Chapter 8

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

Application to Copper and Zinc Problems in the Alamosa River, Colorado

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The Metal Exposure and Transformation Assessment (META4) Simulation Program is a generalized metals transport, speciation, and kinetics model developed for application to a variety of receiving waters. Algorithms for the simulation of crucial metal transformation processes, such as aqueous speciation, sorption/desorption, chemical precipitation/ dissolution, pH dynamics and kinetics were added to the basic structure of the Water Analysis Simulation Program (WASP, Version 4.32), resulting in the META4 model. The modeling of metal dynamics in the Alamosa River downstream of the Summitville Mine Site (CO) was performed to support the Use Attainability Analysis and ultimate goals for remedial actions. Following calibration, the model was used to hindcast metal concentrations for pre-mining conditions, prior to 1873, and conditions prior to

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heap-leach mining beginning in 1984 (pre-Galactic). Results demonstrate much improved water quality conditions in the Alamosa River during both eras. Analysis of data collected after significant metal load reductions at the Summitville mine site (1998) provided a verification of model framework and configuration for the original analysis.

Aquatic resource management strategies for toxic metals, including waste allocation, remedial action (restoration) or total maximum daily loading, are best evaluated by an estimation of the impacts of processes affecting metals concentrations in the water and sediments. These types of analyses are complicated by the fact that metal behavior is non-conservative in aquatic systems and that the transport, transformations, and attenuation depend upon the particular forms of metal present and chemical attributes of the environmental system. A chemical equilibrium simulation routine, based upon a solution approach similar to MINTEQ, was developed as a submodel to the generalized Water Analysis Simulation Program (WASP) to support these analyses. The META4 (Ver. 3.0) submodel addresses metal speciation and kinetics for the metal reactions and uses a solution approach similar to that of MINTEQA2 (Ver. 3.11) developed by, and distributed by EPA (*1*).

Physical and chemical processes that affect the transport of metals are taken into account in the model including advection, dispersion, erosion, sedimentation, and chemical reaction (speciation, adsorption, desorption, precipitation, and dissolution). Algorithms for the simulation of crucial metal transformation processes are thoroughly described in the User Manual (*2*). The modeling procedure is illustrated in Figure 1.

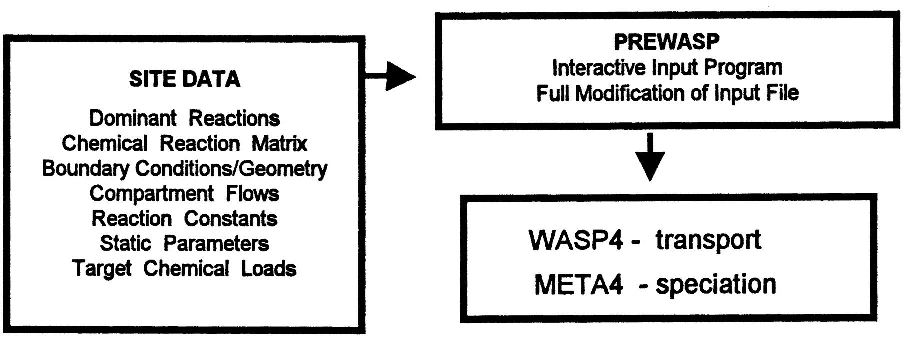

Figure 1. The procedure used for modeling with WASP4/META4.

Some of the advantages of WASP4/META4 are that it can represent 1, 2 or 3-dimensional environments (streams, rivers, reservoirs, multiple benthics), sequential deposition or scouring of benthic bed layers, transient storage, constant or variable pH, numerous point and non-point loads, and multiple metal and major ion reactions, including individual aqueous species. WASP4/META4 was used to model metal dynamics in the Alamosa River downstream of the Summitville Mine (*3*)

