Sampling Considerations at Mining Sites—expanded version

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CLU-IN Webinar Series on
Hardrock Mining Geochemistry and Hydrology

Sampling, Monitoring, and Remediation
at Mine Sites Workshop
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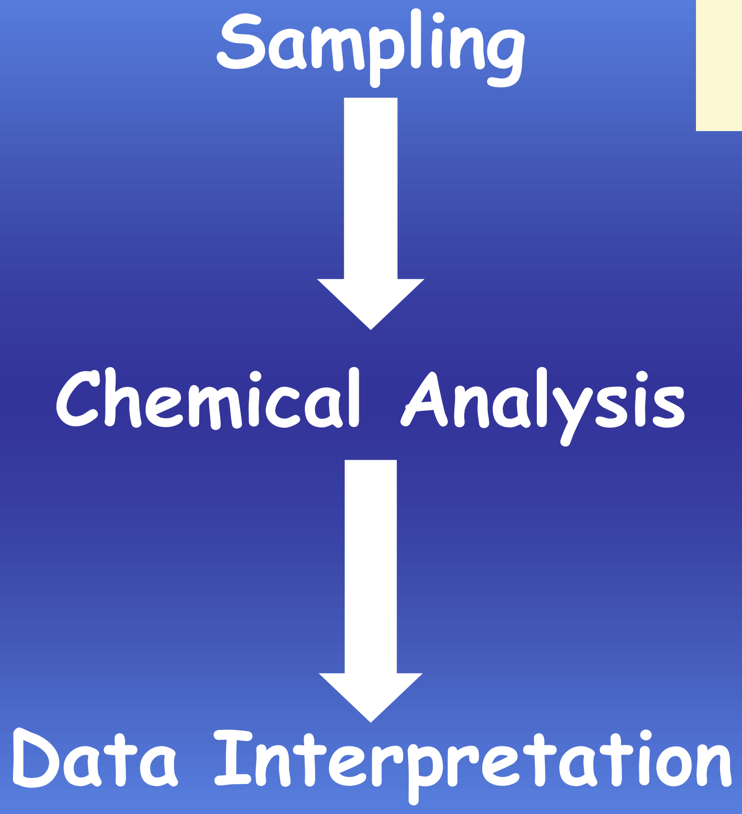
U.S. Department of the Interior
U.S. Geological Survey

Additional Resources Available on CLU-IN Site

- ✓ Expanded version of slides
- ✓ List of references
- ✓ Several papers
  - ○ including 3 chapters from 1999 SEG *Reviews in Economic Geology* (The Environmental Geochemistry of Mineral Deposits)

Sampling is Important!



Sampling

Chemical Analysis

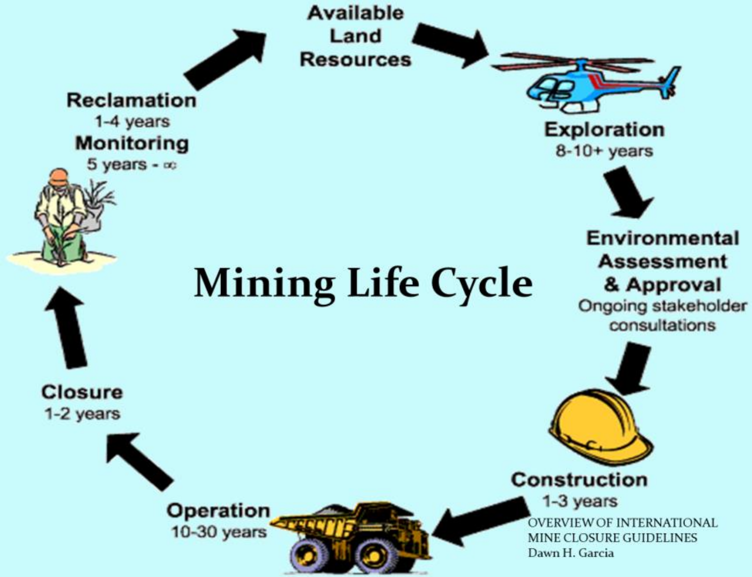
Data Interpretation

"Garbage in, garbage out"

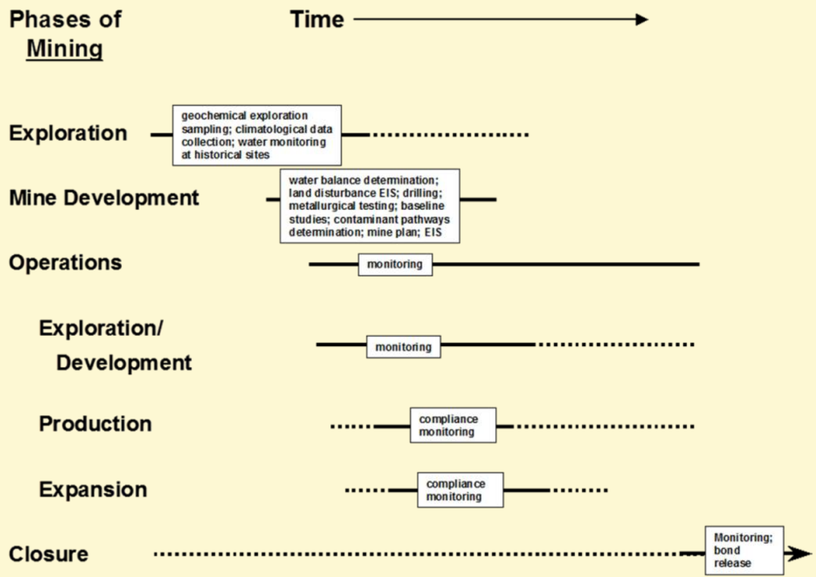
Success of a sampling program depends on

- ✓ Clear definition of sampling objectives
- ✓ Sample quality
- ✓ Sample integrity
- ✓ Sample representativeness

Sampling and Monitoring During the Mining Life Cycle



OVERVIEW OF INTERNATIONAL MINE CLOSURE GUIDELINES
Dawn H. Garcia



Phases of Mining
Time →

Exploration — geochemical exploration sampling; climatological data collection; water monitoring at historical sites

Mine Development — water balance determination; land disturbance EIS; drilling; metallurgical testing; baseline studies; contaminant pathways determination; mine plan; EIS

Operations — monitoring

Exploration/ Development — monitoring

Production — compliance monitoring

Expansion — compliance monitoring

Closure — Monitoring; bond release

- ✓ Sampling and monitoring during ALL phases of the mining life cycle
- ✓ Sampling and monitoring (and planning) for closure throughout the mining life cycle

Russell CLU-IN presentation;
McLemore et al. (2004, 2007, 2009)

Overview of this Presentation

- Importance of understanding controlling processes when designing sampling plans
  - ✓ Geological, hydrological, geochemical, and biogeochemical controls on mine-drainage and natural-drainage water
- Importance of scale when designing sampling plans
- Characterizing source material
- Sampling strategy for solids
- Surface water sampling concerns

Mining Influenced Water (MIW)

- Not limited to low pH
- Allows for characteristics other than low pH
  - ✓ Elevated Fe and/or Al concentrations, elevated non-Fe/Al metal concentrations, elevated sulfate concentrations, elevated total suspended solids
  - ✓ Each requires a different approach to sampling, monitoring, and control
- Characteristics are a function of geology/mineralogy, hydrology, mining technology used

Schmiermund and Drozd (1997); Plumlee et al. (1999); Maest CLU-IN presentation; Nordstrom CLU-IN presentation; Wireman CLU-IN presentation

Importance of Mineralogy

- Role and importance of mineralogy and particle texture often is overlooked
- Mineralogical characterization is necessary
  - ✓ mineralogy and texture are key factors that influence generation of acid rock drainage (ARD)
- There is an overall lack of mineralogical characterization data and examples of interpretation

Kwong (1993); Jambor and Blowes (1998); Plumlee et al. (1999); Hammarstrom and Smith (2002); Diehl et al. (2006, 2008); Parbhakar et al. (2009); Shaw and Mills (Infomine); Smith et al. (2012, 2013); Yager et al. (2013)

Metal Speciation

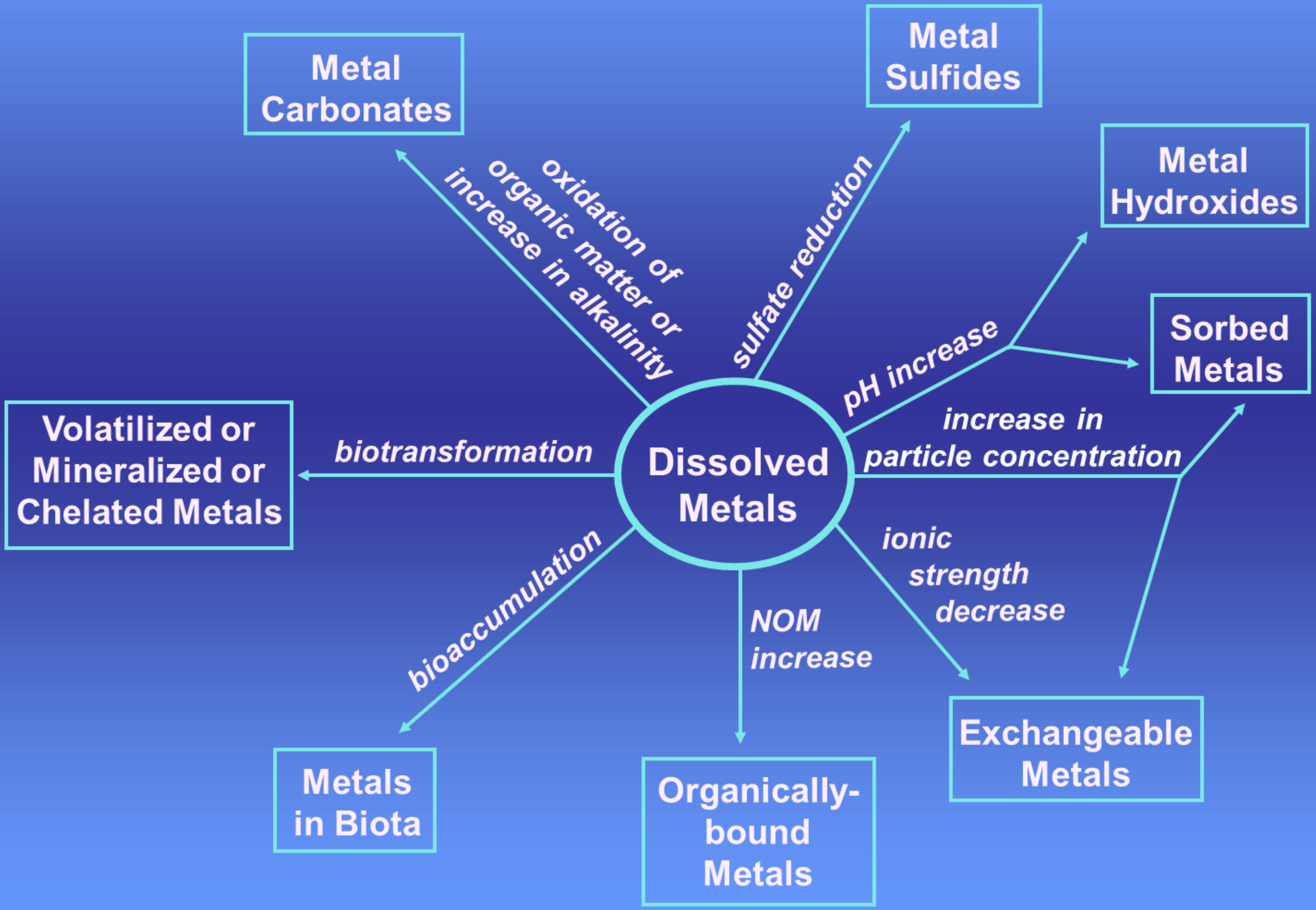
- Key to understanding metal mobility, bioavailability, and toxicity
- Different chemical species of a given metal often have different mobility behavior and toxicological effects
- Forms, transformations, and geochemical environment need to be considered when designing sampling plans
- Appropriate analytical techniques need to be incorporated into planning

