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Sampling Considerations at Mining Sites

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CLU-IN Webinar Series on
Hardrock Mining Geochemistry and Hydrology

Sampling, Monitoring, and Remediation
at Mine Sites Workshop
March 5, 2013

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

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Sampling is Important!

Success of a sampling program depends on

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

Sampling

↓

Chemical Analysis

↓

Data Interpretation

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Russell CLU-IN presentation 3

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

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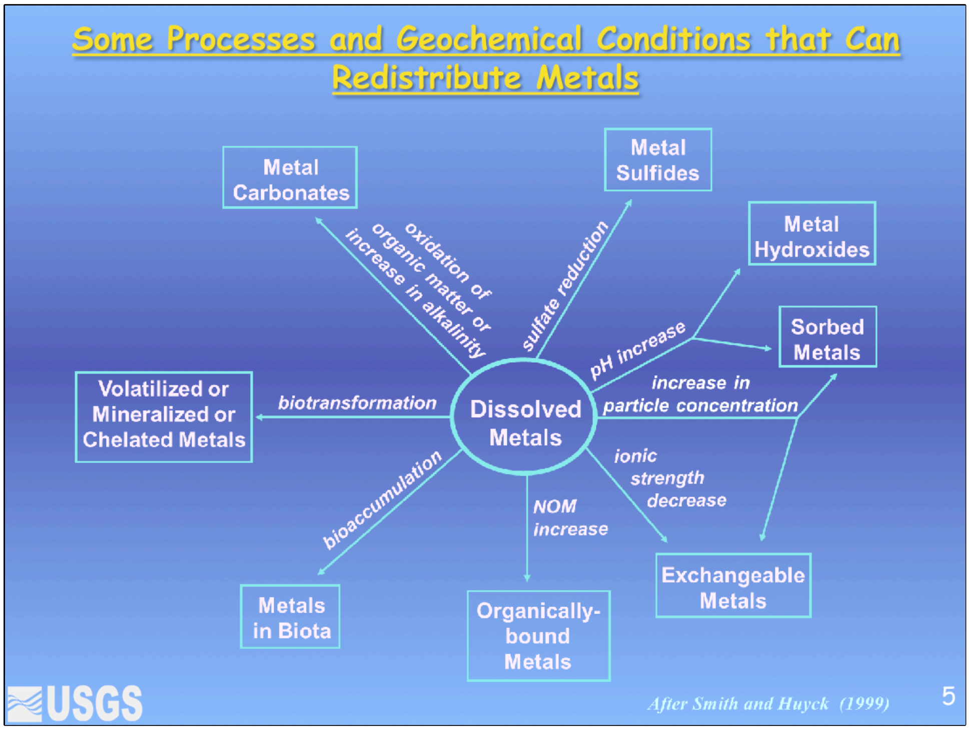
Some Processes and Geochemical Conditions that Can Redistribute Metals
Metal Carbonates
Metal Sulfides
Metal Hydroxides
Sorbed Metals
oxidation of organic matter or increase in alkalinity
sulfate reduction
pH increase
increase in particle concentration
Volatilized or Mineralized or Chelated Metals
biotransformation
Dissolved Metals
bioaccumulation
ionic strength decrease
NOM increase
Metals in Biota
Organically-bound Metals
Exchangeable Metals
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After Smith and Huyck (1999)
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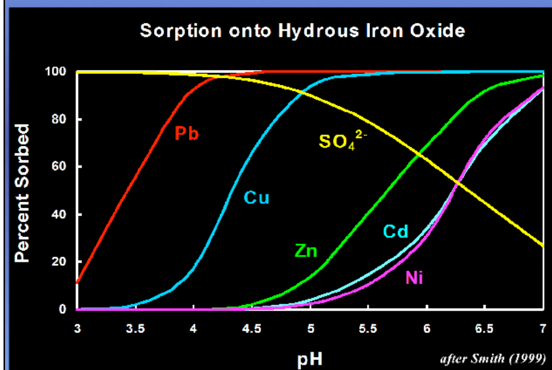
Role of Metal Sorption

