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THE ROLE OF MANGANESE IN TRACE METAL REMOVAL

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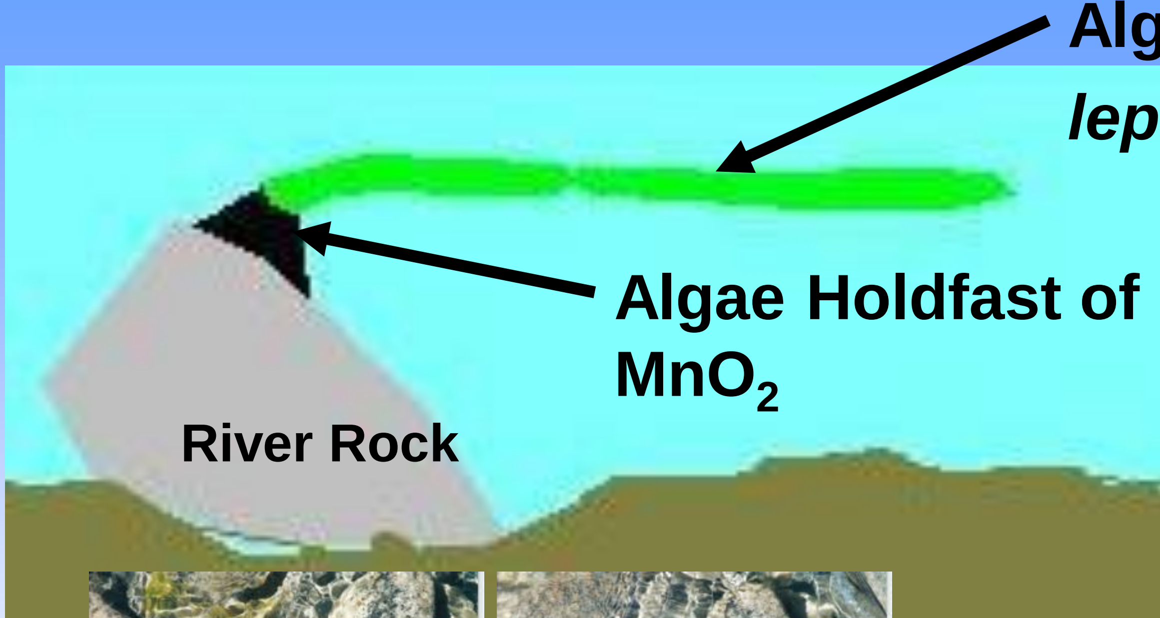
Overview

- Manganese removal
- Manganese and metals
- Case studies
- Soudan mine revisited

Manganese Removal

- Manganese present as Mn^{+2}
- To remove abiotically require pH> 10
- At circumneutral pH, thermodynamically unstable
  - kinetics are super slow
- Primary removal mechanisms are biologically mediated
- Prerequisite, Fe needs to be removed first
- Robbins(Robbins, et al., 1999)
  - 12 different biological mechanisms
  - the most common of which include ***leptothrix discophora*** and ***ulothrix*** algae.
- Burgos (Burgos et al 2010)
  - Fungus plays major role

