Acid-Base Accounting

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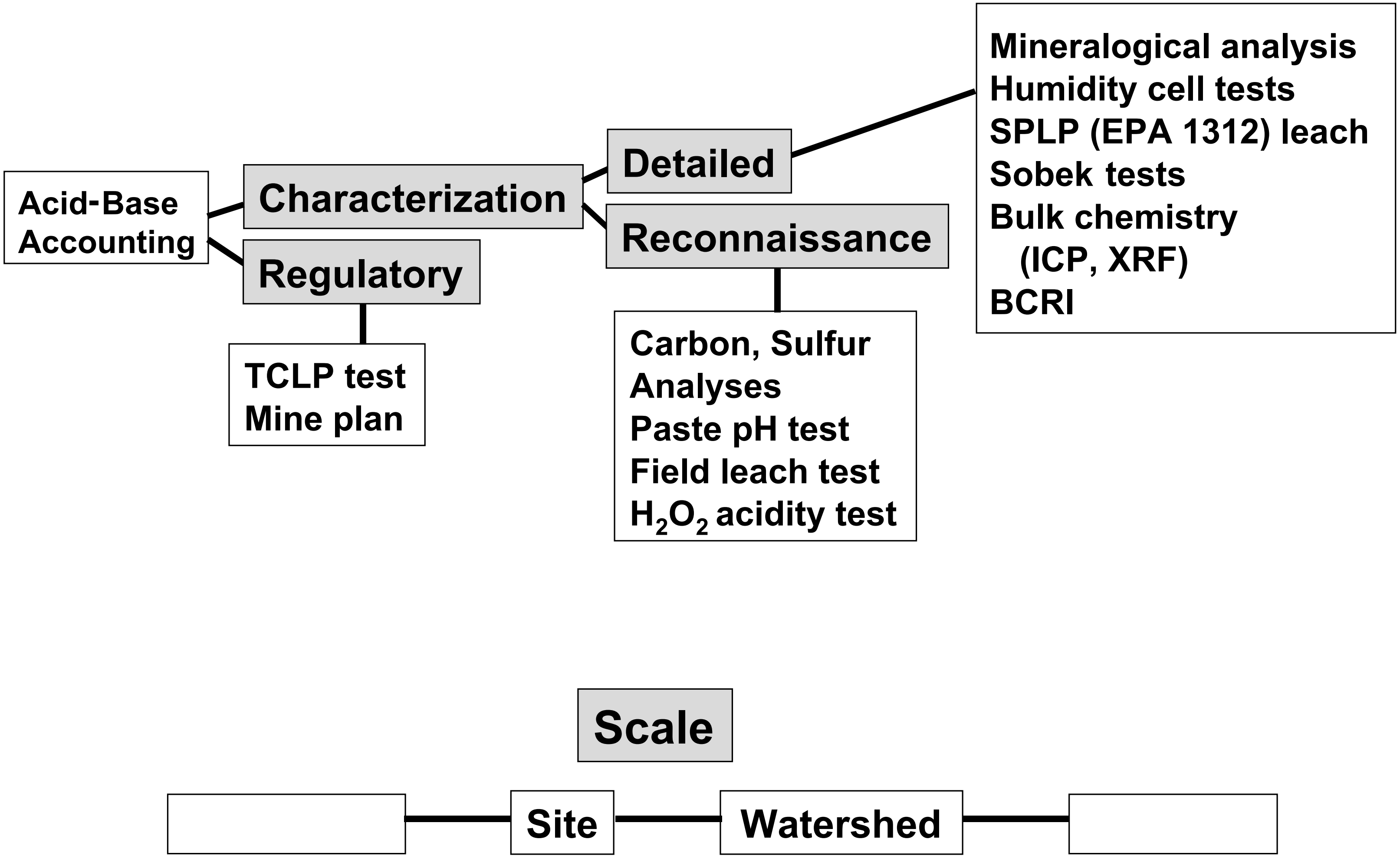
U.S. Department of the Interior

U.S. Geological Survey

Flow Chart for Ranking and Prioritization



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.

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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.

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Some Acid Producing Reactions

pyrite

$$FeS_2\,(s) + (^7/_2)\,O_2\,(g) + H_2O =$$
$$Fe^{2+}\,(aq) + 2\,H^+\,(aq) + 2\,SO_4^{2-}\,(aq)$$

pyrrhotite

$$Fe_{(1-x)}S\,(s) + (2 - {}^x/_2)\,O_2\,(g) + x\,H_2O =$$
$$(1 - x)\,Fe^{2+}\,(aq) + 2x\,H^+\,(aq) + SO_4^{2-}\,(aq)$$

where x ranges between 0.000 and 0.125

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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 (FeS_2)
- Pyrrhotite ($Fe_{1-x}S$)
- Enargite (Cu_3AsS_4)
- Marcasite (FeS_2)
- Arsenopyrite (FeAsS)
- Tennantite ($Cu_{12}As_4S_{13}$)
- Orpiment (AsS)

Acid Neutralization Reactions

above pH 6.4

$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq)$

below pH 6.4

$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq)$

Or

$CaCO_3(s) + H_2SO_4 = CaSO_4(s) + CO_2(g) + H_2O$

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

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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.

