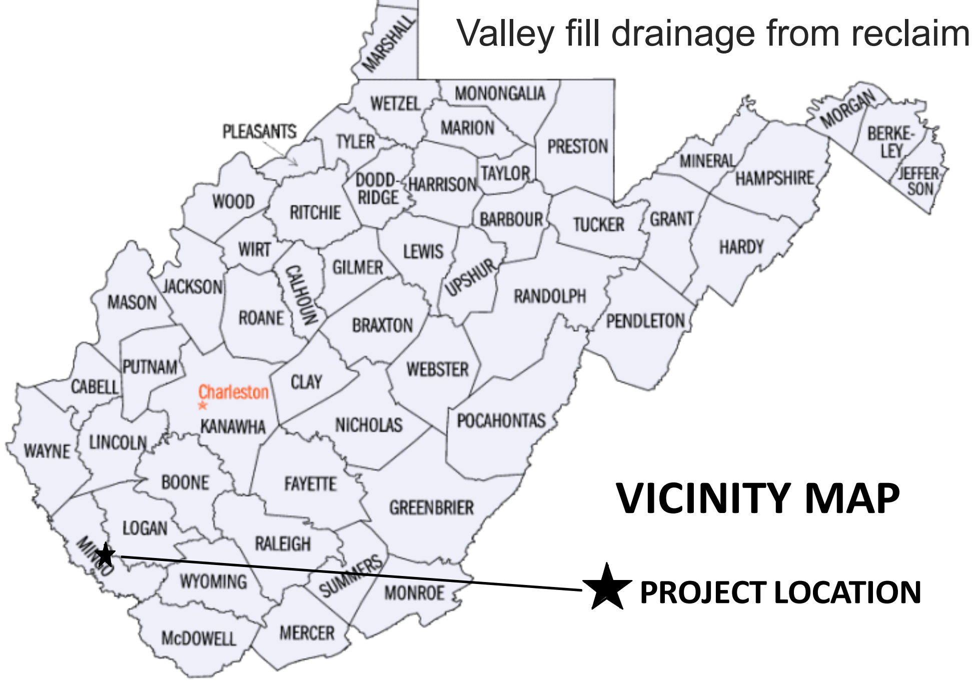
Pilot and Full-Scale Passive Treatment in WV

Overview

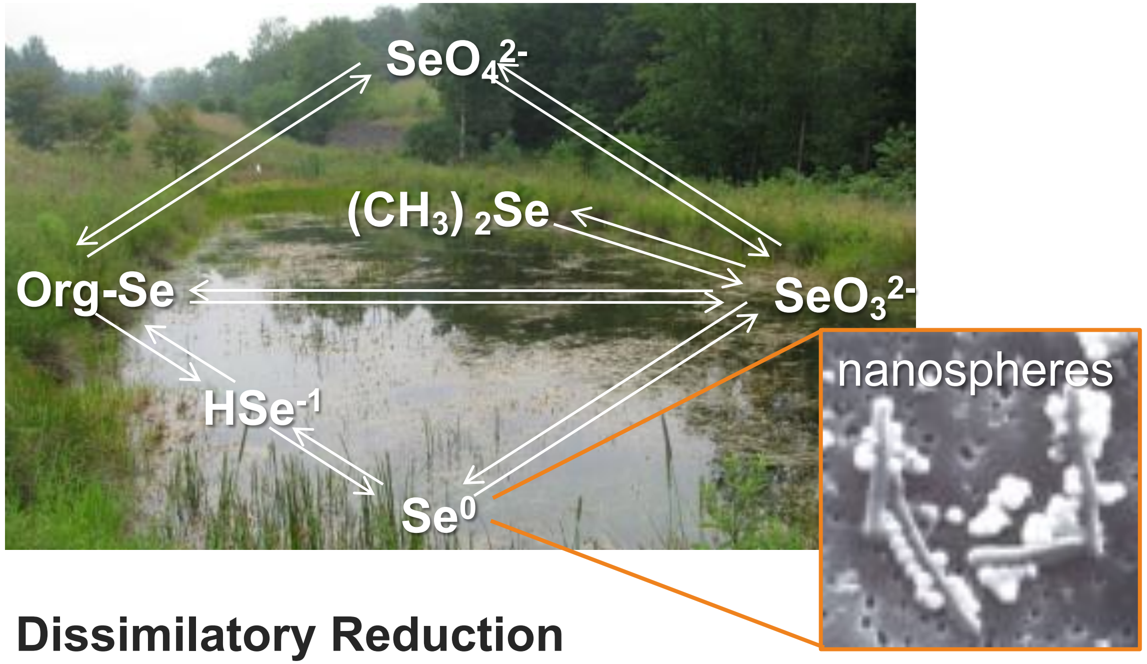
- Two outlets assigned stringent selenium discharge standard:
  - 4.7 ug/L monthly mean
  - 8.2 ug/L daily max
- Conducted barrel studies to formulate substrate, calibrate model
- Designed two distinct systems based on landscape, space, treatment
- First system July 2011
- Second system November 2011

Location

Valley fill drainage from reclaimed mines



Wetland Processing and Storage of Selenium



Dissimilatory Reduction

$SeO_4^{2-} \rightarrow SeO_3^{2-} \rightarrow Se^0 \rightarrow Se^{2-}$

- Anaerobic process (Eh -200 mV, DO<2)
- Distribution in wetland sediments:
  - 0:13:41:46
- Wetlands: 90% reduction 10 - 16 days
- Bioreactors: 90% reduction <1 - 2 days

Volatilization

- Organic + $SeO_3^{2-} \rightarrow (CH_3)_2Se$
- Volatilized from plant tissues
- 5-30% cumulative loss from sediments and plants

Sorption

- Selenite sorbs to sediments and soil constituents: Fe-, Mn- or Al-oxyhydroxides and organic matter

Plant Uptake

- Rapid uptake
- Tissue concentrations increase but not detrimental
- No long term storage in plants; Se transferred to sediments

BCR Pilot Testing in Barrels

Established Substrate Preference and Performance (2010)

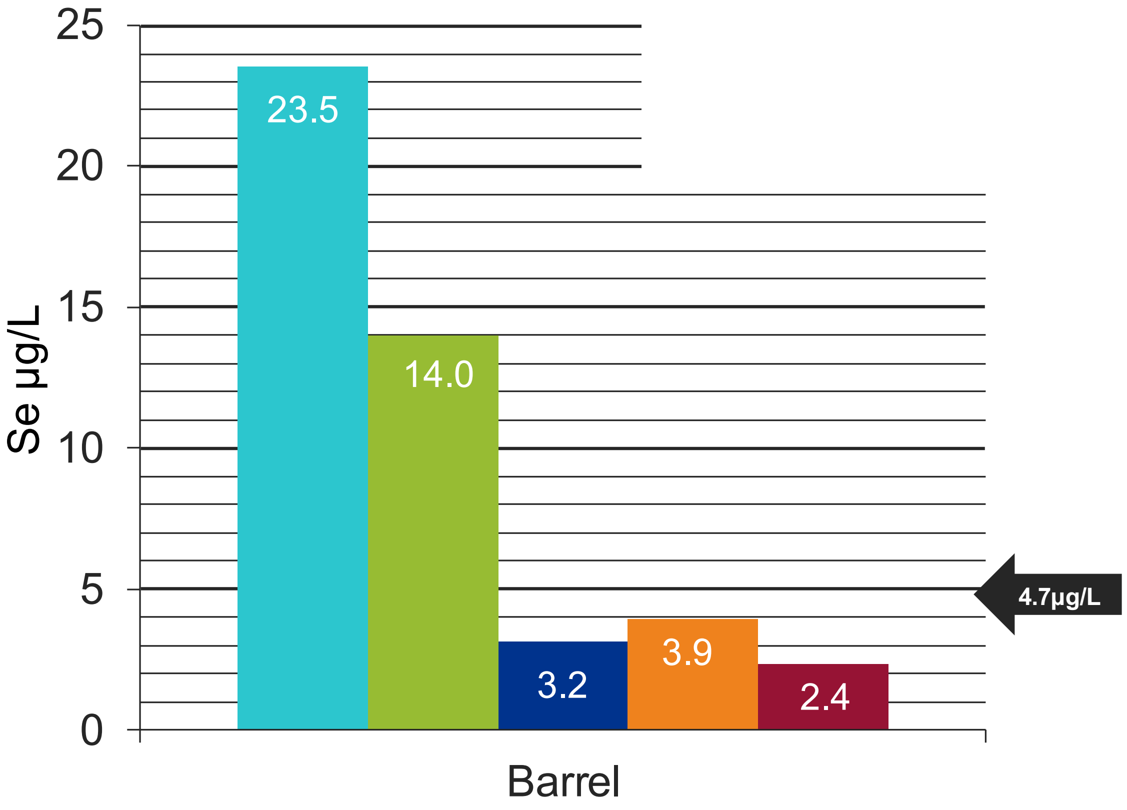
Pilot System (Jun-Sep 2010)

Four Upflow Media Bioreactors (200 L)

Material	**Pilot Barrel** **A**	**B**	**C**	**D**
Woodchips	--	20%	16%	20%
Sawdust	--	20%	47%	30%
Hay	--	15%	16%	20%
Organic Peat	--	20%	--	--
Sphagnum Moss	100%	20%	--	--
Composted Manure	--	--	15%	23%
Limestone Chips	--	5%	6%	7%
Total (by volume)	100%	100%	100%	100%

