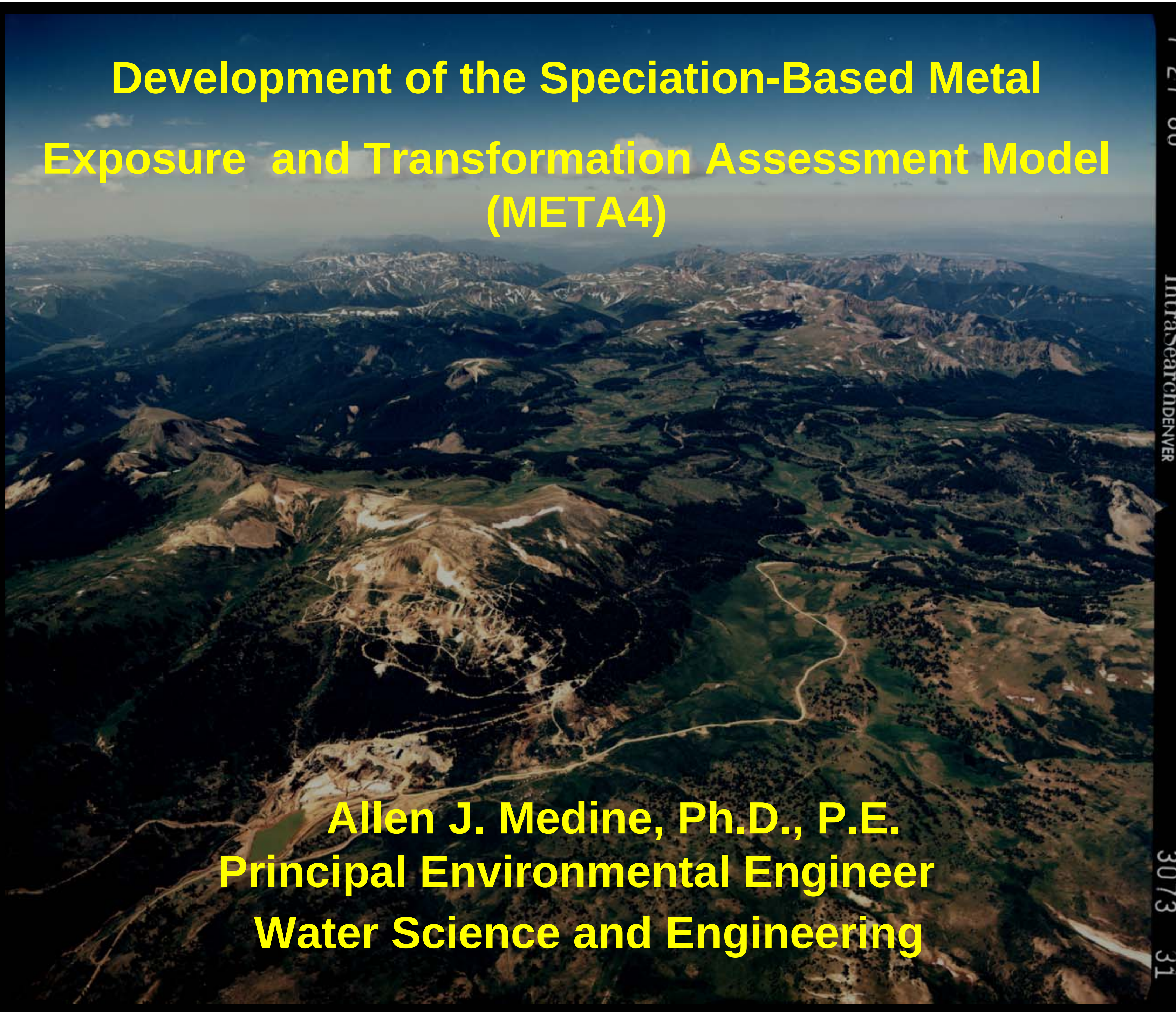
Development of the Speciation-Based Metal Exposure and Transformation Assessment Model (META4)



Allen J. Medine, Ph.D., P.E.
Principal Environmental Engineer
Water Science and Engineering

What Prompted the Development of Metal Transport Model for Mining-Impacted Watersheds?

- Mine-Impacted systems often overly complex,
- Existing data not sufficient for decisions,
- Comprehensive data difficult to obtain,
- Chemical behavior non-conservative, and
- Metal controlling reactions often change as a result of management decisions.

Why Do We Care About Specific Metal Species?

Relations Between Metal Forms

and

- Observed toxicity (Biotic Ligand Model)
- Transformation processes
- Interactions between metals

WASP-META4

Metal Exposure and Transformations Assessment Model

Water Analysis Simulation Program for 1,2 and 3 Dimensions

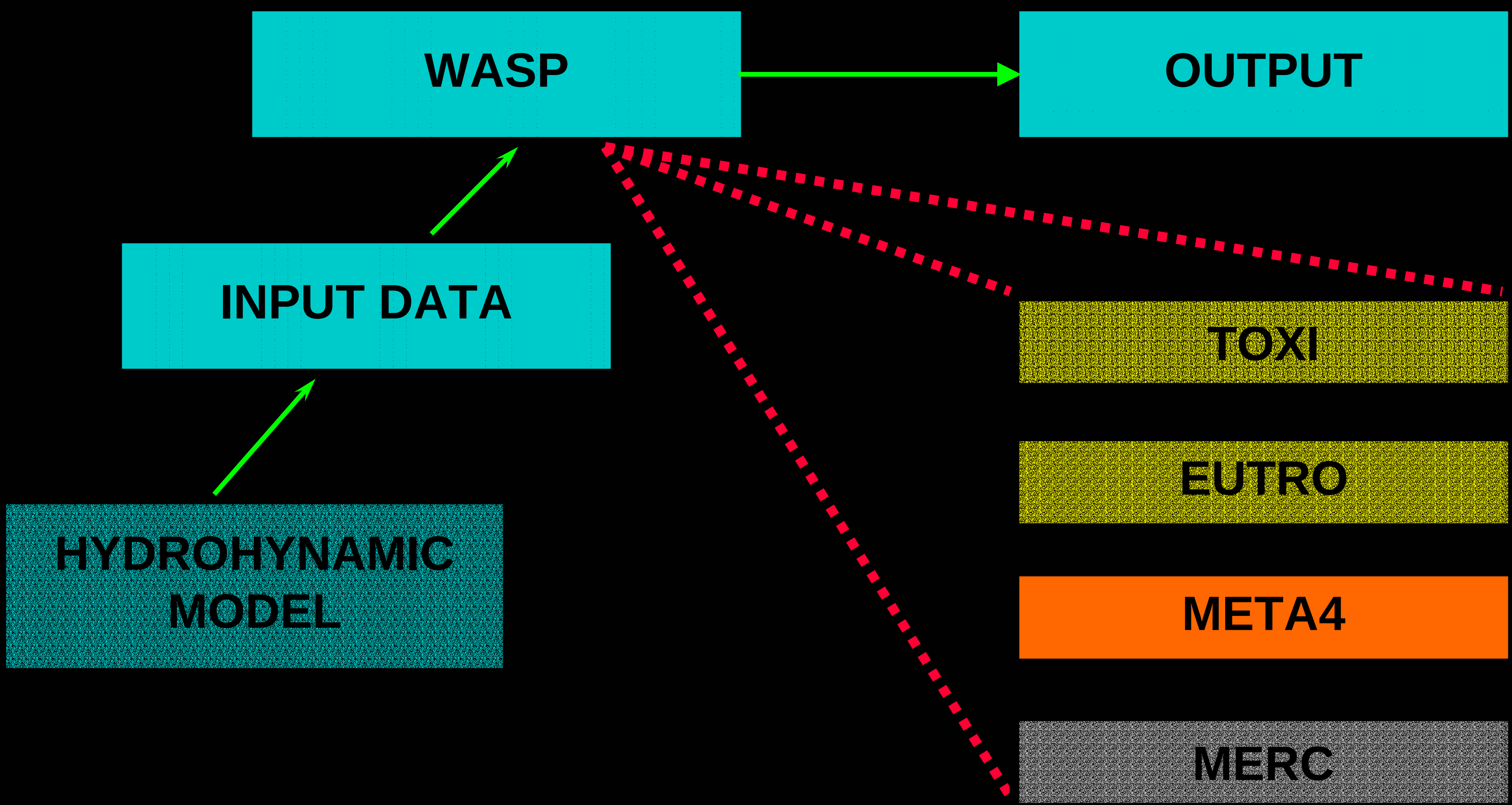
Submodel to Address the Complex Metal Behavior

META4 Originally Evolved from MERC

(James Martin, Robert Ambrose)

Incorporates Metal Speciation Based on MINEQL Mathematics / MINTEQA2 Database

WASP-META4



WASP
OUTPUT
INPUT DATA
HYDROHYNAMIC MODEL
TOXI
EUTRO
META4
MERC

META4 Metal Exposure and Transformations Assessment Model

Model Evolution (1995-2003)

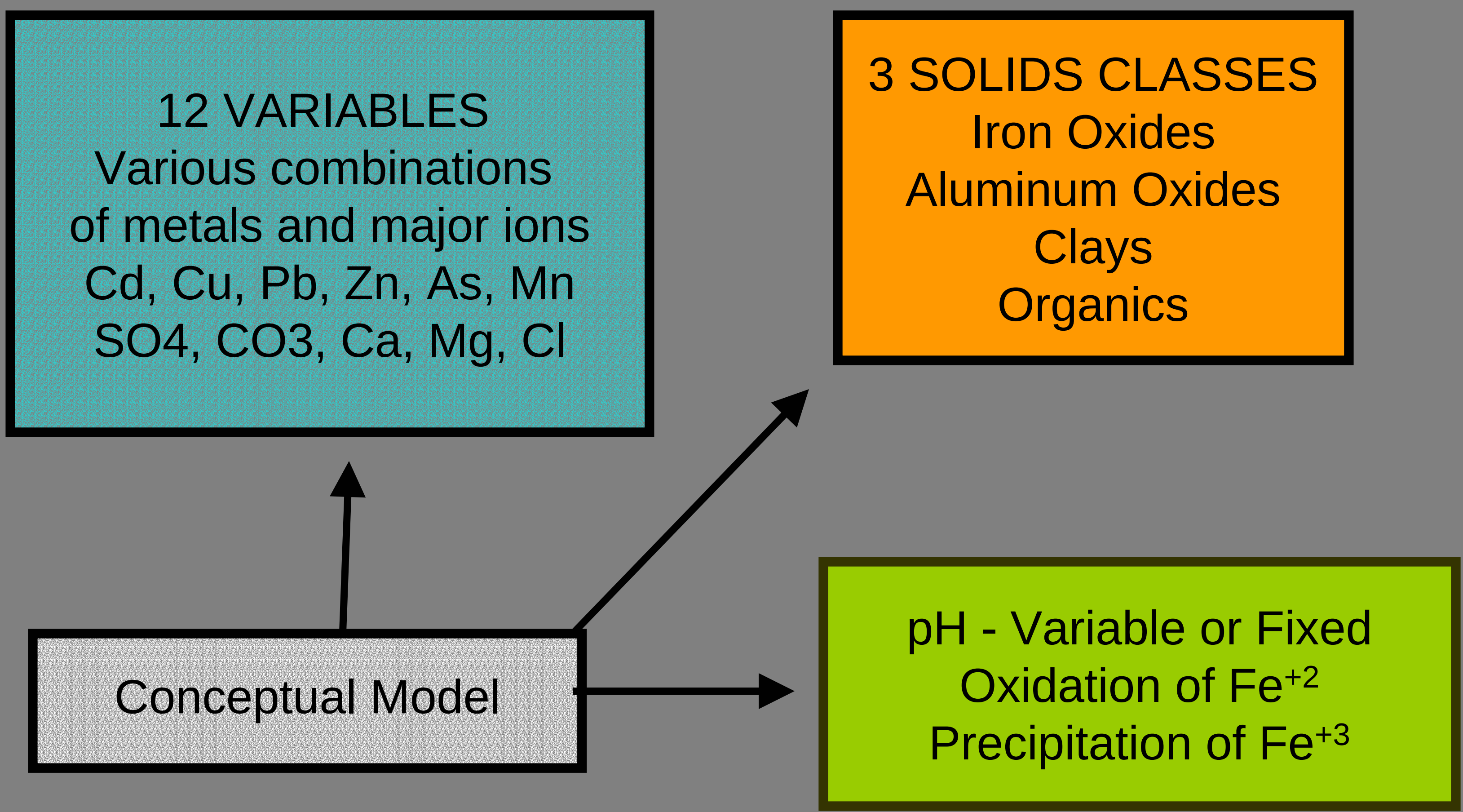
Version 1: First Generation Based on MINTEQA2 and MINEQL Solution Methods, Simple Adsorption Routines

Version 2: Addition of Double Layer Adsorption Option

Version 3: Increase in Variables to 12, Addition of Variable pH Simulation, Preparation of Detailed User Manual

Version 4: Increase in Variables to 16, Minor Change Regarding Iron Oxide Precipitation and Accounting in the Program

META4
Current Model State Variables



Previous Modeling Applications

North Clear Creek	Remedial RI/FS
Alamosa River	Use Attainability, RI/FS TMDL
Clear Creek	Remedial FS
California Gulch	Remedial RI/FS
Blackbird Creek	Restoration NRDA
Big Deer Creek	Restoration NRDA
Whitewood Creek	Dam Failure RD

Previous Modeling Applications
Specific Model Variables

North Clear Creek	**Zn, Cd, Cu, Mn, Pb, Fe(II), Fe(III) SO_4, Ca, Mg, CO_3, Al(III), pH, S1, S2**
Alamosa River	**Zn, Cu, Mn, Fe, Al, pH, CO_3, S1**
Clear Creek	**Zn, Cd, Cu, Mn, S1**
California Gulch	**Zn, Cd, Fe, Pb, S1**
Blackbird Creek	**Cu, S1**
Big Deer Creek	**Cu, S1**
Whitewood Creek	**As, S1**

For each application, majors ions, when not simulated, were treated as parameters.