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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 $CaCO_3$ per ton, or equivalently

parts per thousand $CaCO_3$

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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 $CaCO_3$, it is generally accepted that the material is non-acid producing.
- If the NNP is less than –20 kg/ton $CaCO_3$, it is generally accepted that the material is acid producing.
- NNP values between –20 and 20 kg/ton $CaCO_3$ 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).

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Methods

- <u>**Sobek method (Standard ABA method)**</u>
- <u>**Assumption: oxidation of pyrite by oxygen**</u>

- **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 $CaCO_3$/mole $CaCO_3$: 32g S / mole S**
- **or in standard AP units**

- **31.25 ‰ $CaCO_3$ per % S (‰ is same as kg/ton)**

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Upper limit to pyrite sulfur

- If the material contains ~ 9.5% sulfide sulfur (assuming pyrite), the rest of the material would have to be $CaCO_3$ 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 parts per thousand $CaCO_3$)

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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.

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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.

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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)

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Effect of siderite

- $FeCO_3 + H_2SO_4 = Fe^{2+} + H_2CO_3 + SO_4^{2-}$

  and

- $4Fe^{2+} + O_2 + 4H^+(aq) = 4Fe^{3+} + 2\ H_2O$

  but

- $FeS_2(s) + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+(aq)$

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

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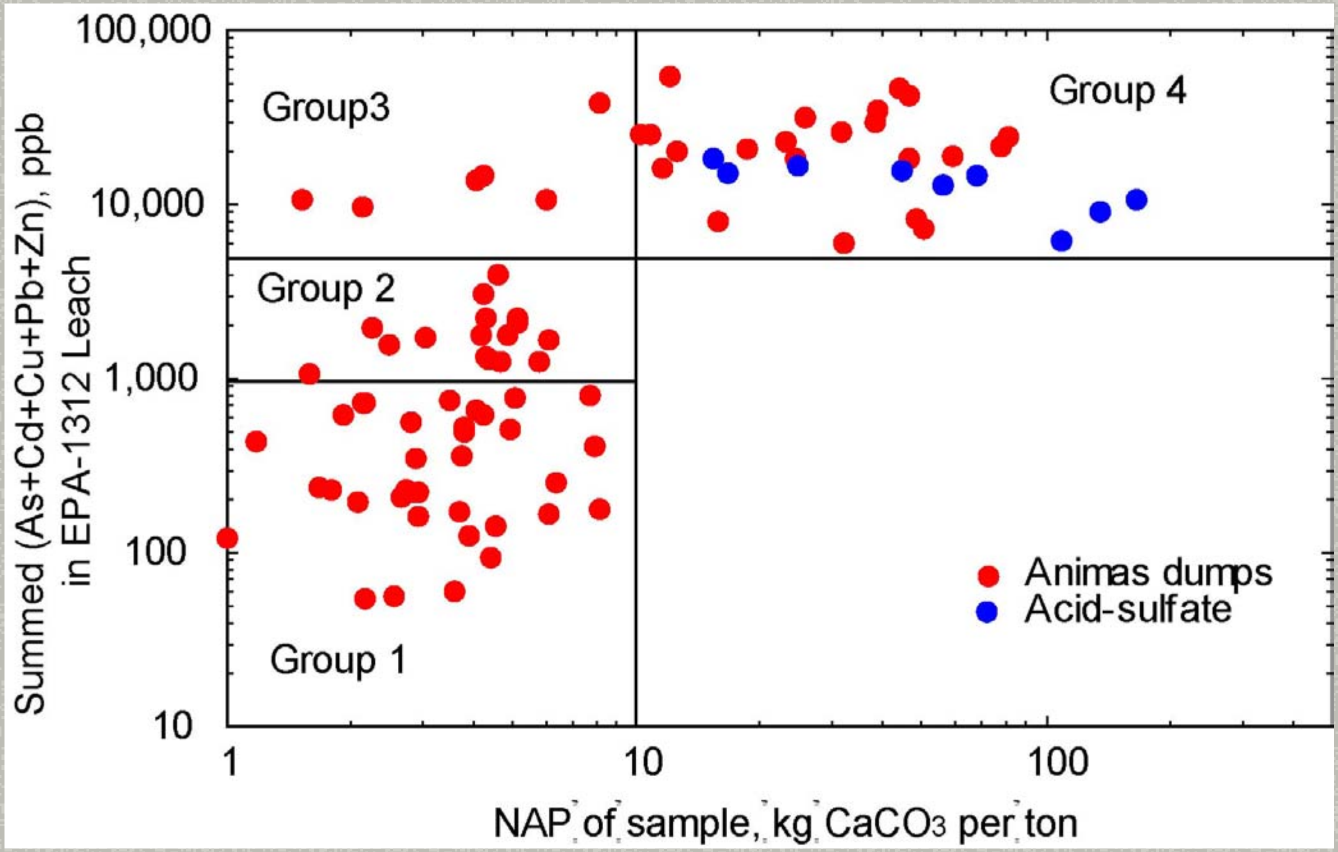
Water-soluble salts in mine waste

