CENTER FOR THE STUDY OF METALS IN THE ENVIRONMENT
Annual Report

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The Center for the Study of Metals in the Environment is a multi-institutional consortium of scientists and engineers working to further the understanding of processes affecting the fate and effects of metals in aquatic and terrestrial ecosystems. Significant gaps in the ability to predict the fate and effects of metals in both aquatic and terrestrial systems continue to hamper appropriate risk assessments and cost-effective risk management. In these situations, decisions include many assumptions and the application of safety factors. The focus of the Center is to develop appropriate information so that regulatory decisions will be based on sound scientific principles. Much of the existing methodology for hazard identification and for risk assessment is based on experience with persistent organic pollutants such as DDT and PCBs. The large differences in environmental behavior and potential for toxicity between organic compounds and metals are not incorporated into these methods. Assessment methodology is currently focused on the extent to which chemicals exhibit PBT (persistent, bioaccumulative, and toxic) characteristics. All three characteristics are important aspects of the assessment of risk, but their applicability to metals and the evaluation of metals data for these criteria differ from organic compounds.

As a replacement for the current methods for evaluating the effect of metals in the environment, the Center is developing a model for the behavior of metal compounds that can be used as a tool in the hazard assessment of metals and metal compounds. This model will include the physical and chemical mechanisms that control the fate and resulting bioavailability of metals discharged to natural waters. In particular the transformations that affect metal fate and toxicity will be included. It is anticipated that it would be similar to the Unit World models, for example EUSES that are used for evaluating PBT organic chemicals. Metal behavior in watersheds, streams, lakes and reservoirs will be considered. The focus of the research efforts is to provide the information necessary to formulate and parameterize the model.

Unit World Model for Metals in Aquatic Environments

Introduction

There is a clear need for methods that can be used for evaluating the environmental hazard associated with the release of metals and metal compounds to the environment (Adams et al., 2000). The purpose of the Unit World Model (UWM) is to provide such a framework. The idea for a UWM comes from the fugacity and regional models developed for organic chemicals (Mackay 1979, 1991, Mackay et al. 1992). Models of this sort have previously been applied in various forms to pesticides (USEPA, 1986) and industrial organic chemicals (European Commission, 1996). The UWM for metals is structured such that it can be used to estimate both the exposure and effects of metal and metal compounds. It will incorporate the necessary metal specific processes that differentiate the behavior of metals from organic chemicals.

Approach

The Unit World Model is designed to represent the major processes that determine the fate and transport of metals in the aquatic environment. In the water column these processes include solubilization for particulate metal compounds, speciation among inorganic and organic dissolved

ligands, and partitioning to suspended particles. The WHAM series of aqueous speciation models (Tipping, 1994) have been extensively calibrated and are well suited for incorporation in the UWM. A metal particle sorption model (SCAMP) has also recently become available (Lofts and Tipping 1998). Although not as well calibrated, it provides a useful starting point.

The sorption of metals to water column particulate matter leads to the transfer of the metal to the bottom sediments. Hence, sediments are the ultimate repositories of metals in aquatic settings. A number of sediment models have been developed that successfully predict levels of sulfide (AVS–Acid Volatile Sulfide) and partitioned metal (SEM) in sediments and resulting fluxes of dissolved metal from the sediments to the overlying water column (Di Toro, 1996; Carbonaro, 1999; Di Toro, 2001). Therefore the frameworks exist for at least most of the processes, in various stages of development, for the water column and sediment compartments.

Effects Concentration and Bioavailability

In addition to the exposure concentrations in the water column and sediment, it is necessary to predict the effects to be expected. The traditional method is to use an effects concentration for the water column and the sediment. For the water column the EPA Water Quality Criteria (Stephan et al., 1985, USEPA 1986, 1996) or the PNEC (Predicted No Effect Concentration) derived following the EU Technical Guidelines (EU, 1996) are possibilities. However, these criteria make only limited bioavailability corrections (for water hardness only). This is a much more critical issue for metals than for organic chemicals. To remedy this situation, the Biotic Ligand Model (BLM) has recently been developed (USEPA, 1999, 2000; Di Toro, et al., 2001; Paquin et al., 2002). It incorporates the WHAM speciation model and in addition models the competitive metal binding at the toxic site of action (the Biotic Ligand). BLMs are currently available for copper and silver (Di Toro, et al., 2001; Santore et al., 2001), zinc (Santore et al., 2002) and are under development for cadmium, nickel and lead.

The situation in the sediment is similar. There are guideline values that do not take bioavailability into account–the sediment PNEC–or which are empirical and therefore are not predictive of individual metal toxicity (e.g. Long and Morgan, 1991; Field et al., 2002).

For metals, EPA has developed sediment quality guidelines that are causally related to metal effects and do take bioavailability into account. They are based on the relative magnitudes of acid volatile sulfide AVS and simultaneously extractable metal SEM, and organic carbon (Di Toro et al., 1990, 1992; Ankley et al., 1993, 1996; USEPA, 2000).

Unit World Model Design and Testing

The design of the UWM is based on the processes required for calculating both the exposure concentration and the variables required for making the bioavailability corrections for the effects concentration. Since the model is expected to be used for site-specific evaluations as well as in regulatory settings, it needs to be predictive to the extent possible. This forces a more complex model structure than would be necessary for a strictly evaluative model with fixed physical, chemical and biological variables. The UWM is being built using a water column/sediment eutrophication model as a basis (Di Toro, 2001). Modern eutrophication models compute most of the required auxiliary variables required for metal modeling–carbon and sulfur cycles–and water column/sediment models for manganese and iron are also available, which are required for metal partitioning.

