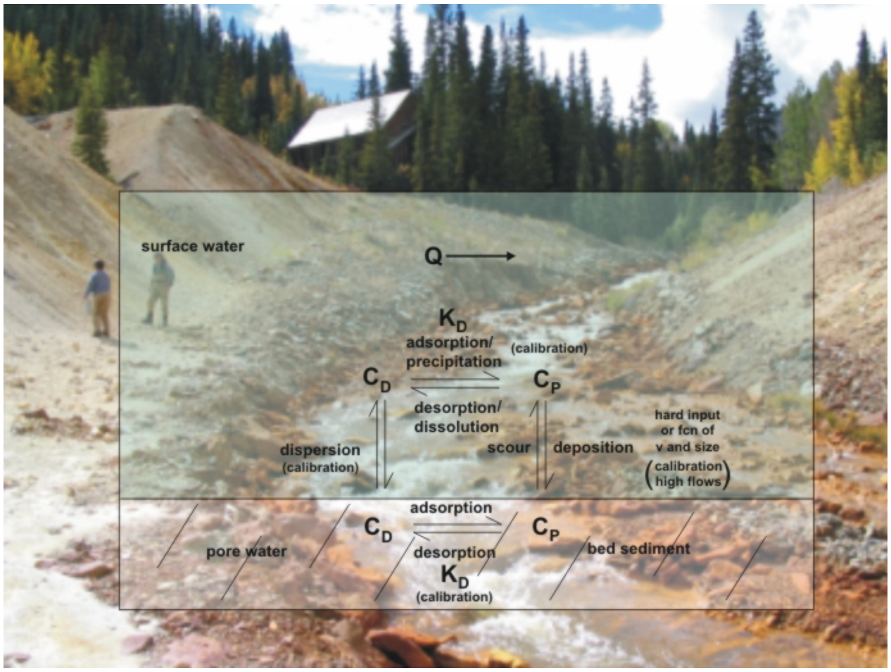
US EPA Region 8

Report Summary of US EPA Metals Fate and Transport Modeling Workshop

Dates: February 13-14, 2007

Location: US EPA Offices, Region 8
1595 Wynkoop St.
Denver, Colorado 80202

June 12, 2007



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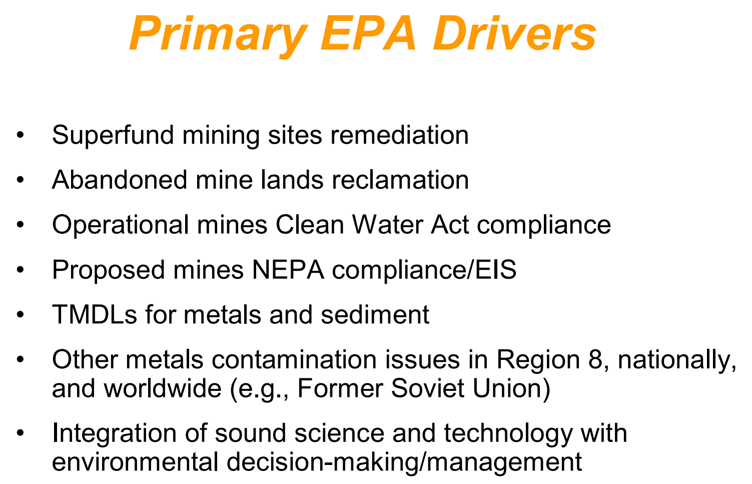


Primary EPA Drivers

- Superfund mining sites remediation
- Abandoned mine lands reclamation
- Operational mines Clean Water Act compliance
- Proposed mines NEPA compliance/EIS
- TMDLs for metals and sediment
- Other metals contamination issues in Region 8, nationally, and worldwide (e.g., Former Soviet Union)
- Integration of sound science and technology with environmental decision-making/management

Figure 1-2
EPA Drivers for Modeling Aquatic Metals Fate and Transport (Caruso)

Section 2
Stream Modeling

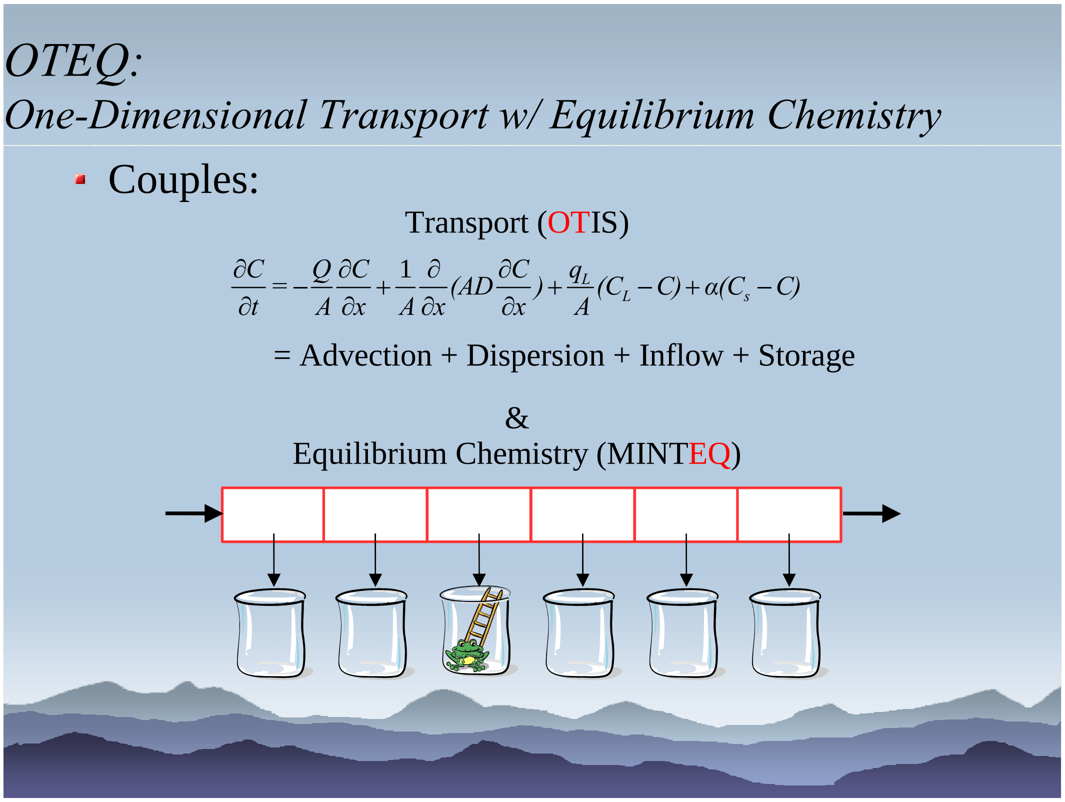
Brian Caruso, EPA Region 8 (Denver, CO), kicked off discussions with an introduction and presentation primarily focused on the EPA Water Quality Analysis Simulation Program (WASP) and related modeling efforts. The unique metals and modeling issues associated with Region 8 were described. These issues include: prevalence of mining impacts with multiple and variable point source loadings, high gradients of the receiving streams, significant hyporheic zone interactions in these streams, snowmelt-driven hydrology, and naturally occurring background metals loads. Most of EPA's metals modeling projects to-date have used WASP, sometimes in conjunction with the Metals Exposure and Transformation Assessment (META4) module, or the US Geological Survey (USGS) One-dimensional Transport with Equilibrium Chemistry (OTEQ) model. A case study of the Upper Tenmile Creek Mining Area Superfund Site (MT) WASP modeling was presented. WASP is a box/compartment stream water quality model that can be applied in one, two, or three dimensions. Previous versions of the model employed a lumped partitioning coefficient, K_D, for simulating metals equilibrium speciation. This approach lumps precipitates and all sorbed forms into a single particulate compartment and all free ions and soluble complexes into a single dissolved compartment. The latest version of the model, however, allows for the simulation of sorption to different types of sorbents (clays, sands, organic solids and solutes) and explicit representation of the oxidation/reduction process. Geochemical processes can be even further represented using the META4 module in WASP, although this module is not yet available in the general WASP release . Other recent, or on-going, advances in WASP include modules for periphyton, sediment nutrient diagenesis, and mercury (Hg). As with META4, many of these advances are not yet available to the public.