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



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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 $CaCO_3$, 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

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Group score for acidity and summed dissolved elements (SDE)

- Group 1, which has low acidity (<10 kg $CaCO_3$/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 $CaCO_3$ /ton) and high SDE (>5,000 μg/L)

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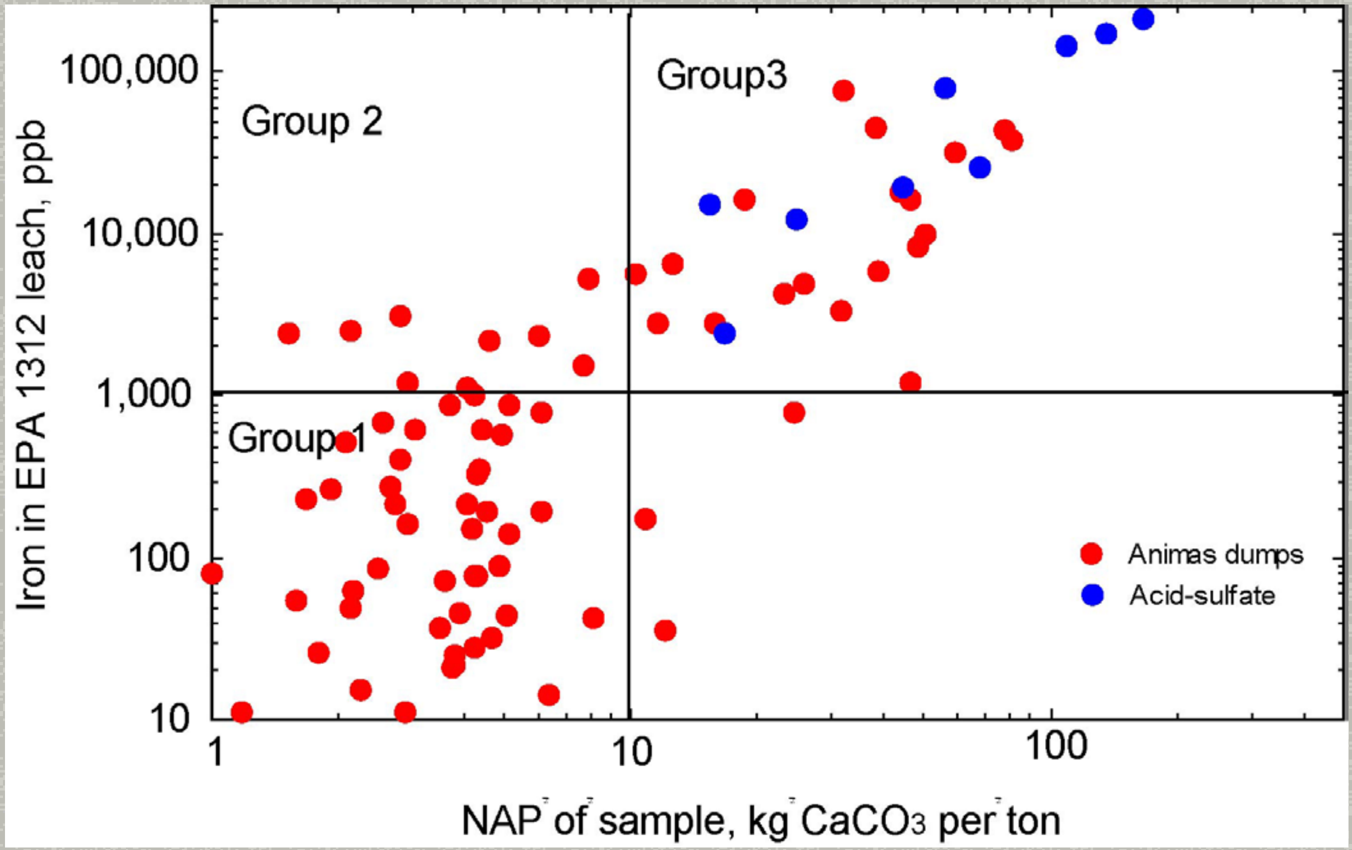
Plot of net acid production (NAP) vs. Iron in EPA-1312 leach