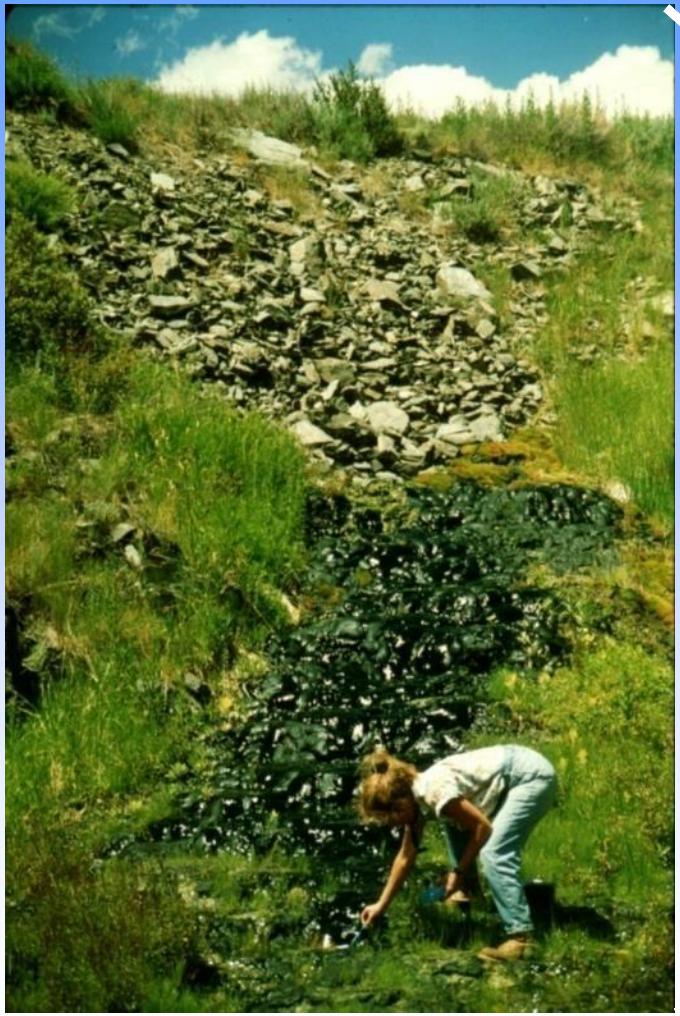
Manganese Oxidation at Neutral pH



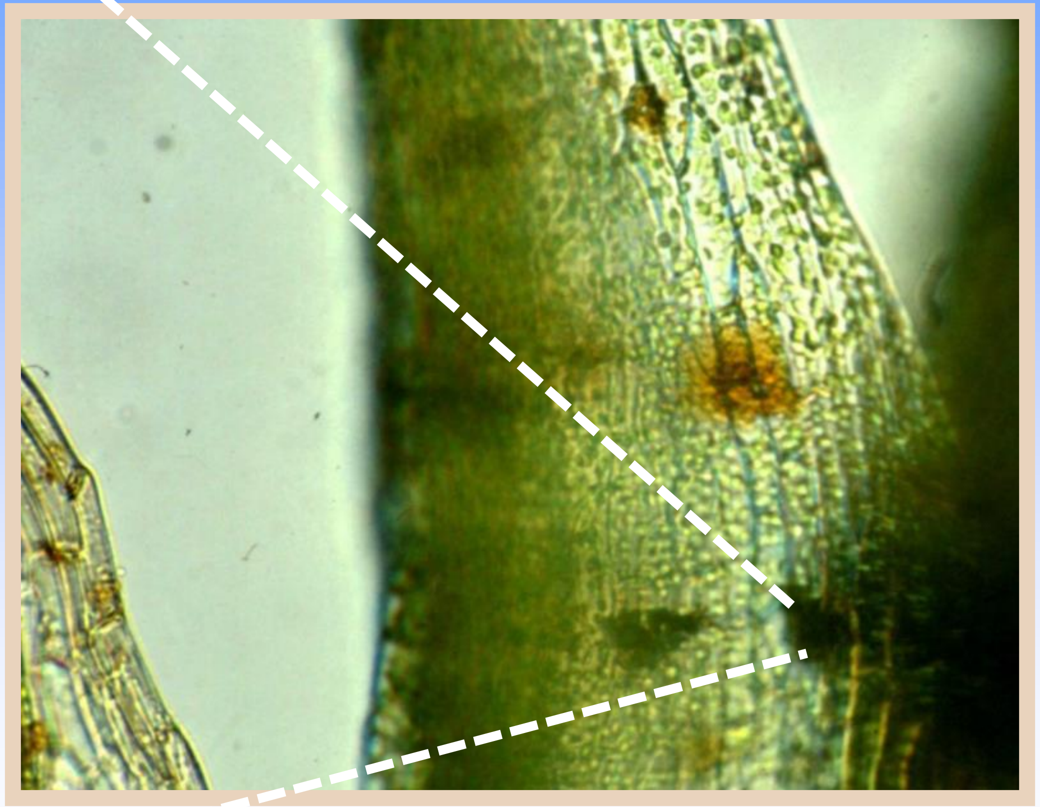
Manganese/algae in outfall from Leadville Colorado (El. 10,000ft/3,050m) WTP in March

Manganocrete from paleo-channel near Prescott, AZ

Iron & Manganese Oxidation on Moss



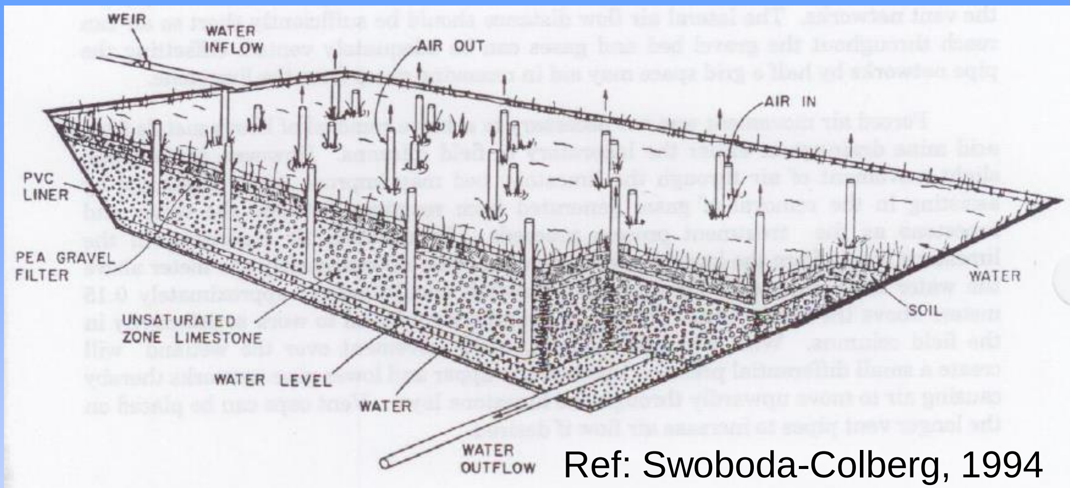
Atlantic City Iron Mine in Wyoming Elev. 8,000 ft (2,500m)



Moss had 39% Mn by Dry Wt!