Tim Cox, CDM (Denver, CO), presented on the numerical approaches employed by many of the currently used stream water quality models and the various forms of potential numerical error associated with these various schemes. These considerations are important for both the general awareness of current modelers and for the development of future numerical models. The potential for numerical dispersion (truncation error), false oscillations, and loss of mass conservation was described and demonstrated for different numerical schemes, including those employed by WASP and OTEQ. These issues are particularly relevant to stream metals modeling because of the conservative nature of metals and the fact that many of the modeled systems are characterized by high gradients, non-uniform flow, and multiple point sources. All of these characteristics make the simulations of such systems more susceptible and sensitive to the described numerical error. Loss of mass conservation in numerical models is particularly concerning. A new analytical derivation was presented that demonstrates the loss of mass conservation for numerical schemes that are based on the non-conservative form of the advection-dispersion equation. This loss of mass conservation is induced when the differential equation is applied in finite difference form to non-uniform flow regimes. Finally, a brief description of "Lagrangian" numerical methods was provided. These methods, many of which have been presented in the literature, eliminate many of the potential problems described but likely at the cost of programming and user complexity.

Allen Medine, Water Science and Engineering (Boulder, CO), presented on the META4 model. META4 is a mechanistic metals speciation model that has recently been developed into a sub-model for WASP. META4 simulates both instant equilibrium reactions and slower kinetic processes. Simulated processes include: metals adsorption / desorption with sediment and organic matter, precipitation, ion exchange, and complexation. Explicit representations of various environmental controls on these processes, including mineral and sediment characteristics, iron concentrations, and pH are also included. In this way, the model can be viewed as a mechanistic improvement, in terms of geochemistry, over the WASP speciation module. A case study of META4 modeling of the North Fork Clear Creek (CO) was presented, including model calibration and verification results and remediation scenario analyses. The modeling results point toward multi-pronged remediation efforts that include reduction of point source flow releases, stabilization of waste piles, erosion controls, contaminated sediment removal, and pH neutralization. The complexities of source areas, and their relationships to hydrology, were noted as major challenges in metals modeling. An integrated approach, using multiple modeling tools, was recommended for modeling metals at a watershed scale. A more user-friendly graphical user interface (GUI) for the META4 model was noted as a future development need.

Barb Butler, EPA ORD (Cincinnati, OH), followed up with a presentation also on metals modeling of the North Fork Clear Creek (CO). This study focused on a comparison of the WASP / META4 coupling with the MINTEQ model in simulating particulate metals in this mining-impacted stream. MINTEQ is a public domain model supported by the EPA that includes a comprehensive database of equilibrium constants. MINTEQ simulates equilibrium speciation only, albeit at a potentially higher level of complexity, while the WASP / META4 combination also includes transport (downstream and vertical settling). Past studies have shown that the metals processing in the targeted system is dominated by sorption and / or co-precipitation with iron (ferric oxyhydroxides, hydrous ferrous oxide (HFO)) and to a lesser extent, manganese oxyhydroxides (HMO), as well as complexation with dissolved organic carbon (DOC). The WASP / META4 model used here included only HFO sorption, while the MINTEQ model also included HMO sorption and complexation with DOC. The results of the modeling comparison show that the WASP / META4 model performed better for simulating high flow conditions, likely due to its incorporation of particulate transport, while MINTEQ generally performed better for simulating low flow conditions. Additionally, it was clear that the WASP / META4 model could be improved by including DOC complexation. For this stream, both models seemed to be lacking representation of an additional sorbent (for zinc) besides HFO and HMO.

Rob Runkel, USGS (Denver, CO), presented an overview of the OTEQ model (Figure 2-1). OTEQ combines the stream transport capability of OTIS (One dimensional Transport with Inflow and Storage) and the geochemistry capability of MINTEQ. Transport mechanisms in the model include advection, dispersion, and transient storage (e.g., hyporheic exchange). The inclusion of transient storage makes the model particularly well-suited for many of the small, high-gradient streams discussed in this workshop. Geochemical processes are simulated with a series of equilibrium speciation equations, primarily targeting sorption / desorption and precipitation / dissolution. A key advantage of this model over others reviewed here is the explicit simulation of the interactions between pH, metal oxide precipitation (e.g., hydrous ferric oxide, HFO), and sorption of other metals onto HFO. OTEQ is public domain software available from the USGS. Two OTEQ case studies were presented: one evaluating remediation alternatives (Mineral Creek, CO) and the other estimating pre-mining conditions (Red Mountain Creek, CO). Potential future enhancements to OTEQ include the incorporation of: kinetically-limiting de-gassing, mechanistic handling of oxidation and reduction, and nutrient and DOC interactions.