North Clear Creek (NCC)

Clear Creek / Central City Superfund Site
Colorado

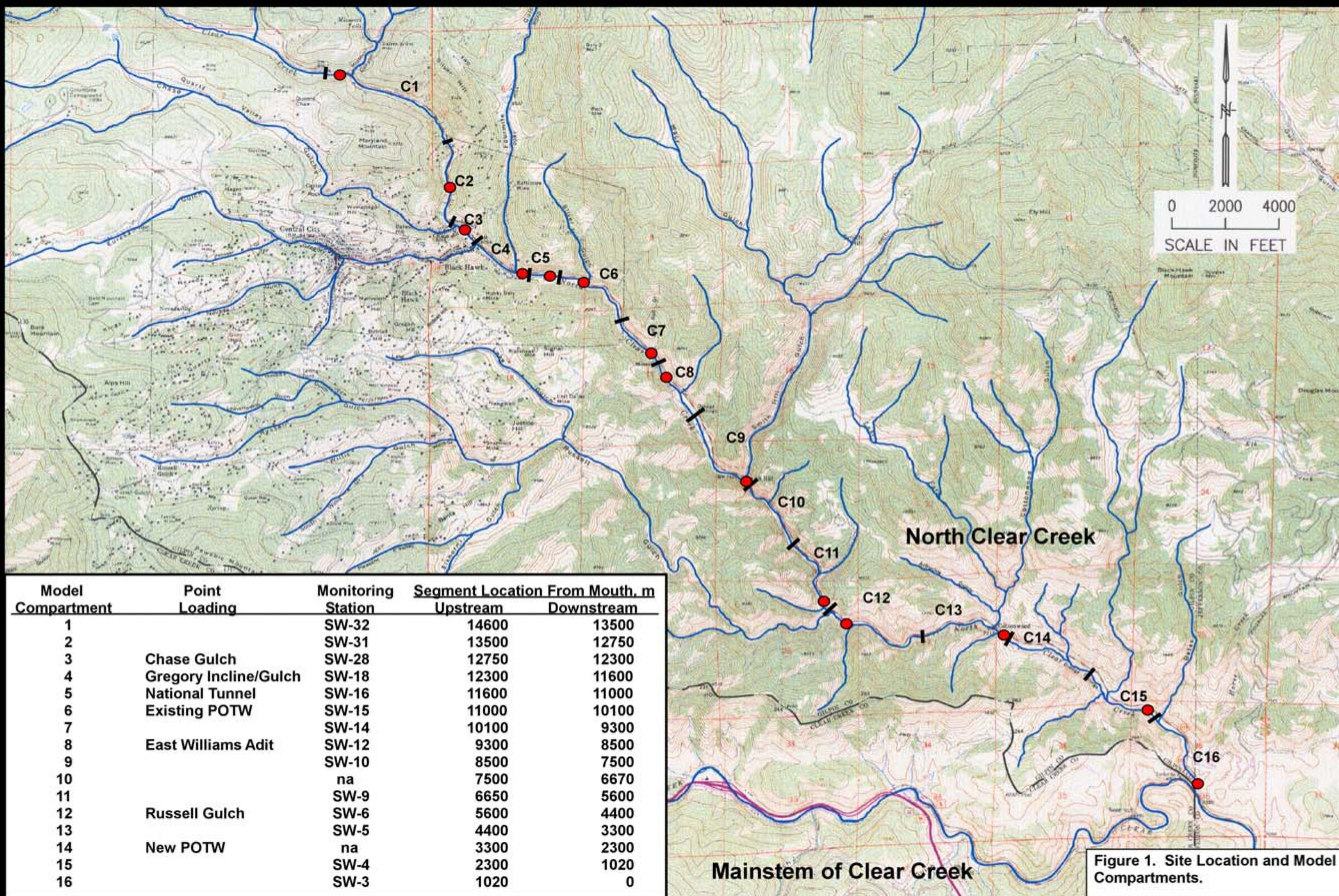
Severe water quality degradation, no fish, limited macroinvertebrates, habitat degradation

Metals responsible for aquatic resource impairment

NCC selected for development and testing of META4

Extensive characterization of surface water, sediment, groundwater interactions, mineral phases, porewater and tributary loadings began in 1994.

Site Location and Model Compartments



Model Compartment	Point Loading	Monitoring Station	Segment Location From Mouth, m Upstream	Downstream
1		SW-32	14600	13500
2		SW-31	13500	12750
3	Chase Gulch	SW-28	12750	12300
4	Gregory Incline/Gulch	SW-18	12300	11600
5	National Tunnel	SW-16	11600	11000
6	Existing POTW	SW-15	11000	10100
7		SW-14	10100	9300
8	East Williams Adit	SW-12	9300	8500
9		SW-10	8500	7500
10		na	7500	6670
11		SW-9	6650	5600
12	Russell Gulch	SW-6	5600	4400
13		SW-5	4400	3300
14	New POTW	na	3300	2300
15		SW-4	2300	1020
16		SW-3	1020	0

Figure 1. Site Location and Model Compartments.

Modeling History for North Clear Creek

- Model used to direct future mainstem sampling and focus sub-basin evaluations
- Evaluated Effects of Trans-basin Diversions
- Evaluated Effects of POTW Relocation
- Evaluated Effects of Contaminated Sediments
- Effectiveness of Feasibility Study Alternatives Evaluated Series of Remedial Actions Directed at Point and Diffuse Loadings in Watershed, Modeling Suggested Limited Fishery

Modeling Activities for 2002-2003

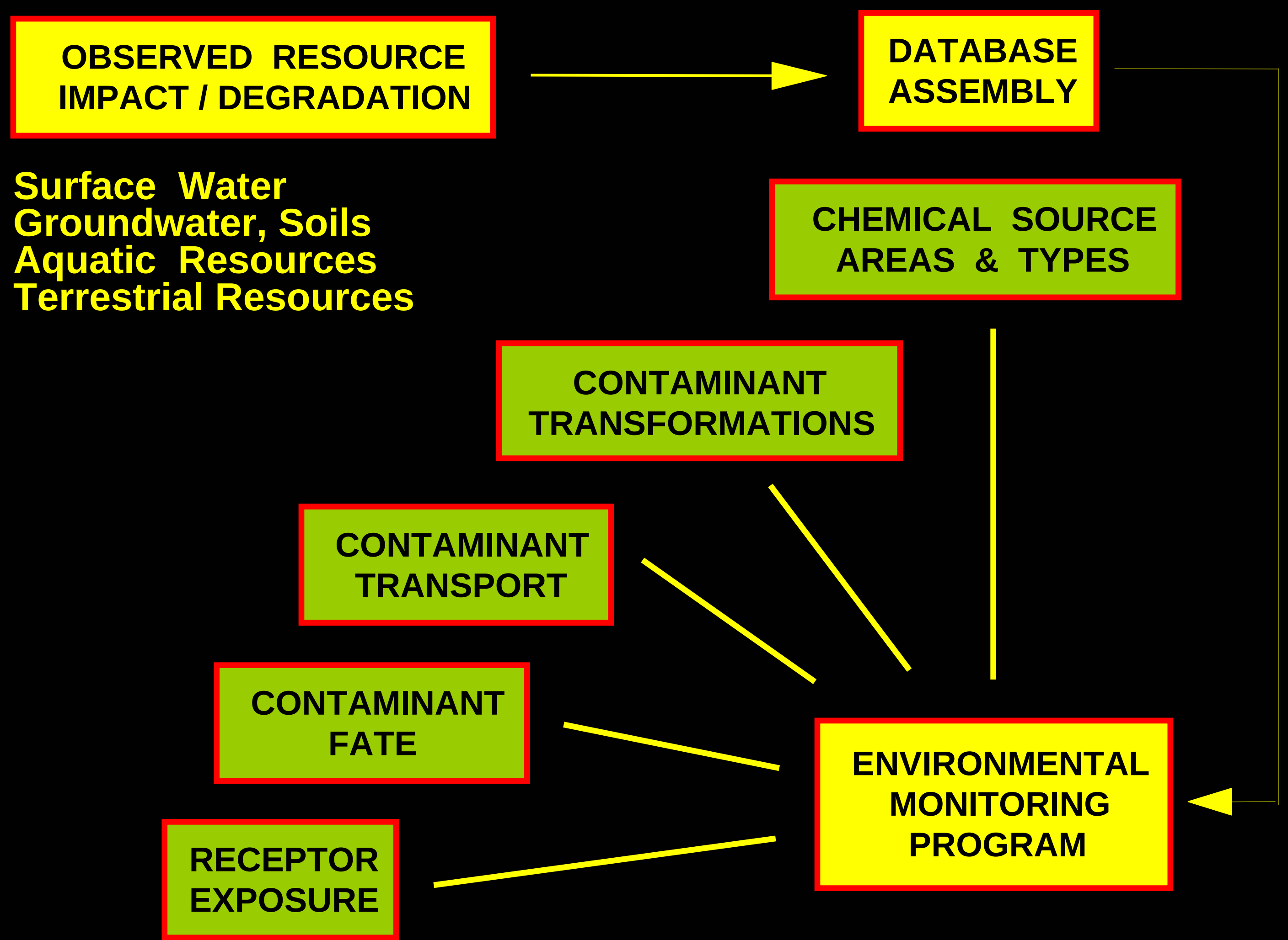
A. Verification of Previous Modeling Effort (1995 data, 6-variables)

B. Modification of the North Clear Creek Model Framework, including chemical reactions needed for 15-variable model, adjustment of compartment locations, some loads and physical characteristics

C. Model Re-Calibration and Verification, calibration and verification of low flow 15-variable model to November 2001 and May 2002 data, respectively

D. Analysis of Scenarios for Water Quality Improvement:

Development of Conceptual Model



Chemical Source Area Types

Primary

Tailings from the Golden-Gilpin Mill

Drainage from the Gregory Incline continues, but the tailings pile was remediated by removal completed in 1994.

Gregory Gulch drainage that contains drainage from the Quartz Hill Tunnel,

Eureka Gulch and Nevada Gulch as well as contaminated sediments
Mill tailings and waste rock which lie along Gregory Gulch upstream from
Black Hawk, including Quartz Hill, Boodle, and others in Gregory Gulch. Some Gregory Gulch piles have been capped or removed.

National Tunnel drainage- Tailings were removed and capped at Clay County.

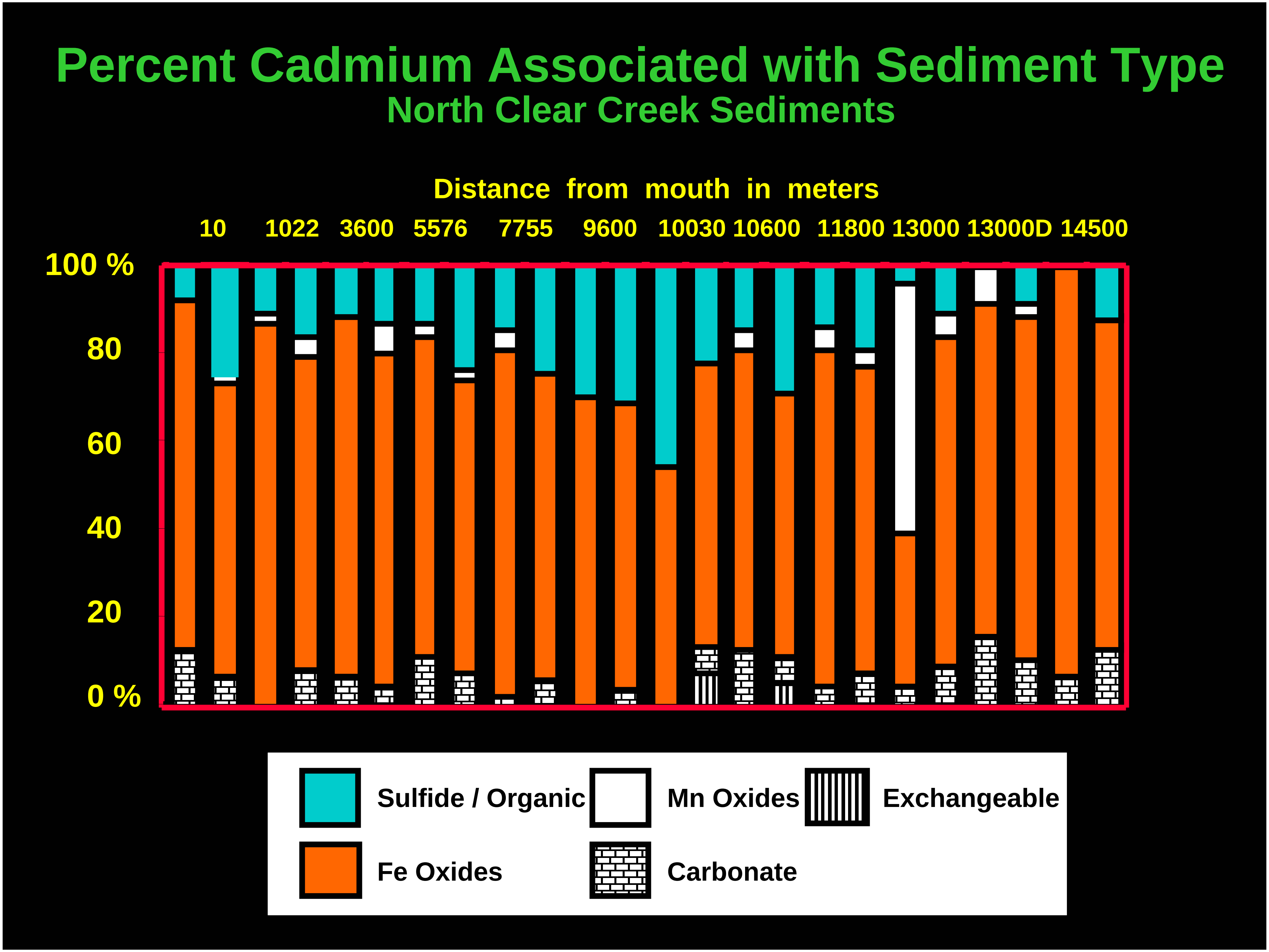
Surface water, sediments and tailings from Chase Gulch and Russell Gulch

Stormwater loadings: Tailings along Gregory Gulch and other tailings piles along North Clear Creek may also significantly affect the chemistry of North Clear Creek and may be major sources of sediment and particulate metals during storm events.

Metal Associations in Sediments

IRON OXIDES ARE EXCELLENT SCAVENGERS OF METALS FROM SOLUTION

- **Fine Grained, Amorphous Compounds**
- **Poorly Crystalized**
- **Large Surface Area**
- **High Cation Exchange Capacity**
- **High Negative Surface Charge**



Percent Cadmium Associated with Sediment Type
North Clear Creek Sediments
Distance from mouth in meters
10
1022
3600
5576
7755
9600
10030
10600
11800
13000
13000D
14500
100 %
80
60
40
20
0 %
Sulfide / Organic
Mn Oxides
Exchangeable
Fe Oxides
Carbonate

Input Data Requirements

Chemical Reaction Matrix

- Mineral and Sediment Types
- Speciation Option (None, Simple,Competitive)
- pH Option, fixed or variable
- Iteration Error and Number of Iterations
- Groundwater- SW Solution Chemistry
- Inorganic Complexation
- Organic Complexation
- Solid Phase Reactions and Control
- Sorption Reactions

Modeling Activities for 2002-2003

A. Verification of Previous Modeling Effort (1995 data, 6-variables).

B. Modification of the North Clear Creek Model Framework, including chemical reactions needed for 15-variable model, adjustment of compartment locations, some loads and physical characteristics.

