Water Quality of Red Mountain Creek

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Overview

• Background
  - Water chemistry
  - Fish
  - Effects of mining
  - Synoptic studies

• Red Mountain Creek
  - Water quality at low flow
  - Premining conditions
Background: Water Chemistry

- Sulfide Oxidation

  Mineralized Ore + Mining (Water & Oxygen)

  → Sulfuric Acid

- Depressed pH

  → Increased solubility for most metals (aluminum, iron, cadmium, copper, zinc...)

Sulfide Oxidation

Mineralized Ore + Mining (Water & Oxygen)

→ Sulfuric Acid

Depressed pH

→ Increased solubility for most metals (aluminum, iron, cadmium, copper, zinc...)
Background: Metal phases

- **“Dissolved”**
  - concentration after filtration
  - Metal solubility is pH-dependent (lower pH, higher concentration)

- **“Total Recoverable”**
  - unfiltered sample
  - dissolved + solids

- **Solids**
  - precipitates (iron, aluminum)
  - sorbed onto other solids (copper, lead, zinc)
### Chemistry by number (pH)

<table>
<thead>
<tr>
<th>Reaction / Removal</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III) Precipitation</td>
<td>3.5</td>
</tr>
<tr>
<td>Al Precipitation</td>
<td>4.5</td>
</tr>
<tr>
<td>Cu Sorption</td>
<td>5.5</td>
</tr>
<tr>
<td>Zn Sorption</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Reactive Transport

- Reaction / Removal
  - Fe(III) Precipitation
  - Al Precipitation
  - Cu Sorption
  - Zn Sorption

- pH
  - 3.5
  - 4.5
  - 5.5
  - 6.5

- Dilution & Reaction

- veta madre
- clean tribs
- Zn

- Dilution
- Dilution & Reaction
- transported solids

- Cu
- Zn

- pH
- Distance

- Concentration of metal ions over distance
  - August 2002
  - April 2002
  - September 2004
Background: Metals & Fish

- Toxicity depends on speciation
  “Free ion” more toxic than complexes

- Lab analysis:
  dissolved concentration = sum of dissolved species

- Example: Corkscrew gulch (pH = 3.2)
  - Dissolved Al = 11.2 mg/L
  - Free ion: Al\(^{3+}\) (22%)
  - Complexes: AlF\(^{2+}\) (3%)
    Al\(\text{SO}_4\)^{+} (70%)
    Al\(\text{SO}_4\)\(^2\)\(^-\) (5%)
Exposure Pathways: Direct Exposure via Water Column

- Adsorption to gill surface (Cd, Cu, Ni, Pb, Zn)
  - impairs oxygen uptake
  - competitive inhibition: hardness ions (Na, K, Ca, Mg) compete with metals for sites, reducing toxicity.
- Diffusion/absorption across cell walls
  - Interferes with metabolism, kidney, & regulation of Na, Cl, Ca
- Toxicity depends on pH, hardness, other constituents
  - example: Free Cu$^{2+}$ depends on pH
    hardness (Mg, Ca) competes with Cu$^{2+}$
    Cu-DOM less toxic than Cu$^{2+}$
Exposure Pathways: Indirect Exposure via Diet

- Ingestion of food or sediment:
  - metals in solid form

- Acidic conditions w/i stomach/GI:
  - low pH causes metals to remobilize (re-dissolve or desorb)
Metals and Fish

Contaminated Headwaters

- Direct Exposure
- Lack of food
- Direct Exposure
- Substrate covered w/ precipitates

Recovery/Depositional Zone (dilution & reaction)

- Impaired: Ingest prey & sediment
- Direct exposure (Zn)

Ouray

- Impaired:
  - Tolerant species only

veta madre
Water Quality Standards

- Aquatic Life Standards (State of CO, CDPHE)
  - Acute (higher concentration, shorter time)
  - Chronic (lower concentration, longer time)
- Some standards are hardness-based
  - Toxicity decreases as hardness increases
  - Higher hardness, higher standard
- Future standards: Biotic Ligand Model
  - Metal interaction w/ gill surfaces
Background: Mining
Contamination from Mining

• Rainfall – Runoff
  - Flush of evaporative salts, fine grain materials, reactive tailings
  - First flush, then dilution
  - High concentration, short duration (acute)

• Adit Discharge
  - continuous release
  - low-flow periods crucial (no dilution)
  - moderate concentration, long duration (chronic)
Rainfall – Runoff