The steps in producing the model are to synthesize the available components into a unified modeling framework, and then to test the model with laboratory and field data for a variety of metals. The testing will begin with experiments in which a suite of metals were added to freshwater (Diamond, 1990) and marine (Santschi, 1987) mesocosms, and a long term dosing experiments to a Canadian lake (Hesslein, 1980). There is one data set (O'Connor 1988) that can be used for calibrating the model to freshwater streams. However, it is somewhat limited and it was not collected using modern clean techniques. It is anticipated that most of the data for streams will need to be generated.

Project Summaries

The Center's Science Advisory Committee (SAC) met in May 2003 to review proposals for research. Nine projects, each of which had been proposed for a 3-year period, were approved. These projects are

Investigator	Institution	Project Title
Ranville, J./ Ross, P.	Colorado School of Mines	Ecotoxicology of Mining-Related Metal Oxides in a High Gradient Mountain Stream
Allen, H. E.	University of Delaware	Modeling Cu and Zn Desorption Kinetics from Soil Particles
Church, T.	University of Delaware	Metal Speciation in Watersheds
Di Toro, D. M./ Farley, K.	University of Delaware Manhattan College	Developing a Unit World Model for Metals in Aquatic Environments
Imhoff, P./ Allen, H. E./ Dentel, S. K.	University of Delaware	Evaluation of Automobile Sources for Metals in Urban Areas
Sparks, D.	University of Delaware	The Impact of Surface Precipitation on Sequestration and Bioavailability of Metals in Soils
Capitani, J.F./ Di Toro, D. M.	Manhattan College University of Delaware	Quantitative Structure Activity Relationships for Toxicity and Fate Parameters of Metal and Metal Compounds
Wronkiewicz, D./ Adams, C. D.	University of Missouri-Rolla	Transport Processes of Mining Related Metals in the Black River of Missouri's New Lead Belt
Meyer, J. S.	University of Wyoming	A Test of the Biotic Ligand Model: Fish Exposed to Time-varying Concentrations of Copper and Zinc

Reports of the results of activities for each of these projects are contained in Appendix I. A brief summary of each project is presented here:

Ranville, J. and Ross, P. Colorado School of Mines "Ecotoxicology of Mining-Related Metal Oxides in a High Gradient Mountain Stream"

The principal objective of the research has been to support the development of the Unit World Model for metal transport in streams. Research has focused on the Clear Creek watershed located west of Denver, Colorado, a high-gradient stream with a large degree of seasonal variation in stream flow due to the predominant contribution of spring snow melt. Investigation of the seasonality of metal transport focused on three sites: CCSW-40, an upstream site on the main-stem of Clear Creek; NCCSW-50, a site on the North Fork, a major tributary draining a mining impacted area; and CCSW-60, a downstream site on the main stem of Clear Creek. During the past two years, samples have been collected monthly during winter and every two weeks for other seasons. Discharge varied from 40-1200 cfs at CCSW-40, 2-120 cfs at NCCSW-50, and 10-1200 cfs at CCSW-60. This variability allowed for the investigation of the relationship between discharge and metal transport.

Although the mine effluents are acidic, dilution and neutralization result in pH's that range from about 6.5 to 8 for all three sites. This pH range favors metal transport on suspended sediments. The

seasonal variation in metal concentrations is quite different depending on the metal investigated. Zinc and manganese show a clear seasonal trend where metal levels are diluted during spring runoff and increase over the summer, fall and winter. This is explained by the variation in the relative contribution to overall stream flow by the mining effluents and the drainage from the watershed. Copper and iron show more annual uniformity but their concentrations are characterized by spikes associated with extreme events. This is consistent with the greater amount of these metals that is associated with particulates, and is likely explained by re-suspension of precipitated bed sediments.

One question to be addressed is whether a simple "K_d" approach will be successful for describing metal partitioning. Normalizing the particulate metal (mg M/ kg) to the total suspended sediment (TSS) and dividing this by the dissolved metal concentration (mg M/ L) gives a "K_d" that can be used to describe metal association. Presuming that the dominant sorbent phase in the suspended sediments is hydrous ferric oxide (HFO), the particulate metals were also normalized to particulate iron content. Assuming HFO = 50% Fe, the Fe-normalized log K_d's for copper [(mg Cu/kg HFO)/(mg Cu/L)] were: 6.1 at CCSW-40, 5.8 at NCCSW-50, and 6.1 at CCSW-60. For zinc, the Fe-normalized log K_d's [(mg Zn/kg HFO)/(mg Zn/L)] were 5.6 at CCSW-40, 4.8 at NCCSW-50, and 5.3 at CCSW-60. To investigate further the role of HFO in metal transport, the field data are being modeled with a surface complexation model (SCM) using the MINTEQA2 code. Our goal is to determine if the SCM approach is superior to a simple K_d to describe metal association with suspended sediments.

Allen, H. E. University of Delaware "Modeling Cu and Zn Desorption Kinetics from Soil Particles"

Our objective is to develop predictive models for kinetics of Cu and Zn desorption from soil particles under effect of both solution chemistry (e.g., pH, dissolved organic matter (DOM), Ca) and soil compositions (e.g., soil organic matter (SOM), soil metal content).

