

Pre-Mining Characterization and Prediction

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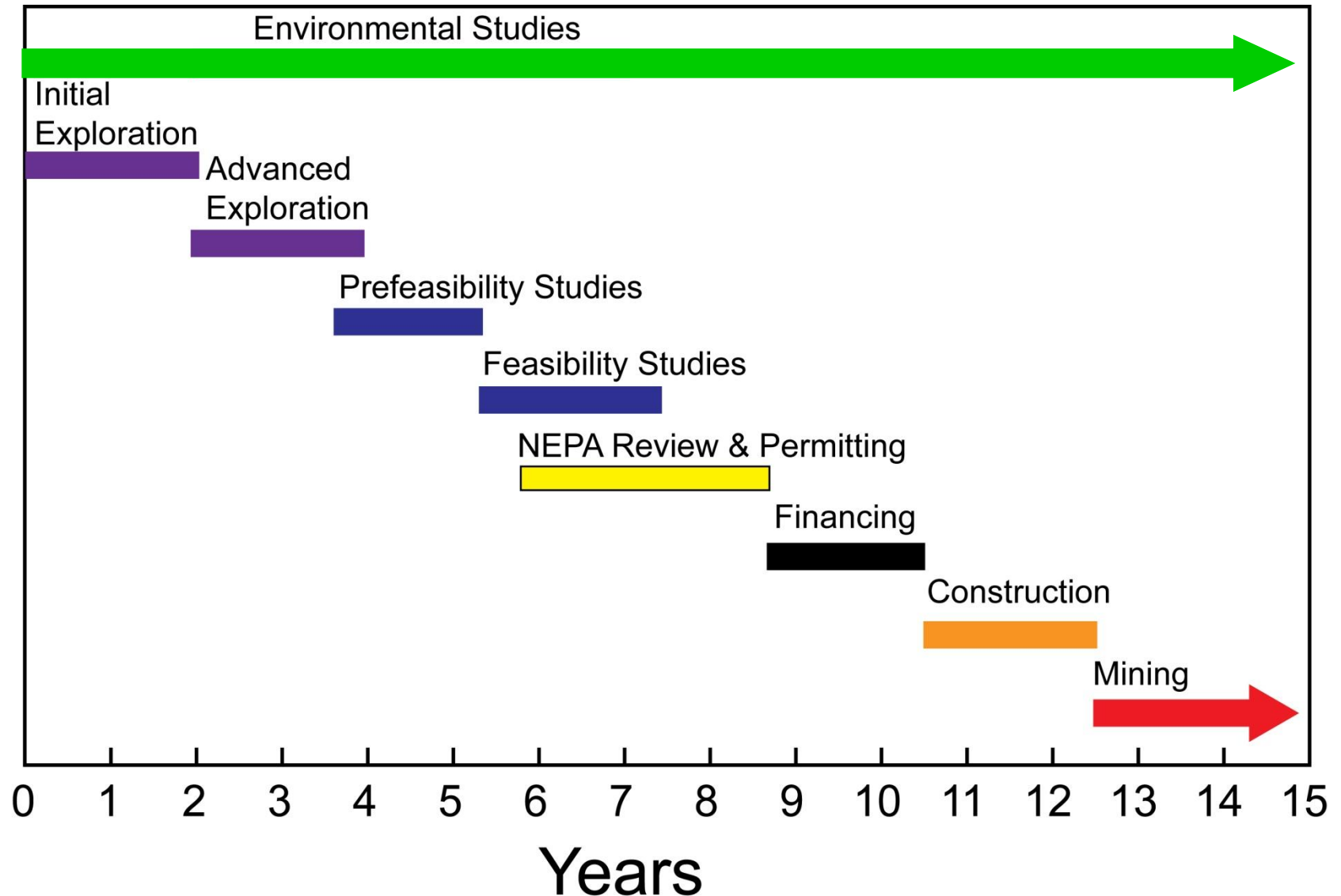
Environmental Geochemistry & Mining

How does it fit in?

What is important?

What do you look for?

“Typical” Time Frame for Mine Project Start Up



Two Main Goals of Environmental Geochemistry

- Characterization of baseline (pre-mining) conditions
 - Establishes monitoring sites.
 - Forms basis of environmental goals for closure.
 - Provides crucial information for design.
- Prediction of behavior of mine wastes
 - Needed to design mitigation and remediation during production and for closure.

Importance of Geochemical Baseline Characterization

- Ore deposits are geochemical anomalies that express themselves in all media:
 - Surface water, groundwater, sediment, soil, biota
- Natural pre-mining geochemical conditions commonly exceed various environmental criteria for surface and ground water, soils, and sediments.
- Difficult to determine pre-mining conditions once mining has started.
- Needs geology as a guide.
- Needs to be done in an up to date regulatory context.
- Provides useful insights for mine planning.
 - Water mass balance.
 - Ground-water chemistry that may need to be pumped during mining.