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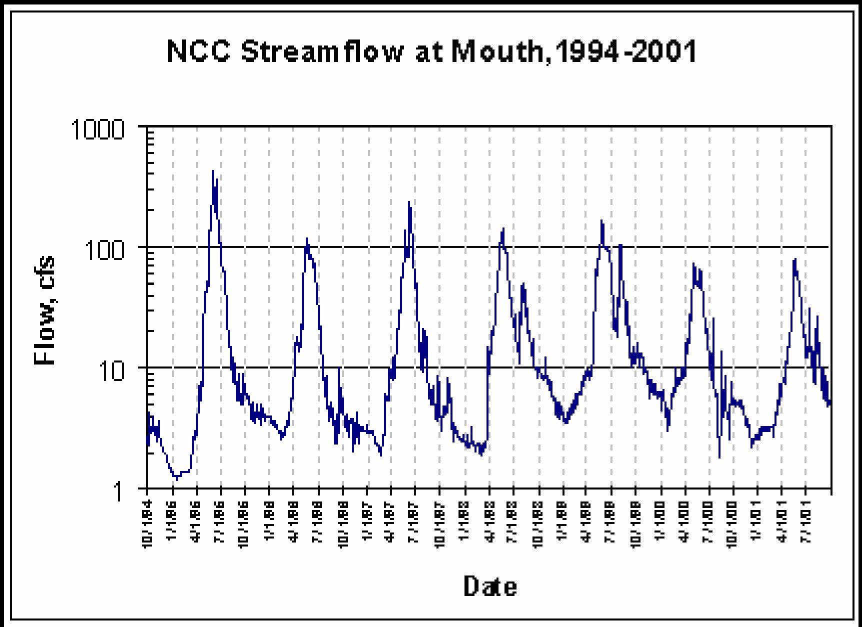
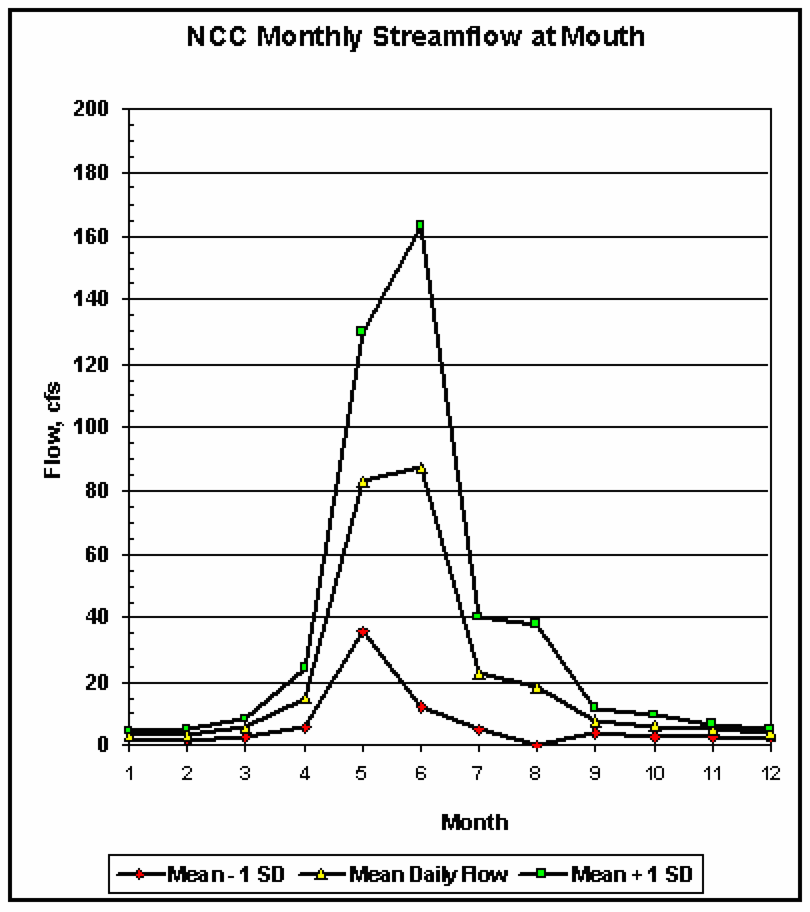
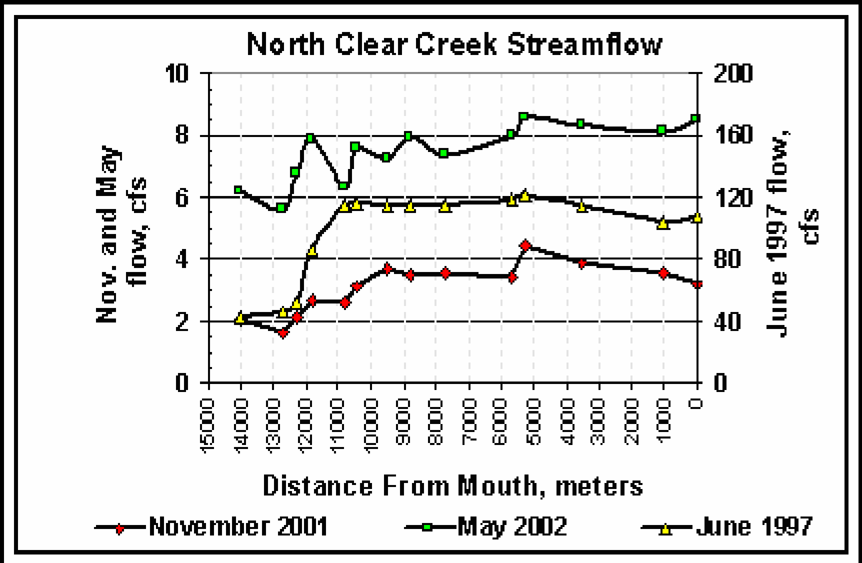
D. Analysis of Scenarios for Water Quality Improvement:

Hydrologic Conditions in North Clear Creek







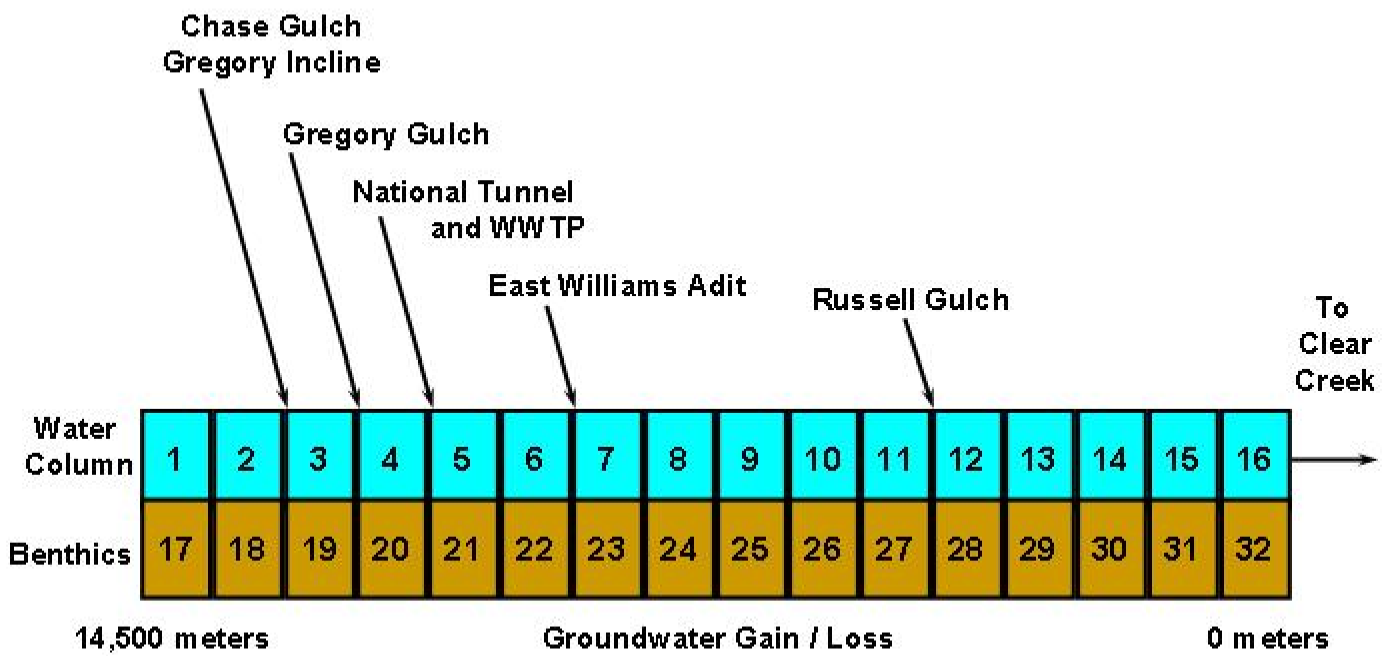
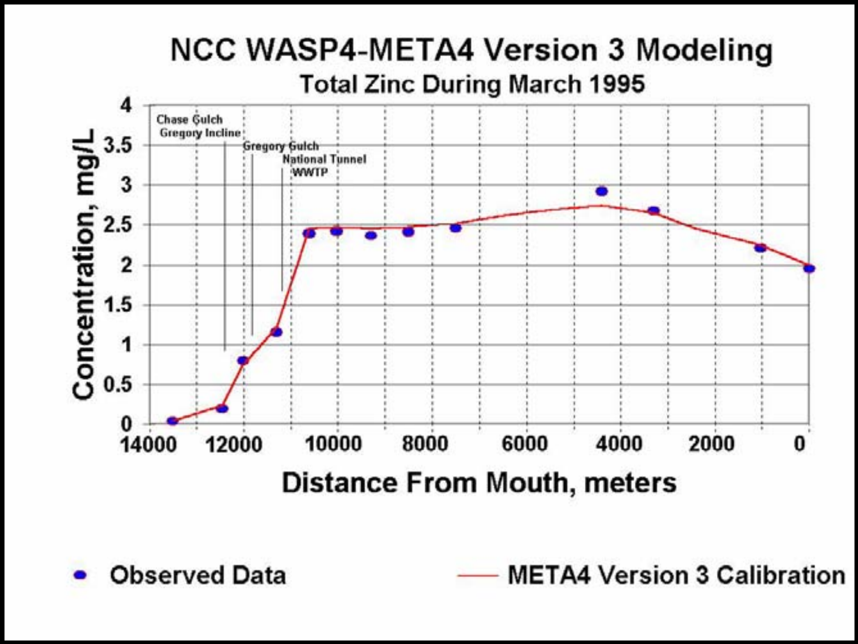
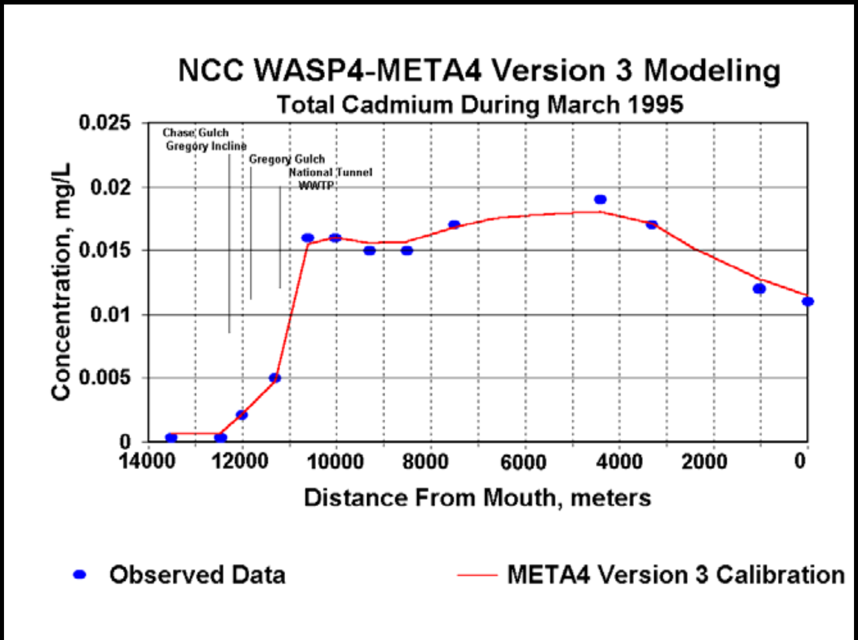


Figure 3. North Clear Creek Model Compartmentalization, 1995 Calibration, META4, V3

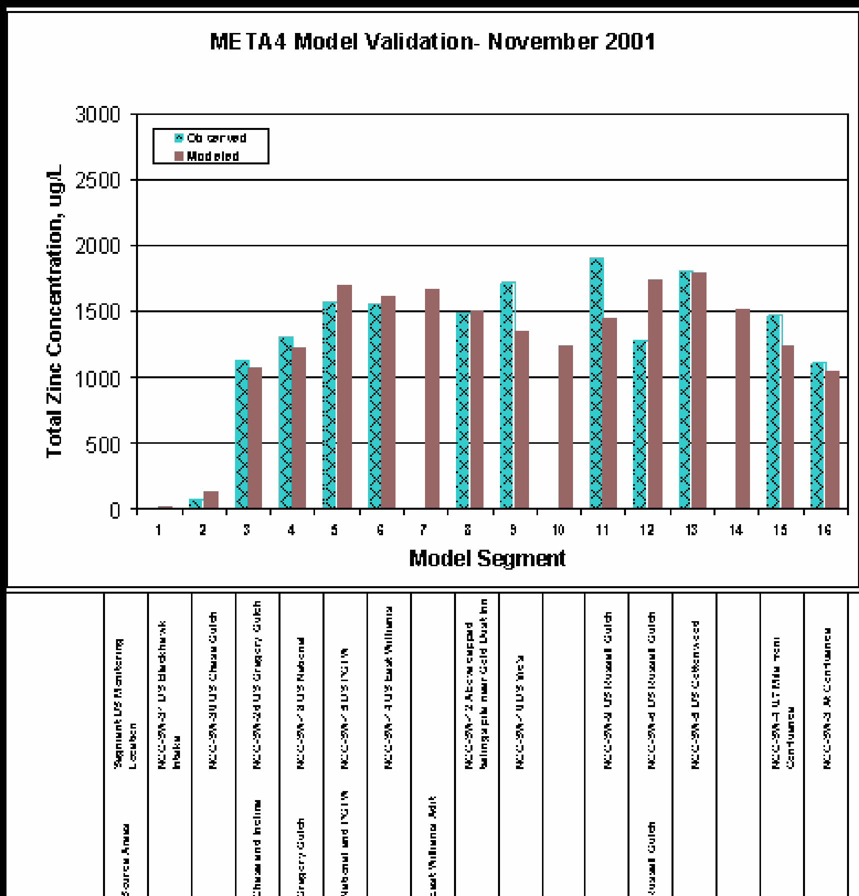
Model Calibration, 1995 Data, META4 - V3