Smith (2007, 2011); Nordstrom (2011); Nordstrom CLU-IN presentation; Butler CLU-IN presentation

Master Variables that Control Metal Mobility

- pH
- Redox conditions
- Temperature
- Inorganic ligands
- Organic ligands (DOC)
- Competition from other ions
- Biological uptake and transformation

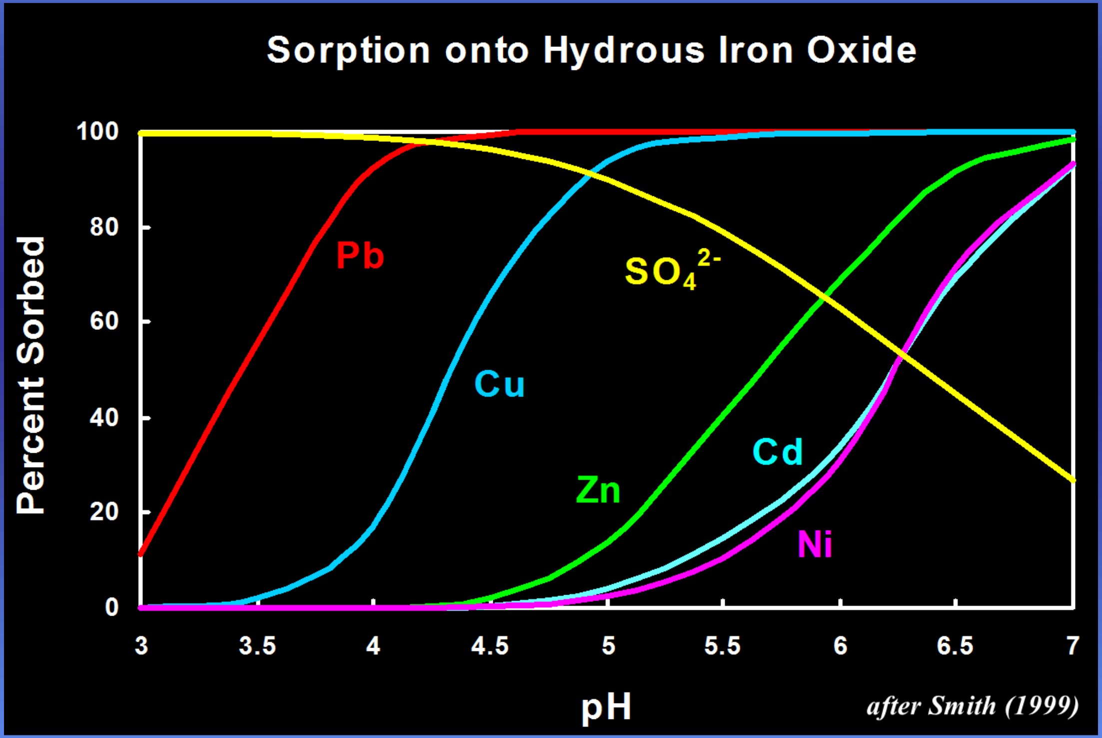
Some Processes and Geochemical Conditions that Can Redistribute Metals



After Smith and Huyck (1999)

Role of Metal Sorption

Sorption largely controls the fate of many trace elements in natural systems



after Smith (1999)

Sorption of metals onto suspended Fe and Al-rich particulates is a predictable function of the metal itself, metal concentration, pH, amounts/types of suspended particulates, and temperature

Smith (1999); Nordstrom CLU-IN presentation; Butler CLU-IN presentation

Characteristics of Elements in Aquatic Systems

Element	Chemical Symbol	Anionic	Cationic	Redox-Sensitive	Commonly Forms Sulfides
Aluminum	Al		X		
Antimony	Sb	X		X	X
Arsenic	As	X		X	X
Barium	Ba		X		
Beryllium	Be		X		
Cadmium	Cd		X		X
Chromium	Cr	X	X	X	
Cobalt	Co		X		X
Copper	Cu		X	X	X
Iron	Fe		X	X	X
Lead	Pb		X	(X)	X
Lithium	Li		X		
Manganese	Mn		X	X	
Mercury	Hg		X	X	X
Molybdenum	Mo	X	X	X	X
Nickel	Ni		X		X
Selenium	Se	X		X	
Silver	Ag		X		X
Thallium	Tl		X	X	X
Thorium	Th		X	(X)	
Uranium	U	X	X	X	
Vanadium	V	X	X	X	
Zinc	Zn		X		X

Smith and Huyck (1999)