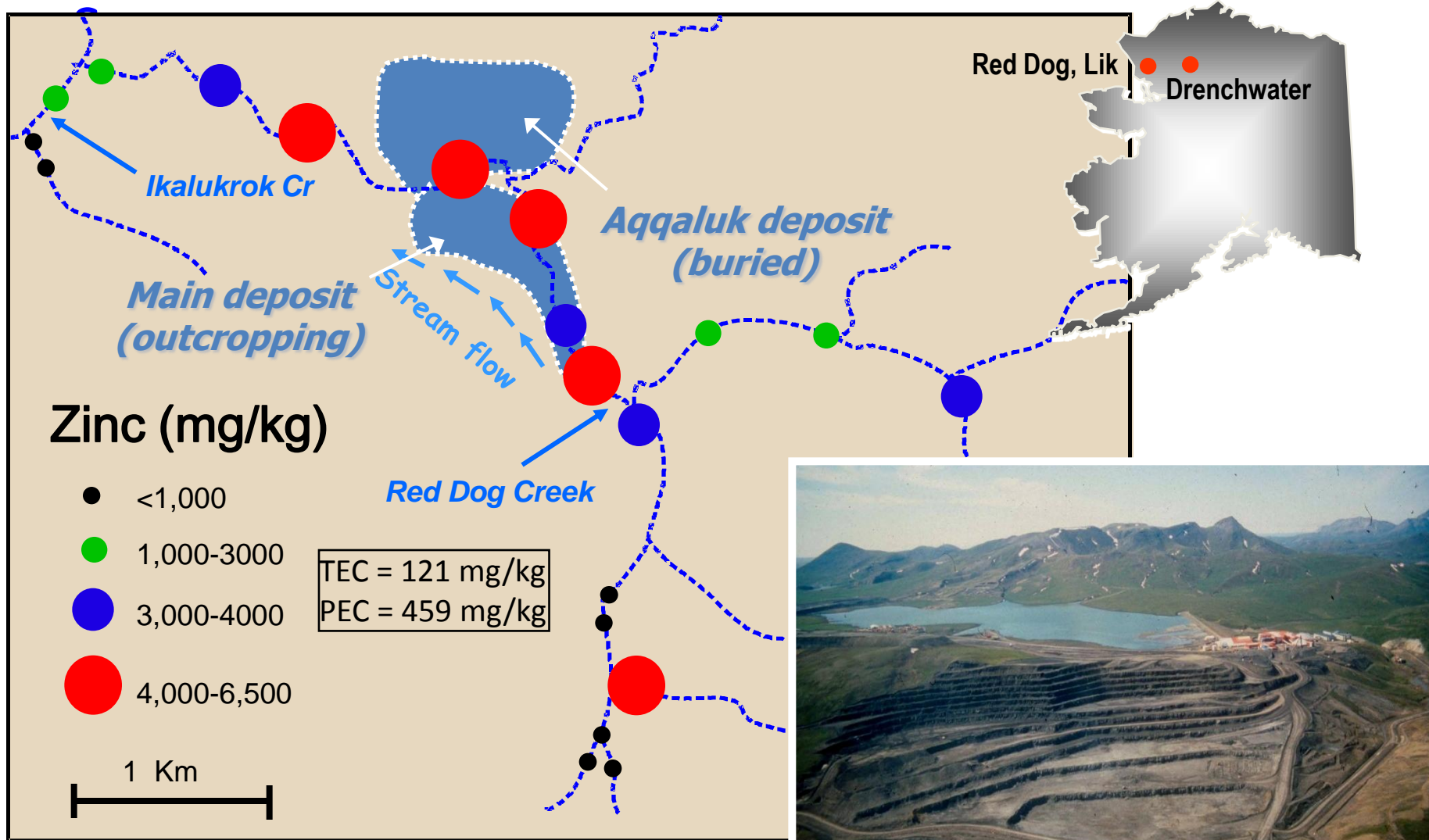


Summitville Mine, Colorado

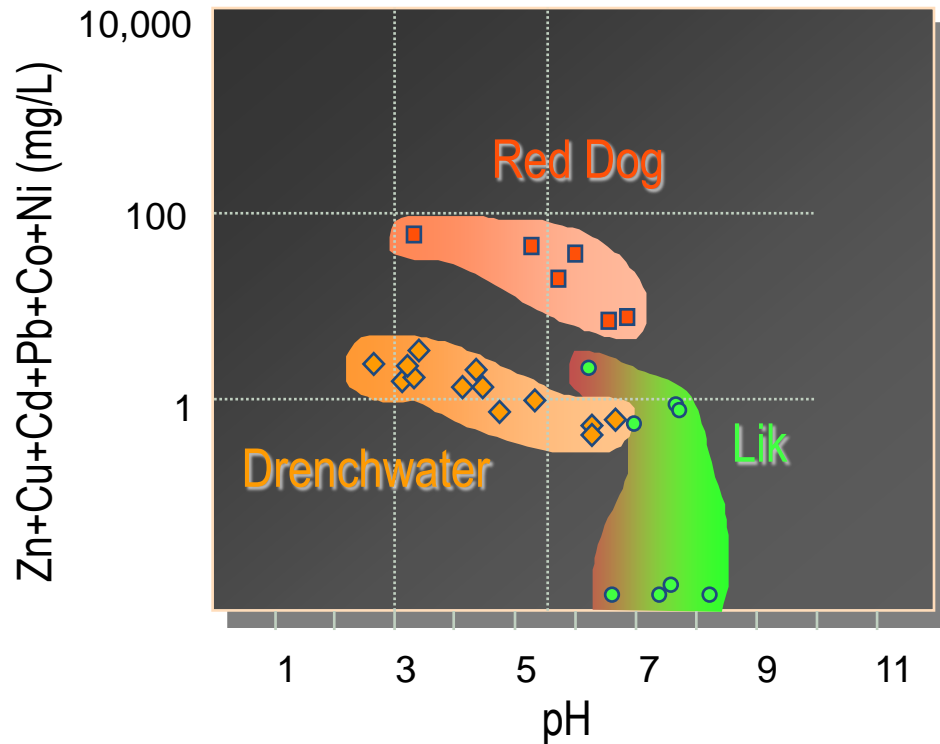
Minor & Trace Elements in Average Rocks

Element	Ultramafic Rocks	Basalt	High-Ca Granite	Low-Ca Granite	Shale	Sandstone	Carbonate Rocks	Residential Soil	Sediment TEC
Al wt %	1.2	8.28	8.2	7.2	8	2.5	0.42	7.7	
Cr mg/kg	1,800	185	22	4.1	90	35	11		43.4
Mn mg/kg	1,560	1,750	540	390	850		1100	1,800	
Fe wt %	9.64	8.6	2.96	1.42	4.72	0.98	0.33	5.5	
Co mg/kg	175	47	7	1	19	0.3	0.1	23	
Ni mg/kg	2,000	145	15	4.5	68	2	20	1,500	22.7
Cu mg/kg	15	94	30	10	45		4	3,100	31.6
Zn mg/kg	40	118	60	39	95	16	20	23,000	121
As mg/kg	0.8	2.2	1.9	1.5	13	1	1	22	9.79
Se mg/kg	0.05	0.05	0.05	0.05	0.6	0.05	0.08	390	
Cd mg/kg	0.05	0.21	0.13	0.13	0.3		0.035	70	0.99
Hg mg/kg	0.01	0.09	0.08	0.08	0.4	0.03	0.04	5.6	0.18
Pb mg/kg	0.5	7	15	19	20	7	9	400	35.8
U mg/kg	0.002	0.75	3	3	3.7	0.45	2.2	230	

Red Dog, Alaska, Pre-Mining Stream Sediment

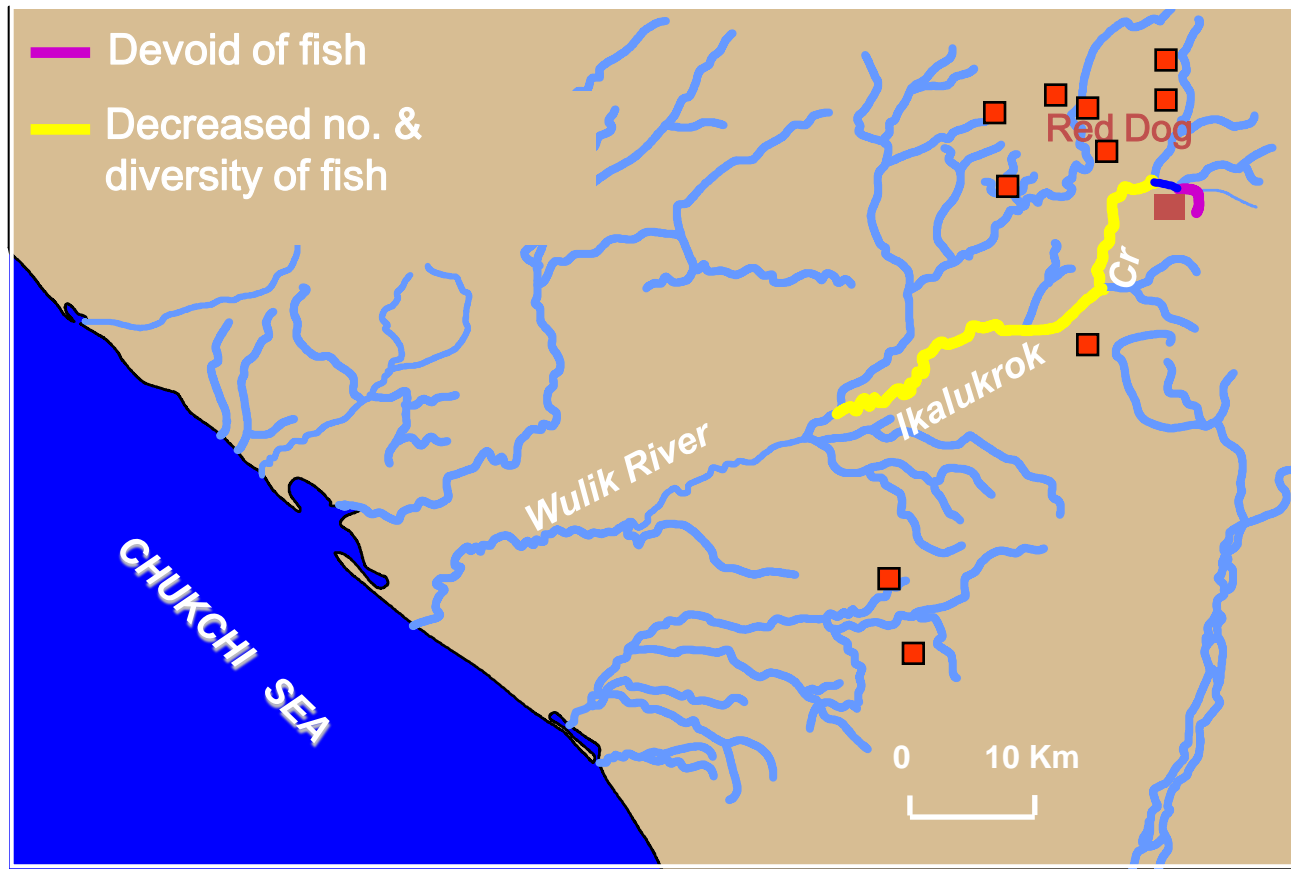


Why pre-mining baseline characterization is important: Red Dog, Alaska



- Sedimentary-Exhalative massive sulfide deposit (Zn, Pb, Ag)
- Exposed at surface prior to mining

Pre-Mining Ecology & Water Chemistry



- Water pH of 2.5-2.8
- High dissolved concentrations of Zn, Cd, Pb, As, Fe, and SO₄

Expectations for Mining Impact Assessment (Section 6)

- Impacts to surface and ground water hydrology
 - Surface water hydrology
 - Ground water hydrology
- Impacts to water quality
 - Background and existing water quality
 - Regional hydrology and hydrogeology
 - Hydrology of mines and waste facilities
 - Solid wastes and materials characterization and management
 - Waste water quality and management
 - Post-closure mine and waste facility water quality
 - Closure and reclamation effects
- Impacts to aquatic resources
- Impacts to wetlands

EPA AND HARDROCK MINING:
A SOURCE BOOK FOR INDUSTRY IN THE NORTHWEST AND ALASKA

January 2003



U.S. Environmental Protection Agency
Region 10
1200 6th Avenue
Seattle, Washington 98101

Additional Information (Appendices)

- Hydrology
- Receiving Waters
- Characterization of Ore, Waste Rock and Tailings
- Effluent Quality
- Wastewater Management
- Solid Waste Management
- Aquatic Resources
- Erosion and Sedimentation
- Wetlands

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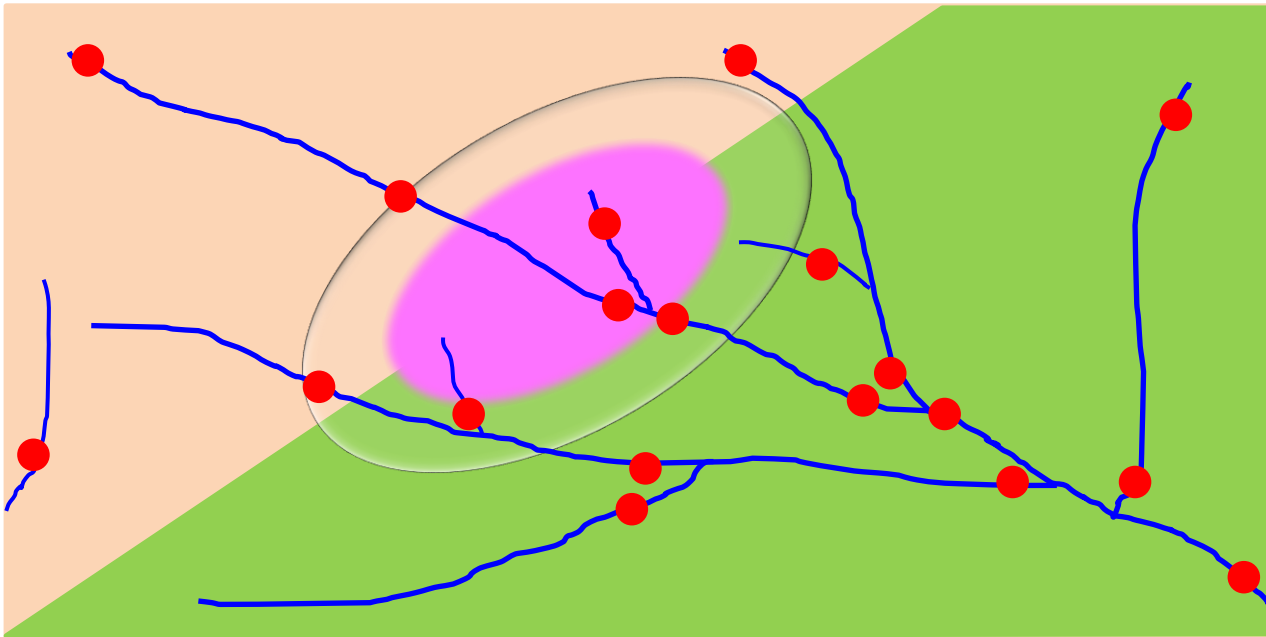
January 2003



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Goals of Baseline Characterization

- Establish sites to monitor environmental performance during mining – away from footprint of the mine.
- Establish closure goals for after mining – within footprint of the mine.




- Design of baseline characterization needs to include geologic and hydrologic context.

Routine Analytical Accessibility

Periodic Table of the Elements 2006

1 H 1.01																	18 He 4.00	
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18	
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95	
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29	
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)								
			58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97		
			90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)		

See "It's Elemental: The Periodic Table"
<http://pubs.acs.org/cen/80th/elements.html>



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- Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), EPA Method 6010A: Cations
- Inductively coupled plasma-mass spectrometry (ICP-MS), EPA Method 6020: Cations
- Ion Chromatography (IC), EPA Method 300: Anions
- Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS): Mercury

Aquatic Risk Assessment Benchmarks

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37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
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Suter, G.W., II, 1996, Toxicological benchmarks for screening contaminants of potential concern for effects on freshwater biota: *Environmental Toxicology and Chemistry*, v. 15, p. 1232-1241.

