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Preliminary Evaluation of Remedial Alternatives Using a Reactive Transport Model: Cement Creek/Animas River

Rob Runkel (runkel@usgs.gov)
U.S. Geological Survey Toxic Substances Hydrology Program

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Overview

- Part I: Study Objectives & Approach
- Part II: Background Info
    - Water Chemistry
    - Reactive Transport Model (OTEQ)
- Part III: Results
    - Concentrations and WQ Standards
    - Loads and Sources
    - OTEQ calibration and remedial scenarios
- Part IV: What next?

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Part I: Study Objectives & Approach

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Study Objective

- Main Objective:

  Use a reactive transport model to evaluate remedial options for Cement Creek

- Data Requirements:
  - Synoptic data set representing “steady-state” conditions
  - Spatial profiles of streamflow and concentration
- Existing data sets:
  - USGS (1996, 1999); diff. conditions: Gladstone treatment
  - EPA/ARSG (recent); lacks spatial resolution
- October 2012 Synoptic

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Approach

- Develop spatial profiles of streamflow & concentration
- Study Reach: Ross Basin to A72 (11.5 miles)
- Previous approach:
  - Tracer Injection to estimate streamflow
  - adv.: provides spatial detail, accurate flow
  - disadv.: time requirements → unlikely to capture "steady state"
- October 2012:
  - Acoustic Doppler Velocimeter (ADV) to estimate streamflow
  - 2 sampling teams & 3 ADVs
  - leapfrog sampling and day-to-day overlap (replication)

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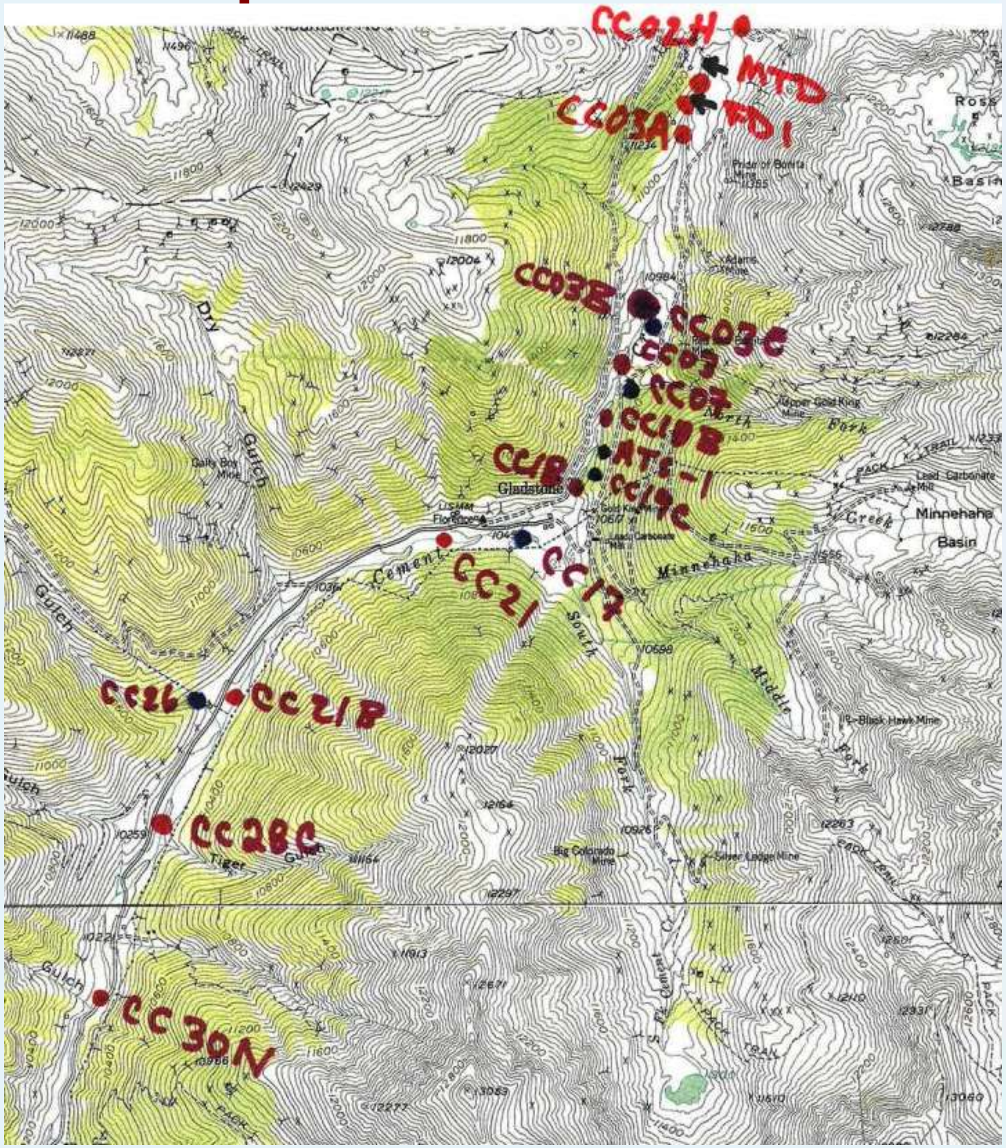
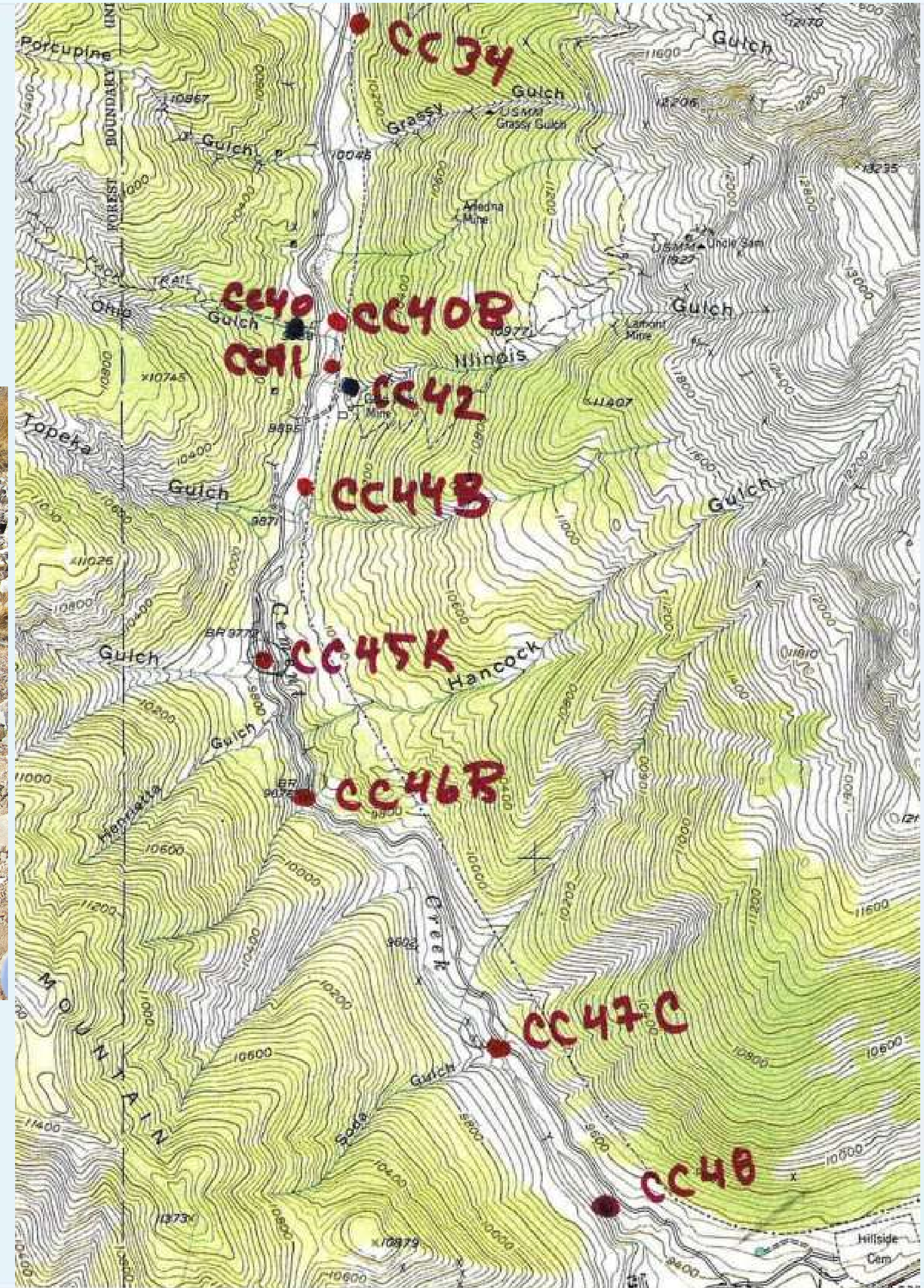
October 2012 Sample Locations

- Chemical "snapshot"
  - 30 stream sites
  - 15 inflows
- Sampled for:
  - pH, Alkalinity
  - cations (Fe, Al, Zn...)
  - anions (SO_4, Cl...)
- leapfrog sampling
- day-to-day replication
- flow from ADV



October 2012 Sample Locations



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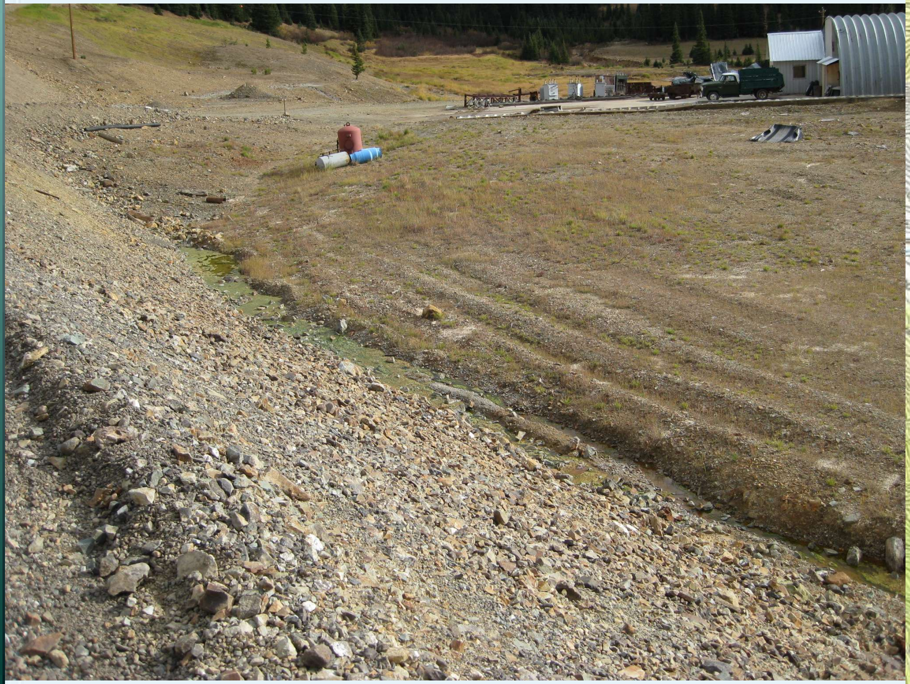
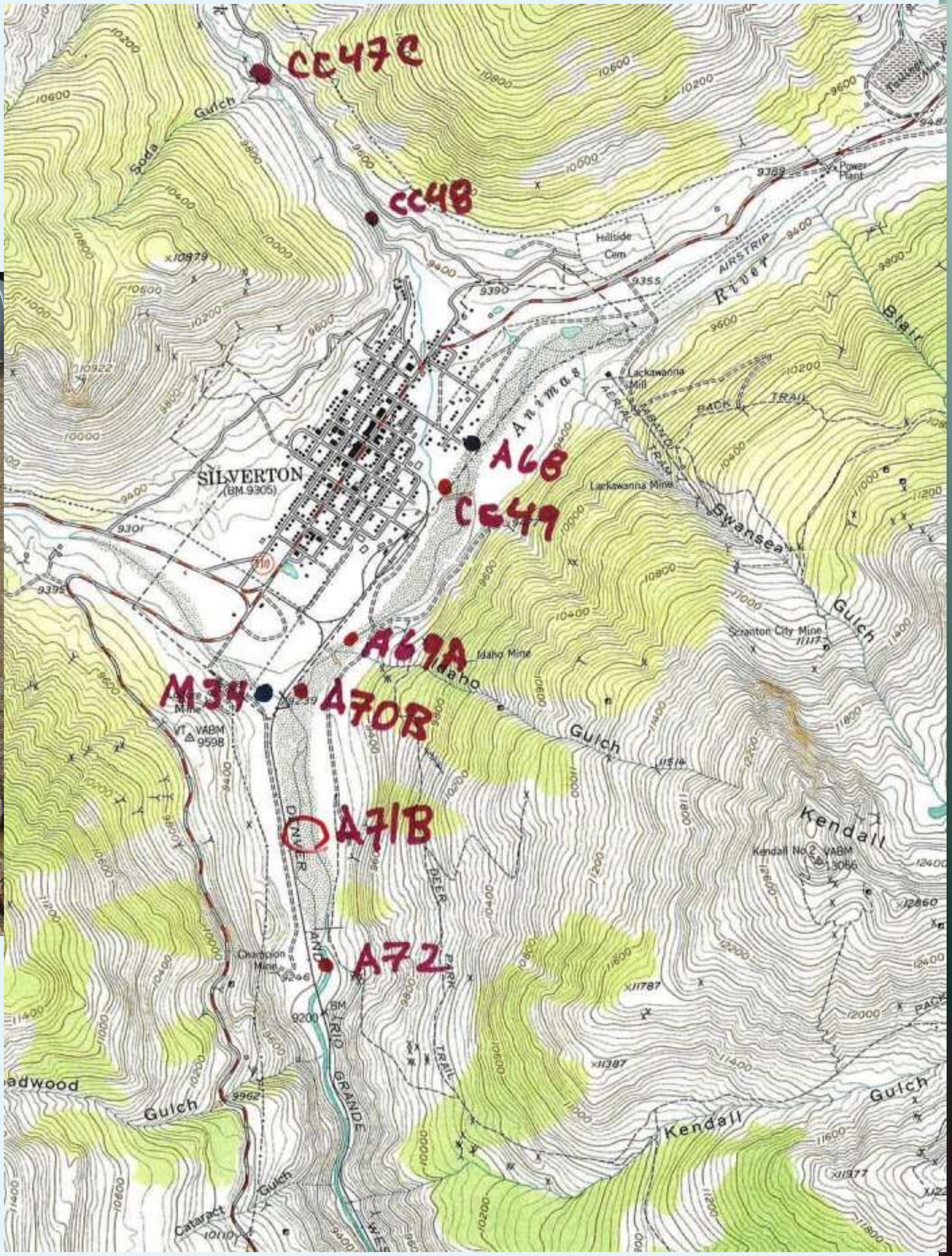
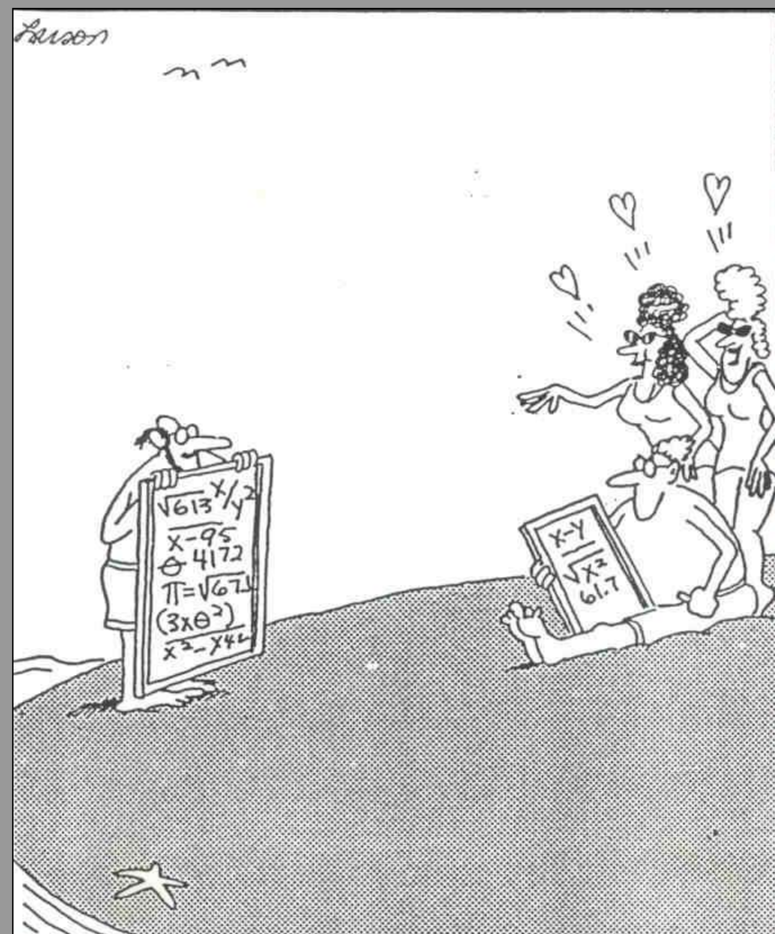
October 2012 Sample Locations





Part II: Background Info:
Water Chemistry & Reactive Transport Model (OTEQ)



