



# Acid-Base Accounting

**David L. Fey, USGS**

**Billings Symposium / ASMR Annual  
Meeting**

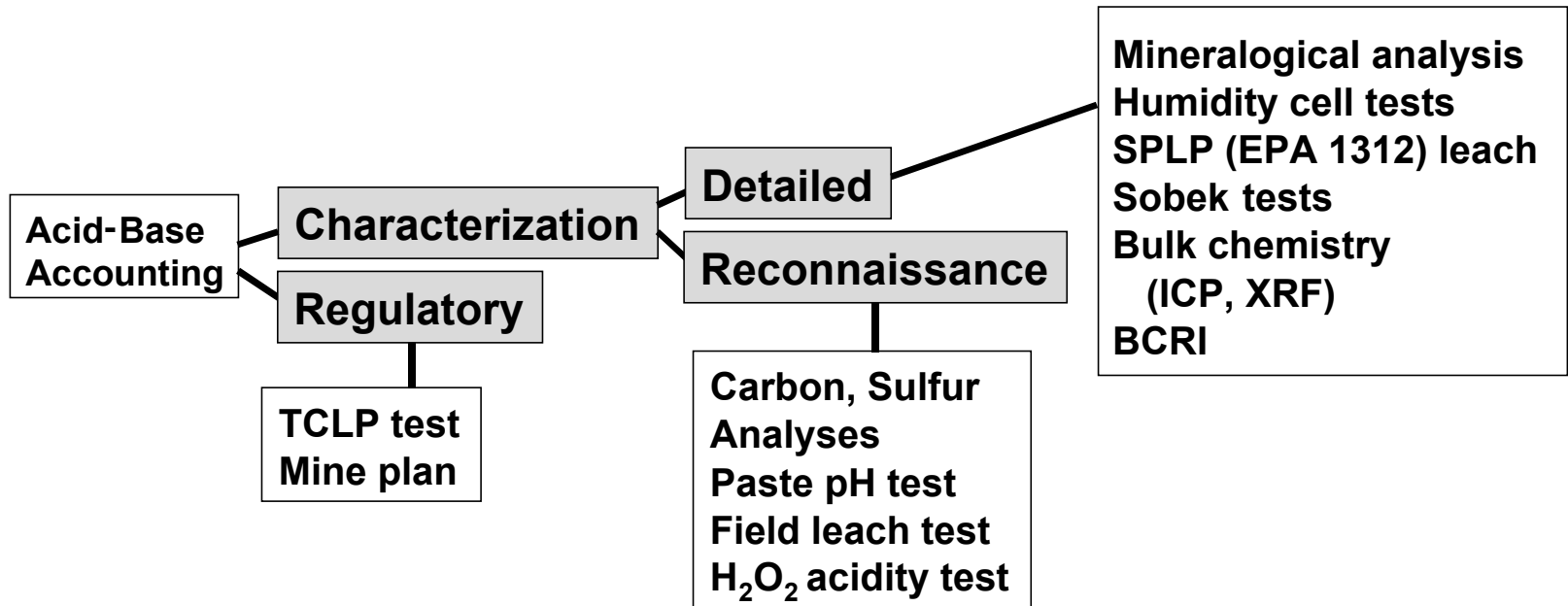
**Assessing the Toxicity Potential  
of Mine-Waste Piles Workshop**

**June 1, 2003**

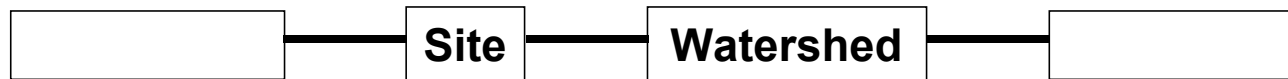
U.S. Department of the  
Interior

U.S. Geological Survey

# Flow Chart for Ranking and Prioritization



## Scale



# Acid-Base Accounting (ABA)

- Who Cares?
- What is it?
- How does one do it?
- What does it mean?

