Determination of Dominant Trace Metal Sequestration Processes in Two Vertical Flow Bioreactors Using Modified Tessier Extractions

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INTRODUCTION

- **Tar Creek Superfund Site**
  - Mayer Ranch, Commerce, OK
  - Over 30 years of unabated mine drainage

- Elevated metals (Fe, Cd, Ni, Pb, Zn), mineral acidity, sulfate

- Elevated alkalinity
  - Net-alkaline discharges with circum-neutral pH

- PTS constructed and began operation in 2008
INTRODUCTION

• Vertical flow bioreactors
  – Thick layer of organic carbon substrate
  – Anoxic, reducing conditions

• Goals = generate bicarbonate alkalinity and remove trace metals as sulfides

• Reality = also removed through sorption and exchange and as carbonates and oxides
INTRODUCTION

• Many methods for evaluating removal products
  – Varied success

• Mineralogical analyses
  – XRD, SEM, TEM, XANES, SXRF, etc.
  – High concentrations of crystalline products preferred

• Total metals
  – Lack of speciation

• Acid-volatile sulfides/simultaneously extracted metals
  – Amorphous vs. crystalline
INTRODUCTION

- Sequential extractions
  - Numerous methods
  - Use specific reagents to extract targeted species
  - Species are operationally defined (e.g., acetic acid soluble)

- Tessier et al., 1979
  - Exchangeable – 1 M MgCl$_2$
  - Carbonate – 1 M NaOAc at pH 5
  - Fe-Mn oxides – 0.04 M NH$_2$OH·HCl in 25% HOAc
  - Organic – HNO$_3$/H$_2$O$_2$ then 3.2 M NH$_4$OAc in 20% HNO$_3$
  - Residual - HClO$_4$/HF
METHODS

• Two VFBR
  – Approx. 49 m x 22 m
  – 45% SMC, 45% wood chips, 10% man-sand

• Water quality evaluated monthly for 18 months

• Nine substrate cores collected at equidistant points
  – June 2010
  – Placed in Ziploc bags
  – Stored at <4°C
  – Returned to CREW labs
METHODS

- Samples dried and subsampled
  - TCLP
  - Total metals
  - Sequential extractions

- Modified Tessier method
  - Added water soluble fraction (e.g., Leinz et al., 2000)
  - Microwave assisted HNO₃ digestion for “residual”

- All fractions analyzed with ICP-OES
  - Matrix adjustments
  - Y internal standard
RESULTS – Water Quality

- Near 100% removal of trace metals in summer months
  - Not as efficient under low temperature conditions

- Reducing conditions present May – October
  - Highest temperatures
  - Lowest effluent concentrations

- No significant differences between north and south
  - Influent and effluent
## Mean Influent and Effluent Water Quality

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent (N)</th>
<th>Influent (S)</th>
<th>Effluent (N)</th>
<th>Effluent (S)</th>
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<td>pH</td>
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<td>6.84</td>
<td>6.81</td>
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<tr>
<td>DO</td>
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<td>0.94</td>
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<td>Alkalinity (mg/L as CaCO₃)</td>
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<td>151</td>
<td>259</td>
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<tr>
<td>Fe</td>
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<td>1.66</td>
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<tr>
<td>Zn</td>
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<td>1.30</td>
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<td>Co</td>
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<td>0.06</td>
<td>0.01</td>
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<tr>
<td>Ni</td>
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<tr>
<td>Mn</td>
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<td>Cd</td>
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<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
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<td>Pb</td>
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<td>0.030</td>
<td>-</td>
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<td>1-2</td>
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<td>SO₄²⁻</td>
<td>2267</td>
<td>2394</td>
<td>2405</td>
<td>2284</td>
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</table>
Temperature (°C) and 1/10 ORP (mV)

- Zinc Concentration (mg/L)
- N IN
- S IN
- N OUT
- S OUT
- Temp
- ORP
RESULTS – Sequential Extractions

- Net increase: Cd, Co, Fe, Mn, Ni, Pb, Zn
- Net decrease: K, Na
- No significant change: Al, As, Ca, Cr, Cu, Mg
- Significant differences between north and south
  - Co – exchangeable, carbonate, organic, residual
  - Zn – carbonate, oxide, organic, residual
Water soluble Exchangeable Carbonate Oxide-bound Organic-bound Residual

Percentage (%) of Total Cobalt

North
South

Water soluble: 3.82, 4.13
Exchangeable: 14.06, 17.98
Carbonate: 28.39, 37.09
Oxide-bound: 9.80, 9.20
Organic-bound: 34.85, 25.08
Residual: 9.08, 6.52
Water soluble Exchangeable Carbonate Oxide-bound Organic-bound Residual

Percentage (%) of Total Nickel

North

South

<table>
<thead>
<tr>
<th>Type</th>
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<th>South</th>
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<td>Oxide-bound</td>
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<td>Organic-bound</td>
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Water soluble Exchangeable Carbonate Oxide-bound Organic-bound Residual Percentage (%) Total Zinc

North

South

Percentage (%)

Water soluble  Exchangeable  Carbonate  Oxide-bound  Organic-bound  Residual

0.07  0.11  0.30  0.45  3.67  7.23  3.93  8.61  69.31  82.22  14.30  9.80

Total Zinc
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<th></th>
<th>Co-N</th>
<th>Co-S</th>
<th>Ni-N</th>
<th>Ni-S</th>
<th>Zn-N</th>
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CONCLUSIONS

• Trace metals are being effectively removed
  – Seasonality indicated

• Large amounts of trace metals retained in organic-bound fraction
  – Co and Ni also high in carbonate fraction
  – Residual fraction not as large as anticipated

• Explore extraction options that include greater specificity, particularly for sulfides

• Potential mineralogical analyses
  – SEM/TEM show promise and are available
ACKNOWLEDGEMENTS

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- Private Landowners
- US Dept. of Education GAANN Program
- ASMR PhD Research Grant 2011
- ASMR Memorial Scholarship, PhD Level 2012
QUESTIONS?
Temperature (°C) and pH

Manganese Concentration (mg/L)

N IN

S IN

N OUT

S OUT

Temp

ORP