Relative Mobility of Chemical Elements Under Different Environmental Conditions

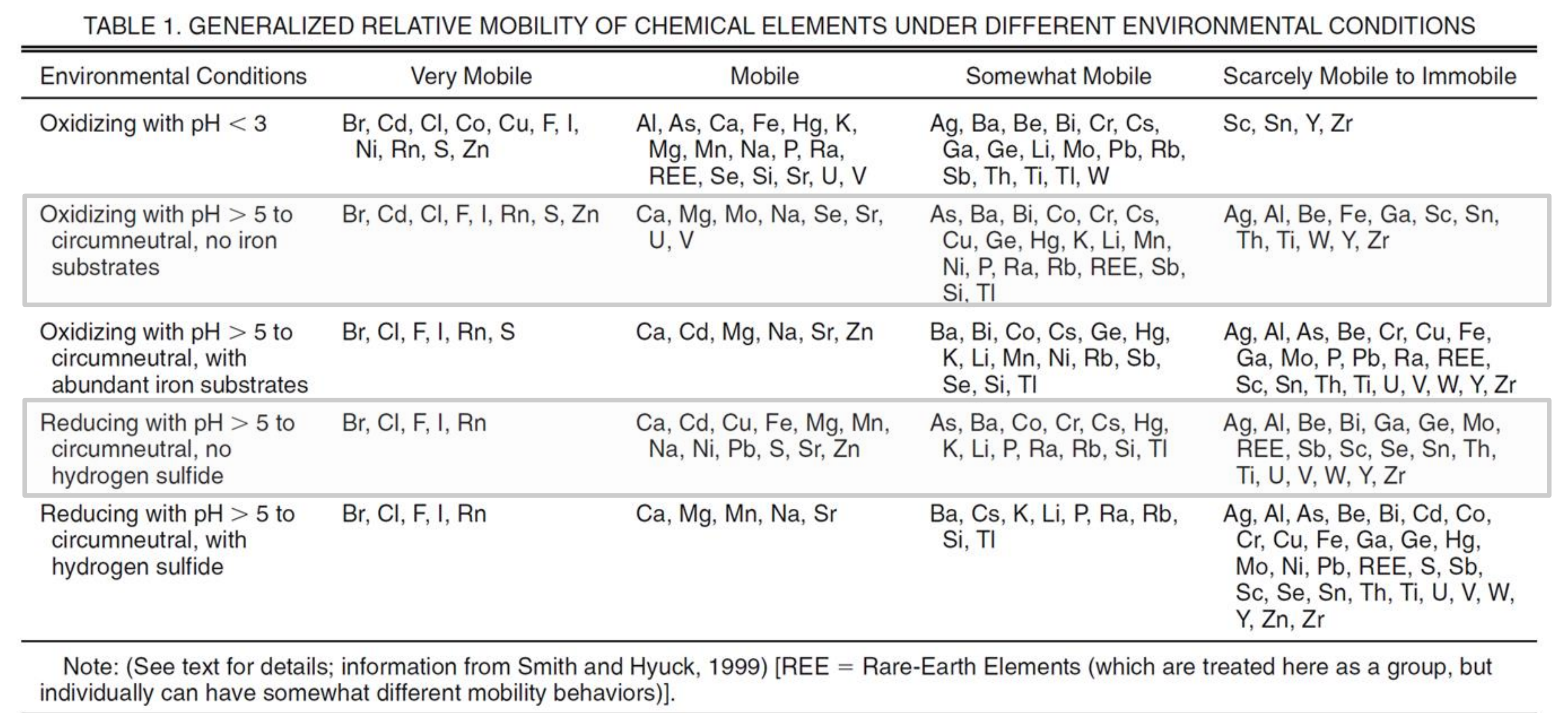


TABLE 1. GENERALIZED RELATIVE MOBILITY OF CHEMICAL ELEMENTS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

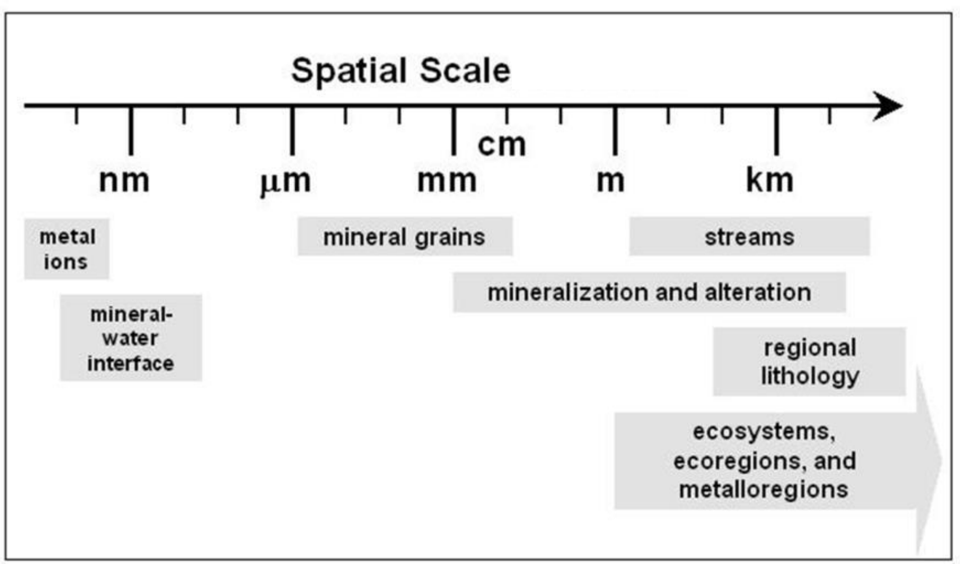
Environmental Conditions	Very Mobile	Mobile	Somewhat Mobile	Scarcely Mobile to Immobile
Oxidizing with pH < 3	Br, Cd, Cl, Co, Cu, F, I, Ni, Rn, S, Zn	Al, As, Ca, Fe, Hg, K, Mg, Mn, Na, P, Ra, REE, Se, Si, Sr, U, V	Ag, Ba, Be, Bi, Cr, Cs, Ga, Ge, Li, Mo, Pb, Rb, Sb, Th, Ti, Tl, W	Sc, Sn, Y, Zr
Oxidizing with pH > 5 to circumneutral, no iron substrates	Br, Cd, Cl, F, I, Rn, S, Zn	Ca, Mg, Mo, Na, Se, Sr, U, V	As, Ba, Bi, Co, Cr, Cs, Cu, Ge, Hg, K, Li, Mn, Ni, P, Ra, Rb, REE, Sb, Si, Tl	Ag, Al, Be, Fe, Ga, Sc, Sn, Th, Ti, W, Y, Zr
Oxidizing with pH > 5 to circumneutral, with abundant iron substrates	Br, Cl, F, I, Rn, S	Ca, Cd, Mg, Na, Sr, Zn	Ba, Bi, Co, Cs, Ge, Hg, K, Li, Mn, Ni, Rb, Sb, Se, Si, Tl	Ag, Al, As, Be, Cr, Cu, Fe, Ga, Mo, P, Pb, Ra, REE, Sc, Sn, Th, Ti, U, V, W, Y, Zr
Reducing with pH > 5 to circumneutral, no hydrogen sulfide	Br, Cl, F, I, Rn	Ca, Cd, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Sr, Zn	As, Ba, Co, Cr, Cs, Hg, K, Li, P, Ra, Rb, Si, Tl	Ag, Al, Be, Bi, Ga, Ge, Mo, REE, Sb, Sc, Se, Sn, Th, Ti, U, V, W, Y, Zr
Reducing with pH > 5 to circumneutral, with hydrogen sulfide	Br, Cl, F, I, Rn	Ca, Mg, Mn, Na, Sr	Ba, Cs, K, Li, P, Ra, Rb, Si, Tl	Ag, Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, Mo, Ni, Pb, REE, S, Sb, Sc, Se, Sn, Th, Ti, U, V, W, Y, Zn, Zr

Note: (See text for details; information from Smith and Hyuck, 1999) [REE = Rare-Earth Elements (which are treated here as a group, but individually can have somewhat different mobility behaviors)].

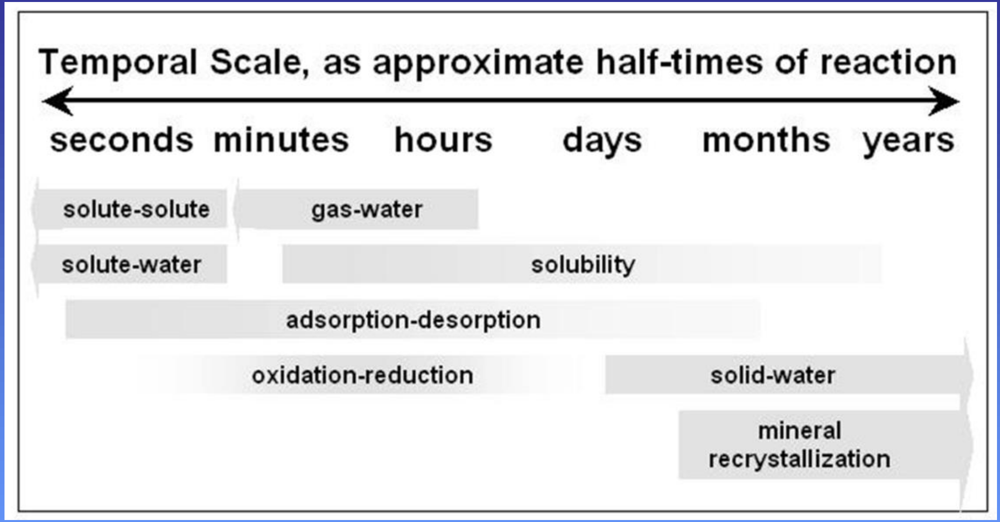
USGS

from Smith (2007)

Spatial and Temporal Scales



Differences in spatial scales of some factors that are influenced by geochemical processes



Differences in rates of some types of reactions that influence metal mobility

- ✓ many reactions involving metals are kinetically controlled or biologically mediated

from Smith (2007); Smith et al. (2000); modified from Wanty et al. (2001) and Langmuir and Mahoney (1984)

Define the Target Population

Target population - the set of all units or elements about which a sample is intended to draw conclusions

- Must be identified prior to sampling
- Defined by objectives of study
- Not an easy decision
- Need to know which media to sample to adequately determine pathways and receptors
- Scale of observation matters
- Must be understandable to users

USEPA (2002)

“Representativeness” of Sample

- Target population must be available to be sampled such that every portion of the material being sampled has an equal chance of being included in the sample
- Randomly collect samples without systematic bias
- Use procedures and sampling devices that prevent segregation and minimize sample variation
- Determining sample representativeness involves careful planning and formulating a proper sampling design
  - ✓ NOT determined by statistical analysis of the data after the fact
  - ✓ MUST document compromises during sampling

Pitard (1993); Ramsey and Hewitt (2005); USEPA (2002)

Common Sampling Concerns

- Sampling error
- Precision requirements
  - ✓ field sampling methods and equipment
  - ✓ sample preparation
  - ✓ laboratory subsampling
  - ✓ analyses
- Sample containers
- Sample preservation and storage
- Sample holding times
- Sampling logistics
- Costs (*but not at the expense of the integrity of the sampling program…*)

Solid, Disaggregated Samples

Sampling Error

- ➢ Improper collection
  - ✓ target population
  - ✓ sampling location
  - ✓ spatial or temporal changes
  - ✓ sampling media
  - ✓ sampling tools
  - ✓ sample containers
- ➢ Contamination
- ➢ Sample preservation and storage
- ➢ Inadequate sample mass

Fundamental Sampling Error

- The source of most sampling errors
- Due to the fact that not all particles have the same composition
- Cannot be eliminated, but can be estimated
- Results in variability and a lack of precision
- Particle size, sample mass, and degree of heterogeneity are important factors

See expanded slides in Additional Resources for more information;
Pitard (1993); USEPA (2002); Smith et al. (2006)

Fundamental Sampling Error, cont.

Pierre Gy's Particulate Sampling Theory:

If the mass of the population to be sampled is greater than ten times the mass of the sample to be collected, then the following formula may be used:

$$\sigma_{FE}^2 = \frac{c\, l\, f\, g\, d^3}{m_s}$$

where

σ_{FE}^2 is the variance of the fundamental error (FE)

c is the mineralogical composition factor (g/cm^3)

l is the liberation factor (dimensionless)

f is the shape factor (dimensionless)

g is the particle size distribution (granulometric) factor (dimensionless)

d is the maximum particle size (cm)

m_s is the sample mass (g)

Pitard (1993); USEPA (2002); Smith et al. (2006)

Fundamental Sampling Error, cont.

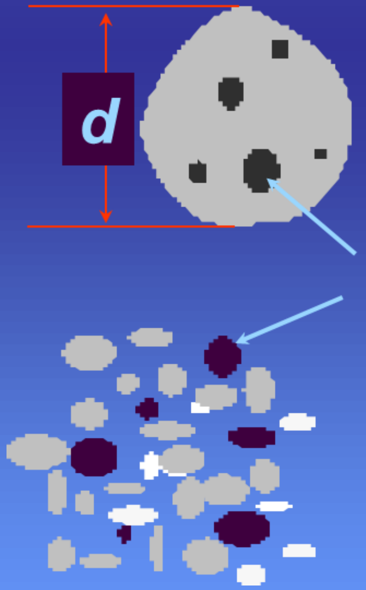
Mineralogical composition factor (*c*) is the maximum heterogeneity generated by the constituent of interest in the target population

- Related to the density of the material containing the constituent of interest (g/cm^3)
- Related to the average concentration of the constituent of interest (as a decimal)
- Can be estimated by dividing the approximate density of the material by the average concentration of the constituent of interest
  - ✓ Assumes complete liberation of the constituent of interest

Pitard (1993)

Fundamental Sampling Error, cont.

Liberation factor (*l*) depends upon whether the constituent of interest is present as separate particles or contained within larger particles



“unliberated”

constituent of interest

“liberated”

Pitard (1993)

Fundamental Sampling Error, cont.

Liberation factor (l) is a correction factor for the mineralogical composition factor (c)

- Dimensionless parameter
- Never greater than 1

  for no liberation, $l = 0$

  for complete liberation, $l = 1$

  for very heterogeneous material, $l \sim 0.8$

  for heterogeneous material, $l \sim 0.4$

  for average material, $l \sim 0.2$

  for homogeneous material, $l \sim 0.1$

  for very homogeneous material, $l \sim 0.05$

Pitard (1993)

Fundamental Sampling Error, cont.

Shape factor (f) relates to the typical shape of particles in the target population

- Dimensionless parameter
- Determined by microscopic examination

for cubes, $f = 1$

for spheres, $f \sim 0.5$ (usual default value)

for flakes (e.g., mica), $f \sim 0.1-0.2$

for elongated particles (e.g., asbestiform), $f > 1$
(can be as large as 10)

Pitard (1993)

Fundamental Sampling Error, cont.