# Who Cares?

- Anyone concerned about the environmental effect from mines
- Those responsible for storing overburden, waste rock, and other mine-waste materials
- Underestimation of the Acid-Production or overestimation of Neutralization Potential can lead to incorrect decisions regarding treatment or storage.

**A typical mine site in the San Juan mountains.  
Steep slopes, ready transport of waste downhill.**

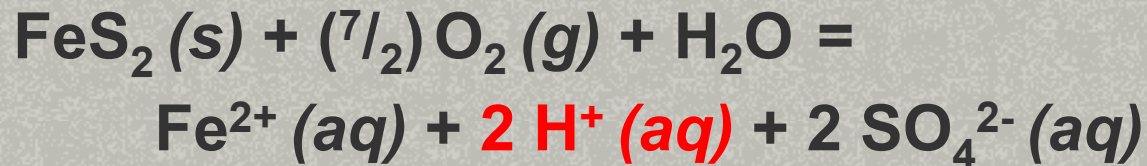


# Acid-Base Accounting: What is it?

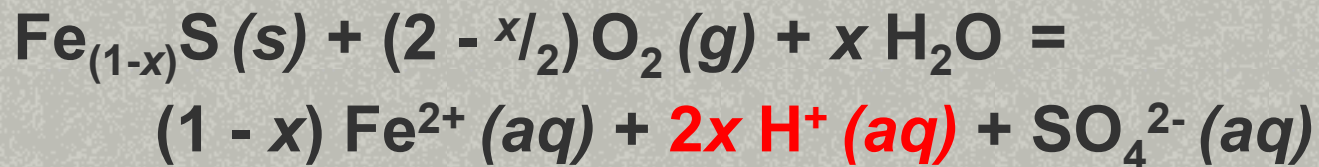
- Acid-Base Accounting (ABA) is the balance between the acid-production and acid-consumption properties of a mine-waste material.
- Minerals in waste material (mostly sulfides; mostly pyrite) react with water and oxygen to produce sulfuric acid.
- This acid is itself detrimental to water quality.
- Acid leaches metals from material and introduces them into environment.

# Some Acid Producing Reactions

## pyrite



## pyrrhotite



where x ranges between 0.000 and 0.125

**Another typical mine site in the San Juan mountains. Steep slopes, ready transport of waste downhill. Draining adit to left.**





# Some acid-generating sulfides

- Pyrite ( $\text{FeS}_2$ )
- Pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ )
- Enargite ( $\text{Cu}_3\text{AsS}_4$ )
- Marcasite ( $\text{FeS}_2$ )
- Arsenopyrite ( $\text{FeAsS}$ )
- Tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ )
- Orpiment ( $\text{AsS}$ )

# Acid Neutralization Reactions

*above pH 6.4*



*below pH 6.4*



*Or*



Other mineral dissolution reactions (chlorite, biotite, other silicates) produce less neutralization and have lower solubilities at moderate pH.

# How does one do it?

- many approaches and methods developed
- acid-producing potential
- neutralization potential of mine-waste material
- early work was applied to coal mining
- Each modification or new method has been developed to address various shortcomings, with the aim to make the end-result estimation as accurate as possible.

# Acid and Neutralization Potential

The aim of these tests is to produce an AP value (Acid Production Potential) and/or an NP value (Neutralization Potential).

Net Neutralization Potential:  $NNP = NP - AP$

And

Neutralization Potential Ratio:  $NPR = NP/AP$

The unit of measurement is kg CaCO<sub>3</sub> per ton,  
or equivalently

parts per thousand CaCO<sub>3</sub>

# Acidic leachate transports metals into headwaters of high mountain stream in San Juan mountains



# NNP and NPR

## interpretation is not simple

- If the NNP is greater than 20 kg/ton  $\text{CaCO}_3$ , it is generally accepted that the material is non-acid producing.
- If the NNP is less than  $-20$  kg/ton  $\text{CaCO}_3$ , it is generally accepted that the material is acid producing.
- NNP values between  $-20$  and 20 kg/ton  $\text{CaCO}_3$  are in the gray range of uncertainty. Kinetic tests may be needed.
- If the NPR value is  $< 1$ , the material is considered acid producing.
- If the NPR value is  $> 3$ , the material is considered non-acid producing (California and Nevada).
- If the NPR value is  $> 4$ , the material is considered non-acid producing (British Columbia).