Site Background

The water quality of the Alamosa River has been impacted by naturally mineralized bedrock in the watershed and by mining activities in the basin that began in the late 19^{th} century and continued through most of the 20^{th} century. Gold was initially discovered at Summitville by early Spanish explorers and then developed by settlers in the San Luis Valley in the 1870s (*4*). Silver, copper and lead have also been produced at the site. The first amalgamation mill was erected in 1875 and, by 1883, the district was the largest gold producer in the state, with nine mills. More recent operations at the site include copper exploration in the late 1960s, gold and copper exploration in the late 1970s, and further gold prospecting in the early 1980s. In 1968, significant disturbances were evident at the base of the mountain (12 acres). Wightman Fork, the stream leaving the site, was an orange-red color downstream. By 1980, the additional disturbed area increased to 33 acres.

In 1984, Galactic Resources Limited (SCMCI) obtained a permit to operate a heap leach gold mining operation. Construction of the leaching pad and operation began in the summer of 1986. Twenty million tons of rock were removed from an open pit in the 3 years of operation. Development of the open pit resulted in the increase of copper concentrations emanating from the Reynold's Adit from approximately 25 mg/L to a high of 650 mg/L (*5*); inaccurate water-balance predictions and pump breakdowns caused direct release of cyanide and copper contaminated fluids; and placement of sulfide rich waste rock piles caused acid drainage and metals contamination in Wightman Fork. The disturbed area at the site increased to 633 acres. Numerous operating, environmental, and financial problems led to bankruptcy of the company in 1992. The USEPA initiated Emergency Response Actions in December, 1992 to control contaminant releases from the site.

Alamosa River Study Area

The study area for this report includes the Alamosa River and tributaries upstream of Terrace Reservoir. Major tributaries that have significant impacts on water quality in the Alamosa River include Wightman Fork, Iron Creek, Alum Creek and Bitter Creek. Wightman Fork contributed the greatest mass of copper and zinc to the river. For example, during 1993, copper and zinc loadings were, in general, 100X greater from Wightman Fork compared to other tributaries (*6*). Other tributaries generally provide dilution water that tend to improve overall water quality (Figure 2).

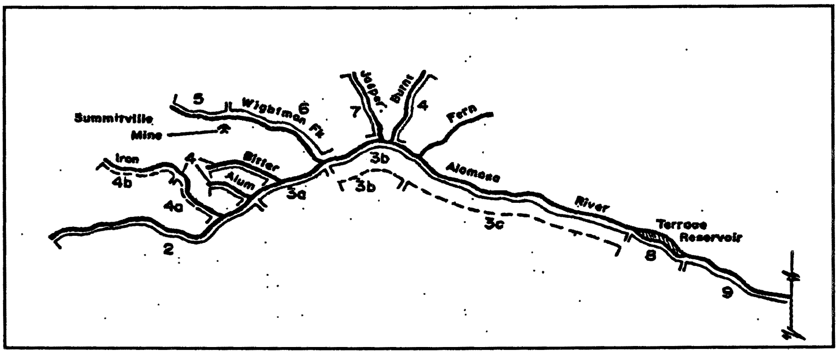

Figure 2. Study area for the Alamosa River modeling showing Colorado State River Segments (Source: 6).

The Use Attainability Assessment (UAA) as well as recent USEPA monitoring indicated that water quality standards in the basin were not being met due to a combination of the natural geologic conditions and metals contamination due to mining. The UAA also discussed historic aquatic life uses in the basin (*6*). Anecdotal evidence from local persons and a variety of other Forest Service, Division of Wildlife, and USEPA data are reported to indicate that the Alamosa River supported at least a limited fishery until 1990. While there is evidence of mining activity in the upper Alamosa River, it was determined to be a minimal influence of stream water quality.

Conceptual Model for Metals Dynamics in the Alamosa River

The Conceptual Model for contaminant source, transport, transformations, fate, and resource impacts indicates that the primary mechanisms responsible for metal transport in surface waters are advection and dispersion. Advection is typically the dominant process responsible for metal transport in dynamic surface waters such as streams. However, in the stream sediment layer, or benthos, where water velocities are much lower, dispersion may become a significant mechanism for chemical release and transport. Additional dilution and chemical input from adjacent tributaries and alluvial groundwater contribute to the observed concentrations of contaminants in the Alamosa River.