Granulometric factor (g) accounts for the different sizes of particles in the target population

- Dimensionless parameter
- Decreases with presence of fine particles
- Never greater than 1

for same-size particles, $g = 1$

for noncalibrated material (e.g., jaw crusher), $g \sim 0.25$

for calibrated material, $0.5 < g \leq 1$

for sieved material (e.g., bracketed consecutive sieve sizes in a series), $g \sim 0.55$

for naturally calibrated material (e.g., rice), $g \sim 0.75$

Pitard (1993)

Fundamental Sampling Error, cont.

Maximum particle size (*d*)

- Opening size of the square mesh retaining no more than 5% oversize material
- In units of centimeters

Pitard (1993)

How to Determine Sample Mass

Always want the fundamental error to be less than 16%, so for 15%

$$\sigma_{FE}^2 = \frac{c\,l\,f\,g\,d^3}{m_s} = 0.0225$$

$$m_s = \frac{c\,l\,f\,g\,d^3}{0.0225}$$

Calculate sample mass by defining values for parameters

Pitard (1993)

Grouping and Segregation Error

- Due to the fact that not all particles are randomly distributed
  - ✓ size, shape, concentration
  - ✓ temporal differences
  - ✓ segregation
- Can be reduced
  - ✓ random sampling
  - ✓ collection of multiple increments

Incremental Sampling – see next presentation by Crumbling

See expanded slides in Additional Resources for more information; Pitard (1993); USEPA (2002); Smith et al. (2006); CLU-IN ITRC Soil Sampling and Decision Making Using Incremental Sampling Methodology

Need to Collect more Sample Mass when

Increasing particle size

Increasing heterogeneity

Low constituent concentration

Increasing desired degree of confidence

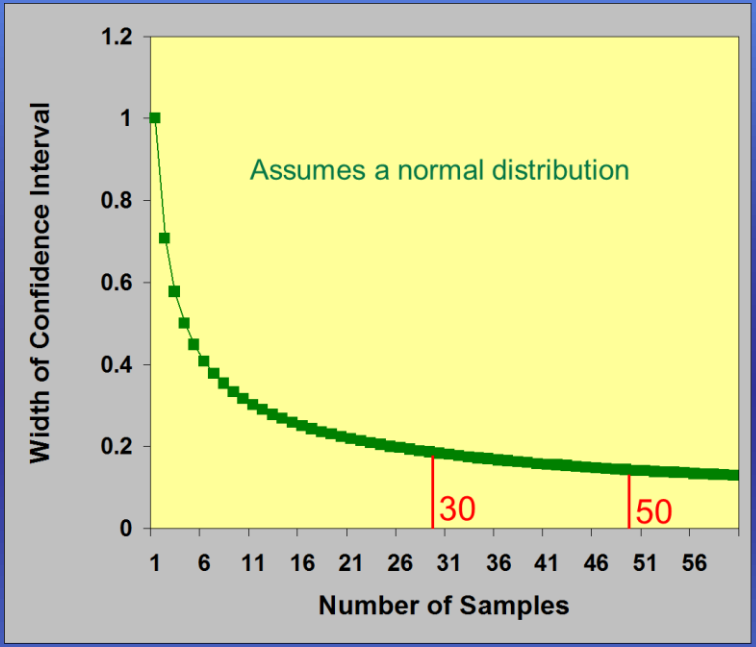
How Many Samples?

There is no "cookbook" approach

Consider an iterative approach

Need to take into account

- ✓ Heterogeneity
  - ○ distributional
  - ○ compositional
  - ○ morphological
- ✓ Degree of accuracy
- ✓ Variability of constituents
- ✓ Composite?



Pitard "rule of thumb" that a sample should be made up of at least 30 increments

Pitard (1993); Runnells et al. (1997); USEPA (2002); Price (2009)

How Many Samples?

Price (2009; p. Ch8-8): "The recommendation here and previously is that the final sampling frequency be determined site specifically based on the variability of critical parameters, prediction objectives and required accuracy."

Runnells et al. (1997): "Briefly, the method is based on the use of a statistical approach to determine, illustrate, and defend the adequacy of the sampling. [We do] not believe that there is a "correct" number of samples for characterizing a facility. That is, there is no general rule that can (or should) be followed, such as a given number of samples per ton of tailings, per acre of impoundment, or per foot of drillcore. Each facility is different, and the adequacy of sampling must be tailored to the facility."

Pitard (1993; p. 187): "As a rule of thumb based on numerous experiments, a sample should be made up of at least 30 increments."

USEPA (2002): *Guidance on Choosing a Sampling Design for Environmental Data Collection*

Sampling Mine Piles

Heterogeneity

Distributional

Morphological
(size and shape)

Compositional

USGS Sampling Strategy for Screening Mine Piles

- **Needs**
  - ✓ Screening and prioritizing mine piles
  - ✓ Statistically based
  - ✓ Field friendly
  - ✓ Cost effective
- **Question Addressed**
  - ✓ What are the potential metal contributions from mine piles at various mine sites?
    - ○ average properties = composite samples
- **Sampling Concerns**
  - ✓ Heterogeneity
    - ○ compositional, spatial, particle size
  - ✓ Sampling errors

Smith et al. (2000, 2002, 2003, 2006, 2007)

Sampling Strategy for Screening Mine Piles, cont.

- Target Population
  - ✓ Based on question to be addressed
  - ✓ Mine-waste pile
  - ✓ Surficial material (upper 15 cm)
  - ✓ <2 mm fraction (dry sieved)
- General Sampling Plan
  - ✓ Obtain a composite sample of the target population
  - ✓ Subject sample to leaching procedures to evaluate potential metal release to adjacent stream and shallow groundwater

Smith et al. (2000, 2002, 2003, 2006, 2007)

Sampling Strategy for Screening Mine Piles, cont.

- **Minimize Grouping and Segregation Error:**
  - ✓ Divide mine-waste dump into at least 30 cells of roughly equal surface area and randomly collect a surficial sample from each cell
- **Examine Average Properties and Minimize Cost:**
  - ✓ Combine cell samples into a mine-dump composite sample
- **Define Fundamental Error:**
  - ✓ Dry sieve the mine-dump composite sample to <2 mm (final composite sample should weigh at least 1,000 g (1 kg) after sieving)

Pitard (1993); Smith et al. (2000, 2002, 2003, 2006, 2007)

Sampling Strategy for Screening Mine Piles, cont.

One 30-increment dump-composite sample collected using this sampling strategy contains as much information, relative to average value, as 30 individual grab samples at $^1/_{30}$ of the analytical cost

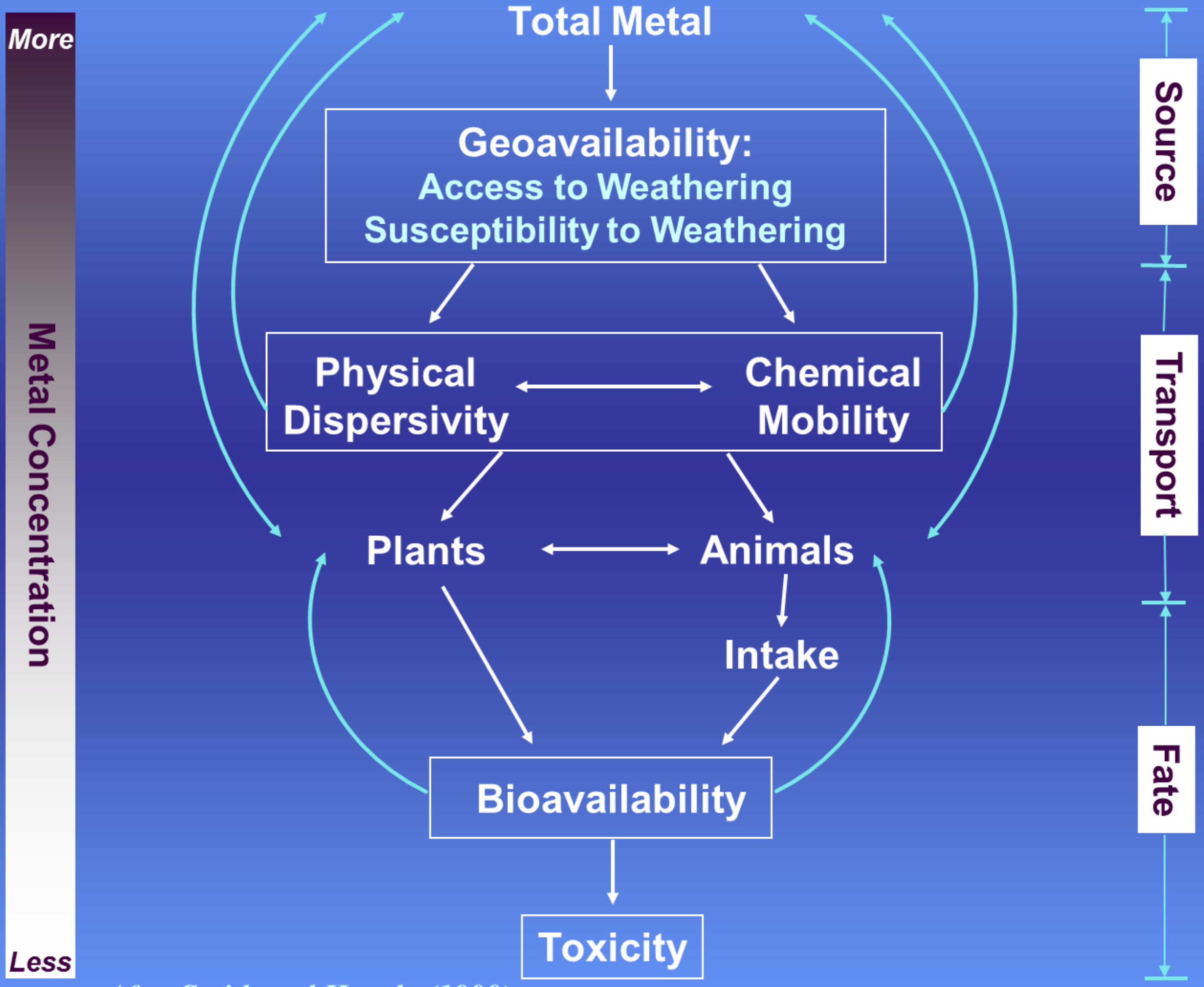
Smith et al. (2000, 2002, 2003, 2006, 2007)

Sampling Strategy for Screening Mine Piles, cont.

