The Solubility of Metals and Their Coincident Release Alamosa River Basin Soils, Colorado

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Texas A&M University
Introduction

- Several land uses depend on Alamosa River water
- Summitville Mine drainage and volcanic geology contribute to metal and acid contamination
- Terrace Reservoir is a sink/source for metals
- Alamosa River is contaminated
- Irrigation methods may contribute to increased metal concentrations (4 days)
- Mn is above water regulation standards
Summitville Gold Mine
Acidic metal-rich puddles, Summitville open pit
Natural Acidic Iron Spring
Objectives

- Impact of reduction/pH on the solubility of metals
- Time effect of waterlogged conditions on metal concentrations
- Coincident release of metals
- Plan for watershed-scale modeling
Alamosa River above Terrace Reservoir
Terrace Reservoir Inlet
Alamosa River below Terrace Reservoir
# Soil Physical Characteristics

<table>
<thead>
<tr>
<th>Soil Name</th>
<th>pH</th>
<th>EC&lt;sub&gt;e&lt;/sub&gt; (ds m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>CEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mogote-V</td>
<td>7.9</td>
<td>31.43</td>
<td>26.1</td>
</tr>
<tr>
<td>Mogote-A</td>
<td>6.3</td>
<td>2.12</td>
<td>21.4</td>
</tr>
<tr>
<td>La Jara-V</td>
<td>6.6</td>
<td>5.26</td>
<td>22.0</td>
</tr>
<tr>
<td>La Jara-A</td>
<td>5.1</td>
<td>2.71</td>
<td>16.1</td>
</tr>
</tbody>
</table>
Redox column
Nernst (Redox) Equation

Redox and pH impact metal availability

\[ \text{Eh (mV)} = \text{E}^o - \frac{59}{n} \log \left[ \frac{\text{Red}}{\text{Ox}} \right] + 59 \left( \frac{m}{n} \right) \text{pH} \]

Eh = Measure of intensity of reduction or oxidation
E^o = Standard electrode potential (V or mv)
n = # of moles of e- participating in reaction
m = concentration (moles/liter)
Initial Eh (mV) Reduced Species Appear

<table>
<thead>
<tr>
<th>Oxidized Species</th>
<th>Reduced Species</th>
<th>Initial Eh (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>N$_2$O, N$_2$ (g)</td>
<td>+300</td>
</tr>
<tr>
<td>MnO$_2$, Mn$^{4+}$</td>
<td>Mn$^{2+}$</td>
<td>+200</td>
</tr>
<tr>
<td>Fe(OH)$_3$, Fe$^{3+}$</td>
<td>Fe$^{2+}$</td>
<td>+100</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>S$^{2-}$</td>
<td>-120</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>CH$_4$</td>
<td>Below -200</td>
</tr>
</tbody>
</table>
Results

- pH, EC, and CEC are lowest for soils irrigated with Alamosa River water
- pH strongly impacts metal solubility-Mn$^{2+}$ remains solubilized at low pH
- OM% significantly impacts metal concentrations
- Treated columns: -350 mV to +600 mV
- Untreated columns: +50 mV to +600 mV
Results continued

- 12-36 hours is statistically significant for metal release with waterlogged conditions
- All systems reached a low enough Eh to support Mn reduction
- Mn increased up to 213 times in magnitude under reduced conditions
- No direct correlation of coincident release of Cu, Ni, and Zn but Ni and Zn follow Mn$^{2+}$ pattern
1. \[ \text{MnO}_2 + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + \text{H}_2\text{O} \]

2. \[ \log (\text{Mn}^{2+}) = 41.4 - 2pE - 4pH \]

3. \[ \text{Mn}^{2+} + \text{H}_2\text{CO}_3 = \text{MnCO}_3 + 2\text{H}^+ \]

4. \[ \log (\text{Mn}^{2+}) = 8.8 - \log (\text{CO}_2) - 2pH \]
pH = 6.0
At lower pH, solubility is greater
pH = 7.0

