Word Document --- 4 pages of text for Proceedings Paper
16 slides (prepared in PowerPoint) for Presentation based on Paper

January 29, 1999 -- Submitted to
U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999--Volume 1- Contamination from Hardrock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A,, Morganwalp, D.W., and Buxton, H.T., eds..

Theory and(or) Reality: Analysis of Sulfate Mass-balance at Summitville, Colorado Poses Process Questions About the Estimation of Metal Loadings

By Kenneth E. Bencala and Roderick F. Ortiz

ABSTRACT

Characterization of in-stream metal loading from acid mine drainage includes identification of location, discharge, and solute concentrations of inflows to the stream. In using the tracer injection and synoptic sampling method we recognize that drainage from a mine site enters a stream through distributed, dispersed, and ill-defined inflows. The veracity of the method relies upon implicit assumptions related to catchment hydrology, stream hydraulics, and chemical reactivity. As a practical examination of methodology, we analyzed the ambient sulfate data collected during a metal loading characterization of the inactive mine site at Summitville, Colorado. This analysis may be thought of as a 'successive mass-balance comparison.' The results lead us to pose the following issues which can be addressed in further study at acid mine drainage sites:

1. Catchment hydrology: Will extensive chemical sampling in the near-stream zone of the catchment characterize the connections between the stream and its catchment?
2. Stream hydraulics: Will the in-stream water be 'well-mixed' in the complex physical and chemical environments typical of acid mine drainage?
3. Chemical reactivity: Will the amount of sulfate removal be sufficiently slight for this constituent to be useful as an operational ambient tracer?

Although each issue is framed as a methodological issue, resolving each requires study at the process scale. Resolving each of these issues would enhance the degree of process interpretation in the characterization of metal loading using the tracer injection and synoptic sampling method.

INTRODUCTION

A set of quantitative factors influencing the impact of drainage into a stream from a mine site includes the location, discharge, and solute concentrations of inflows to the stream. Conceptually identifying these factors appears to be trivial. One might envision walking along the stream, observing the inflows, noting their location, measuring their discharge and obtaining samples for chemical analysis. In practice drainage from a mine site enters a stream through visible inflows as well as, distributed, dispersed, and ill-defined subsurface flows.

We have been using a combination of tracer injections and synoptic sampling (Kimball, 1997) as a methodology for this quantitative identification of inflow factors. Analysis of the steady tracer injection yields estimates of in-stream discharge along the stream reach of interest. Synoptic sampling of water both in the stream and in areas of visible drainage are then used, with the discharge data, to estimate mass-flow of chemical constituents in the streams and the identified inflows. Typically, the injected tracer will be one or more of the salts of chloride, bromide, sodium, or lithium (Bencala and others, 1990). Also, the ambient constituents of interest will be trace metals (Kimball, 1997) of environmental interest and the metals iron, aluminum, and manganese (Kimball and others, 1994), whose solid precipitates influence the transport of other constituents.

In this paper we analyze the ambient concentration data for sulfate. Sulfate likely is incorporated to some degree into the precipitates coating a mine drainage streambed (Kimball and others, 1994; Bigham and others, 1990, 1996). However, concentration of sulfate typically is high and relative loss in precipitates is low. Thus, while not ideally conservative, sulfate may act as a useful ambient tracer (Bencala and others, 1987 and 1990). The analysis presented is a succession (that is, moving downstream) of mass-balance comparisons in which the mass-balance of in-stream sulfate is recomputed at each sampled site. This analysis is part of an ongoing effort to assess the veracity of the field methods, specifically as the methods rely upon implicit assumptions related to catchment hydrology, stream hydraulics, and chemical reactivity. The results of the analysis lead us to pose process questions about the estimation of metal loadings.