This sampling strategy could be adapted to the sampling of other target populations, such as

- ✓ individual waste-dump lobes
- ✓ pit bench
- ✓ dump lift
- ✓ geologic unit
- ✓ other "operational" units
- ✓ soils
- ✓ vegetation
- ✓ flood sediment from Hurricane Katrina

Total Concentration vs Geoavailability



After Smith and Huyck (1999)

USGS

Russell CLU-IN presentation

Field Screening

Price and Errington (1998); USEPA (2001); Smith et al. (2002, 2003, 2006); Price (2005, 2009); Stewart et al. (2006)

USGS Field Leach Test (FLT)

- Extraction ratio 20:1 (same as USEPA methods 1311 and 1312)
  - ✓ most readily soluble constituents in the sample can be dissolved without exceeding saturation limits
  - ✓ provides sufficient sample to obtain desired measurements and elemental analyses
- Add 1.0 L deionized water to 50.0 g of a <2 mm (-10 mesh) sample
- Hand shake for 5 min, allow to settle for 10 min
- Determine pH and specific conductance on the leachate
- Filter leachate through a 0.45-µm syringe filter and preserve for analyses

Hageman and Briggs (2000); Smith et al. (2000); Al-Abed et al. (2006); Hageman (2007); Smith et al. (2007)

USGS

Field Leach Test, cont.

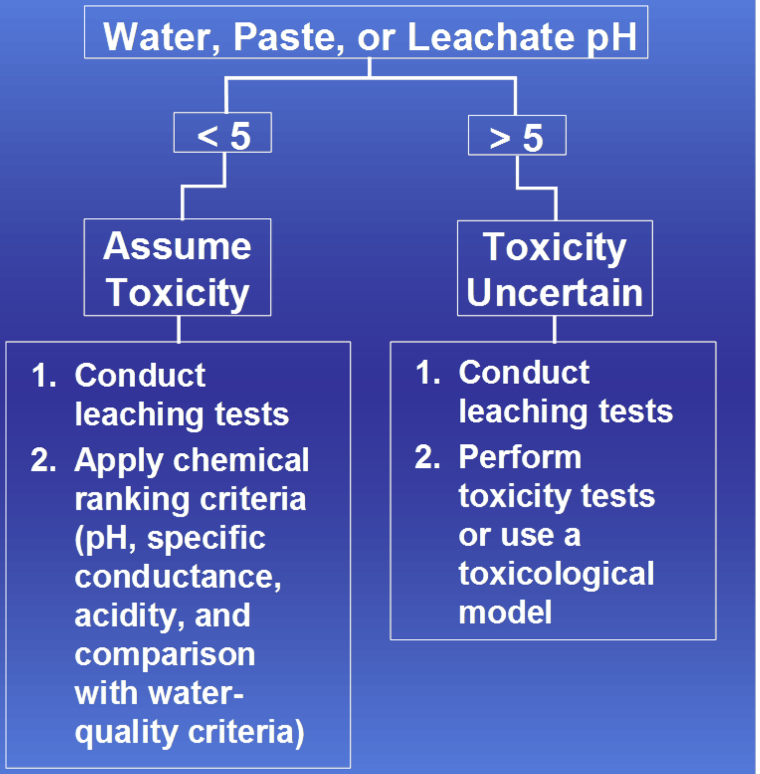
- When used in conjunction with the sampling technique described earlier, it can be performed onsite with only sub-samples of preserved leachate returned to the lab for analyses
- Has been used extensively for characterization of historical mine-waste piles throughout the continental United States and Alaska
- Has also been used to leach a broad spectrum of other matrices
    - ✓ naturally mineralized soils, agricultural soils, mine-waste pile drill core intervals, mining influenced wetland sediments, World Trade Center dusts, volcanic dusts, atmospheric dusts, and forest fire burned soils

Hageman and Briggs (2000); Smith et al. (2000);
Al-Abed et al. (2006); Hageman (2007); Smith et al. (2007)

Mining Waste Decision Tree

A simple screening procedure to determine potential toxicity to the aquatic environment

CHEMICAL CRITERIA



Water, Paste, or Leachate pH

< 5

Assume Toxicity

1. Conduct leaching tests
2. Apply chemical ranking criteria (pH, specific conductance, acidity, and comparison with water-quality criteria)

> 5

Toxicity Uncertain

1. Conduct leaching tests
2. Perform toxicity tests or use a toxicological model

PHYSICAL CRITERIA

1. Conduct on-site assessment
    - a) Size and estimated volume of waste-rock pile
    - b) Presence of cementation crusts
2. Apply physical ranking criteria (erosional features, presence of a vegetative kill zone, presence of vegetation on the pile, and proximity to a stream)

from Wildeman et al. (2007)

Both Criteria are Important

- ✓ Chemical rates availability of contaminants
- ✓ Physical rates ability to deliver contaminants

USGS

Sampling for Prediction Studies

- Determine degree of variability
- Different rock types, alteration
- Mineralogical and microscopic examination
  - ✓ degree of liberation
  - ✓ solubility controls
  - ✓ grain size and texture
- Need complete geochemical characterization
- "Representative" samples

USGS

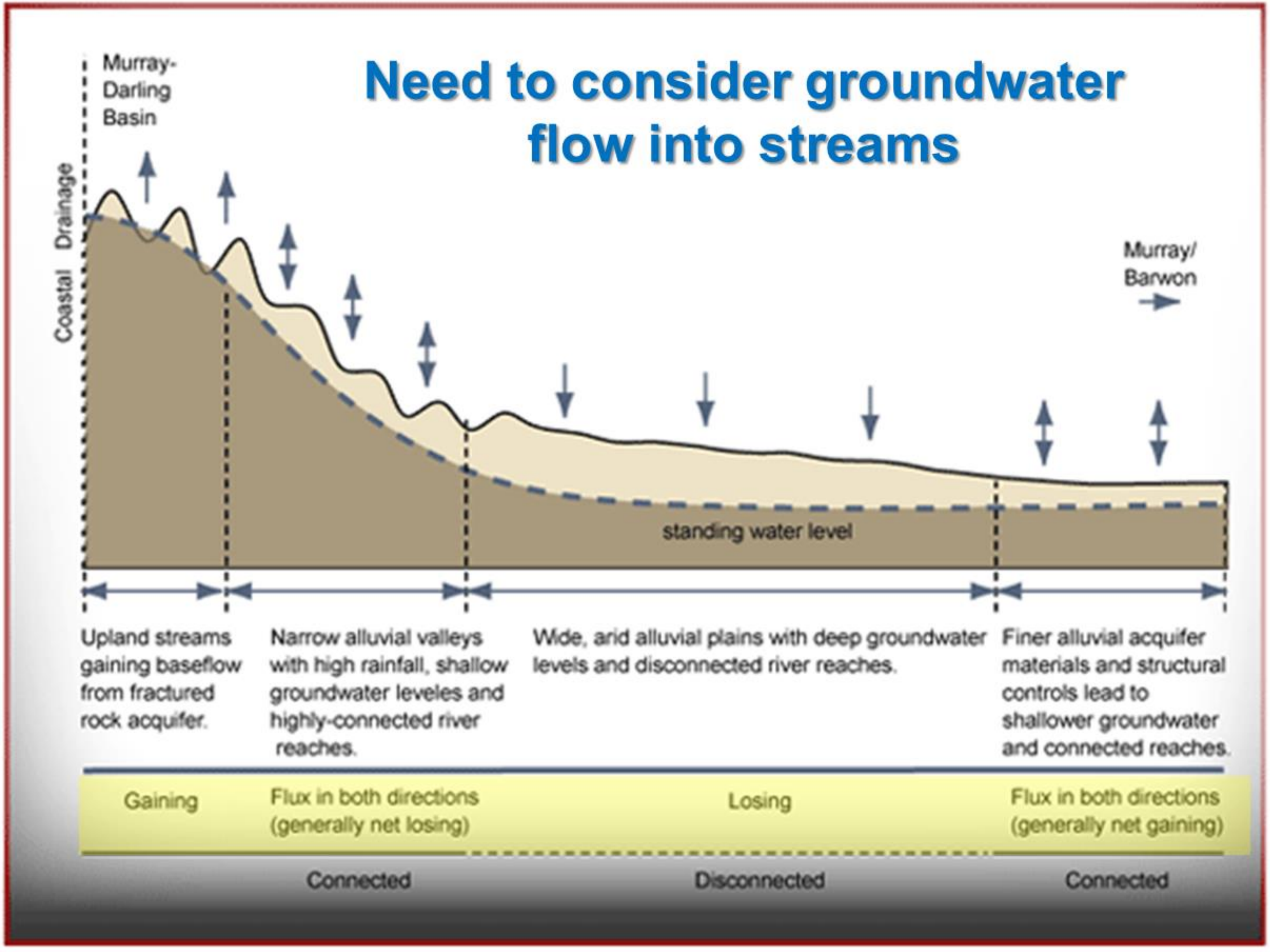
Maest CLU-IN presentation; Maest and Kuipers (2005)

Surface Water Sampling Considerations

Challenges in Collecting Surface-Water Samples at Mining Sites

- Aqueous metal concentrations are highly variable in space in mineralized and mined areas
  - ✓ Location in catchment
  - ✓ Underlying lithology
  - ✓ Weathering of ore deposits or wastes
  - ✓ Climate
  - ✓ Geochemical processes
- Aqueous metal concentrations are highly variable in time in mineralized and mined areas
  - ✓ Seasonal
  - ✓ Streamflow (storms)
  - ✓ Daily

Interaction of Groundwater and Surface Water



Need to consider groundwater flow into streams

Upland streams gaining baseflow from fractured rock acquifer.

Narrow alluvial valleys with high rainfall, shallow groundwater leveles and highly-connected river reaches.

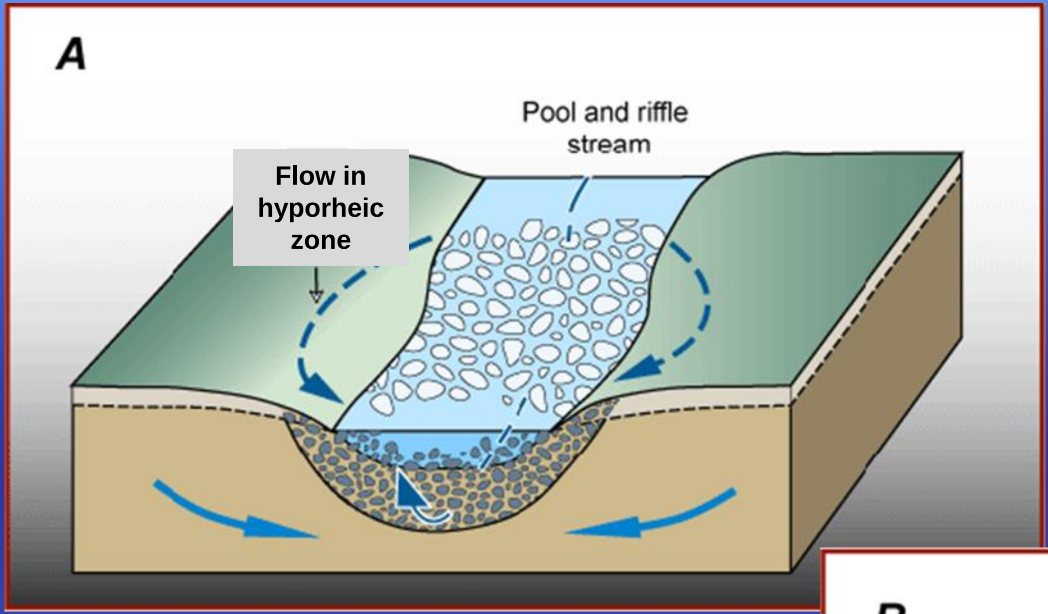
Wide, arid alluvial plains with deep groundwater levels and disconnected river reaches.