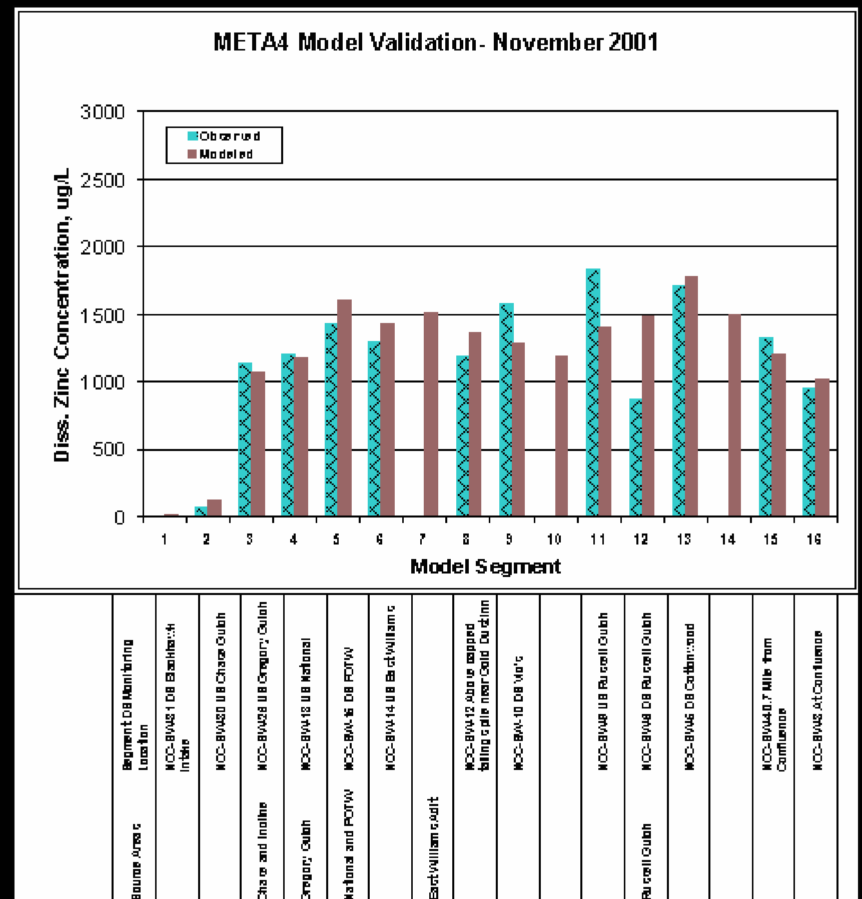


Total metal and dissolved metal concentrations in the benthic region agreed well with both total and porewater analyses. The relative percent errors for the surface water and benthic total and dissolved metals were generally within 5%. The RPDs for each paired data for observed and modeled metal concentration was generally well below 10%.

Model Verification, November 2001, META4 - V3
Total and Dissolved Zinc

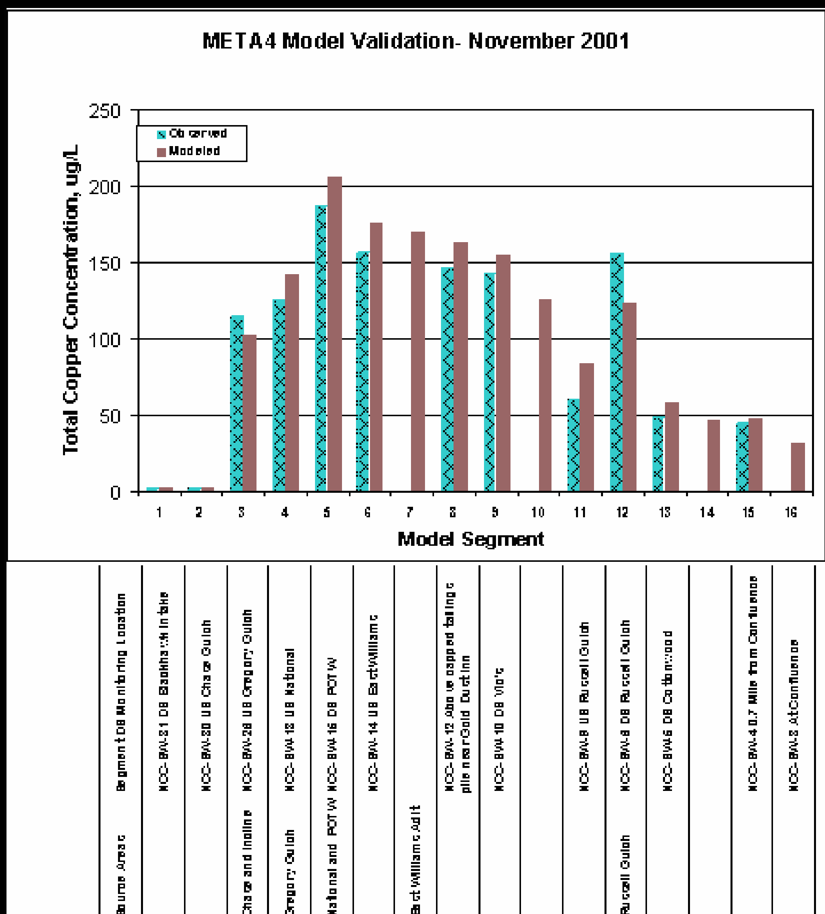


Relative percent error = 25.2% Segments 1-16
Relative percent error = 11.9% Segments 3-16

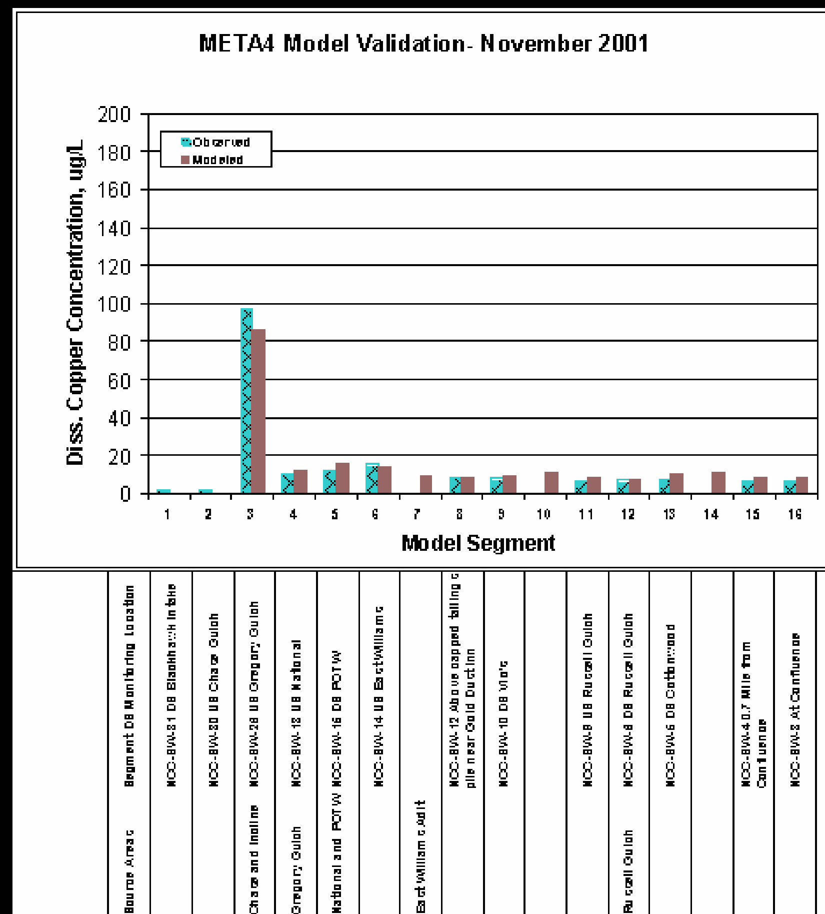


Relative percent error = 26.9% Segments 1-16
Relative percent error = 14.6% Segments 3-16

Model Verification, November 2001, META4 - V3
Total and Dissolved Copper



Relative percent error = 12.5% Segments 1-16
Relative percent error = 14.2% Segments 3-16



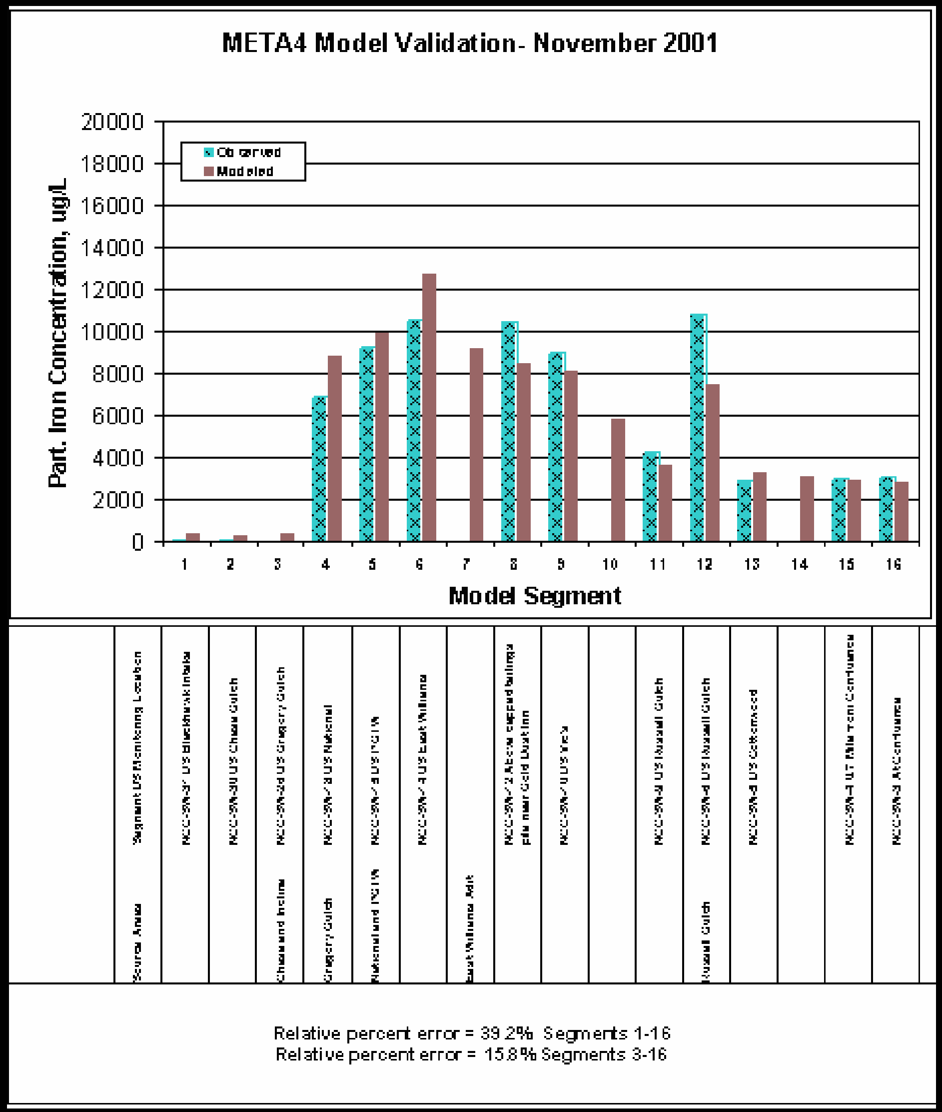
Relative percent error = 37.2% Segments 1-16
Relative percent error = 17.3% Segments 3-16

Model Verification, November 2001, META4 - V3

Particulate Iron produced from Fe(II) → Fe(III) oxidation and subsequent iron oxide precipitation

Dissolved iron peaks just below Gregory Gulch at NCC-19 (26.7 mg/L) and decreases to 13.1 mg/L at NCC-16 (above the POTW and below National Tunnel).

A further decrease to in dissolved iron to 1.26 mg/L was observed upstream of the east Williams Adit (NCC-14). The observed decrease illustrates the oxidation of ferrous iron to ferric iron and subsequent chemical precipitation and corresponding effect on dissolved copper.



Modeling Activities for 2002-2003

A. Verification of Previous Modeling Effort (1995 data, 6-variables).

B. Modification of the North Clear Creek Model Framework, including chemical reactions needed for 15-variable model, adjustment of compartment locations, some loads and physical characteristics.

C. Model Re-Calibration and Verification, calibration and verification of low flow 15-variable model to November 2001 and May 2002 data, respectively. High Flow analysis is not presented.

D. Analysis of Scenarios for Water Quality Improvement:

Transformation and Speciation Reactions - Copper

Model Species:

Zn^{+2} Cd^{+2} Cu^{+2} Pb^{+2} Fe^{+2} Fe^{+3} Fe-Oxide

SO_4^{-2} Ca^{+2} Mg^{+2} $CO3^{-2}$ H^{+} Al^{+3} Mn Al-Oxide

Copper Speciation Reactions:

Cu^{+2} $CuSO_{4(aq)}$ $CuOH^{+}$ $Cu(OH)_2^0$

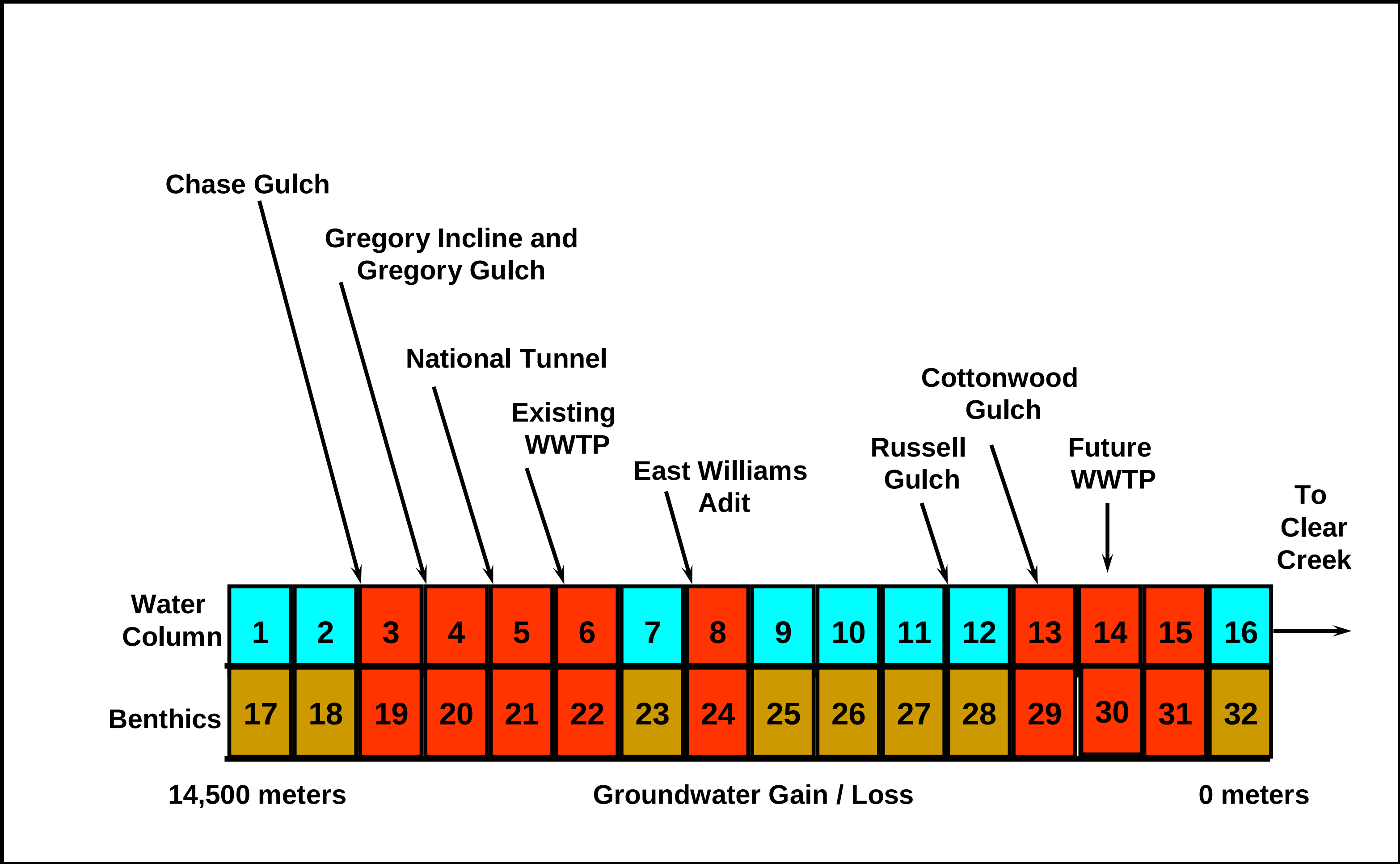
$CuHCO_3^{+}$ $CuCO_{3(aq)}$ $Cu(CO3)_2^{-2}$

Sorbed: Cu-FeOx(Strong) Cu-FeOx(weak)

Major Ion Reactions: Ca^{+2} Mg^{+2} $CO3^{-2}$ SO_4^{-2}

Precipitates: Determined from MINTEQA2, MINEQL+, data

Model Compartmentalization



The red compartments represent those that were changed during the 2002 calibration of the model from the previous model applications.