Eh (mV) vs. log (Mn$^{2+}$) plot for different Mn oxide and carbonate species at pH 7.0:
- MnO$_2$
- MnCO$_3$/$-3.52$
- MnCO$_3$/$-2.52$
- MnCO$_3$/$-1.52$
- MnCO$_3$/$-.52$
<table>
<thead>
<tr>
<th>Soil Name</th>
<th>Treatment (Dextrose)</th>
<th>Triplicate Response</th>
<th>pH (Hour) Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mogote-V</td>
<td>Untreated</td>
<td>3/3</td>
<td>12-60</td>
</tr>
<tr>
<td>Mogote-V</td>
<td>Treated</td>
<td>3/3</td>
<td>12-48</td>
</tr>
<tr>
<td>Mogote-A</td>
<td>Untreated</td>
<td>1/3</td>
<td>12-24</td>
</tr>
<tr>
<td>Mogote-A</td>
<td>Treated</td>
<td>3/3</td>
<td>12-36</td>
</tr>
<tr>
<td>La Jara-V</td>
<td>Untreated</td>
<td>3/3</td>
<td>12-36</td>
</tr>
<tr>
<td>La Jara-V</td>
<td>Treated</td>
<td>3/3</td>
<td>12-36</td>
</tr>
<tr>
<td>La Jara-A</td>
<td>Untreated</td>
<td>1/3</td>
<td>12-24</td>
</tr>
<tr>
<td>La Jara-A</td>
<td>Treated</td>
<td>3/3</td>
<td>12-24</td>
</tr>
</tbody>
</table>
# Average + or – Redox Column Metal Concentration in Soil Solution

<table>
<thead>
<tr>
<th>Soil Name</th>
<th>Treatment</th>
<th>Cu ppm</th>
<th>Fe ppm</th>
<th>Mn ppm</th>
<th>Ni ppm</th>
<th>Zn ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N</td>
<td>Yes</td>
<td>+4.0</td>
<td>+5.9</td>
<td>+74.6</td>
<td>+9.2</td>
<td>+3.0</td>
</tr>
<tr>
<td>M-N</td>
<td>No</td>
<td>+3.7</td>
<td>+39.5</td>
<td>+131</td>
<td>+2.8</td>
<td>+1.5</td>
</tr>
<tr>
<td>M-A</td>
<td>Yes</td>
<td>+1.4</td>
<td>+10.0</td>
<td>+213</td>
<td>+4.5</td>
<td>+23.9</td>
</tr>
<tr>
<td>M-A</td>
<td>No</td>
<td>+2.2</td>
<td>+45.2</td>
<td>+2.2</td>
<td>+45.2</td>
<td>+183</td>
</tr>
<tr>
<td>L-N</td>
<td>Yes</td>
<td>+1.1</td>
<td>+10.8</td>
<td>+44.3</td>
<td>+1.6</td>
<td>+3.5</td>
</tr>
<tr>
<td>L-N</td>
<td>No</td>
<td>+1.6</td>
<td>+13.9</td>
<td>+47.2</td>
<td>+2.3</td>
<td>+1.0</td>
</tr>
<tr>
<td>L-A</td>
<td>Yes</td>
<td>+1.3</td>
<td>-9.7</td>
<td>+6.3</td>
<td>+1.9</td>
<td>+6.2</td>
</tr>
<tr>
<td>L-A</td>
<td>No</td>
<td>+1.4</td>
<td>-13.7</td>
<td>+30.5</td>
<td>+3.0</td>
<td>+6.1</td>
</tr>
</tbody>
</table>
Mogote-Alamosa Flood Untreated

$y = -0.139 + 0.0156x$

$R^2$ Value = 0.97
Mogote-Alamosa Flood Treated with Dextrose

\[ y = -1.90 + 0.167x \]

0.80 R\(^2\) value

<table>
<thead>
<tr>
<th>Hours</th>
<th>Mn ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.03</td>
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<tr>
<td>12</td>
<td>2.10</td>
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<tr>
<td>24</td>
<td>4.18</td>
</tr>
<tr>
<td>36</td>
<td>6.25</td>
</tr>
<tr>
<td>48</td>
<td>8.33</td>
</tr>
<tr>
<td>60</td>
<td>10.40</td>
</tr>
</tbody>
</table>