OTEQ:
One-Dimensional Transport w/ Equilibrium Chemistry

- Couples:

Transport (OTIS)

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

= Advection + Dispersion + Inflow + Storage

&
Equilibrium Chemistry (MINTEQ)

Figure 2-1
OTEQ Model Summary Slide (Runkel)

Andrea Marion, University of Padua (Italy), presented recent research on residence time modeling of hyporheic flows and a modification of the widely-used transient storage model (TSM) approach. The STIR (Solute Transport in Rivers) model represents a mechanistic improvement over the TSM, as it allows for separation of physical processes at different temporal and spatial scales. In fact, the TSM breaks down for exchange with deep hyporheic zones, while the STIR model does not. The STIR model numerics are based on describing the statistical properties of contaminant residence times in different compartments of the physical domain. Tracer tests and controlled condition experimental work can be used to calibrate different parts of the model independently. This is an advantage over the lumped TSM approach where it is difficult to separate out processes during calibration. For example, because of differing residence times, calibration of the STIR model can separate side pool storage from hyporheic storage and passive diffusive exchange from benthic pumping (vertical advection).

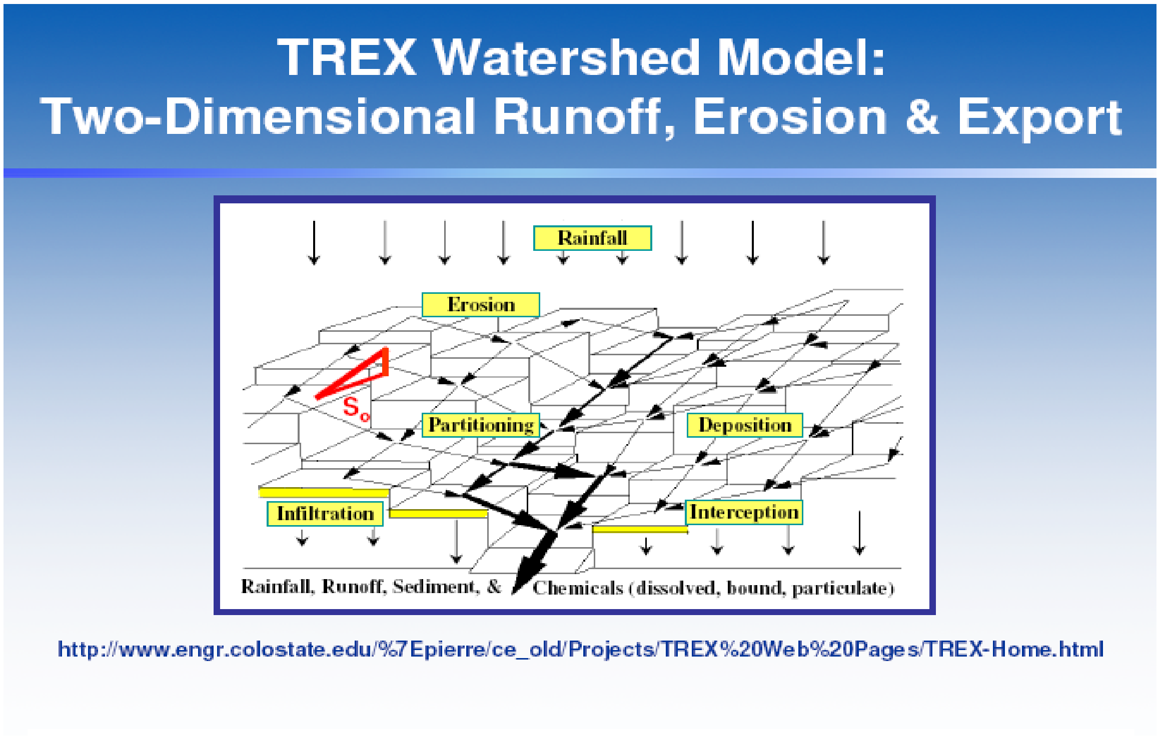
Kevin Rader, University of Delaware (Newark, DE) and Center for the Study of Metals in the Environment (CSME) funded by EPA, described the development of a Unit World model for metals fate and transport in streams and rivers. The term "Unit World" describes a domain consisting of typical environmental compartments. Probabilistic methods are used to capture the variability and uncertainty associated with stream metals in the model simulations of loadings and dilution. In this approach, upstream concentrations and flows are defined with probability distributions generated from measured data sets. These upstream distributions are then used to calculate downstream (mixed) concentration probability distributions. Metals speciation is calculated in the model using the WHAM6 (Windermere Humic Aqueous Model) algorithm and includes sorption and desorption to organic and inorganic solids, precipitation, and complexation. Although not described, the model also calculates settling and resuspension of particulate metals and downstream transport of both dissolved and particulate forms. Finally, the model incorporates the Biotic Ligand Model (BLM), also developed at CSME. This model calculates the biological toxicity of the simulated metals concentrations as a function of multiple water quality parameters, such as DOC, and incorporating the results of past empirical studies. The BLM converts the calculated concentrations to "toxic units" (ratio of predicted concentrations to toxicity levels). Application of the model to the Leadville/California Gulch Superfund Site (CO) was briefly described. The uniqueness of the Unit World model presented, relative to other reviewed models, lies in the probabilistic handling of loads and dilution and the conversion to toxicity via the BLM.

Jim Ranville, Colorado School of Mines (Golden, CO), presented on metals modeling of the mining-impacted North Fork Clear Creek (CO) using a combination of MINTEQ and the BLM. MINTEQ provides the metals speciation predictions while the BLM provides the resulting toxicity predictions. Dr. Ranville described the "three Cs" of bioavailability: concentration, competition (for biotic ligand sites), and complexation (with dissolved organic matter and alkalinity). Time-series simulation results for a two-year period (2002 – 2004) were presented for the target reach. Downstream transport and spatial variations were not incorporated into the modeling. Manganese, zinc, and sulfates show a clear correlation to hydrology, with peak concentrations occurring during low flow periods and minimum concentrations occurring during high flow (snowmelt) periods. These data do, however, show an "early flush" spike in concentrations at the beginning of the snowmelt period. Copper and iron exhibit more spikey patterns and less of a seasonal trend, and appear to be more closely correlated with storm events. These metals appear to be dominated by the solid phase in this system. Toxicity simulation results for zinc (measured in toxicity units) show large variability during the simulation period, with apparent peaks occurring during the early high flow period. A close (negative) correlation between toxicity and hardness levels is seen. Laboratory toxicity experiments were used to validate the BLM results. The BLM approach is an improvement over past practices of setting criteria based on hardness only.