Water Quality Criteria (Aquatic or Human Health)

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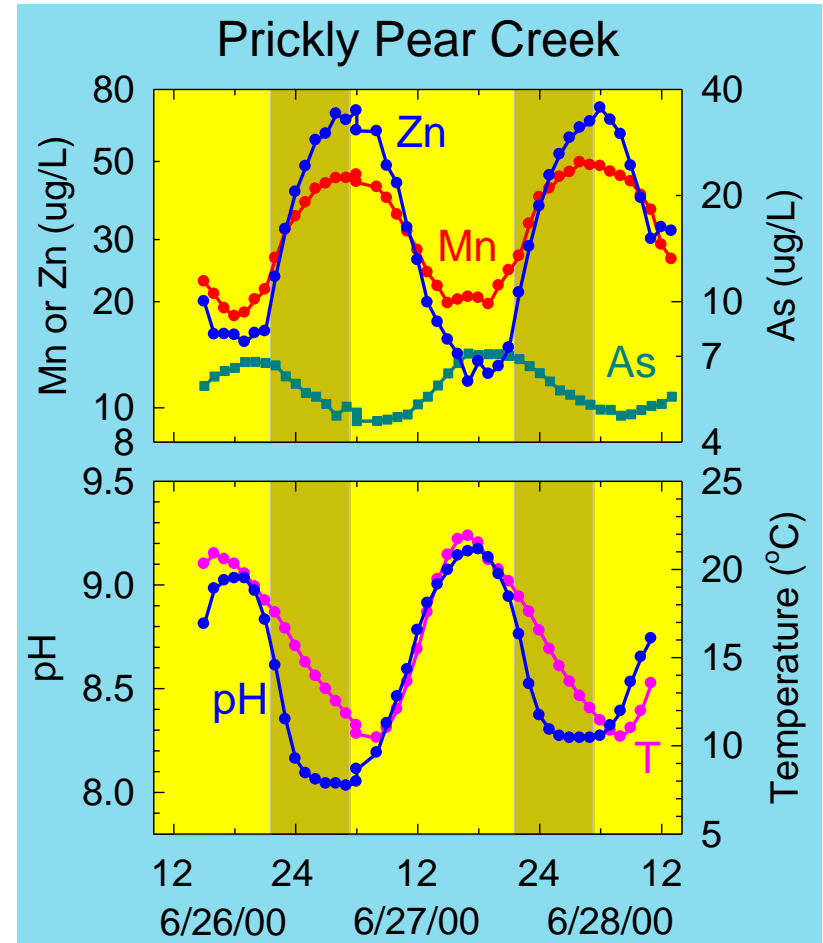
USEPA Environmental Criteria

Element	Human	Health	Aquatic	Ecosystem
Media	Residential Soil	Drinking Water	Acute Surface Water Toxicity	Sediment PEC
Units	mg/kg	µg/L	µg/L	mg/kg
Al	77,000	200	750	
As	23	10	340	33.0
Cd	70	5	2*	4.98
Cr	280	100	570	111
Cu	3,100	1,300	13*	149
Fe	55,000	300		
Hg	6.7	2	1.4	1.06
Mn	1,800	50		
Mo	390			
Ni	1,600		470*	4.86
Pb	400	15	65*	128
Se	390	50		
U	230	30		
V	78			
Zn	23,000	5,000	120*	459

*Aquatic criteria in green vary with water hardness

Baseline Characterization for Monitoring (and Closure)

- Needs to capture the range of natural geochemical variations.
- Needs to use geology as a guide.
- Needs to use hydrology as a guide.
- Diurnal (diel) variations in surface-water chemistry are not uncommon.
- Needs to be done in a current regulatory context.



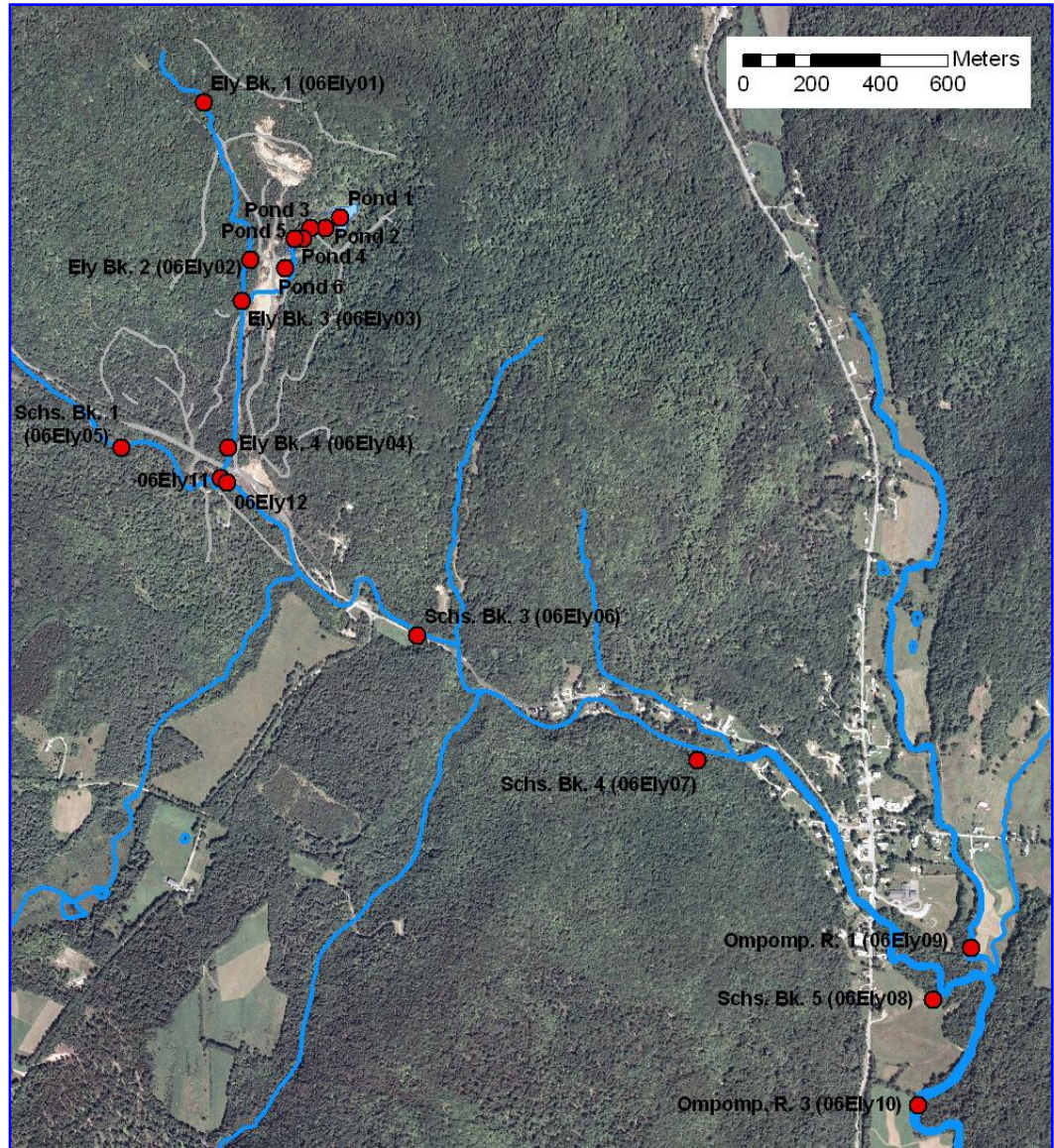
Nimick et al. (2010)

Quality Assurance/Quality Control (QA/QC)

- Procedures to assess the quality of your data
- Water chemistry
 - Blanks (analyzing distilled, deionized water) 1:20
 - Duplicates 1:20
 - Reference waters vs. spiked samples
 - (Charge balance)
- Soils and Sediments
 - ~~Blanks~~
 - Duplicates 1:20
 - Reference materials

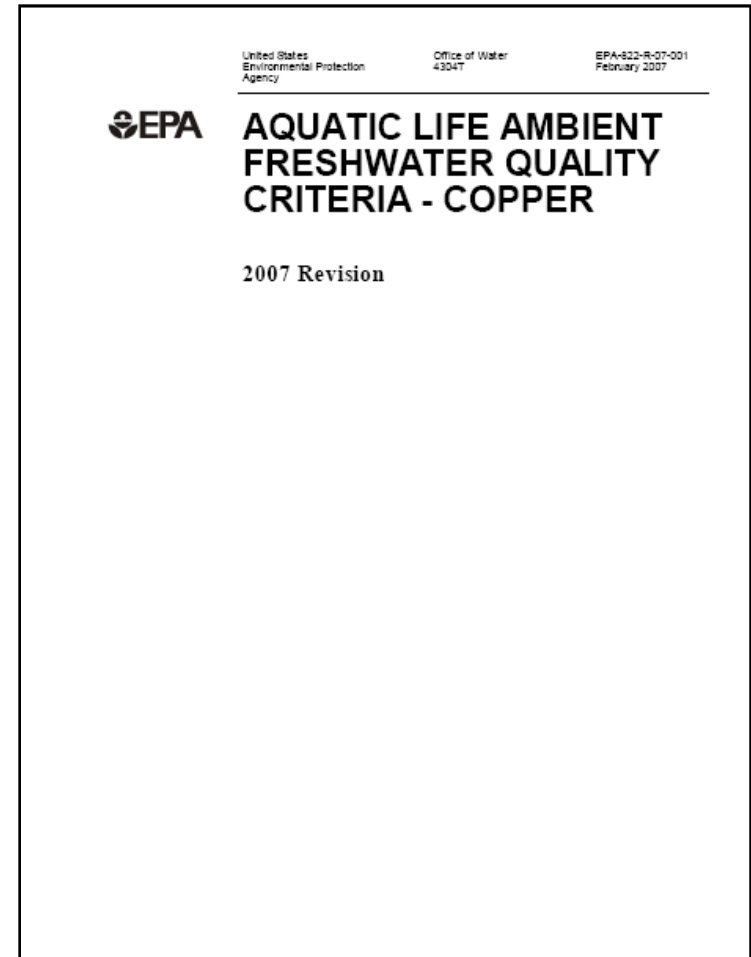
Ely Mine Superfund Site, Vermont, USA

- Today's problem: metal-rich AMD.
- Acid in Ely Brook is rapidly neutralized by Schoolhouse Brook.
- Metals persist downstream.