Analysis of existing data indicates that the Alamosa River upstream of Station 45.5 (above Wightman Fork) and Wightman Fork are the major contributors to metal degradation in Alamosa River below the confluence with Wightman Fork (Colorado State Segments 3b and 3c). Chemical sinks within the Alamosa River include coprecipitation and sorption losses to the bed region, alluvial system transfers, and settling of particulate metals.

Adsorption of dissolved species is the most significant attenuation process for copper; zinc adsorption is limited when pH is less than 6.5. In many surface waters affected by mining, including the Alamosa River, it is generally accepted that sorption of metals to iron oxyhydroxides is the dominant chemical process regulating the dissolved concentrations of metals in waters and sediments (*7*). Chemical precipitation of Fe and Al is very rapid under pH conditions greater than 4 while pH's greater than 6.0 accentuate the sorption properties of suspended and bed sediments for copper. While adsorptive processes are very effective in removing metals from the water column, the equilibration of the sediment porewater with the contaminated sediments will generally result in the contaminated porewater. Stream flow changes that result in an increase in sediment resuspension can lead to significant releases of dissolved metals to the overlying water column during such transient events.

Modeling Alamosa River Water Quality

The modeling of the Alamosa River basin included the area from Wightman Fork downstream to Terrace Reservoir in southern Colorado (Figure 2). The objective of the modeling was to evaluate the likely pre-mining (1873) and pre-Galactic (1984) metal concentrations in the Alamosa River and potentially achievable environmental conditions. A pre-mining and pre-Galactic analysis of both the Alamosa River upstream of Wightman Fork (AR45.5) and Wightman Fork (WF0.0) was needed to serve as point sources (upper boundary condition) to the model segments downstream of Wightman Fork. Evaluation of current and historical water quality data was performed to provide an estimate of seasonal conditions in Wightman Fork prior to SCMCI's operations and prior to mining (*3*), and these estimates were then used as input to the META4 model. The model input at AR45.4 (upstream boundary) for the calibration was based on a September, 1995 synoptic sampling conducted by the USGS while the model inputs developed for pre-SCMCI and pre-mining for copper, zinc, iron, manganese and aluminum are shown in Tables 1 and 2.

Table 1. Pre-Mining concentrations in the Alamosa River below the mouth of Wightman Fork (AR 45.4)

	Concentrations (μg/L)							
	Winter		Spring		Summer		Fall	
	Mean	85th-ile	Mean	85th-ile	Mean	85th-ile	Mean	85th-ile
Cu (Diss)	36.9	35.1	11.7	30.5	7.58	19.1	13.7	22.1
Zn (Diss)	105	91.8	22.4	60.0	26.5	41.2	44.8	82.2
Fe (Total)	6,680	7,790	4,410	10,900	2,010	5,100	5,710	8,940
Mn (Diss)	565	557	126	378	124	207	282	544
Al (Diss)	3,550	4,370	422	2,380	112	215	1,440	2,340

Table 2. Pre-Galactic concentrations in the Alamosa River below the mouth of Wightman Fork (AR 45.4)

	Concentrations (μg/L)							
	Winter		Spring		Summer		Fall	
	Mean	85th-ile	Mean	85th-ile	Mean	85th-ile	Mean	85th-ile
Cu (Diss)	211	233	88.6	179	141	154	136	158
Zn (Diss)	127	137	57.2	94.0	82.6	131	147	268
Fe (Total)	6,920	8,290	4,590	11,100	2,540	6,000	6,210	9,780
Mn (Diss)	580	647	189	503	224	405	475	929
Al (Diss)	3,460	4,420	456	2,440	197	334	1,540	2,500

Modeling Framework for the Alamosa River

Based on the Conceptual Model, the relevant, interacting physical-chemical processes that affect overall water quality were included in the modeling framework. The water quality conditions used for the inputs to the model represented the worst case seasonal water quality observed in the Alamosa River above Wightman Fork and as estimated for Wightman Fork at the mouth. The fall and winter periods represent the greatest degradation of water quality for copper and zinc in the Alamosa River downstream of Summitville. Of these two seasons, the best monitoring data for modeling was available for only the fall period; consequently, the model simulations were based on fall flow conditions.