Background: Water Chemistry

- Mineralized Ore + (Water & Oxygen)

  → Sulfuric Acid → lowers pH → elevates metals
- "Total Recoverable"
  - unfiltered sample: dissolved + solids
  - solids: Fe and Al hydroxides precipitate
    Cd, Cu, Zn, etc sorb onto Fe & Al
- "Dissolved"
  - filtered sample
  - pH-dependent solubility (low pH→high conc)

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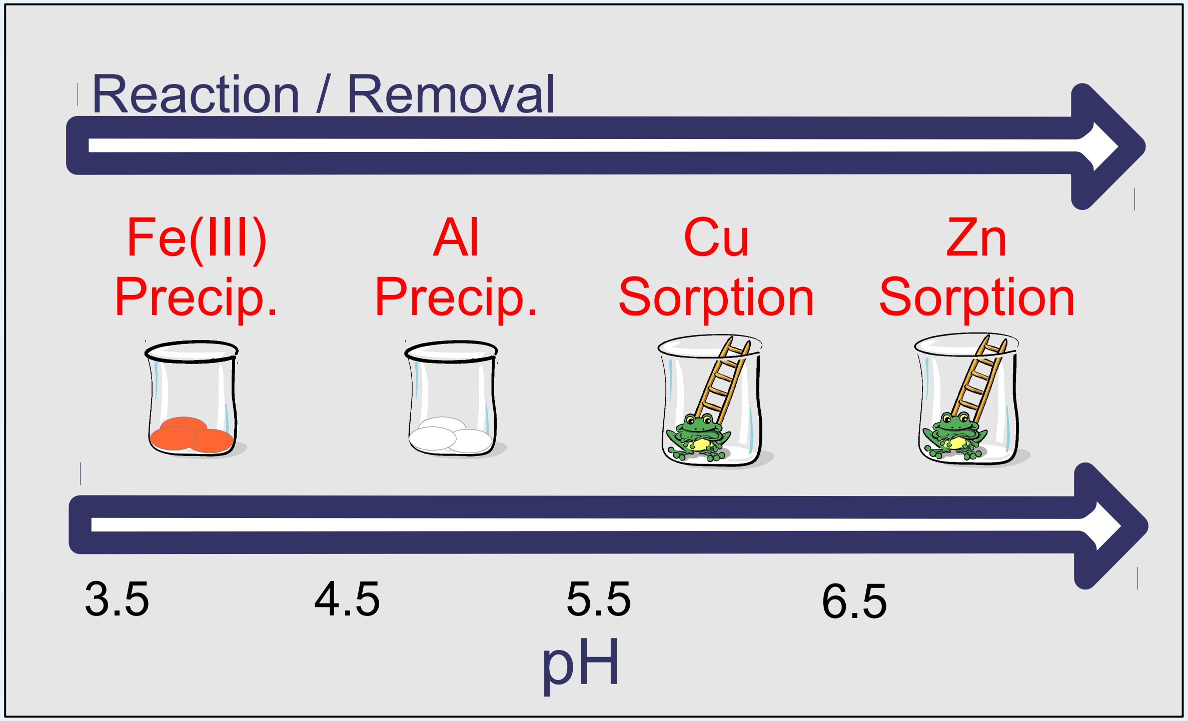
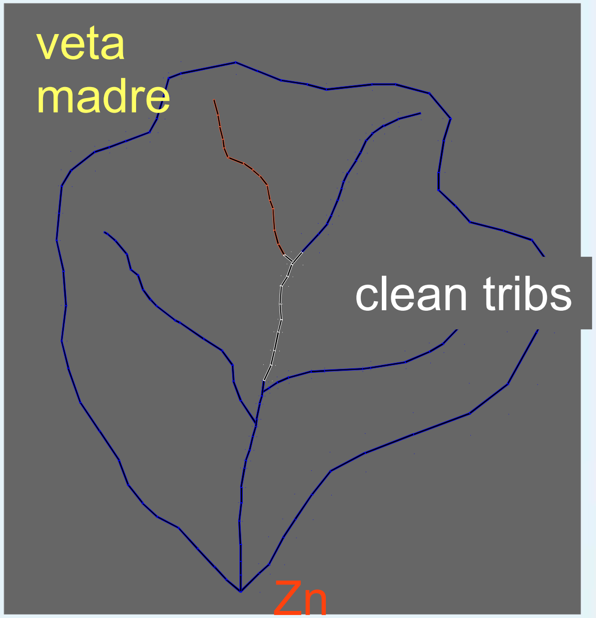
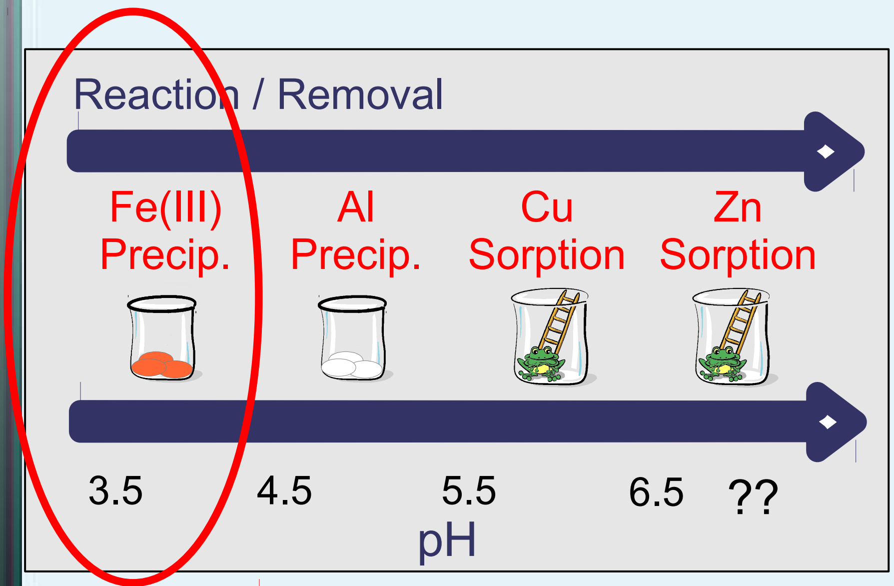
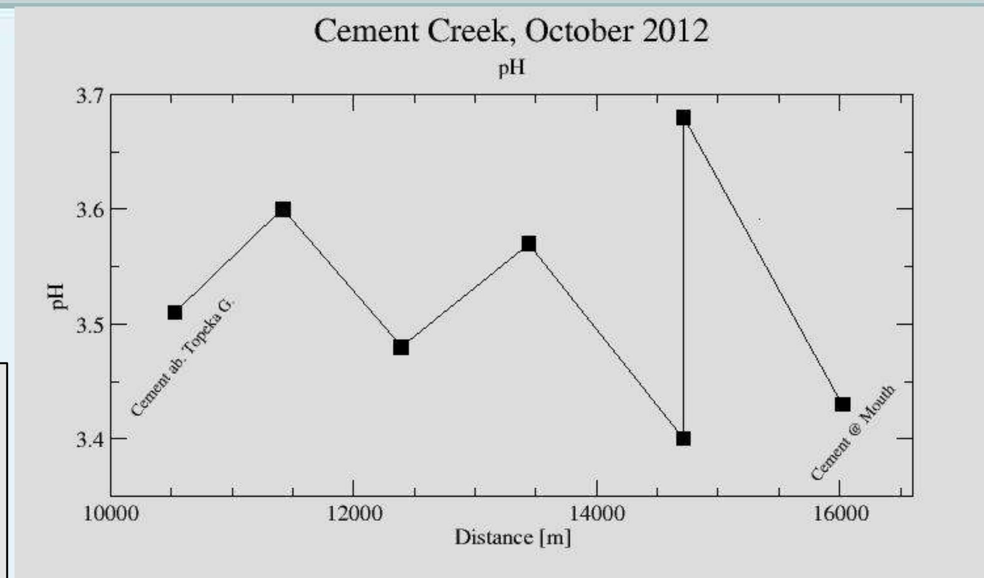
Reactive Transport

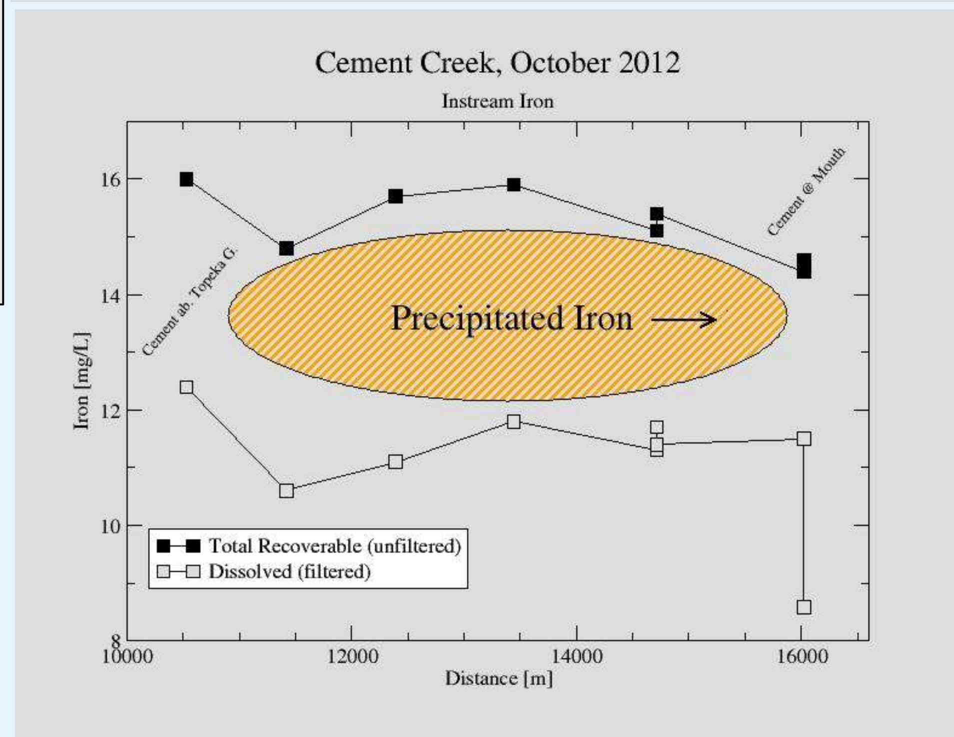




Reactive Transport







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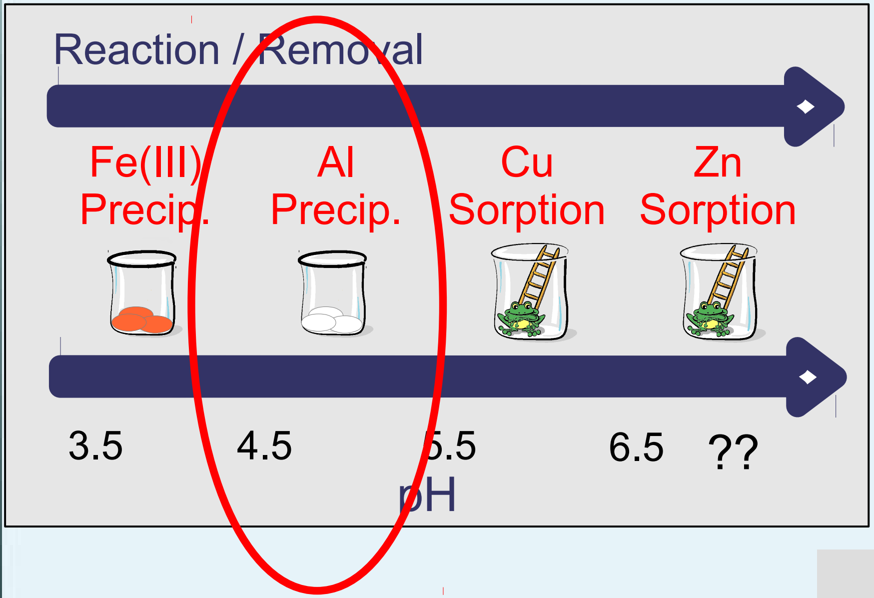
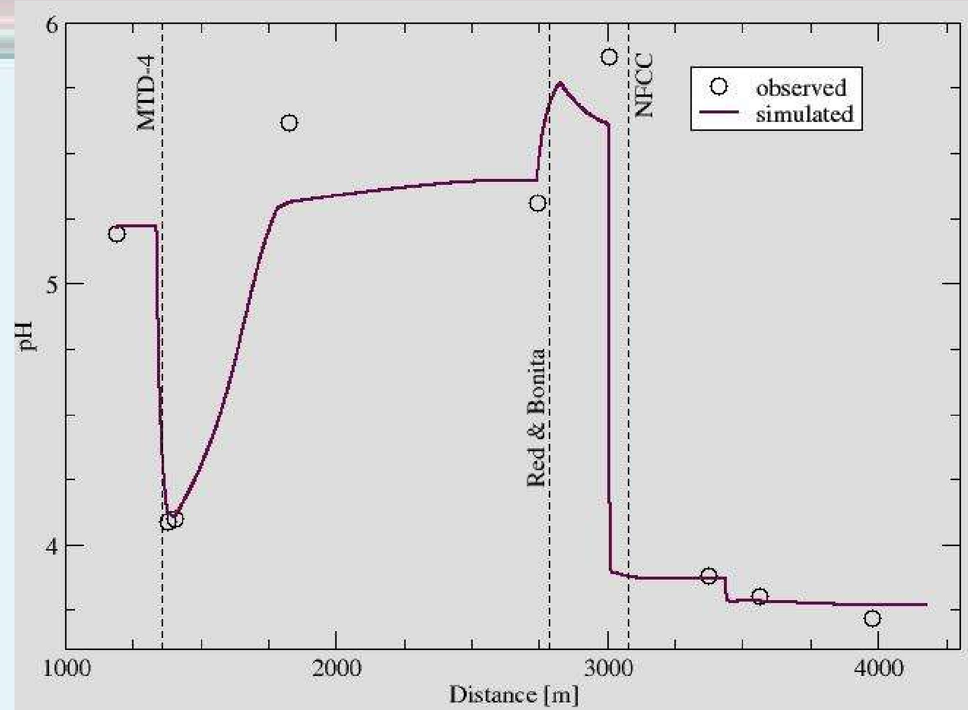
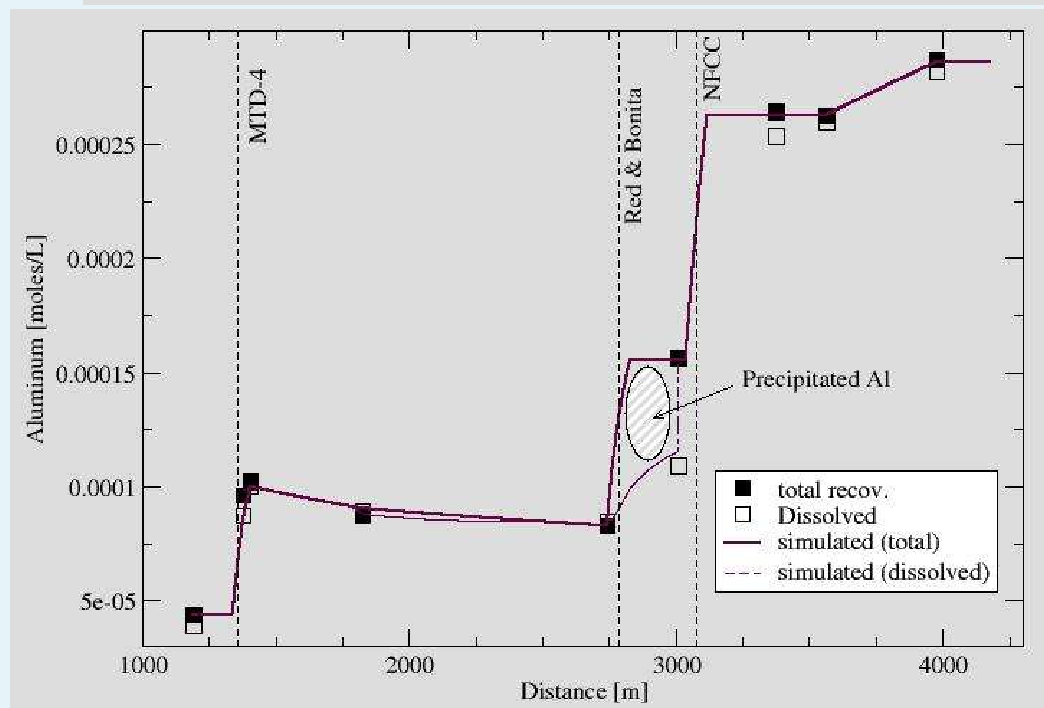
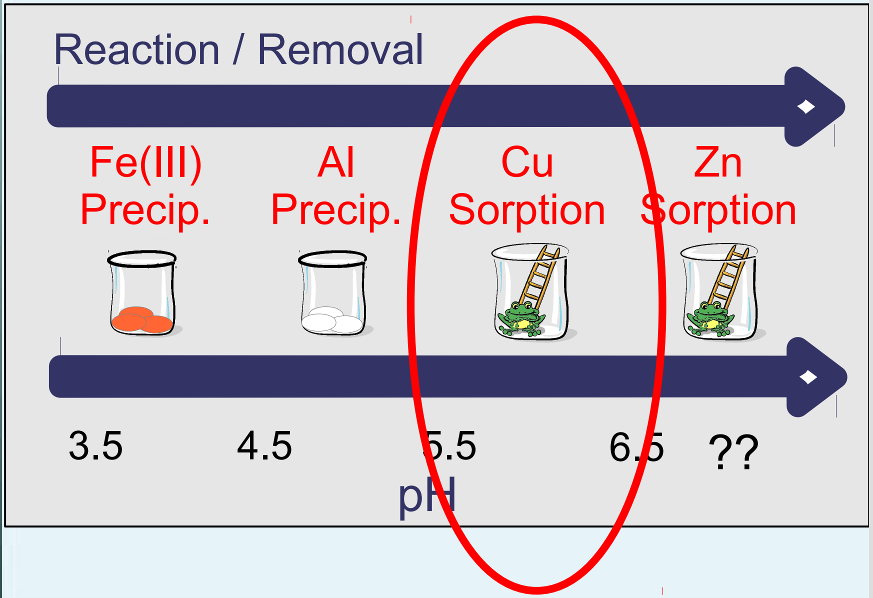
Reactive Transport