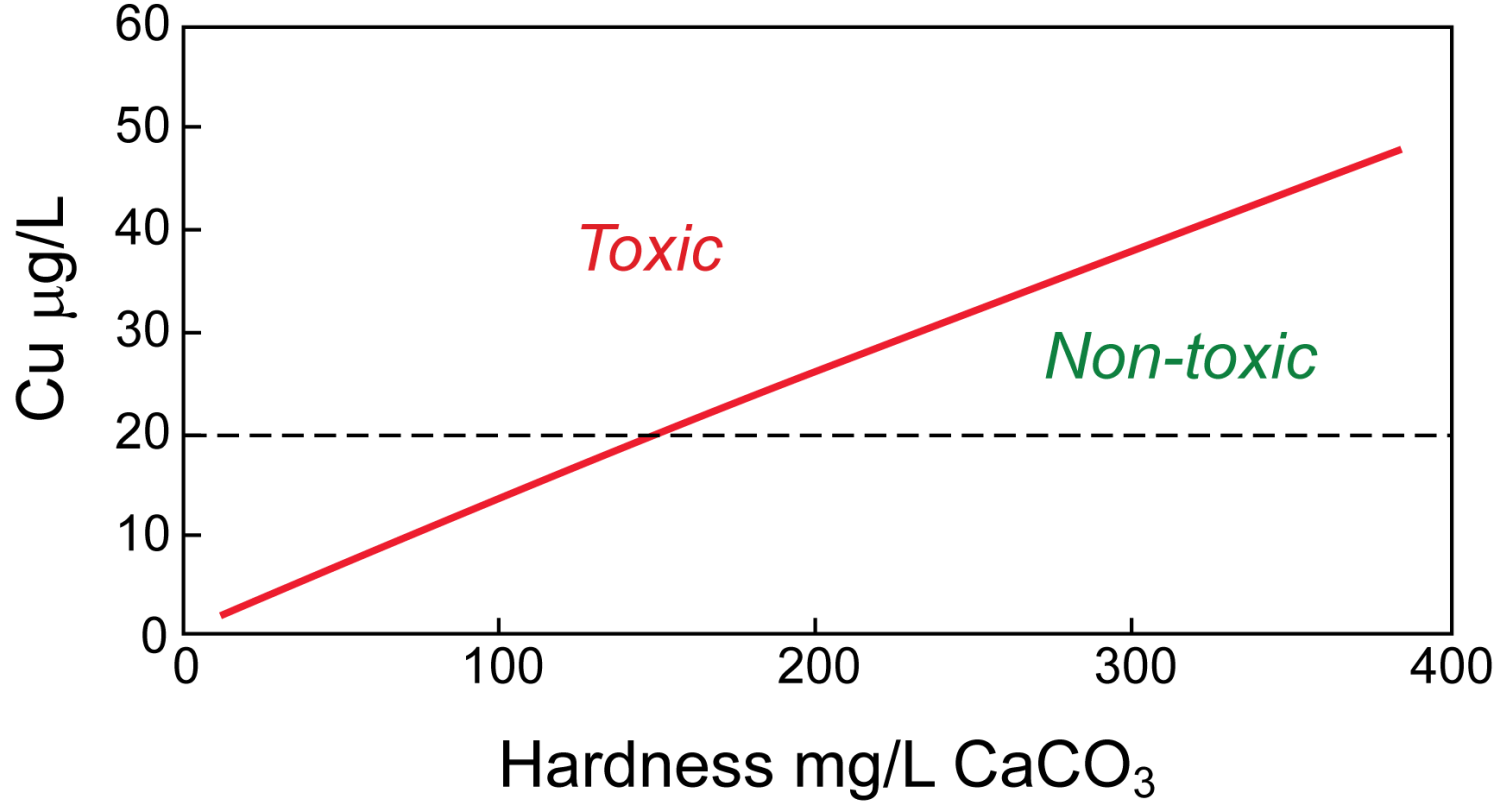
Surface-Water Environmental Criteria

- USEPA and the world community are changing from hardness based criteria to “Biotic Ligand Model” (BLM) criteria.
- At present, BLM is only adopted in USA for Cu.



http://water.epa.gov/scitech/swguidance/waterquality/standards/current/upload/2009_04_27_criteria_copper_2007_criteria-full.pdf

Surface Water Ecosystems: Acute Copper Toxicity



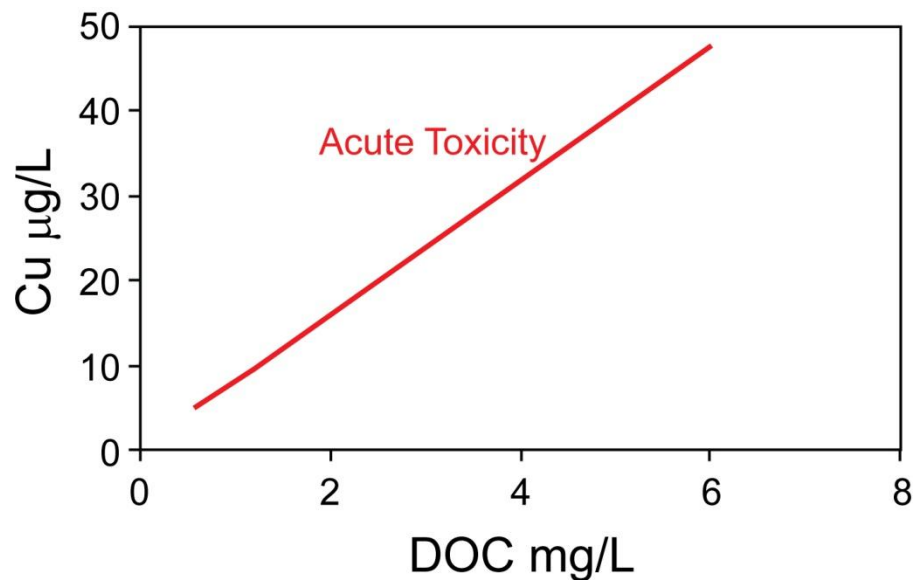
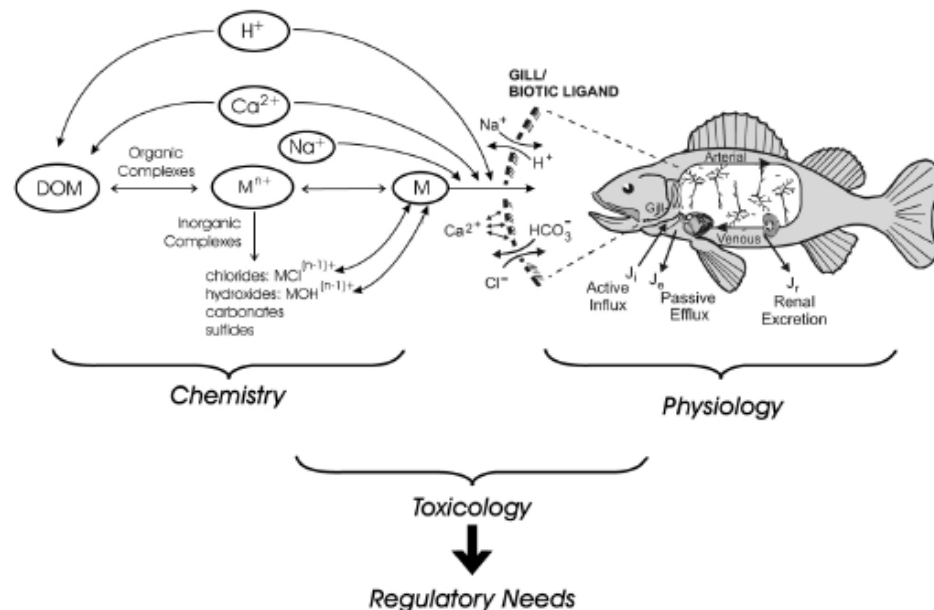
$$\text{Hardness (mg/L CaCO}_3\text{)} = 2.5 \text{ Ca (mg/L)} + 4.1 \text{ Mg (mg/L)}$$

Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Nickel (Ni), Silver (Ag), Zinc (Zn)

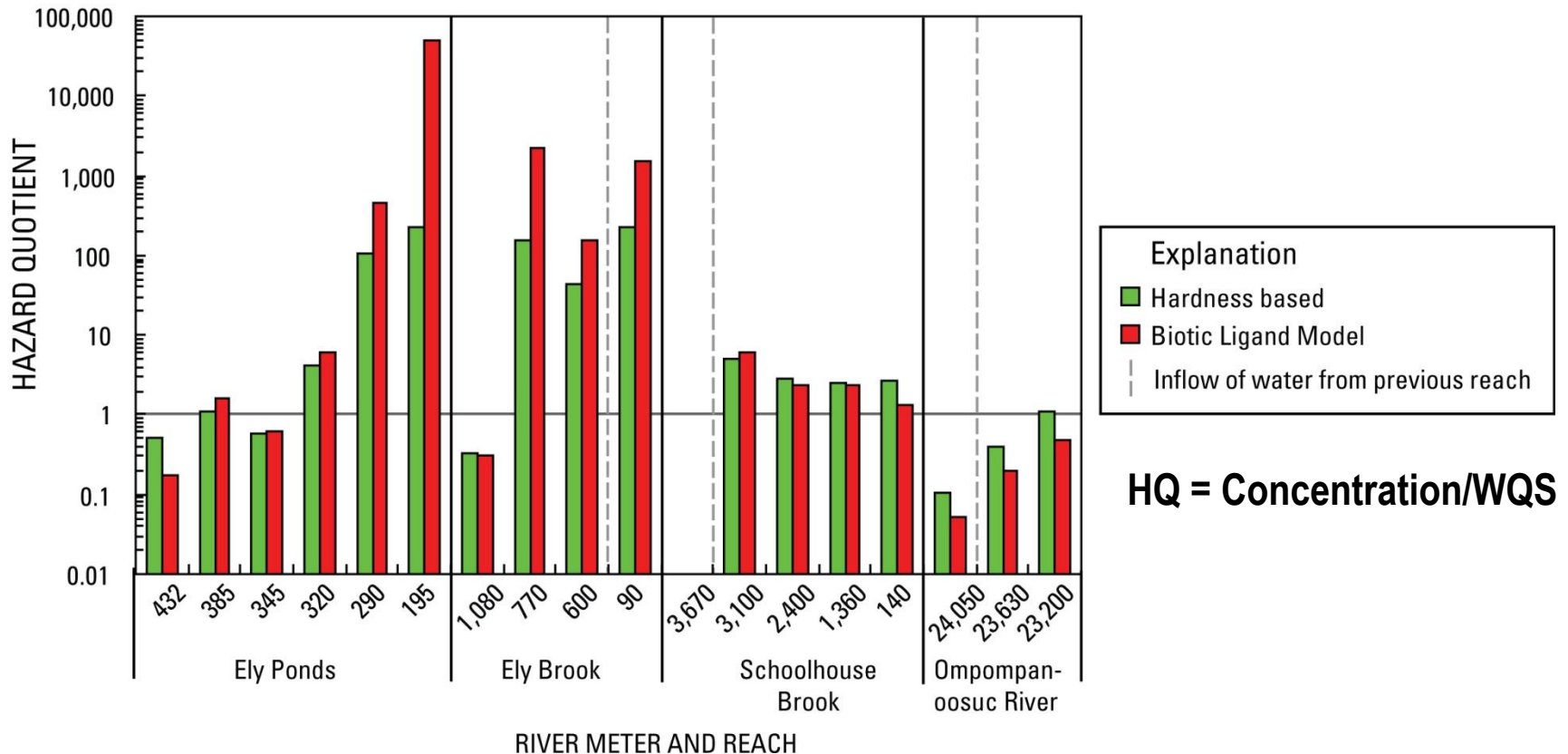
<http://water.epa.gov/scitech/swguidance/standards/current/>