$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$

Manganese Removal Beds



Ref: Swoboda-Colberg, 1994

MRBs can be operated as saturated beds or as trickling filters; Fe must be removed first

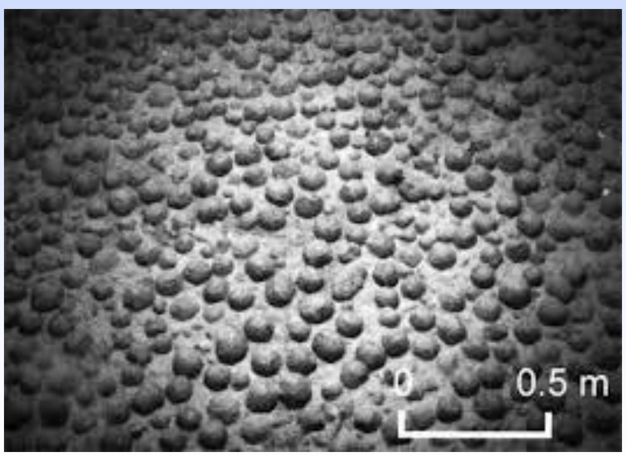
Courtesy of Bob Hedin

Manganese Removal

- **Zero order model**
  - Removal occurs at a constant rate
  - Removal independent of Mn concentration
  - Areal removal rate
  - 5 $gm/m^2/day$
- **First order model**
  - Rose and Means, 2005
  - Removal function of
    - Surface area
    - Mn concentration
    - Time

Manganese and Metals

- Ability of manganese to adsorb metals is well documented (Tebo, et al. 2004)
- Deep sea nodules



Periodic Table of Passive Treatment (2008)

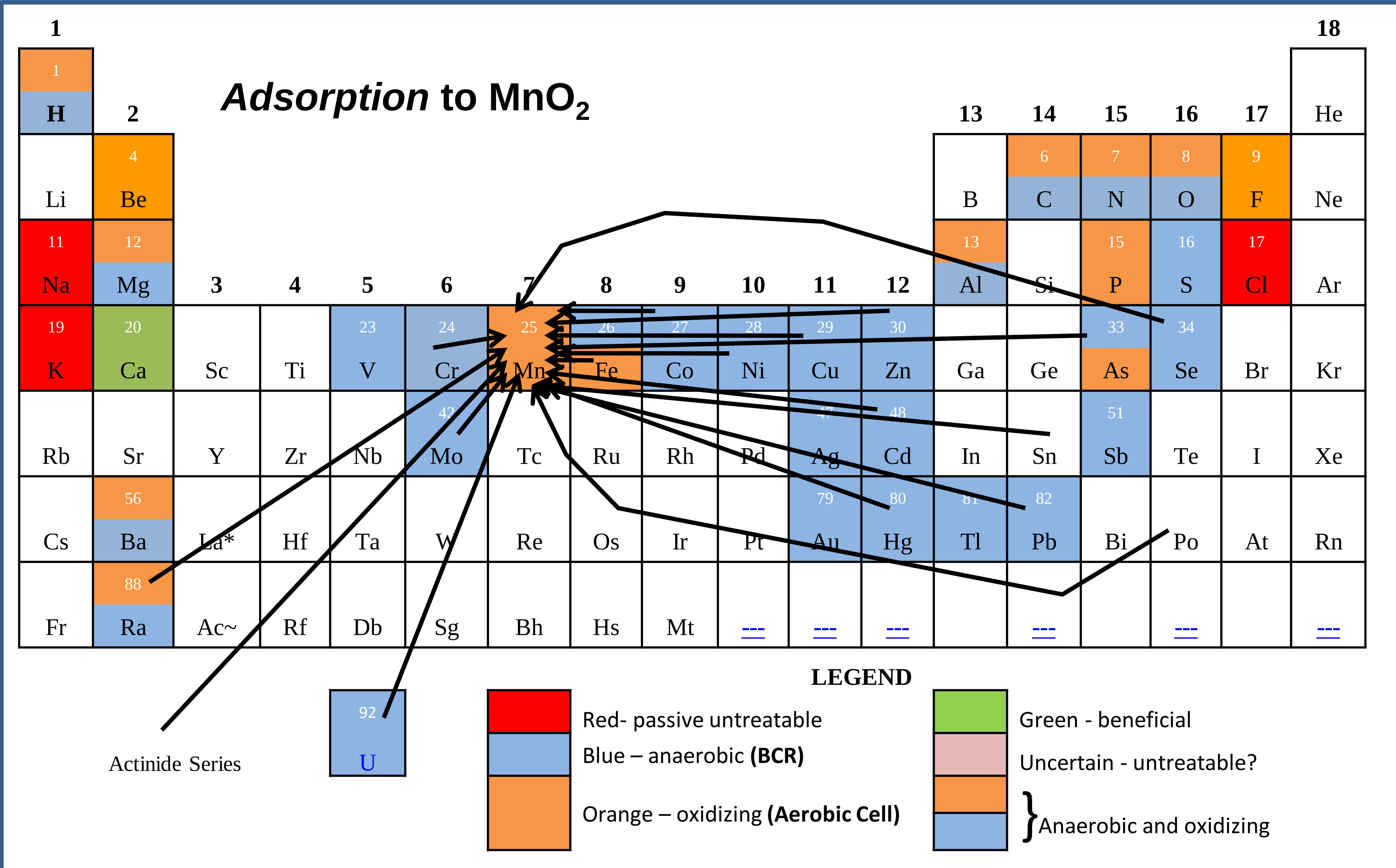
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	He
Li	4 Be											B	6 C	7 N	8 O	9 F	Ne
11 Na	12 Mg											13 Al	Si	15 P	16 S	17 Cl	Ar
19 K	20 Ca	Sc	Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	Ga	Ge	33 As	34 Se	Br	Kr
Rb	Sr	Y	Zr	Nb	42 Mo	Tc	Ru	Rh	Pd	47 Ag	48 Cd	In	Sn	51 Sb	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~	Rf	Db	Sg	Bh	Hs	Mt	---	---	---		---		---		---