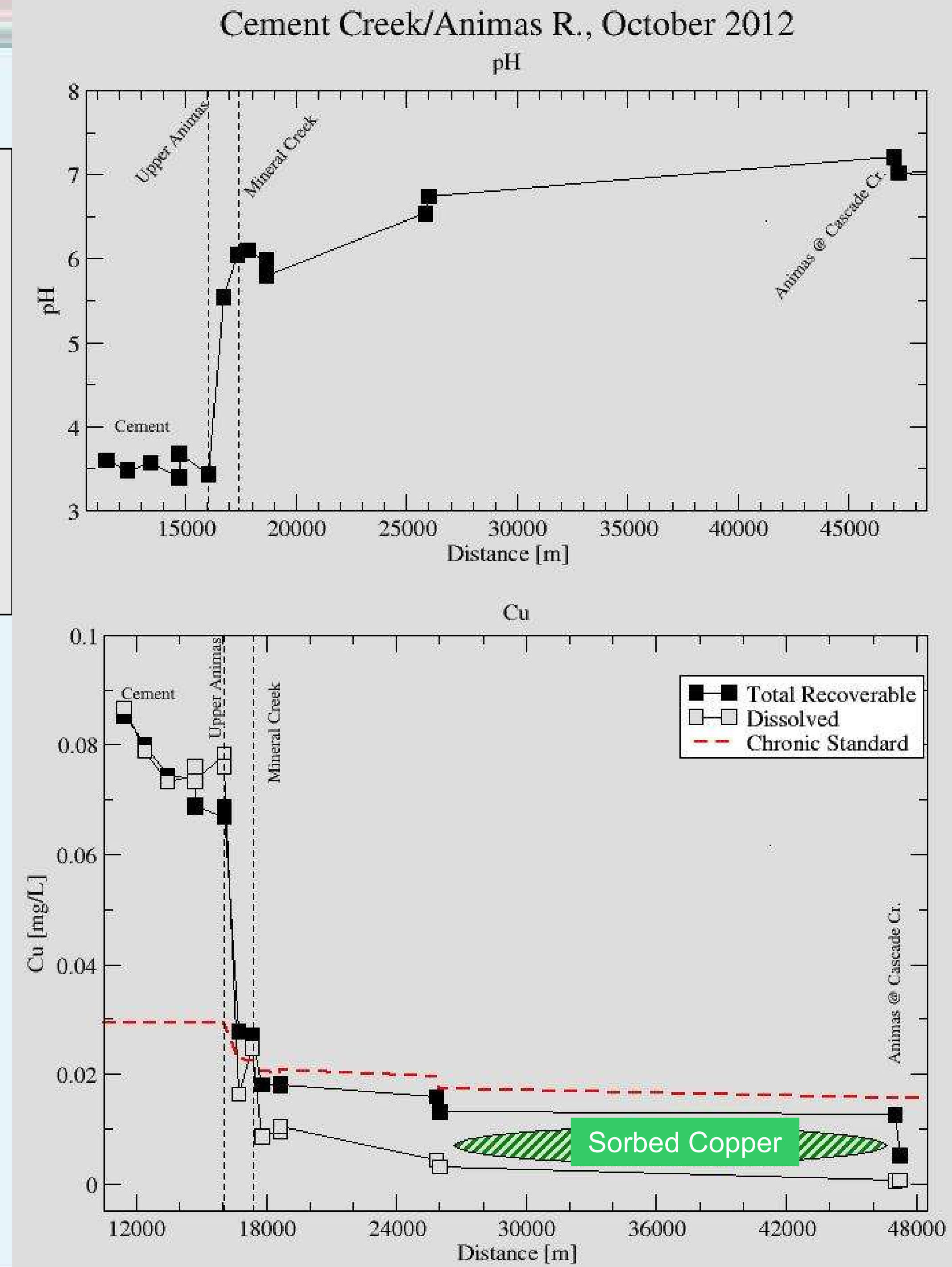






Reactive Transport





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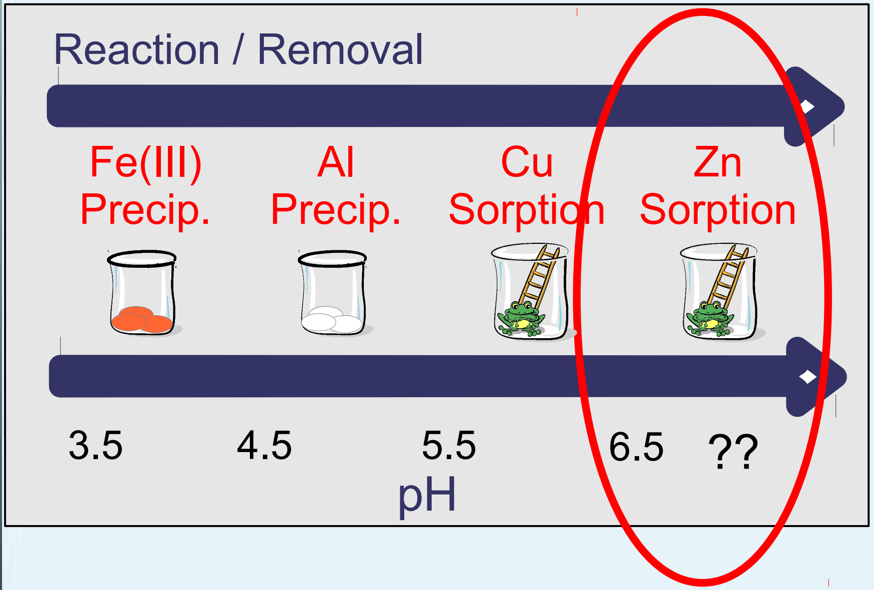
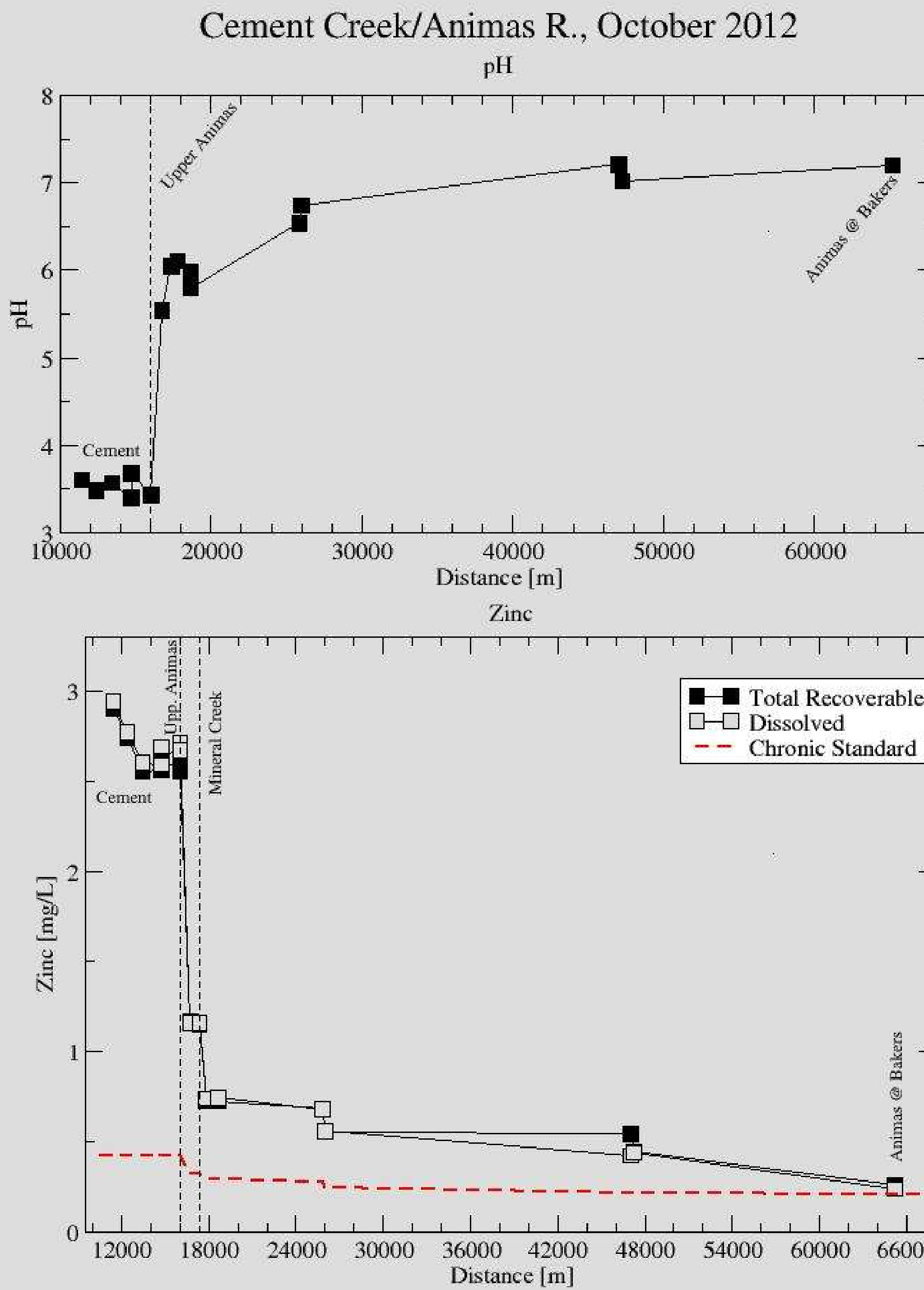
Reactive Transport





Reactive Transport

- Quantify interplay between:

  Hydrology: Advection, Dispersion, Storage, Inflow
  Geochemistry: Precip./Dissolution, Sorption, pH

  - OTEQ: One-dimensional Transport w/ Equilibrium Chemistry

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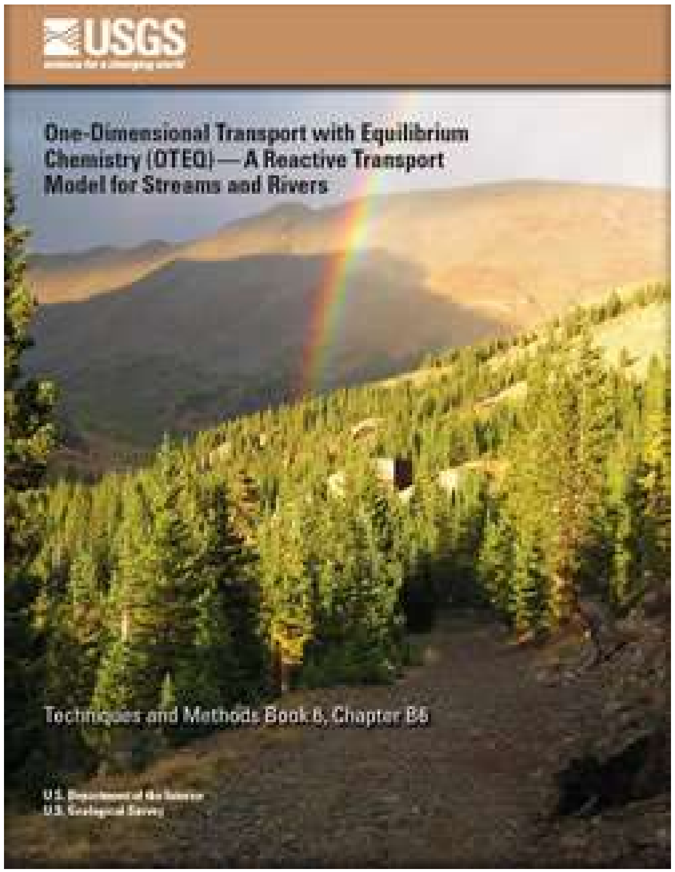
OTEQ:

One-dimensional **T**ransport w/ **EQ**uilibrium Chemistry



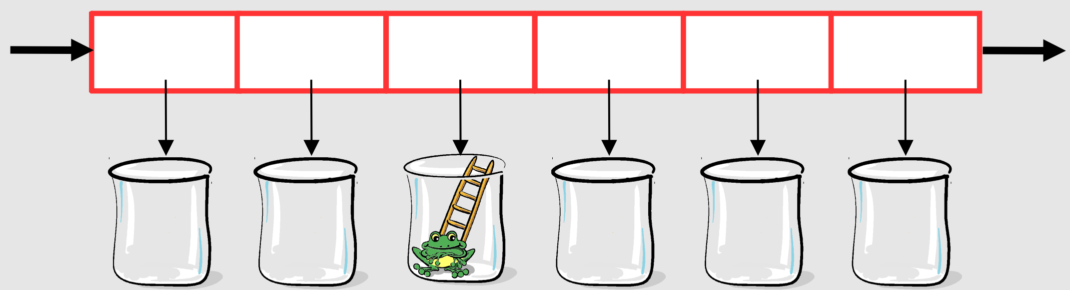
Transport (OTIS)

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_{LIN}}{A}(C_L - C) + \alpha(C_S - C)$$

= Advection + Dispersion + Inflow + Storage

&

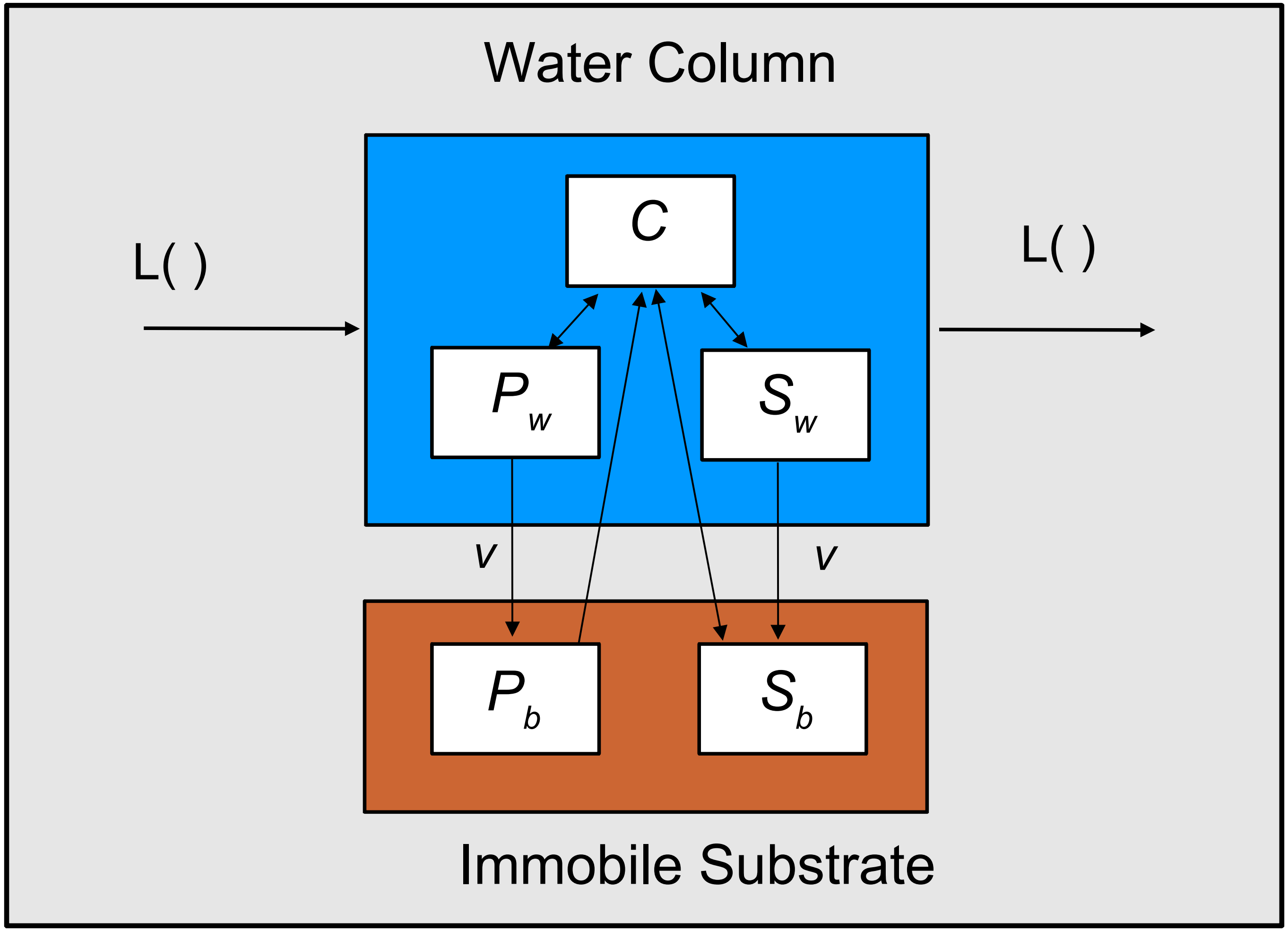
Equilibrium Chemistry (MINTEQ)



http://water.usgs.gov/software/OTEQ

Conceptual Surface Water System

$$T = C + P_w + P_b + S_w + S_b$$



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Part III: Results

"It's the largest outhouse in the San Juan Mountains – an 8-holer"
– Bill Simon, August 2005

Part III: Data Set Quality Assurance

- Data “Backbone” – Spatial Streamflow Profile
  – Essential starting point for loading analysis & modeling

- Multiple means of estimating streamflow provide redundancy:
  - ADV (primary technique);
    multiple measurements due to sample overlap
  - stream gages
  - flume measurements
  - slug injections

- Mass balance calculations to develop spatial profile of streamflow.