Surface Water: Biotic Ligand Model Data Requirements

- pH
- Na
- K
- **Ca**
- **Mg**
- Chloride
- Sulfate
- Alkalinity
- **Dissolved Organic Carbon (DOC)**



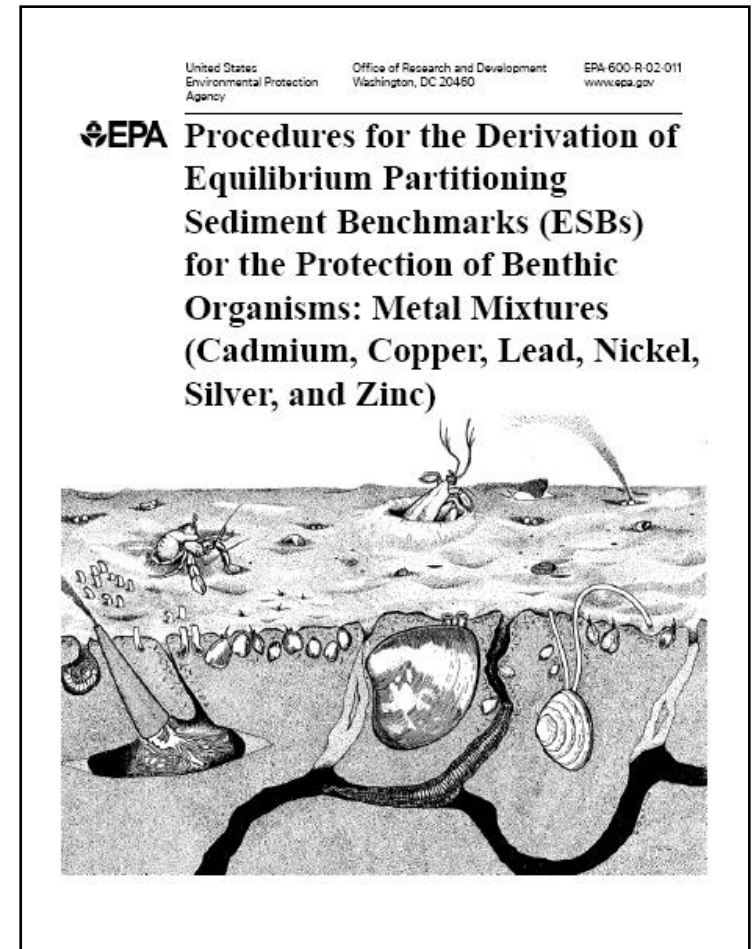
Ely Mine Superfund Site, Vermont, USA



- Hardness-based and biotic ligand-based approaches yield grossly similar results.
- Some reaches the hardness-based criteria are more restrictive; in other the BLM criteria are more restrictive.

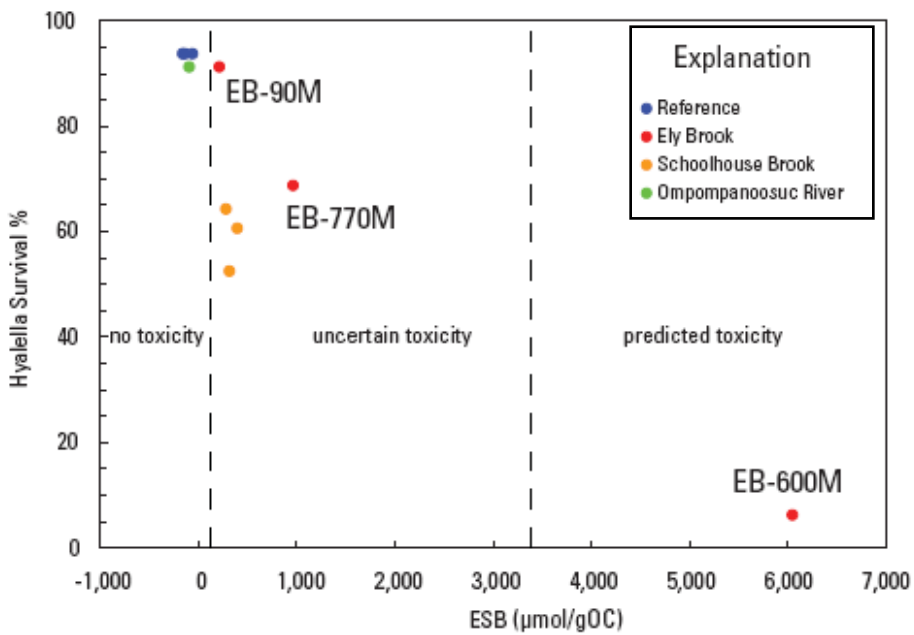
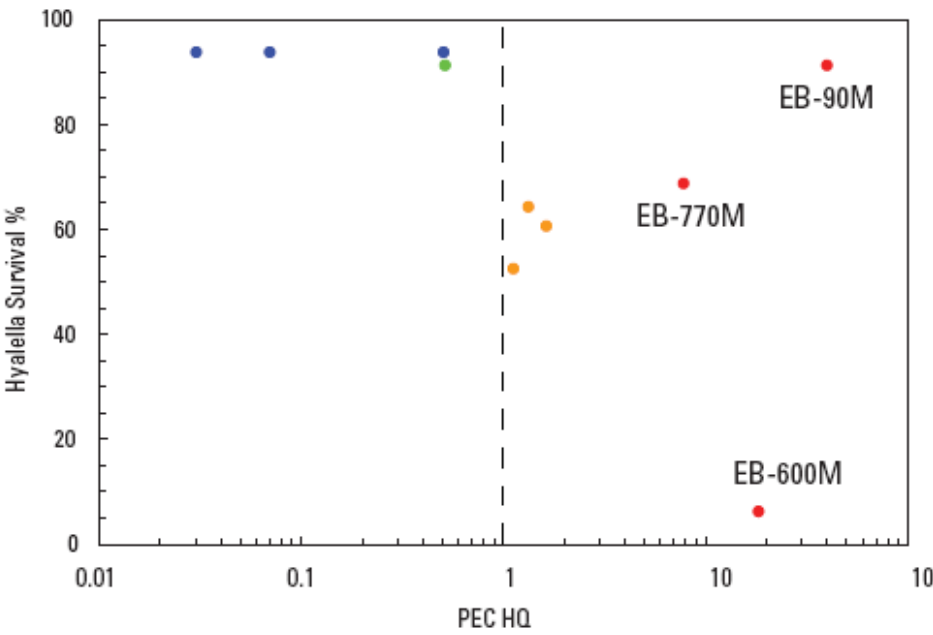
Equilibrium Partitioning Sediment Benchmarks

- Criteria are called “Equilibrium Partitioning Sediment Benchmarks” (ESBs)
- Use measurements of:
 - Acid volatile sulfur (AVS)
 - Simultaneously extractable metals (SEM)
 - Organic carbon (OC)
- $ESB = (\sum SEM - AVS) / f_{OC}$



http://www.epa.gov/nheerl/publications/files/metalsESB_022405.pdf

Probable Effects Concentrations vs. Equilibrium Partitioning Sediment Benchmarks



- At the Ely abandoned mine, ESB approach better explains laboratory bioassay results than PEC approach.
- ESB requires more extensive analytical suite (SEM, AVS, f_{OC})