Actinide Series: 92 U

LEGEND

- Red- passive untreatable
- Blue – anaerobic **(BCR)**
- Orange – oxidizing **(Aerobic Cell)**
- Green - beneficial
- Uncertain - untreatable?
- } Anaerobic and oxidizing

2013 Periodic Table of Passive Treatment (Revisited)



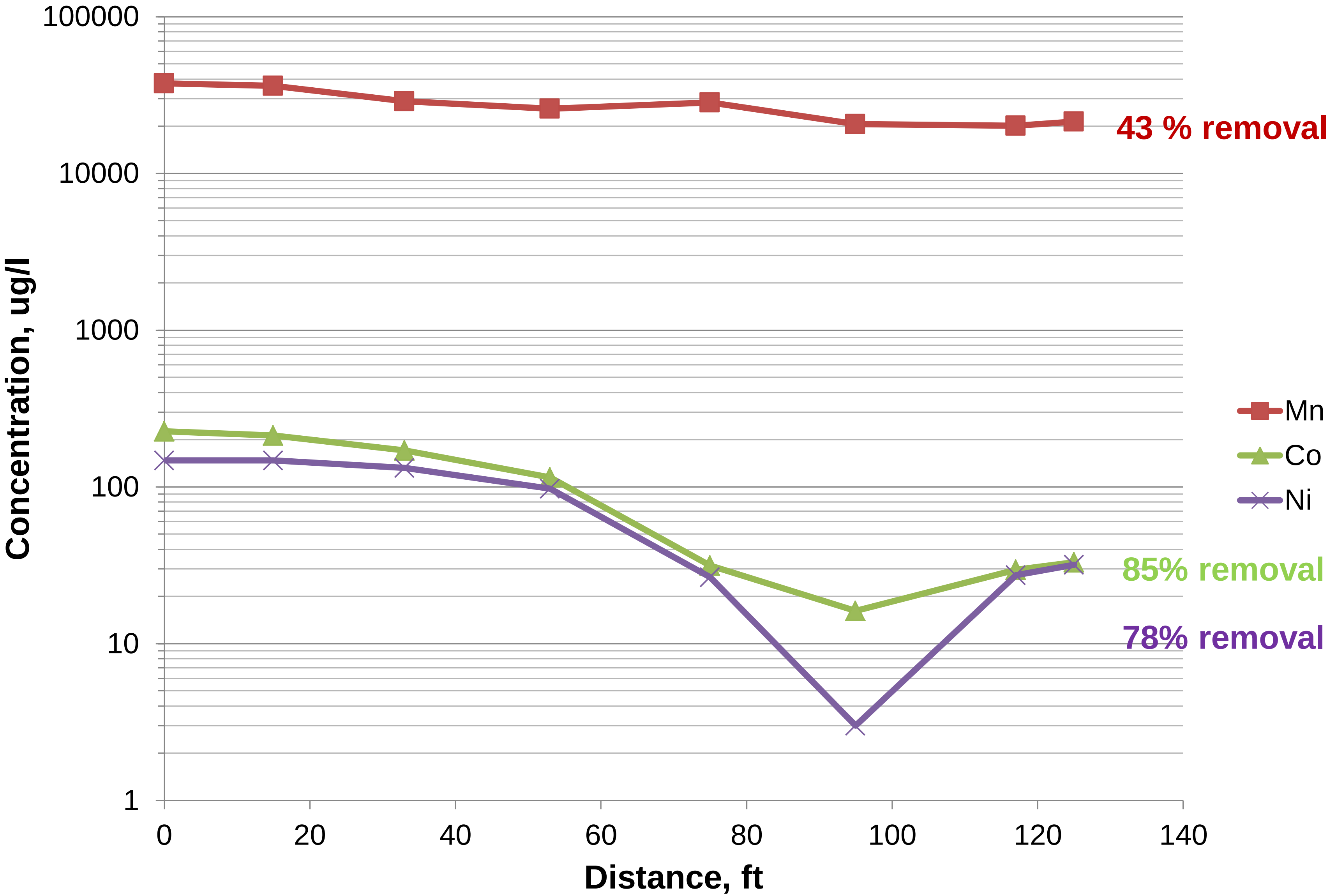
Case Studies

Desale

Desale Treatment Systems

- Forebay
- Vertical Flow Pond
  - 1 ft compost
  - 2ft limestone
- Settling pond
- Wetland
- Horizontal limestone bed
- Treatment began in 2000

Desale 2, Metal concentrations within limestone bed, July 2004



Pilot tank study

Jennings Results, Dissolved metals, concentrations in mg/l

Site	pH	Flow (ml/min)	Fe	Mn	Co	Ni	Zn