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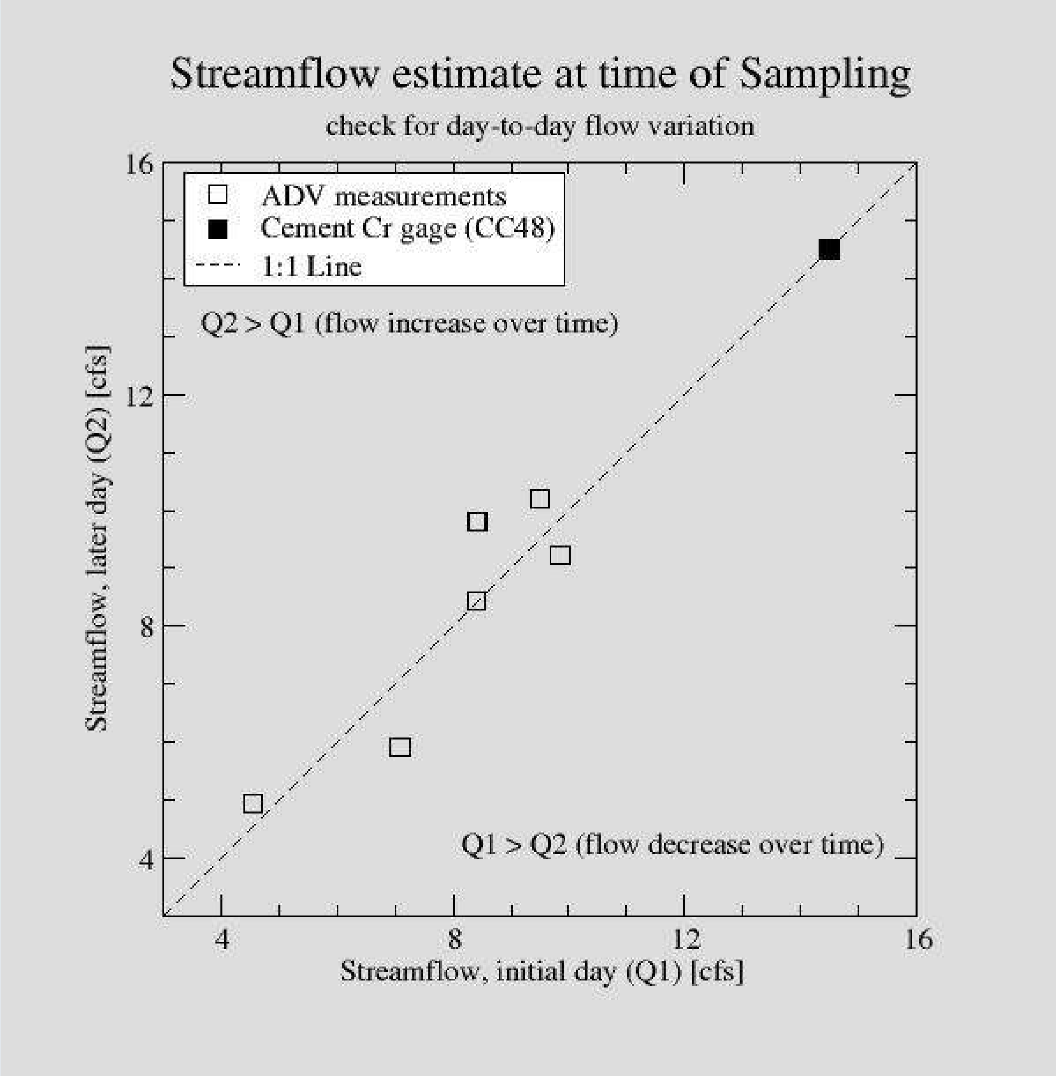
Do synoptic data represent “steady-state” conditions?

Loading analysis & modeling assume streamflow and concentration do not vary with time.



<u>Constant Streamflow?</u>

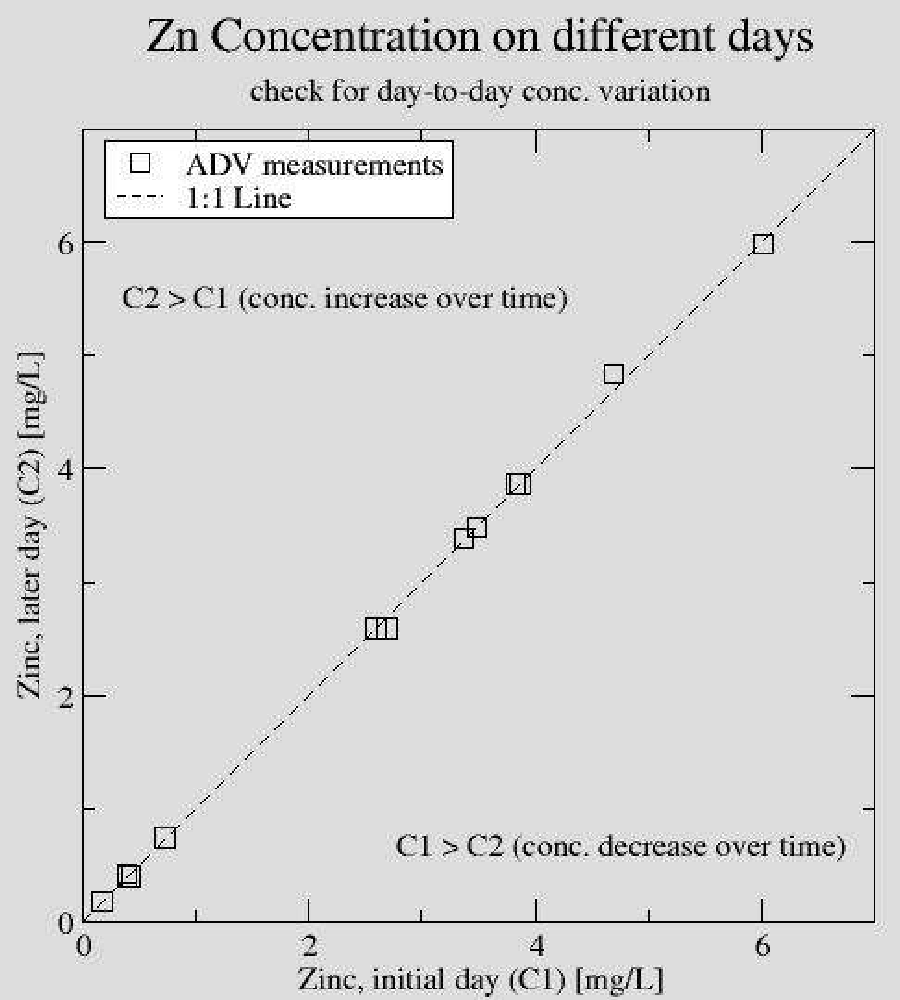
Cement Cr gage shows no change

ADV measurements on both sides of 1:1 line:

→ variability in ADV estimates > change in streamflow

Do synoptic data represent "steady-state" conditions?

Loading analysis & modeling assume streamflow and concentration do not vary with time.



<u>Constant loading & rxn?</u>

C1 & C2, good/great agreement:

Al, Ca, Cd, Co, Cu, F, Mg, Mn, Na, Sr, SO4, Zn

more variable:

pH, Fe, K, Ni, Pb

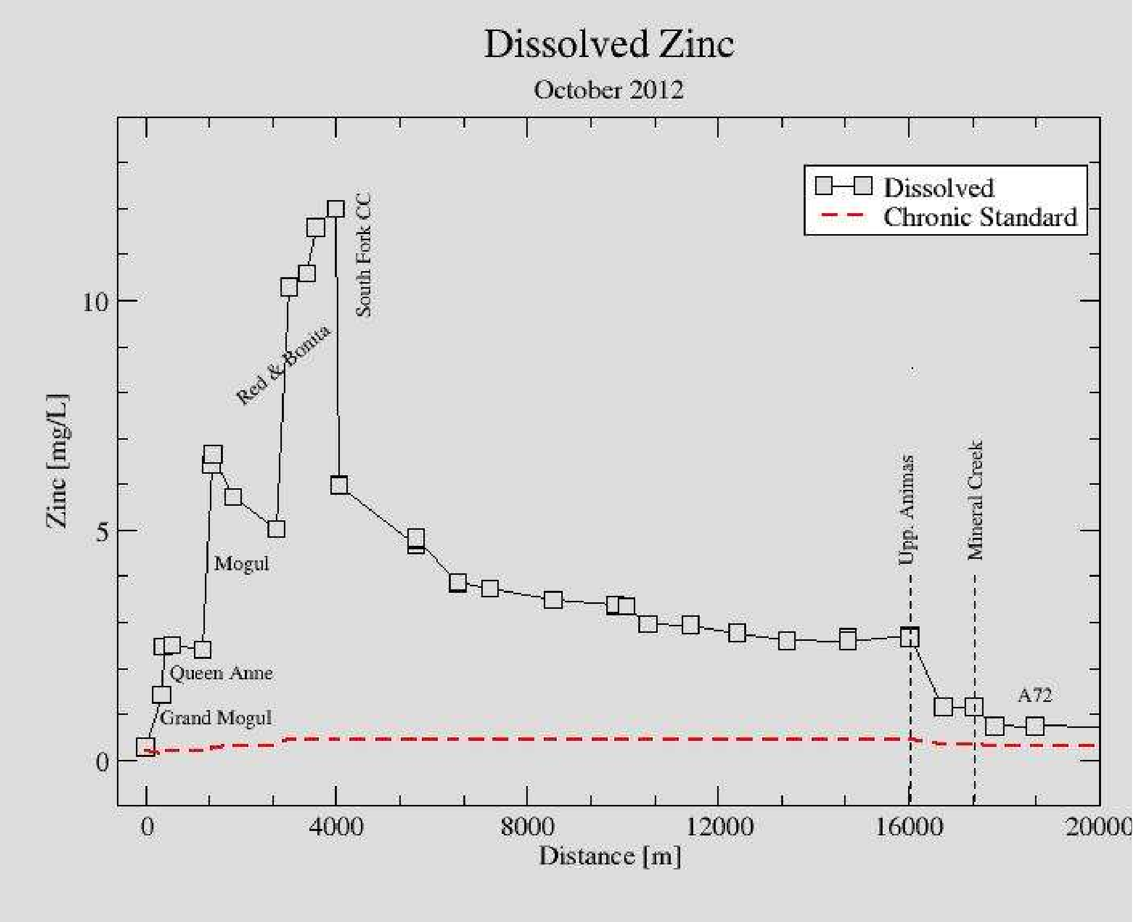
→ data represent approximate steady state conditions

<u>Mineral Cr:</u> Al on 10/2 and 10/4 v. diff.

<u>A68:</u> diel variation of pH, Zn

Part III: Results

Concentrations and Water Quality Standards



Above std, entire study reach:

Al, Cd, Zn

Above std, top to Cascade Cr:

Fe

Above std, Mogul to Mineral:

Mn

Above std, top to cement mouth:

Cu

Above std, sub1 to cement mouth:

Pb

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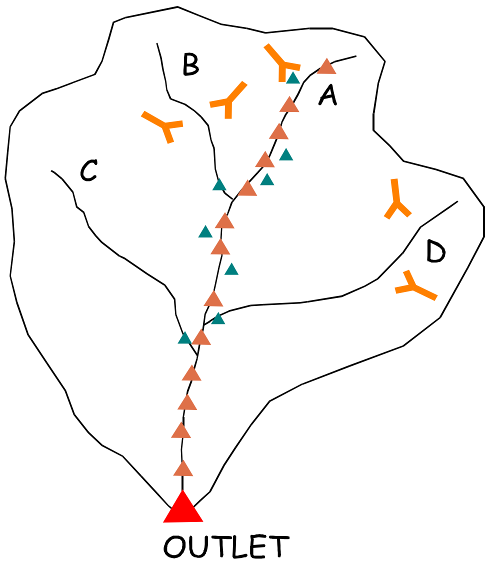
Part III: Results – Loads & Sources



Synoptic Sampling, October 2-4, 2012

- Synoptic Study:

  Spatial profiles of Streamflow & Conc.

- Load (mass / time) = flow * concentration
- → Spatial profiles of mass load
- \+ changes in mass load used to identify source areas

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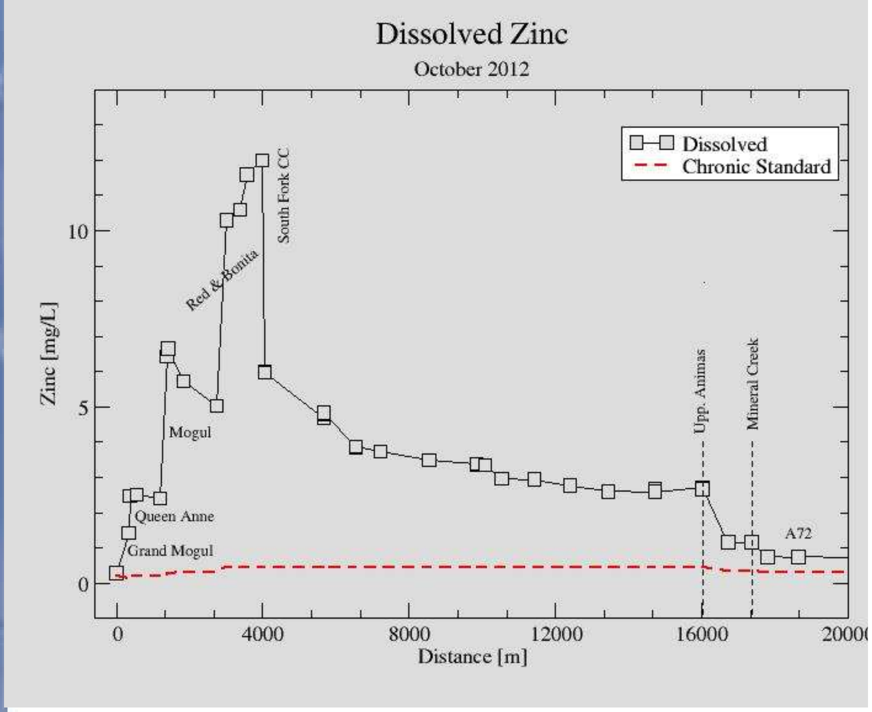
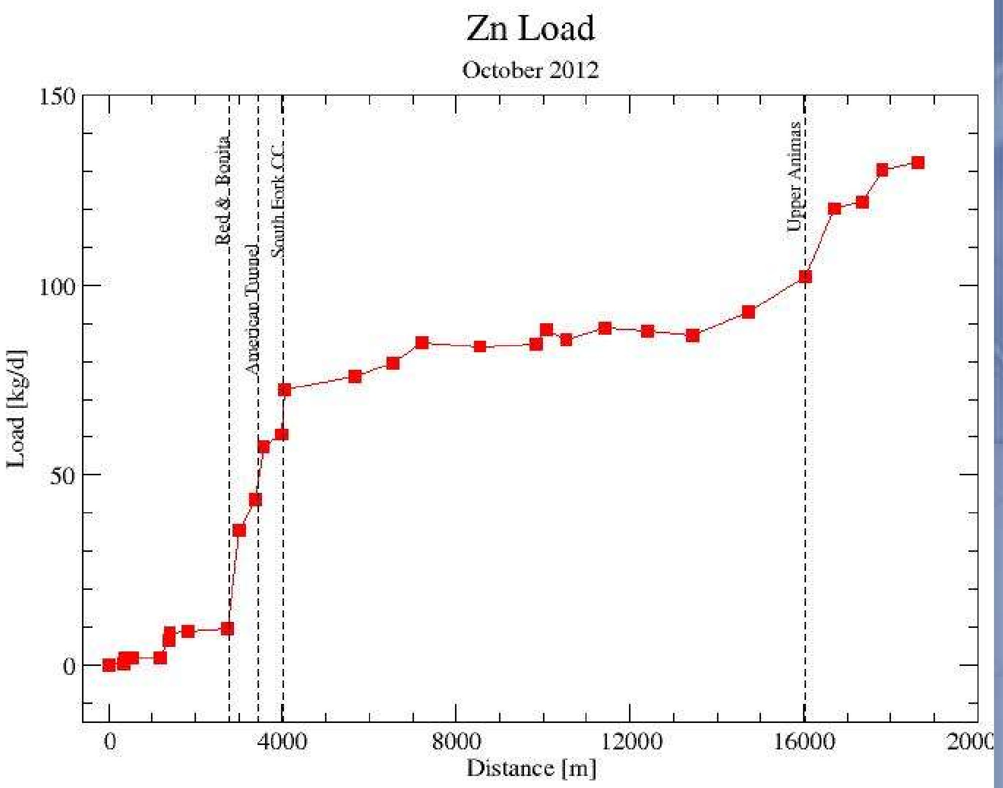
Part IV: Results – Loads & Sources





