Bioreactor and Vertical Wetland Remediation of Metal Contaminated Mining-Influenced Water

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Removing Toxic Metals from Water

- Metals need to be removed from water due to their toxicity
- Do not degrade but change forms: dissolved and particulate
- Metal forms determine bioavailability and bioaccessibility
- Metal precipitation is a common metal removal mechanism but its is not sustainable

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Mining-Influenced Water (MIW)

- There are above half million abandoned mines in the U.S. (46K in public lands)
- Acidic MIW is formed when iron sulfides are oxidized to sulfates allowing metal dissolution from mine waste
- Challenging due to sites location, weather, and variable flowrates

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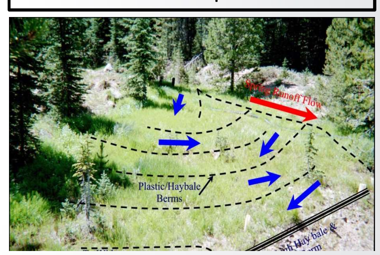
Mine Water Treatment Options: Active and Passive Systems

- Physical treatment removes particles, but not dissolved metals
- Chemical and biological remediation generate precipitates to remove dissolved salts and metals
- Systems designed as passive or active
- Treatment selection depends on: MIW quality, desired effluent quality, cost, site accessibility and surface area available, etc.

Active Systems
Require minimal inputs of resources once in operation

Image taken from www.waterworld.com

Passive Systems
Require continuous input to sustain the process



Underground SRBR at the Peerless Jenny King site, MT

- **Sulfate-reducing bioreactors and constructed wetlands are two important passive systems used to remove dissolved metals from MIW**

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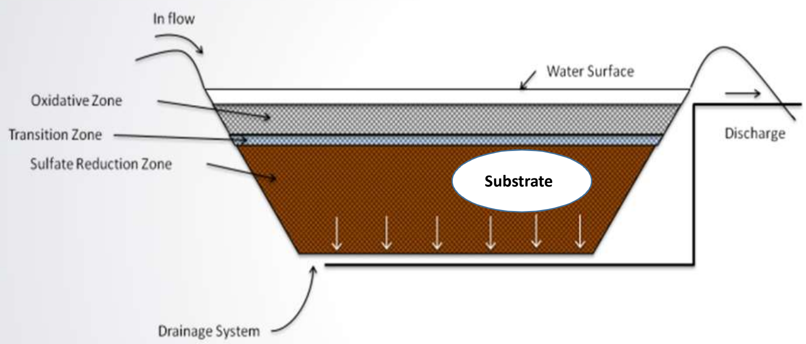
Passive Systems: Sulfate-Reducing Bioreactors (SRBRs)



- **Sulfate concentration in the influent is key**
- Main reactions:

$$SO_4^{2-}{}_{(aq)} + 2CH_2O_{(aq)} \rightarrow H_2S_{(aq)} + 2HCO_3^-{}_{(aq)} \quad (1)$$

$$M^{2+}{}_{(aq)} + H_2S_{(aq)} \rightarrow MS(s)\downarrow + 2H^+{}_{(aq)} \quad (2)$$

Where $M^{2+} = Zn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}$ and CH_2O is the substrate

- Metal precipitation to sulfide and metal adsorption are the main removal mechanisms

- The substrate is a carbon sources that acts as an electron donor for the sulfate reduction
- It promotes bacterial growth and also filters the created sludge
- It usually contains an alkaline source to neutralize influent acidity

SRBRs Design Parameters

Design parameters

- pH: SRBs thrive at pH 5-8
- Oxidation-reduction potential: Eh<0
- Hydraulic retention time (HRT=Q/V): 24 h to 168 h

Substrate

- Organic materials available at the sites are usually a low-cost option: sawdust, nut shells, wood chips, manure, etc.
- Crushed crab shells and other food waste have been successfully used as substrates for various studies
- Buffering capacity to neutralize influent acidity