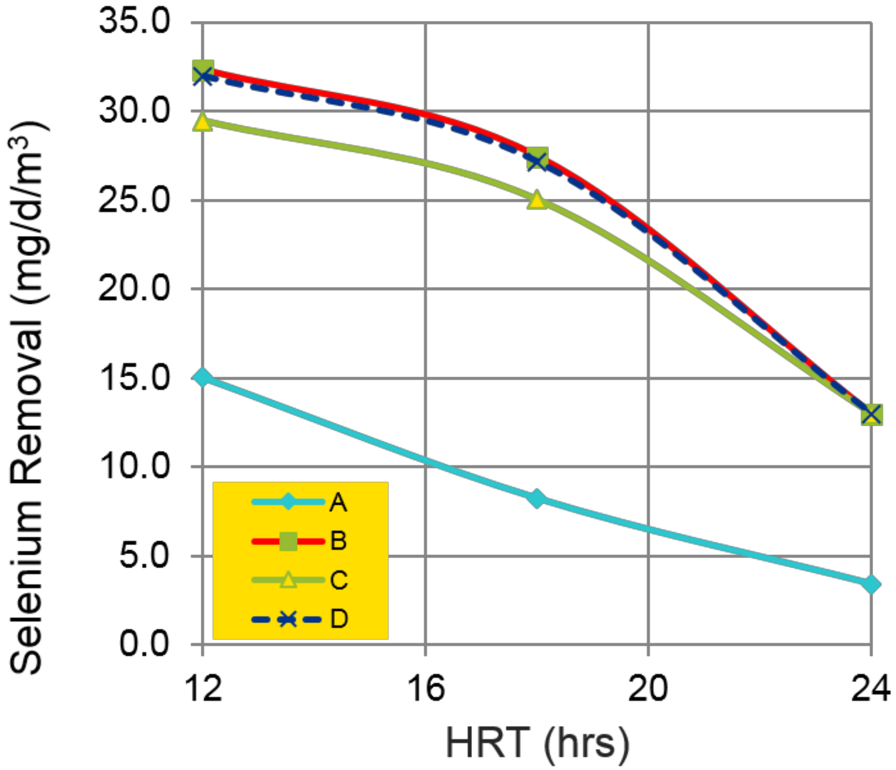
Four Organic Media (OM) Substrates

Average Total Se by Barrel

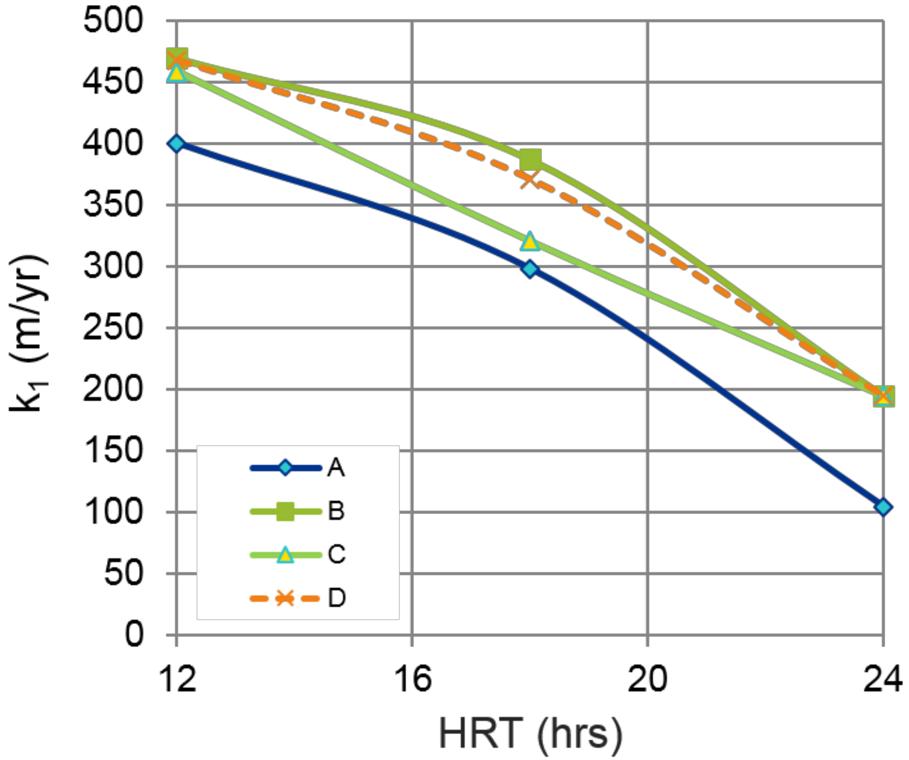


Pilot Established Removal Rates for Target Hydraulic Residence Times

Zero-order volumetric

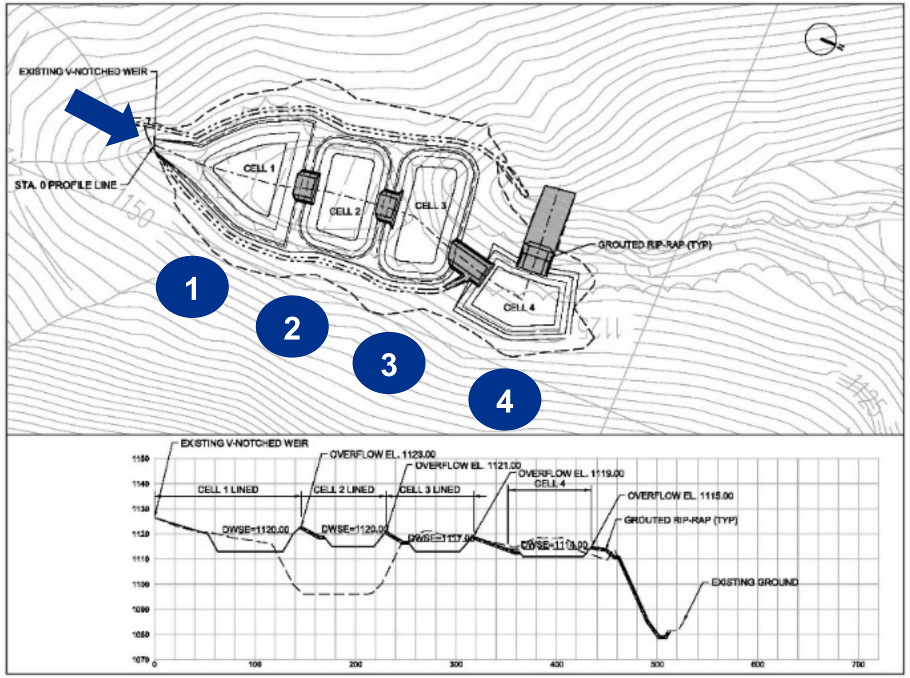


First-order area-based



Case History (2011-present)

Full-Scale BCR System for Coal Mine Drainage Se Treatment

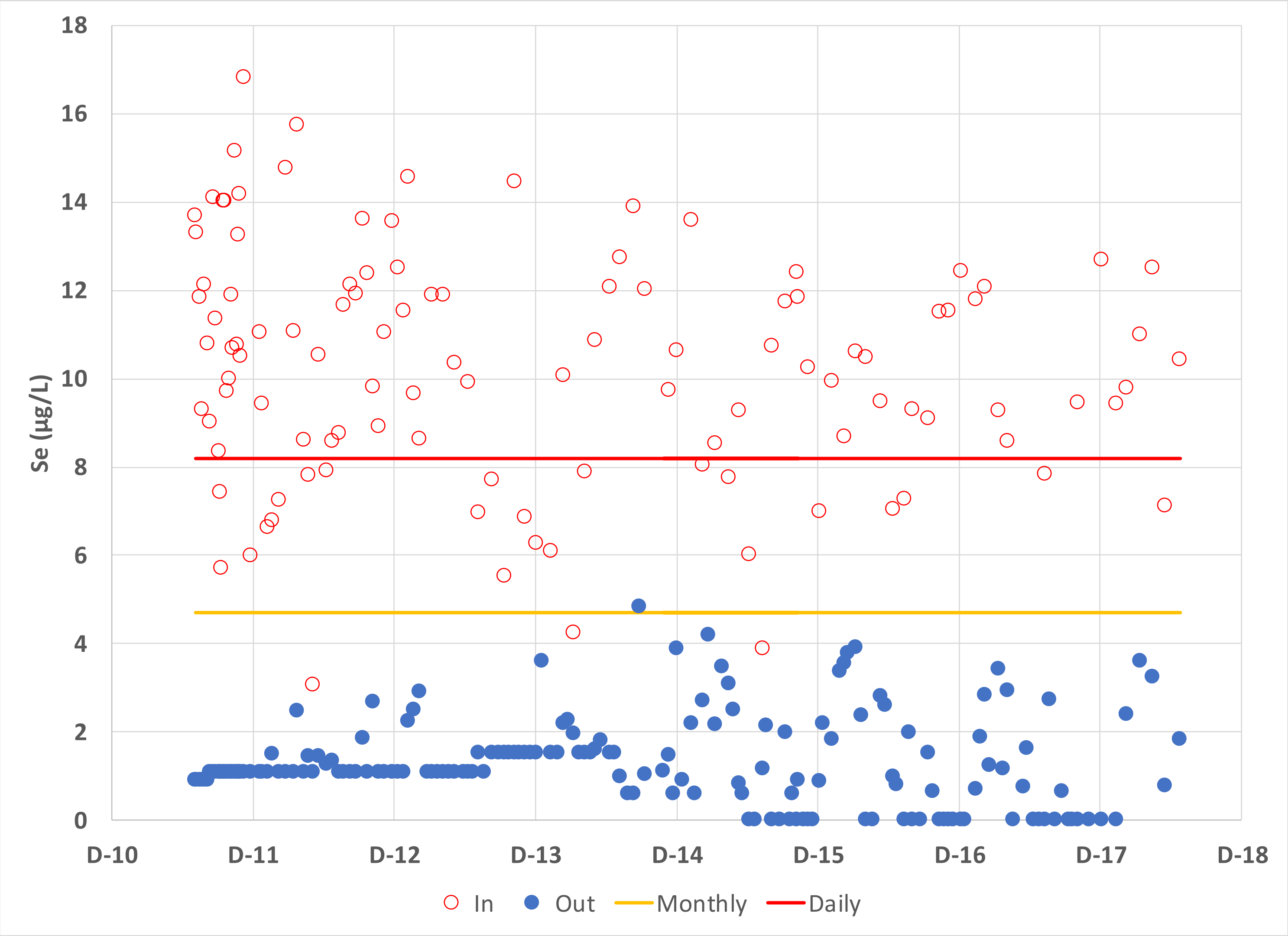


Source: CH2MHILL (2012)

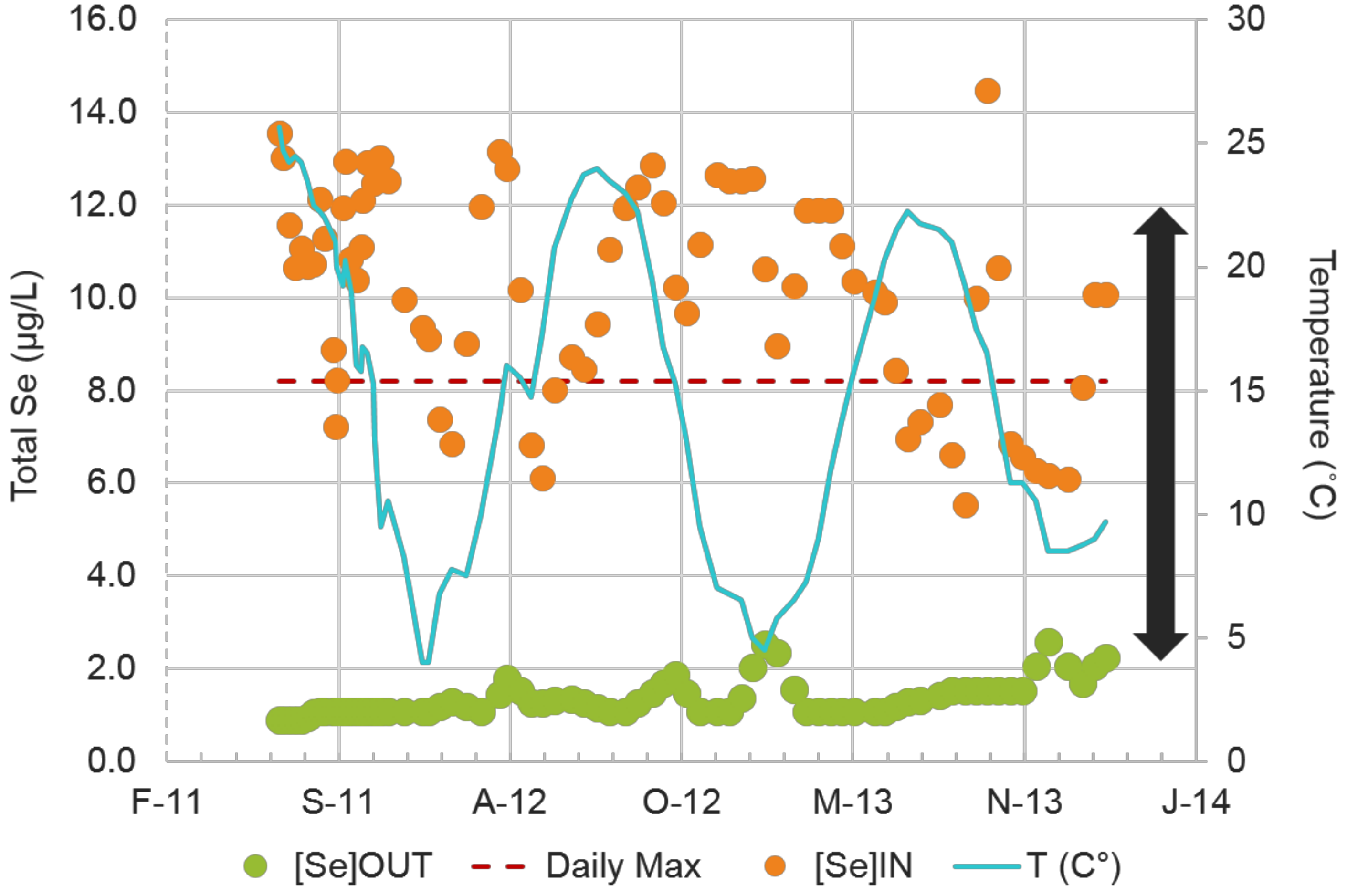
- 60 gpm base flow
- 100 gpm max
- 12 µg/L mean Se to <4.7

- Replace existing sed pond
- Four cells-in-series:
  1. 0.13 ac Downflow BCR
     Barrel “B” mix
  2. 0.14 ac Anaerobic upflow bed
     Barrel “A” peat
  3. 0.16 ac Fill-and-drain wetland
     Gravel; siphon level control
  4. 0.11 ac Surface flow marsh

System Consistently Meets Discharge Criteria



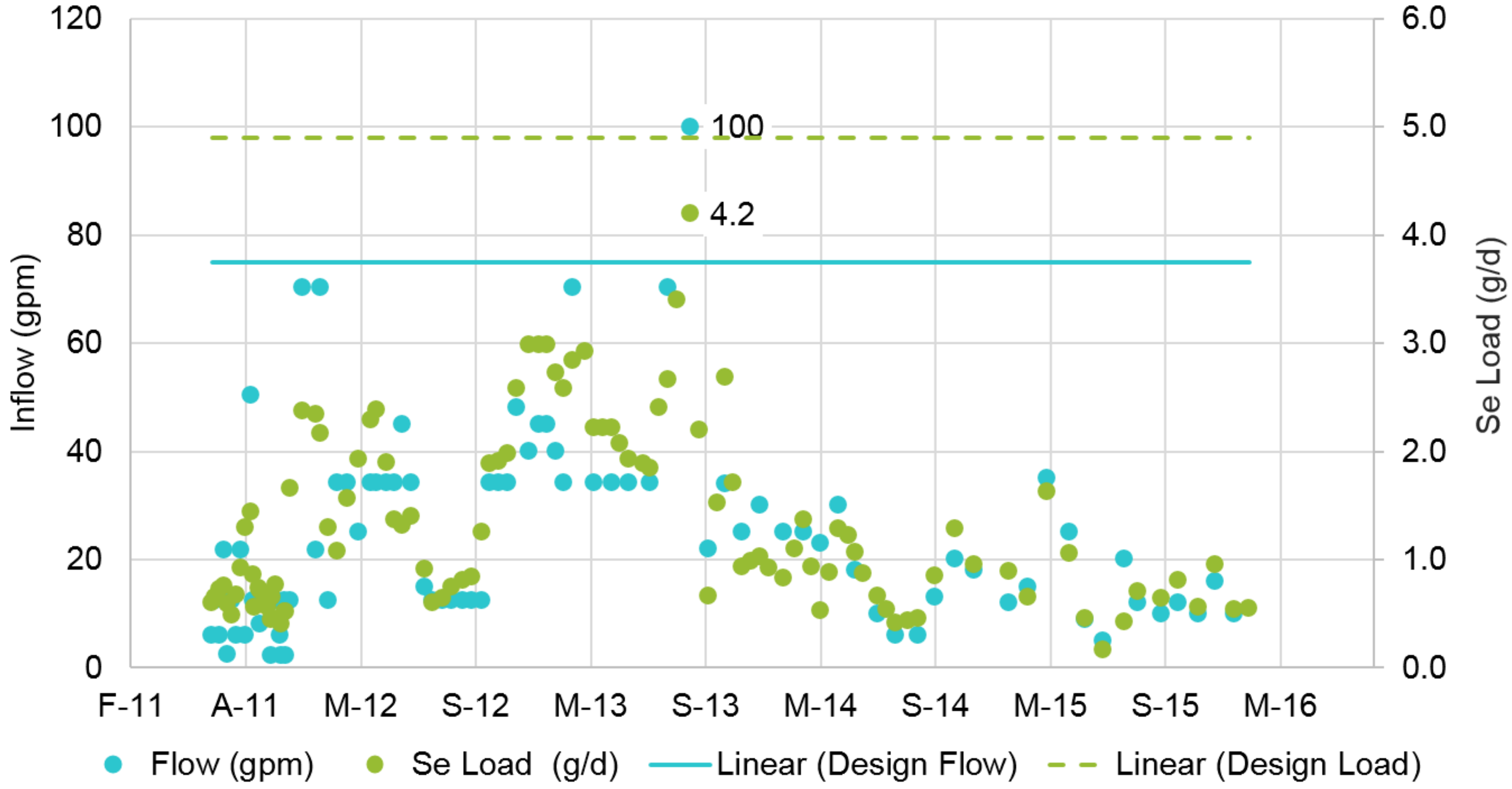
Selenium Meeting Daily Criterion Year-Round