Cu and Zn desorption experiments were conducted with a stirred-flow method. We used two spiked soils collected from Delaware and Maryland which have similar soil compositions. DOM was collected from Edisto River in South Carolina. The experiment was design to test different solution conditions, including four pHs (5.5-7.2) which covered general soil solution pH range, four DOM concentrations (3.8 – 15 mg/L) which are common DOM concentrations in surface water, four Ca concentrations (1 mM to 10 mM) and four flow rates (0.5 to 4 mL/min). We found increase of pH inhibited both Cu and Zn desorption rates which corresponds to less proton competition at higher pH. DOM greatly enhanced the Cu desorption rate, but it had little effect on Zn desorption. This is due to stronger binding ability of Cu to DOM than Zn. Ca had a much smaller effect compared with pH and DOM when Ca concentration varied from 1 mM to 10 mM. Increase of flow rates also increased both Cu and Zn desorption. Overall, pH and DOM are two key solution parameters controlling Cu desorption kinetics, but for Zn pH is the dominant solution factor.

One adsorption/desorption kinetics model was developed based on mass balance of the flow system in this study. We considered that soil metal was bound in two different kinds of sites, one fast release site and one slow release site. The distribution of metals between these two sites may be dependent on the total metal concentrations. For Cu, at low soil metal concentrations, one slow release site is enough to describe Cu desorption kinetics. For Zn, two sites, one fast and another slow site, are necessary. The fast release site contributed the Zn release in the beginning time period and the slow release site accounted for the slow "bleeding" of Zn. Different from most previous models, we incorporated basic chemical reactions between metals and soil particles into our model. These include proton competition, metal and DOM complexation, and SOM dissolution from soil particles. All experimental data were fit globally and then we obtained one unique set of kinetics parameters that can be applied to different conditions. Based on our model results, the pH effect can be handled as proton competition for the soil surface binding sites which affected adsorption/desorption rate coefficients. The DOM effect is through DOM complexing solution metal ions which decreased metal ions re-adsorption

onto soil particles. Cu forms strong Cu-DOM complexes which have comparable reaction kinetics compared with Cu and soil particles adsorption/desorption, but Zn does not. The rate coefficients obtained from our model are similar for the two soils we used. This supported our assumption that SOM content is the most important soil parameter controlling Cu and Zn desorption kinetics. In the modeling, we also found adsorption kinetics experiment is necessary to identify the two sites and understand the mechanisms.

Church, T. University of Delaware "Metal Speciation in Watersheds"

We are sampling waters in both fresh (Potomac) and marine (Delaware Inland Bay) watersheds. The sampling spans the range of pristine, urban and estuarine conditions.

Confirmed is the high proportion of particulate metals in the main stem of the Potomac even at high flow, as was observed previously under average flow. This is unlike most major Potomac tributaries where the metal loading was observed to be predominantly dissolved. Thus one aim of the modeling will be to ascertain the underlying cause of this gross redistribution. One hypothesis is that this is caused by the marked increase in pH during warmer seasons and downstream in the mainstem. This is consistent with increasing eutrophication and net photosynthesis, and perhaps organic ligands bound to surface active particles. Here also, there is a presence of reduced sulfur in the hundreds of micro-molar range. Presumably, this is due to reduction of the dominant anion sulfate from either acid rain or mine drainage. As these exceed by an order of magnitude the levels of dissolved Cu and Zn, it is possible that sulfide complexation could exert dominant control of the inorganic speciation and availability that could rival the organic complexes in strength, if not in amount.

In the saline Inland Bay Watersheds, sulfide complexation dominates organic complexation. This is evident during the electrochemical analysis of Zn for example in the presence of organic ligand-bound zinc. In the presence of sulfide under reducing conditions, the fraction of organic ligand-bound zinc vanishes. Indicated are different Zn-organic ligands in surface waters (2 separate ligands observable) and bottom waters (only one ligand observable). These have different ligands based on the increase in current at different potentials. However, these ligands make up only a fraction of the total Zn. Other stronger complexes exist and may be related to sulfide. In any case, dominant Zn-sulfide complexes form when sulfide is added or present at levels higher than the Zn concentration.

Di Toro, D. M. University of Delaware and Farley, K. Manhattan College "Developing a Unit World Model for Metals in Aquatic Environments"

The objective of our study is therefore to develop a more reliable model for regulatory decision making. For this purpose, we are considering an intact aquatic environment (i.e., a "unit world") for several idealized environments including a stratified lake, a shallow lake, a high-gradient stream, and a low-gradient stream or river. Based on discussions at a workshop held at the University of Delaware in February 2003, development of the "unit world" model is following a three tiered approach with consideration given to simple and more complex models to describe the fate and effects of metals in lakes, rivers and streams.

Initial emphasis in the project has been on lakes. For Tier 1, we are developing a simple modeling tool that describes the fate and effects of metals in a vertically well-mixed lake over an active sediment layer. The distribution of metals between dissolved and particulate phases is described by partitioning to DOC and POC using the WHAM V formulation (Tipping 1994). This approach has been tested using data from enclosure studies in a Canadian soft water lake (Perch Lake: Diamond et al. 1990) and a Swiss high alkalinity, hard water lake (Lake Baldegg: Gachter and Mares, 1979). Results show that the simple partitioning Tier 1 model can be fitted to metal data from the Perch Lake and Lake Baldegg enclosures. Metal partition coefficients for the water column were described reasonably well using WHAM V for zinc, iron and mercury in Perch Lake, and zinc and copper in Lake Baldegg. For other metals including cobalt in Perch Lake and mercury, cadmium and lead in Lake Baldegg, WHAM

V underpredicted the partitioning of metals, an occurrence that may possibly be explained by $Co_3O_4(s)$ precipitation in Perch Lake and carbonate precipitation in the high alkalinity waters of Lake Baldegg. Overall, the Tier 1 modeling studies yielded promising results, especially in the ability of WHAM V to calculate changes of up to an order of magnitude in metal partition coefficients due to the differences in the water chemistry for the two lakes. The Tier 1 model is currently being extended to assess metal bioavailability and fate by direct incorporation of the Biotic Ligand Reactions (DiToro et al., 2001; Paquin et al., 2002) into the modeling framework.

