Sampling Considerations at Mining Sites

Kathleen S. Smith
U.S. Geological Survey, Denver, CO
ksmith@usgs.gov

CLU-IN Webinar Series on
Hardrock Mining Geochemistry and Hydrology

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

Additional Resources Available on CLU-IN Site

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

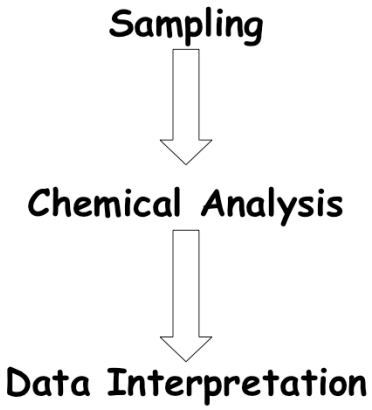
USGS

2

Sampling is Important!

Success of a sampling program depends on

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



USGS

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**

USGS

4

Some Processes and Geochemical Conditions that Can Redistribute Metals

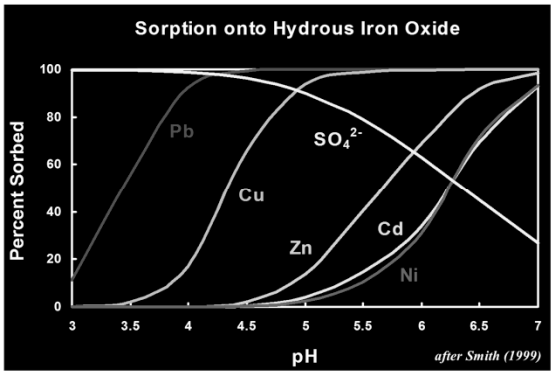
USGS

After Smith and Huyck (1999)

5

Role of Metal Sorption

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



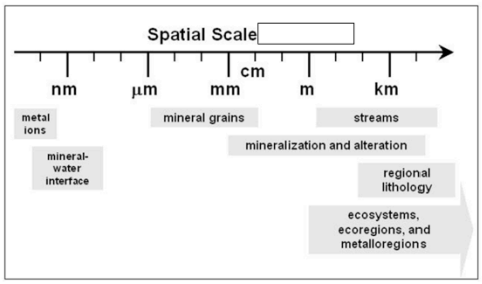
Sorption of metals onto suspended Fe and Al-rich particulates is a predictable function of the metal itself, metal concentration, pH, amounts/types of suspended particulates, and temperature

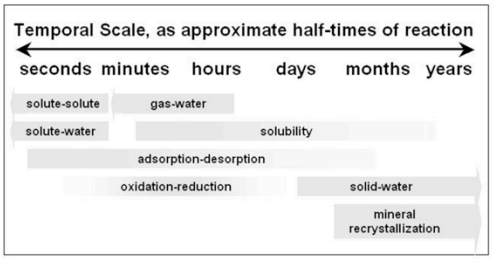
Smith (1999); Nordstrom CLU-IN presentation; Butler CLU-IN presentation

USGS

6

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)

USGS

7

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

USGS

USEPA (2002) 8

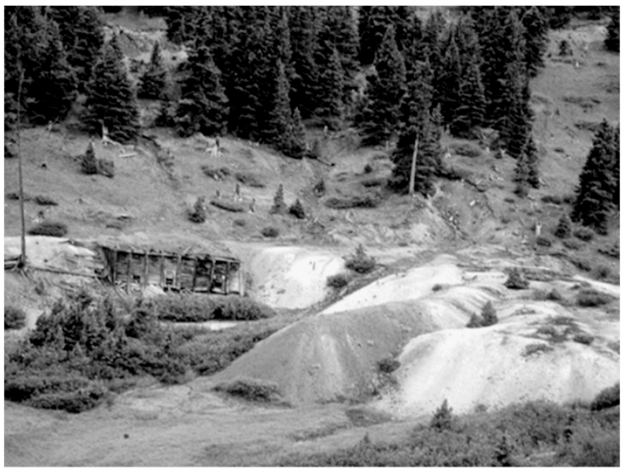
"Representativeness" of Sample

- 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

USGS

Pitard (1993); Ramsey and Hewitt (2005); USEPA (2002) 9

Sampling Solid, Disaggregated Samples



USGS

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)