SUCCESSIVE MASS-BALANCE COMPARISON

Kimball (1997) gives an application-oriented discussion of the 'Tracer injection and synoptic sampling method for metal loading characterization.' Underlying the development of the methodology, research investigations in two acidic and metal-enriched streams have been described in Bencala and others (1987 and 1990) and Kimball and others (1994). Following the approach discussed by Kimball(1997), we estimate in-stream discharge and constituent mass-flow (discharge times concentration) at several sites along a stream study-reach. Further, by sampling areas of visible drainage into the stream, we estimate the concentration of constituents to the stream. Thus, progressing successively from one sampled, in-stream site to the next, we can sum the mass-flow at the upstream site with the inflow between the two sites to do a mass-balance comparison with the mass-flow at the downstream site.

Sulfate Data

In this paper, we do the successive mass-balance comparison on the sulfate data collected during a metal loading characterization in Wightman Fork adjacent to the inactive mine site at Summitville, Colorado. The in-stream discharges were estimated from injected chloride tracer data. The study reach for analysis in this paper was 1,748 meters in length, with discharge increasing from 4.6 L/s to 28.0 L/s along this reach and ten sampled, in-stream sites. Nine areas of visible drainage into the stream also were sampled, which correspond to the nine subreach intervals bracketed by the in-stream sites. The estimated discharges from these effective inflows ranged from a slight seepage of 0.1 L/s up to a well-defined tributary with a discharge of 9.9 L/s. Sulfate concentrations in the stream ranged between 48 mg/L and 341 mg/L. Sulfate concentrations in the inflows ranged between 5 mg/L and 2,428 mg/L; a range that is clearly reflective of an upland catchment environment impacted by the mine site.

Summation of Inflow Mass-Flow

Within each of the nine subreaches (delineated by up- and downstream, in-stream samples and an interspersed inflow sample) the downstream sulfate mass-flow was compared to the sum of the upstream and inflow sulfate mass-flows. The maximum in-stream sulfate mass-flow was in excess of 9 g/s. Six of the mass-balance comparisons agreed to within 0.2 g/s. A major disagreement was along a 100m subreach in which sulfate mass-flow increased significantly from approximately 0.9 g/s to in excess of 7 g/s at the downstream sampling site. The in-stream discharge increased 5.1L/s within the subreach. The measured sulfate concentration of the identified inflow within the subreach was almost 2,200 mg/L. Thus the sulfate mass-flow for the inflow within the subreach was approximately 11 g/s. The summation of the upstream sulfate mass-flow in this subreach with the inflow sulfate mass-flow was approximately 12 g/s; that is, almost double the observed downstream value.

DISSCUSSION AND ISSUES FOR FURTHER STUDY

Several of the successive sulfate mass-balance comparisons agreed within 10 percent of the maximum in-stream sulfate mass-flow. This agreement is a verification of internal consistency of the field methodology using the tracer injection and synoptic sampling to identify the inflows into the stream. These results are by no means an independent test. There were subreaches in which the mass-balance comparisons were in substantial disagreement. Such disagreements are not, in themselves, indicative of quantitative errors in estimation of in-stream discharge or the in-stream mass-flow of any constituent. Such disagreements are instructive in that they indicate issues in the field methodology for which further process study might enhance overall the estimation of metal loadings. The mass-balance computations include information about both the mass-flow of a constituent through inflows to stream and the mass-flow of a constituent within the stream channel. The interpretation of the mass-balance computations is further based on information about the conservative nature of the constituent. Below we pose, as questions, three distinct issues.

Catchment Hydrology

Will extensive chemical sampling in the near-stream zone of the catchment characterize the connections between the stream and its catchment? Much of the water in an upland stream did not enter the stream as discrete inflows. Hydrometric study of the flow of water within the catchment might include detailed mapping of the subsurface water table in selected areas. Alternatively, topographic analyses might be used to identify the likely contributing catchment source areas. Chemical sampling in the near-stream zone might most effectively be viewed as providing additional mass-balance constraints on the bounds of hydrometric interpretations.