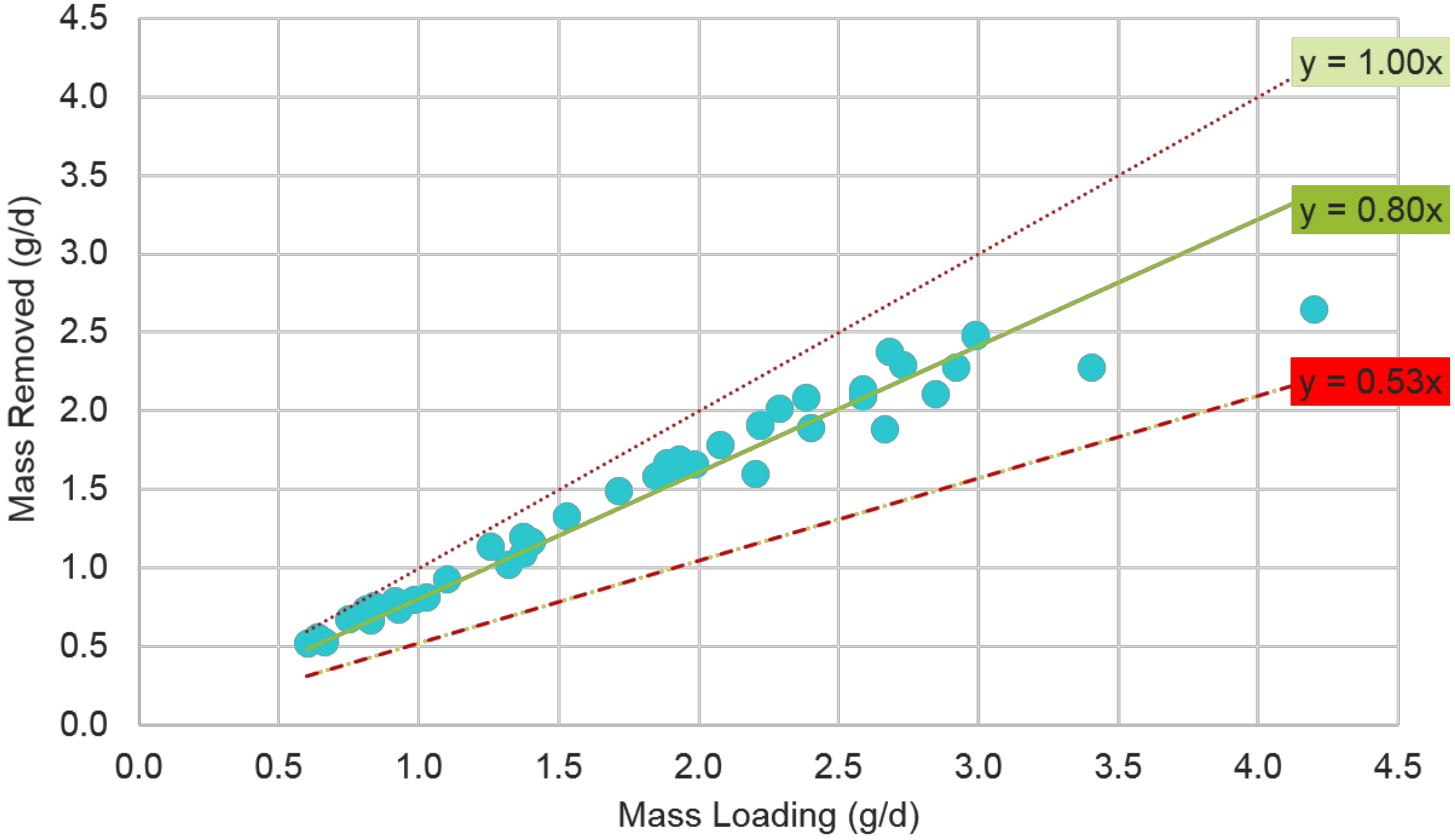
µg/L	In	Out
Average	10.24	1.32
Max	14.47	2.57
Min	5.53	0.90
Range	8.9	1.7

First Five Years

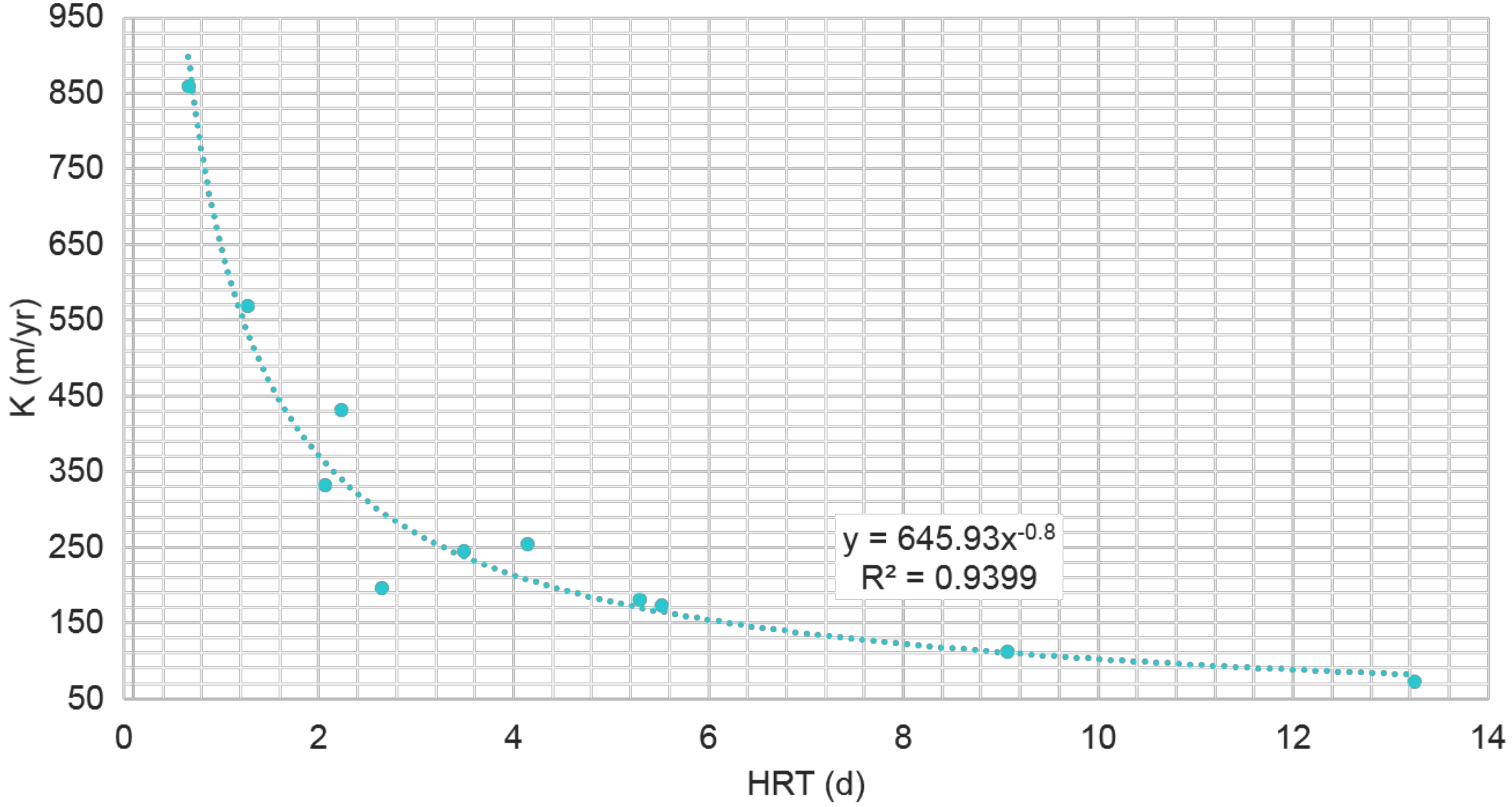
Five-fold Variation in Flow and Load



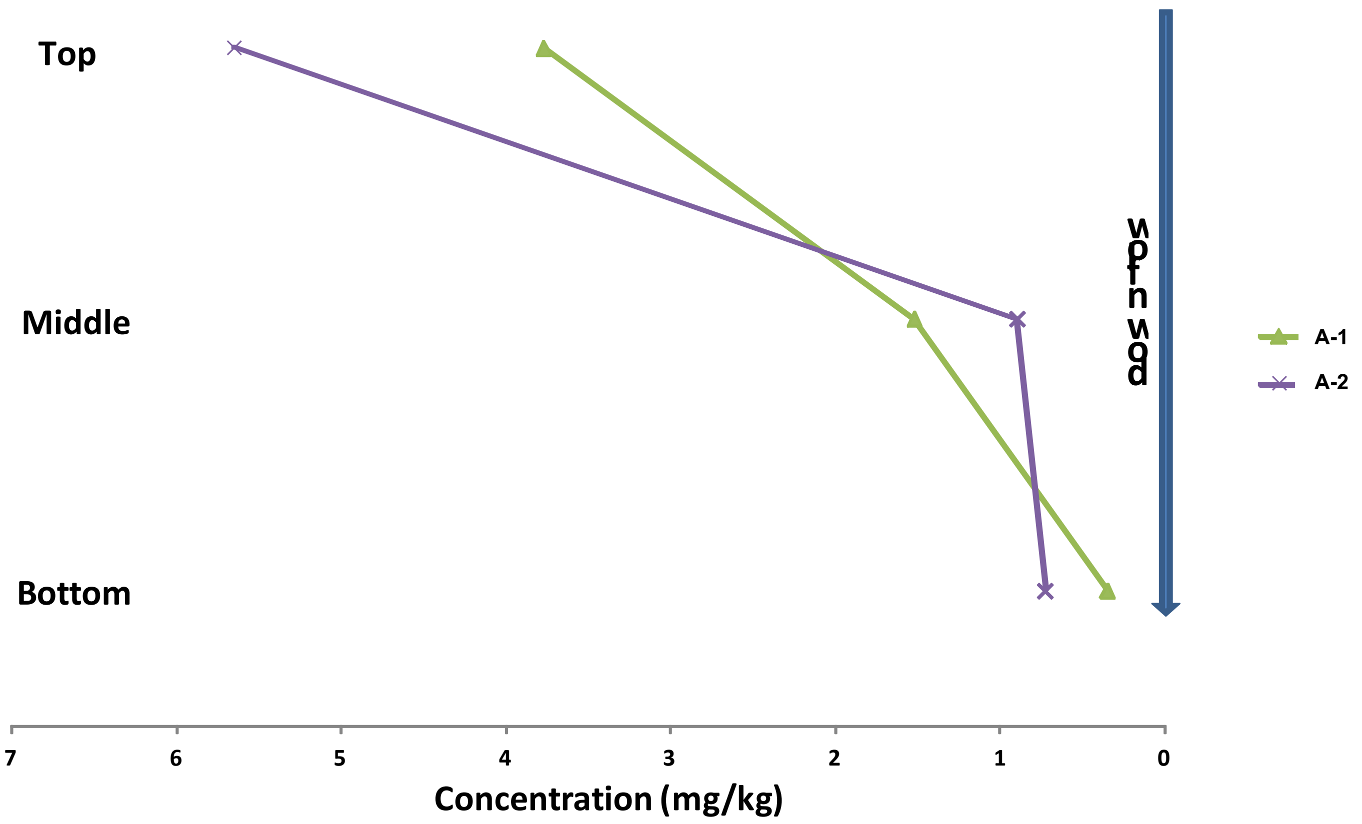
Removal Rate Sustained Substantial Margin Through Loading Rate Increase