Finer alluvial acquifer materials and structural controls lead to shallower groundwater and connected reaches.

Gaining	Flux in both directions (generally net losing)	Losing	Flux in both directions (generally net gaining)
Connected	Connected	Disconnected	Connected

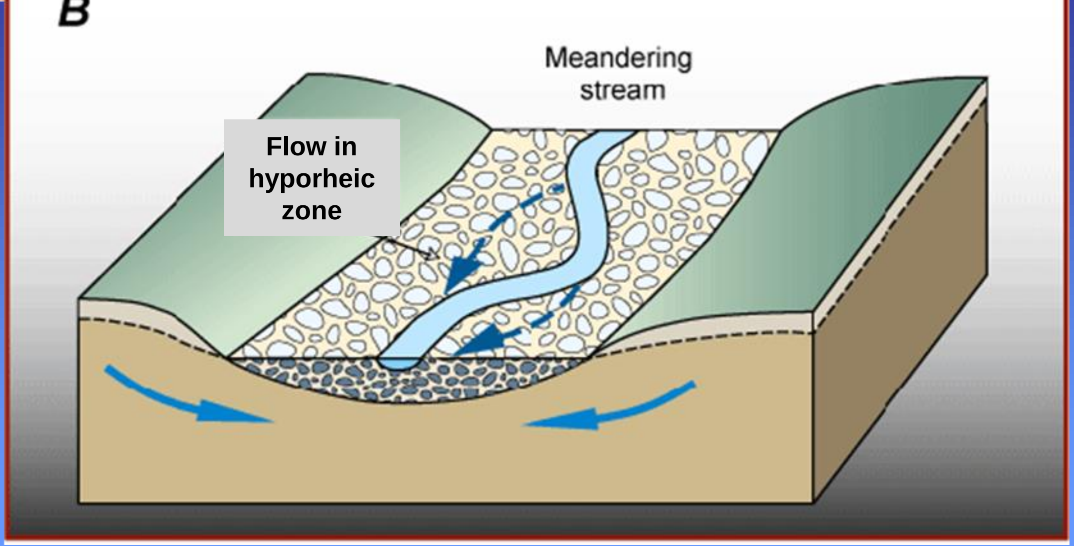
from Braaten and Gates (2002); Wireman CLU-IN presentation

Hyporheic Flow



Interactions at the surface-water/groundwater interface can play an important role in the concentration and load of constituents and can have significant environmental influences on biogeochemical processes (Bencala, 2005)

The hyporheic zone is a region beneath and lateral to a stream bed where there is mixing of shallow groundwater and surface water



Winter et al. (1998); Bencala (2005)

What is a Diel Cycle?

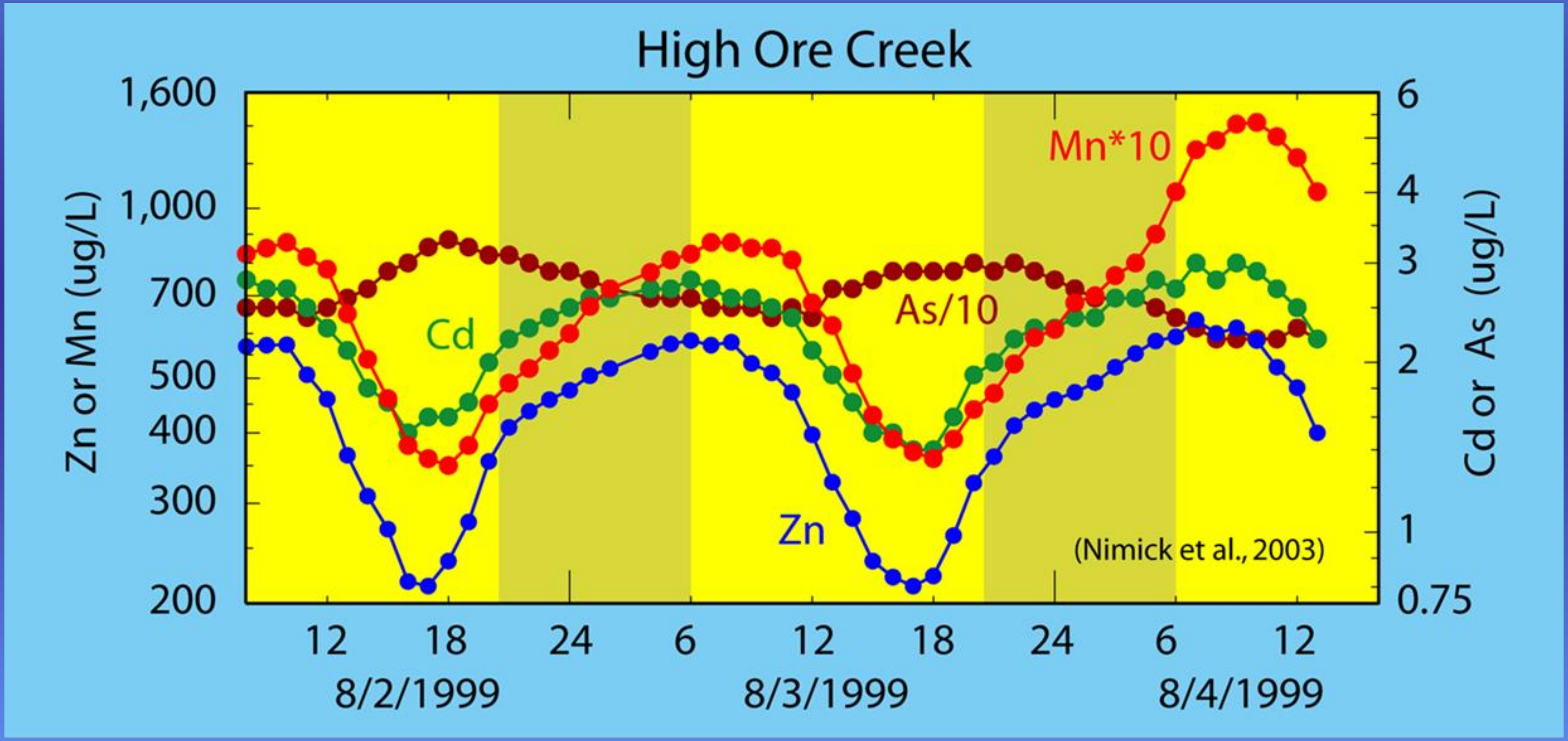
Diel – involving a 24-hour period that usually involves the day and adjoining night

Processes:

- ✓ Stream flow (evapotranspiration causes up to 20% change; snowmelt pulses)
- ✓ Water temperature (influences rates of reactions; mineral and gas solubility)
- ✓ Photosynthesis
- ✓ Photochemical reactions

Diel Processes in Neutral and Alkaline Streams

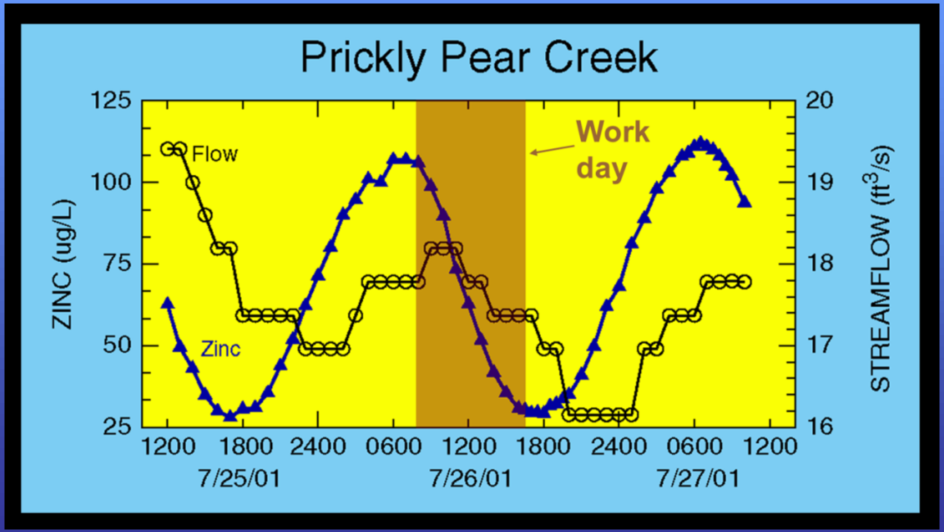
Note: (1) the large fluctuation in metal concentrations during each 24-hour cycle (shaded=nighttime); (2) arsenic is in opposite phase with cations; (3) applies to near-neutral to alkaline streams (not so critical at lower pH)

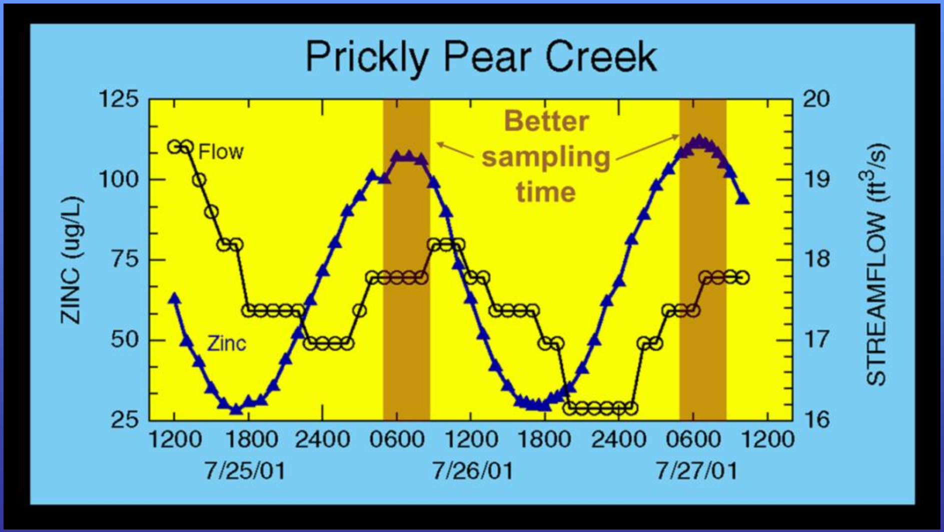


Arsenic	Cadmium	Manganese	Zinc
22-33 μg/L	1.4-3.0 μg/L	35-142 μg/L	214-634 μg/L
50%	110%	306%	196%