Input	6.6	131	28.4	17.1	0.13	0.19	0.06
Outflow	7.3	109	0.5	12.4	0.04	0.09	0.02
% removal			98	27	69	53	67

Metal Removal Rates

Site	Mn	Co	Ni
	gm/m^2/day	mg/m^2/day	mg/m^2/day
Desale 2	7.4	89	53
Jennings, pilot study	2.7	53	59

Nickel removal in wetlands ~ 40 mg/m^2/day

Solids Analysis

Minerals

Phase Name	Composition	Weight %
Birnessite	$NaMn_2O_4 \cdot 1.5H_2O$	Major
Todorokite	$NaMn_3O_6 \cdot 3H_2O$	Major
Takanelite	$CaMn_4O_9 \cdot 3H_2O$	Varied
Calcite	$CaCO_3$	5 – 10

Solids Analysis

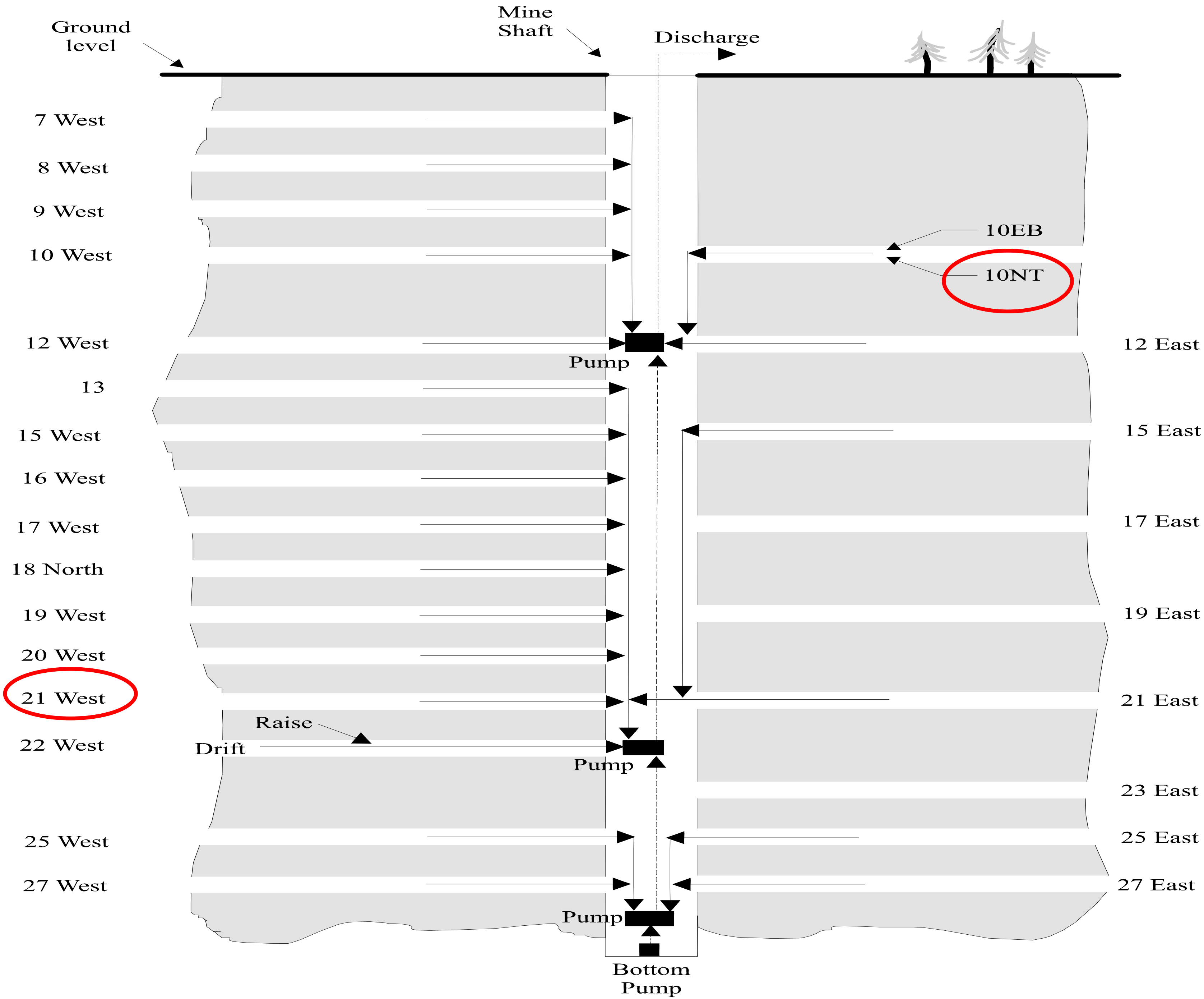
Site	MnO	Co mg/kg	Ni	Zn
	%	mg/kg	mg/kg	mg/kg
Desale 1 -A	52.9	6130	2800	2830
Desale 1 -B	52.4	5020	3120	3270
Desale 2	36.6	2480	1120	1400
Pilot Tank	17.3	2370	2330	731