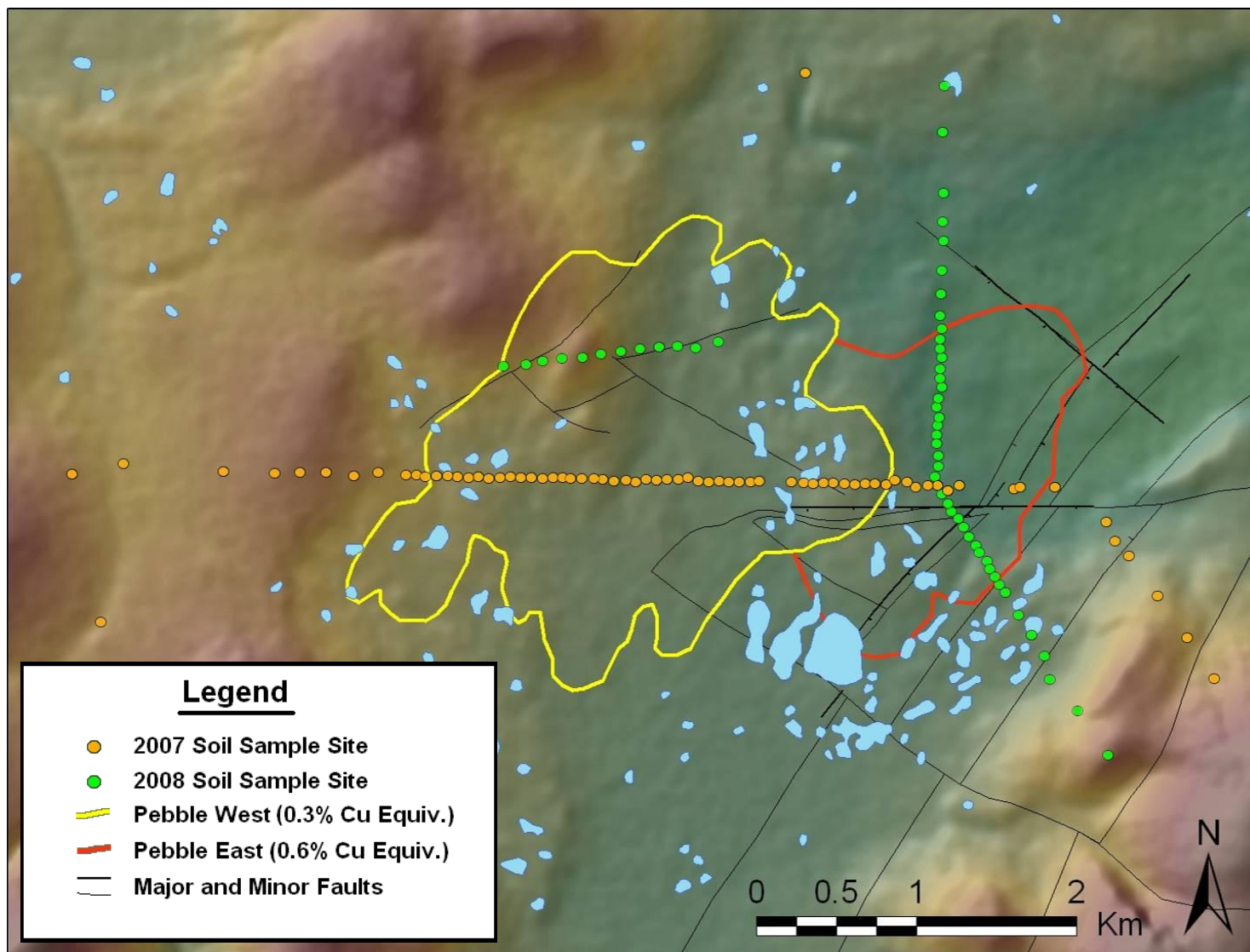


Baseline Characterization for Closure

- Insights from exploration geologists will improve process and product.
- Ore deposits are geochemical anomalies that can commonly and naturally exceed environmental criteria.
- They express themselves in all media:
 - Groundwater
 - Surface water
 - Sediment
 - Soil
- Needs to include up-gradient and down-gradient of deposit (streams, groundwater, glaciers, etc.)

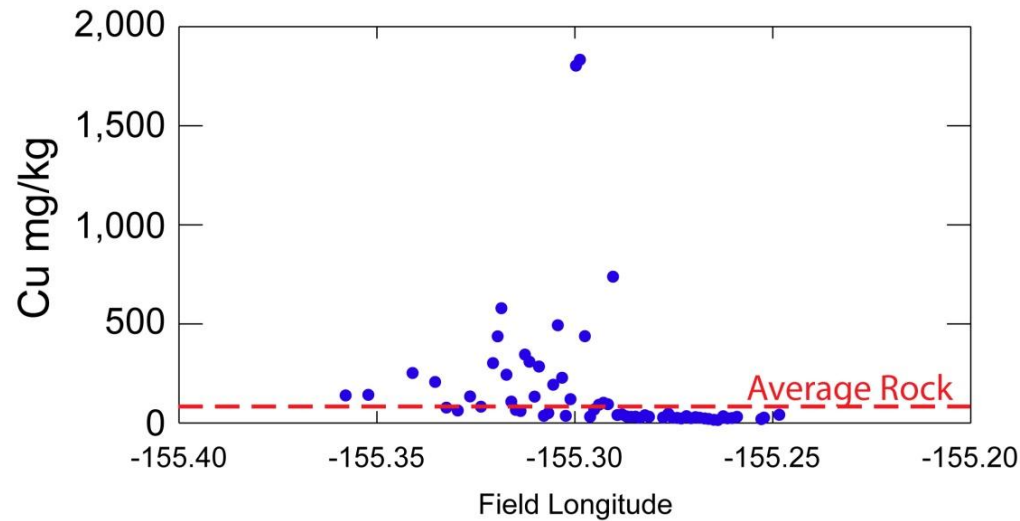
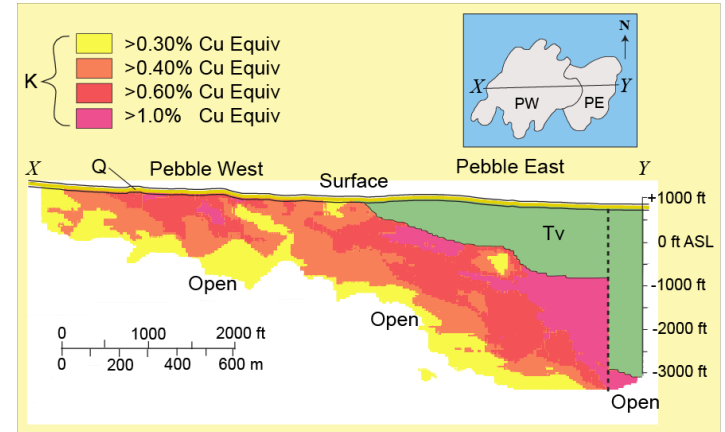


Pebble Deposit (SW Alaska): Soil Traverses



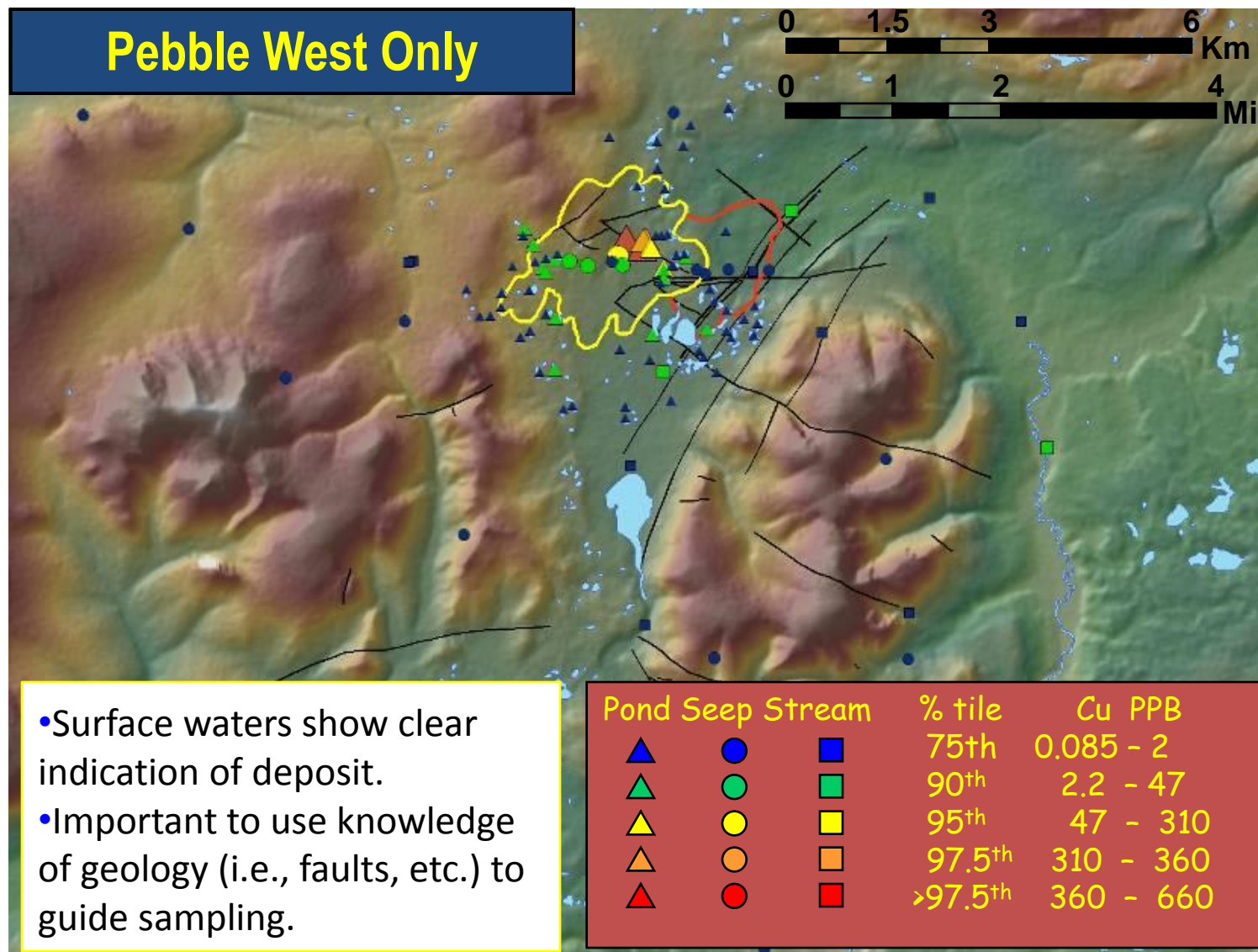
Soil Characterization

- Porphyry copper deposit
 - Very large (10 billion tonnes)
 - Copper, gold, molybdenum
- Goal is to characterize natural variations
 - Both highs and lows.
- Exploration department will likely have soil survey maps
 - Samples may not have been analyzed as extensively as needed.
 - Maps can serve as guide for effective baseline survey.
- Requires statistically significant data sets for both mineralized areas and unmineralized areas.