Nimick et al. (2003)

Time of Sampling is Important





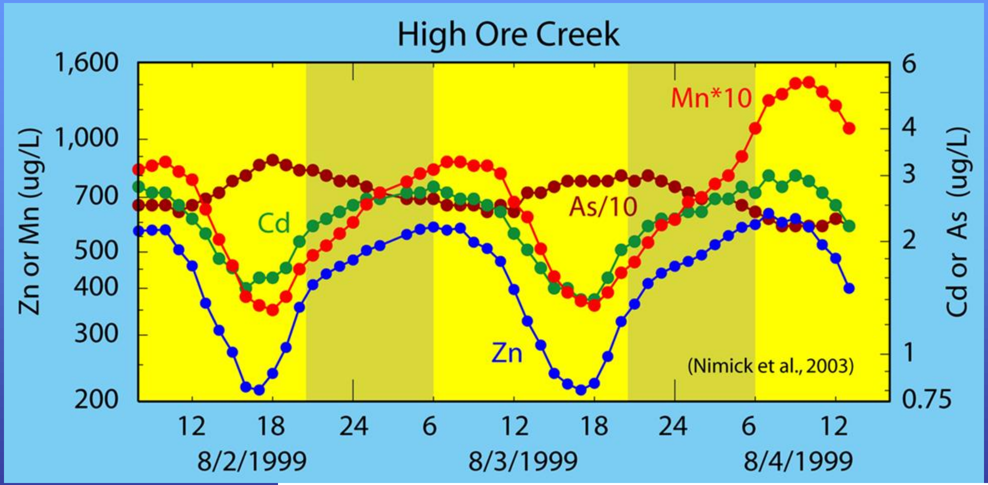
What is realistic?

- ✓ Be aware of diel cycles
- ✓ If a site is repeatedly sampled, it should be sampled at the same time of day each time it is visited
- ✓ Record the time of day a sample is collected

USGS

Nimick et al. (2011)

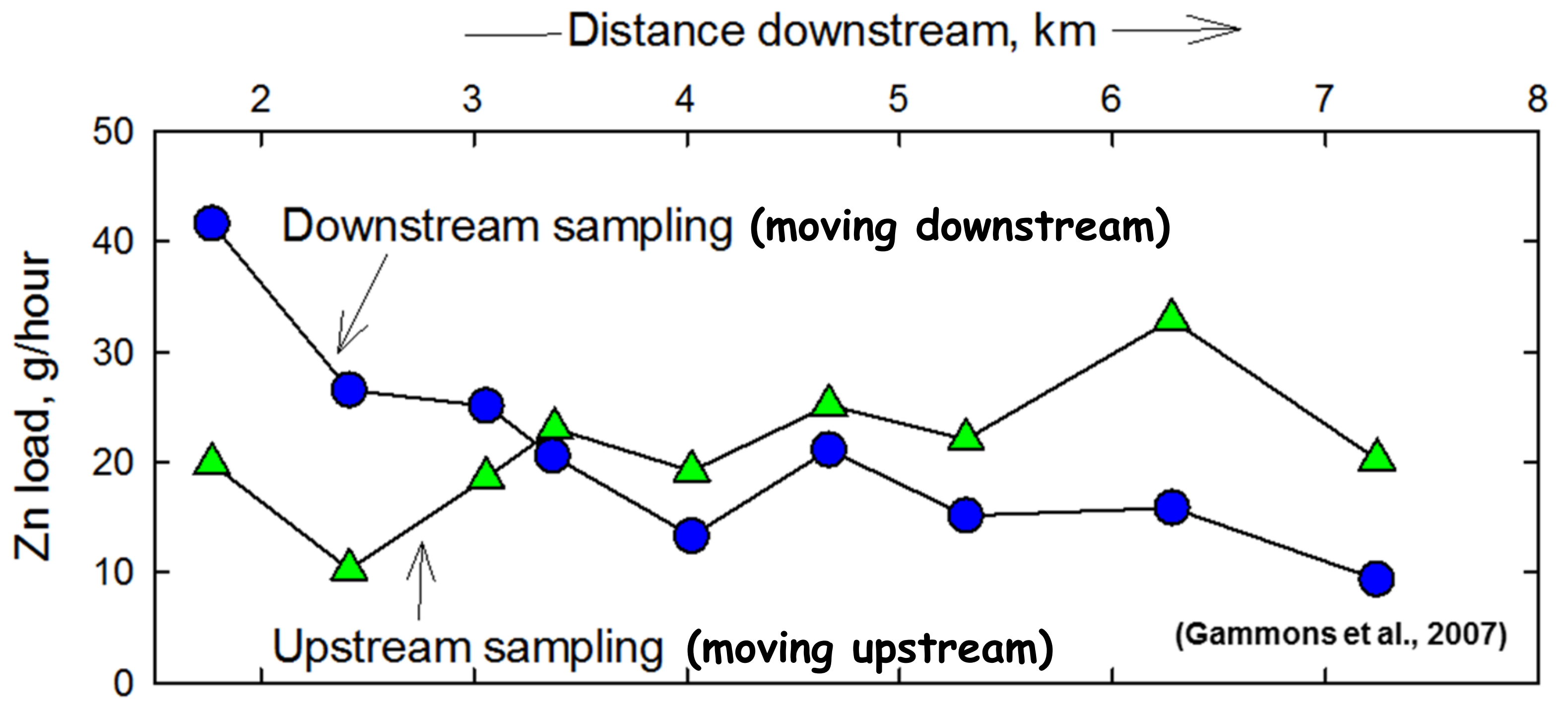
Short-Term Variability



High Ore Creek

(Nimick et al., 2003)

Different findings when sampled moving upstream vs moving downstream during the day



Downstream sampling **(moving downstream)**

Upstream sampling **(moving upstream)**

(Gammons et al., 2007)

Gammons et al. (2007)

Short-Term Variability, cont.

The previous slide shows data from a one-day study in a mining influenced stream where one sampler consecutively collected samples going upstream, and another sampler consecutively collected samples going downstream. The sampler who moved downstream concluded that the zinc load steadily decreased downstream, and the sampler moving upstream concluded that the zinc load increased downstream (and that zinc sources existed along the stream). In reality, the average zinc load over the 24-hour period was relatively constant and the differences observed by the samplers were due to diel (24-hour cycle) variations (Gammons et al., 2007).

Gammons et al. (2007)

Magnitude of Diel Cycles for Dissolved Trace Elements

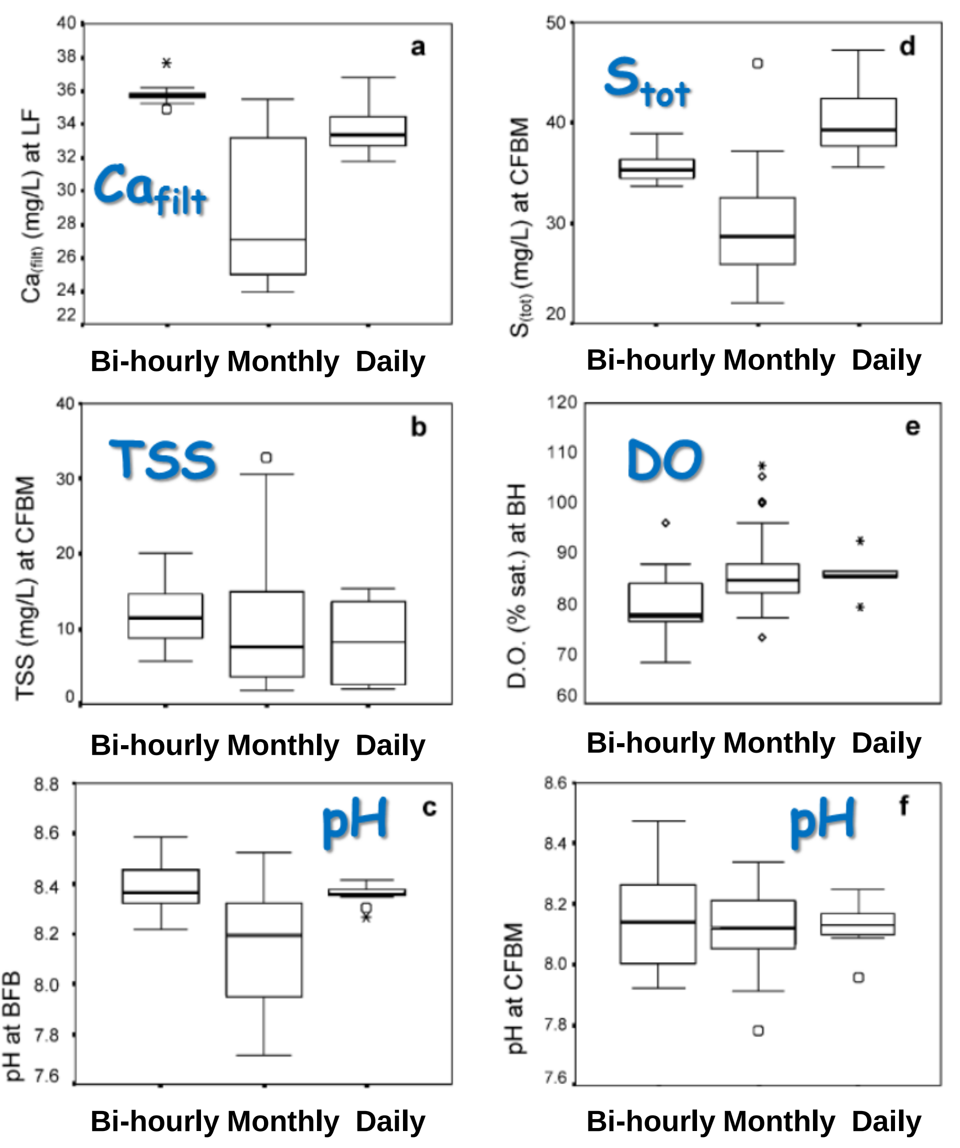
Trace Element[1]	Maximum Daily Increase (%) [2]	Number of Diel Samplings[2]
As	54	>25
Cd	330	12
Cu (pH = 6.8 – 7)	140	3
Cu (pH > 7)	<10	12
Methyl Hg	93	2
Mn	306	20
Ni	167	1
Pb	--	0
REE	830	2
Se	<10	1
Zn	800	>35