Section 3
Watershed Modeling

Pierre Julien, Colorado State University (Ft. Collins, CO), led off the discussions on metals modeling at the watershed scale with a presentation on the Cascade of Planes in Two Dimensions and Sedimentation (CASC2D-SED) model. This spatially-distributed, event-based model simulates watershed runoff hydrology in two dimensions, channel flow in one dimension, and sediment erosion and transport. The model uses detailed, but readily available, GIS-based physical data to describe watershed topography and drainage characteristics down to a 30-meter grid scale. The presentation focused on grid size impacts on simulation accuracy. Results of a case study on the Goodwin Creek watershed (MS) indicate that hydrology can be accurately simulated at a grid size of up to 1000 meters, while sediment simulations are best for grid sizes under 100 meters. Model snowmelt simulations were also discussed and demonstrated. Future work may focus on incorporating a more mechanistic representation of the snowmelt process that will take advantage of the detailed data available, including terrain geometry, slope and exposure, vegetation, and land use. This model has been used for the Leadville/California Gulch Superfund Site (CO) and has significant potential for applied modeling of runoff, erosion, and sediment transport (including tailings and waste rock) during precipitation and snowmelt events in mountain watersheds in the semi-arid western U.S.

Mark Velleux, HydroQual (Mahwah, NJ), followed up on Dr. Julien's presentation with a discussion on applications of the Two-Dimensional Runoff, Erosion, and Export (TREX) watershed fate and transport model (Figure 3-1). TREX evolved from the CASC2D-SED hydrologic model described above and incorporates the same runoff and routing algorithms. It was noted that the importance of using a fully distributed watershed model, with respect to metals source remediation, is that it allows the user to identify key source areas, such as waste piles, within the watershed. TREX uses the same hydrology and sediment loading algorithms as CASC2D but also overlays the contaminant fate and transport dynamics of the WASP model. Overland erosion of sediments in TREX is simulated as a function of topography, flow hydraulics, soil type, and land use (modified version of the Universal Soil Loss Equation). Channel erosion is simulated as a function of channel hydraulics and sediment particle characteristics (modified Engelund and Hanson Equation). Metals speciation, as in WASP, is simulated using a simple "lumped" partitioning coefficient, K_D and assumes instantaneous equilibrium. An application to the California Gulch (CO) mine-impacted watershed was described, including calibration and validation water quality simulations. For this study, the model helped in locating specific metals source areas. An interesting result of the study was that many of the simulated water quality parameter concentrations, particularly total suspended solids, exhibit a hysteresis effect, where the rising limb concentrations are significantly greater than those associated with the falling limb. Future work on this model will likely focus on improving the snowmelt algorithm, incorporating surface and groundwater interactions, and moving toward continuous modeling capabilities.



TREX Watershed Model:
Two-Dimensional Runoff, Erosion & Export

http://www.engr.colostate.edu/%7Epierre/ce_old/Projects/TREX%20Web%20Pages/TREX-Home.html

Figure 3-1
TREX Model Summary Slide (Velleux)

Billy Johnson, U.S. Army Corps of Engineers (USACE, Vicksburg, MS), presented on a watershed water quality model developed primarily to simulate explosive compounds from various sources across a watershed. The approach employed couples a generalized fate and transport module (Contaminant Transport Transformation and Fate, CTT&F) with a grid-based, spatially distributed watershed hydrology model, very similar to the CASC2D model described above. The water quality module includes four-phase equilibrium partitioning. The simulated metals phases are: dissolved, precipitated, sorbed to sediment particles, and sorbed to dissolved organic carbon. The model also includes up to seven different biochemical transformation processes: biodegradation, hydrolysis, oxidation, photolysis, dissolution, chemical transformation with daughter products, and a user-defined reaction. Downstream advection and dispersion are also explicitly simulated. In this way, the model is more generalized and flexible, with respect to water quality, than either the CASC2D or TREX models described above. Application of the models, simulating explosives (TNT, RDX) in the Camp Shelby (MS) watershed, was described.

Mark Velleux, filling in for John England (U.S. Bureau of Reclamation, Denver, CO), presented on the simulation of extreme storms and resulting flood hydrographs using numerical modeling. His approach involved a stochastic representation of the location of storm events within a watershed in combination with the TREX hydrologic model.

Monte Carlo simulations involving 1000 iterations of a defined storm event at different locations in a watershed are used to capture the uncertainty associated with the exact location of the storm events. The TREX model then calculates and routes the resulting runoff and stream flow. Output is in the form of flood frequency curves. A case study of the Arkansas River Basin (CO), and a 1 in 200-year event, was presented. This case study demonstrates the power of this approach and also the ability of the TREX model to simulate large watersheds (12,000 km^2). This work was motivated primarily by dam construction considerations but does have relevance to metals watershed modeling due to the potential large load of metals during these extreme events.

Ann Maest, Stratus Consulting (Boulder, CO), described a study that evaluated past environmental impact statements (EISs) for hard rock mines in which water quality impacts from the mines were characterized and predicted using modeling and experimental work. The use of numerical models in these studies was summarized. Of the 71 mines included in the study, 56 percent used some type of numerical model for predictions of water quantity, quality, or both. None of the 56 percent actually used what could be considered a comprehensive watershed model. However, various components of small watershed dynamics were modeled using combinations of focused hydrologic models (e.g. HEC-1, WASHMO, MODFLOW) and/or water quality models (e.g., RUSLE, PHREEQC, MINTEQ). It was recommended that proprietary models not be used to support EISs due to their lack of transparency. A process scheme was recommended for developing mining site models in support of mitigation planning. It was noted that a key to successful modeling of these sites is a quantification of uncertainty.