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



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

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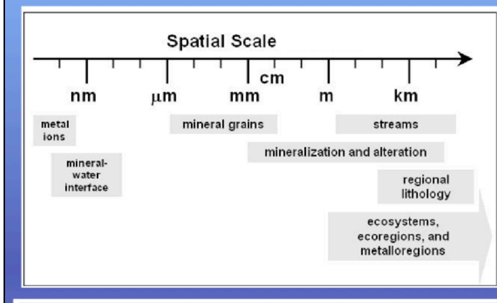
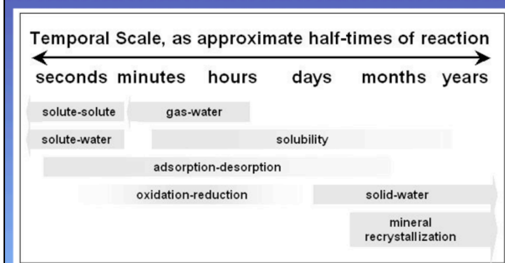
Spatial and Temporal Scales



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)

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Define the Target Population

- 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

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USEPA (2002)

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"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
  - ✓ CANNOT be determined by statistical analysis of the data after the fact
  - ✓ MUST have flexibility to document compromises during sampling

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

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Sampling Solid, Disaggregated Samples

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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)

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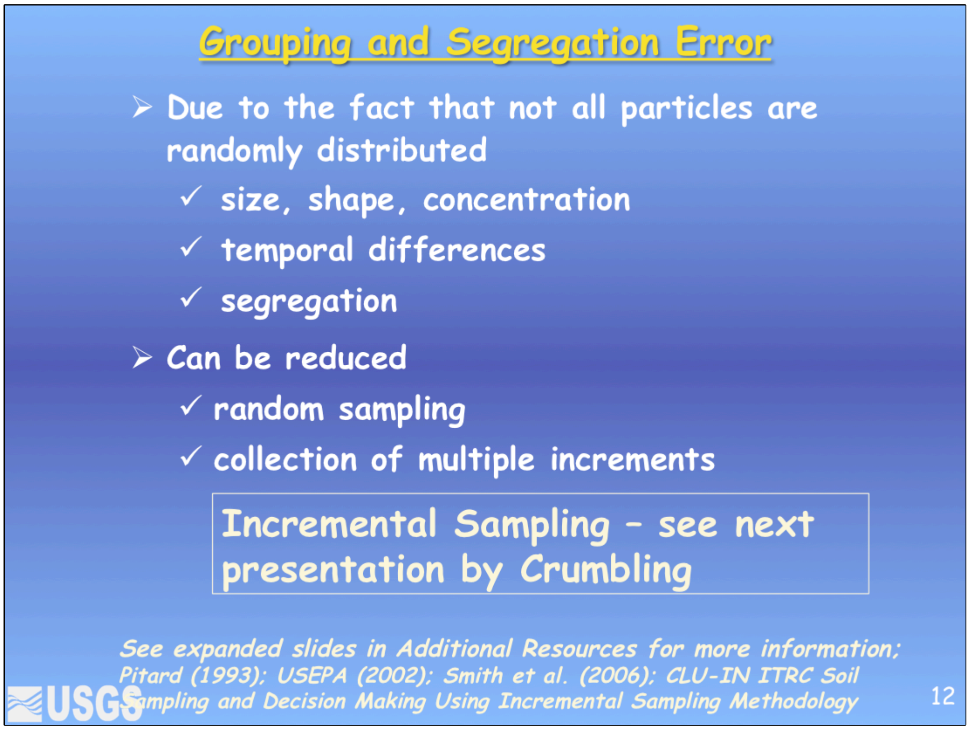
Grouping and Segregation Error
Due to the fact that not all particles are randomly distributed
size, shape, concentration
temporal differences
segregation
Can be reduced
random sampling
collection of multiple increments
Incremental Sampling – see next presentation by Crumbling
See expanded slides in 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
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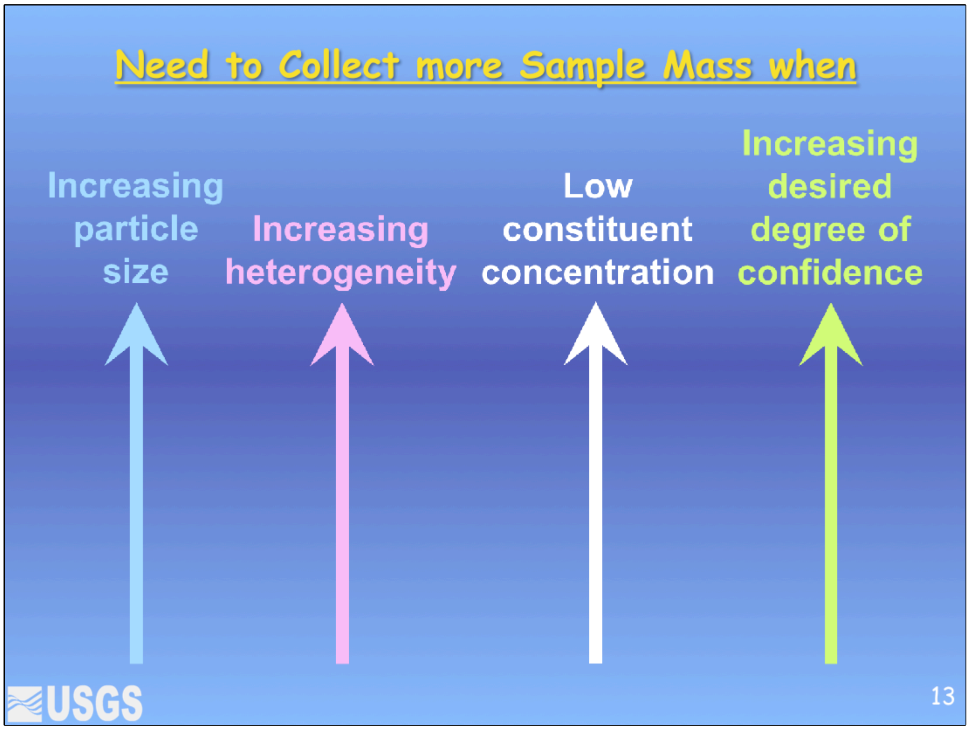
Need to Collect more Sample Mass when
Increasing particle size
Increasing heterogeneity
Low constituent concentration
Increasing desired degree of confidence
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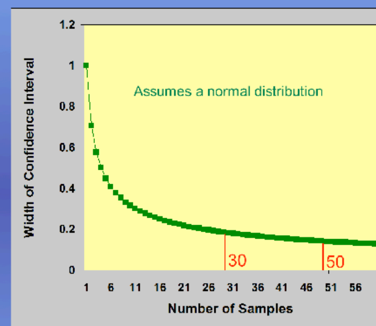
How Many Samples?