Removal Rate Decreases with Increasing Hydraulic Residence Time

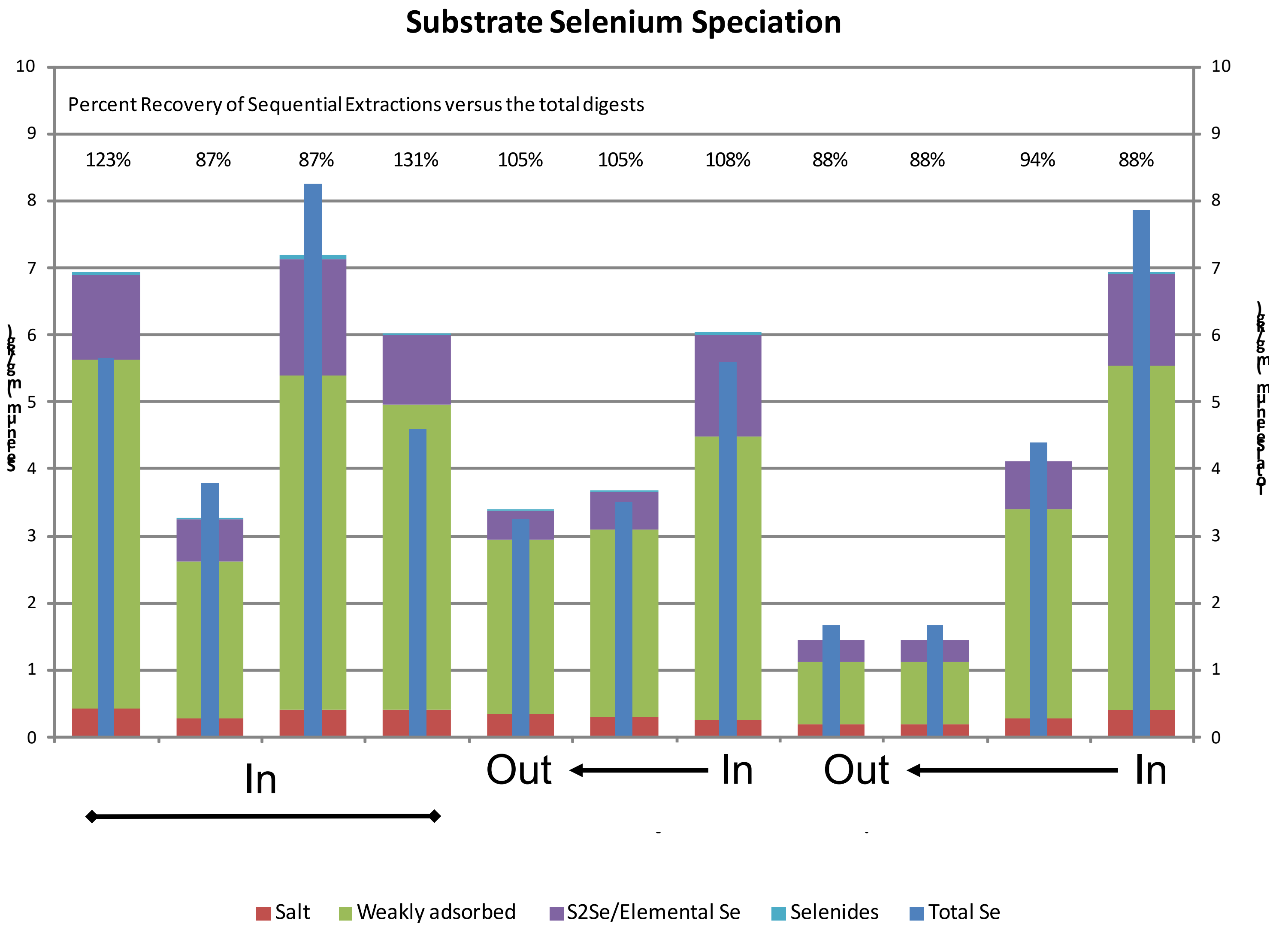


Barrel Selenium Profile Reflects First-Order Process (2011-2012 Pilot)


Outlet 033 Substrate Total Selenium Concentration

Vertical Distribution and Speciation of Selenium

Reduction, Sorption, Volatilization (2011-2012 Pilot)



Source: CH2MHILL (2012)

Post-BCR

Flow Needs Polishing

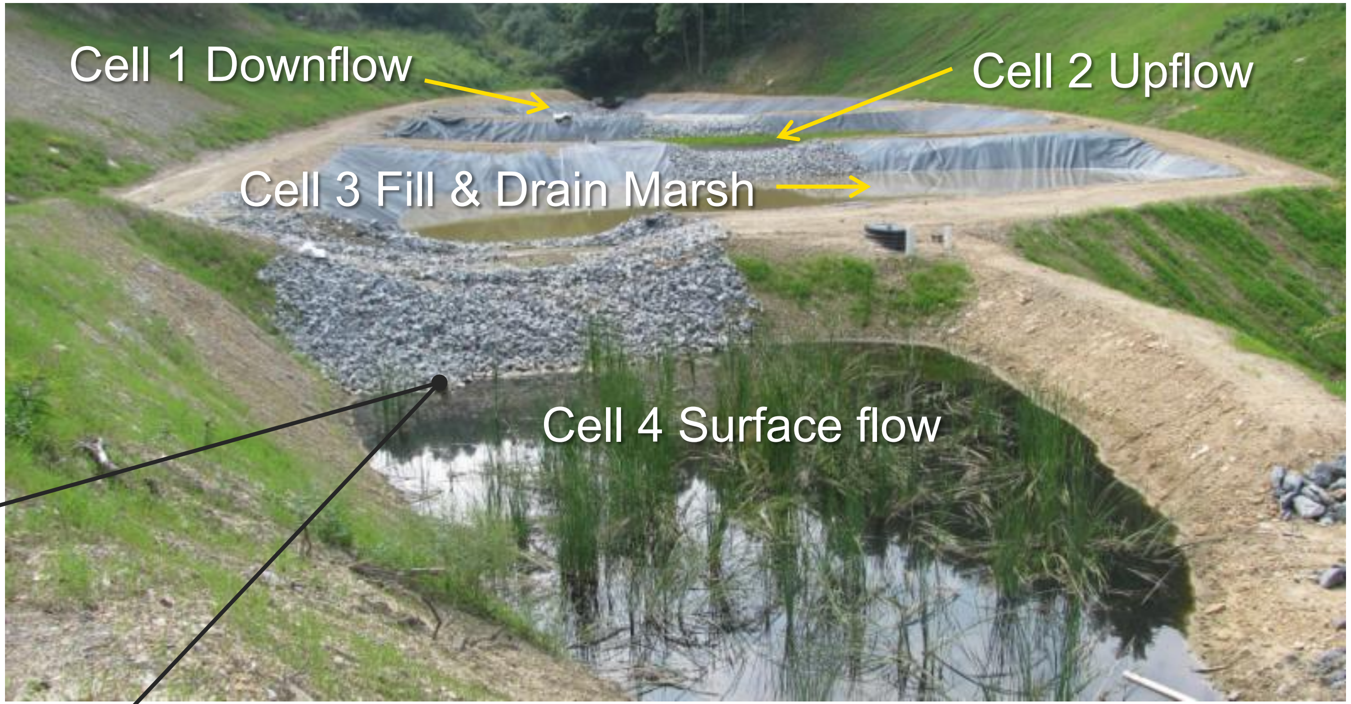
- Initial organic color will be high
- Inorganic color often white/ yellow precipitate (elemental sulfur), the oxidation result when pH not optimum for conversion to sulfate
- BOD and COD also elevated
- > Addition of oxygen to system

Completed Passive Se Treatment System

Parameter	Influent	Cell 1 Effluent	Cell 2 Effluent	Final Effluent
BOD	13	30	26	11
COD	11	43	84	24
NO_2+NO_3-N	3.6	1.5	2.4	1.2
Total Phosphorus	0.28	0.09	0.13	0.1

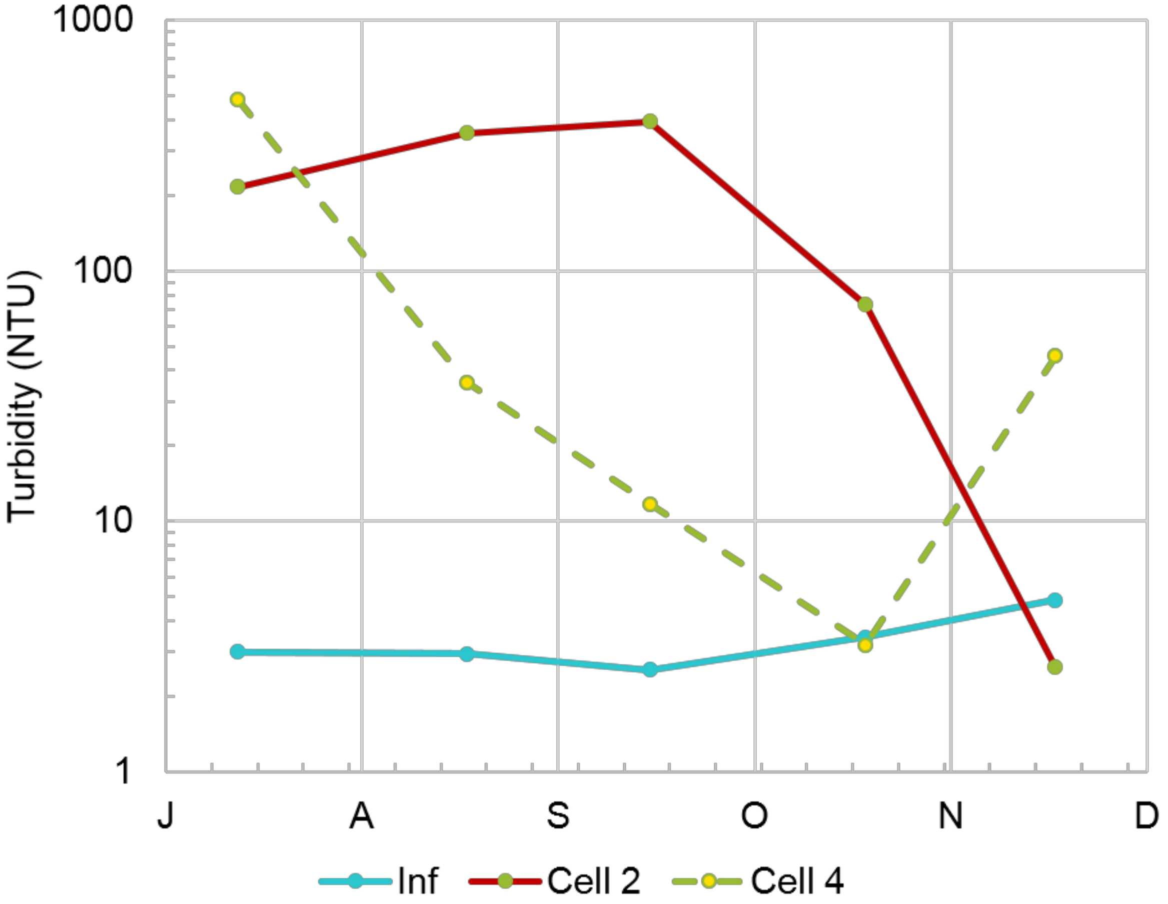
All units = mg/L

[a] Monitoring data from February through July 2012



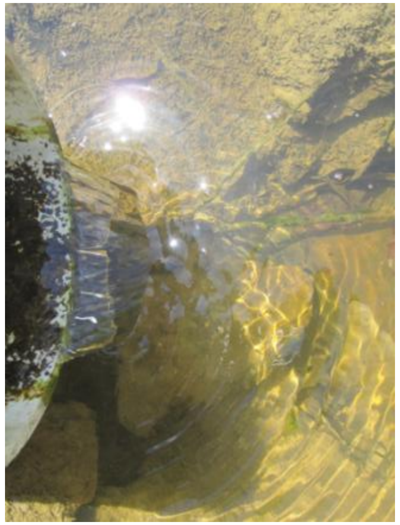
Source: Thomas, R. (2011)

Polishing Wetlands Reduced Turbidity by 83%



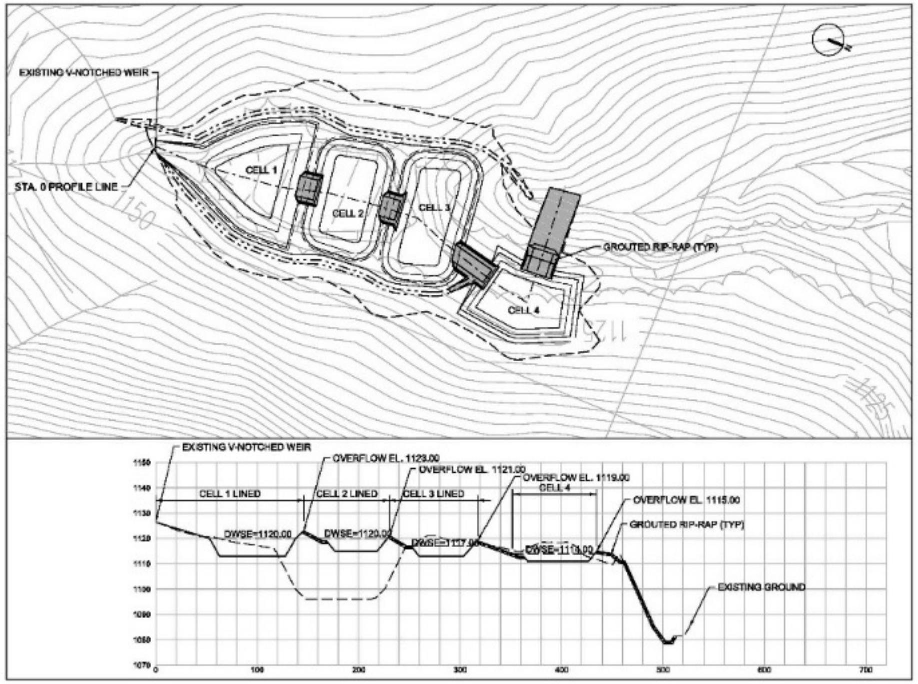
Cell 2

Cell 3 into Cell 4



Coal Mac Selenium Treatment System

Natural Systems	Conventional Systems
BCR+wetland footprint fits (just)	Can be made to fit
Construction $765K	Construction $18MM
Natural processes	Engineered processes
O&M $15K/yr	O&M $500K



Passive Designs Currently Being Implemented

VDF BCR

VUF Peat

HSSF Polishing

Conclusions

Coal Mac Se BCR System Demonstrates Robust System Longevity

Key Points

- 8 years continuously compliant performance
  - No indication of reduction in lifespan
- O&M was budgeted for $15K/yr, reality ~$5K/yr in weekly monitoring
  - No substrate adjustment needed
- Averaging <$0.32/1000 gallons treated
  - Includes hypothetical substrate replacement ~20yrs
- Award-winning “innovative” project