USGS

11

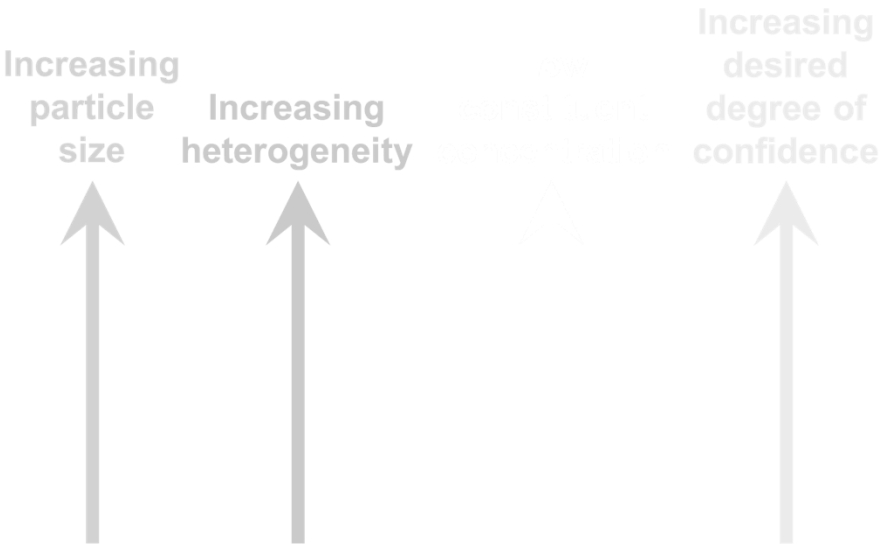
Grouping and Segregation Error

- 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



USGS

13

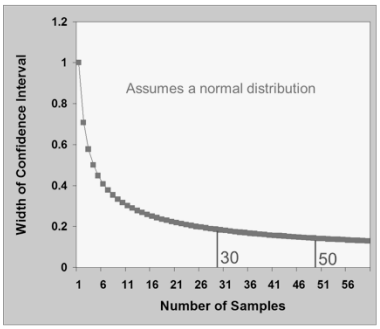
How Many Samples?

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

USGS

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

14

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

16

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)

USGS

17

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

USGS

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

18

Sampling Strategy for Mine Piles, cont.

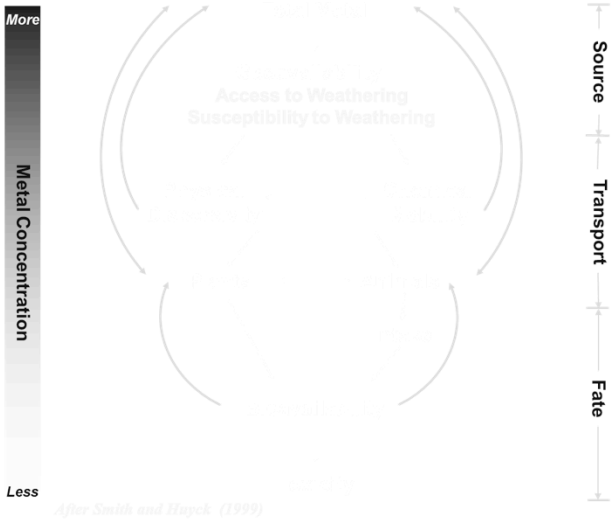
This sampling strategy could be adapted to the sampling of other target populations, such as

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

USGS

19

Total Concentration vs Geoavailability



After Smith and Huyck (1999)

USGS

Russell CLU-IN presentation 20

Surface Water Sampling Considerations

USGS

21

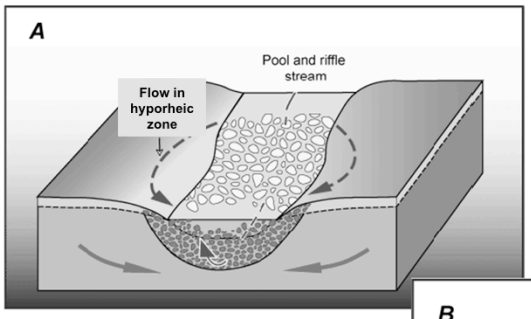
Challenges in Collecting Surface-Water Samples at Mining Sites