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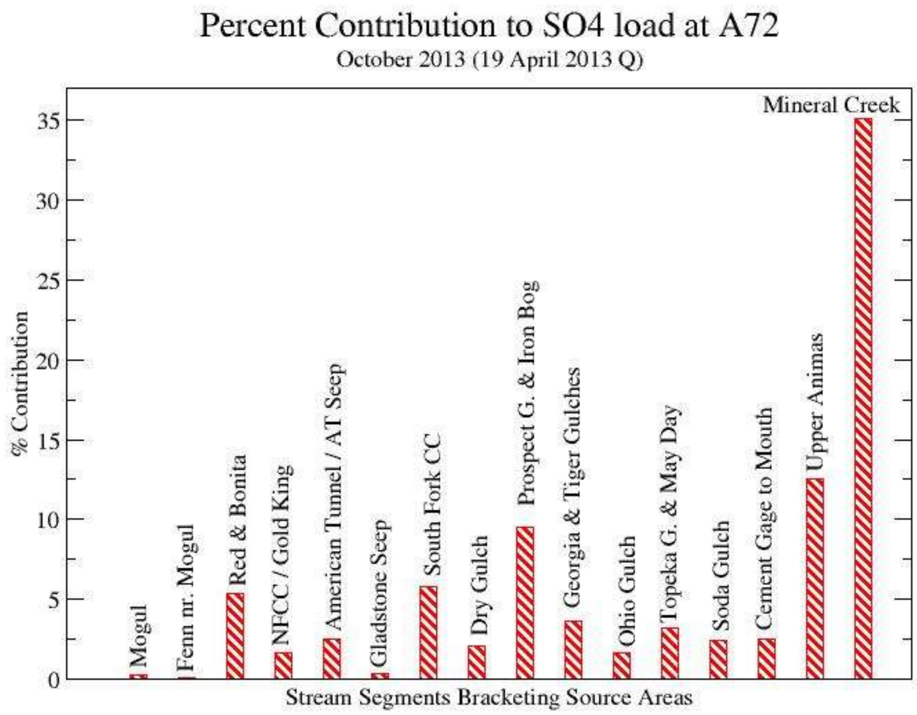
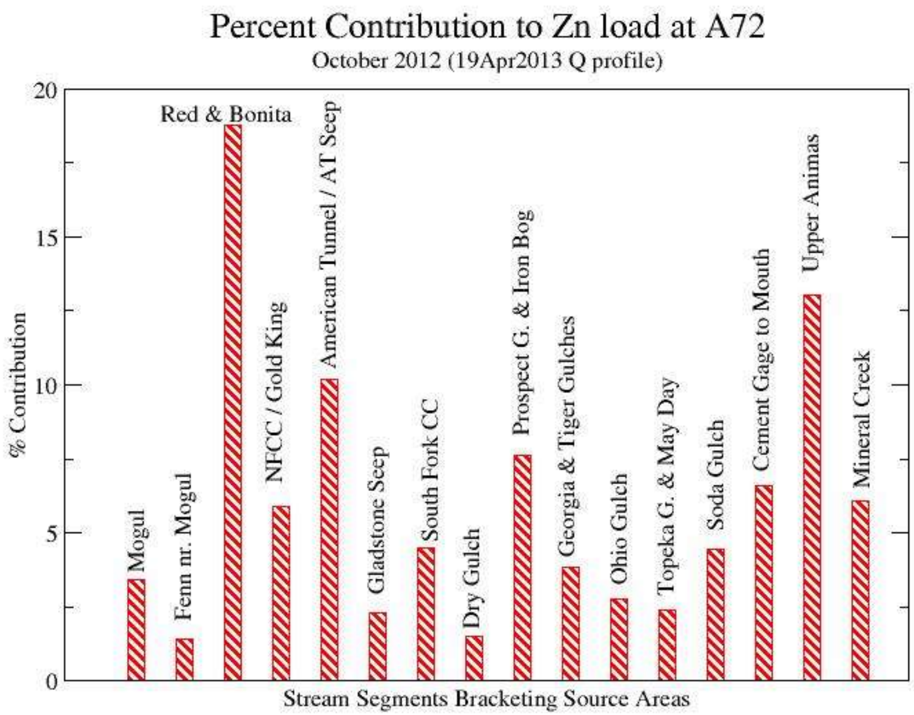
Part III: Results – Loads & Sources





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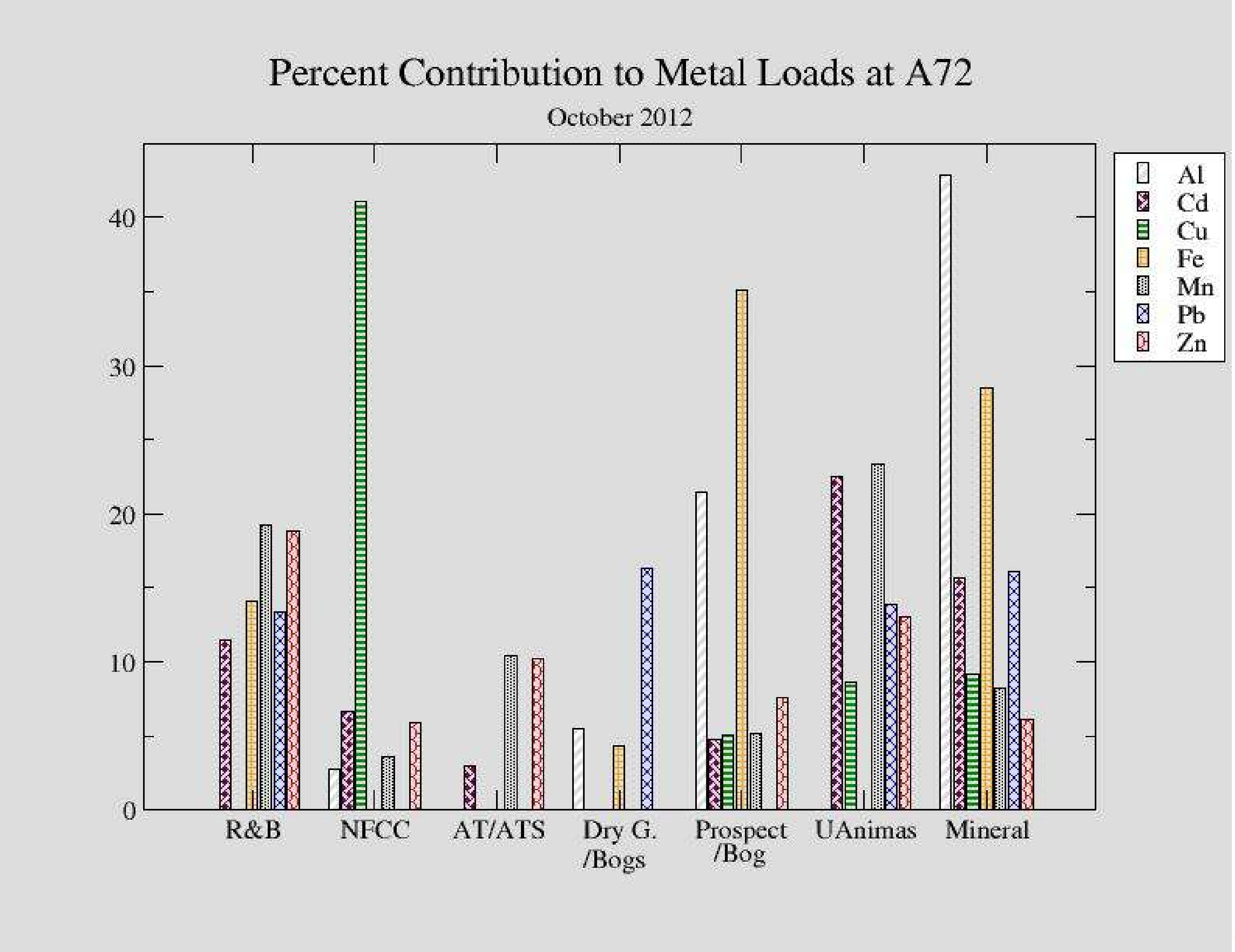
Part III: Results – Loads & Sources



Part III Results:
Reactive transport modeling

"Making predictions is difficult,
especially when it's about the future"

– Casey Stengel or Yogi Bera or some physicist dude

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Study Objective

- Main Objective:

  Use a reactive transport model to evaluate remedial options for Cement Creek

- Data Requirements:
  - Synoptic data set representing “steady-state” conditions
  - Spatial profiles of streamflow and concentration

- Doing the 2-Step:
  - Model Calibration: Reproduce existing conditions
  - Prediction: Modify calibrated model to reflect remediation

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Model Calibration: Reproduce existing conditions

- Components:
  - Al, As, Cd, Cu, Fe(II), Fe(III), H+, Ni, Pb, SO_4, Zn, Ca, CO_3
- Reactions:
  - precipitation: $Fe(OH)_3$, $Al(OH)_3$
  - sorption of As, Cd, Cu, Pb, and Zn onto HFO
  - oxidation of Fe(II)
  - degassing of CO2
- Model Input:
  - spatial streamflow profile (1 flow / site based on QA)
  - inflow chemistry (synoptic sampling)
  - equilibrium constants (MINTEQ database)

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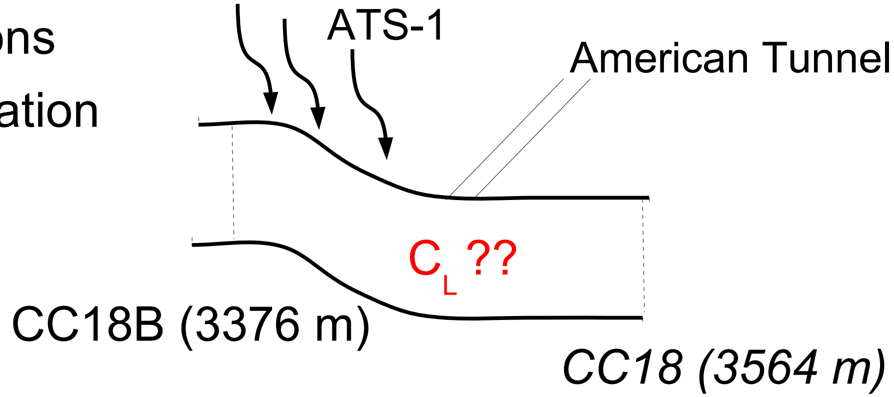
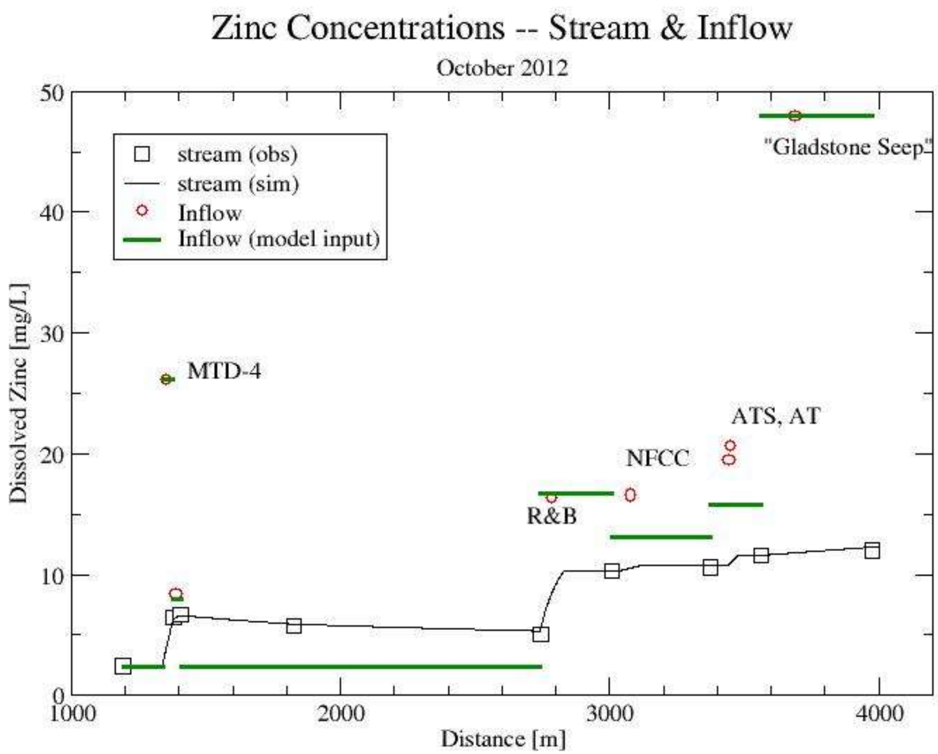
Model Calibration: Reproduce existing conditions

- Model input: inflow chemistry (synoptic sampling)
  - Reaches w/ multiple inflow observations
  - Reaches w/ a single inflow observation, but multiple inflows
  - Reaches w/o inflow observations
    - historical observations
    - no historical observation



Model Calibration: Inflow Chemsitry (C_L)



Set CL to reproduce stream data

Zinc – input values realistic

check other elements →
Fe CL > observed data, for example

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When calibrating:
Error on the side of caution

Possible outcomes of Predictions vs. Reality

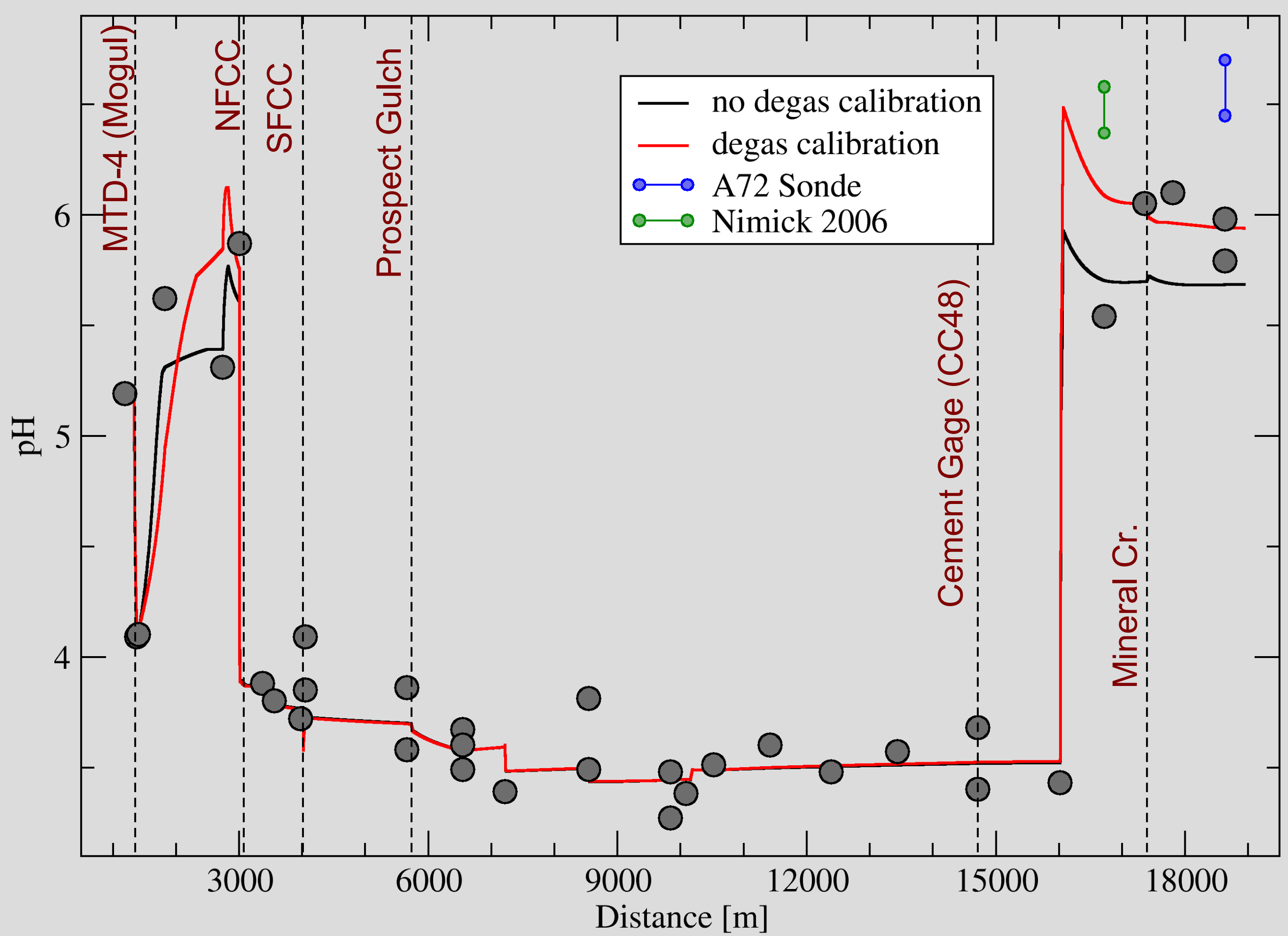
Table 1. Water Quality Standard Assessment (WQSA).