# Methods

- Sobek method (Standard ABA method)
- Assumption: oxidation of pyrite by oxygen
- The earliest and still much-used method estimates the acid potential based on the sulfur content
- each mole of sulfur produces two moles of acid
- neutralized by one mole of calcium carbonate
- The mole ratio of sulfur to calcium carbonate is therefore 1:1. The weight ratio is then:
  - 100 g  $\text{CaCO}_3$ /mole  $\text{CaCO}_3$  : 32g S / mole S
  - or in standard AP units
  - 31.25 ‰  $\text{CaCO}_3$  per ‰ S (‰ is same as kg/ton)

## Upper limit to pyrite sulfur

- If the material contains ~ 9.5% sulfide sulfur (assuming pyrite), the rest of the material would have to be  $\text{CaCO}_3$  to meet the 3:1 criterion.
- This provides an upper boundary for sulfide content (that is, if sulfide sulfur is > 9%, no test is needed: it's acid producing).
- $(9.5 * 31.25 * 3 = 891 \text{ parts per thousand } \text{CaCO}_3)$



## Neutralization Potential by reaction with acid and back-titrating

- The NP in the Sobek test is determined by reacting the sample with HCl, and back-titrating with NaOH.
- The strength and amount of HCl to use is estimated with a “fizz test.”
- Introduces a large uncertainty in the final NP calculated.
- With a stronger amount of initial acid, the solution reacts at a lower pH and involves phases that would not react at the more realistic pH of the real situation.
- Therefore, the simple Sobek test tends to overestimate the NP of a material, and this affects the AP/NP ratio. The presence of siderite (iron carbonate) can greatly affect the laboratory determination of NP.

## Modified Sobek Method

- This method is similar to the Sobek method, but bases the AP on *sulfide* sulfur rather than *total* sulfur.
- Using total-sulfur analyses can lead to error if non-acid producing sulfates such as gypsum and barite are present.
- Also, the NP test uses an ambient temperature digestion at pH 1.5 to 2.0 (less acidic than standard method), and a titration endpoint of 8.3 instead of 7.0.
- This method can miss acidity produced by sulfates, such as copiapite. Mineralogical knowledge of the material is an important adjunct to the chemical tests.

## British Columbia Research Initial Test (BCRI)

- AP based on total S content. NP is determined by titrating a stirred mixture of mine waste and water with strong sulfuric acid to a pH of 3.5.

## NP (pH6)

- Developed by Lapakko, is similar to the BCRI test
- 1.0 N sulfuric acid is used as titrant
- The endpoint is pH 6
- This test is designed to give the “effective NP,” or the calcium carbonate equivalent NP available at pH 6.



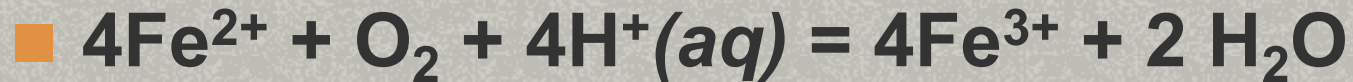
## Concerns with traditional approaches

- Presence of sulfide minerals other than pyrite
- Presence of acid-producing minerals that aren't sulfides
- Presence of carbonate minerals that don't produce alkalinity
- Presence of non-carbonate minerals that can buffer acidity (e.g., chlorite, biotite)