Although the Tier 1 model provides a reasonable description of metal behavior in the lake enclosure studies, the model has two major shortcomings: 1) DOC and POC concentrations are considered as fixed quantities in model calculations, and 2) sulfide generation and metal sulfide precipitation, which are important processes in binding metals in sediments, are not considered. We are therefore constructing a more complex Tier 2 model that considers a layered water column that is subject to thermal stratification, and includes descriptions for algal dynamics, organic matter decomposition, and nutrient cycling. Organic carbon decomposition, sulfide generation and nutrient recycling from sediments are also being considered by linking the water column model to the Sediment Flux Model (Di Toro, 2001). Metal-specific processes such as partitioning of metals to DOC, POC and algae, metal sulfide precipitation, and binding to the "biotic ligand" will then be added to the Tier 2 model. The completed model will allow us to assess time-variable fate and effects of metals in lakes, and allow more detailed evaluations of metal loadings and other external forcing factors. The Tier 3 model for lakes will follow a similar framework and will likely include more detailed spatial resolution for site-specific applications of the model.

A similar development of a "unit world" model for rivers and streams is also underway. To date, we have analyzed field data from Clear Creek in Colorado and the Big River in Missouri. (These data are being collected as part of other Center projects.) Preliminary results show that total metal concentrations in the streams are largely described using a simple dilution model. More detailed evaluation of the data is underway. Because of the mineralogy of the two watersheds, we anticipate that our simple Tier 1 modeling approach for lakes will need to be expanded to include not just the affects of transport, but also the partitioning of metals to iron oxide surfaces (e.g., following the approach of Dzombak and Morel, 1993).

Imhoff, P., Allen, H. E., and Dentel, S. K. University of Delaware "Evaluation of Automobile Sources for Metals in Urban Areas"

Artificially brake pad particles were generated by grinding or sanding brake pads removed from our test automobiles. Grinding generated particles approximately 5 to 10 times larger than natural debris, while sanding produced particles of similar size (1-10 μm) to those collected from the wheels and hubs of automobiles, what we term "natural" wear debris. Specific surface areas and Cu composition differed between the artificial and natural particles. For sanded particles, which were expected to be most similar to natural debris, specific surface areas differed by as little as 30% and up to a factor of 10 between artificial and natural particles, depending on the vehicle type. Cu contents also differed among particle type depending on the vehicle, with differences ranging from 40% to a factor of 10, with Cu content always higher for the artificial particles than the natural particles.

Selected artificial and natural wear debris were analyzed using SEM and XEDS to assess particle sizes and distribution of elements on particle surfaces. SEM analyses verified that the artificial (sanded) and natural particles were of similar size. XEDS data suggest that some elements are preferentially distributed among particles. For example, in natural particles Fe was primarily associated with the largest particles while Cu appears to be associated with smaller particles. This may have implications for the rate of Cu leaching from natural wear debris.

For buffered leaching solutions with pH = 4.2-4.3, 80% to 100% of the Cu in the artificial and natural particles was leached after 6 days in batch reactors. This "dissolved" Cu was operationally

defined as Cu passing 0.45-micron filter, and most was Cu^{+2}. For the natural particles, the Cu dissolved quickly with over 80% of the mass leached in the first 24 hours, for the brake wear debris analyzed thus far. For the artificial particles, the rate of dissolution was typically slower, with more than 100 hours required for greater than 80-90% of Cu to be leached.

Brake pad wear debris (artificial and natural) from one automobile was leached using the synthetic rainwater. The initial pH = 4.2-4.4, but this quickly increased to pH greater than 6.0 after 5 hours, eventually reaching a stable pH = 6.8 after 90 hours for the natural particles. For this leaching solution and set of natural particles from a single vehicle, only 7-8% of the Cu in the natural particles was leached after 150 hours. The smaller mass leached from the synthetic rainwater versus the buffered solution with pH = 4.2-4.3 is likely due to differences in pH.

Sparks, D. University of Delaware "The Impact of Surface Precipitation on Sequestration and Bioavailability of Metals in Soils"

The objectives of this study are to investigate the formation and residence time of metal precipitate phases, particularly metal hydroxides, in contaminated soils under a range of environmental conditions and the effect this formation has on metal availability and sequestration in field contaminated soils. Sorption, sequestration, and precipitation of metals within the soil matrix are critical processes affecting contaminant speciation, toxicity, transport and bioavailability. Unfortunately, there is a lack of fundamental understanding of these processes in natural soil systems at a molecular, mechanistic level. In order to improve the decision making process and develop reliable risk assessment methods, it is necessary to acquire a more thorough understanding of the processes controlling metal mobility, speciation and bioavailability in contaminated soils.

Previous research has shown that polynuclear metal hydroxide complexes and surface precipitates can form on the surfaces of clay minerals and metal oxides for a number of metals of environmental interest, particularly Ni, Zn and Cr. Research from our group has shown that Ni and Zn sorption on Al-bearing clay minerals, metal oxides, and soils results in the formation of mixed metal-Al hydroxide precipitates similar to layered double hydroxides, rather than the metal hydroxide compounds found in non-Al bearing minerals. As the surface precipitates age, metal release decreases substantially, indicating increased stability of the metal hydroxide phases. Thus, these phases may play an important role in reducing metal mobility and bioavailability in natural systems. While mixed metal-aluminum hydroxide phases have been observed primarily on model substrates. Roberts et al. (2002) showed that mixed metal-Al hydroxide phases formed on the clay fraction from a Delaware soil when reaction pH was greater than 6.8, and Nachtegaal et al. (2004) have recently shown that both mixed metal-Al and metal phyllosilicate phases occur in Zn-contaminated and remediated soils, respectively, from Belgium. However, questions still remain as to the prevalence of metal hydroxide precipitates in field contaminated soils and, particularly, under what environmental conditions (soil pH, organic content, etc.) their formation and stability occurs.