		Observed Data (MC2)	
		Attainment	Non-attainment
Best Estimate Simulation	Attainment	Correct Assessment	Type I Error: False Positive
	Non-attainment	Type II Error: False Negative	Correct Assessment

Runkel et al., Envir. Sci. & Tech., 2012

To avoid Type I errors:
Overestimate concentrations/Underestimate attenuation

pH Calibration



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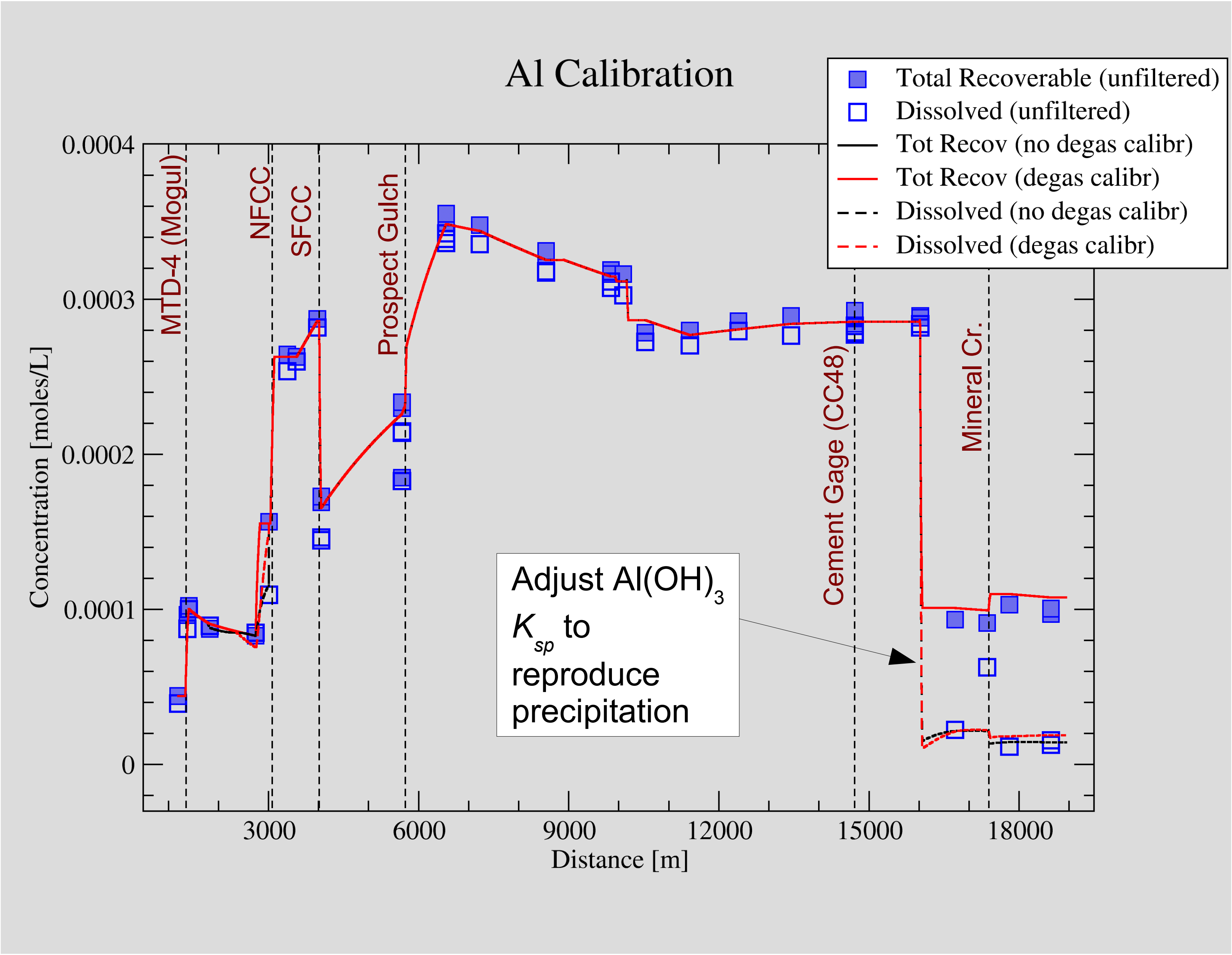

Al Calibration
Total Recoverable (unfiltered)
Dissolved (unfiltered)
Tot Recov (no degas calibr)
Tot Recov (degas calibr)
Dissolved (no degas calibr)
Dissolved (degas calibr)
MTD-4 (Mogul)
NFCC
SFCC
Prospect Gulch
Cement Gage (CC48)
Mineral Cr.
Adjust Al(OH)3
Ksp to
reproduce
precipitation
Concentration [moles/L]
0.0004
0.0003
0.0002
0.0001
0
3000
6000
9000
12000
15000
18000
Distance [m]

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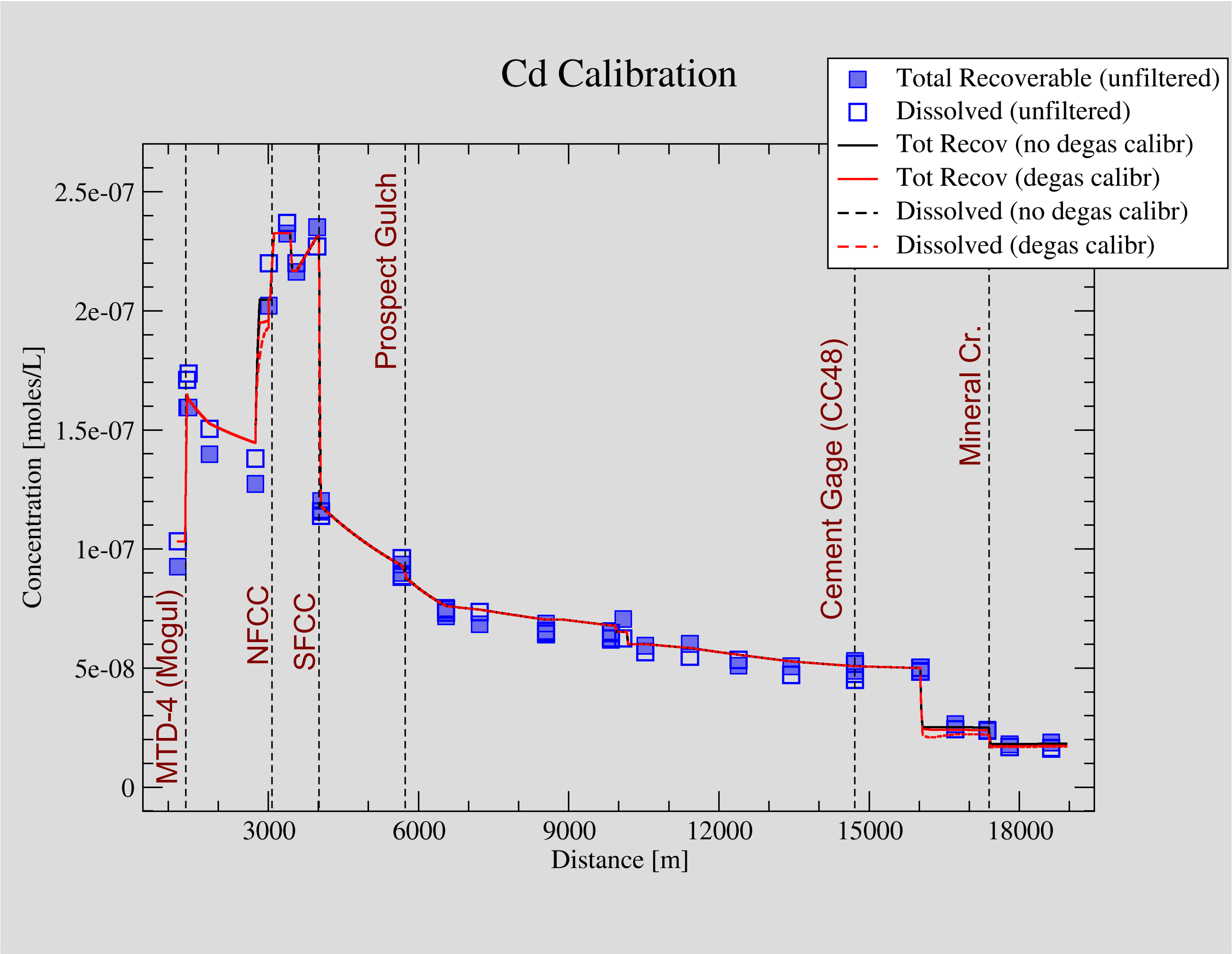
Cd Calibration
Total Recoverable (unfiltered)
Dissolved (unfiltered)
Tot Recov (no degas calibr)
Tot Recov (degas calibr)
Dissolved (no degas calibr)
Dissolved (degas calibr)
Concentration [moles/L]
Distance [m]
2.5e-07
2e-07
1.5e-07
1e-07
5e-08
0
3000
6000
9000
12000
15000
18000
MTD-4 (Mogul)
NFCC
SFCC
Prospect Gulch
Cement Gage (CC48)
Mineral Cr.

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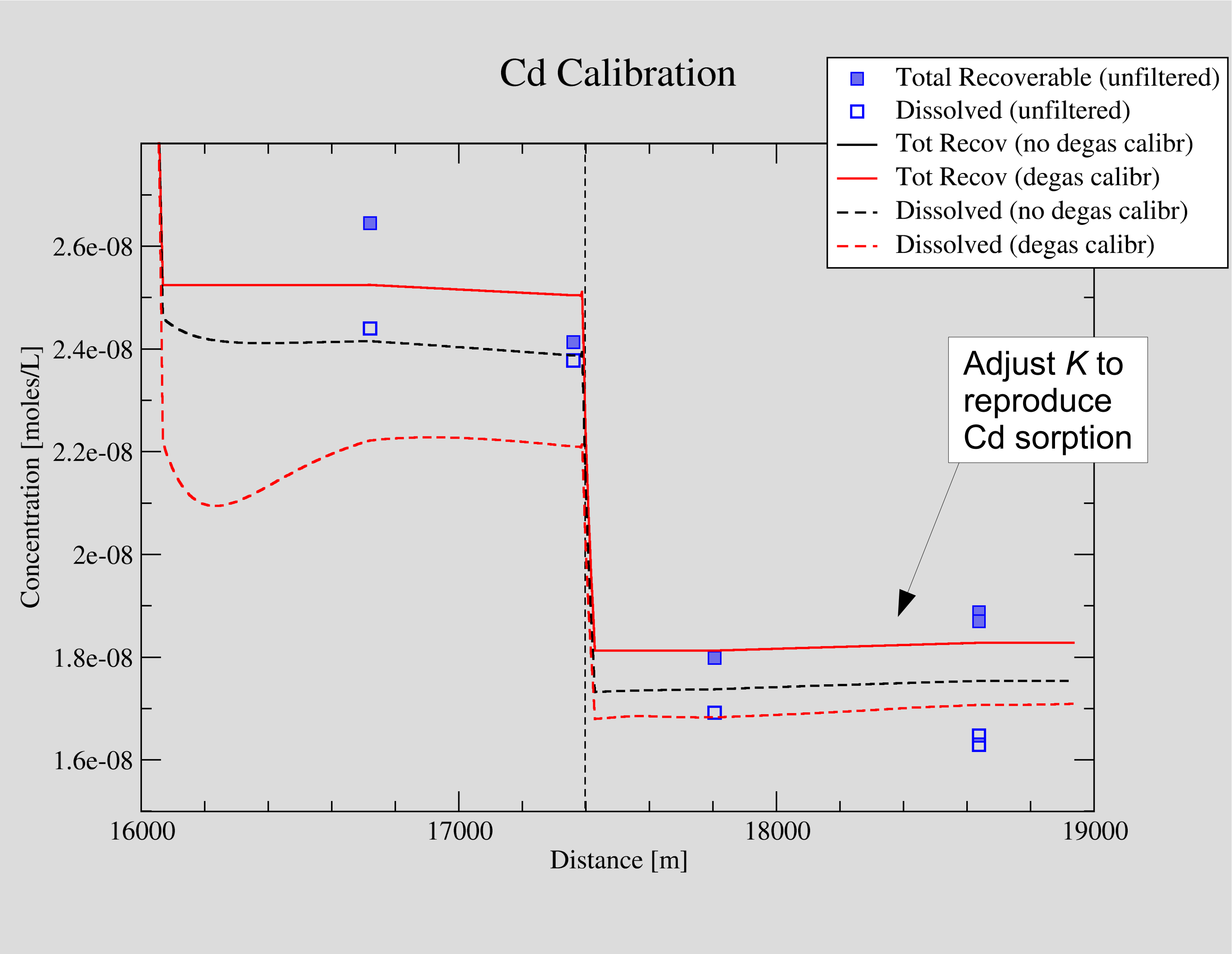
Cd Calibration
Total Recoverable (unfiltered)
Dissolved (unfiltered)
Tot Recov (no degas calibr)
Tot Recov (degas calibr)
Dissolved (no degas calibr)
Dissolved (degas calibr)
Adjust K to reproduce Cd sorption
Concentration [moles/L]
2.6e-08
2.4e-08
2.2e-08
2e-08
1.8e-08
1.6e-08
16000
17000
18000
19000
Distance [m]

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Predicting Effects of Remediation

- Modify calibrated model to reflect proposed remedial action
- Remedial Scenarios:
  - Plug Red & Bonita Adit (100% reduction)
  - 1996 Treatment Plant Conditions

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Predicting Effects of Remediation
Role of Uncertainty

- Estimates of post-remediation water quality are uncertain
- Calibration (low pH) → Estimation (increased pH)
- Sources of Uncertainty:
  - form of precipitates and solubility products
  - surface complexation (sorption) constants
  - uncalibrated rxns (e.g. Zn sorption)
  - effect of degassing
  - variation in low flow water quality

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Role of Uncertainty
Factor #1: Equilibrium Constants

- Solubility Products for Precipitation of Al & Fe
  - known to vary over a wide range
  - default K_{sp} values modified during calibration
- Surface complexation constants for sorption of As, Cd, Cu, Ni, Pb, Zn
  - defaults based on best estimates of Dzombak & Morel
  - default K values modified during calibration (As, Cd, Cu)
- Dealing w/ Uncertainty:
  - consider predictive simulations w/ both calibrated values and defaults

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Role of Uncertainty
Factor #2: Gas Exchange

- Calibrated model w/o degassing errs on the side of caution (under-predicts pH)
- Calibrated model w/ degassing reproduces observed data
- Dealing w/ Uncertainty:
  - consider predictive simulations w/ and w/o degassing

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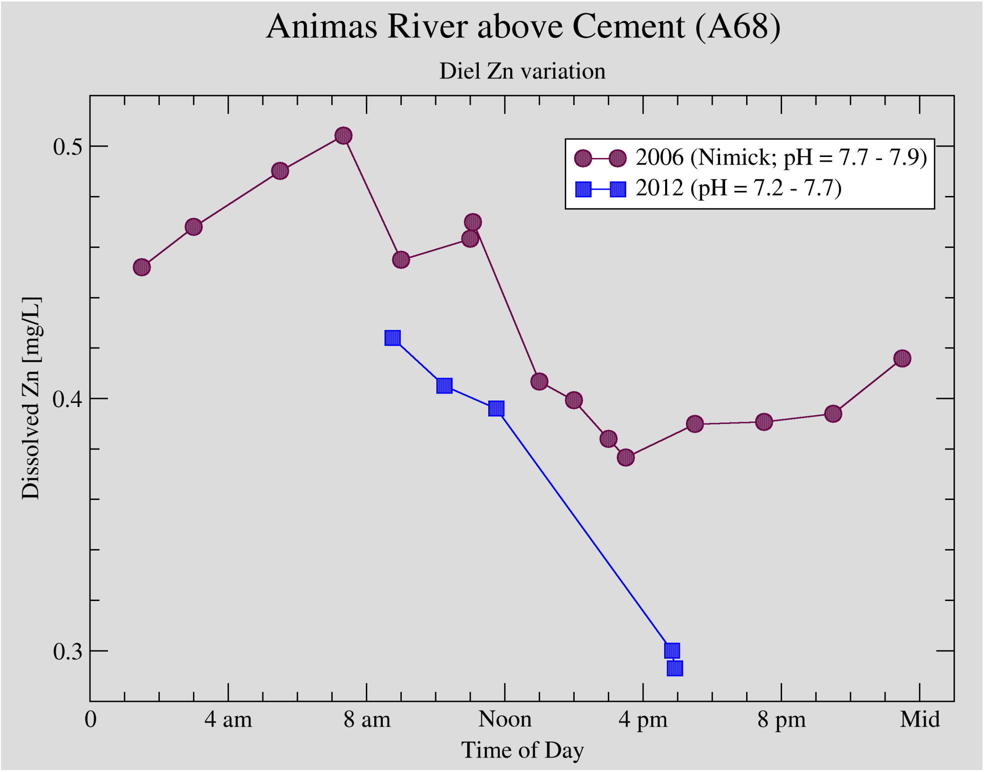
Role of Uncertainty
Factor #3: Variation in low-flow water quality