Replicate 1
Replicate 2
Replicate 3
Mogote-Alamosa Flood Untreated

Graphs showing the relationship between Mn ppm and Eh (mV) over time, with separate graphs for Eh and pH.
Mogote-Alamosa Flood Untreated

Graphs showing data for Eh (mV), Zn ppm, Eh (mV), and pH over time in hours.
Mogote-Alamosa Flood Treated with Dextrose
Discussion

- Coprecipitation and adsorption mechanisms uncertain—Mn$^{2+}$ is ionic (availability shifts as pH changes)
- Sequential Extraction vs. EPA 3050 (800 ppm)
- Eh decreases rapidly because e$^-$ acceptors are overwhelmed by microbial activity
- Time may be the limiting factor affecting Mn$^{2+}$ concentrations
Summary

• Mn increases the most compared to Cu, Fe, Ni, and Zn
• Mn release is highest for Alamosa River irrigated soils
• Mn consistently exceeds Colorado Water Standards
• Waterlogged time and organic matter significantly affect reduced metal concentrations
• pH and Eh impact metal behavior
Conclusions

• Redox processes may be controlled through irrigation management minimizing dissolution of soluble metals
• Limit further degradation of water quality
• Laboratory redox simulations are inconsistent and must be used with caution when results are used for a field environment
Metal transport in SWAT

- Ann: Need to link watershed to in-stream processes
- Jeff: break watershed down to landscape units/include slope/pedology?
- Virginia: Economics of sampling
- Karim: Uncertainty/Continent Scale
- Armen/Stefan: C addition (based on simplified pool)
- Balaji: sediment particles size: 5 classes
- Dr. Thibodeaux: how much stress can system take
- EPIC & SWAT
Pools

- Exchangeable Ions + Surface Adsorption
- Organic Matter + Microorganisms
- Plant residues
- Minerals + Solid Phases
- Nutrient Uptake by Plants
- Air pathways
- Manures, Biosolids (soil amendments)
Problems/Future

- Timestep: sub-hourly
- Issues of data collection techniques
- Defined transport phases
- Define trends re: soil heterogeneity
- Sequence of processes
- Mineral surfaces are irregular re: chemical rxns & soln
- Need extensive database for mechanisms into transport model
- pH needs to be dynamic
Factors Controlling Rates

• Hydrologic Inputs (Tile Drains, Precipitation, Snow, Percolation, Evaporation)
• Soil Erosion (topsoil, slope)
• Water Removal (groundwater, deep aquifer, seepage, surface runoff)
• Saturated/Waterlogged conditions (Redox)
• Environmental system equilibrium
• Dynamic reactions/metabolic energy rxns/diffusion gradient
SWAT Database & Model
Parameter Inputs for Consideration

- pH (dependency), adsorption/desorption parameters (hysteresis), Kd
- Soil texture/dominant mineralogy (2:1 clays) has to be included/Transformations
- CEC (# of exchange sites limited), Vp (CO2)
- Ionic Strength & correction; activities calc from thermodyn soil-metal specific eqns & Solubility eqns.—process-based
- Solubility Constants/pKa, pKb/fast and slow rxns
- Chemical rxn rates; Temperature (lab exp are at 25C)
- Chemical residence time: change to dependence on flow velocity (Ann) vs. concentration at outlet of watershed
- water transport is essential (no water = no movement)
- Where is data available? at/above/below point sources (Forest inlet/outlet; WWTPs; septic systems, urban areas, Reservoirs, CAFOs)
- Need to input Fe, Al, Ca for pH range of interest
- Processes included: coprecipitation? Transformations? Sorption to sed? Resuspended sed?
- How much information should be required for input?
- What data is reasonable to expect user to have?
- Uncertainty? Repeatability?
- Mass balance approach? At WAS scale? Most results are from lab experiments…
### Table 10.1 Equilibrium Reactions of Iron Minerals and Complexes at 25°C