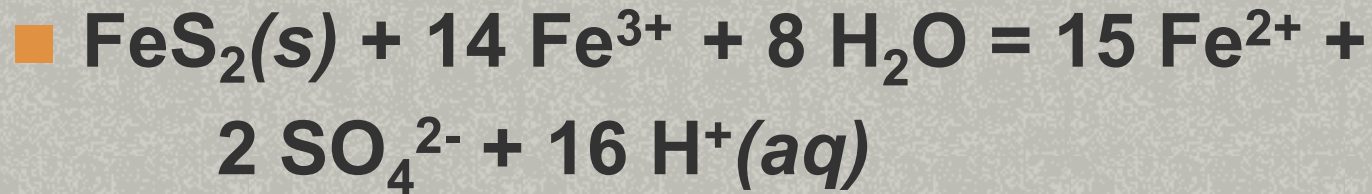
## Effect of siderite



*and*



*but*



## Hydrogen Peroxide-based Tests

- A hydrogen peroxide digestion of waste material produces acid by oxidizing sample pyrite.
- The resulting acid may be partially or wholly consumed by available neutralizing material.
- The filtered solution is titrated to pH 7 with NaOH to measure how much acidity is left.
- Provides an empirical measure of NNP that doesn't rely on assumptions about mineralogical residence.
- It does not, however, provide the individual AP and NP values, and so a NPR is not calculable.

**Field method of water analysis that  
has nothing to do with this talk**





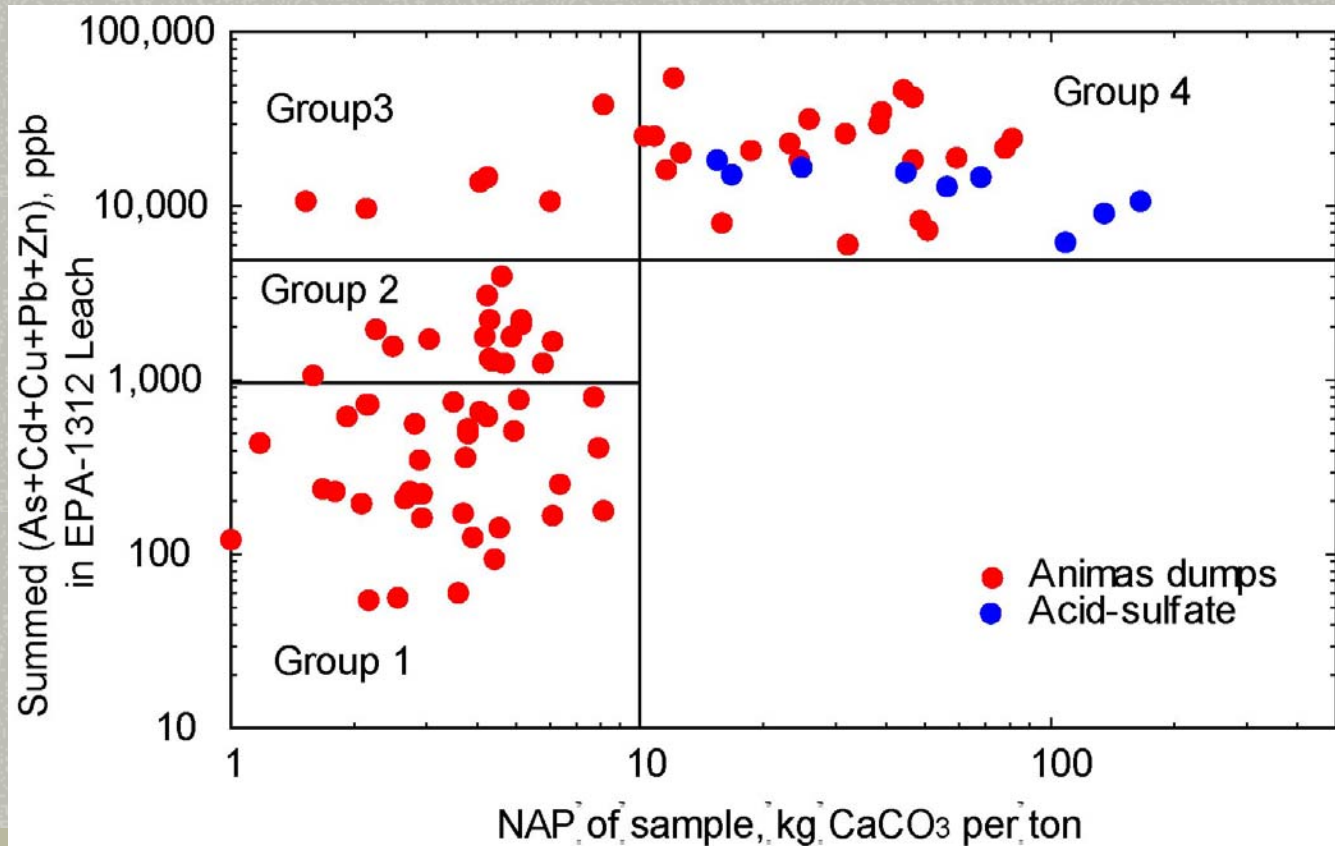
# What does it mean?