And now a word from Soudan....

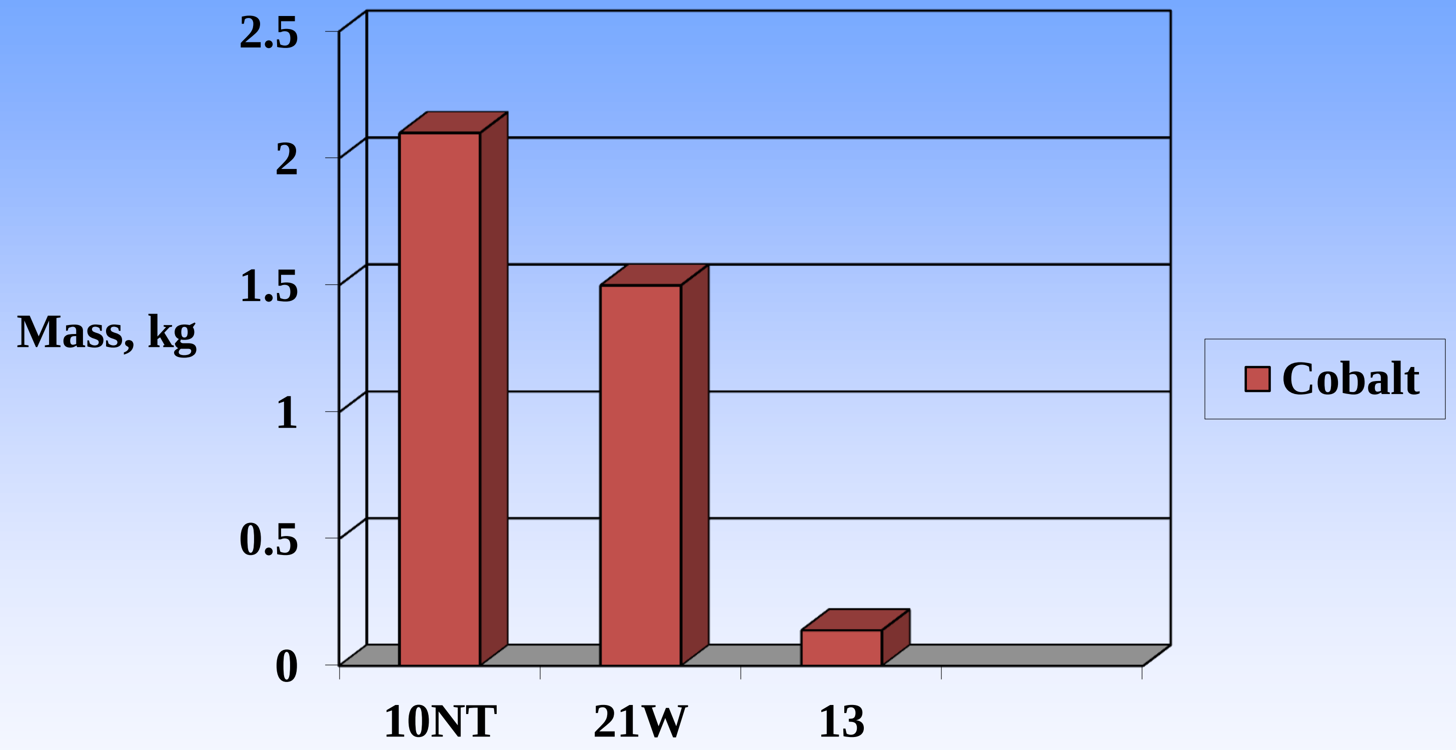
Background

- Minnesota's oldest and deepest iron mine
  - Began in 1882
  - Ended 1962
- US Steel donated mine to state
  - DNR developed a state park 1965