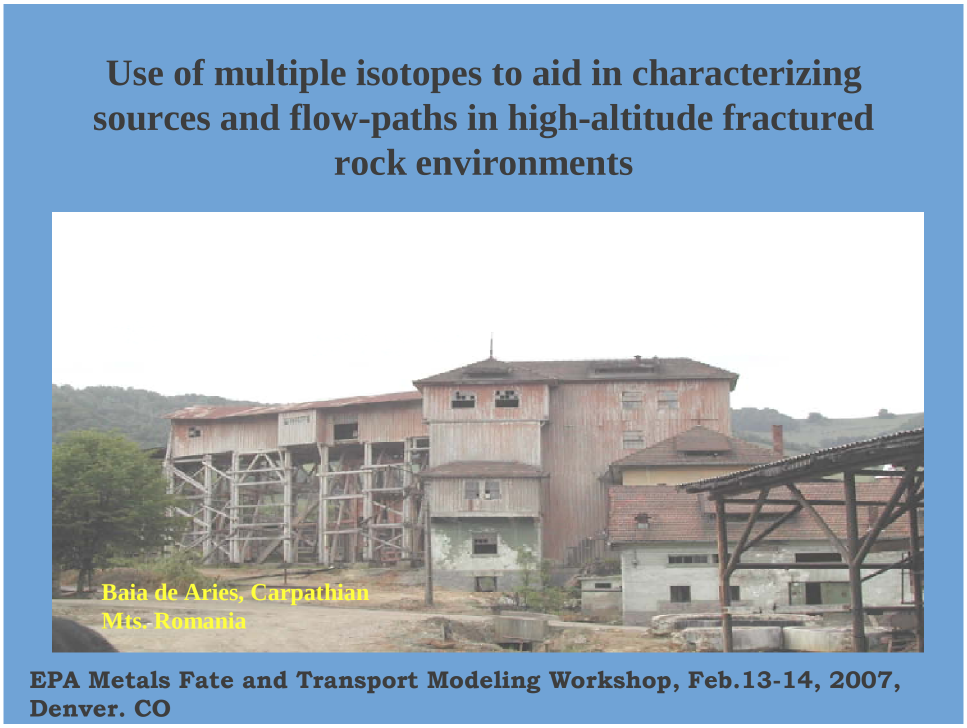
Section 4
Process-Level Modeling and Characterization

Focused modeling and empirical work on specific components of stream and watershed systems is clearly critical to the success of modeling such systems at a larger scale. The presentations summarized below describe such process-level work. This type of work provides important data and information for stream and watershed metals fate and transport modeling.

Ann Maest (previously referenced) reported that of the 71 mine sites reviewed in their study, nearly 90 percent performed some type of site-specific geochemical characterization of waste piles in support of their EIS. Most of these characterization studies involved a combination of static (single snapshot), kinetic (long term, time-variable), and short-term leach tests to evaluate waste contamination potential. Over 50 percent of the reviewed mine sites used numerical modeling, at some level, to support the characterization and to provide predictive analyses.

Ken Bencala, USGS (Menlo Park, CA), presented on hyporheic flow exchanges in stream solute transport and on the need to understand and characterize such processes. A case study of Mineral Creek (CO) was described where tracer studies and stream and shallow well sampling were used to define hyporheic exchanges. Results of this study indicate a mixture of source waters in the hyporheos contributing variable solute loads to the stream. Additionally, in the studied reach, vertical advective upwelling was infrequently observed. This result is consistent with indications of hyporheic flows with significant longitudinal (down-valley) components. The transient storage model (TSM) has proved to be an effective tool for characterizing hyporheic exchanges of solute, primarily through the interpretation of field data. Published studies of solutes in the hyporheic zone have increased rapidly over the past ten years indicating the increased recognition of these areas as important components of stream ecosystems. Future work should focus on gaining a better understanding of the variable timescales of different types and downstream locations of hyporheic exchanges; the catchment physical (and measurable) properties that determine flow paths; and the overall impacts of hyporheic exchanges on catchment hydrology.

Mike Wireman, EPA Region 8 (Denver, CO), described field research performed at the Mary Murphy Mine (CO) that used multiple isotopes to assess metals sources and groundwater flow paths (Figure 4-1). The Mary Murphy Mine was mined in the 1860s and 1870s primarily for gold, silver, lead, zinc, and copper. Site stabilization work has been ongoing since 1991. The roles of interflow versus baseflow, and characterization of the groundwater flow paths through elaborate underground mine workings, were primary focuses of this research. Oxygen, tritium, sulfur, helium, and uranium isotopes were used to define sources and flow paths. Conservative tracers were also used in this study as a basis of comparison. Study results indicate that inflow to mine



Use of multiple isotopes to aid in characterizing sources and flow-paths in high-altitude fractured rock environments

Baia de Aries, Carpathian Mts. Romania

EPA Metals Fate and Transport Modeling Workshop, Feb.13-14, 2007, Denver. CO

Figure 4-1
Metals Source Assessment Presentation Opening Slide (Wiremen)

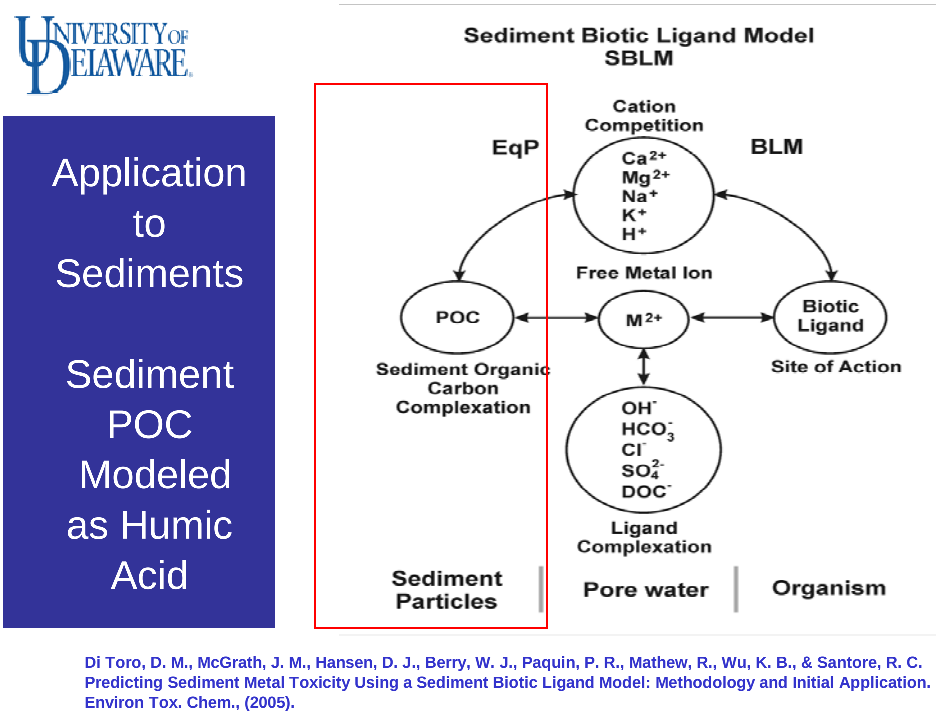
workings is primarily groundwater recharge from snowmelt and that there are multiple groundwater flow systems. The isotope data also allowed for the identification of a specific underground source area for metals contamination in receiving waters.