- 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

USGS

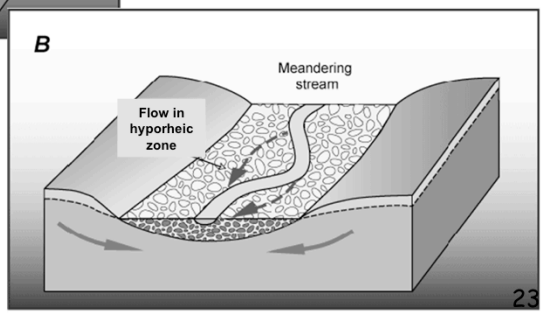
22

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)

USGS

23

What is a Diel Cycle?

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

Processes:

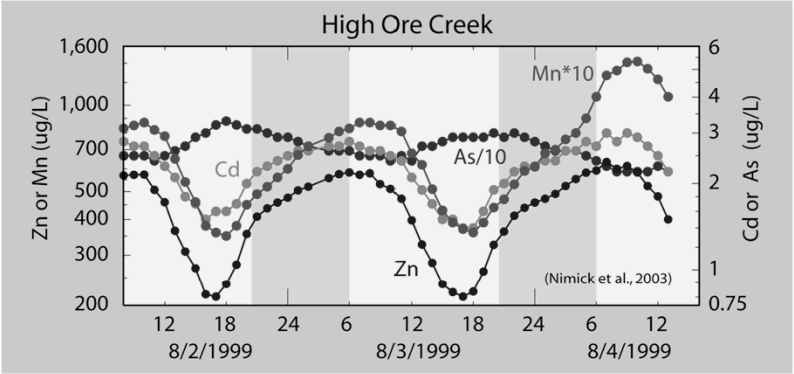
- ✓ **Stream flow (evapotranspiration causes up to 20% change; snowmelt pulses)**
- ✓ **Water temperature (influences rates of reactions; mineral and gas solubility)**
- ✓ **Photosynthesis**
- ✓ **Photochemical reactions**

USGS

24

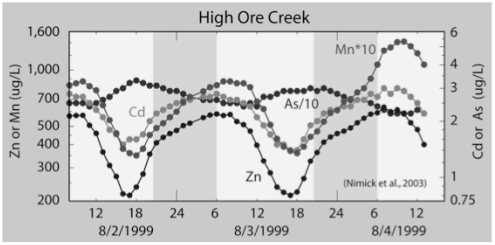
Diel Processes in Neutral and Alkaline Streams

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)

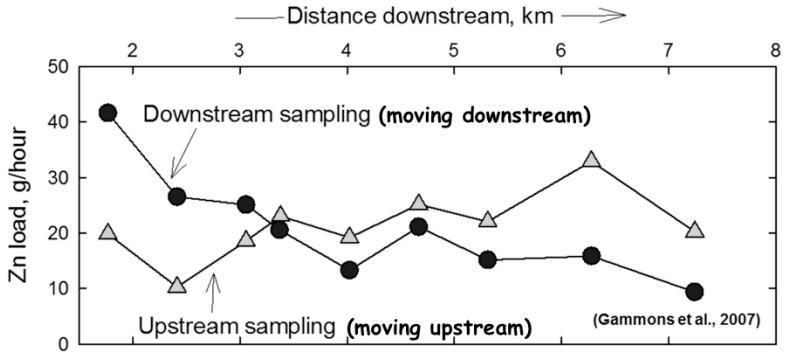


Nimick et al. (2003)

Short-Term Variability



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



Gammons et al. (2007)