Modeling Approach

The META4 model simulates transport of flows and loads through compartments in the water column and underlying sediment as equilibrium chemistry is calculated for each segment, including the interactions with adjacent compartments. The modeling process involved the evaluation of site data as shown in Figure 1. Model input data included volumetric flows, metal loading rates, and inflow metal concentrations. Other data needs included calculation time step, model compartmentalization, cell volume, channel geometry, volumetric flow rates, and metal-sorbent reaction constants. Channel geometry and compartments volumes were estimated from time of travel information for the fall monitoring data collected by the USGS (September, 1995).

More complex sediment modeling, as used within META4, required a delineation of the importance of dominant mechanisms which affect accumulation of metals in sediments and potential releases of metals from sediments. The accumulation of metals in sediments generally includes five major mechanisms: 1) adsorption onto fine-grained materials, including oxides, 2) precipitation of trace element compounds, 3) coprecipitation with Fe, Al and Mn oxides/carbonates, 4) association with organic matter, and 5) incorporation in crystalline minerals. Due to the dominance of the sediment sorption reactions by iron precipitates, only adsorption to iron was simulated in the model. The model configuration included copper and zinc speciation as affected by the composition of major water quality variables. The major parameters used to describe the speciation of metals, and the corresponding effects on sorption and desorption by the sediments, include H^+, CO_3^{-2}, Ca^{2+}, SO_4^{2-}, Mg^{2+}, Cu^{2+}, Zn^{2+} and three classes of adsorbing solids: Solid1 (iron oxides), Solid2 (aluminum oxides), and Solid3 (residual source/sink surfaces).

Chemical Reactions

The reactions to be included in the META4 submodel for WASP4 were determined after a series of chemical speciation calculations using MINTEQA2 (Versions 3.11). Using a variety of water quality conditions, including estimates of future conditions, only the reactions that represented a significant percentage of each individual metal were included in the model. Generally, reactions were excluded if they comprised less than 0.2 percent of the dissolved metal concentration. The two-layer sorption model (diffuse layer or double layer model) as implemented in the geochemical model MINTEQA2 is regarded as the most representative approach for modeling metal sorption to iron oxides and was used for the modeling. Constants for hydrous iron oxide sorption of copper and zinc to strong and weak sites were based on literature (*7*).

Model Calibration

The modeling for Segments 3b and 3c (Wightman Fork to Fern Creek: Fern Creek to Terrace Reservoir) of the Alamosa River includes 14 surface water compartments along the main channel along with the corresponding 14 benthic compartments for each water column compartment (Figure 3). Model compartments were developed from information concerning the physical and chemical characteristics of stream reaches (i.e. slope, hydrology, sediment type) and locations for major loads to the system.

The specification of overall model details including control parameters, system configuration, hydrology, boundary conditions, reactions, loadings and other model parameters were developed for the model input file. The model was calibrated to the September, 1995 monitoring data. The initial calibration activity, following the balancing of flows and travel time, included the simulation of a conservative anion (to check on flow balancing) and total suspended solids (TSS represented by particulate iron) within the Alamosa River from Wightman Fork to Terrace Reservoir. After solids were calibrated, subsequent steps included the combined calibration of benthic metal concentrations and total/dissolved metal in the water column of each compartment (*3*).

Sediment conditions for the adsorbed fraction of zinc and copper were determined from Terrace Reservoir data (*8*). The data showed that the operationally defined labile zinc and copper in the sediments were about 49.2 ± 5.26 % and 23.1 ± 3.62 % of the total sediment burden of these metals. The iron oxide fraction for iron was approximately 21.8 ± 7.10 % of the total iron content. The conditions were used to describe the partitioning of copper and zinc to the sediments as reflected in double layer sorption model used in WASP4/META4.