Case Study 2

Mayer Ranch Passive Treatment System

- Target artesian discharges of net alkaline mine water
- Multiple process units for sequential treatment
- Focus on Unnamed Tributary watershed (200 ha)
- Location of Original Discharge from Mine Pool after closure
  - Mayer Ranch
- Dr Robert Nairn, University of Oklahoma
  - all of data present in this section is credited to OU/CREW

Tri-State Mining District

Picher, OK 1926

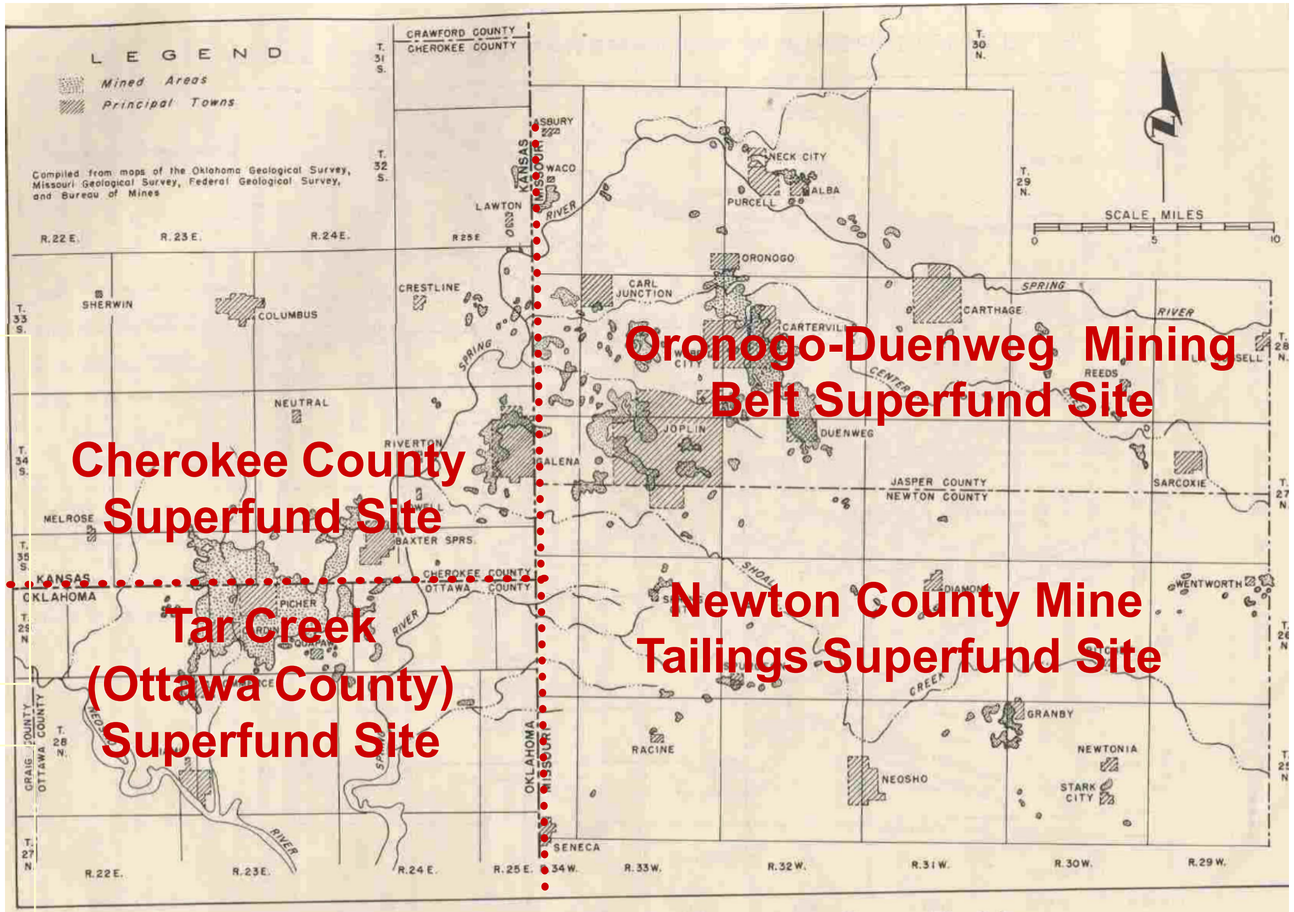
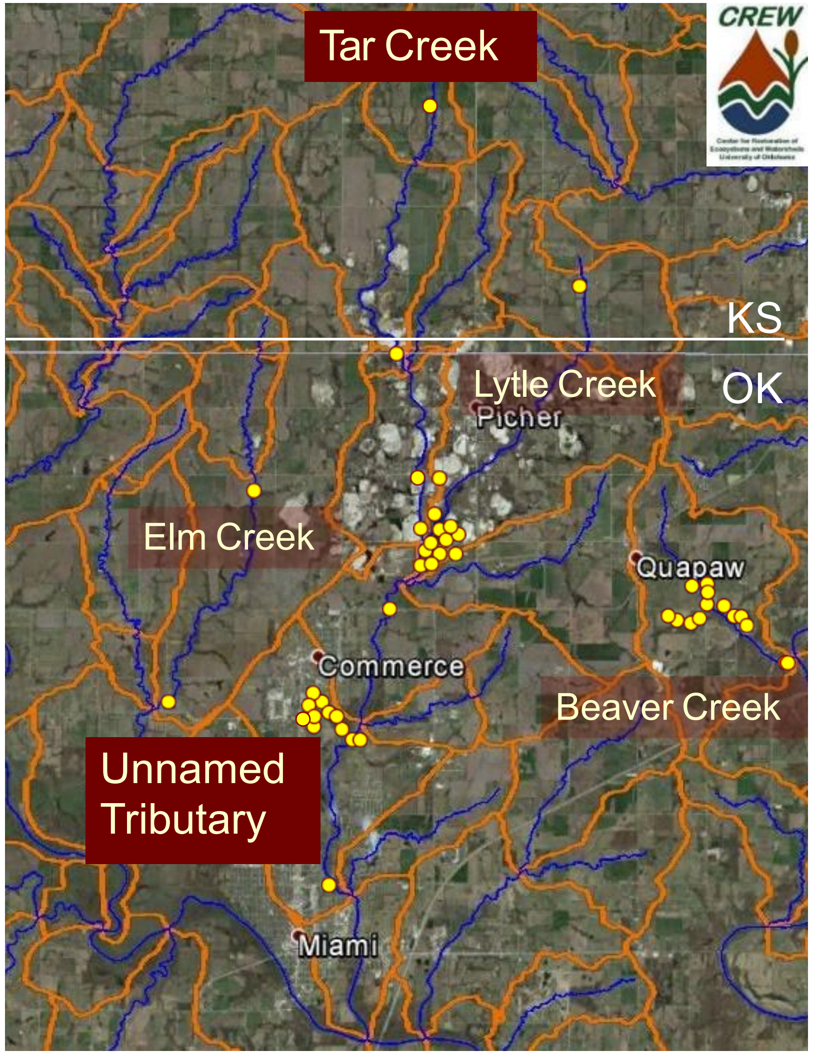


FIGURE 1. - Principal Part of Tri-State Zinc-Lead District, Showing Mined Areas.

Tar Creek Superfund Site



- Mining 1890s-1960s
- 1979: discharge to surface
  - First from 2 abandoned boreholes on the **Mayer Ranch** Property in Commerce, Oklahoma
- National Priorities List (1983)
- Elevated Fe, Zn, Cd, Pb, As in water, chat, soils and biota

- Mining "mega-site"
  - >1000 surface hectares
  - 500 km of tunnels, 2600 open shafts and boreholes.
  - 94 million m3 contaminated water
- Six Communities & Ten Native American Tribes

University of Oklahoma comprehensive watershed monitoring

- 1997 - 2018
- Streams, point (artesian discharges), nonpoint (waste pile runoff / leachate) sources

Mayer Ranch

Annual Mass Loadings (kg/yr)

Fe	~88,730
Zn	~6,210
Cd	~5
Pb	~10

> “EPA concurs with the State's conclusion that the surface water conditions are irreversible”
> (2005)

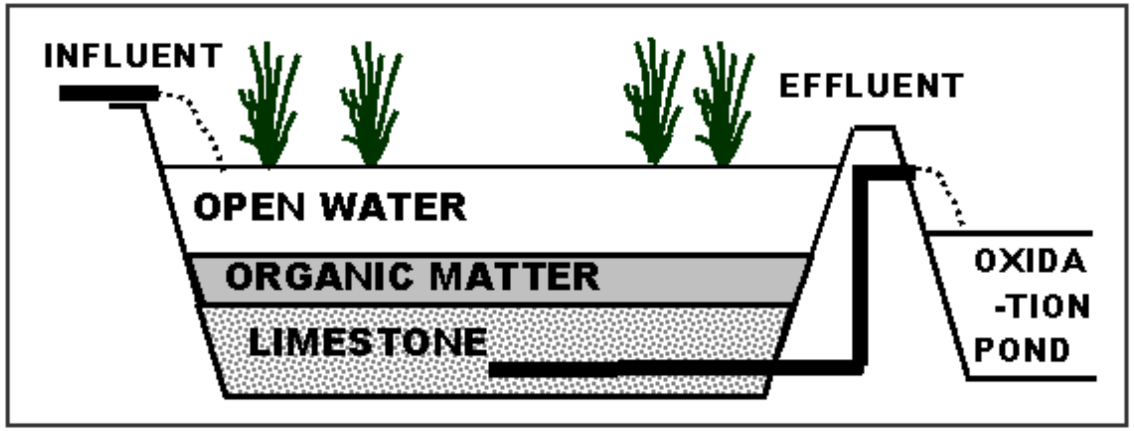
www.epa.gov/superfund/sites/fiveyear/f94-06003.pdf

Mayer Ranch

Passive Treatment Concept

- Ponds
  - Precipitation and sedimentation
- Aerobic Marsh
  - Precipitation and Solids Trapping
- Biochemical Reactors
  - Trace metal removal
  - SRB-mediated reduction
- Aerobic Polishing
- Limestone Beds
  - Add alkalinity
  - Zn carbonate precipitation

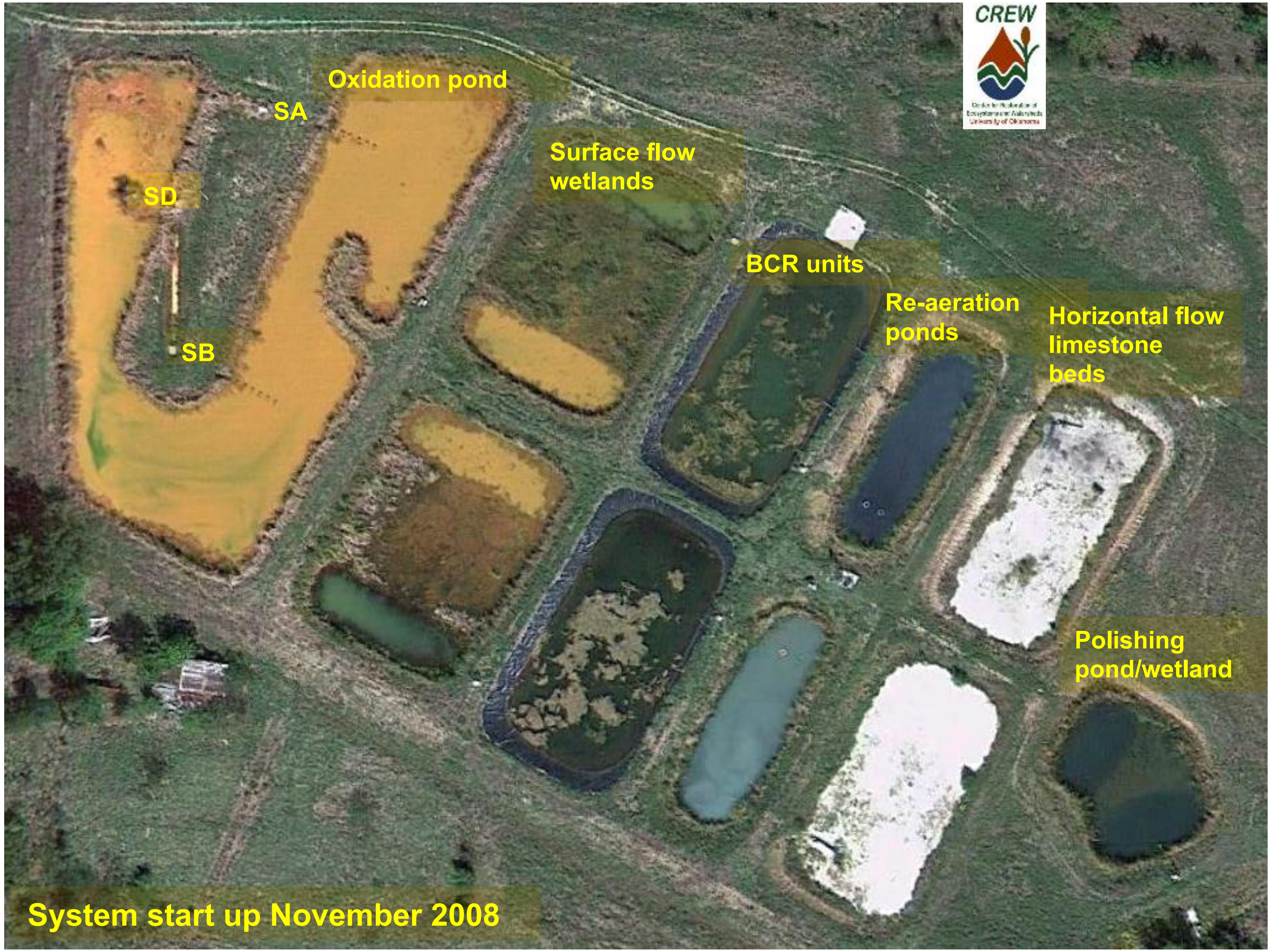
Biochemical Reactor



Mayer Ranch

Passive Treatment System

- USEPA funding 2004-10
- Ecological engineering field research site for OU
- Designed for 1000 L/min flow rate
- Six distinct process units
  - 8 in parallel for total of 10 cells
- First PTS in entire Tri-State Mining District
- Continuous operation since 11/2008
- Limited O&M
- Elevated Fe, Zn, Pb, Cd, As influent
- Discharge meets criteria