The specific hypotheses being tested in this research are:

- 1. The formation of polynuclear metal hydroxide complexes and surface precipitates, particularly layered double hydroxides, could play a significant role in trace metal speciation and sequestration in contaminated soils with pH levels ≥ 6.5.
- 2 Formation of these precipitates sequesters metals into stable phases of low bioavailability, reducing their toxicity to the surrounding ecosystem.

Testing of the first hypothesis involves a two-step approach. In the first step, metal speciation studies of laboratory contaminated soils will be used to determine the parameters controlling the formation of layered double hydroxide (LDH) phases. The role of environmental variables such as pH, organic matter and aluminum solubilization from the underlying clay substrates will be carefully examined. The results of these initial experiments will be used to screen our database of approximately

40 contaminated soils for those which can potentially support the formation of these LDH phases. Soils meeting these criteria will then be examined to determine whether these phases are actually present, and whether they contribute substantially to the overall speciation of the contaminant metal. In both steps of this project, speciation information will be obtained primarily through the use of x-ray absorption spectroscopy. BIOMET analysis of metal bioavailability in these soils will be carried out to determine the effect of precipitate formation on metal sequestration and toxicity.

XAFS results from three soils (Berry land loamy sand, Matapeake silt loam, and Fort Ellis clayey soil) spiked with a Ni containing solution indicate the presence of mixed nickel-aluminum hydroxide precipitate phases at pH $\geq$ 7 in the Berryland and Matapeake soils. Kinetic studies indicate that formation of these LDH phases can occur within 12-24 hours under favorable conditions. The presence of higher concentrations of organic matter can significantly retard the rate of precipitate formation, although these effects are less noticeable as the pH increases. Desorption experiments are also consistent with the formation of surface precipitate phases, while longer aging times result in decreased release of Ni from the soils where LDH phases are present. These results suggest that the availability of Al for release from the mineral substrate plays a dominant factor in determining whether Ni-Al hydroxide phases form in soils. Organic matter also may inhibit formation of these phases, particularly at lower pH. Preliminary thermodynamic analysis indicates that the stability of these phases would increase with the presence of carbonate or silicate anions in the interlayer. An evaluation of whether the increased long term stability of these precipitates results from surface transformations to phyllosilicate phases is ongoing.

Capitani, J.F. Manhattan College and Di Toro, D. M. University of Delaware "Quantitative Structure Activity Relationships for Toxicity and Fate Parameters of Metal and Metal Compounds"

The purpose of this research project is to develop quantitative structure activity relationships (QSARs) for metals for which little or no experimental information exists. The parameters of interest are those required for the Unit World Model. Unlike the most studied metals, Cd, Cu, Ni, Pb, and Zn, or metals that have recently been of concern, for example Ag, very little data are available for the rest, particularly the transition metals in the third and fourth rows and the lanthanides. The Unit World Model uses both the WHAM partitioning model and the biotic ligand model (BLM). WHAM requires complexation constants to humic and fulvic acid sites in order to predict partitioning to DOC and POC. In addition the BLM requires the binding constant and critical site density of the BLM. These are the parameters for which QSARs will be developed.

The QSARs will be developed in two steps. First relationships between the parameters of interest and binding constants to simple ligands will be developed. An example is the regression equation suggested by Tipping between the metal- humic acid binding constant in WHAM and metal-lactate binding constants. This regression requires that both these binding constants are known. However, for many metals, the metal-lactate binding constant is unknown. Therefore the second step is to compute the metal-ligand binding constant using quantum chemical methods. This can be done in a number of ways. The simplest is to do the computation in the gas phase, using a simplified representation of water. These results are used to establish a regression of the gas phase – aqueous phase metal-ligand binding constant. These two regressions are then used to predict the parameter for the other metals. The quantum chemical method is used to compute the gas phase binding constant to the simple ligand. Then the two regressions are used to predict the aqueous phase metal - simple ligand binding constant and the WHAM and BLM constants.

Preliminary results for the regression of the WHAM humic acid and fulvic acid binding constant to the metal-hydroxide binding constant. In both cases the Log Ks are for the metal-proton replacement reaction.

$$M^{2+} + HL \rightarrow H^+ + ML^+$$
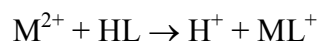
The strong binding of Hg influences the regression. However without Hg, the regression is still quite good: $R^2 = 0.95$ and 0.86 becomes $R^2 = 0.90$ and 0.72. We have also developed regression of the WHAM humic acid and fulvic acid binding constant to the metal- acetic acid benzoic acid binding constants. The idea is to use a molecular fragment – acetic acid or benzoic acid -- that more closely resembles the carboxylic acid groups that are thought to be the binding sites for metals in humic and fulvic acids. The benzoic acid results are quite promising and since benzoate is a carboxylic group attached to a benzene ring – much like the humic and fulvic acid sites – they have a chemical basis. The slopes of the regressions are nearly one (0.91) for humic acid and close to one (0.74) for fulvic acid.