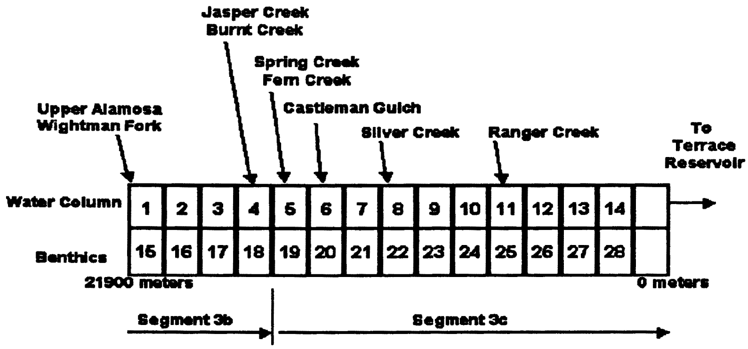

Figure 3. Model compartmentalization, upper boundary and tributary locations.

The results of the calibration for water column total zinc and total copper are shown in Figures 4 and 5, respectively (dissolved copper and zinc were nearly equal to total metals and are not shown). Both total and dissolved metals in the water column compartments show excellent agreement with observed data and represent the combined effects of loading, dilution, partitioning and attenuation. Three observed data points were available for comparison at AR43.6, AR41.2 and AR34.5 for the September, 1995 modeling. The relative percent difference for each paired data for observed and modeled metal concentration is generally well below 5%. Following calibration, a Monte Carlo simulation was used to describe the potential pre-Galactic and pre-mining water quality.

Monte Carlo Simulation of Pre-Galactic and Pre-Mining Chemistry

The model simulations performed for pre-Galactic and pre-mining included calculations of both dissolved and total zinc and copper in the various model compartments from Wightman Fork downstream to Terrace Reservoir. From a modeler's perspective, addressing uncertainty in the application of numerical modeling to Summitville was central to sound decision-making. Sensitivity analysis followed by uncertainty analysis provided a greater ability to make informed decisions. One of the more basic aspects of uncertainty analysis was statistical in nature and was based on a comparison of the calibrated model with the observed distributions of metal concentrations as described below (Calibration Prediction Error). Obviously, this comparison is not possible for the pre-mining and pre-Galactic scenarios. To address the model uncertainty associated with input parameters, it was decided that Monte Carlo simulation, widely used in water quality modeling, would best reflect this uncertainty.

After a number of model sensitivity runs, it was determined that the uncertainty could be best reflected by varying copper and zinc concentrations in the Alamosa River (above Wightman Fork) and in Wightman Fork. Input files for 100 simulations were randomly constructed from the statistical distribution of the original data sets from WF0.0 and AR45.5 for the upstream boundary condition. After the input files were assembled to describe the pre-Galactic and pre-mining chemical inputs in the first model compartment (as described for Tables 1 and 2), the model was run and the data entered into a database management program for analysis.