System start up November 2008

Mayer Ranch

Water Quality Changes

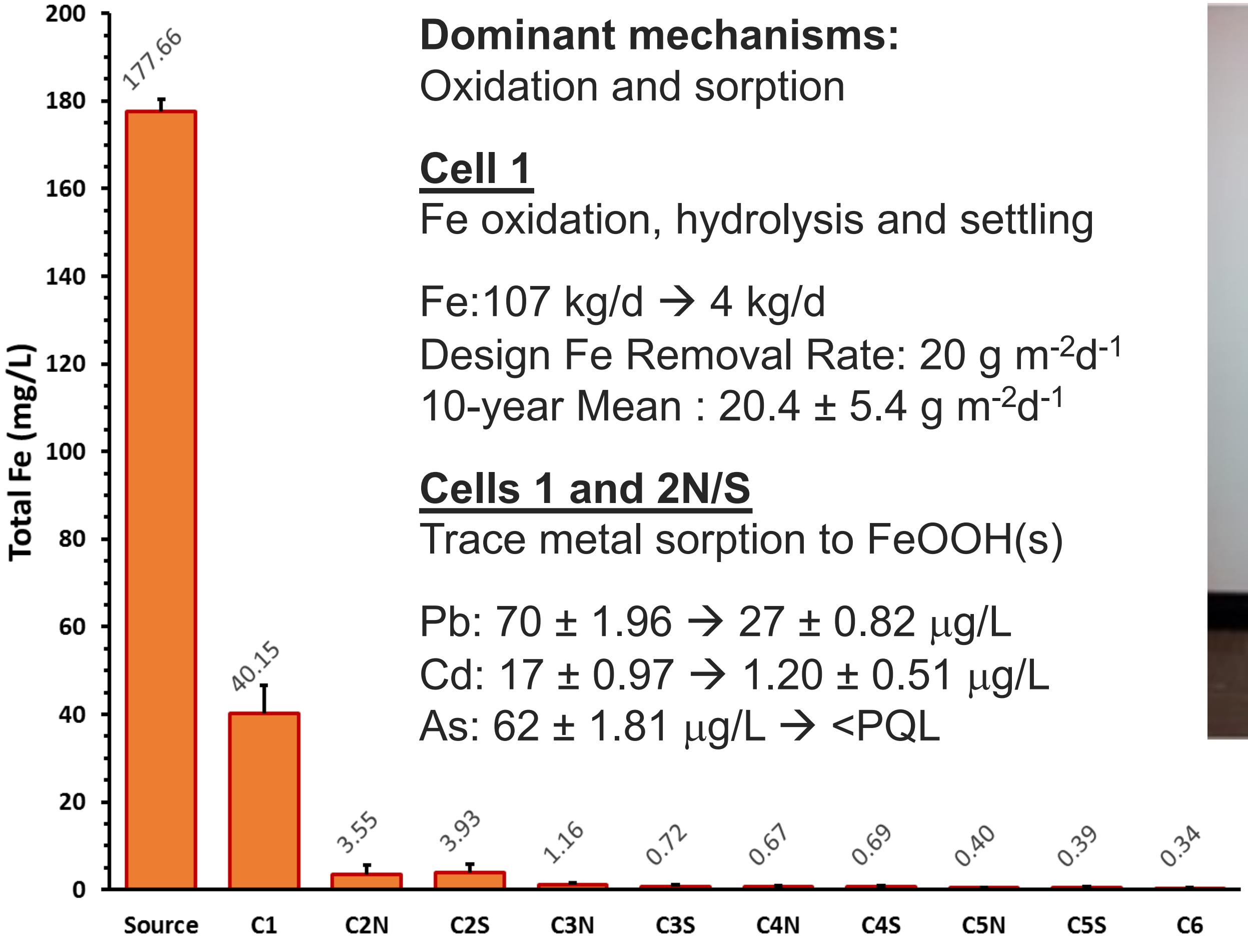
	In (n=82)	Out (n=43)
pH	5.95	7.02
Alk_T (mg/L)	393	224
Fe_T (mg/L)	192	0.13
Zn_T (mg/L)	11	0.25
Ni_T (mg/L)	0.97	0.15
Cd_T (μg/L)	17	<PQL
Pb_T (μg/L)	60	<PQL
As_T (μg/L)	64	<PQL
SO_4^{-2} (mg/L)	2239	2057

MRPTS
oxidation cell
under construction,
fall 2008

MRPTS
oxidation cell
during managed
drawdown,
winter 2017

Mayer Ranch PTS

Total **Iron** Changes



Dominant mechanisms:
Oxidation and sorption

Cell 1
Fe oxidation, hydrolysis and settling

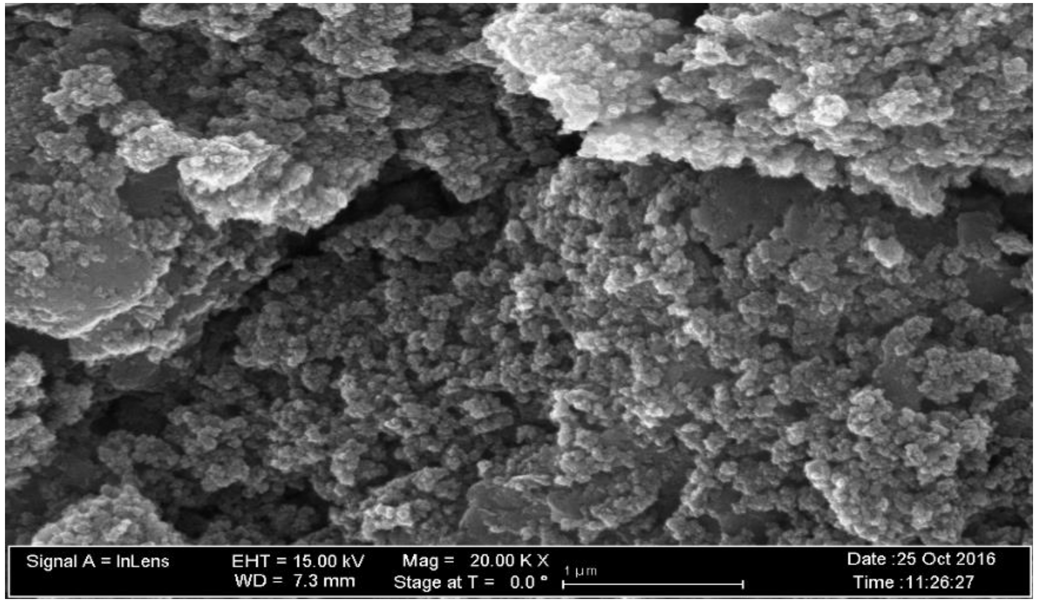
Fe:107 kg/d → 4 kg/d
Design Fe Removal Rate: 20 g $m^{-2}d^{-1}$
10-year Mean : 20.4 ± 5.4 g $m^{-2}d^{-1}$

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

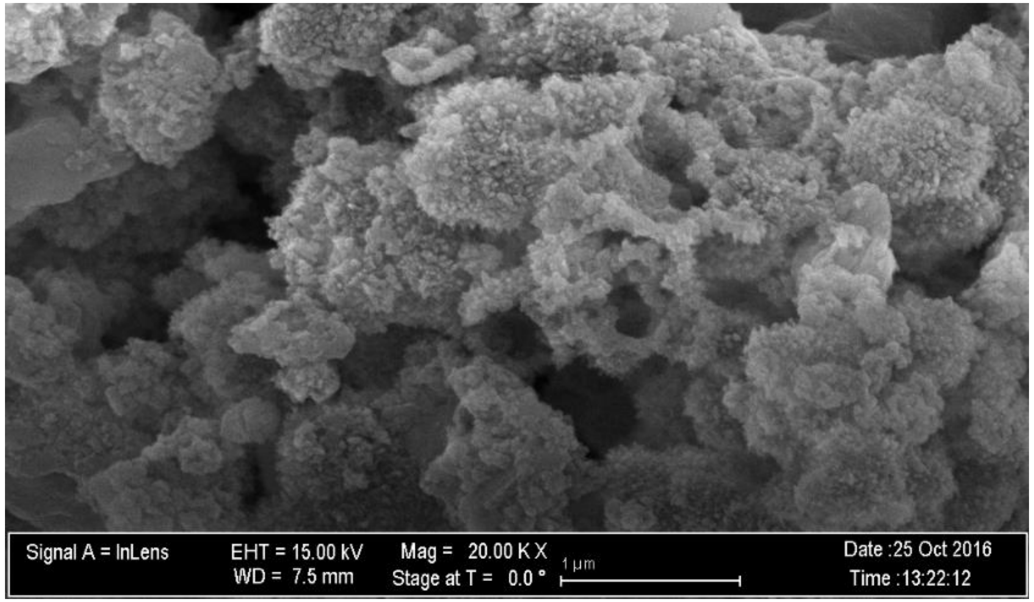
Pb: 70 ± 1.96 → 27 ± 0.82 µg/L
Cd: 17 ± 0.97 → 1.20 ± 0.51 µg/L
As: 62 ± 1.81 µg/L → <PQL

Mayer Ranch PTS

Total **Iron** Changes



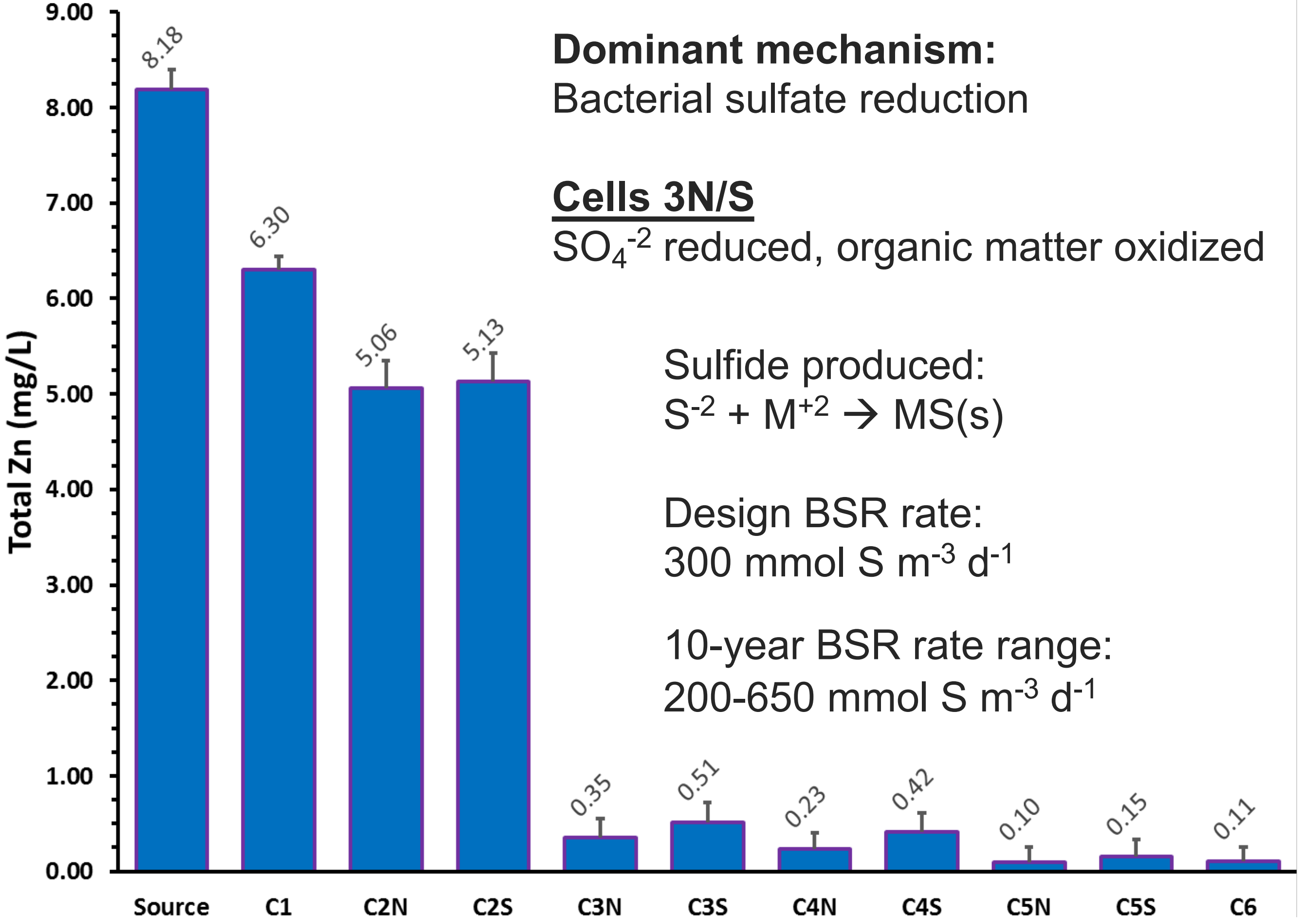
Amorphous ferrihydrite typical of Cell 1 and Cell 2N/2S **surface** samples