David Parkhurst, USGS (Denver, CO), presented on the PHREEQC model, which simulates metals geochemistry and solute transport in aqueous environments. PHREEQC is a equilibrium speciation model that includes one-dimensional reactive transport. It includes both ion association and Pitzer specific interaction models and rigorously simulates surface complexation reactions. The model has been shown to provide an excellent description of surface complexation in laboratory settings, but extension to field settings is needed. The model currently lacks the ability to simulate metals sorption to organic compounds. However, it does offer a generalized kinetic capability in which the user writes kinetic expressions for incorporation into the model. Model transport algorithms were not discussed. The PHAST model is a three dimensional extension of the PHREEQC algorithms to groundwater systems.

Kirk Nordstrom, USGS (Boulder, CO), presented on conceptual work and data analysis illustrating the challenges of geochemical modeling of aluminum (Al) and iron (Fe) in acidified surface and ground waters. A large set of geochemical data from seven western mining sites (Iron Mtn., Leviathon, and Penn Mine, CA; Summitville and Upper Animas, CO; Questa, NM; and Gilt Edge Mine, SD) was used to support the analysis presented. By way of review, the major controls on Al and Fe concentrations in acidic waters were presented. Al concentrations in acidic waters depend on weathering rates, hydrolysis and precipitation rates (which have pH dependencies that vary for surface versus ground waters), and organic complexing. Little else affects Al concentrations in these types of waters. Iron concentrations in acidic waters depend on redox conditions, hydrolysis rates, level of acidity, and organic complexing. A major conclusion of the work presented is that, at near-neutral pH values and in the presence of normal concentrations of dissolved organic carbon, most Al and Fe will be organically complexed.

Dominic Di Toro, University of Delaware (Newark, DE), presented on metals toxicity assessments and the BLM. Dr. Di Toro summarized much of the relevant work done over the past 20 years in the area of metals toxicology. This work has shown that there are many confounding factors affecting metals biological toxicity. The setting of criteria in the past has been flawed, because regulators have focused on a single total concentration value for each metal of concern without an understanding of these confounding factors. In fact, much of the published experimental data for metals has shown that there is no correlation between total metals concentrations, by themselves, and toxicity. Correlations are seen only when a more mechanistic representation of the various environmental factors that affect bioavailability is applied. The BLM, developed at the CSME, provides such a mechanistic model. This model can be viewed as an important link between metals concentration modeling and the assessment of risk posed by the concentrations. It simulates metals speciation using algorithms from the WHAM model, and uses past empirical studies to assess biological toxicity based on sediment and water column concentrations. DOC and sulfide concentrations have been shown to be strong determinants of bioavailability of metals, and these interactions are key features of the BLM. For example, if an excess of sulfides is present then essentially all metals form sulfide complexes and become non-bioavailable. Consequently, toxicity is negligible. Alkalinity, pH, and hardness are also important factors in determining metals toxicity and are incorporated in the BLM. Experimental results have shown that, in sediments, it is the pore water concentration (rather than the bound concentrations) that determines toxicity. Thus, another key component of the BLM is the prediction of pore water metals concentrations as functions of sediment-bound mass using equilibrium partitioning (Figure 4-2). The BLM has been adopted by EPA for copper criterion assessment and is in the process of being applied to other metals.

Rich Carbonaro, Manhattan College (New York, NY), further reviewed the current BLM research and development, specifically in the area of predicting metal binding to natural organic matter (NOM). All organic carbon molecules are different and have different metals binding capacities based on their molecular structure. The methods being developed for the BLM utilize linear free energy relationships that relate metal binding strength to proton binding strength. Data sets from the literature for 24 metals have been used to parameterize this relationship. The linear free energy relationship model represents an advancement over the current NOM / metals simulations employed by WHAM and the current BLM.



Application to Sediments

Sediment POC Modeled as Humic Acid

Di Toro, D. M., McGrath, J. M., Hansen, D. J., Berry, W. J., Paquin, P. R., Mathew, R., Wu, K. B., & Santore, R. C. Predicting Sediment Metal Toxicity Using a Sediment Biotic Ligand Model: Methodology and Initial Application. Environ Tox. Chem., (2005).

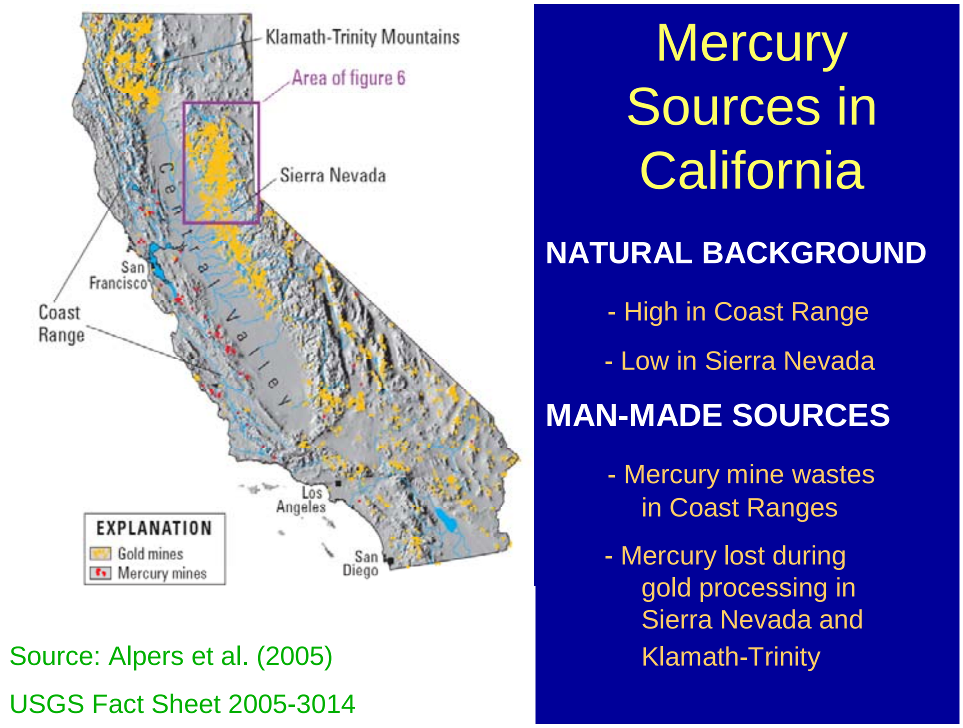
Figure 4-2
Summary of Sediment Biotic Ligand Model (DiToro)

Kevin Farley, Manhattan College (New York, NY), presented on a recently developed "Unit World" model for metals in lakes. The model simulates a single, well-mixed water column overlying a sediment layer and includes both metals speciation dynamics (partitioning, precipitation, organic carbon and sulfur cycling and metals impacts, and complexation) and biological toxicity calculations. The biological toxicity simulations follow the BLM described above. The model includes a user-friendly, visual basic interface and the intention is to make the model useable for both regulators and researchers. The simulation of internal water quality dynamics in this model appears to be on par with the most rigorous of the stream water quality modules described above but also includes the added feature of biological toxicity calculations. The model appears to be well-suited for use in combination with many of the watershed loading models described above.