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Equilibrium Reaction</th>
<th>log K'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(OH)₃(amorp) + 3 H⁺ ⇄ Fe³⁺ + 3 H₂O</td>
<td>3.54</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OH)₂(soil) + 3 H⁺ ⇄ Fe³⁺ + 3 H₂O</td>
<td>2.70</td>
</tr>
<tr>
<td>3</td>
<td>½γ-Fe₂O₃(maghemite) + 3 H⁺ ⇄ Fe³⁺ + ½ H₂O</td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>γ-FeOOH(lepidocrocite) + 3 H⁺ ⇄ Fe³⁺ + 2 H₂O</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>½α-Fe₂O₃(hematite) + 3 H⁺ ⇄ Fe³⁺ + ½ H₂O</td>
<td>0.09</td>
</tr>
<tr>
<td>6</td>
<td>α-FeOOH(goethite) + 3 H⁺ ⇄ Fe³⁺ + 2 H₂O</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td><strong>Other Fe(III) Minerals</strong></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>FeCl₃(molysite) ⇄ Fe³⁺ + 3 Cl⁻</td>
<td>13.25</td>
</tr>
<tr>
<td>8</td>
<td>Fe₂(SO₄)₃(c) ⇄ 2Fe³⁺ + 3SO₄²⁻</td>
<td>2.89</td>
</tr>
<tr>
<td>9</td>
<td>KFe₃(SO₄)₂(OH)₆(jarosite) + 6 H⁺ ⇄ K⁺ + 3 Fe³⁺ + 2SO₄²⁻ + 6 H₂O</td>
<td>-12.51</td>
</tr>
<tr>
<td></td>
<td><strong>Fe(III) Hydrolysis</strong></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Fe³⁺ + H₂O ⇄ FeOH⁺²⁻ + H⁺</td>
<td>-2.19</td>
</tr>
<tr>
<td>11</td>
<td>Fe³⁺ + 2H₂O ⇄ Fe(OH)₂⁺ + 2H⁺</td>
<td>-5.69</td>
</tr>
<tr>
<td>12</td>
<td>Fe³⁺ + 3H₂O ⇄ Fe(OH)₃⁺ + 3H⁺</td>
<td>-13.09</td>
</tr>
<tr>
<td>13</td>
<td>Fe³⁺ + 4H₂O ⇄ Fe(OH)₄⁺ + 4H⁺</td>
<td>-21.59</td>
</tr>
<tr>
<td>14</td>
<td>2Fe³⁺ + 2H₂O ⇄ Fe₂(OH)₃⁺ + 2H⁺</td>
<td>-2.90</td>
</tr>
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<td></td>
<td><strong>Fe(III) Complexes</strong></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Fe³⁺ + Cl⁻ ⇄ FeCl⁺²⁻</td>
<td>1.48</td>
</tr>
<tr>
<td>16</td>
<td>Fe³⁺ + 2Cl⁻ ⇄ FeCl₂⁺</td>
<td>2.13</td>
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<tr>
<td>17</td>
<td>Fe³⁺ + 3Cl⁻ ⇄ FeCl₃⁺</td>
<td>0.77</td>
</tr>
<tr>
<td>18</td>
<td>Fe³⁺ + Br⁻ ⇄ FeBr⁺²⁻</td>
<td>-0.60</td>
</tr>
<tr>
<td>19</td>
<td>Fe³⁺ + 3Br⁻ ⇄ FeBr₃⁺</td>
<td>0.04</td>
</tr>
<tr>
<td>20</td>
<td>Fe³⁺ + F⁻ ⇄ FeF⁺²⁻</td>
<td>0.60</td>
</tr>
<tr>
<td>21</td>
<td>Fe³⁺ + 2F⁻ ⇄ FeF₂⁺</td>
<td>9.20</td>
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<tr>
<td>22</td>
<td>Fe³⁺ + 3F⁻ ⇄ FeF₃⁺</td>
<td>11.70</td>
</tr>
<tr>
<td>23</td>
<td>Fe³⁺ + NO₂⁻ ⇄ FeNO³⁺</td>
<td>1.00</td>
</tr>
<tr>
<td>24</td>
<td>Fe³⁺ + SO₂⁴⁻ ⇄ FeSO₃⁺</td>
<td>4.15</td>
</tr>
<tr>
<td>25</td>
<td>Fe³⁺ + 2SO₂⁴⁻ ⇄ Fe₂(SO₄)₃⁺</td>
<td>5.38</td>
</tr>
<tr>
<td>26</td>
<td>Fe³⁺ + H₂PO₄⁻ ⇄ FeH₂PO₄⁺</td>
<td>5.43</td>
</tr>
<tr>
<td>27</td>
<td>Fe³⁺ + H₃PO₄⁻ ⇄ FeH₃PO₄⁺ + H⁺</td>
<td>3.71</td>
</tr>
</tbody>
</table>