Wronkiewicz, D. and Adams, C. D. University of Missouri-Rolla "Transport Processes of Mining Related Metals in the Black River of Missouri's New Lead Belt"

The West Fork of the Black River lies in a bicarbonate dominated river system which runs through Missouri's actively-mined New Lead Belt. Water chemistry, sediment composition, particle size distribution, mineral speciation, and stream flow data are being evaluated to characterize heavy metal transport processes during varying hydraulic events. Water and sediment samples have been taken and analyzed quarterly at six sites along the West Fork for seven separate time periods. Additional samples were also gathered in order to sample rising water conditions due to a storm event, to obtain data from locations upstream from the sampling reach, and to characterize the water quality and metals content of the tailings effluent as it enters the West Fork.

Five of the seven sampling periods exhibited normal flow conditions (no precipitation or disturbance events during sampling). Average flows on the West Fork of the Black River were estimated to vary between 34 and 288 cubic feet per second (cfs) during normal flow conditions. Average estimated flow was calculated using data taken at 12:00 noon at the Lesterville and Annapolis USGS gauging stations (downstream from our sampling sites), along with considering relative watershed sizes for the two gauging station locations and for the sampling sites along the West Fork.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) data for unfiltered water samples collected during normal flow conditions showed maximum lead and zinc concentrations of 6.7 μg/L and 163 μg/L, respectively. Lead concentrations were below the EPA Drinking Water Action Level for Pb (15 μg/L) except for samples taken at two sites samples during storm flow which had unfiltered sample lead concentrations of 65 and 21 μg/L. Lead concentrations showed no relation to flow while zinc concentrations generally increased with increasing flow.

Sediment samples showed a wide range of lead and zinc concentrations (3-960 mg/kg Pb and 4-2488 mg/kg Zn). Optical microscopy and Scanning Electron Microscopy (SEM) analyses of sediment samples indicated that metals were incorporated in manganese and iron oxyhydroxide minerals and coatings on sediment grains. Metal sulfides were not found in any sediment samples.

Analyses on a limited number of sediment samples did not show that organic content had statistically significant correlations with metals, but metal content generally increased with increasing organic content.

Meyer, J. S. University of Wyoming "A Test of the Biotic Ligand Model: Fish Exposed to Time-varying Concentrations of Copper and Zinc"

Our goal is to determine if the biotic ligand model (BLM) can be used to accurately predict the toxicity of Cu or Zn to fathead minnows (FHM; *Pimephales promelas*) under time-varying combinations of water quality parameters [e.g., pH, alkalinity, hardness, dissolved organic carbon (DOC) concentration, and/or meal concentration]. With initial funding from the Center for the Study of Metals in the Environment and part of the Year 1 funding for the current project, we conducted Zn toxicity tests in 2002 and 2003 to help parameterize the Zn BLM. Although a Cu BLM has been available for several

years, only a preliminary Zn BLM was available at the beginning of this project. Results of our toxicity tests of the modifying effects of major inorganic ions and dissolved organic matter (DOM) on Zn toxicity were used by HydroQual, Inc. to modify the preliminary model (see below), resulting in the most recent "research-only" Zn BLM that was made available earlier this year. With both BLMs in hand, we are using the remainder of Year 1 and all of Year 2 funding to conduct experiments with time-varying water quality parameters and Cu or Zn concentrations during Summer and Fall 2004.

In the toxicity tests conducted in support of development of the Zn BLM, we exposed larval FHM ($\leq$24 h old at beginning of the tests) to Zn for 96 h in a variety of water quality conditions (i.e., a series of pH values from 6 to 9; elevated concentrations of Ca, Mg or Na; and elevated concentrations of DOM from several sources). We conducted the tests in either flow-through mode (the pH tests and some of the Ca, Mg and Na tests) or static-renewal mode (some of the Ca, Mg and Na tests, and all DOM tests). Our standard dilution water (22°C, pH 7.5, alkalinity ~30 mg/L as $CaCO_3$, hardness ~50 mg/L as $CaCO_3$, DOM <0.5 mg C/L) was a mixture of well water and reverse-osmosis (RO) water, in which one water quality parameter was varied per test.

In the pH series, the 96-h Zn LC50 was slightly lower at intermediate pH values (~8) than at the extremes of the range we tested (pH 6 and 9), in general agreement with the preliminary Zn BLM. In tests with the major inorganic cations, we demonstrated that Ca^{2+} is protective against Zn toxicity to larval FHM but Mg^{2+} and Na^+ are not (whereas all three cations had been shown to protect *Daphnia magna* against Zn toxicity). In tests with DOM from a variety of sources, 96-h Zn LC50s did not increase until the DOC concentration exceeded 10 mg C/L. The protectiveness against Zn toxicity did not vary considerably among the DOM sources (Cypress Swamp, Edisto River, Suwanee River, and Wilmington Wastewater Treatment Plant), and the presence of high NaCl concentrations in some of the DOM isolates (caused by pre-treating the water with a Na-exchange resin) did not alter the protective effect of a low-Na DOM isolate (Suwanee River) to which we added 18 mM NaCl. Based in part on these results, the Zn BLM was modified to (1) approximately halve the density of Zn-binding sites on DOM and (2) decrease the Na-gill binding constant for FHM (but not for *D. magna*).

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APPENDIX I

Research Project Reports

Ecotoxicology of Mining-Related Metal Oxides in High Gradient Mountain Stream

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The principal objective of the research has been to support the development of the Unit World Model for metal transport in streams. The Unit World Model requires field data sets for calibration. Given that much of the previous data has been collected for lotic systems, data on high-gradient systems is lacking. These systems are expected to be more complex due to the variability in hydrologic conditions. We have focused on the Clear Creek watershed located west of Denver, Colorado. Clear Creek is a high-gradient stream which has a large degree of seasonal variation in stream flow. This is due to the predominant contribution to stream flow of snow melt during spring. Investigation of the seasonality of metal transport focused on three sites: CCSW-40, an upstream site on the main-stem of Clear Creek; NCCSW-50, a site on the North Fork, a major tributary draining a mining impacted area; and CCSW-60, a downstream site on the main-stem of Clear Creek. During the past two years, samples have been collected monthly during winter and every two weeks for other seasons. Discharge varied from 40-1200 cfs at CCSW-40, 2-120 cfs at NCCSW-50, and 10-1200 cfs at CCSW-60. This variability allowed for the investigation of the relationship between discharge and metal transport.