Stream Hydraulics

Will the in-stream water be ‘well-mixed’ in the complex physical and chemical environments typical of acid mine drainage? Within a subreach (demarcated by an upstream and a downstream in-stream water sample) there actually will be multiple inflows and sources of solutes. In effect, an upland stream is always gaining water from the catchment (or at least exchanging water with the catchment through the hyporheic zone). Any sample of stream water might be capturing a flux of inflow water and constituents. Hydrometric and topographic study of the streambed might be used to identify sections of stream with minimal hydrologic connection to the catchment.

Chemical Reactivity

Will the amount of sulfate removal be sufficiently slight for this constituent to be useful as an operational ambient tracer? The analysis of the internal consistency presented in this paper could be extended to include analysis based on geochemical equilibrium to identify both potential over saturation of mineral phases or likely sorption reactions. The practical focus of studies in acid mine drainage has been on metal loadings. Possibly analyses of other major ions might be used in mass-balance comparisons complementing the use of sulfate.

SUMMARY

The analysis of sulfate mass-balance at Summitville, Colorado was internally consistent in several subreachs of Wightman Fork. Substantial disagreements also were shown. From these disagreements we pose issues in the field methodology for which further study might enhance the overall method. The mass-balance computations are based on information about sulfate mass-flow through inflows, sulfate mass-flow within the stream and sulfate geochemistry. Thus, issues arise in catchment hydrology, stream hydraulics, and chemical reactivity. Although each issue is framed as a methodological issue, resolving each requires study at the process scale. Resolving each of the issues would enhance the degree of process interpretation in the characterization of metal loading using the tracer injection and synoptic sampling method.

REFERENCES

Bencala, K.E., McKnight, D.M., and Zellweger, G.W., 1987, Evaluation of natural tracers in an acidic and metal-rich mountain stream: Water Resources Research, v. 23, no. 5, p. 827-836.

Bencala, K.E., McKnight, D.M., and Zellweger, G.W., 1990, Characterization of transport in an acidic and metal-rich mountain stream based on a lithium tracer injection and simulations of transient storage: Water Resources Research, v. 26, no. 5, p. 989-1000.

Bigham, J.M., Schwertmann, U., Carlson, L., and Murad, E., 1990, A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters: Geochimica et Cosmochimica Acta, v. 54, p. 2743-2758.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., and Wolf, M., 1996, Schwertmannite and the chemical modeling of iron in acid sulfate waters: Geochimica et Cosmochimica Acta, v. 60, p. 2111-2121.

Kimball, B.A., 1997, Use of tracer injections and synoptic sampling to measure loadings from acid mine drainage: U.S. Geological Survey Fact Sheet 245-97, 4 p.

Kimball, B.A., Broshears, R.E., Bencala, K.E., and McKnight, D.M., 1994, Coupling of hydrologic transport and chemical reactions in a stream affected be acid mine drainage: Environmental Science and Technology, v. 28, p.2065-2073.

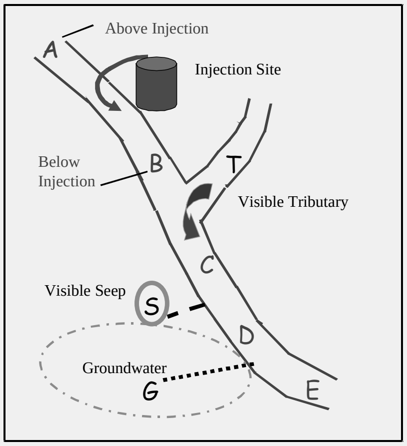
AUTHOR INFORMATION

Kenneth E. Bencala, U.S. Geological Survey, Menlo Park, California (kbencala@usgs.gov , http://nrp.usgs.gov/nrp/proj.bib/bencala.html)

Roderick F. Ortiz, U.S. Geological Survey, Pueblo, Colorado (rfortiz@usgs.gov)