### Table 10.1 (Continued)

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Equilibrium Reaction</th>
<th>log K'</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>Fe(c) ⇄ Fe²⁺ + 2e⁻</td>
<td>15.98</td>
</tr>
<tr>
<td>29</td>
<td>Fe³⁺ + e⁻ ⇄ Fe²⁺</td>
<td>13.04</td>
</tr>
<tr>
<td>30</td>
<td>Fe₃O₄(magnetite) + 8H⁺ + 2e⁻ ⇄ 3Fe²⁺ + 4H₂O</td>
<td>35.69</td>
</tr>
<tr>
<td>31</td>
<td>Fe₃O₄(magnetite) + 8H⁺ ⇄ 3Fe²⁺ + e⁻ + 4H₂O</td>
<td>-3.42</td>
</tr>
<tr>
<td>32</td>
<td>Fe₅(OH)₉(ferrosic oxide) + 8H⁺ + 2e⁻ ⇄ 3Fe²⁺ + 8H₂O</td>
<td>43.75</td>
</tr>
<tr>
<td>33</td>
<td>Fe₅O₉S₉(wustite) + 0.10e⁻ + 2H⁺ ⇄ 0.95Fe²⁺ + H₂O</td>
<td>12.42</td>
</tr>
<tr>
<td></td>
<td><strong>Fe(II) Minerals</strong></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>FeO(c) + 2H⁺ ⇄ Fe²⁺ + H₂O</td>
<td>13.48</td>
</tr>
<tr>
<td>35</td>
<td>Fe(OH)₂(c) + 2H⁺ ⇄ Fe²⁺ + 2H₂O</td>
<td>12.90</td>
</tr>
<tr>
<td>36</td>
<td>FeCl₂(lawrencite) ⇄ Fe²⁺ + 2Cl⁻</td>
<td>9.00</td>
</tr>
<tr>
<td>37</td>
<td>FeCO₃(siderite) + 2H⁺ ⇄ Fe²⁺ + CO₂(g) + H₂O</td>
<td>7.92</td>
</tr>
<tr>
<td>38</td>
<td>FeSO₄(c) ⇄ Fe²⁺ + SO₄²⁻</td>
<td>2.65</td>
</tr>
<tr>
<td>39</td>
<td>FeSO₄·7H₂O ⇄ Fe²⁺ + SO₄²⁻ + 7H₂O</td>
<td>-2.46</td>
</tr>
<tr>
<td>40</td>
<td>FeSiO₃(c) + 2H⁺ + H₂O ⇄ Fe²⁺ + H₂SiO₄</td>
<td>14.79</td>
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<tr>
<td>41</td>
<td>Fe₂SiO₄(fayalite) + 4H⁺ ⇄ 2Fe²⁺ + H₄SiO₄</td>
<td>19.76</td>
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<td><strong>Fe(II) Hydrolysis</strong></td>
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<tr>
<td>42</td>
<td>Fe²⁺ + H₂O ⇄ FeOH⁺²⁻ + H⁺</td>
<td>-6.74</td>
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<td>43</td>
<td>Fe²⁺ + 2H₂O ⇄ Fe(OH)₂⁺ + 2H⁺</td>
<td>-16.04</td>
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<td>Fe²⁺ + 3H₂O ⇄ Fe(OH)₃⁺ + 3H⁺</td>
<td>-31.99</td>
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<td>45</td>
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<td>-46.38</td>
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<td>3Fe²⁺ + 4H₂O ⇄ Fe₃(OH)₄⁺ + 4H⁺</td>
<td>-45.39</td>
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<td><strong>Fe(II) Complexes</strong></td>
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<tr>
<td>47</td>
<td>Fe²⁺ + 2Br⁻ ⇄ FeBr₃⁺</td>
<td>0.00</td>
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<tr>
<td>48</td>
<td>Fe²⁺ + 2Cl⁻ ⇄ FeCl₂⁺</td>
<td>-0.07</td>
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<td>49</td>
<td>Fe²⁺ + 2F⁻ ⇄ FeF₂⁺</td>
<td>0.03</td>
</tr>
<tr>
<td>50</td>
<td>Fe²⁺ + H₂PO₄⁻ ⇄ FeH₂PO₄⁺</td>
<td>2.70</td>
</tr>
<tr>
<td>51</td>
<td>Fe²⁺ + H₃PO₄⁻ ⇄ FeH₃PO₄⁺ + H⁺</td>
<td>-3.60</td>
</tr>
<tr>
<td>52</td>
<td>Fe²⁺ + SO₄²⁻ ⇄ FeSO₄⁺</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Fe₃O₄·xH₂O + 8H⁺ + 2e⁻ ⇄ 3Fe²⁺ + xH₂O  40.65
i.e. of Database needs