In the Clear Creek system, the metal sources are from abandoned mine sites that release acidity and dissolved metals. Direct erosion of metal-containing mining wastes or contaminated soils into the stream is generally considered to be minor, except for short-term storm events. Thus, metal-association with suspended sediments arises primarily from in-stream processes including precipitation, sorption, and re-suspension. The oxidation of ferrous iron and the neutralization of the acidic effluents after mixing with the stream results in the formation of iron-rich suspended sediments. The iron contents of the suspended sediments vary with stream flow and range from 1-20 % for CCSW-40, 4-45% for NCCSW-50; and 1-15 % for CCSW-60.

Although the mine effluents are acidic, dilution and neutralization result in pH's that range from about 6.5 to 8 for all three sites. This pH range favors metal transport on suspended sediments. The fraction of copper transport by suspended sediments ranges from 25-80% at CCSW-40; 60-100 % at NCCSW-50; and 30-90 % at CCSW-60. For zinc the ranges are: 5-60% for CCSW-40; 5-45 % at NCCSW-50; and 6-80% at CCSW-60. Additional sites along the North Fork have been sampled less frequently to further investigate the partitioning of metals to suspended sediments as they are transported downstream from the metal inputs.

The seasonal variation in metal concentrations is quite different depending on the metal investigated. Zinc and manganese show a clear seasonal trend where metal levels are diluted during spring runoff and increase over the summer, fall and winter. This is explained by the variation in the relative contribution to overall stream flow by the mining effluents and the drainage from the watershed. Copper and iron show more uniformity over season but their concentrations are characterized by spikes associated with extreme events. This is consistent with the greater amount of these metals that is associated with particulates, and is likely explained by re-suspension of precipitated bed sediments.

An important first step in developing the Unit World Model is in understanding the partitioning of metals between dissolved and sediment phases. This is likely to be more complex in a stream system compared to a lotic system. This may be especially true for a high-gradient stream like Clear Creek. One question to be addressed is whether a simple "K_d" approach will be successful for describing metal partitioning. Normalizing the particulate metal (mg M/ kg) to the total suspended sediment (TSS) and dividing this by the dissolved metal concentration (mgM/L) gives a "K_d" that can be used to describe metal association. Over the dates sampled, for copper the average log K_d [(mgCu/kg TSS)/(mgCu/L)] was found to be 5.2 for CCSW-40, 5.4 for NCCSW-50, and 5.1 for CCSW-60. The K_d's varied by about a factor of two over the two year sampling period, with no obvious seasonal trends. For zinc, the log K_d[(mgM/kg TSS)/(mgM/L)] was 4.8 for CCSW-40, 4.4 for NCCSW-50, and 4.4 for CCSW-60. The variation in K_d was similar to that found for copper.

Presuming that the dominant sorbent phase in the suspended sediments is hydrous ferric oxide (HFO) the particulate metals were also normalized to particulate iron content. Assuming HFO = 50% Fe, the log K_d's for copper [(mg Cu/kg HFO)/(mg Cu/L)] were: 6.1 at CCSW-40, 5.8 at NCCSW-50,

and 6.1at CCSW-60. For zinc, the log K_d's [(mg Zn/kg HFO)/(mg Zn/L)] were 5.6 at CCSW-40, 4.8 at NCCSW-50, and 5.3 at CCSW-60. To further investigate the role of HFO in metal transport, the field data are being modeled with a surface complexation model (SCM) using the MINTEQA2 code. Our goal is to determine if the SCM approach is superior to a simple K_d to describe metal association with suspended sediments. One current product of the research is the extensive seasonal database on the distribution of metals between dissolved and particulate phases. An additional product is an evaluation of two methods for determining the amount of metal associated with suspended sediments. This involved comparing direct analysis of digested suspended sediments to the difference in the analysis of filtered and unfiltered samples.

Future work will include applying the SCM to evaluating the role of different metal oxides (HFO, HMO) on metal transport. The SCM will be applied to both field data for suspended sediments and also laboratory investigations of pH-dependant metal sorption to HFO. HFO was prepared in the laboratory by raising the pH of an acidic mine effluent. This will be compared to bed sediments collected from sites downstream of mining inputs. We will also be evaluating a long-term (10 years of quarterly sampling) data set on dissolved and particlulate metal that has obtained for a large number of sites within the Clear Creek watershed by the Colorado Division of Public Health and Environment. Finally we plan at least two more sampling trips to obtain high spatial sampling along the North Fork to improve the dataset for investigating the downstream transport of dissolved and particulate metals.

Introduction

Acid-mine drainage (AMD) is an important source of metal contamination in regions of current or past mining of sulfide ores. AMD impacted streams pose toxicity risks to a variety of aquatic and sediment-dwelling organisms. In the Blackhawk-Central City area of the Colorado Mineral Belt, gold, silver, copper, lead, and zinc were extensively mined in the late 1800's (Wildeman et al., 1974; Cunningham et al., 1994; U.S. EPA, 1999). Effects from these past mining activities are still seen today in the Clear Creek Watershed (Ficklin and Smith, 1994; Morris et al., 1999). For example, the North Fork of Clear Creek (NFCC), a major tributary of Clear Creek, does not support fish in locations below AMD inputs (U.S. EPA and CDPHE, 1997).