- Two case histories using Peroxide NAP method of Lapakko and Lawrence (1993)
  - 1) Animas River, southwest Colorado
  - 2) Boulder River, Jefferson County, Montana
- Watershed scale studies
- Polymetallic vein deposits
- Volcanic and plutonic terrane
- Approximately 120 samples of mine waste analyzed for NAP *and* EPA-1312 leach

## Water-soluble salts in mine waste



# Plot of net acid production (NAP) vs. summed metals in EPA-1312 leach



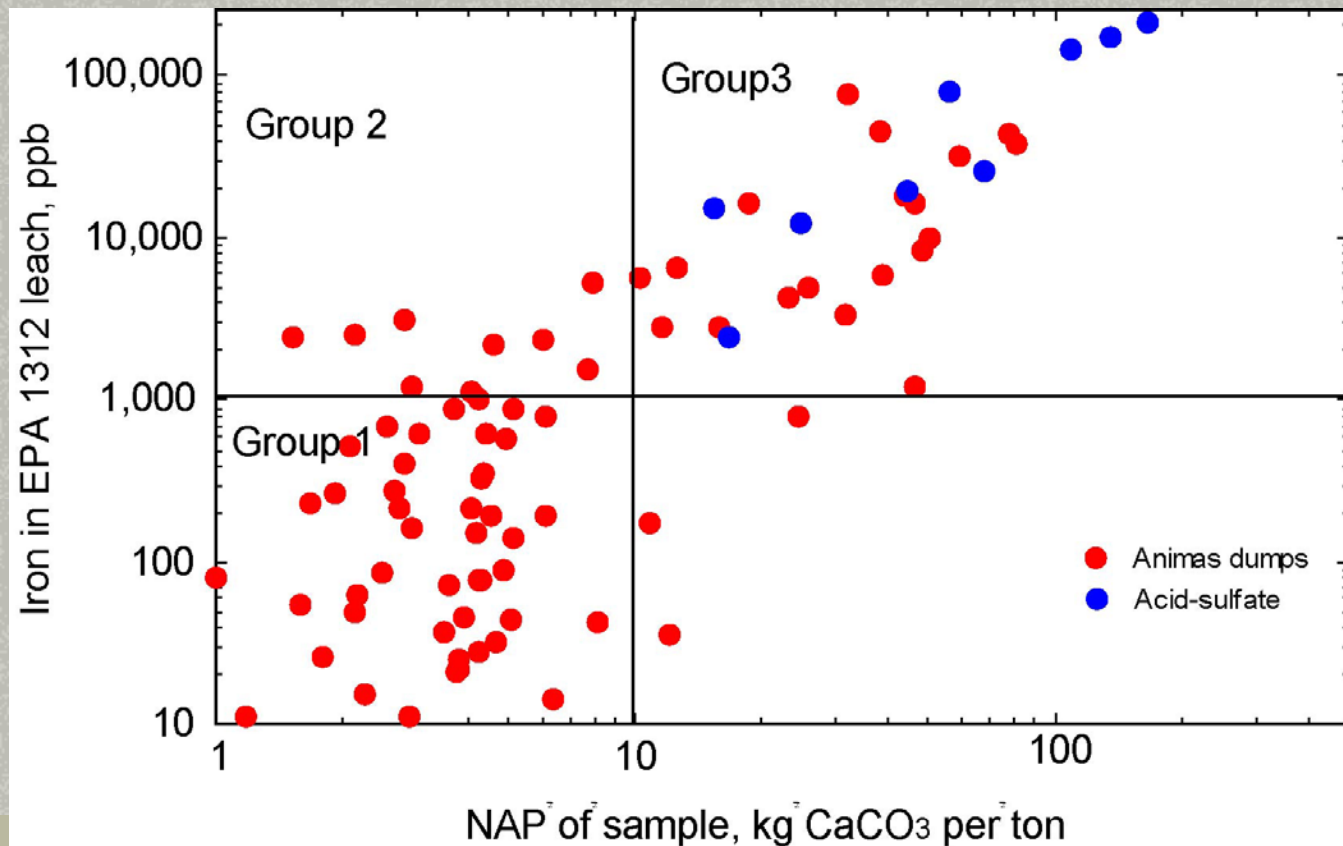
## ***Chemical* potential of mine waste to be an environmental concern**