- Need to establish soil-water chemical database
- 1. filtered concentration filtered through 0.001-um pore-size membrane (dissolved species)
- 2. colloidal concentration filtered through 0.45-um pore size membrane (subtract (1))
- 3. suspended particulate by unfiltered sample then subtract #1 & 2
- Need samples from several soil types
- compare rates of transport vs. chemical reaction rate
- Treatment of metals by wetlands, hyperaccumulators, etc.
- Methods of analysis (EPA 3050 vs. Sequential Extraction)
If want more detail then need a dataset with log K data, corrections if ionic strength changes (Na); Mass action eqns are written in terms of activities to be able to apply to all ionic strengths; ionic strength corrections can use $b^*1$ for ionic strength term or the Davies Debye-Huckel expression (which depends only on the charge of the species) used to calculate activities.
Model databases

- Models: PHREEQC: reaction/transport model—ion association modelling approach
- TRANSPEC (metal fate-TRANsport and SPECiation/complexation model; for surface aquatic systems for cationic metlas
- PHROPITZ: reaction/no transport
- MINTEQA2/PRODEFA2: Geochemical Assessment Model for Environmental Systems; equilibrium speciation model used to calculate equil [ ] of dilute aq soln in lab or natural systems
State of the Union:

• HAS: SWAT: sub-hourly runoff, plant uptake and decomposition framework, partitioning coefficient, dynamic OM pool, air pressure, database soil amendments,

• NEEDS: scale, pH range, landscape unit incl. mineralogy (major limitation), soil chemical and physical database (estimation of parameters not in DB); input soil-M eqns @ particular pH and $I$

• GOAL: metal availability/transformations
Goal: to provide a method for assessing the fate of heavy metals in soil.

- Soil layer
  - Homogeneously low permeability
  - High permeability at some spots
- Macropore flow
- Soil-Water Matrix flow
- pH > 6
- pH ≤ 6
- Small capacity for adsorption
- Large capacity for adsorption

Infiltration rate:
- ≥ 400 mm/y
- < 400 mm/y

Distance to water:
- ≥ 2 m
- < 2 m
The retardation of heavy metal cations in the soil matrix estimation

Results

Retardation factor: soil matrix & transport rate

Retardation Factor

<table>
<thead>
<tr>
<th>pH</th>
<th>5.5</th>
<th>6</th>
<th>6.5</th>
<th>7</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>3.5</td>
<td>4</td>
<td>4.5</td>
<td>5</td>
<td>5.5</td>
</tr>
<tr>
<td>Cu,Cr</td>
<td>5</td>
<td>5.5</td>
<td>6</td>
<td>6.5</td>
<td>7</td>
</tr>
<tr>
<td>Pb,Hg</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

Rf depends on pH, type of metal, content of organic material, MW, solubility, vapor pressure...

FIELD STUDIES

Transport rate (mm/year)

Retardation Factor

3 4 5 6 7 8 9 10 11 12.0
Discussion/Questions?