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 $CaCO_3$/ton) and dissolved iron less than 1,000 μg/L
- Group 2, which has low acidity (<10 kg $CaCO_3$/ton) and dissolved iron greater than 1,000 μg/L
- Group 3, which has high acidity (>10 kg $CaCO_3$ /ton) and dissolved iron greater than 1,000 μg/L

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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

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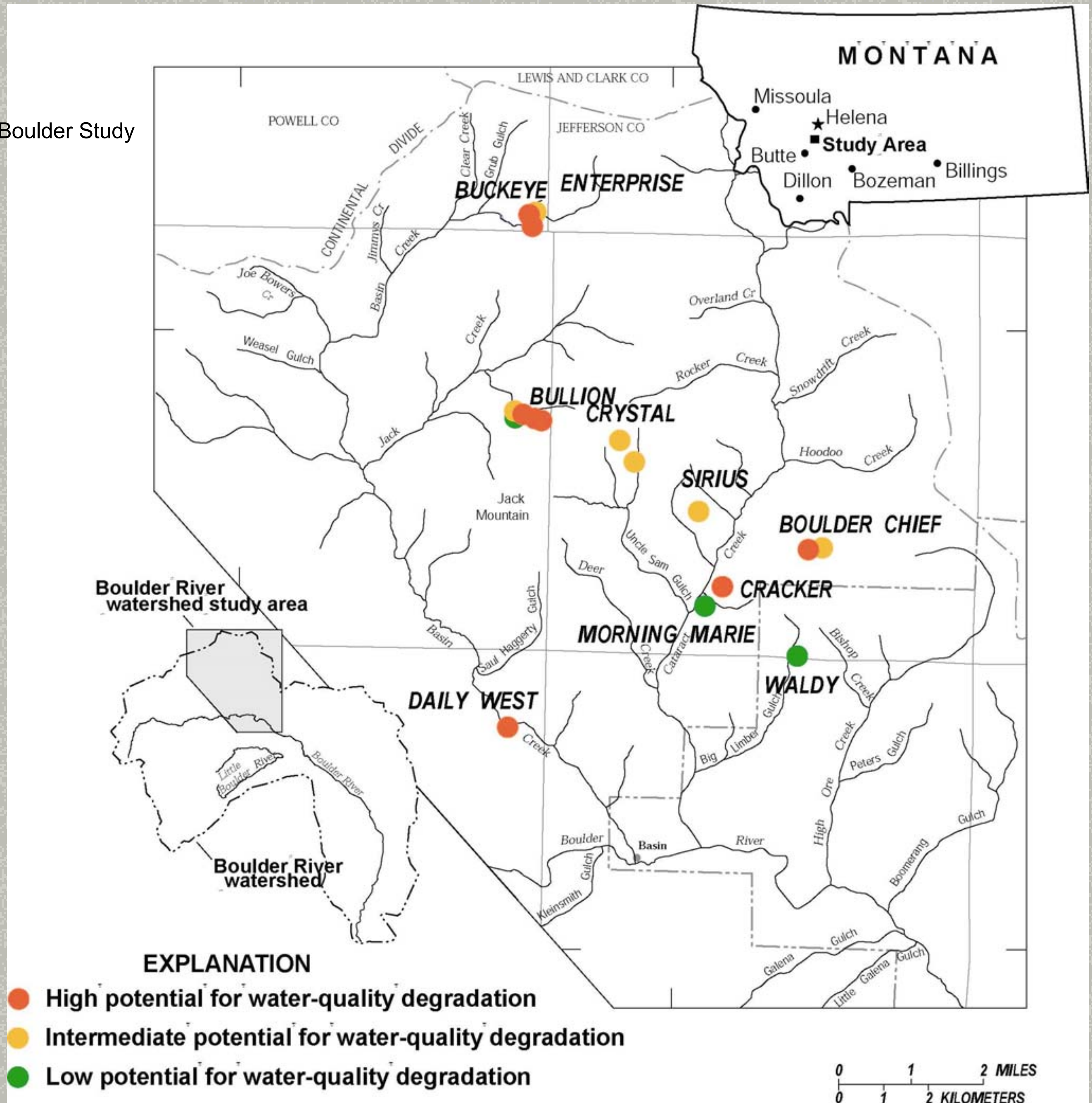
The size of the waste pile also influences the ranking

- 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



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