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

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

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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

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Sampling Mine Piles

Heterogeneity

Distributional

Morphological
(size and shape)

Compositional

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Sampling Strategy for Mine Piles

1. Divide pile into at least 30 cells of roughly equal surface area and randomly collect a surficial sample from each cell
2. Combine cell samples into a mine-pile composite sample
3. Dry sieve the mine-pile composite sample to <2 mm
4. Final composite sample should weigh at least 1 kg after sieving

See expanded slides in Additional Resources for more information

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

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Sampling Strategy for Mine Piles, cont.

1 composite sample is analyzed instead of 30 grab samples

One 30-increment mine-pile 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

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Smith et al. (2000, 2002, 2003, 2006, 2007) 18

Sampling Strategy for 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

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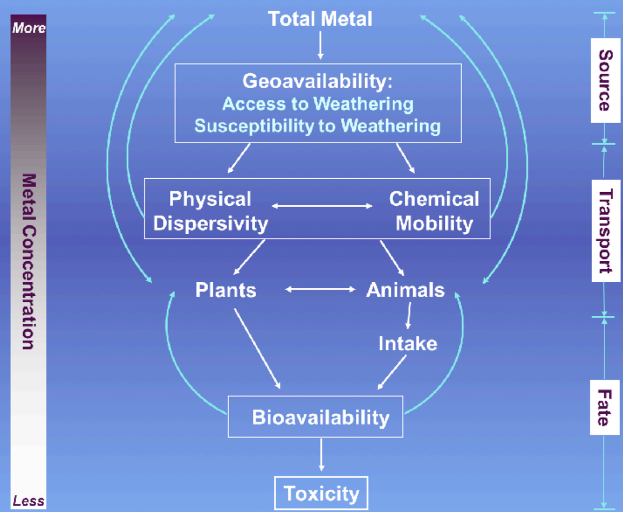
Total Concentration vs Geoavailability