EPA

Bench-Scale SRBRs

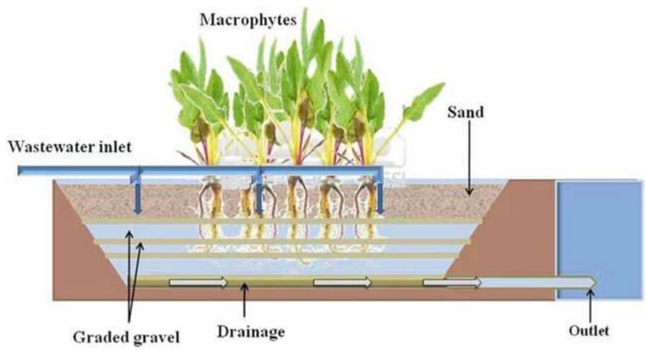
- Long-term experiments needed to find the capacity of the substrate
- Short-term experiments determine metal removal efficiency
- Potential to remove recalcitrant metals (e.g. Zn, Mn)
- Aqueous and gas phases routinely sampled for efficiency evaluation
- Spent substrate sampled to confirm metal removal mechanisms

Pilot-Scale SRBRs

- Larger system with hydraulics closer to a field system
- True passive system: uses gravity to control influent and effluent flowrate, not pumping
- Substrate porosity is critical to avoid clogging
- More difficult to keep a long-term stable operation

Vertical Constructed Wetlands

- Constructed wetlands (CW) combine biological, chemical and physical processes for water remediation with plant uptake
- Vertical wetlands (VW) feed the influent through a distribution system from the top, creating a vertical flow
- Use less space than horizontal flow wetlands,
- Suffer less clogging and have lower operational costs



Source: https://www.researchgate.net/publication/277325727_Phytoremediation_in_Constructed_Wetlands/figures?lo=1

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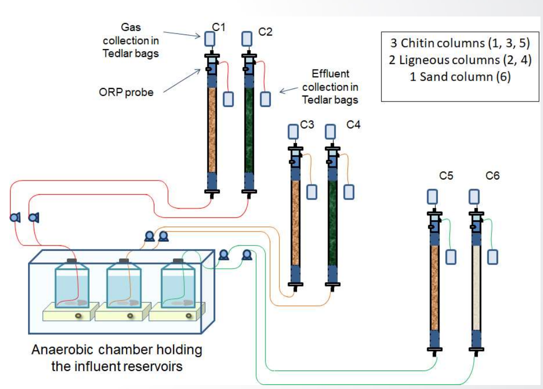
Experimental Design and Influent Water Characterization

Parameter	Unit	Influent Water	Chitinous Columns Effluent Untreated	Chitinous Columns Effluent Pretreated	Ligneous Columns Effluent Untreated	Ligneous Columns Effluent Pretreated
Operational period	Weeks	N.A.	66	105	12	50
pH	**pH units**	**2.48**	**6.39**	**7.08**	**5.41**	**5.36**
Zn	**mg/L**	**76.5**	**0.25**	**0.25**	**1.67**	**0.42**
Sulfate	**mg/L**	**2600**	**656**	**713**	**1547**	**792**
Al	mg/L	14.4	0.60	<0.1	7.09	0.15
Cu	mg/L	6.74	0.04	<0.007	0.071	0.01
Fe	mg/L	204	17.26	<0.105	6.29	1.09
Mn	mg/L	2.90	1.75	0.29	5.55	2.13
Alkalinity	mg/L Ca CO_3	570	1475	1500	568	255
Dissolved oxygen	mg/L	1.50	<1	<1	<1	<1

- **Objective: to determine zinc removal efficiency with a chitinous substrate and compare it to a ligneous substrate**
- HRT range 48-96 h
- To avoid iron content reduction during storage time, the influent reservoirs were placed in an anaerobic chamber
- Pretreatment removed Al, Cu, Fe and Mn