Section 5
Mercury (Hg) Modeling

Nick Loux, EPA ORD (Athens, GA), presented on the challenges facing development of Hg models. A simple Hg simulation module is available in the current version of WASP, but lacks a mechanistic representation of many of the important processes associated with Hg in aquatic environments. Dr. Loux's talk focused on both the air-water interface exchange and water column speciation. Air-water exchange rates for all gases are dependent on a number of factors, including temperature, windspeed, water turbulence, Henry's Law constants, and potentially rainfall. Confounding factors affecting exchange rates specific to Hg include the fact that gaseous Hg is difficult to measure due to the sensitivity of the analytical equipment to sunlight and the fact that aqueous Hg exhibits a significant diel variation. Ionic Hg species in aqueous solutions undergo a large suite of competitive equilibrium reactions with environmental ligands such as hydroxides, chlorides, and sulfides. MINTEQ does an adequate job of simulating the aqueous speciation of Hg, but more data is needed to define the large number of equilibrium constants.

Charlie Alpers, USGS (Sacramento, CA), presented on modeling Hg loads in a mining-impacted watershed using the LOAD ESTimator (LOADEST) model (Figure 5-1). LOADEST is an empirical model developed by the USGS, and freely available to the public, that predicts time-variable mass loadings from a watershed using gaged flows and empirical regressions. These regressions describe contaminant loads as a function of flow and any number of other explanatory variables, such as time and season. Application of the model to mercury and sediment modeling in California mined watersheds and into receiving reservoirs was described. Sources of Hg in California watersheds include high background levels (coastal ranges), Hg mines, and gold mines (Hg lost during processing). For the study sites, there is a positive correlation between methyl Hg and stream temperature, and the highest Hg concentrations were measured during summer low flow periods. There was also an apparent seasonal variability in the relationship between Hg concentration and stream discharge. The hysteresis in concentration versus flow profiles, as described above, was also evident in the case study data presented here. Incorporating this behavior into the LOADEST model is a potential area of future work. In general, this type of empirical approach appears to be a good option when only downstream loads are of interest (rather than upstream mechanisms) and when both concentration and flow data are abundant.



Source: Alpers et al. (2005)

USGS Fact Sheet 2005-3014

Mercury Sources in California

NATURAL BACKGROUND

- High in Coast Range
- Low in Sierra Nevada

MAN-MADE SOURCES

- Mercury mine wastes in Coast Ranges
- Mercury lost during gold processing in Sierra Nevada and Klamath-Trinity

Figure 5-1
California Mercury Load Modeling Background Slide (Alpers)

Section 6
Synthesis and Discussion

The workshop included three open discussion forums during the course of the two days. Brian Caruso of EPA Region 8, facilitated these sessions. Key points of these discussions are summarized below.

The first session focused on stream metals models and the question of "are existing metals modeling tools good enough?" In other words, are the available models adequate, particularly with respect to stream modeling, to meet the needs of the regulatory, scientific, and engineering communities in tackling metals contamination problems? The general consensus was that the existing stream metals modeling tools are, for the most part, "good enough". It was agreed that the lumped K_D approach, employed by older versions of WASP and used in many past EPA studies, is probably valid over only a narrow range of systems. These could include systems with circum-neutral pH and metals concentrations that are not near saturation so that precipitation reactions are not dominant. However, it was also agreed that the more sophisticated available alternatives are generally adequate for those systems that fall out of this range; e.g., META4 and OTEQ which couple the equilibrium chemistry of MINTEQ with the transport simulations of WASP and OTIS, respectively. That being said, it was noted that all of these models are "living" tools and will continue to be updated and enhanced in the future. In this vein, the term "model validation" was discouraged as it implies a final "stamp of approval" for a model to be used in the future without the discretion that is needed. It was generally agreed that the term "model evaluation" may be more appropriate for describing the broad approach of applying, testing, and refining these models for better performance with time and for evolving needs.

Discussion during the first session also focused on the fact that, while the necessary numerical tools may be available, the data to adequately test, evaluate, parameterize, and further refine these models are lacking. The rate of model development has outpaced the supporting data collection, likely primarily due to cost and other resource constraints. In particular, there has been little opportunity to perform "post auditing" on the developed models due to both a lack of long-term data sets and funding. Future efforts should focus on data collection, as well as experimental controlled studies, designed specifically to test, evaluate, and better parameterize the existing modeling tools. The concept of a "study" watershed for collaborative, long-term model development and evaluation was discussed. The general lack of support from agency management and decision-makers for model application and evaluation, due to a number of factors, was also discussed as a major factor inhibiting further successful development and use of these models.

The second discussion session focused on watershed metals models. Participants raised many of the same issues as described above. In general, the existing watershed models, particularly for metals, need further testing and evaluation using real data. However, it was recognized that the collection of such data is more complicated for watersheds compared to streams. There are more parameters to quantify, and many of those parameters, such as antecedent soil conditions and groundwater organic carbon concentrations, are very difficult to measure. In fact, truly calibrated water quality watershed models are hard to find in past work. An approach discussed in this workshop for calibration and evaluation of watershed models is to utilize output probability distributions as a basis of comparison rather than relying on single-scenario, deterministic results. The bioavailability of predicted concentrations should also be included in such evaluations. It was noted that tracers, both added and natural, may be a good option for calibrating watershed models as they can help define both hydrologic pathways and specific contaminant sources.