Slide 1

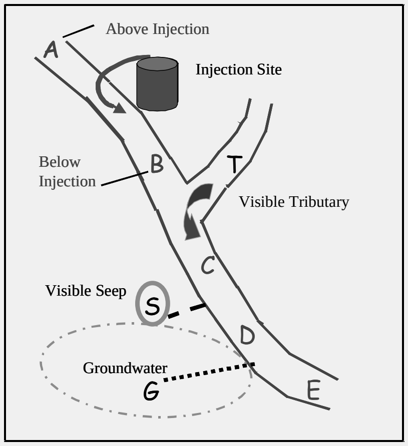
Conceptual Stream



- Well-defined Channel
- Distinct Inflows
  - Tributaries
  - Seeps, springs
  - Ground-water discharge

Slide 2

Conceptual Mass-Balance



- Mass-flow at each stream site
  $M_x = C_x \ Q_x$
- Discrete Inflows
  $Q_i = Q_y - Q_x$
- Known Concentration
  Ci
- Downstream Mass-flow
  $M_y = C_x Q_x + C_i Q_i$

Theory and/or Reality: Analysis of Sulfate Mass-balance at Summitville, Colorado - - Process Questions About the Estimation of Metal Loadings

Ken Bencala Rodger Ortiz
Menlo Park, CA Pueblo, CO
U.S. Geological Survey

Slide 4

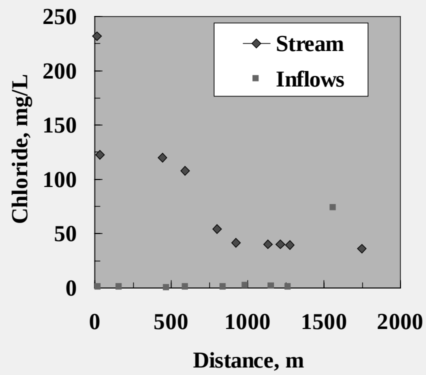
Theory and/or Reality: Analysis of Sulfate Mass-balance
- Process Questions -

- Summitville Injection/Experiment
  - Estimation of Sulfate Mass-flow
- Inflows
  - Internally Consistent?
  - Representative?
- Chemical Reactivity
- Stream Hydraulics
- Catchment Hydrology