Becomes Paul's career project 1994


Ground level
Mine Shaft
Discharge
7 West
8 West
9 West
10 West
10EB
10NT
12 West
12 East
Pump
13
15 West
15 East
16 West
17 West
17 East
18 North
19 West
19 East
20 West
21 West
21 East
Raise
22 West
Drift
Pump
23 East
25 West
25 East
27 West
27 East
Pump
Bottom Pump

Cobalt Mass



pH	2.5
Fe	57 mg/l
Al	12 mg/l
Mn	1 mg/l
Cu	0.054 mg/l
Co	0.16 mg/l
Flow	1 gpm

pH adjustment test

Parameter	initial	Step 1	Step 2
pH	2.5	4.2	5.6
Fe	57.3	9.6	4.0
Al	12.0	7.3	0.08
Cu	0.05	0.08	<0.008
Co	0.16	0.15	0.13

All metals in mg/l

Use of a Dispersed Alkaline Substrate and Limestone Beds to Treat Acid Mine Drainage at Soudan Mine, Minnesota

Approach

Dispersed Alkaline Substrate (DAS)

- Fine grained alkaline reagent
  - –Limestone sand
- Coarse inert matrix
  - –Wood chips

Rationale

Increase pH

Remove Fe, Al.Cu

Reduce clogging

Approach

Limestone Bed

- Coarse grained limestone
- Increase pH
- Remove manganese
- Adsorb cobalt

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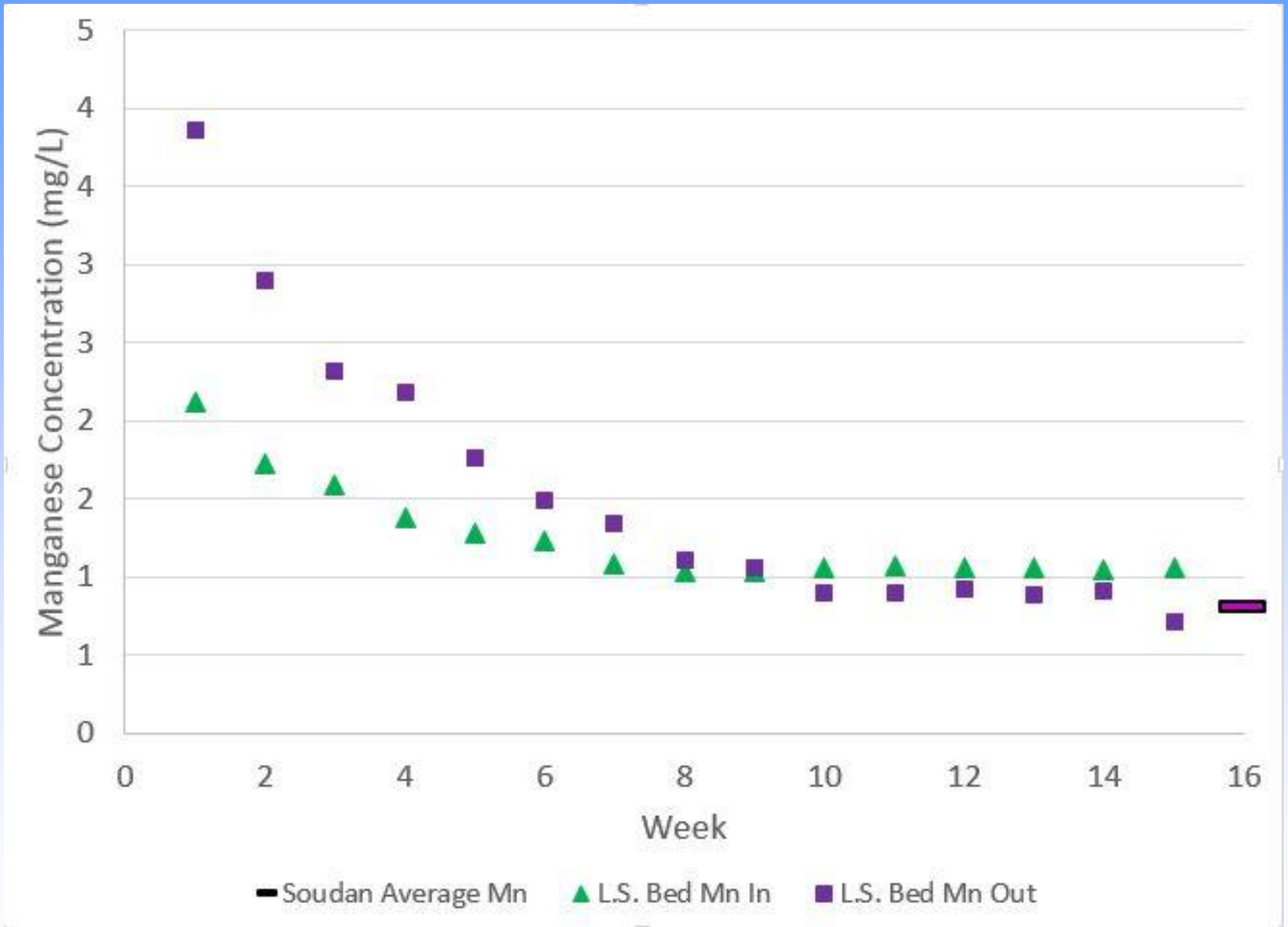
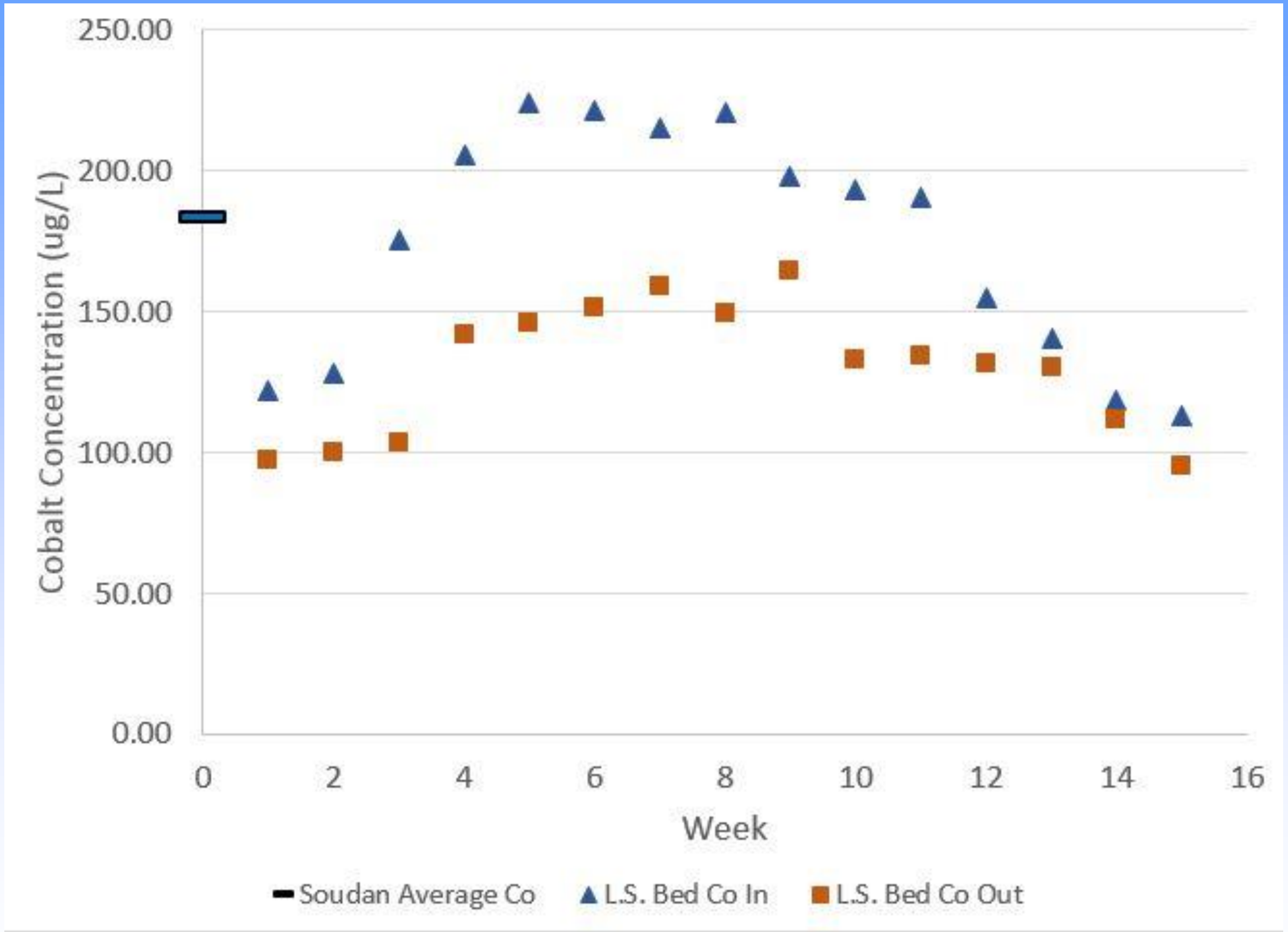
Experimental Setup

Results,Mn



Manganese Concentration (mg/L)
5
4
4
3
3
2
2
1
1
0
0
2
4
6
8
10
12
14
16
Week
Soudan Average Mn
L.S. Bed Mn In
L.S. Bed Mn Out

Results, Co


250.00
200.00
150.00
100.00
50.00
0.00
Cobalt Concentration (ug/L)
0
2
4
6
8
10
12
14
16
Week
Soudan Average Co
L.S. Bed Co In
L.S. Bed Co Out


1.52 ml/min
GSA
PHOTO SCALE/GROSS GUIDE
IN
CM
Grain Size Scale
mm

Conclusions

- Manganese oxides can remove trace metals
- Removal rates similar to wetland treatment
- Soudan story will never end
- See you in Spokane

Looking for answers?