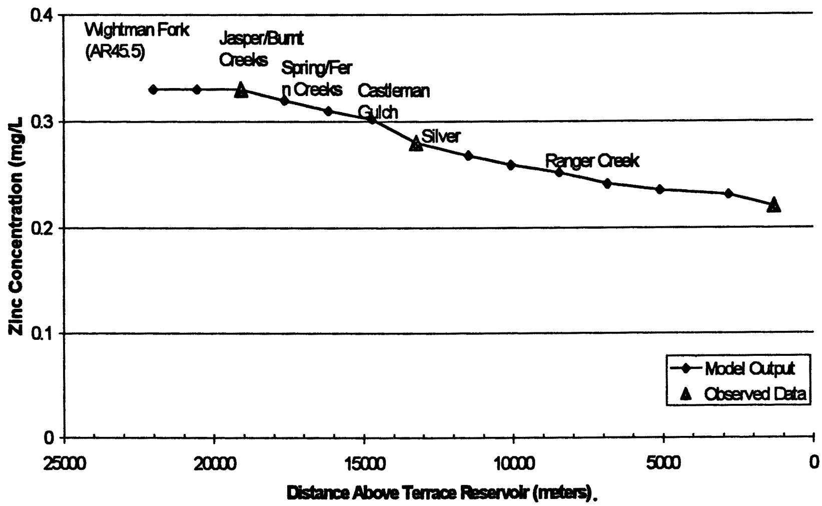

Figure 4. Model calibration for total zinc during September, 1995.

Pre-Galactic Water Quality

The pre-Galactic water quality for copper and zinc during fall (Figures 6-7) likely represent the worst-case seasonal values in the Alamosa downstream of Wightman Fork. Copper concentrations show a pronounced effect of the iron oxide partitioning in the water column and well as reduced transport of copper due to retention by stream sediments.

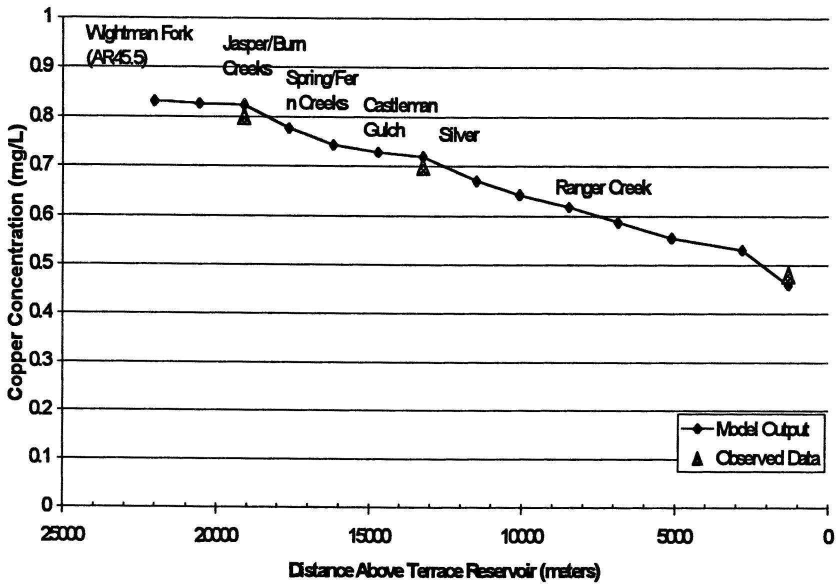

Figure 5. Model calibration for total copper during September, 1995.

Concentrations of dissolved and total zinc were nearly identical and indicated the limited partitioning of zinc to the iron oxides at pH conditions in the Alamosa River (<7.0) for the pre-Galactic scenario. While the concentration of total copper is reduced by 82% from Wightman Fork to Terrace Reservoir through combined adsorption (to bed sediments) and dilution, the zinc concentration is reduced by 47%. Zinc and copper are both removed to the bed sediments, although zinc is removed less efficiently. If pH were in the range of 7.5-8.0 in the system, both zinc and copper adsorption would be enhanced and the associated dissolved metal in the water column would be decreased further.

Pre-Mining Water Quality

The pre-mining water quality for copper and zinc during fall time is shown in Figures 8-9 and, as for copper, would represent the highest seasonal concentrations for both dissolved and total metals in the Alamosa River downstream of Wightman Fork. Total copper concentrations decrease by 66%

while total zinc concentration decreases by only 16%. The main difference between the efficiencies of removal is again related to system pH. Modeling indicates that during the pre-mining era the dissolved copper and zinc concentrations would be below 4 μg/L and 50 μg/L, respectively, and would not result in significant impacts to fisheries. Pre-Galactic concentrations are higher and were found to be below 30 μg/L and 130 μg/L, respectively, in the lower portion of the Alamosa River below Silver Creek. The water quality for other seasons is expected to have been better than these estimates and would have likely permitted fisheries to be established as far upstream as Spring and Fern Creek under the pre-Galactic modeling scenario.