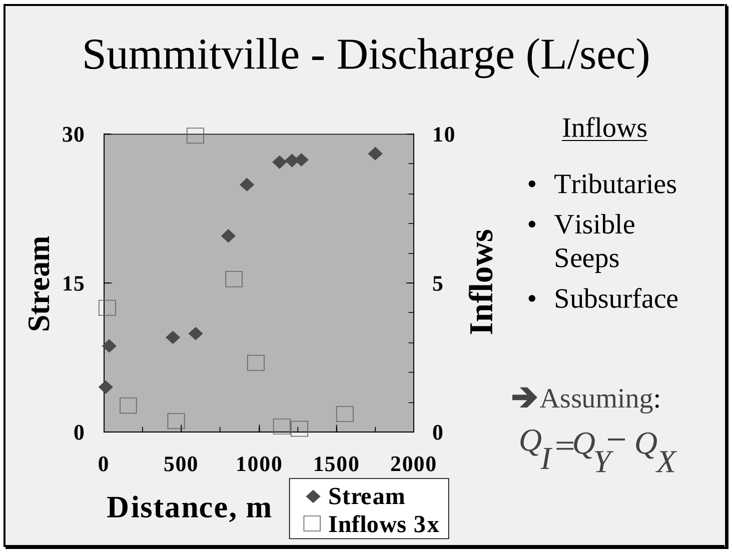
Summitville - Chloride Tracer

<u>Illustrate Issues</u>

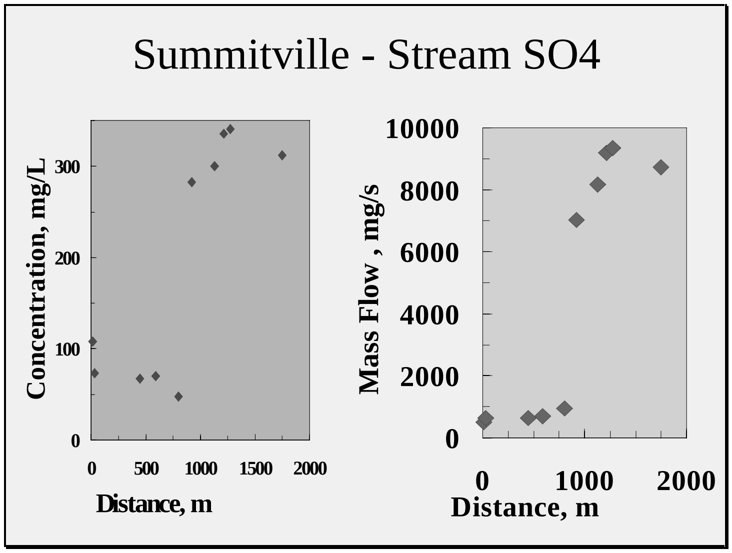
- Ten Stream Samples
  - 2x dilutions
- Nine Inflows
  - Concentrated Inflow

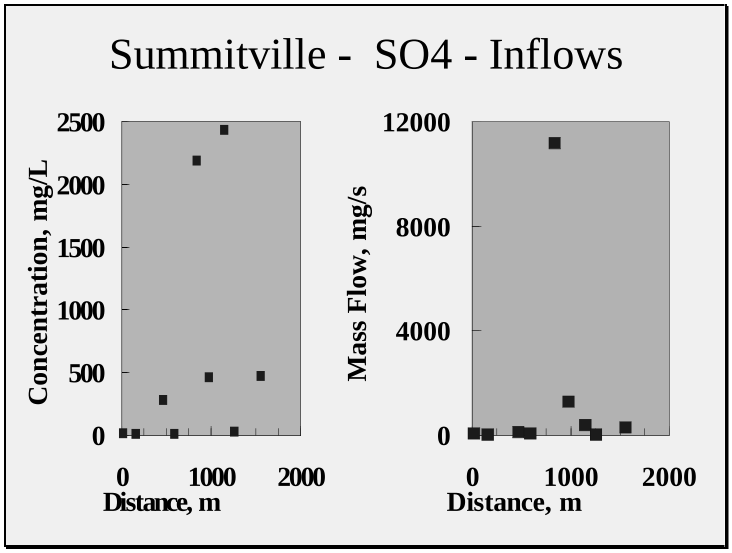


Slide 6


Summitville - Discharge (L/sec)
30
15
0
Stream
10
5
0
Inflows
0
500
1000
1500
2000
Distance, m
Stream
Inflows 3x
Inflows
• Tributaries
• Visible Seeps
• Subsurface
➔Assuming:
$Q_I = Q_Y - Q_X$

Slide 7


Summitville - Stream SO4
Concentration, mg/L
300
200
100
0
0
500
1000
1500
2000
Distance, m
Mass Flow , mg/s
10000
8000
6000
4000
2000
0
0
1000
2000
Distance, m


Summitville - SO4 - Inflows
Concentration, mg/L
2500
2000
1500
1000
500
0
0
1000
2000
Distance, m
Mass Flow, mg/s
12000
8000
4000
0
0
1000
2000
Distance, m

Inflow Concentrations Internally Consistent?