Bench-Scale Experimental Design



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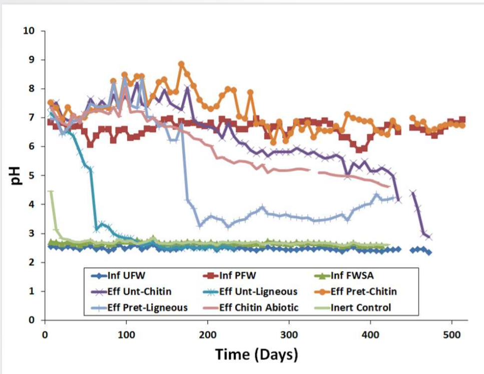
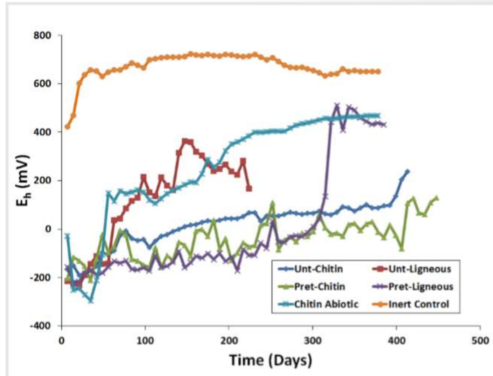
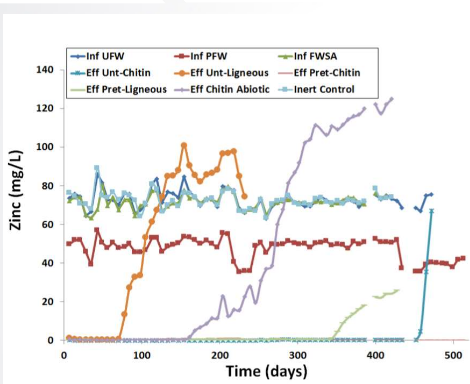
Results: pH and E_h

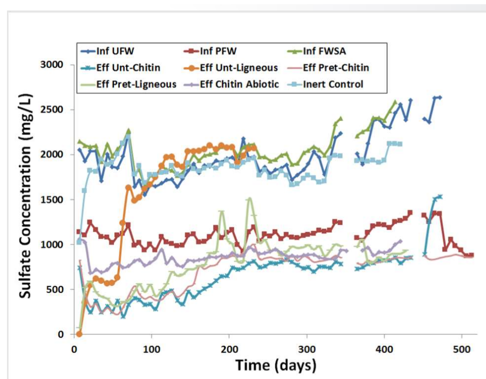




- pH in the ligneous columns decreased much faster than in chitinous columns due to the lack of buffering capacity
- The longer operational time of the pretreated columns was a result of the lower acidity of the influent
- Pretreatment extended the operational period for both substrates

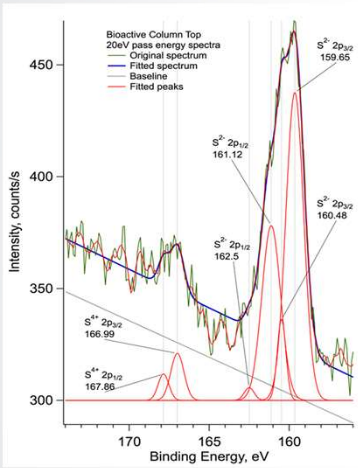
Results: Zinc and Sulfate Removal



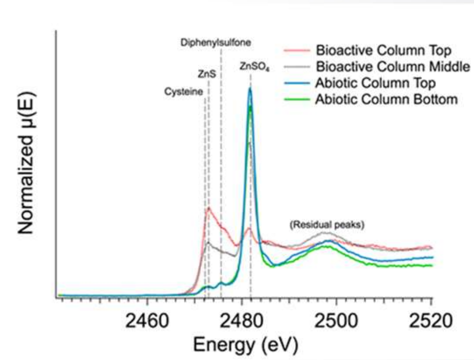


- The chitinous columns had higher sulfate reduction and higher zinc removal rates
- The ligneous columns were quick to suffer from zinc breakthrough due to a rapid increase in pH
- Zinc precipitated as ZnS according to a Visual Minteq simulation

Zinc Speciation in the Solid Residues



XPS spectral fitting in the Bioactive Column



XANES spectra of the experimental solid residues

- **ZnS confirmed with XPS and XANES**
- **ZnS found at higher concentration in the bioactive column than in the abiotic column, while $ZnSO_4$ was dominant in the abiotic column**

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Pilot-Scale Reactor (Trench Design)