- Plot the sum of (As+Cd+Cu+Pb+Zn) in ppb vs. the NAP as measured from peroxide test
- Can break up the data points into 4 different Groups, separated by NAP and metal concentration values
- Note that above 10 kg/ton  $\text{CaCO}_3$ , all samples from this study released more than 5,000 ppb summed metals (Group 4)
- Note that some samples with low acidity can still release high summed metals (Group 3); this is often zinc

## Group score for acidity and summed dissolved elements (SDE)

- Group 1, which has low acidity (<10 kg CaCO<sub>3</sub>/ton) and <1,000 μg/L SDE
- Group 2, which has low acidity and moderate SDE (between 1,000 and 5,000 μg/L)
- Group 3, which has low acidity and high SDE (>5,000 μg/L)
- Group 4, which has high acidity (>10 kg CaCO<sub>3</sub>/ton) and high SDE (>5,000 μg/L)

# Plot of net acid production (NAP) vs. Iron in EPA-1312 leach



## Group score for acidity and dissolved iron

- Iron plotted separately, or would dominate the plot
- Iron a problem either as a toxic component or as reactant in acid-producing reactions
- Group 1, which has low acidity (<10 kg CaCO<sub>3</sub>/ton) and dissolved iron less than 1,000 μg/L
- Group 2, which has low acidity (<10 kg CaCO<sub>3</sub>/ton) and dissolved iron greater than 1,000 μg/L
- Group 3, which has high acidity (>10 kg CaCO<sub>3</sub>/ton) and dissolved iron greater than 1,000 μg/L