After Smith and Huyck (1999)

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Russell CLU-IN presentation 20

Surface Water Sampling Considerations

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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

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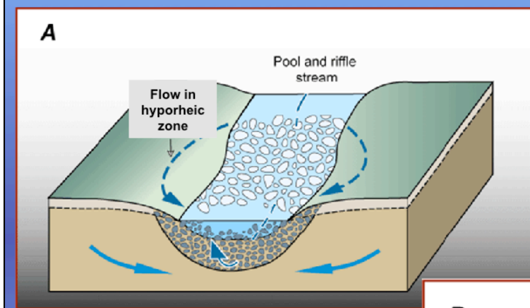
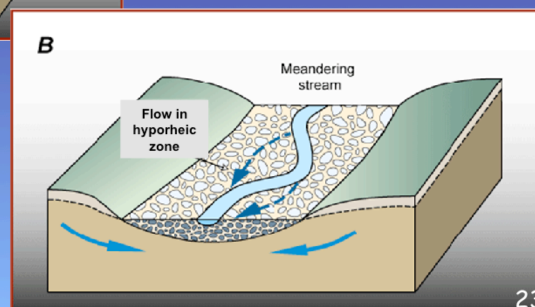
Hyporheic Flow

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)

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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

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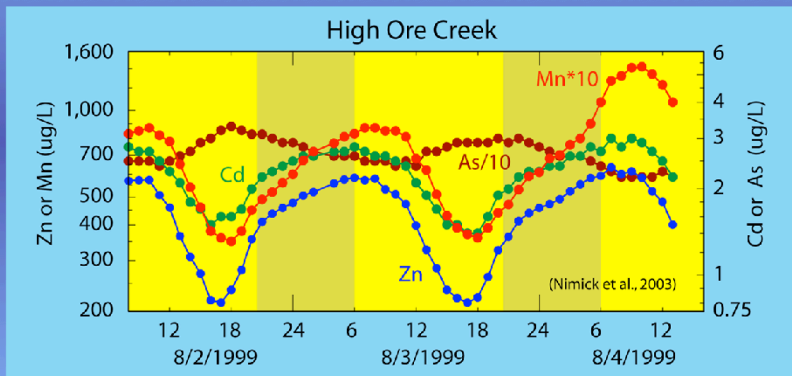
Diel Processes in Neutral and Alkaline Streams

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%

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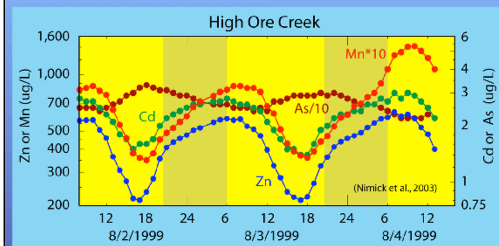
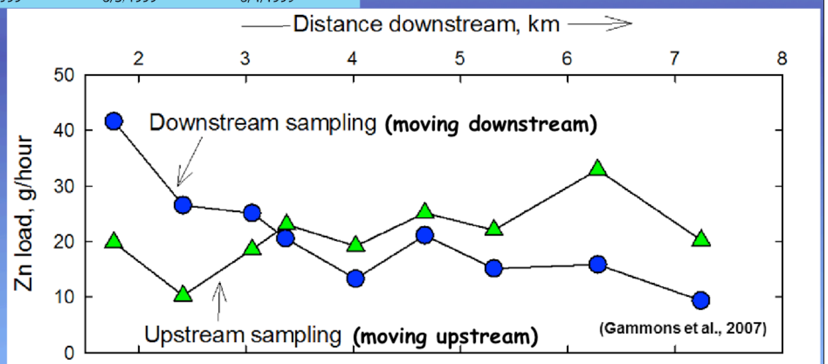
Nimick et al. (2003) 25

Short-Term Variability



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



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Gammons et al. (2007) 26

Temporal Sampling Scales

Short-term (daily) variations can be similar in magnitude to longer (monthly) timescales

- Monthly variations are dominated by snowmelt and precipitation dynamics
- Daily-scale variations are dominated by episodic events
  - ✓ Thunderstorms, similar in magnitude to early spring flush
  - ✓ Diel cycles