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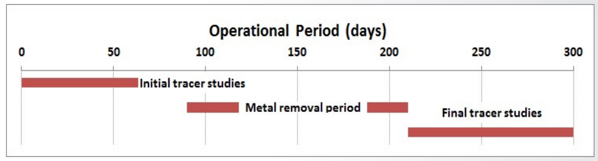
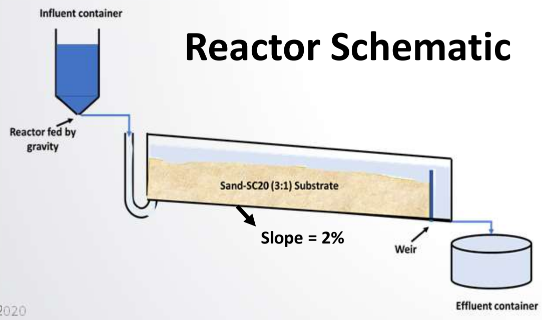
Pilot-Scale Reactor Design and Objectives

- To study the hydraulic parameters of the pilot-scale trench reactor that will eventually be scaled up to a field-scale reactor – HRT, hydraulic conductivity
- To evaluate metal (Mn, Zn) and sulfate removal in the pilot-scale reactor using a chitin product as substrate
- To compare operational parameters with those obtained in the bench-scale study



Reactor Schematic



Dimensions

Width	3.01 cm
Length	238.3 cm
Depth	8.55 cm
Reactive Volume	13.26 L

Substrate

Chitin/Sand	1/3
Total mass	10.3 kg
Substrate Depth	6.5 cm
Carbon mass in the substrate	783 g

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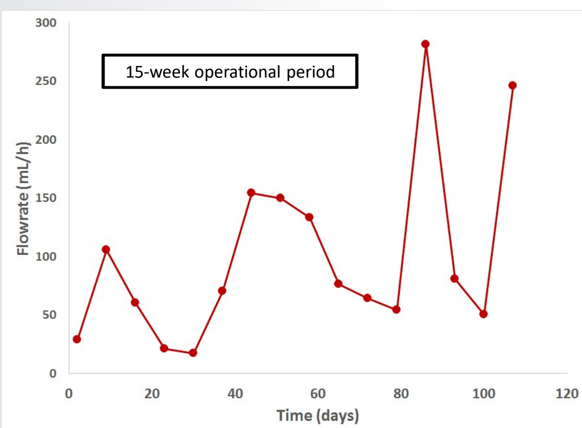
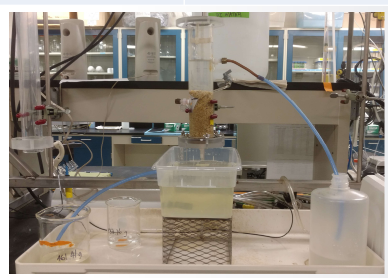
Pilot-Scale: Flowrate and substrate's hydraulic conductivity



Flowrate fluctuations reflect valve manipulations done to increase the flowrate that decreased due to clogging of the effluent outlet and reduction of hydraulic conductivity of the substrate

Substrate condition	Hydraulic conductivity (mL/h)
Fresh substrate	105.4 ± 134.0
Spent substrate	0.890 ± 0.669



*Hydraulic conductivity was measured by EPA Method 9100

- Hydraulic conductivity reduction caused reduction in the flowrate, hence we were in need of opening the effluent valve frequently to keep a flow
- A possible solution could be increasing the sand/chitin ratio in the substrate from 3/1 to 10/1