## Aspects of the leachate chemistry groups

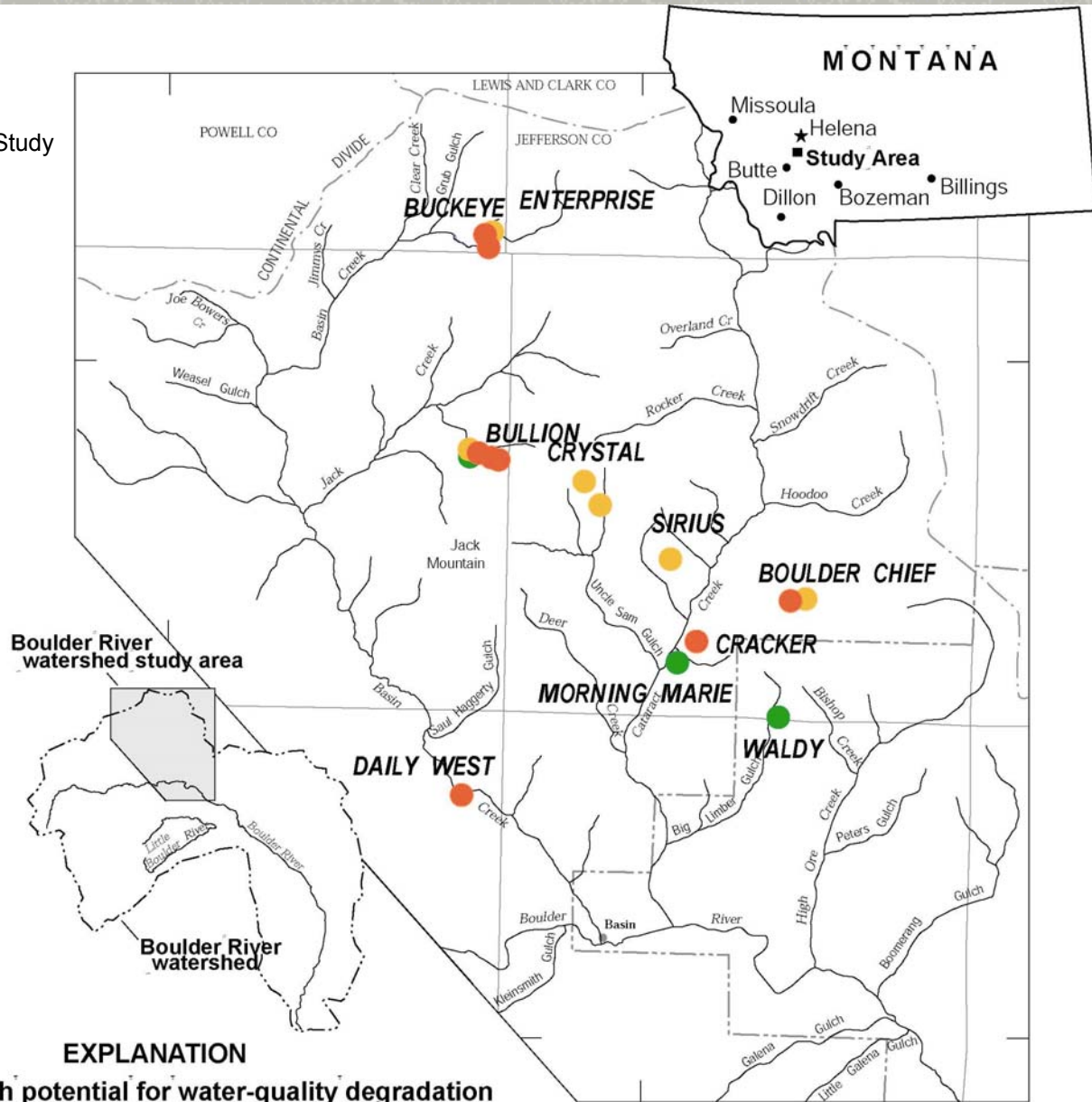
- **NAP > 10 kg/ton produce metal-rich leachates**
- **NAP < 10 kg/ton can produce either metal-poor or metal-rich leachates**
- **Near-neutral pH or near-zero acidity leachate can contain high zinc concentrations**



# The size of the waste pile also influences the ranking

- for size <500 tons, Group 1
  - for size between 500 and 2,500 tons, Group 2
  - for size >2,500 tons, Group 3
  - (this size ranking only for this study)
- 
- Add the Group scores from summed dissolved metals, dissolved iron, and size for range of 3 to 10. Rank of 3 means low, rank of 10 means very high potential for environmental effect
  - Should still account for other site factors, such as draining adits, proximity to ground or surface water, water flowing across dumps, and others

Map of Boulder Study area



**EXPLANATION**

- High potential for water-quality degradation
- Intermediate potential for water-quality degradation
- Low potential for water-quality degradation