Modeling Activities for 2002-2003

A. Verification of Previous Modeling Effort (1995 data, 6-variables).

B. Modification of the North Clear Creek Model Framework, including chemical reactions needed for 15-variable model, adjustment of compartment locations, some loads and physical characteristics.

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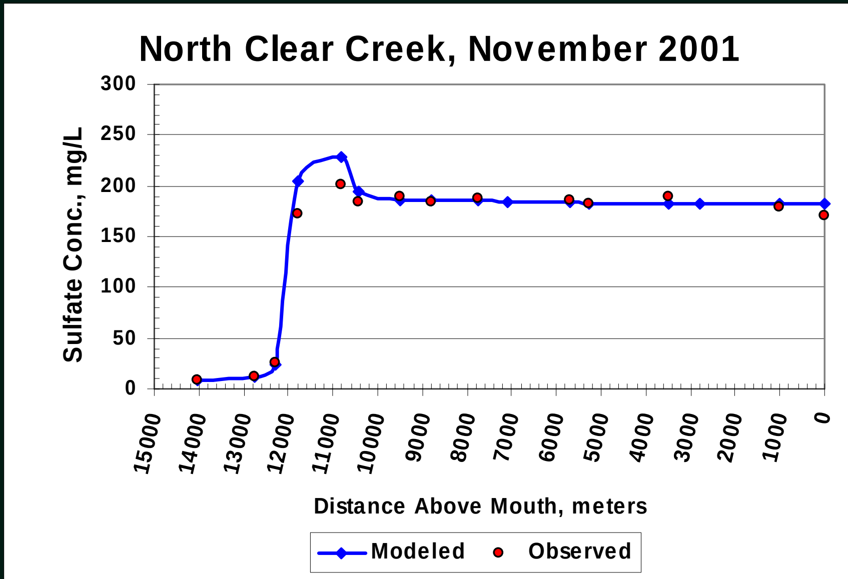
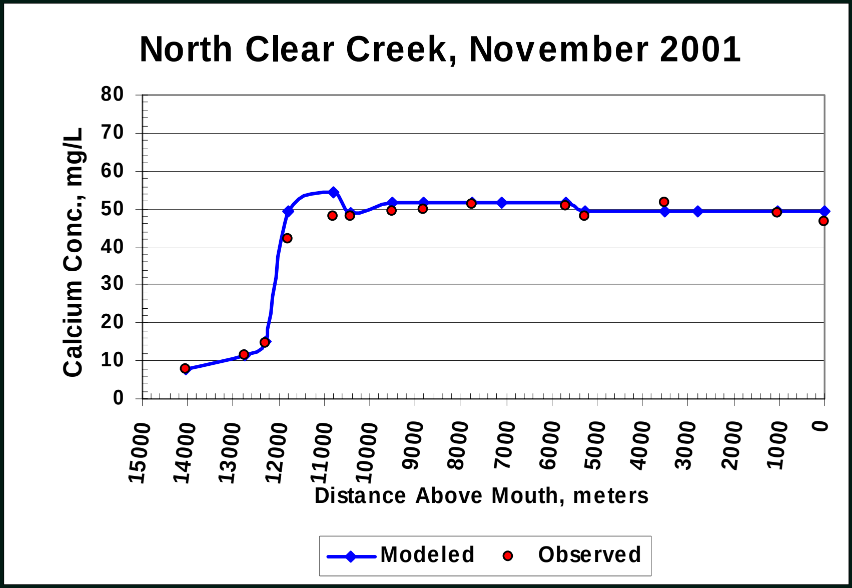
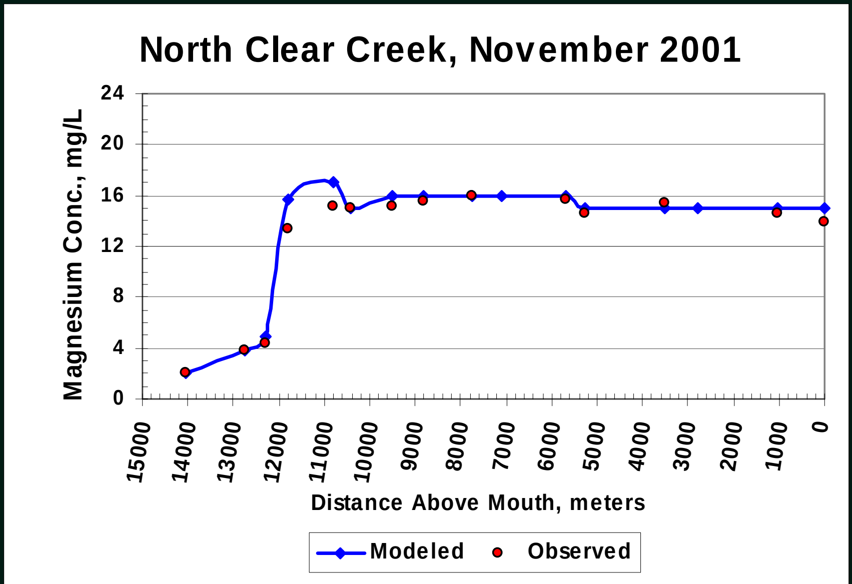
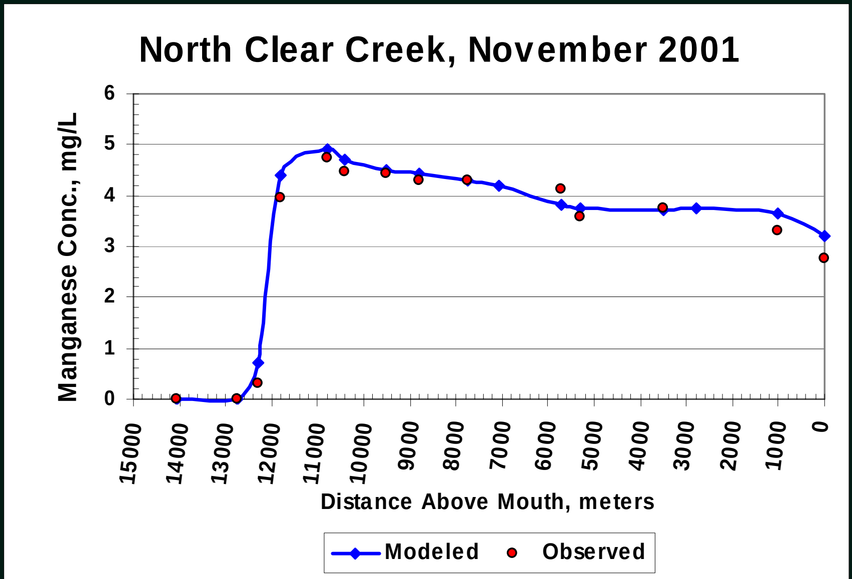
D. Analysis of Scenarios for Water Quality Improvement:

Major Ion Calibration – November 2001





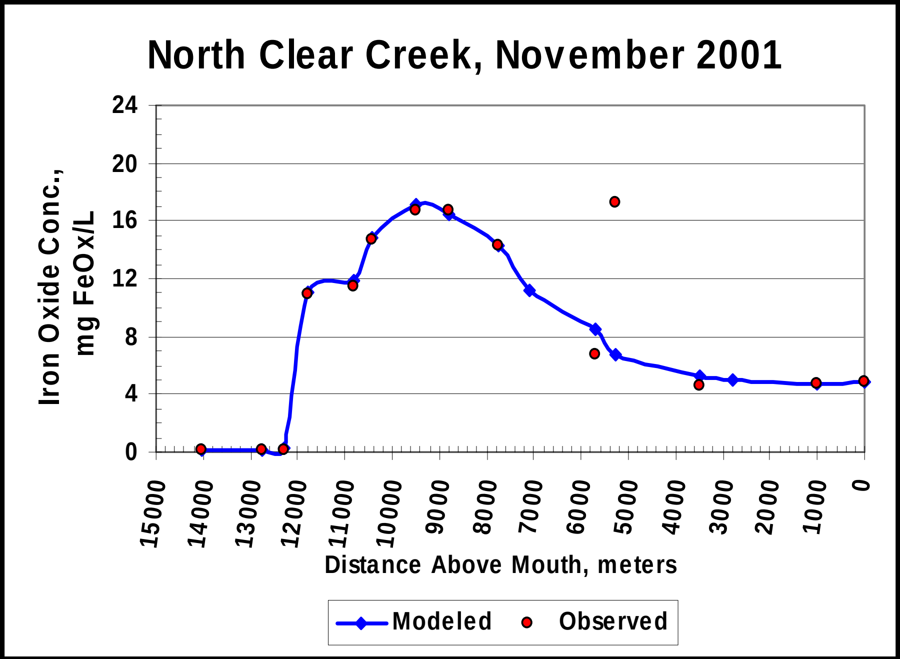


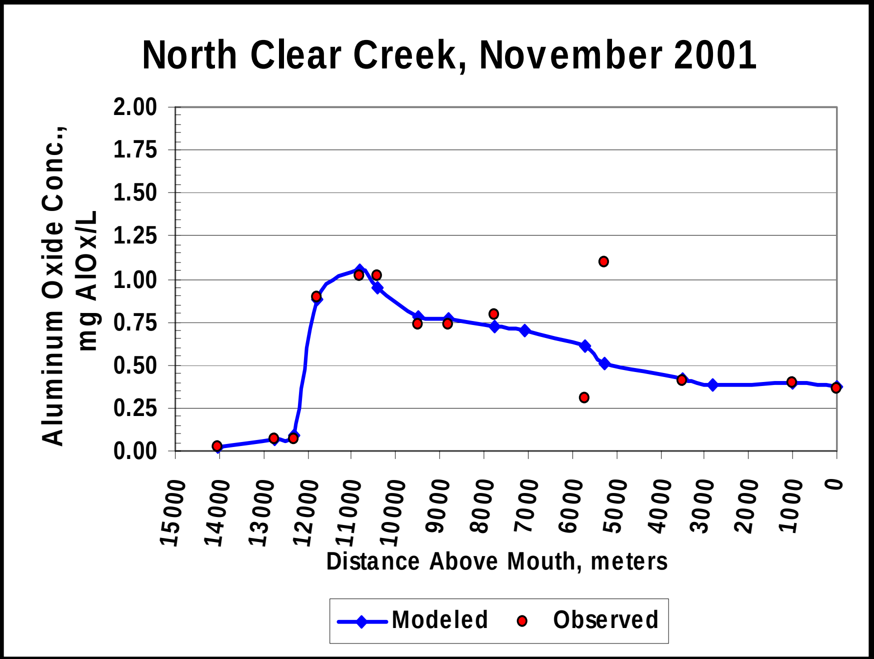


Precipitated Fe and Al Calibration – November 2001

Particulate Iron produced from kinetically driven Fe(II) → Fe(III) oxidation reaction and the subsequent iron oxide precipitation