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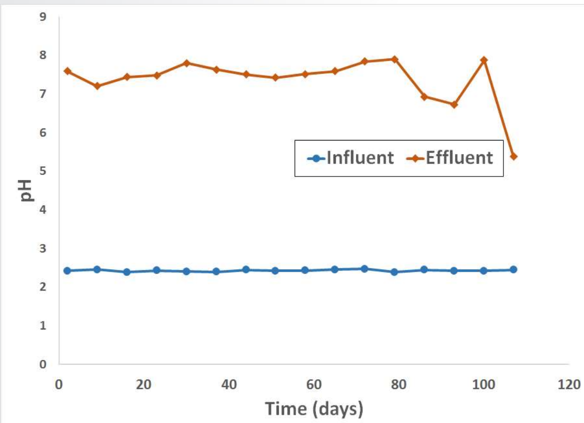
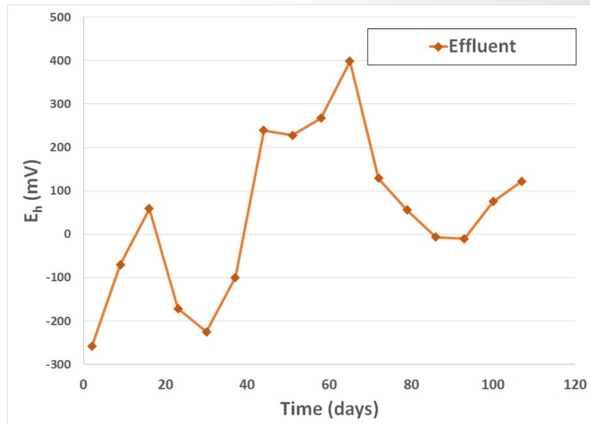
Pilot-Scale: pH and E_h

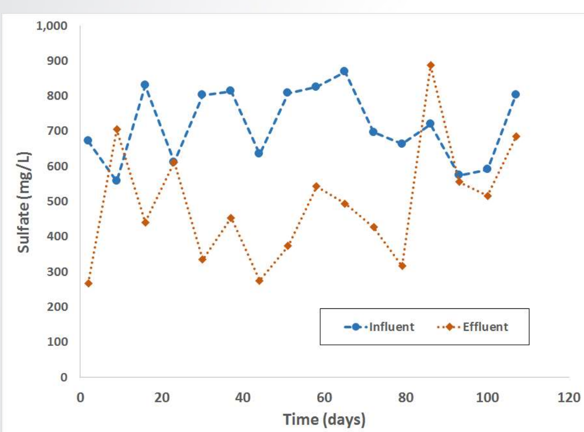


In spite of the flowrate fluctuations, pH remained stable in the effluent, until a decrease in the 15th week

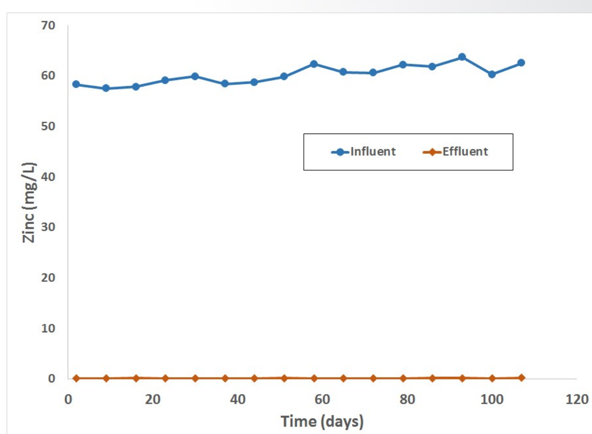


Oxidation-reduction potential fluctuated influenced by flowrate changes. Was positive for an important period.

Pilot-Scale: Sulfate and Zinc Removal



Sulfate reduction was consistent, except for a peak at the 12th week of operation. Consistent with a high peak in flowrate



In spite of the flowrate fluctuations Zinc removal was complete and steady (Zn<0.3 mg/L effluent)

Bench vs Pilot Scale Results Comparison

Parameter	Bench-Scale (Columns) Reactors	Pilot-Scale (Trench) Reactor
Operational period	74 weeks	15 weeks
Hydraulic Retention Time (HRT)	96 and 48 h m - stable	24-250 h - variable
Sulfate Removal Rate	Up to 6 $mmol/m^3/d$	Up to 1.2 $mmol/m^3/d$
Metal Removal	Mn breakthrough at 300 days, Zn did not reach breakthrough	Mn breakthrough at 105 days, Zn did not reach breakthrough
Mn and Zn Effluent Concentrations	Mn: 0.01-0.1 mg/L Zn: 0.1-0.3 mg/L	Mn: 0.5-1 mg/L Zn: 0.1-0.2 mg/L