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

USGS

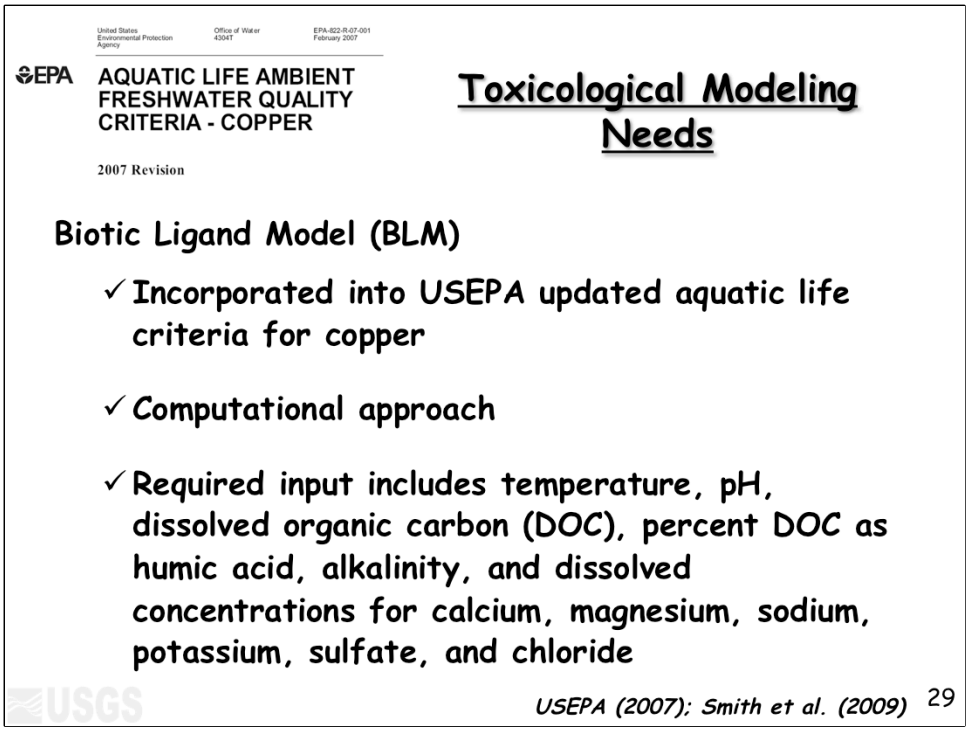
Nagorski et al. (2003) 27

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

USGS

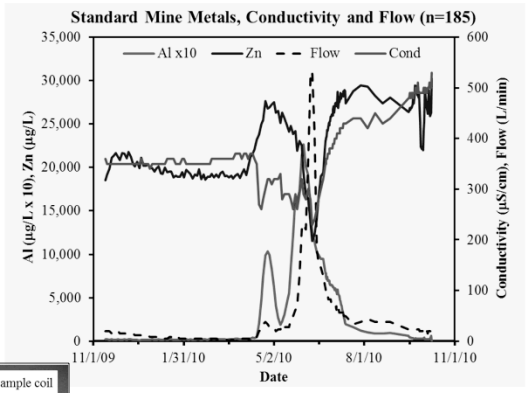
Nordstrom CLU-IN presentation; Nordstrom (2004) 28

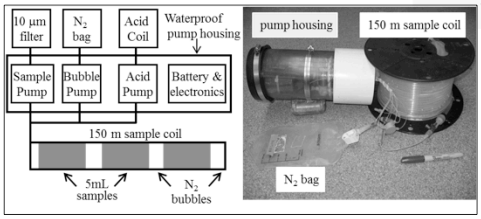

United States Environmental Protection Agency
Office of Water 4304T
EPA-822-R-07-001 February 2007
EPA
AQUATIC LIFE AMBIENT FRESHWATER QUALITY CRITERIA - COPPER
2007 Revision
Toxicological Modeling Needs
Biotic Ligand Model (BLM)
✓ Incorporated into USEPA updated aquatic life criteria for copper
✓ Computational 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
USGS
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

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

USGS

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

31

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) 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

USGS

Smith (2011) 33

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

USGS

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

USGS

35

Acknowledgements

Funding through the U.S. Geological Survey
Mineral Resources Program and the
Toxic Substances Hydrology Program

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

Any use of trade, product, or firm names in this presentation is for descriptive purposes only and does not imply endorsement by the U.S. Government.

USGS

36

Thank you

Available on CLU-IN site (Additional Resources):

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

USGS

37