Inflow concentrations are set during calibration

Inflow concentrations are known to vary:



Dealing w/ Uncertainty:

Conduct "worst case" simulations where Mineral Creek and Upper Animas inflow concentrations are set equal to the max concentrations (2006/2012)

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Dealing w/ Uncertainty

- Sensitivity Analysis
  - Factors
    - Equilibrium constants: calibrated vs. defaults
    - Gas Exchange: with vs. without
    - Inflow concentrations: calibrated vs. worst case
  - Factorial design: $Nlevels^{Mfactors} = 2^3 = 8$ simulations
- 8 simulations for each remedial scenario
  - provides range of possible outcomes
  - "best estimate" = calibrated degas model
  - compare results based on median

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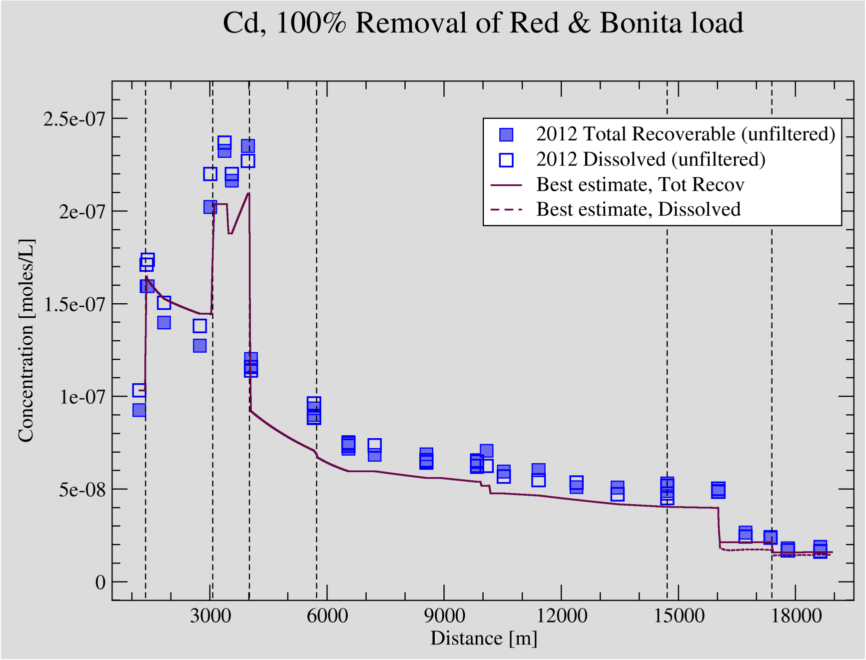
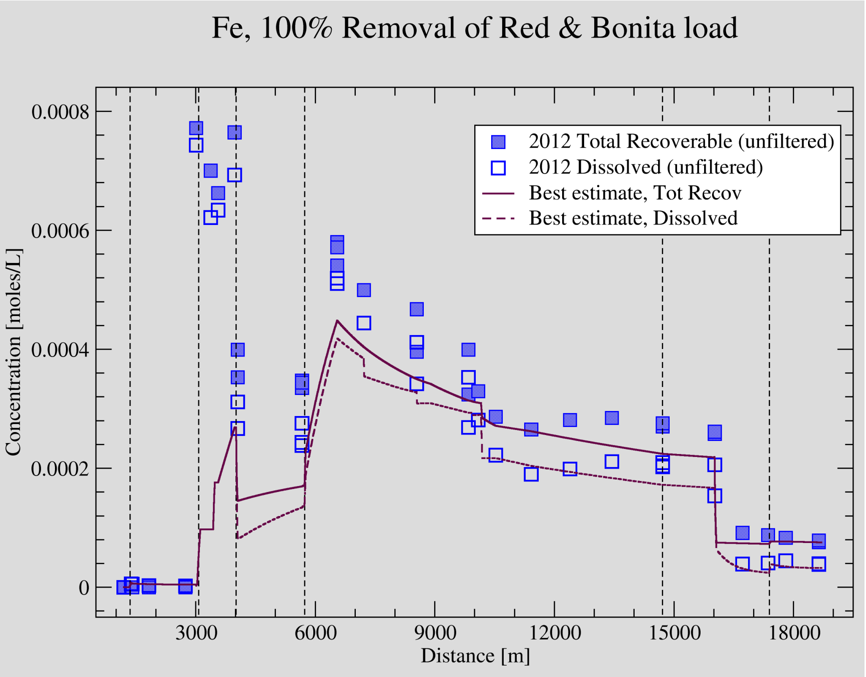
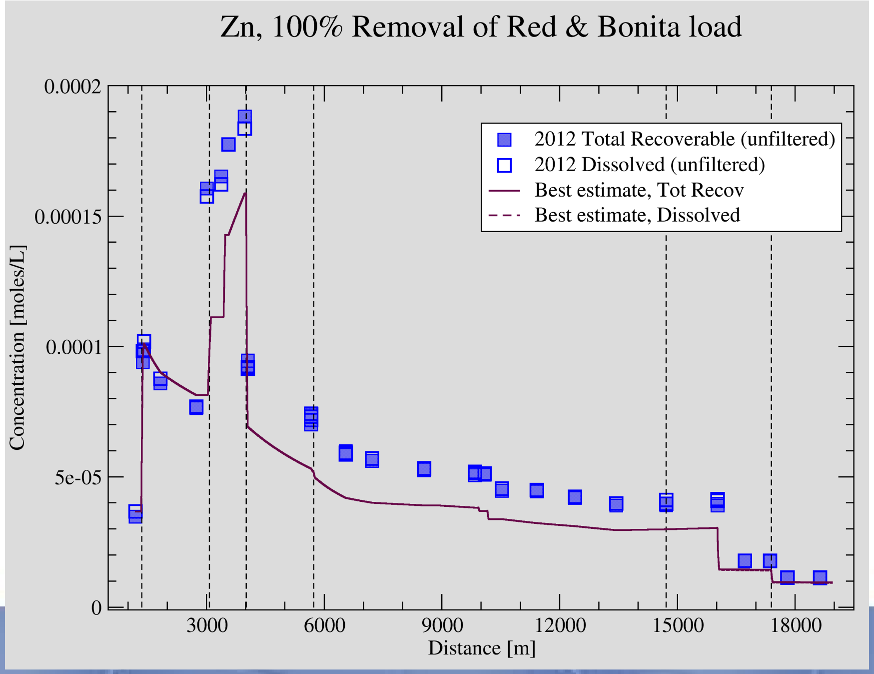
Remedial Scenario #1: 100% removal of R&B load

Modify the calibrated model such that no water enters between the two stream sites that bracket the Red & Bonita

Results: 100% removal of Red & Bonita load







pH & Al – v. similar to existing conditions

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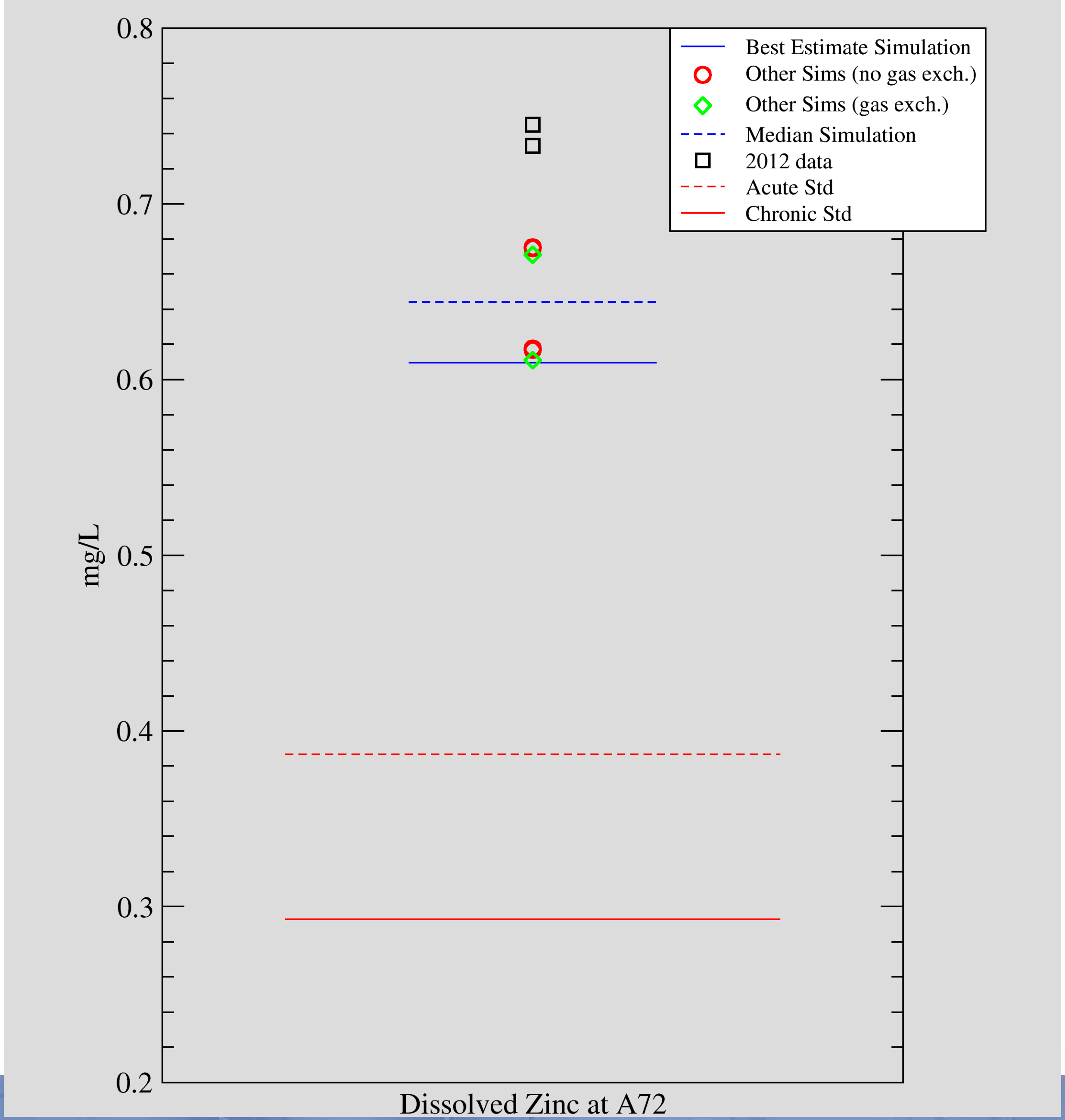
Results: 100% removal of Red & Bonita load



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Normalized Results

- Concentrations vary between constituents – normalize to allow for comparison

$$C_{norm} = 100 * (C_{pred} - wqstd)/(C_{2012} - wqstd)$$

$C_{norm} = 100 \rightarrow$ Prediction = 2012 conditions

$C_{norm} = 0 \rightarrow$ Prediction = chronic water quality std

$C_{norm} < 0 \rightarrow$ Prediction < chronic water quality std

$C_{norm} > 100 \rightarrow$ Prediction > 2012 conditions

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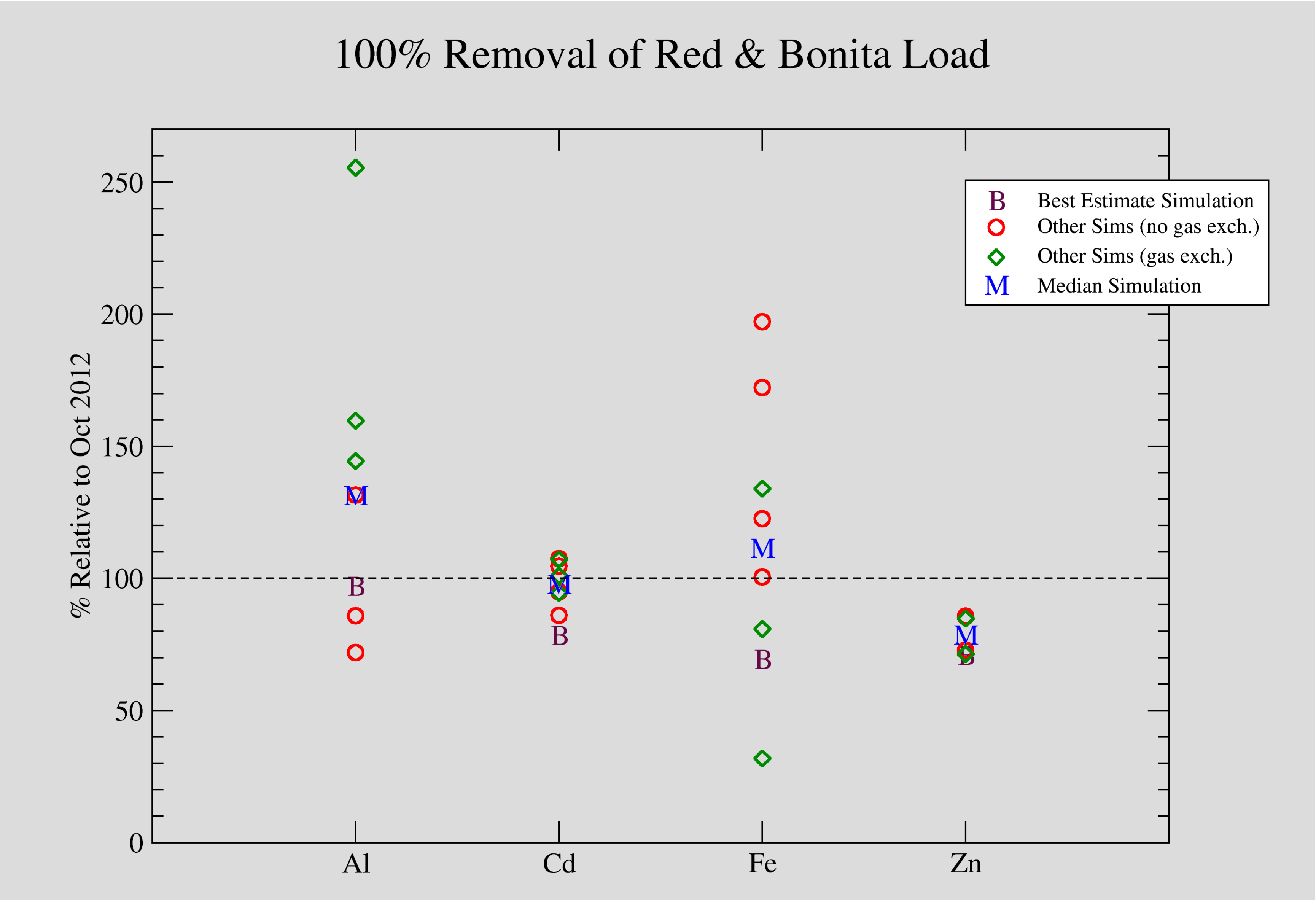
Normalized Results



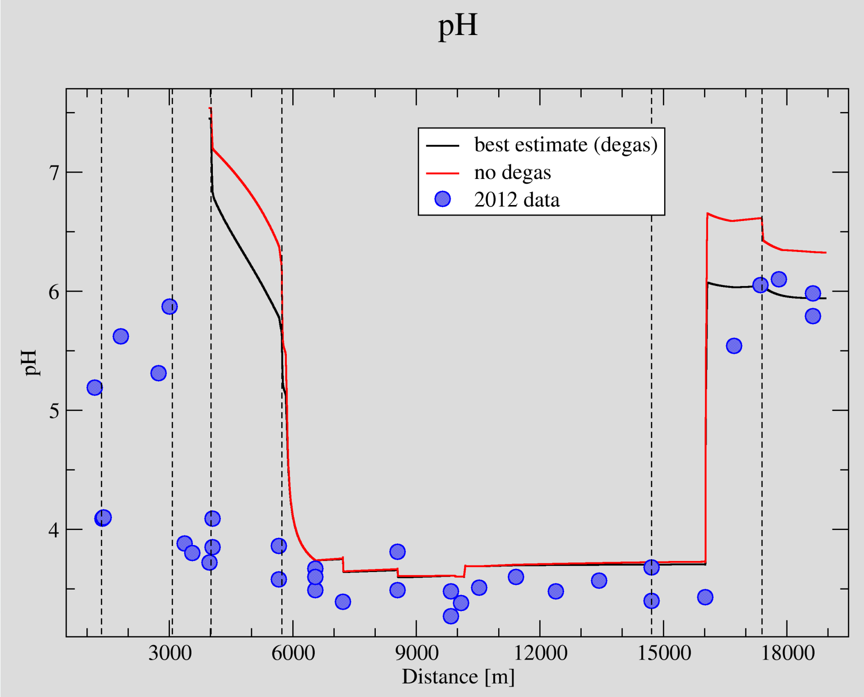
Remedial Scenario #2: 1996 Treatment Conditions