- Sampled
  - Consistent Mass-Flow?

$$C_I(Q_I) + C_X Q_X \stackrel{?}{=} C_Y Q_Y$$

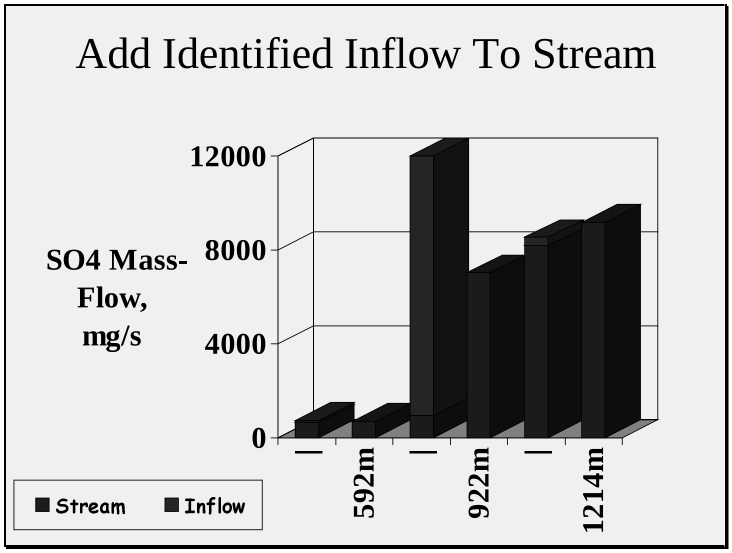
- Calculated
  - Representative?

$$\overline{C}_I \stackrel{?}{=} \frac{(C_Y Q_Y - C_X Q_X)}{(Q_I)}$$

➔Assuming:

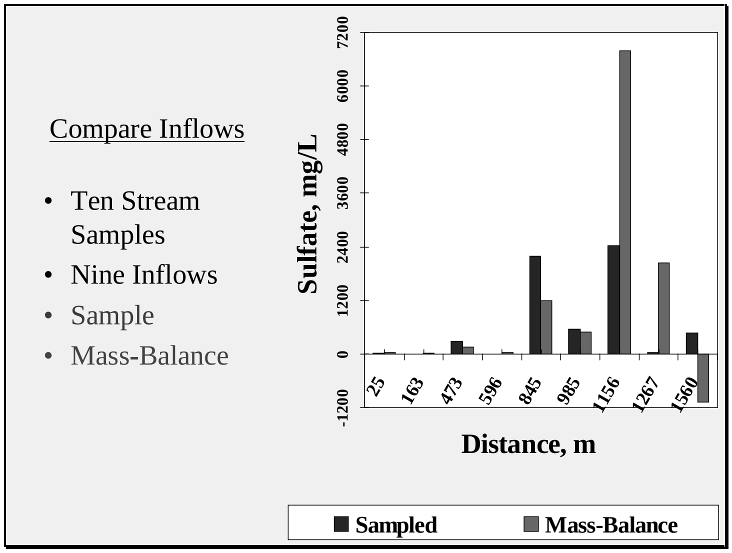
$$Q_I = Q_Y - Q_X$$

Slide 10

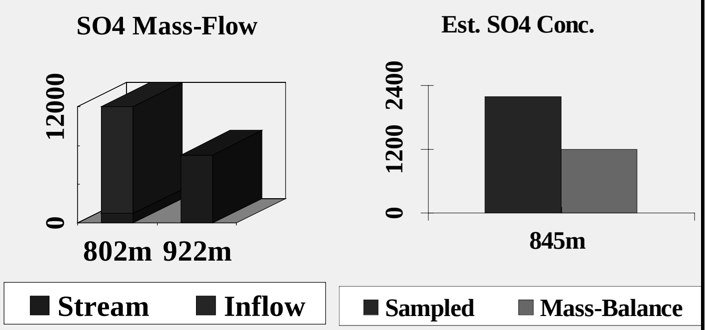


Add Identified Inflow To Stream
SO4 Mass-Flow, mg/s
12000
8000
4000
0
592m
922m
1214m
Stream
Inflow

Slide 11


Compare Inflows
• Ten Stream Samples
• Nine Inflows
• Sample
• Mass-Balance
Sulfate, mg/L
7200
6000
4800
3600
2400
1200
0
-1200
25
163
473
596
845
985
1156
1267
1560
Distance, m
Sampled
Mass-Balance