Waters: Cu by HR-ICPMS

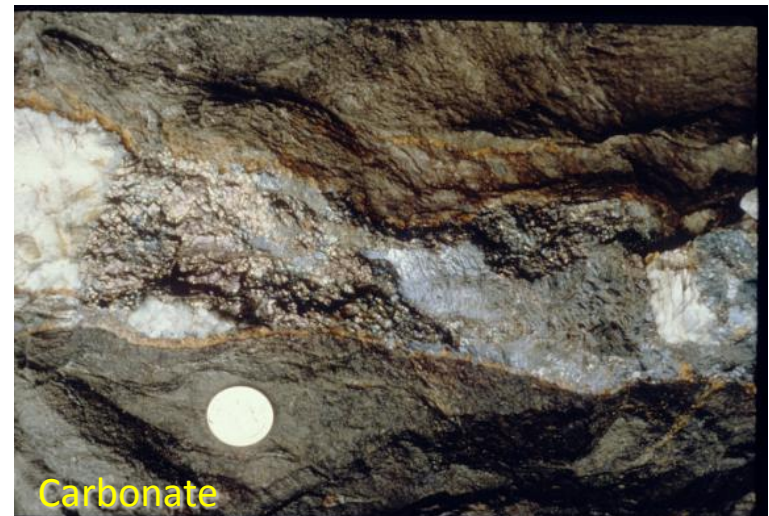
Pebble West Only



Prediction

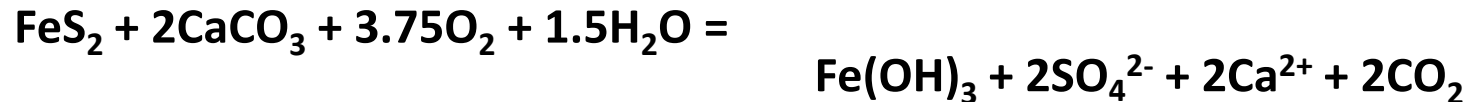
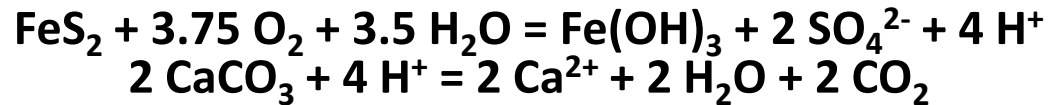
Ore & Alteration Characterization

- Mineralogy
 - Trace element hosts
- Geochemistry
- Acid-Base Accounting
 - Sulfide Minerals
 - Carbonate Minerals



Static Tests:

Acid-Base Accounting: Pyrite vs. Calcite (sort of...)



$$\text{NNP} = \text{NP} - \text{AP}$$

$$\text{NP/AP}$$

AP: Acid-producing potential

NP: Acid-neutralizing potential

NNP: Net neutralizing potential

AP

NP

ΣS

ΣCO_3^{2-}

S^{2-}

SO_4^{2-}

Calcite

Siderite

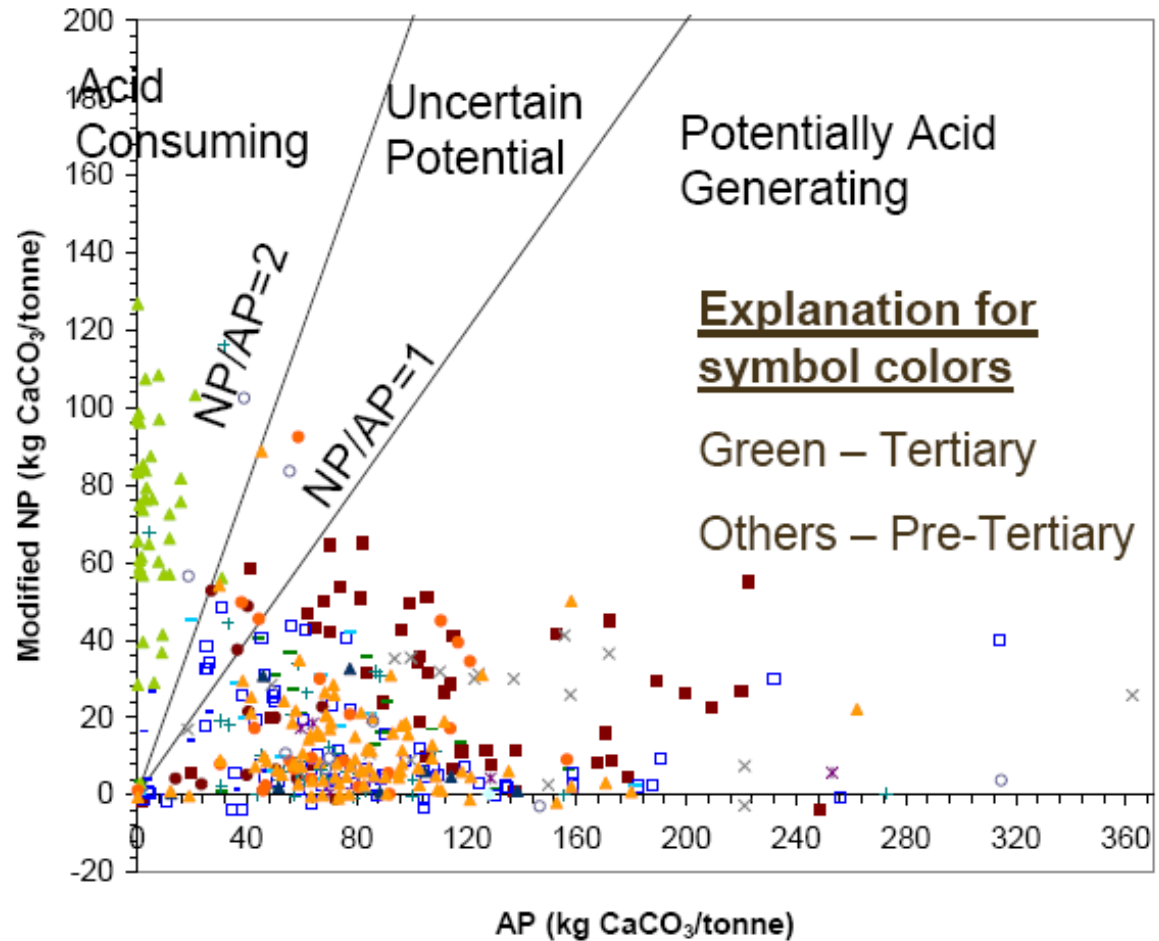
Pyrite

Anhydrite

Melanterite Jarosite

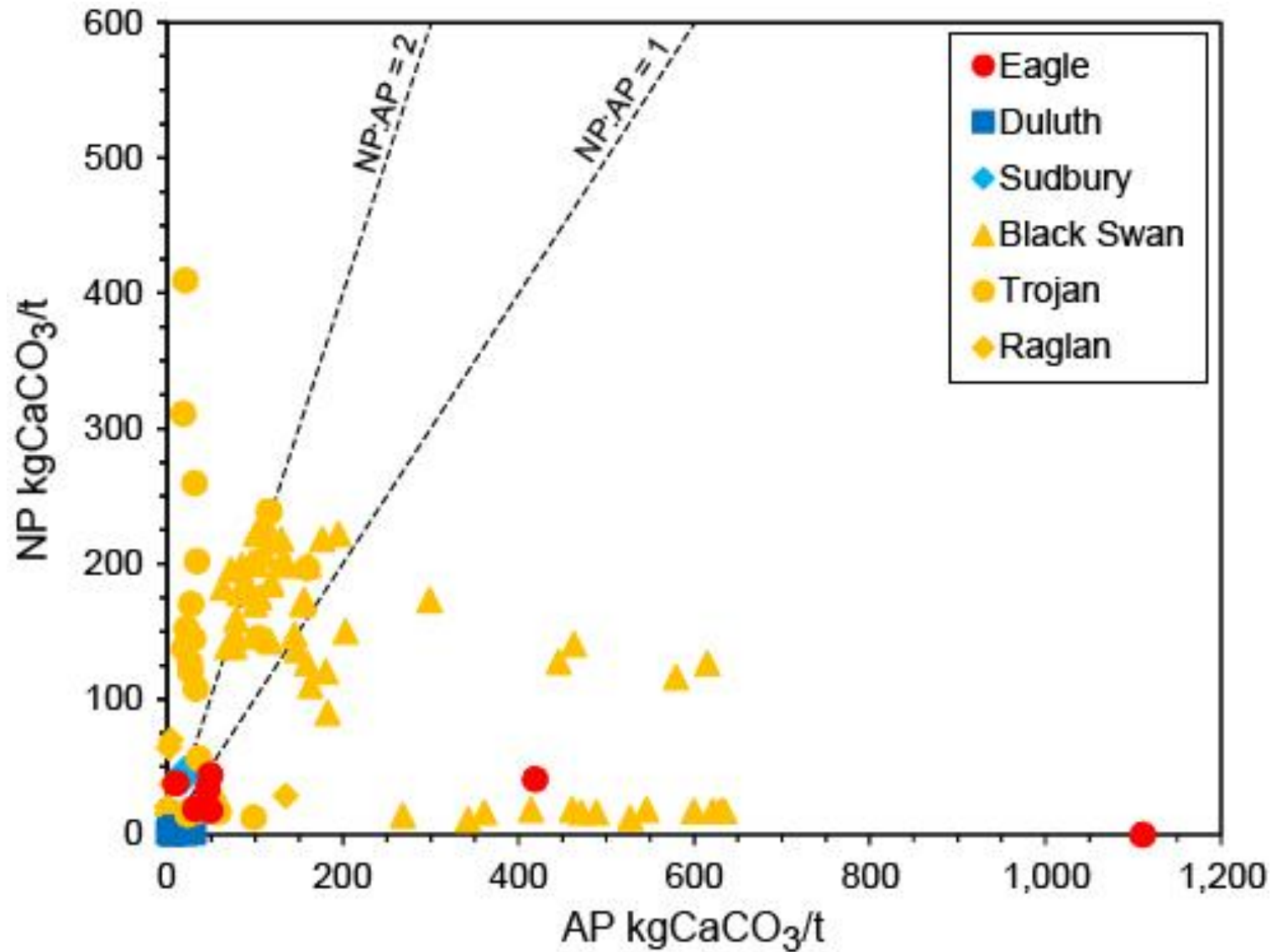
Acid-Base Accounting

- Goal is to determine which material needs special handling and which does not.
- $NP/AP < 1$: PAG
- $2 > NP/AP > 1$: Uncertain
- $NP/AP > 2$: Acid Consuming