RED RIVER, NEW MEXICO

[Graph showing discharge data with a peak on 9/18 and sample collected on 9/18]
Rainfall – Runoff

A. Discharge (CFS)

B. pH

- SO₄ (mg/L)
- Zn (µg/L)
Characterization of Low-Flow Conditions

- Metal concentrations often highest when streamflow is the lowest
- Characterize sources that contribute metals on a continuous basis (adits and acidic seeps)
- Focus of what follows
Characterization of low-flow conditions: Synoptic Studies

• Basic problem
  - Many potential sources, scarce $$
  - **Goal**: set clean up priorities
  - **Approach**: Spatial loading profiles

• Approach to watershed characterization
  - Tracer-dilution (streamflow)
  - Synoptic sampling (concentration)
  - Metal loads (streamflow x concentration)
Monitoring vs. Source Characterization

Water Quality Monitoring

- Single location, multiple times

Synoptic Sampling

- Multiple locations, single day
Source characterization: Synoptic Studies

- Many sources, few $$
- Prioritize sites, Evaluate options
- Estimate loads:

\[ Load = \text{mass/time} \]

Streamflow \times \text{Concentration}
Streamflow by Tracer-dilution

- Small streams: Standard method difficult to apply
- Synoptic sampling: measure flow at many sites
The Tracer-Dilution Method

Tracer: Salt solution

Dilution → Streamflow
Tracer-dilution observed dilution → Streamflow estimate
Synoptic Sampling

- **Goal**: ID sources @ fine spatial scale

- **Approach**:
  - subdivide into segments (bracket source areas)
  - sample at segment endpoints

- **Example**:
  - 5 kilometer study reach
  - 100-200 m segments
Synoptic Sampling: Red Mountain Creek Headwaters

- 5 km: Red Mountain pass to Ironton Park
- Spatial snapshot of:
  - streamflow (tracer dilution)
  - concentration (synoptic)
  - load (flow x concentration)
- Samples, August 2002:
  - 48 stream sites
  - 29 inflows
Geochemistry of Red Mountain Creek, Colorado, under low-flow conditions, August 2002

Stream @ 200-350 Meters
Confluence of West & East Branches

Stream @ 658 m (East)

Inflow @ 673 m (West)
Manhole Discharge
Right Bank Inflow, 965 meters
Downstream of Idarado (Start of Tailings Pipeline)

Stream @ 1360 m
Stream @ Cty Bridge (1950 m)
Inflow near American Girl Mine (2930 m)
Neutral pH Inflow, 2992 m
Stream, upstream of McIntyre Gulch, near Silver Bell Mine (3285 m)
Left bank inflow, 3740 meters
Stream above Corkscrew Gulch
(4275 meters)
Engineering (5135 m)
End of the Line, Cty Rd 20 (5377 m)
Stream & Inflow Samples

- Raw: 'Total Recoverable' = Dissolved + Solids
- Filtered: 'Dissolved'

- pH
- Metal concentrations – total & dissolved
- Tracer concentration → streamflow estimate
Stream & Inflow pH

Acidic stream
Acidic inflow (E)
Neutral inflow (W)
E-W: Geology
Dissolved Aluminum: Stream & Inflow

Dissolved Concentration [mg/l] vs. Distance [meters]

- **Stream**
- **Right Bank Inflow (East)**
- **Left Bank Inflow (West)**
- **Acute Standard**

- **East vs. West Exceeds Stds**

**Locations:**
- 965 m (Manhole)
- 1950 m (City Bridge)
- 2634 m (Champion Gulch)
- 2930 m (nr. American Girl)
- 2634 m (Champion Gulch)
- 4335 m (Corkscrew Gulch)
Iron: Stream & Inflow

Distance [meters]

Concentration [mg/l]

- Stream - Dissolved
- Right Bank Inflow (East)
- Left Bank Inflow (West)
- Stream - Total Recov.