1. Near-neutral to alkaline streams unless otherwise noted

2. See Nimick et al. (2011) for references

For diel behavior in acidic- to neutral-pH streams, see Gammons et al. (2005) and Nimick et al. (2011)

Temporal Sampling Scales



Note that short-term variations are similar in magnitude to longer timescales

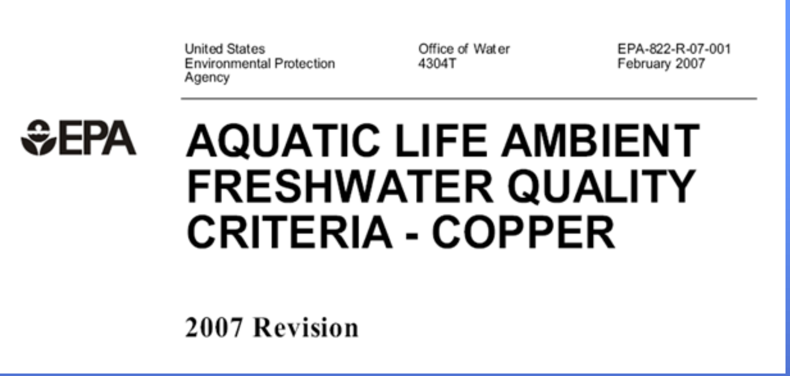
- ✓ Monthly dominated by snowmelt and precipitation dynamics
- ✓ Daily dominated by episodic events
- ✓ Bi-hourly is diel changes

Nagorski et al. (2003)

Geochemical Modeling Needs

- Necessary to have complete dissolved water analyses
  - ✓ Including major, minor, and trace elements (both anions and cations), pH, temperature
  - ✓ Iron speciation (and other elements of concern)?
- Additional important determinations
  - ✓ Specific conductance, alkalinity, TDS, and redox conditions
  - ✓ Suspended sediment?
  - ✓ Consider definition of "dissolved"
- Focusing sampling activities solely on regulated constituents often results in incomplete or incorrect characterization, which could lead to potentially costly problems later
  - ✓ Limits utility of data
  - ✓ Unanticipated issues may be discovered later

Nordstrom CLU-IN presentation; Nordstrom (2004)



United States Environmental Protection Agency
Office of Water 4304T
EPA-822-R-07-001 February 2007

EPA

AQUATIC LIFE AMBIENT FRESHWATER QUALITY CRITERIA - COPPER

2007 Revision

Toxicological Modeling Needs

Biotic Ligand Model (BLM)

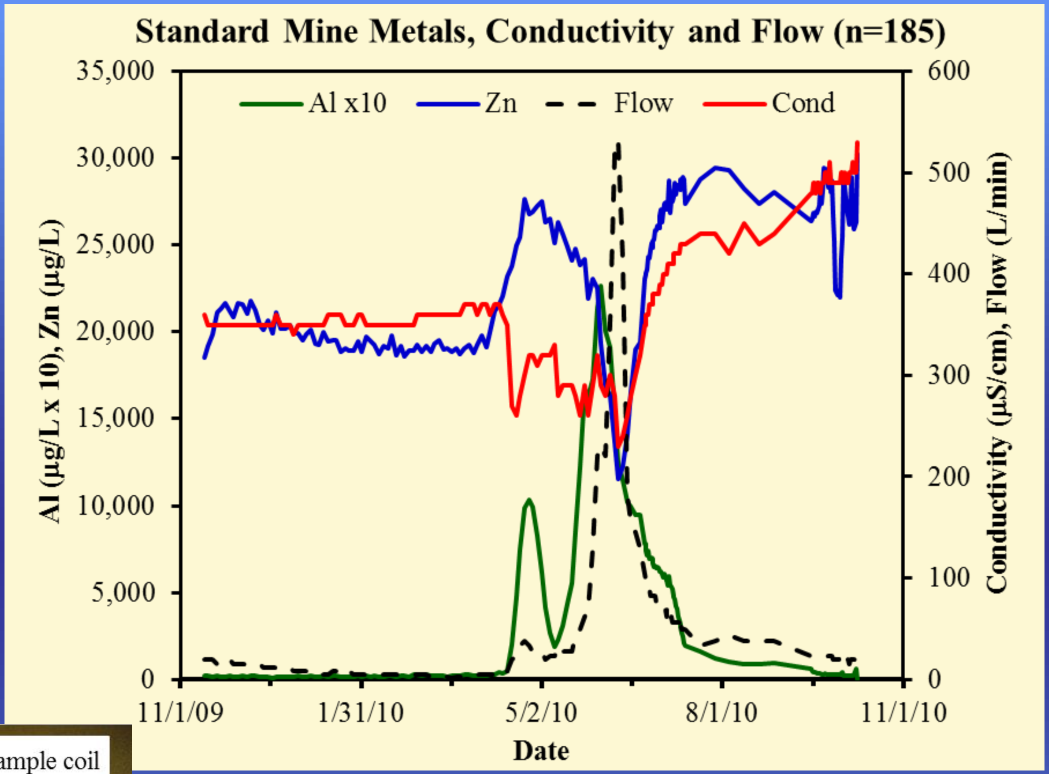
- ✓ Incorporated into USEPA updated aquatic life criteria for copper
- ✓ Computational approach
- ✓ Required input includes temperature, pH, dissolved organic carbon (DOC), percent DOC as humic acid, alkalinity, and dissolved concentrations for calcium, magnesium, sodium, potassium, sulfate, and chloride

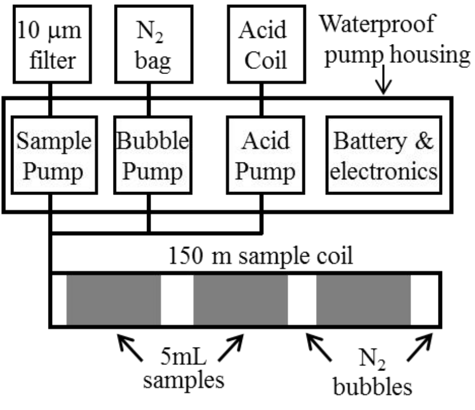
USEPA (2007); Smith et al. (2009)

MiniSipper (segmented water sampler)

High resolution *in situ* remote sampling

- ✓ 250 5-mL discrete or integrated samples
- ✓ 12-month long deployments
- ✓ Event triggers can change sampling





10 µm filter

N_2 bag

Acid Coil

Waterproof pump housing

Sample Pump

Bubble Pump

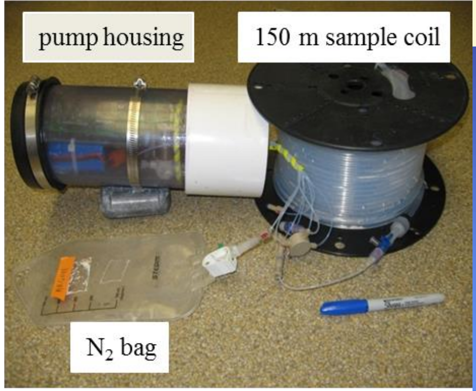
Acid Pump

Battery & electronics

150 m sample coil

5mL samples

N_2 bubbles



Bubble separation

10 µm filtration

Inline acidification

Chapin and Todd (2012)

Concentration vs Load

(Depends on the question…)

Concentration

- Regulatory criteria based on concentrations
- Toxicological data relate to concentrations

Load at Catchment Outlet

- Product of concentration and stream discharge
- TMDL (Total Maximum Daily Load; load capacity of the receiving water)
  - ✓ Fixed point monitoring
  - ✓ Temporal trends
  - ✓ Not adequate to identify sources

Mass-loading Approach

- Combines tracer-injection and synoptic-sampling methods
  - ✓ Provides spatial detail
  - ✓ Can determine metal attenuation
  - ✓ Can identify and compare sources within catchment
  - ✓ Includes groundwater and hyporheic flow

Kimball et al. (2002, 2007); Walton-Day et al. (2012)

Tracer Injections

- Determine how much metal enters a stream
  - ✓ mass loading (concentration x discharge)
- Determine how much metal stays in a stream
- Provide accurate discharge measurements
  - ✓ difficult to obtain in mountain streams
- Differentiate between multiple sources
- Monitor effectiveness of remediation efforts
- Usually combined with instantaneous sampling
  - ✓ Collection of samples from many locations during a short period of time, typically within about 20 min, during minimum period on cation diel curves

USGS

Kimball (1997)

Surface Water Sampling Suggestions

- Use experienced personnel to collect water samples
- Be consistent in sampling procedures, locations, and time of day
- Conduct stream-water discharge measurements
- Ensure that stream water is well mixed at sampling locations
- Account for natural variability by nesting short-term studies within long-term studies
  - ✓ Encompass variable climatic and hydrologic conditions
  - ✓ Short-term (daily) variations can be similar in magnitude to seasonal variations
- Sample over the entire hydrograph

Smith (2011)

Surface Water Sampling Suggestions, cont.

- For comparison between sites, collect samples simultaneously under similar hydrologic and diel cycle conditions
- Sample high-flow and transient hydrologic events
  - ✓ Obtain an estimate of flushing of constituents from soils, mining wastes, hyporheic zones, etc. in a catchment
- Need adequate water-quality information
  - ✓ Complete dissolved chemical analyses, including major, minor, and trace cations and anions, and dissolved organic carbon
- Communicate with the laboratory to ensure that adequate sample volumes are collected and proper sample preservation is used

Smith (2011)

Surface Water Sampling Strategies

(from Gammons and Nimick, 2010)

- Chronic standards
  - ✓ Sample at equal time intervals to obtain a 4-day mean
- Acute standards
  - ✓ Pick sample time to coincide with the daily maximum
- Temporal or spatial analysis
  - ✓ Always sample at same time or collect 24-hour samples
- Comparison of loads (temporally or spatially)
  - ✓ Collect samples and measure flows over at least 24 hours

Acknowledgements

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R. Schmiermund and K. Walton-Day provided very helpful suggestions for this presentation

Thank you

Available on CLU-IN site (Additional Resources):

- ✓ Expanded version of slides
- ✓ List of references
- ✓ Several papers