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

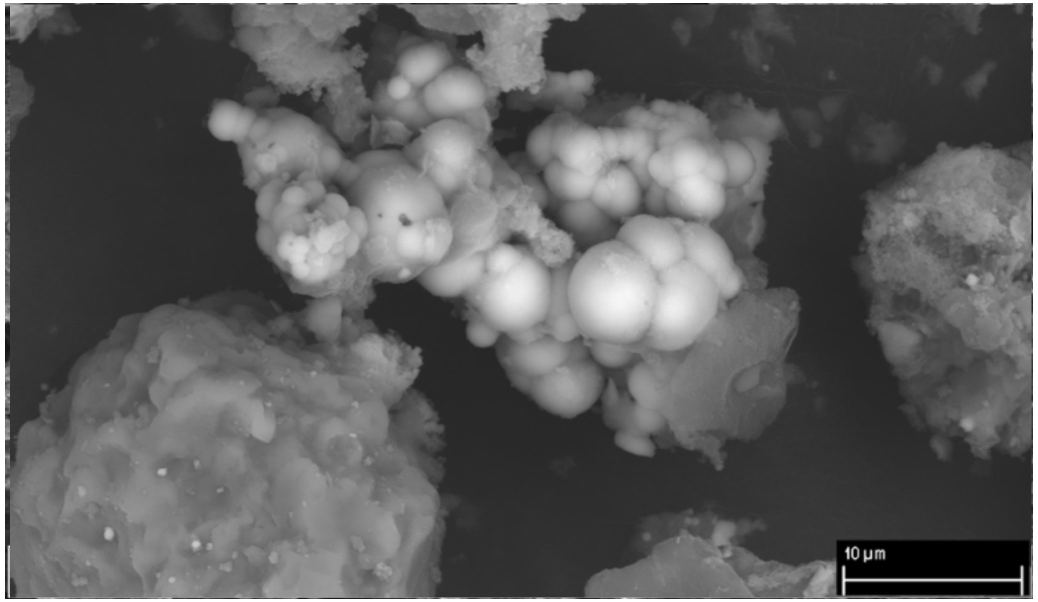
Sulfide produced:
$S^{-2} + M^{+2} \rightarrow MS(s)$

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

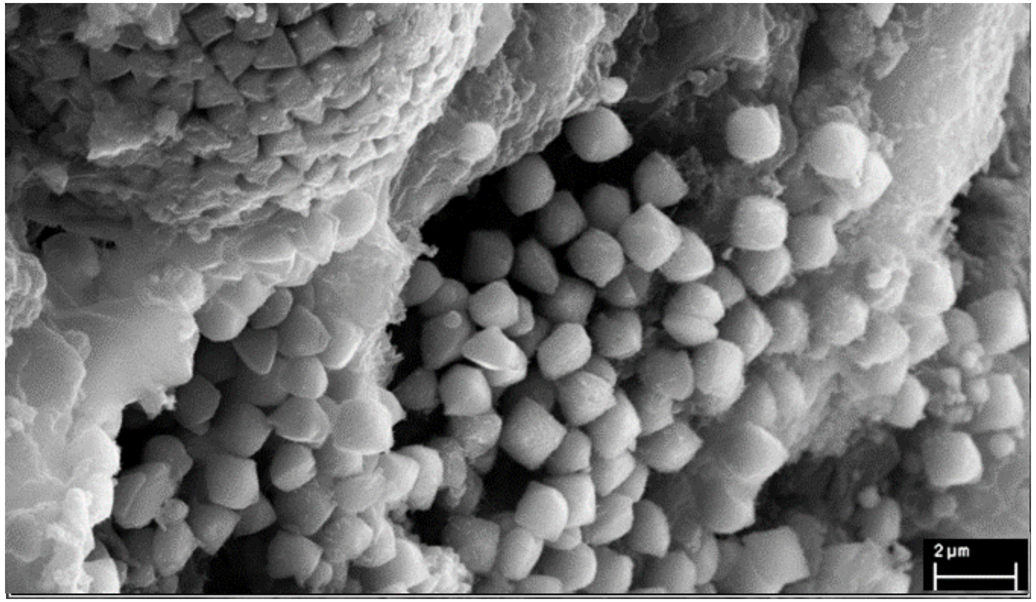
10-year BSR rate range:
200-650 mmol S m^{-3} d^{-1}