965 m (Manhole)
1950 m (Cty Bridge)
2634 m (Champion Gulch)
2930 m (nr. American Girl)
4335 m (Corkscrew Gulch)
Arsenic Concentrations: Stream & Inflow

- **Stream - Dissolved**
- **Right Bank Inflow (East)**
- **Left Bank Inflow (West)**
- **Stream - Total Recov.**
- **Acute Std**

**Arsenic Concentrations**:
- **965 m (Manhole)**
- **1950 m (Cty Bridge)**
- **2634 m (Champion Gulch)**
- **2930 m (nr. American Girl)**
- **4335 m (Corkscrew Gulch)**
Source characterization: Metal loads

- Concentration = mass / volume
- Streamflow = volume / time
- Conc (M/V) x Flow (V/T) = mass/time = load
- Total Recoverable loads:
  
  Al, As, Cd, Cu, Fe, Pb, Zn
Total Recoverable Zinc Load

Increases in Instream Load

Identify Major Sources

965 m (Manhole)
1950 m (Cty Bridge)
Champion G.
Nr American Girl
Corkscrew Gulch
Total Recoverable Cadmium Load

- Load [mg/second]
- Distance [meters]
- Percent Contribution

Key Points:
- 965 m (Manhole)
- Corkscrew Gulch
- Champion G.
- Nr. American Girl
Source #1: Manhole Discharge
(RBI @ 965 meters)

- The Gold Medals:
  Highest Contribution for Al, As, Cd, Cu, Fe, Zn (28-44 %)

- The Bronze:
  3rd Highest for Lead
Source #2: Upstream of Injection

- Gold Medal: Pb (21%)
- Silver Medals: As, Cu
- Bronze Medals: Al, Fe
- 4th: Cd, Zn
Source #3: Champion Gulch (RBI @ 2634 meters)

- Silver Medals:
  Al (24%), Cd (14%), Fe (15%)

- The Bronze: Zn

- 5th: Cu
Source #4: Near American Girl (RBI @ 2930 meters)

- Silver Medal: Zn (16%)
- The Bronze: Cd (11%)
- 4th: Al, Fe
Conclusions: RMC at Low-Flow

- Four sources account for most of the load: Al (83%), Cd (61%), Fe (72%), Zn (69%)
  - Few sources to treat
  - Point sources easier to treat
- East side of watershed controls loading
- Metal concentrations > Aquatic Standards (Al, Cd, Cu, Pb, Zn – entire study reach)
- Low pH → w/ the exception of As and Fe, metals are not removed by reactions (w/i study reach)
Are the 2002 Low-flow Results Still Valid?
Are the 2002 results still valid?

Moran & Wentz
Fall 1972

30 years

This study
Aug 2002
Thanks to:

**Ouray County:**
Connie Hunt & Cty Board

**US EPA:**
Carol Russell & Bill Schroeder

**USGS Toxic Substances Hydrology Program**

**Local talent:**
Don Batchelder, Christopher Pikes, Walt Rule, Alan Staehle, Karin Stanley, Marianne Zegers
Pre-mining Water Quality

- Some streams are naturally acidic and metal-rich (example: Upper Snake River, CO)
- Red Mountain Creek may have been acidic & metal-rich BUT no one was there to sample
- Generic, state-wide water quality standards may not be appropriate
- Pre-mining concentrations may be used to set site-specific standards
- Pre-mining concentrations must be estimated
Estimating Premining Water Quality

- Variety of methods available
  - all have their pros & cons
  - use in combination to develop range
  - accuracy unknown
- Simulation-based approach using OTEQ
One-dimensional Transport with Equilibrium Chemistry (OTEQ)

- Reactive Transport
  - Advection/Dispersion
  - Precipitation/Sorption
  - pH dependence
- Post-remediation WQ
  - Summitville
  - Little Cottonwood UT
  - Mineral Creek (hypoth.)
  - Peru Creek (upcoming)
- Premining WQ

http://water.usgs.gov/software/OTEQ
Estimating Premining WQ: OTEQ

- **Step 1:** Calibrate model to existing conditions (results in Red)
  - Fit model to synoptic data
  - Streamflow from tracer-dilution
  - Inflow concentrations from synoptic samples
Estimating Premining WQ: OTEQ

- Step 2: Replace mining-affected inflows with inflow representing 'natural background'

Right-bank Inflow @ 564 m
Estimating Premining WQ: OTEQ

- Step 3: Estimate Premining WQ (results in blue)
  
  - Results at bottom of study reach:
    
    pH higher: 4.7
    
    Al lower: exceeds standards
    
    Cd lower: meets standards
Premining Simulation Results


- Results are for demonstration purposes only (see caveats in paper)

- Nonetheless:

  Red Mountain Creek was probably acidic and metal rich prior to mining
Thank You

“It’s the largest outhouse in the San Juan Mountains – an 8-holer”
– Bill Simon, August 2005