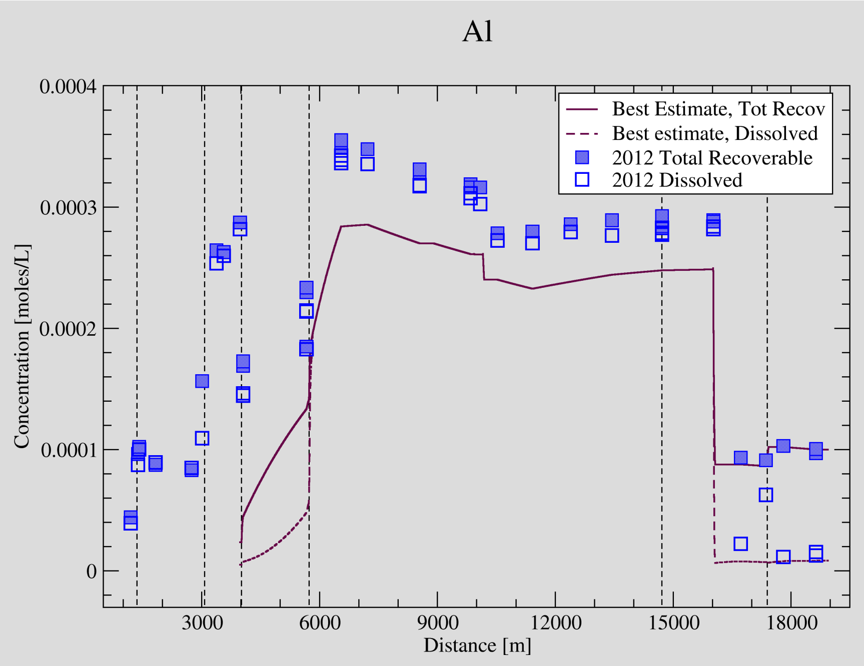
1996: Gladstone treatment system collected most of the water upstream of the South Fork

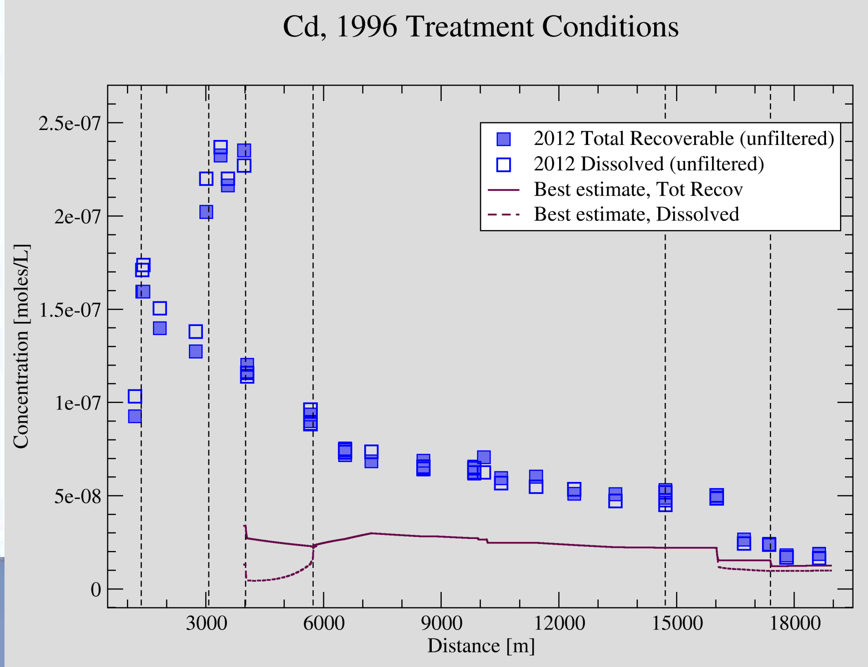
Move upstream boundary (above Mogul) to just above South Fork.

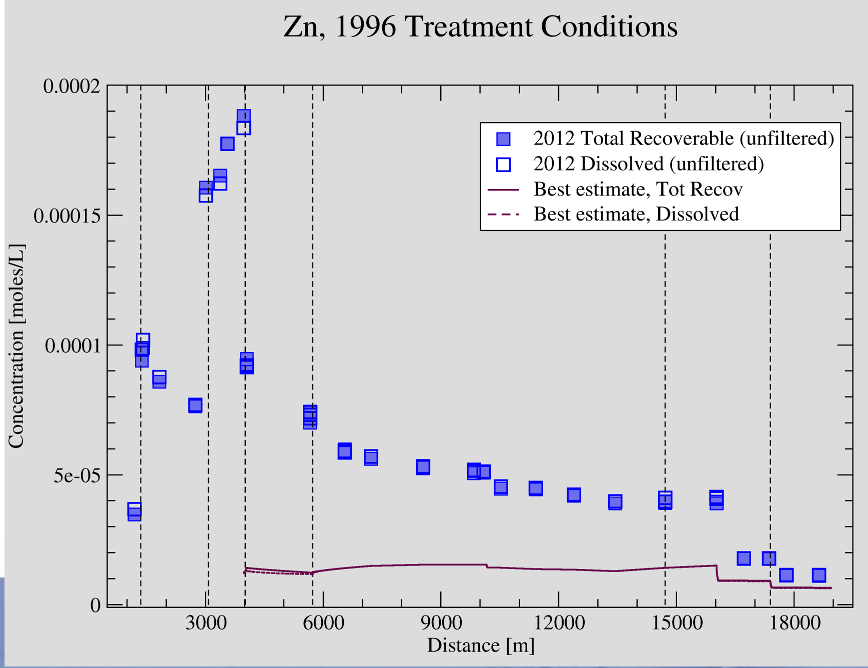
Specify upstream boundary chemistry based on 1996 data for Cement Creek, just downstream of the treatment system

Results: 1996 Treatment Conditions



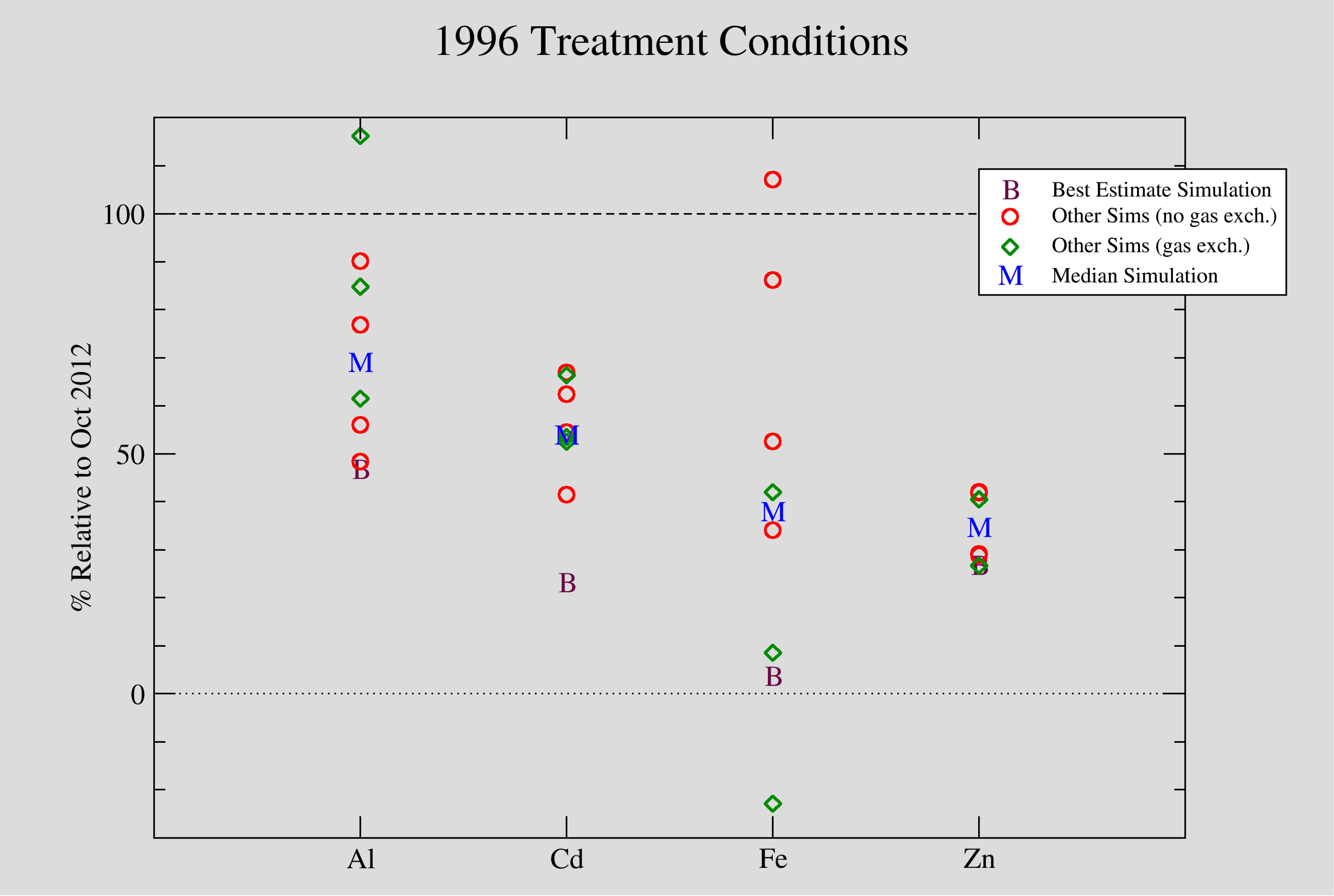






USGS

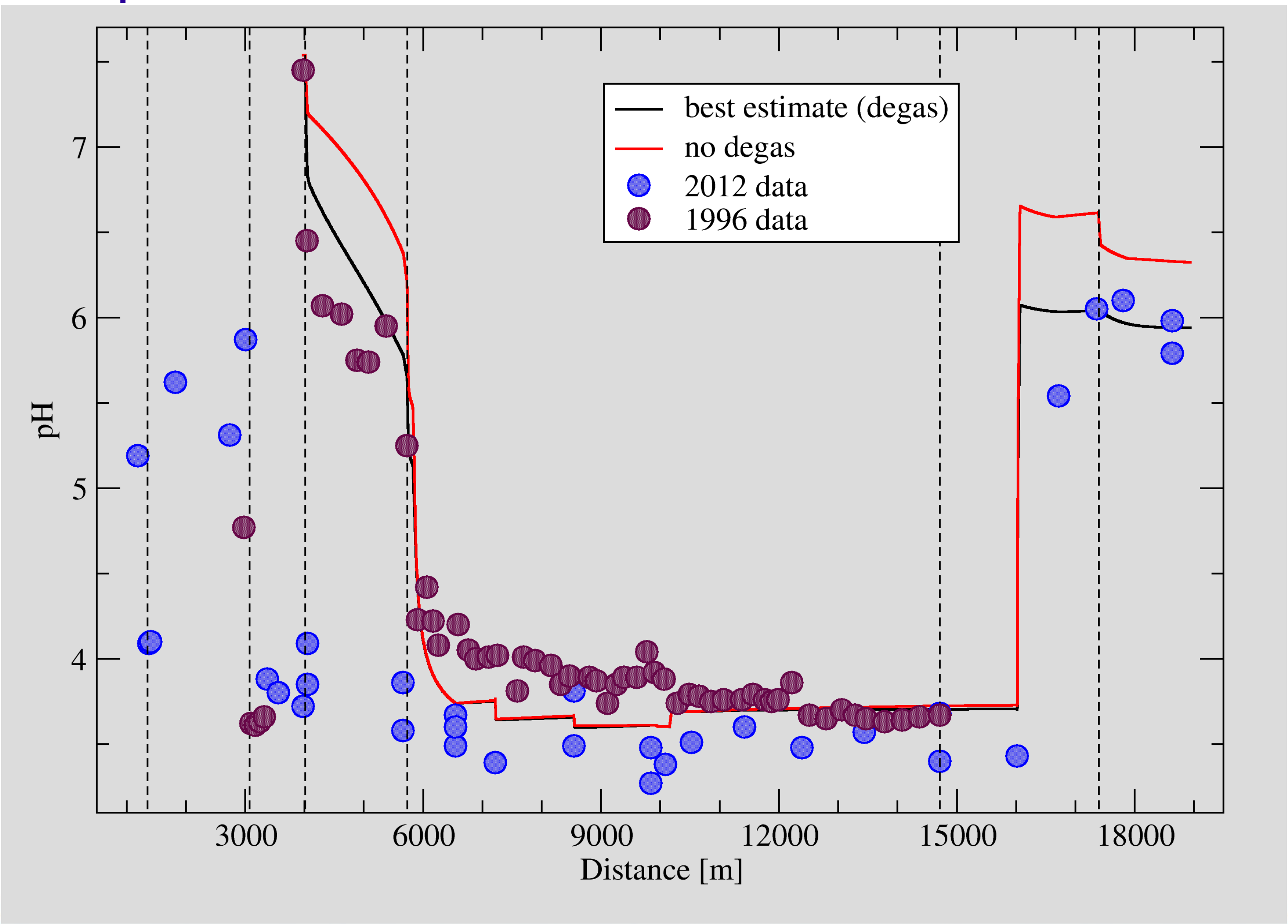
Results: 1996 Treatment Conditions



USGS

Model "Validation"

Comparison of Treatment Simulation w/1996 Data



USGS

Normalized Results, Revisited

Median Values (n=8)

	Al	Cd	Fe	Zn
R&B Plug	132	98	112	79
1996 Treatment	69	54	38	35

Best Estimate Simulation

	Al	Cd	Fe	Zn
R&B Plug	97	79	69	71
1996 Treatment	47	23	4	27

USGS

Summary

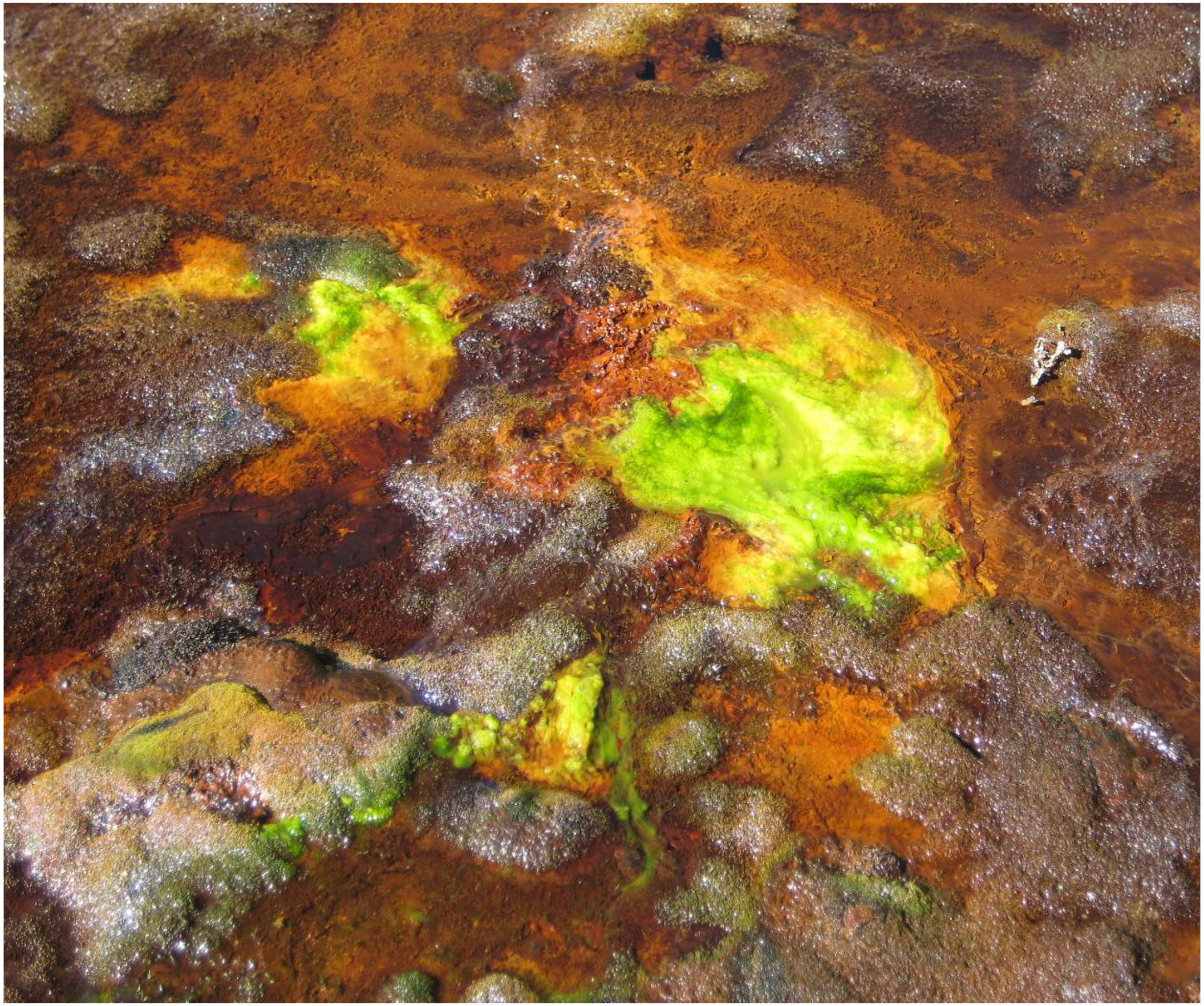
- Neither scenario results in the attainment of chronic water quality standards at A72
- Cement Creek is an appropriate focus for Fe & Zn
- Cd: need to consider U. Animas & Mineral
- Al: need to consider Mineral Creek

USGS

Middle Fork Mineral Creek
"White Death"

USGS

Next Steps?



Thank you!