Pebble Porphyry Cu-Mo-Au deposit, AK
<http://www.pebblepartnership.com>

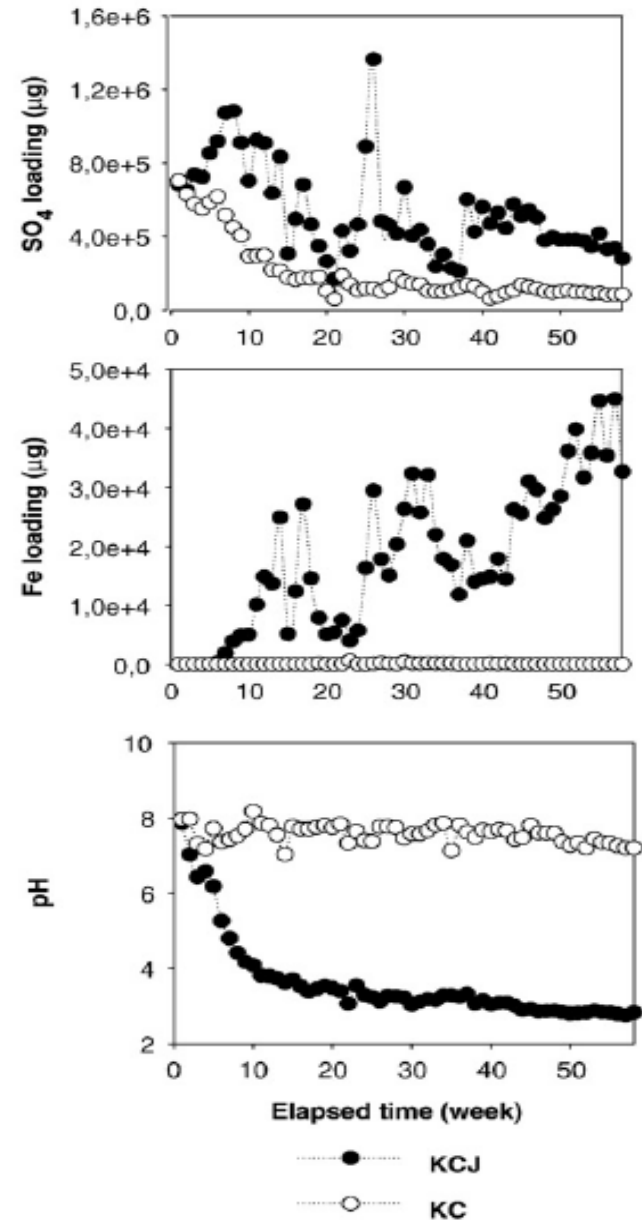
ABA: Ni-Cu(-PGM) Deposits



Humidity-Cell (Kinetic) Tests

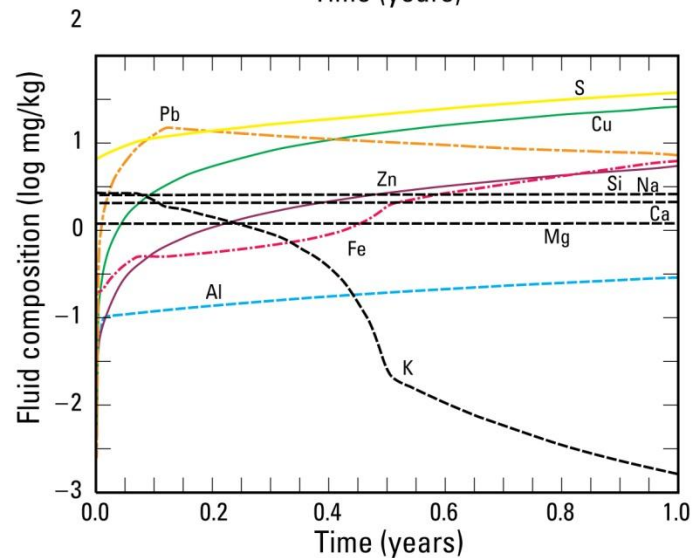
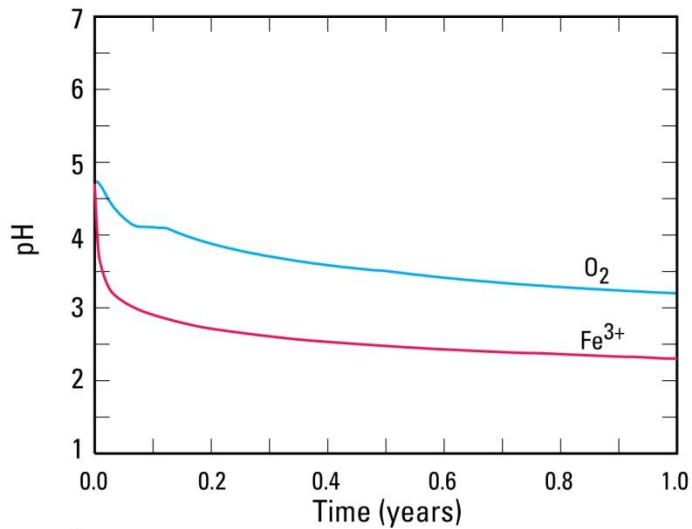


- Long-term behavior
- 1 kg sample
- 7-day cycle: 3 days dry air, 3 days humid air, 1 day leach (0.5 L)

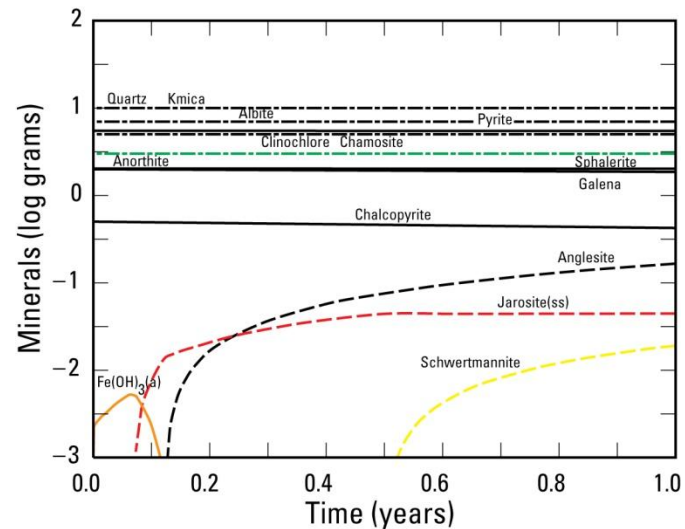


From: Ardaou et al. (2009)

Modeling




- Chemical interactions in solution
- Rates of dissolution of various minerals
- Equilibrium state of system
- Combines several “models”



Water Quality Criteria or Drinking Water Standards

Periodic Table of the Elements 2006

1 H 1.01																	18 He 4.00																																				
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18																																				
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																																				
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80																																				
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29																																				
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	(209)	85 At (210)	86 Rn (222)																																				
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)																																											
																																																					
<p style="text-align: right;">See "It's Elemental: The Periodic Table" http://pubs.acs.org/cen/80th/elements.html</p>																																																					
<table border="1"> <tr> <td>58 Ce 140.12</td> <td>59 Pr 140.91</td> <td>60 Nd 144.24</td> <td>61 Pm (145)</td> <td>62 Sm 150.36</td> <td>63 Eu 151.97</td> <td>64 Gd 157.25</td> <td>65 Tb 158.93</td> <td>66 Dy 162.50</td> <td>67 Ho 164.93</td> <td>68 Er 167.26</td> <td>69 Tm 168.93</td> <td>70 Yb 173.04</td> <td>71 Lu 174.97</td> <td colspan="4"></td> </tr> <tr> <td>90 Th 232.04</td> <td>91 Pa 231.04</td> <td>92 U 238.03</td> <td>93 Np (237)</td> <td>94 Pu (244)</td> <td>95 Am (243)</td> <td>96 Cm (247)</td> <td>97 Bk (247)</td> <td>98 Cf (251)</td> <td>99 Es (252)</td> <td>100 Fm (257)</td> <td>101 Md (258)</td> <td>102 No (259)</td> <td>103 Lr (262)</td> <td colspan="4"></td> </tr> </table>																		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97					90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)				
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Suter, G.W., II, 1996, Toxicological benchmarks for screening contaminants of potential concern for effects on freshwater biota: Environmental Toxicology and Chemistry, v. 15, p. 1232-1241.

Mine Waste Characterization

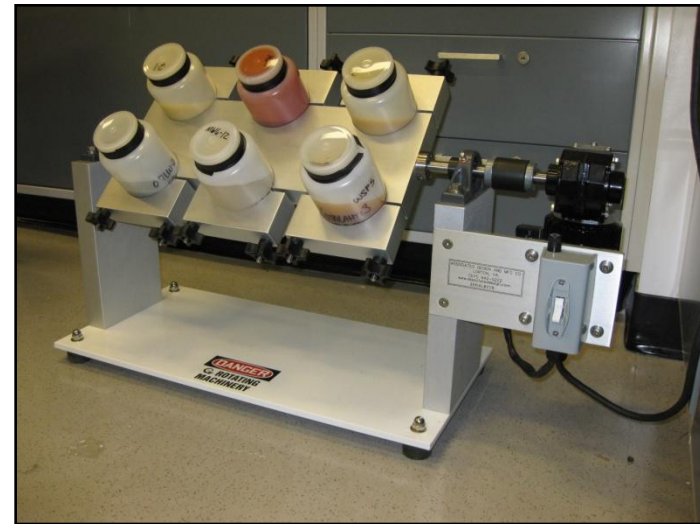
Bulk Chemistry of Solids: Compare to:

- Soil guidelines (human health)
- Sediment guidelines (aquatic health)

Leachate Chemistry: Compare to:

- Drinking water guidelines (human health)
- Surface water guidelines (aquatic health)

- NOT an answer to a questions.
- A tool for asking intelligent questions
- NOT a replacement for site specific studies.



Rating Table

Deposit	VMS				Orogenic Gold				Taconite			
Target	Human Health		Ecosystem Health		Human Health		Ecosystem Health		Human Health		Ecosystem Health	
Pathway	Soil	Drinking Water	Sediment	Surface Water	Soil	Drinking Water	Sediment	Surface Water	Soil	Drinking Water	Sediment	Surface Water
Ag	1	1		1	1	1		1	1	1		1
Al	1	3		5	1	1		1	1	1		1
As	3	1	5	1	5	5	5	5	5	5	3	1
Cd	1	5	5	5	1	1	3	1	1	1	1	1
Cr	1	1	1	1	1	1	3	1	1	1	3	1
Cu	1	1	5	5	1	1	3	1	1	1	3	1
Fe	3	3		3	1	1		1	3	3		1
Ni	1	1	1	1	1	1	3	1	1	1	1	1
Pb	5	5	5	3	1	1	3	1	1	1	1	1
Zn	1	1	5	5	1	1	1	1	1	1	1	1
AP/pH	5	5		5	1	1		1	1	1		1

Rating Table

Deposit	<i>Magmatic Ni-Cu MS</i>				<i>Low Sulfide PGM</i>			
Target	Human Health		Ecosystem Health		Human Health		Ecosystem Health	
Pathway	Soil	Drinking Water	Sediment	Surface Water	Soil	Drinking Water	Sediment	Surface Water
Ag	1	1		1	1	1		1
Al	1	3		5	3	1		3
As	1	1	1	1	1	5	1	1
Cd	1	5	5	5	1	1	1	1
Cr	3	1	5	3	1	1	5	1
Cu	1	3	5	5	1	1	5	1
Fe	5	3		3	1	1		1
Ni	3	1	5	5	1	1	5	1
Pb	1	1	5	1	1	1	3	1
Zn	1	1	3	5	1	1	3	1
AP/pH	5	5		5	1	1		1

Summary

- Goals need to include establishment of monitoring sites for use prior, during, and after mining.
- Goals also need to include documentation of pre-mining geochemical landscape within the footprint of the proposed mine, especially in all regulated media (groundwater, surface water, sediment, soil).
- Insights from exploration geologists will be invaluable because of their knowledge of geologic and geochemical features of the deposit.