The final discussion session of the workshop reiterated many of the conclusions described above. Existing metals modeling tools need further application, evaluation and testing, and this process needs to be supported by better data collection. This need is evident in the results of the Stratus Consulting, Inc. (Ann Maest) EIS review. Among other things, this review showed that, of the 15 mines investigated with existing surface water quality standard exceedances, 11 had predicted no exceedances (given the planned mitigation) at the time of the EIS. In other words, nearly 75% "got it wrong" using a variety of predictive methods. Clearly, improvements in the use and accuracy of numerical models for these types of systems are needed. Along these lines, it was recommended that models be used to guide sampling programs, and that programs iterate between modeling and data collection. Models should also generally be applied and evaluated more, with the proper empirical support, by the regulatory community. Skepticism needs to be overcome through further model evaluation, education, and increased interaction between scientists/model developers and regulatory decision-makers. Well-executed modeling studies have the potential to contribute to greater success and long term cost savings in monitoring and remedial activities. As a component of these activities, the cost of the modeling can be a fraction of the total investment. Workshop participants suggested that EPA should continue to facilitate and enhance the interaction between model developers and users.

Other significant points raised during the final discussion session include:

- Hg, which has garnered a lot of attention by EPA recently, is in a "different category" than other metals. It is more complex than the other metals, is in need of significant research and model development, and also requires additional data collection for model development and application
- An inventory, and comparison, of both available metals modeling tools and available data sets would be very valuable
- DOC is an often-overlooked parameter in data collection, given its importance to metals modeling, and toxicity assessments
- Models are valuable tools for interpreting existing data and understanding processes, in addition to their use in projecting future conditions

- EPA should identify "benchmark" models and ensure that they are maintained and updated.

The workshop concluded with the general consensus that the event was highly valuable to those in attendance and a significant step in the right direction toward improving metals fate and transport modeling, as well as communicating about such models. The EPA was congratulated on hosting a valuable workshop, and follow-up discussions, along with appropriate funding for future technical meetings,were recommended.

Appendix A
List of Attendees

US EPA Metals Fate and Transport Modeling Workshop
Region 8 Office, Denver, CO
February 13-14, 2007

ATTENDEES

	Name	Email	Organization	Presentation Title
1	Brian Caruso	caruso.brian@epa.gov	EPA ORD & Region 8 - Denver, CO	EPA metals fate and transport modeling issues in high-elevation, mining-impacted watersheds and streams
2	Tim Cox	CoxTJ@cdm.com	CDM - Denver, CO	Numerics and mass conservation considerations of metals stream transport models
3	Al Medine	amedine@comcast.net	Water Science and Engineering - Boulder, CO	Metals Exposure and Transformation Assessment (META4) model
4	Barb Butler	butler.barb@gmail.com	Colorado School of Mines - Golden, CO/ EPA ORD - Cincinnati, OH	Comparing equilibrium and transport modeling predictions to observed particulate metal transport in a mining-impacted stream
5	David Parkhurst	dlpark@usgs.gov	USGS - Denver, CO	Current capabilities of reaction and transport models PHREEQC and PHAST
6	Rob Runkel	runkel@usgs.gov	USGS - Denver, CO	One-dimensional Transport with EQuilibrium chemistry (OTEQ): An equilibrium-based model for reactive transport in streams and rivers
7	Andrea Marion	marion@idra.unipd.it	University of Padua, Italy	Residence time modelling of hyporheic flows
8	Ken Bencala	kbencala@usgs.gov	USGS - Menlo Park, CA	Tracer identification of groundwater-surface water interactions and hyporheic exchange flows: sorting through non-point sources to in-stream loading
9	Mike Wireman	wireman.mike@epa.gov	EPA Region 8 - Denver, CO	Use of mutliple isotopes to asses sources and flowpaths
10	Pierre Julien	pierre@engr.colostate.edu	Colorado State University - Ft Collins, CO	CASC2D/TREX development history and/or grid-scale effects for erosion and/or snowmelt simulation
11	Mark Velleux	mvelleux@hydroqual.com	Hydroqual - Mawah, NJ	Simulation of watershed-scale metals transport: Application to California Gulch
12	Billy E. Johnson	Billy.E.Johnson@erdc.usace.army.mil	USACE ERDC Environmental Laboratory - Vicksburg, MS	USACE's development of a watershed-scale contaminant transport and fate model, lab tests and Camp Shelby
13	John England	jengland@do.usbr.gov	Bureau of Reclamation, Flood Hydrology - Denver, CO	Simulating extreme storms, implications for modeling transport at different spatial scales
14	Kirk Nordstrom	dkn@usgs.gov	USGS - Boulder, CO	Problems with geochemical modeling of iron and aluminum in acidified surface and ground waters
15	Ann Maest	amaest@stratusconsulting.com	Stratus Consulting - Boulder, CO	Predicting water quality at hardrock mines
16	Dominic DiToro	dditoro@ce.udel.edu	University of Delaware	Water Column, Sediment and Soil Criteria for Metals: Applications of the Biotic Ligand Model
17	Kevin Rader	Krader@ce.udel.edu	University of Delaware	Developing a Unit World Model for Metals in Rivers and Streams
18	Kevin Farley	kfarley@manhattan.edu	Manhattan College - NY	Unit World Model for Metals in Lakes
19	Rich Carbonaro	richard.carbonaro@manhattan.edu	Manhattan College - NY	Applications of linear free energy relationships for modeling metal binding to natural organic matter
20	Jim Ranville	jranvill@mines.edu	Colorado School of Mines - Golden, CO	Seasonal variations in metal speciation and predicted toxicity in the North Fork of Clear Creek
21	Nick Loux	Loux.nick@epa.gov	EPA ORD - Athens, GA	Issues in Simulating Elemental Hg Air/Water Exchange and Aqueous Monomethylmercury Speciation
22	Charlie Alpers	cnalpers@usgs.gov	USGS - Sacramento, CA	Estimation of mercury, methylmercury, and sediment loads in Sierra Nevada rivers using LOADEST
23	James Martin	jmartin@engr.msstate.edu	Department of Civil Engineering, Mississippi State University	None
24	Katie Walton-Day	kwaltond@usgs.gov	USGS - Denver, CO	None
25	Kathleen Smith	ksmith@usgs.gov	USGS - Denver, CO	None
26	Philip Verplanck	plv@usgs.gov	USGS - Boulder, CO	None
27	Seema Shah-Fairbank	sshah@engr.colostate.edu	Colorado State University - Ft Collins, CO	None
28	Marcella Hutchinson	hutchinson.marcella@epa.gov	EPA Region 8 - Denver, CO	None
29	Roger Olsen	olsenrl@cdm.com	CDM - Denver, CO	None
30	Daniel Reeder	dreeder@summitusa.net	Summit Technical Resources - Denver, CO	None