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Adding Vertical Wetlands as a Polishing Step

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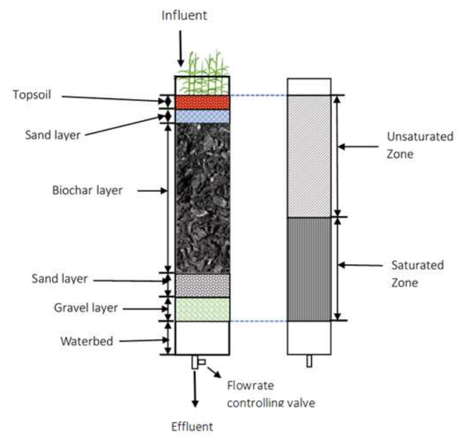
Vwet as a Polishing Step

- Aerobic Vwet remove metals by adsorption, complexation, precipitation, and plant uptake
- Increase in dissolved oxygen
- Increase pH
- Recalcitrant metals (e.g. Zn, Mn) could be further reduced
- Might not have an impact on sulfate reduction



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Conclusions

- Chitinous substrates (crushed crab shells) have an important potential to be used as a substrate in SRBRs
- They can be effective in Zn and Mn removal (two metals known as difficult to remove)
- Further research is needed with non-traditional substrates that may increase the operational period
- Vertical wetlands can be a great additional to further decrease metals and increase oxygen

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SRBRs Publications

Al-Abed, S.R., Pinto, P.X., McKernan, J., Feld-Cook, E., Lomnicki, S.M., 2017. Mechanisms and effectivity of sulfate reducing bioreactors using a chitinous substrate in treating mining influenced water. Chem. Eng. J. 323, 270-277.

Pinto, P.X., Al-Abed, S.R., McKernan, Comparison of the efficiency of chitinous and ligneous substrates in metal and sulfate removal from mining-influenced water, J Environ Manage, 227, 321-328.

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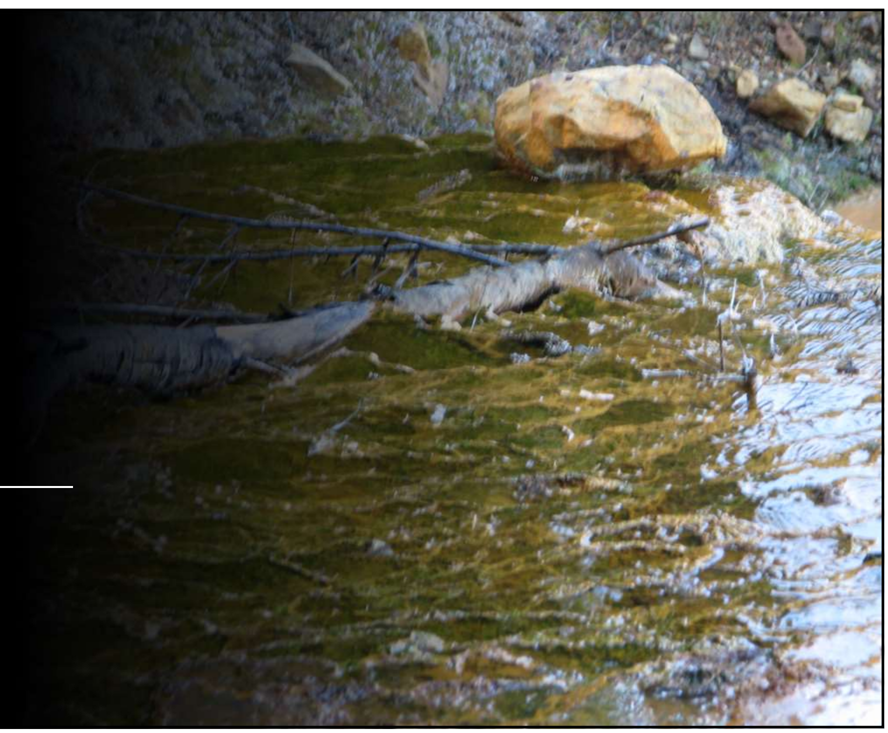
Thank you!



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