Thank You
Hysteresis

Hysteretic $\Theta(h)$ as measured by traditional pressure plate (PP) versus continuous flow method (CFM)

Silty clay loam

Soil Water Tension, $h$ (cm)

Water Content, $\Theta$

- $MDC$ (PP)
- PWSC (PP)
- $MWC$ (CFM)
- PWSC (CFM)
- MDC (CFM)
- $+95$ CL
- $-95$ CL
Materials and Methods

• Soils are from top 12 inches of profile
• Two virgin sites - nonirrigated, uncultivated
• Two contaminated sites - Alamosa River water
• Redox columns, Pt electrodes, 1% dextrose
• Sequential extraction
• XRD
Redox columns using Pt electrodes

Why different?
• 1. log K (stability constant) (correct for I; s/b moderate for natural water 1.45 mol/kg(nonsaline)
• 2. dissolved inorganic carbon (CO2, HCO3-, and CO32-) aka Total CO2
• 3. High Ionic Strength and redox reactions i.e. CO2 degassing leads to calcite pcp
• 4. Alkalinity: need to add Ca species and complexes to SWAT
• 5. correct for Eh reference electrode (Ag/AgCl pair)
• **EPA HAWQS:** As, Cd, Cu, Fe, Hg, Zn

• Langmuir
  • \( C/q = 1/(Kb) + C/b \)

• \( Q = \) moles of species adsorbed per kg soil
• \( K = \) constant
• \( C = \) soluble concentration mol L\(^{-1}\)
• \( B = \) adsorption capacity mol kg\(^{-1}\)

• If data reaches a plateau at high concentrations then can use Langmuir model (also use Langmuir for pesticides when amount = less than amount of adsorption capacity)
• Mass action exp for Kd (ml/g)

\[ K_d = \frac{\text{mass of adsorbate sorbed (} A_i \text{)}}{\text{mass of adsorbate in soln (} C_i \text{)}} \text{ based on } A + C_i = A_i \]

Where 
- \( A \) = free or unoccupied surface ads sites
- \( C_i \) = total dissolved adsorbate remaining in soln at equil
- \( A_i \) = amount of adsorbate on the solid at equilibrium

Chemical retardation, \( R_f \): \( R_f = \frac{V_p}{V_c} \)

Where 
- \( V_p \) = velocity of water through a control volume
- \( V_c \) = velocity of contaminant through a control volume

The \( R_f \) term does not equal unity when solute interacts with soil therefore, \( R_f > 1 \) due to solute sorption to soils; if \( R_f < 1 \) = caused by anion exclusion
La Jara-Virgin Untreated

\[ y = -0.0898 + 0.00522 \times x \]

\[ R^2 = 0.83 \] value
La Jara-Virgin Treated with Dextrose

\[ y = -0.05642 + 0.00745 \times x \]

0.67 \( R^2 \) value

Mn ppm

Hours

0 12 24 36 48

0.01 0.11 0.22 0.32 0.43 0.53 1.30 1.66 2.02 2.38 2.74 3.10

Replicate 1
Replicate 2
Replicate 3
La Jara-Alamosa Flood Untreated

$y = -0.233 + 0.0394x$

0.98 $R^2$ value
La Jara-Alamosa Flood Treated with Dextrose

$y = 0.0676 + 0.0180x$

$R^2$ value = 0.91
Mogote-Virgin Untreated

- Eh (mV)
- Mn ppm
- pH
- Mn ppm

Graphs showing the changes in Eh (mV), Mn ppm, and pH over hours for Mogote-Virgin Untreated conditions.
Mogote-Virgin Treated with Dextrose
a-c. SEM-EDS image of the cross-section of a soil particle saturated with 10 mg P L$^{-1}$. D-e. SEM-EDS image of the cross-section of a water treatment residual particle with 1000 mg P L$^{-1}$. Both individual (a-b and d-e) and joint (c and f) element maps are presented. A map that shows a color that cannot be distinguished into its elemental colors indicates an association between those elements. The lower P concentration is mostly found at the perimeter of the particle while the high P concentration is found at the interior as well as the perimeter of the particle.
Fig. 10.3 The hydrolysis species of Fe(III) in equilibrium with soil-Fe.