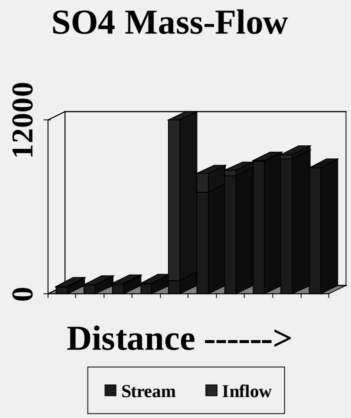
Major SO4 Mass Inflow

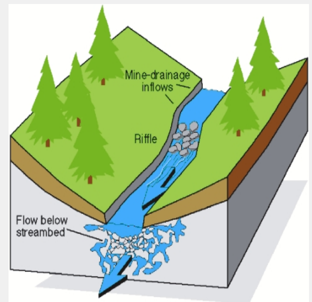


SO4 - Ambient 'Tracer'? - Internal Consistency?
- Reactive? - Fe Colloids? -

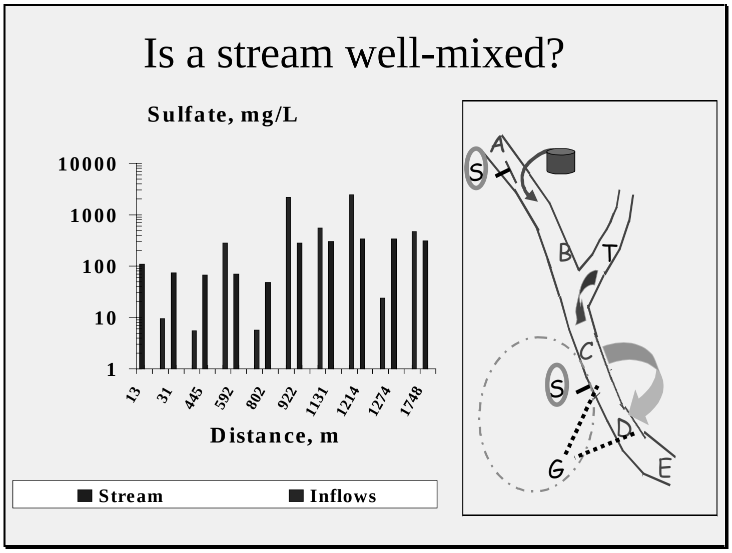
Slide 13

Sampling Inflows To Stream?





Slide 14

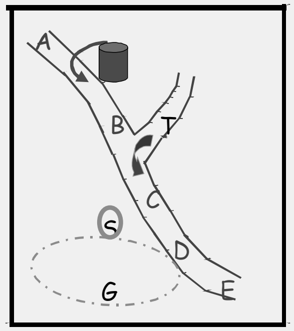

Is a stream well-mixed?
Sulfate, mg/L
10000
1000
100
10
1
13
31
445
592
802
922
1131
1214
1274
1748
Distance, m
Stream
Inflows
A
S
B
T
C
S
D
G
E

Slide 15

People

Rodger Ortiz
Pat Edelman
Sheryl Ferguson
Bob Stogner
Bob Broshears
Katie Walton-Day
Larry Schemel

Ken Bencala
Briant Kimball
Rob Runkel
Linda Gerner
Tracy Yager
Fred Rossi
Jon Evans
Marisa Cox



Offices --
- Pueblo, CO Subdistrict
  - NRP - Menlo Park
    - Utah and Colorado Dist.

$$$ --
- EPA
  - AML
    - Toxics

- Summary -
Sulfate Mass-Balance at Summitville

- Internal consistency with several inflows
- Further work is indicated:
  - ‘Inflow’ as a catchment scale process
  - ‘Well-mixed’ as a stream-catchment issue
  - Sulfate as an ‘ambient tracer’
- The truth is in the stream