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Nagorski et al. (2003) 27

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

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Nordstrom CLU-IN presentation; Nordstrom (2004) 28

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

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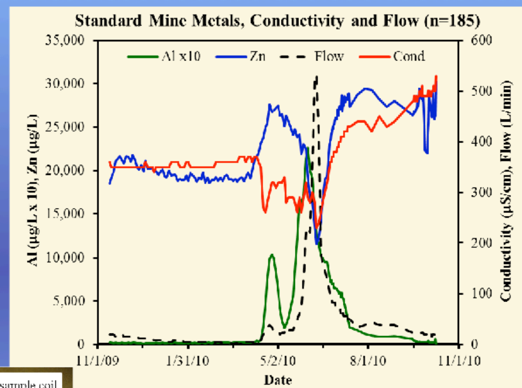
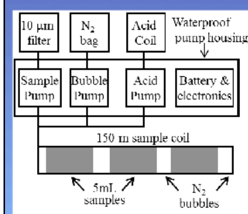
USEPA (2007); Smith et al. (2009) 29

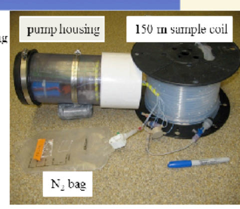
MiniSipper (segmented water sampler)

High resolution *in situ* remote sampling

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







Bubble separation

10 µm filtration

Inline acidification

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Chapin and Todd (2012) 30

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

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

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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

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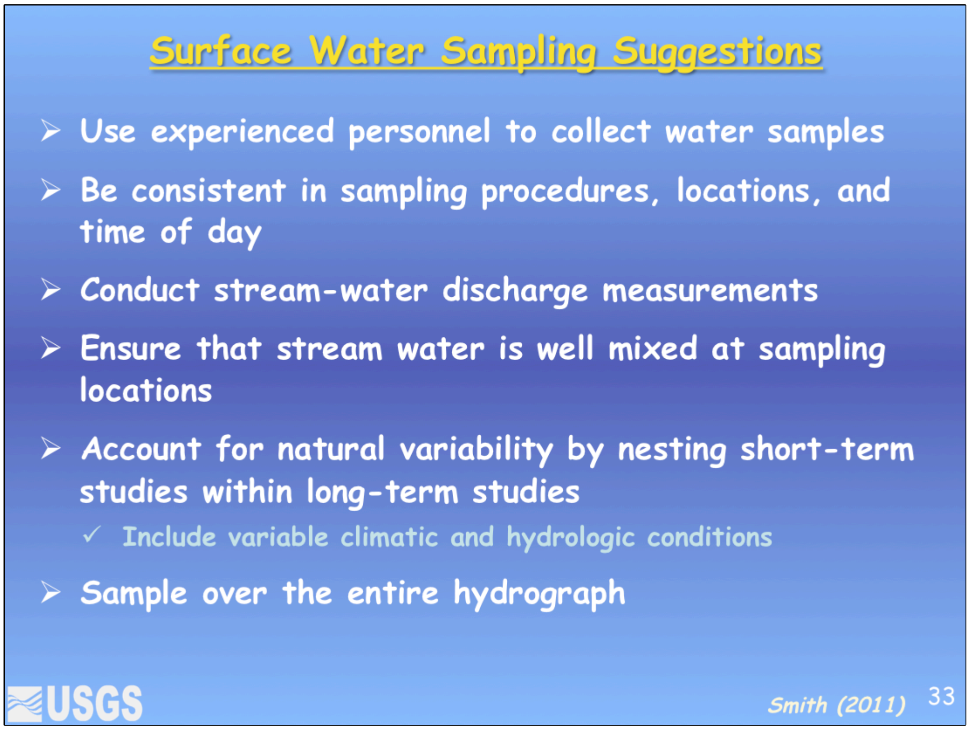
Kimball (1997) 32


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
Include variable climatic and hydrologic conditions
Sample over the entire hydrograph
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Smith (2011)
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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 DOC)
- Communicate with the laboratory to ensure that adequate sample volumes are collected and proper sample preservation is used

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Smith (2011) 34

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

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Acknowledgements

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

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Thank you

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