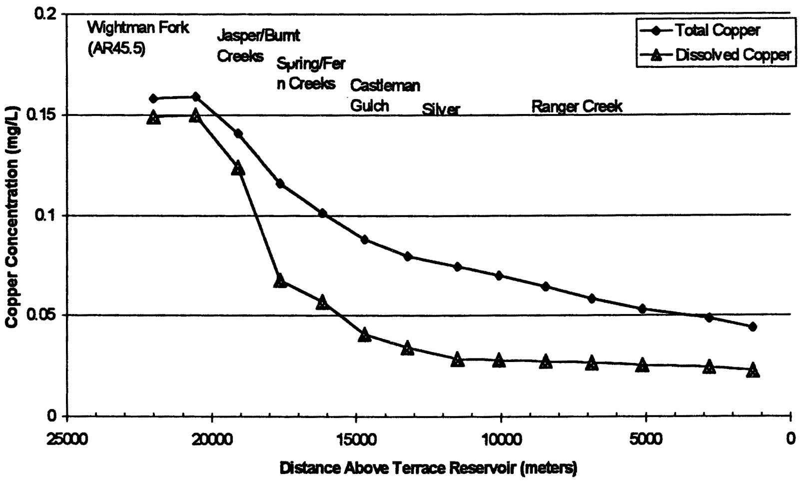

Figure 6. Simulated Pre-Galactic copper concentrations during fall.

Summary and Conclusions

This modeling study evaluated the likely pre-mining (prior to 1873) and pre-Galactic (prior to 1984) concentrations in the Alamosa River downstream of Wightman Fork. Following model calibration, Monte Carlo simulations estimated water quality after calculating the effects of adsorption, advection, settling, dilution, and dispersion. The Monte Carlo simulation provided an assessment of model uncertainty with respect to the boundary conditions. The combined effects of these processes indicate that in the pre-Galactic scenario, using worst-case fall conditions, 82% of the copper and 47% of the zinc were removed, and in the pre-mining scenario 66% of the copper and 16% of the zinc were removed in the Alamosa River between Wightman Fork and Terrace Reservoir. Based on water quality standards and anecdotal evidence, the modeled concentrations in the Alamosa River would have been adequate to support a fishery in the river prior to mining, and in the pre-Galactic period, would likely have supported a fishery in the river downstream of Fern and Spring Creeks.

Acknowledgement

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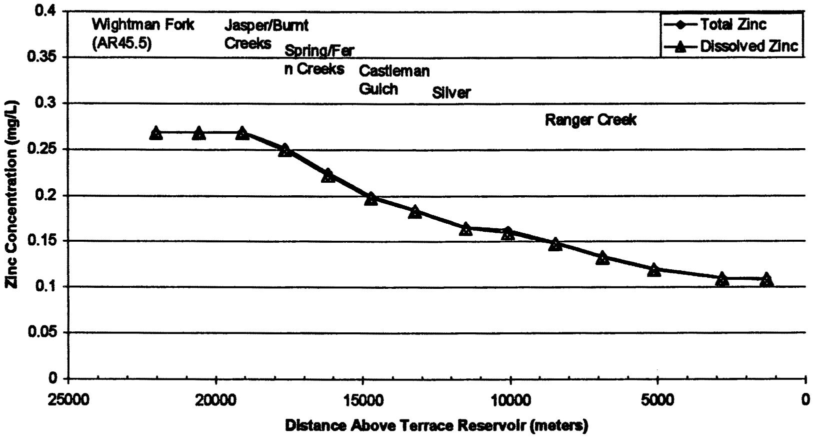

Figure 7. Simulated Pre-Galactic zinc concentrations during fall.