Aluminum controlled by aluminum hydroxide precipitation

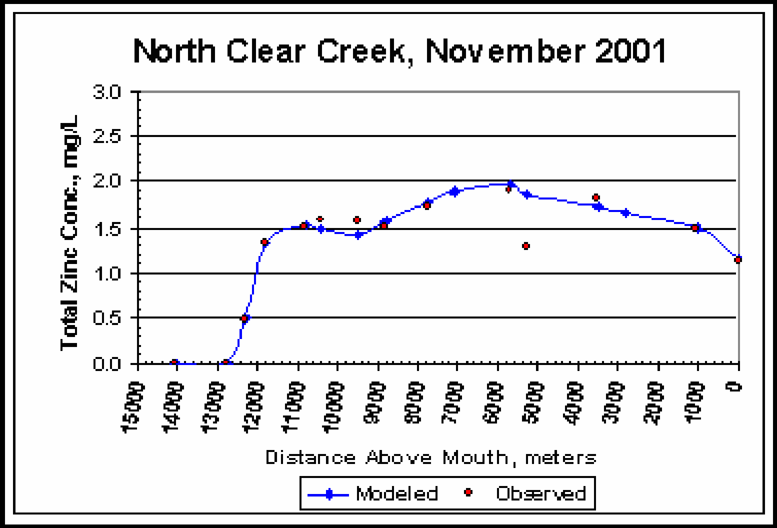


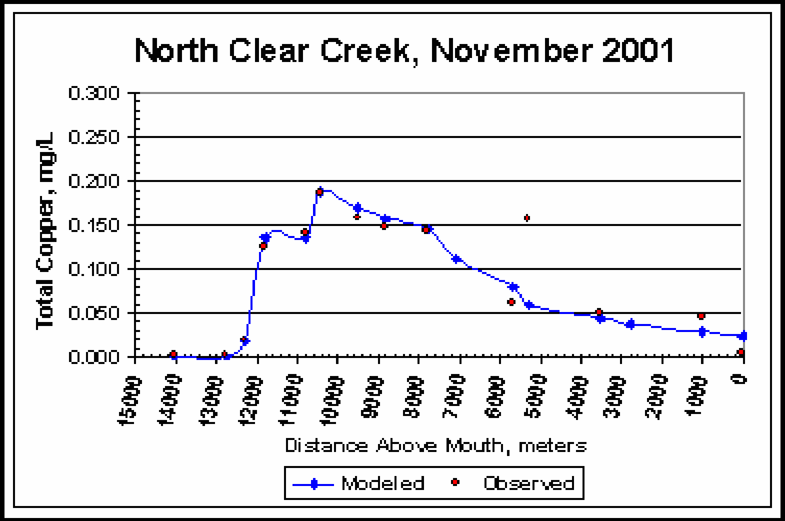


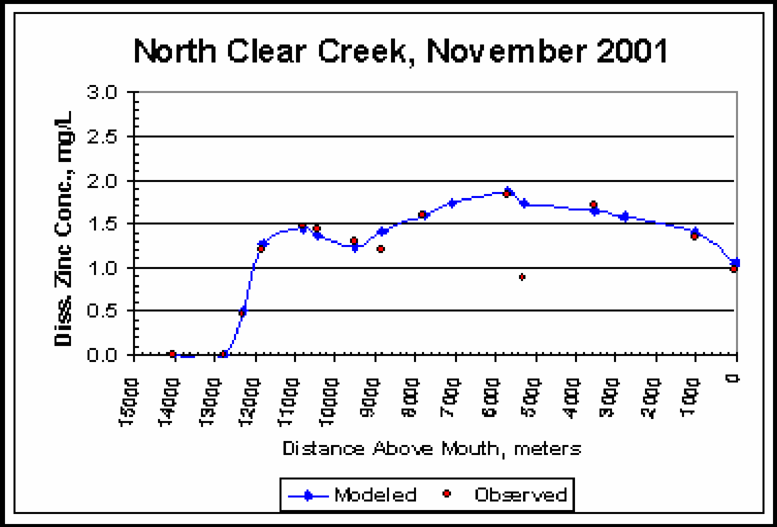
INPUT FILE REACTION DATA

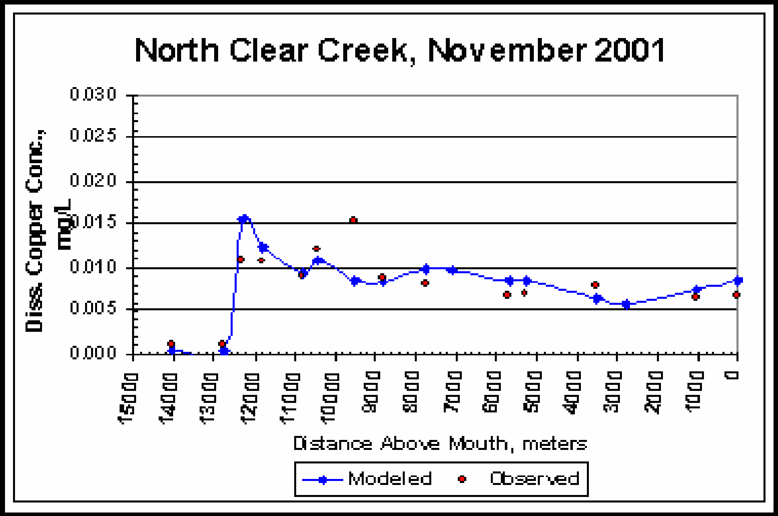
OXIDATION	1				
IRON	7				
FE(II)	51	1.3	FE(III)	71	4.1
RATE,DAY-1	91	8.639E-11	Q10	111	1.0
PH-EFFECT	131	1	DEPEND	151	25
CONSTANT	171	-1.75			

Zinc and Copper Calibration – November 2001









November 2001 Calibration Statistics

Low-Flow Modeling – November 2001
Calibration Statistics

PARAMETER	RPD Relative % Difference	Maximum Observed Value, mg/L	Error Range mg/L	Project Objectives
Sulfate	5.44	201	-6.3 to 32.9	
Calcium	4.88	51.5	-2.3 to 7.6	
Magnesium	5.58	16	-0.4 to 2.3	
Manganese	12.07	4.56	-0.3 to 0.47	
FeOx	8.46	10.86	-0.28 to 1.70	
AlOx	11.37	0.58	-0.07 to 0.3	
pH	NA	NA	-0.20 to 0.02	+/- 1.0 unit
Zinc, Total	4.04	1.9	-0.14 to 0.09	+/- 15% or 0.1mg/L
Zinc, Dissolved	5.54	1.83	-0.07 to 0.23	+/- 15% or 0.1mg/L
Copper, Total	11.37	0.187	-0.017 to 0.021	+/- 15% or 0.1mg/L
Copper, Dissolved	20.98	0.0154	-0.007 to 0.005	+/- 15% or 0.1mg/L
Cadmium, Total	21.14	0.00626	-0.003 to 0.0003	
Cadmium, Dissolved	23.42	0.00546	-0.0031 to 0.0001	
Lead, Total	NA	0.0102	-0.0354 to 0.0056	
Lead, Dissolved	NA	0.00056	-0.0003 to 0.0004	

Following the detailed specification of system geometry, boundary conditions and initial conditions, the model was calibrated for both high-flow (June 1997) and low-flow (November, 2001) conditions. Data collected during May 2002 were used for model verification. These data provided the recent and complete field monitoring data that would be acceptable for modeling purposes. The initial calibration activity, following the balancing of flows and travel time, included the simulation of conservative substances (sulfate, calcium, magnesium) followed by the calibration of total recoverable iron, total recoverable aluminum and pH. After solids and pH were calibrated, subsequent steps included the combined calibration of reactive chemicals (zinc, copper, cadmium, lead, manganese) in both the water column and benthic regions. Chemical inputs were obtained by mass balance analysis and MINTEQA2 simulations from available monitoring data for the flow periods modeled. The results of the calibration indicated a relative percent error between observed and calculated concentrations in the stream of generally less than 15% except when the concentrations of a given variable were very low (below 10 ug/L).

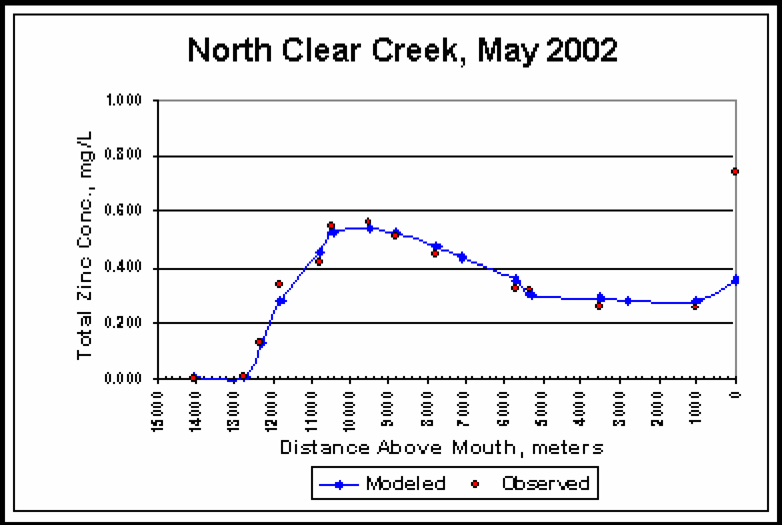
Model Verification May 2002 Data

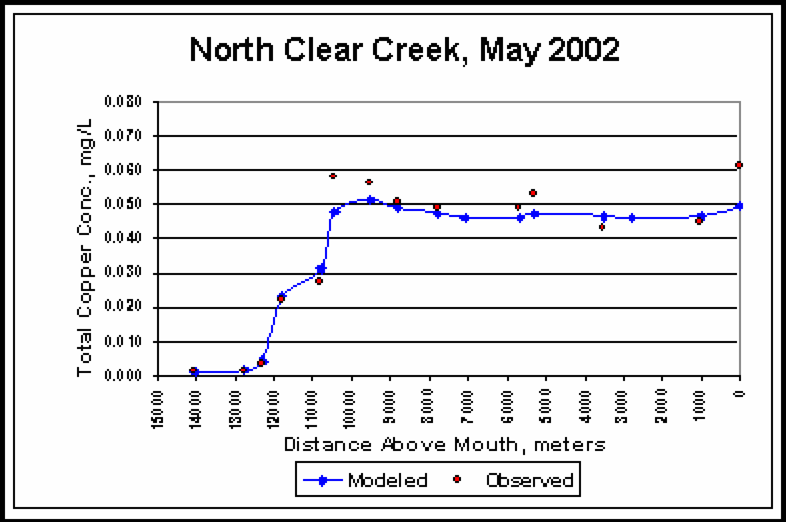
The model was verified using data collected during May 2002. While the May period often represents a high flow time, the flow rate during May 2002 was 8.5 cfs and not reflective of a high flow period. It was judged that these data would be acceptable for model verification This was confirmed during verification analysis; results for two of the target metals, zinc and copper (Figures 27 to 30) indicated that the relative percent errors for the model were as follows:

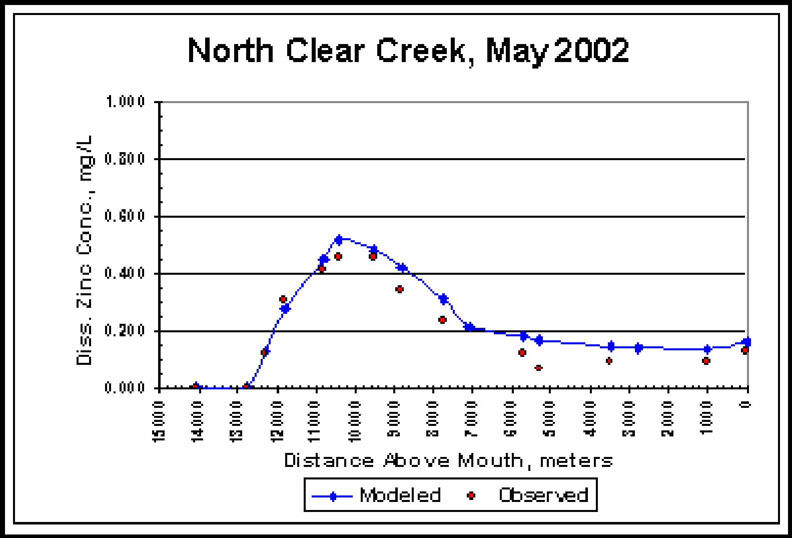
Zn, total	12.6%
Zn, dissolved	27.7%
Cu, total	9.7 %
Cu, dissolved	10.63%

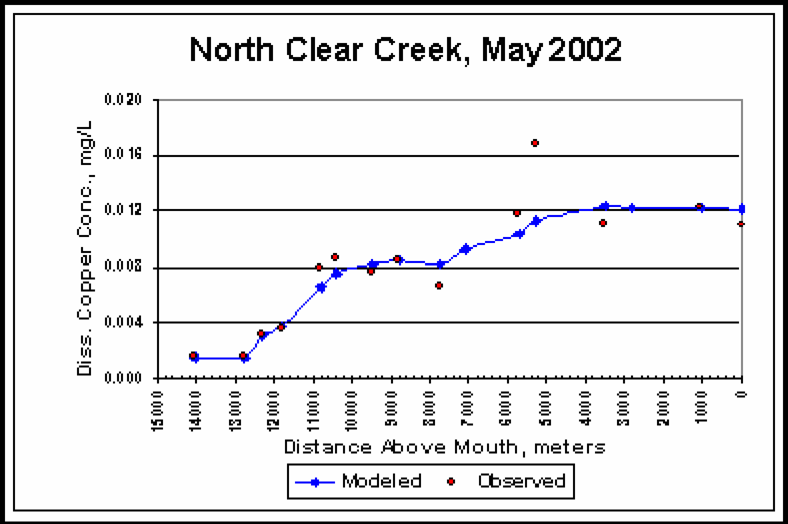
Results of the model verification indicate that the low flow model could be used within the flow events represented by both November 2001 and May 2002, or up to about 10 cfs with acceptable results.

May 2002 Verification – Illustrated with Zinc and Copper









Modeling Activities for 2002-2003

A. Verification of Previous Modeling Effort (1995 data, 6-variables)

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C. Model Re-Calibration and Verification, calibration and verification of low flow 15-variable model to November 2001 and May 2002 data, respectively

D. Analysis of Scenarios for Water Quality Improvement:

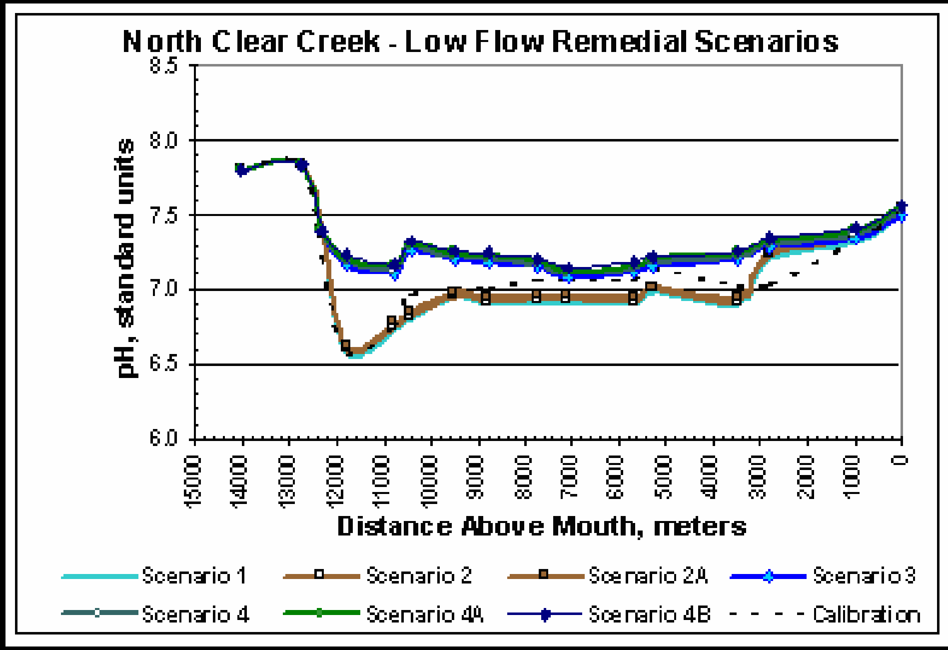
Analysis of Scenarios for Water Quality Improvement:

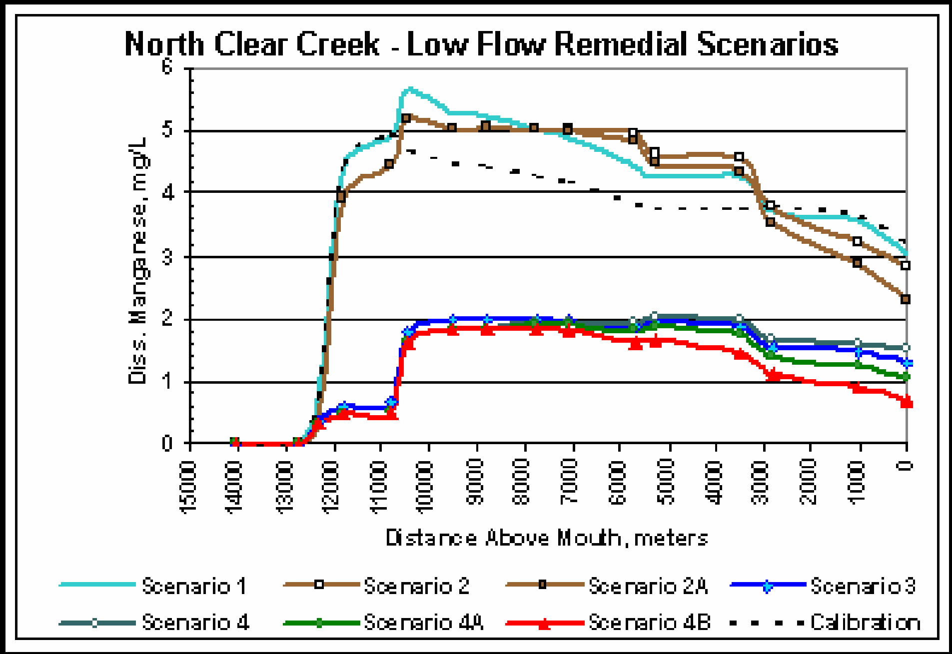
Scenario	Description
1	Relocation of WWTP (POTW) downstream
2	Sediment remediation at 33% reduction in upper Gregory Gulch and Russell Gulch
2A	Sediment remediation at 67% reduction in upper Gregory Gulch and Russell Gulch
3	Point source treatment, including Gregory Incline and National Tunnel
4	Scenario 2 and 3 combined
4A	Scenario 2A and 3 combined
4B	Scenario 3 and sediment remediation at 80% reduction in upper Gregory Gulch and Russell Gulch

[1]