Mayer Ranch PTS

Total **Zinc** Changes



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

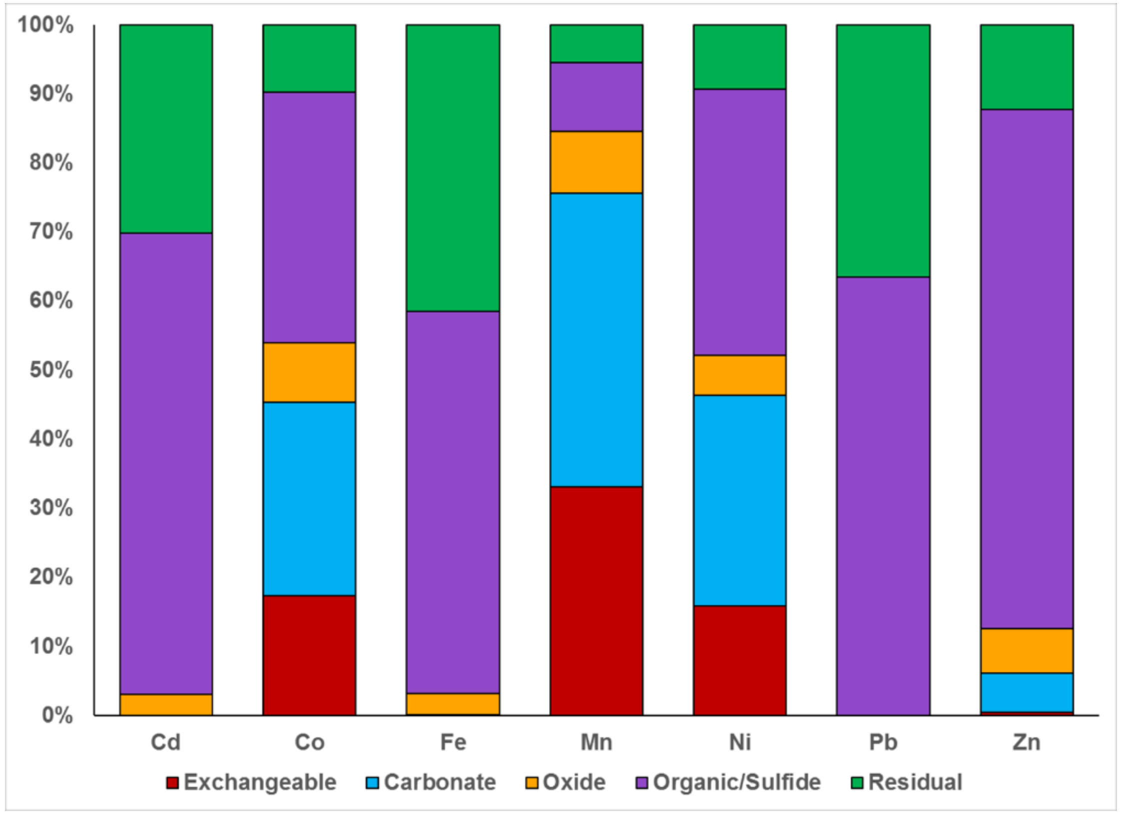


FeS2 aggregation and framboidal pyrite in VFBR substrates

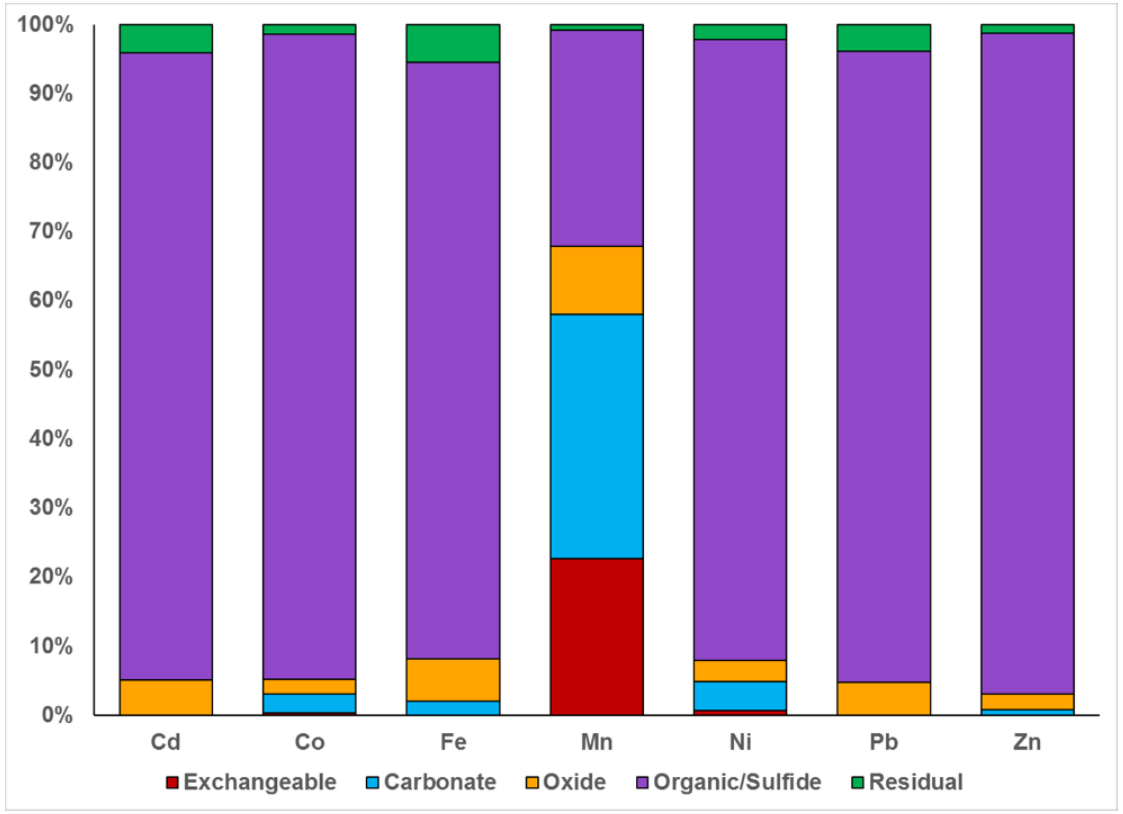
Mayer Ranch PTS

Total **Metal** Changes

2010 VFBR Sequential Extractions

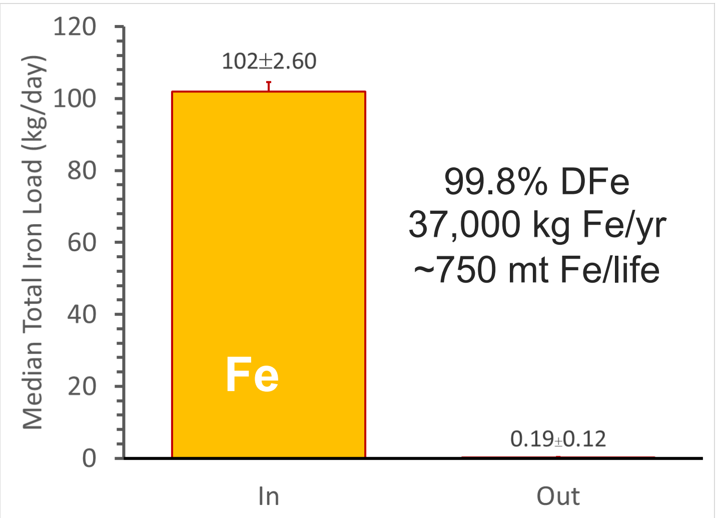


2014 VFBR Sequential Extractions

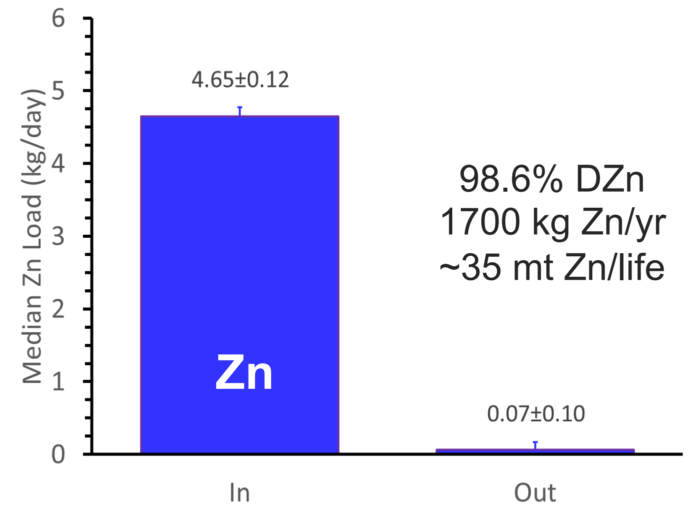


Mayer Ranch PTS

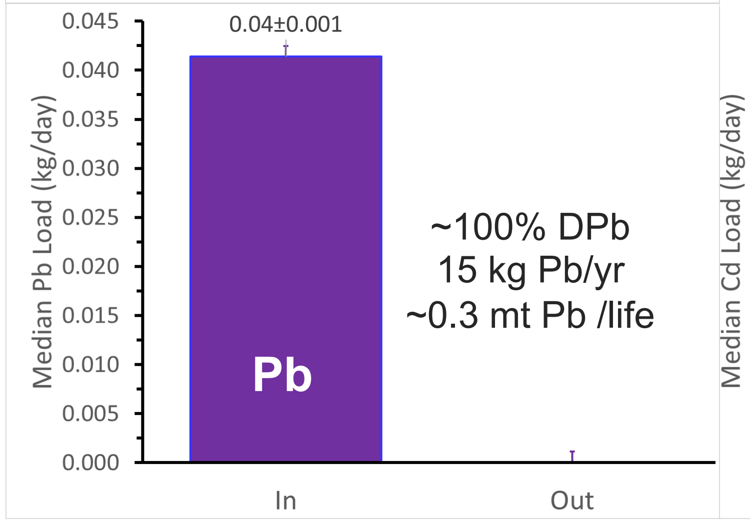
Contaminants of Concern



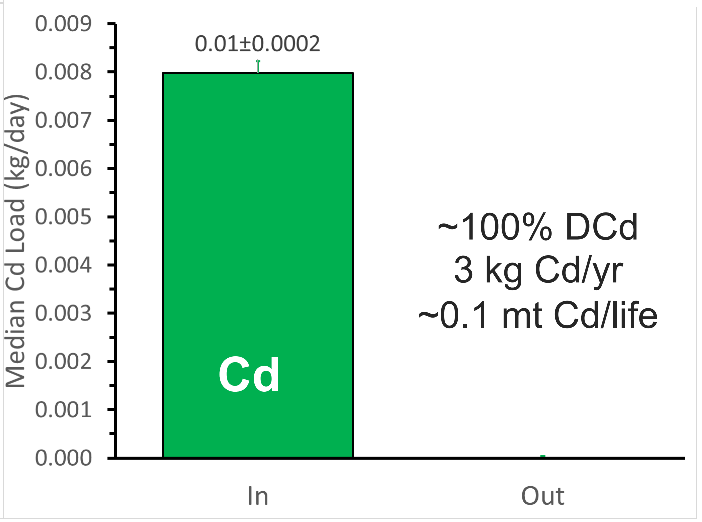
99.8% DFe
37,000 kg Fe/yr
~750 mt Fe/life



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



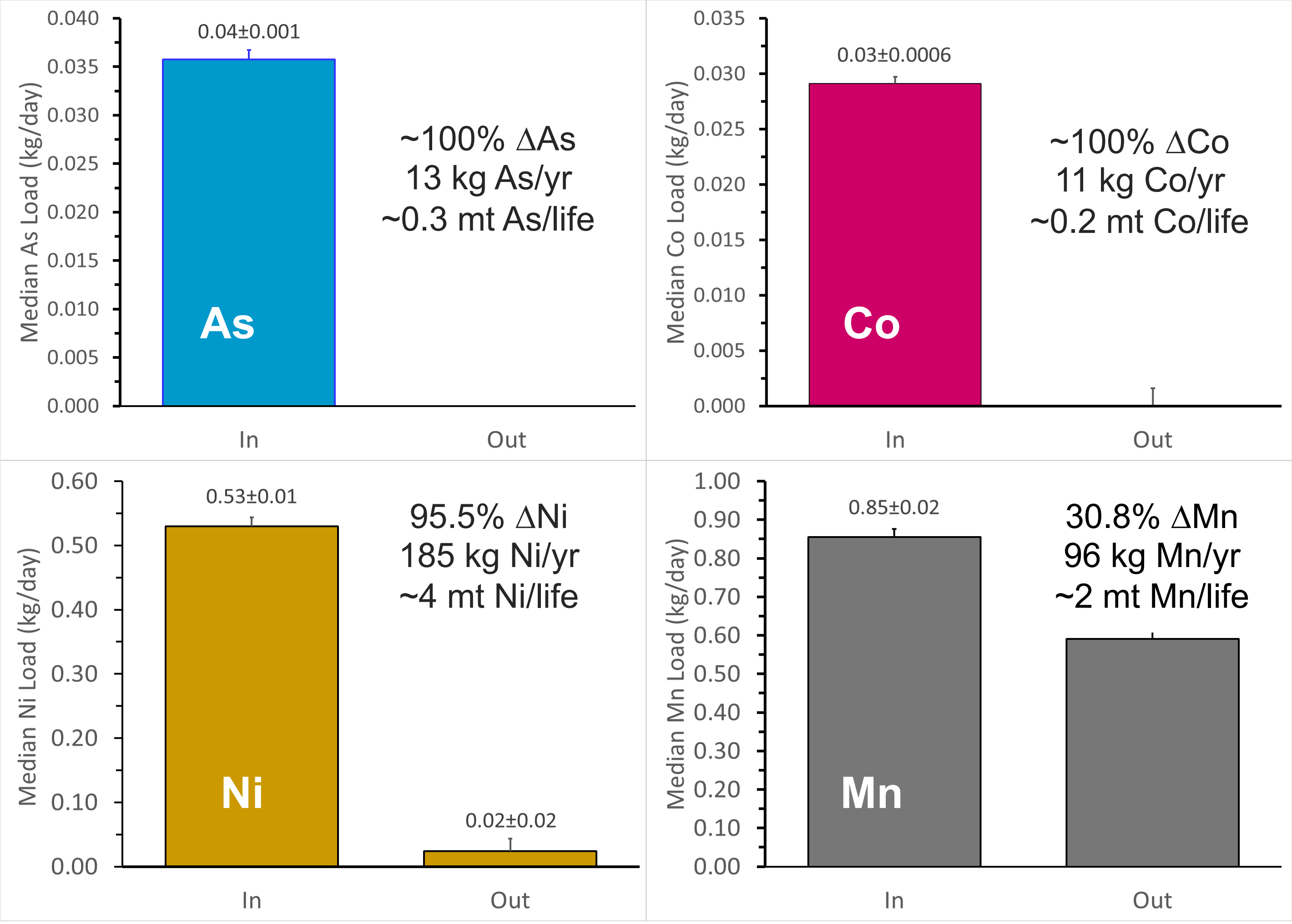
~100% DPb
15 kg Pb/yr
~0.3 mt Pb /life



~100% DCd
3 kg Cd/yr
~0.1 mt Cd/life

Mayer Ranch PTS

Other Metals



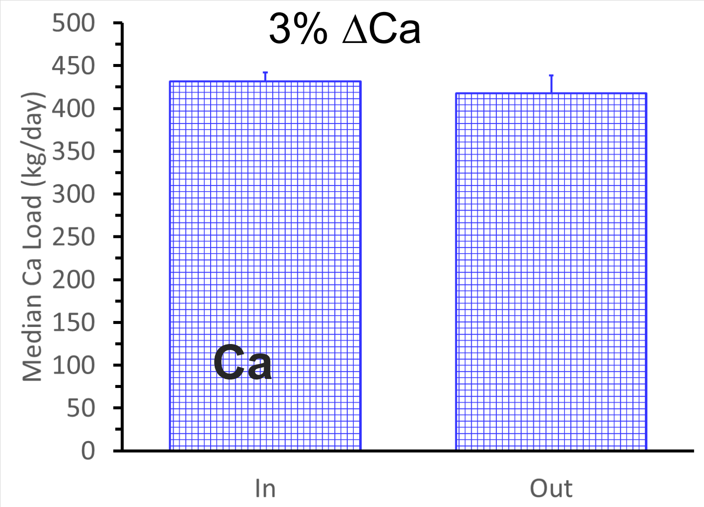
~100% ΔAs
13 kg As/yr
~0.3 mt As/life

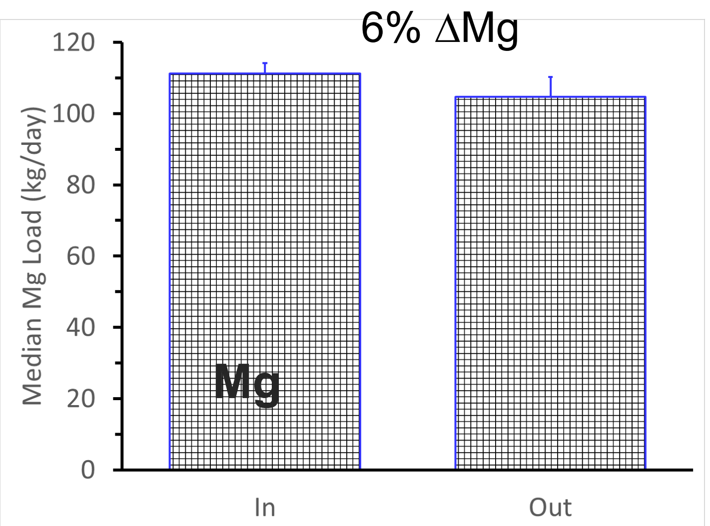
~100% ΔCo
11 kg Co/yr
~0.2 mt Co/life

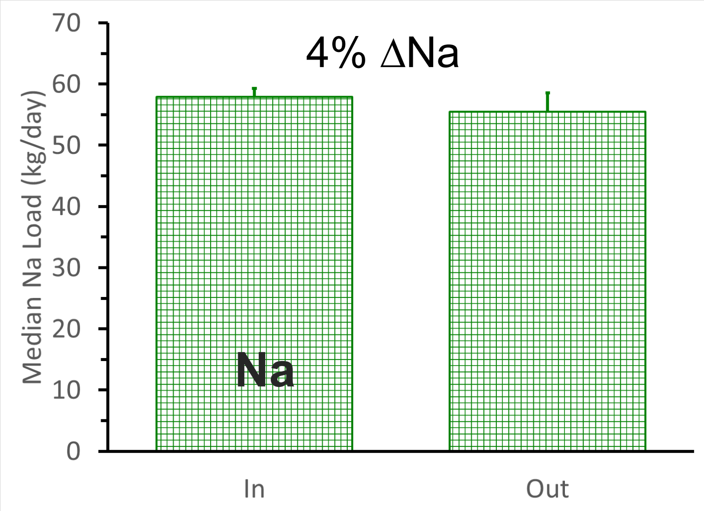
95.5% ΔNi
185 kg Ni/yr
~4 mt Ni/life

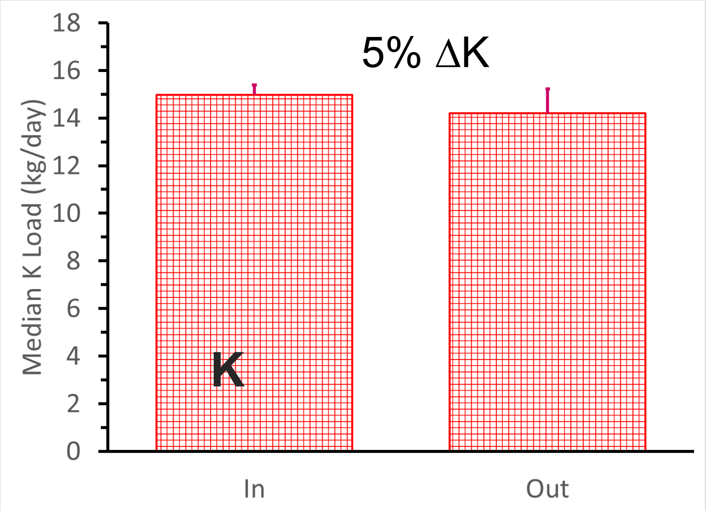
30.8% ΔMn
96 kg Mn/yr
~2 mt Mn/life

Mayer Ranch PTS
Base Cations









Mayer Ranch PTS

BCR Maintenance

- After 9 years of operation both BCR units showed significant decrease in permeability

- Both units drained and the substrate “flipped” in attempt to recovery the hydraulic properties

Changes in Hydraulic Conductivity

-

	K (m/day)	
	North BCR	South BCR
2008 (pre-construction)		
Laboratory-Falling Head	4.77	4.77
2016 (8-years operation)		
Laboratory-Falling Head	0.51	---
Field-Falling Head	0.13	0.31
Modified Infiltrometer	0.19	0.17
Slug Test	1.25	0.43
2017 (after flipping)		
Field-Falling Head	4.5	4.5

“Major” O&M Costs

	Oxidation Pond	BCR
2 x 8” x 5’ Inlet AgriDrains	$1200	---
Equipment (Takeuchi TB153)	$1500	$1900
Stone (for ramp)	---	$700
Labor	$1000	$1500
Misc. (pipe, fuel etc.)	$700	$200
Total	**$4400**	**$4000**

“Major” O&M < $10K ($840/yr)
All monitoring and regular O&M ~ $10K/yr

Conclusions

Mayer Ranch Passive Treatment System Maintenance Substains Longevity

Key Points

- 10 years consistent performance
  - No reduction in water quality performance
  - Maintenance restored hydraulic function
- Routine maintenance is land & water-based
  - Animals, vegetation, storms, people
- Annual O&M was <$10K/year
  - BCR substrate “flip” performed for $4K
- Average <$0.10/1000 gallons treated
- ITRC “Success Story”

Conclusions

Biochemical Reactors Meet Longevity and Performance Requirement

- Biochemical reactor technology based on long-term performance of natural systems
- Carbon depletion and hydraulic conductivity are potential impacts to longevity
- Case histories demonstrate good performance (8-10yrs)
  - No adverse performance trends; no indication of carbon-depletion
  - No costly substrate replacement
  - Hydraulic property of the substrate may be a concern before carbon depletion
  - Lower cost operations demonstrated

Acknowledgements

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- Thanks to engineering and science staff at Jacobs.

JACOBS

Questions

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Jim Bays is a Professional Wetland Scientist and a Technology Fellow in Natural Treatment Systems with Jacobs. With more than 40 years of experience, Jim specializes in planning and design of natural treatment systems for water quality improvement. His current focus is on passive treatment of selenium and the use of wetlands for treating membrane concentrate.

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