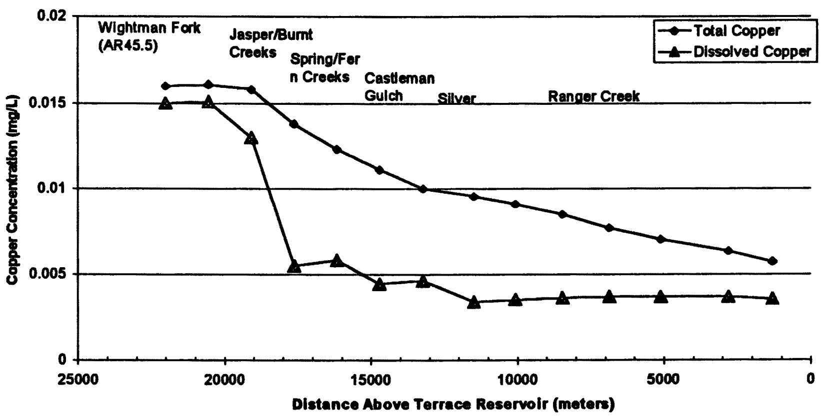

Figure 8. Simulated Pre-mining copper concentrations during fall.

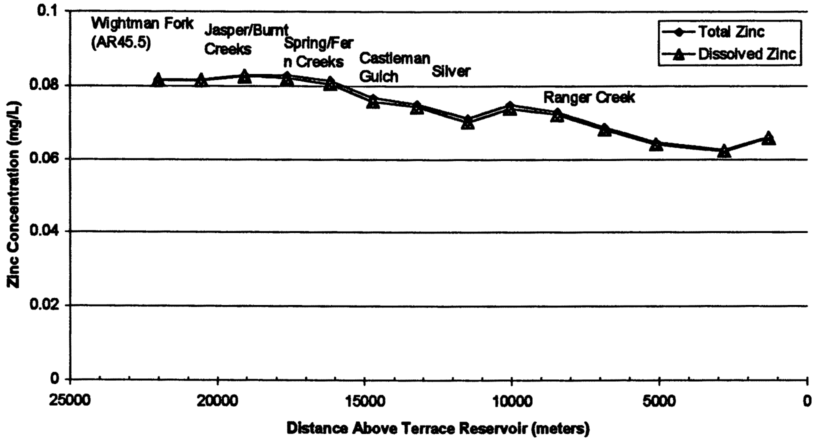

Figure 9. Simulated Pre-mining zinc concentrations during fall.

Literature Cited

1. Allison, J. D.; Brown, D. S.; Novo-Gradac, K. J. MINTEQA2/PRODEFA2, Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, EPA/600/3-91/021, USEPA, 1991.
2. Martin, J. L.; Medine, A. J. META4 - Metal Exposure and Transformation Assessment Model, Model Documentation for Version 3, December, 1998.
3. Medine, A. J. Technical Assessment of Pre-Mining and Pre-Galactic Water Quality for Wightman Fork and the Alamosa River. USEPA, National Risk Management Research Laboratory, Cincinnati, OH, 1997.
4. Shriver, D. R. History of the Summitville Mining District. The San Luis Valley Historian, Volume XXII (1), 1990.
5. Pendleton, J. A.; Posey, H. H.; Long, M. B. Characterizing Summitville and Its Impacts: Setting the Scene. In: Proc.: Summitville Forum '95. CO Geol. Survey, Special Publication 38, Denver, Colorado, 1995.
6. CDPHE. Use Attainability Assessment, Alamosa River Watershed through 1996. Posey, H. H.; Woodling, J.; Campbell, A.; and Pendleton, J. A. USEPS and Colorado WQCC, July 12, 1996.
7. Dzombak, D. A.; Morel, F. M. M. *Surface Complexation Modeling, Hydrous Ferric Oxide*. John Wiley and Sons, New York, 1990.
8. Horowitz, A. J.; Robbins, J. A.; Elrick, K. A.; Cook, R. B. Bed Sediment-Trace Element Geochemistry of Terrace Reservoir, near Summitville, Southwestern Colorado. USGS, Open-File Report 96-344, 1996.