Remediation Scenarios

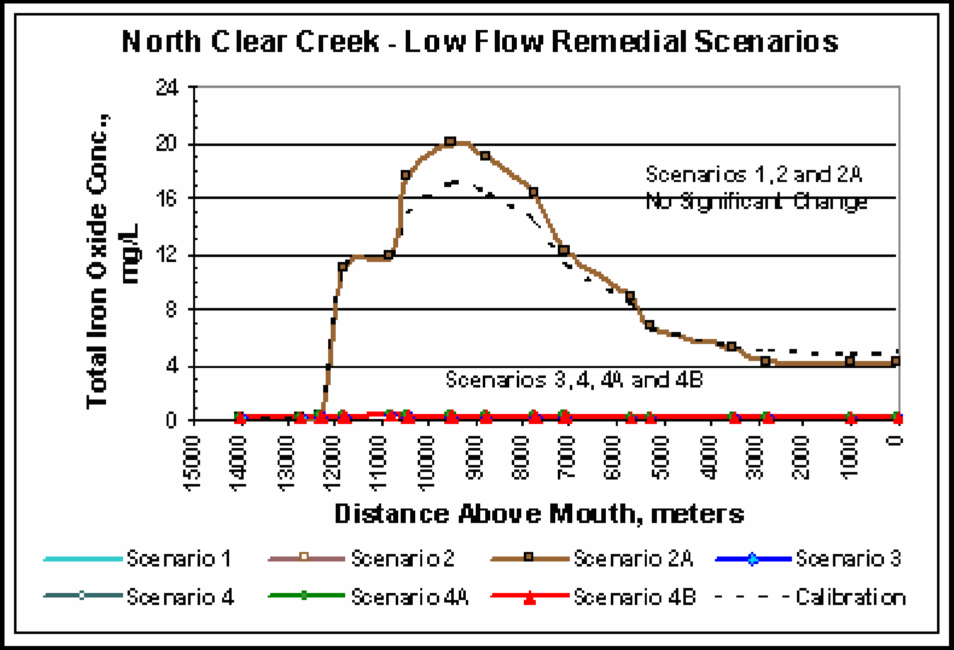
pH and Manganese

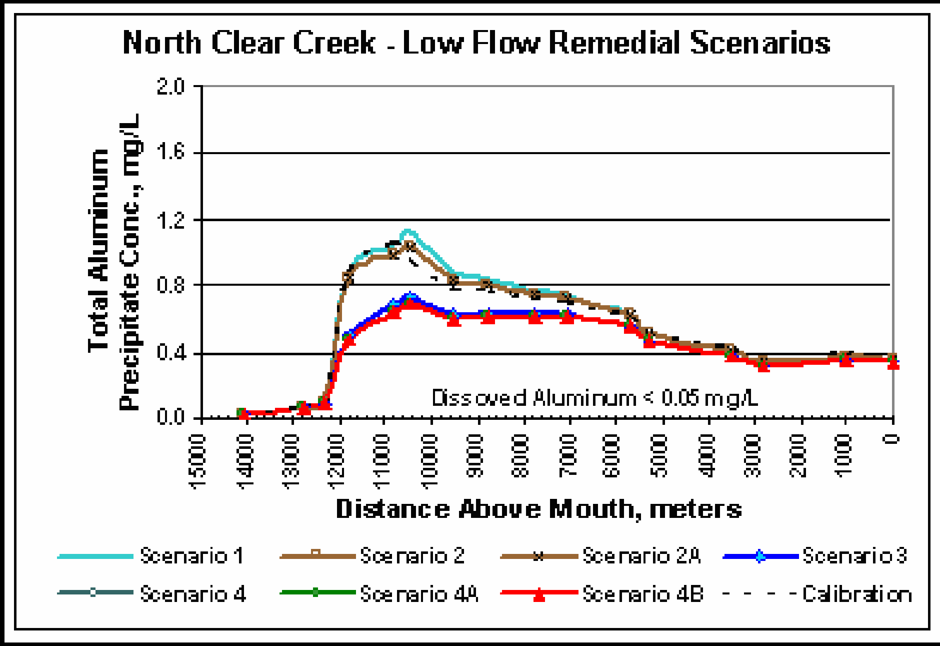




Remediation Scenarios

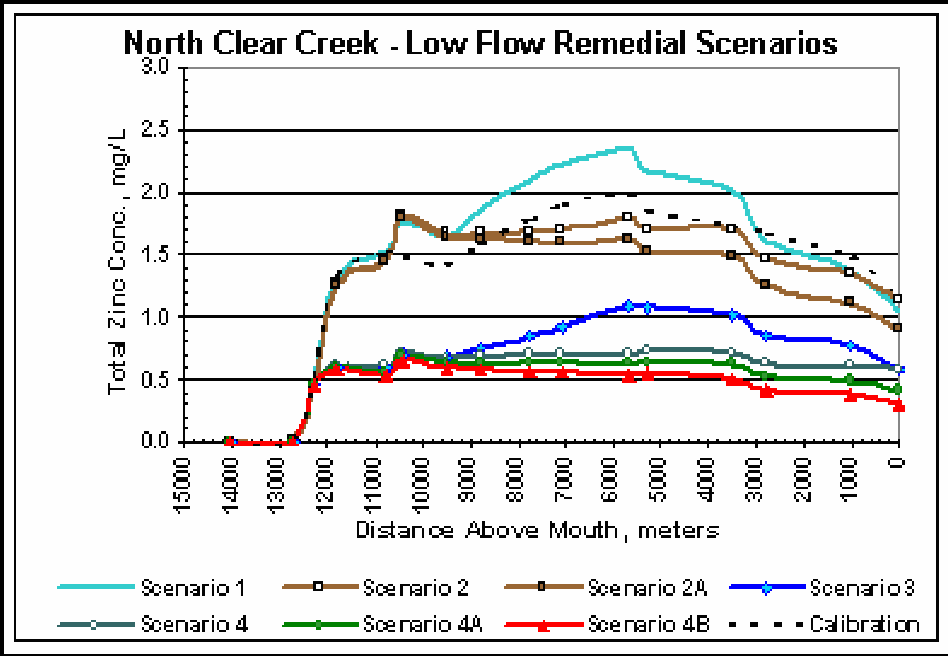
Iron and Aluminum

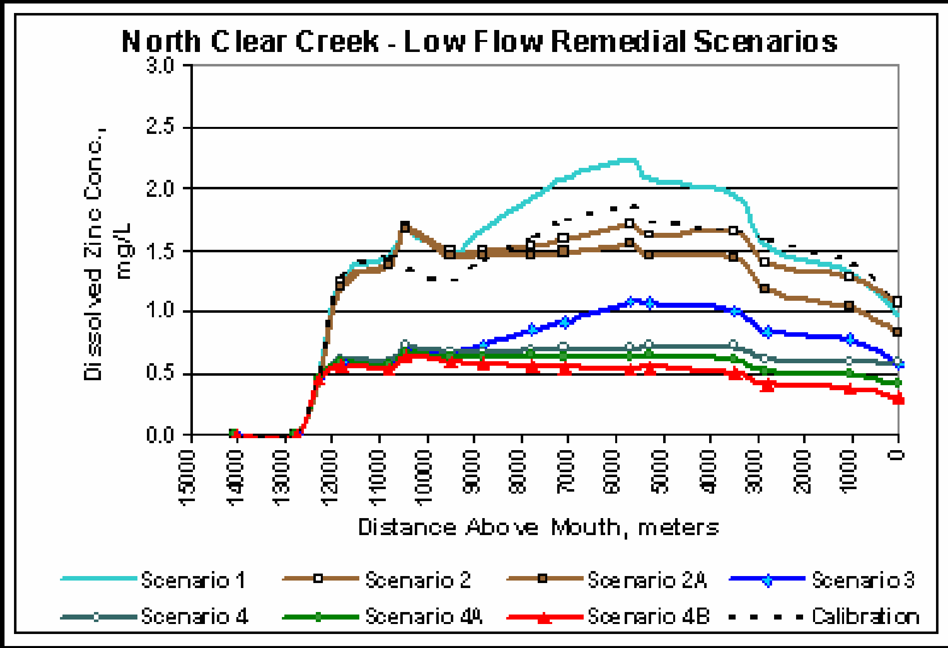




Remediation Scenarios

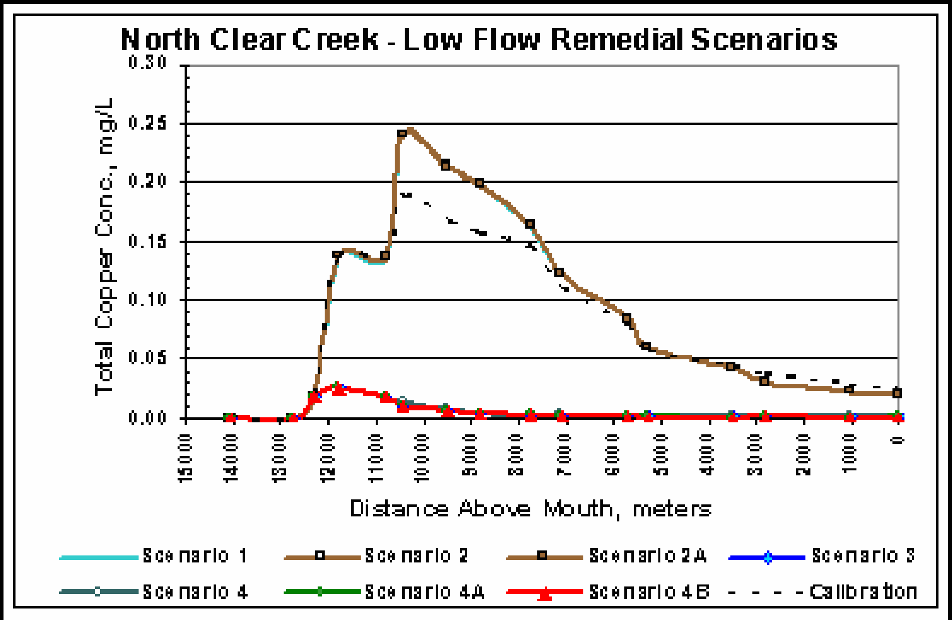
Total and Dissolved Zinc

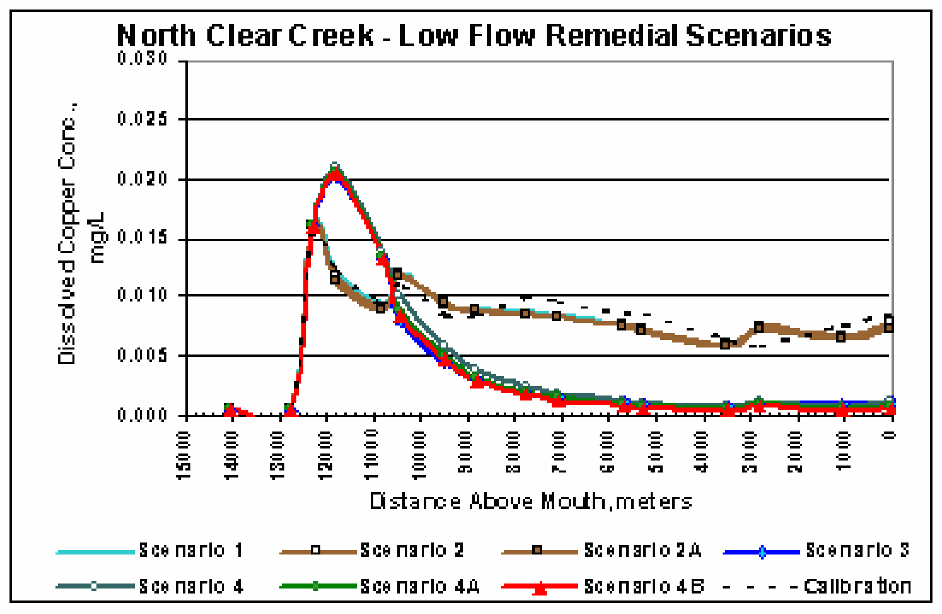




Remediation Scenarios

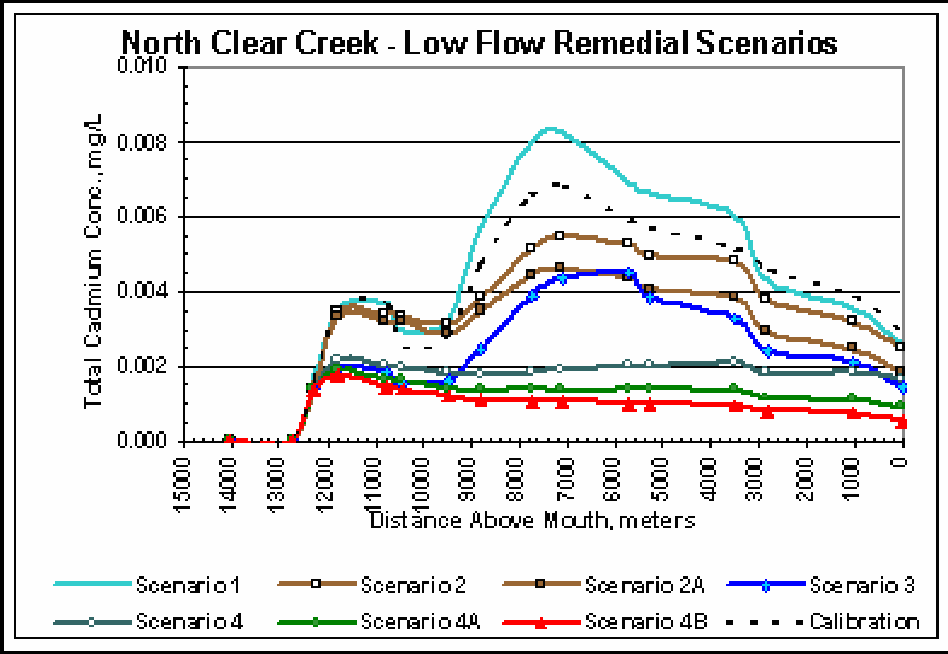
Total & Dissolved Copper

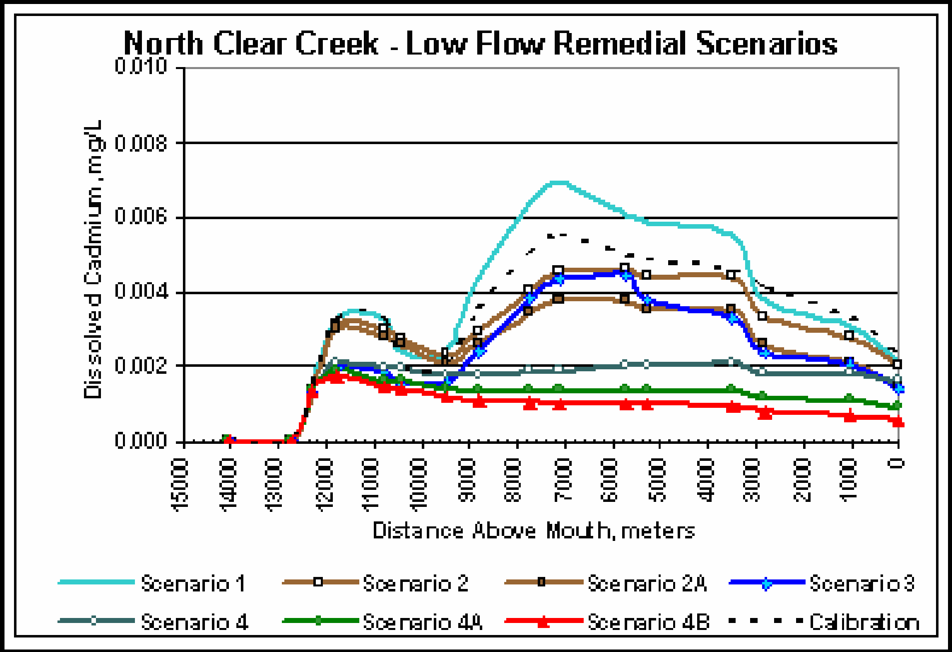




Remediation Scenarios

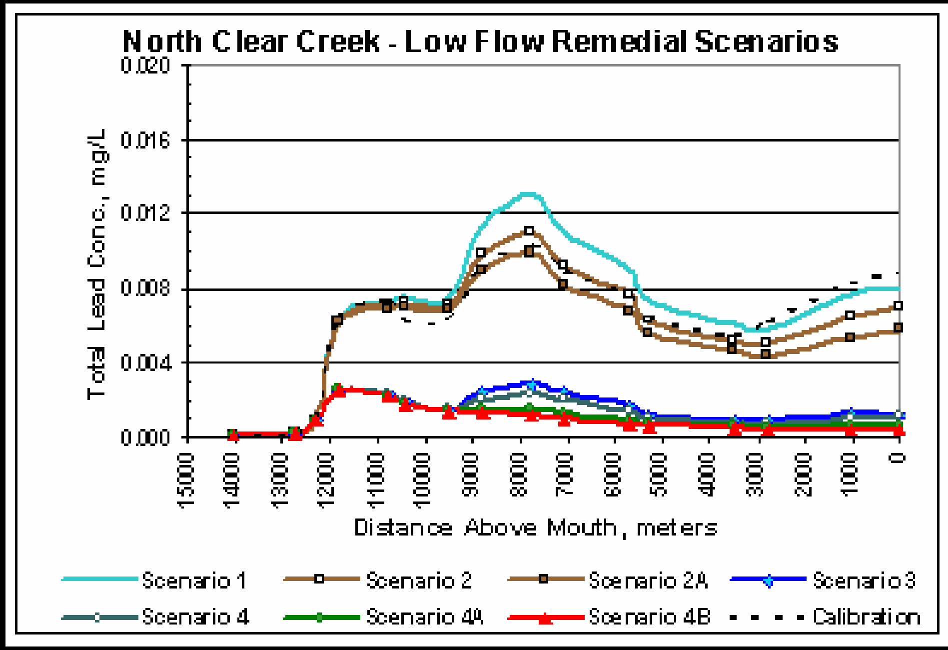
Total & Dissolved Cadmium

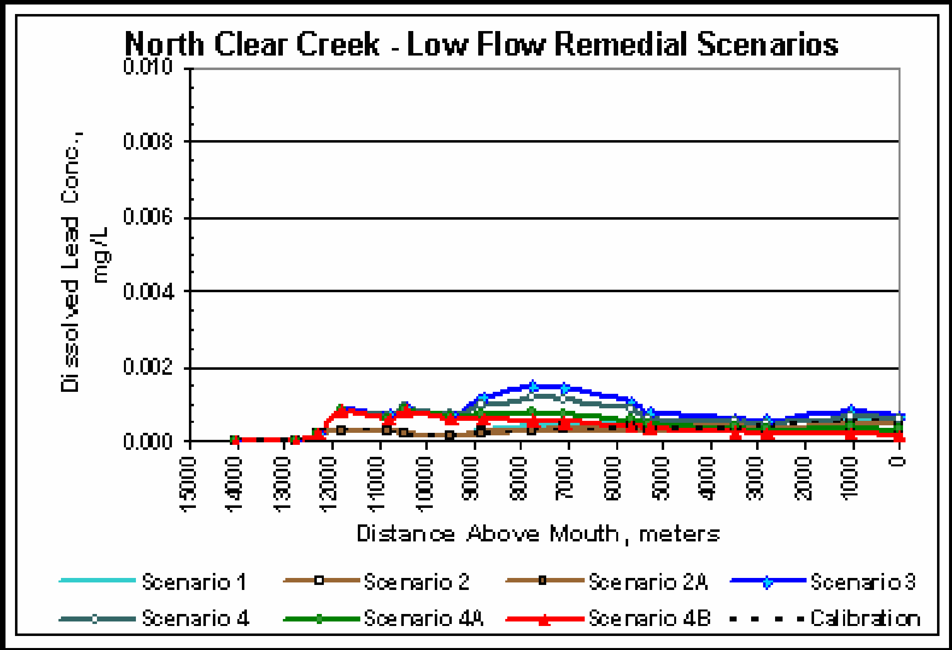




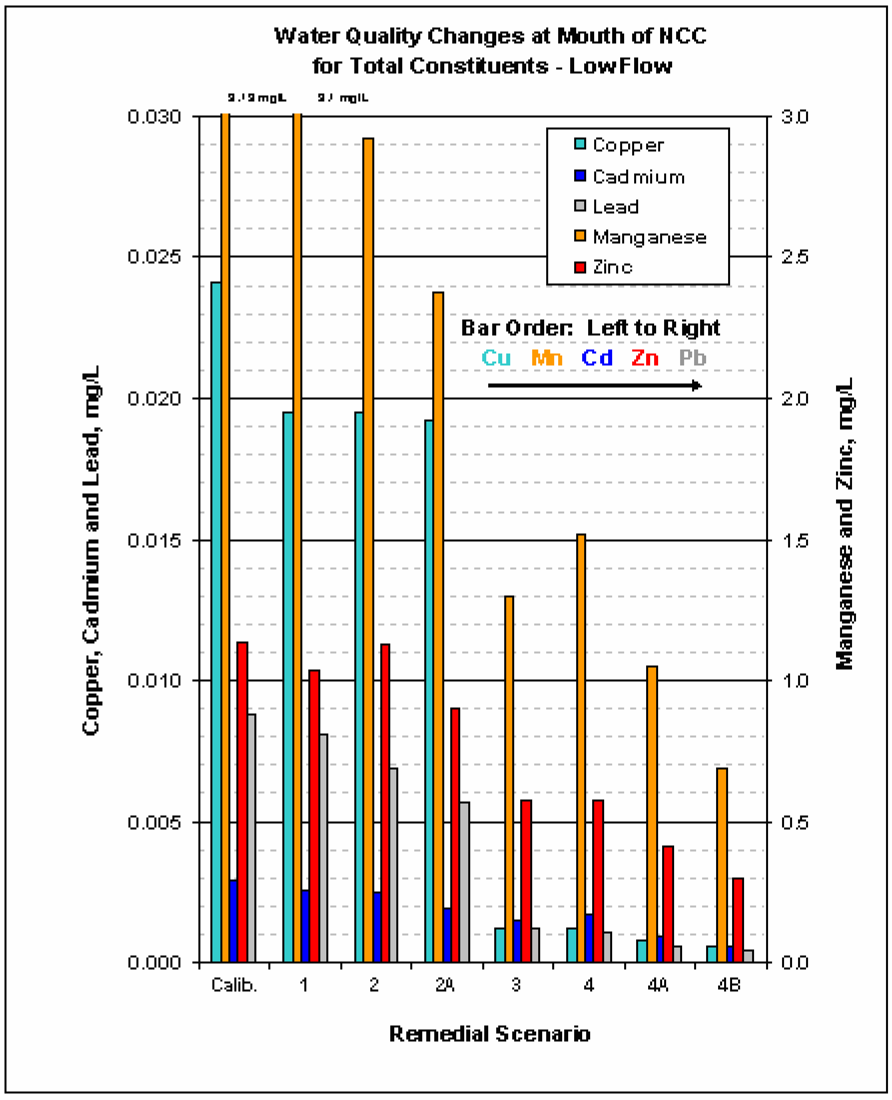
Remediation Scenarios

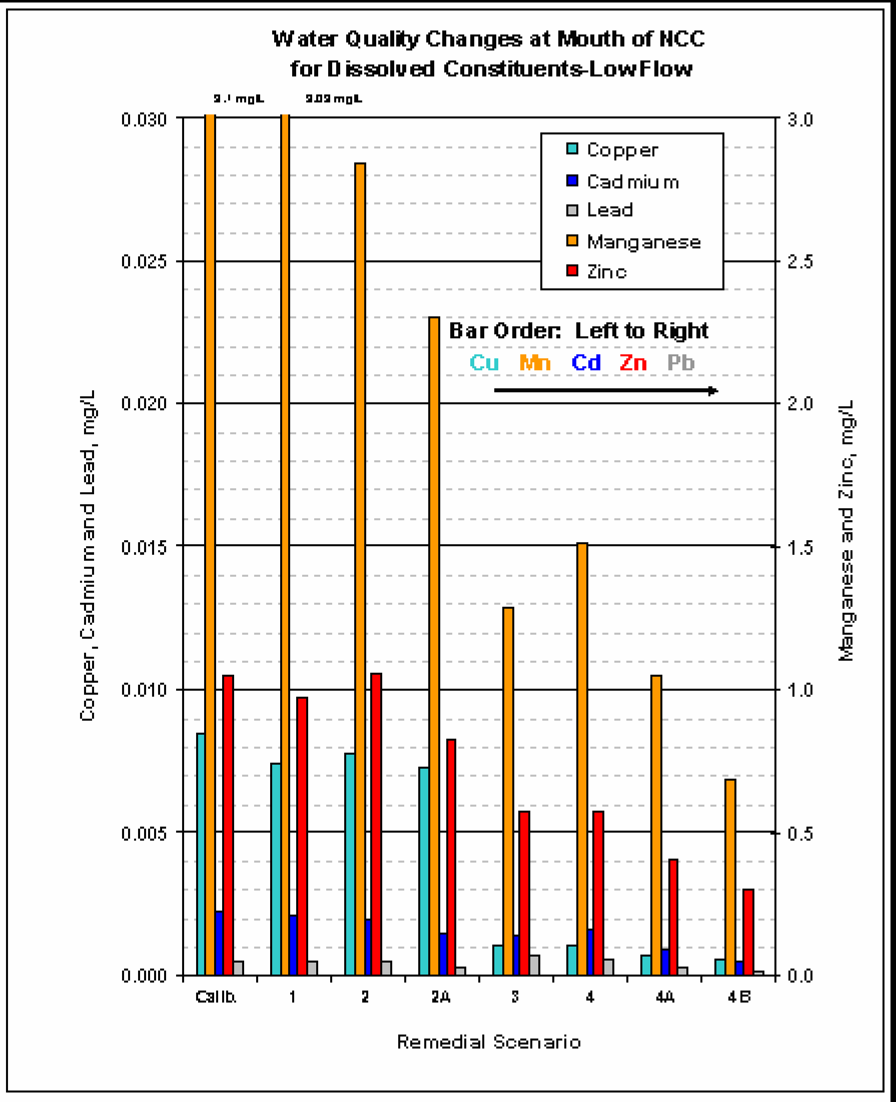
Total & Dissolved Lead





Comparative Summary of Remedial Scenarios





Conclusions

The most challenging parameter with respect to restoration of water quality within the basin and the attainment of water quality standards and a potential Brown trout fishery was zinc during the low-flow periods and copper during the high flow periods. Dissolved lead and cadmium were judged to be within brown trout fishery limits.

As evident from a review of the modeling results, additional combined remediation above individual point source control or sediment remediation (Scenarios 1, 2, 2A or 3) is needed to address high concentrations of dissolved manganese, zinc and cadmium still observed at the mouth under. Combined Remediation Scenarios 4, 4A and 4B, while showing limited additional improvement in water quality for copper and lead, result in additional improvement in manganese, zinc and cadmium concentrations approaching 1 mg/L, 0.3 mg/L and 0.0005 mg/L, respectively.

To reach these targets (Mn, Zn and Cd concentrations approaching 1 mg/L, 0.3 mg/L and 0.0005 mg/L, respectively) requires a thoughtful approach to reducing the erosion of contaminated sediments into the stream from Gregory Gulch and Russell Gulch along with significant point source removal efficiency.

Conclusions

The projected effectiveness of the remedial actions was sensitive to metal loadings but also to system pH, iron concentration and residual sediment metal concentrations.

Modeling underscored the need for an integrated approach to managing metal loading controls from multiple sources within a river basin

To determine proper control of both natural and mining-related loadings, as necessary for TMDL analyses, remedial action or restoration analyses, META4 can provide a defensible allocation of loadings with the mainstem

The author would like to acknowledge the support of EPA’s National Risk Management Research Lab in Cincinnati, Mr. Edward Bates and David Reisman, Project Managers and EPA Region VIII, Ms. Holly Fliniau and Mr. Ron Abel, Remedial Project Managers (Clear Creek /Central City Superfund Site) for providing the funding to develop and improve META4.