AMD enters NFCC, near the towns of Blackhawk and Central City, and results in high concentrations of heavy metals, including iron, zinc, copper, and manganese in the water and the associated sediments. Once the metal-laden water mixes with the upstream NFCC water, there is a transformation from ferrous to ferric iron. This results in the visible precipitation of colloidal ferric oxyhydroxides. These colloids can scavenge other metals present in the water column, and can either be transported downstream or aggregate and then settle to the bed sediment (Stumm, 1992; Schemel et al., 2000).

Sediments accumulated on the streambed can be resuspended and transported. Deposition and scouring of metal-laden bottom sediments is mostly controlled by flow conditions in the stream. NFCC is an example of a high-gradient mountain stream, where flows are quite variable over the year and depend on seasonal (snow-melt, fall/winter low-flow) and short-term (localized rain storms) weather conditions. In addition, drought during 2002 resulted in the lowest recorded flows for Clear Creek and likely affected metal transport.

One goal of this research was to examine the spatial and temporal trends in both dissolved and suspended metal concentrations. A spatial study of NFCC was conducted in May 2002 and June 2004 with the Colorado Department of Public Health & Environment (CDPHE). Collection of temporal data at several sites in NFCC and the main stem of Clear Creek (CC) are ongoing. Both the dissolved phase and suspended sediments were analyzed for a variety of metals. This report presents and discusses spatial and temporal data (May 2002 to June 2004) for Fe, Cu, and Zn. The results of the chemical analyses were used to determine the relative importance of suspended versus dissolved transport of metals over the study period.

Methods

Sample Collection:

For the spatial study, water samples were collected along a reach of the North Fork Clear Creek with the assistance of the CDPHE in May 2002 and June 2004. All sites for which data were collected in 2002 are indicated on Figure 1. A subset of these sites were sampled in June 2004.   For the temporal study, water samples were collected 1 to 2 times per month starting in May 2002 at three sites (Kermit's SG, NFSG, and Golden SG) shown on Figure 1.
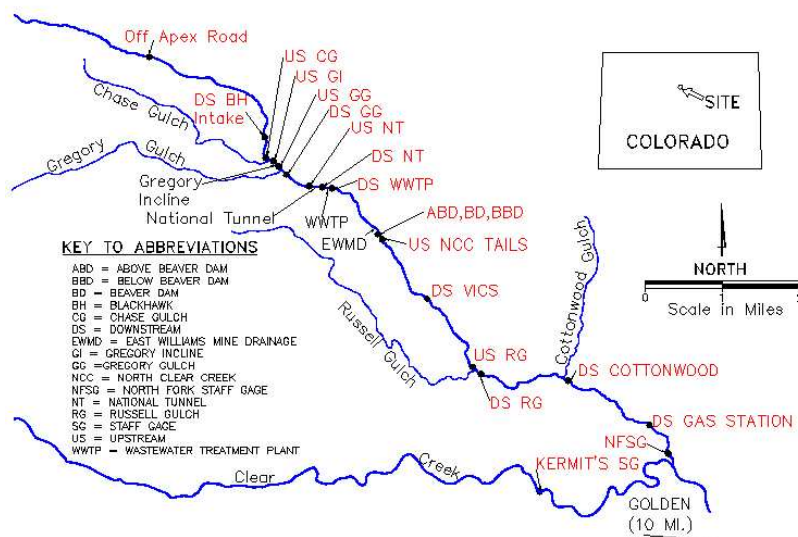
Figure 1.   Spatial and Temporal Study Sites, North Fork Clear Creek (NFCC), Colorado.

All water samples were grab samples collected in high-density polyethylene (HDPE) bottles. Bottles were rinsed three times with the stream water before sample collection. The bottles were placed below the surface water and then filled by moving the bottle through the water column. It was assumed that the water was well mixed due to the turbulent nature of the stream and thus, samples were not depth integrated. Water was filtered in the field using 25 mm filter holders (Gelman) with disposable 0.45-micron (Supor-450) filters. Filtered and raw water samples were acidified with metal-free hydrochloric acid to a pH < 2. Unfiltered samples were also collected for total organic carbon, alkalinity, and particle-size analysis (organic carbon and alkalinity results are not presented).

NFSG flow data were obtained from the U.S. Geological Survey (USGS) Lakewood, Colorado office.

Analytical Methods:

Temperature and pH were measured in the field; all other analyses were performed in the laboratory. All alkalinity measurements were conducted at the Colorado School of Mines (CSM) using a HACH kit and titrating to the Bromocresol-Green endpoint. For the May 2002 spatial study, the USEPA Region VIII Laboratory, using Inductively Coupled Plasma Spectroscopy (ICP-Mass Spectroscopy for Cd, Cu, Pb, and Ag and ICP-Atomic Emission Spectroscopy for all other elements), assessed the majority of samples for metal concentrations. Metals from sites ABD, BD, and BBD were measured by CSM using a Perkin-Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). All metal analyses for the temporal study were performed at CSM. Samples were analyzed for total and dissolved metals on a Perkin-Elmer Optima-3000 ICP-AES using EPA

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Method 200.7. TOC measurements were performed at CSM by high-temperature combustion using a Shimadzu TOC-500 instrument.

Results and Discussion

Spatial Studies:

AMD inputs to NFCC include Gregory Gulch, Gregory Incline, National Tunnel, and, to a lesser degree, the East Williams Mine Adit. Each of these locations is indicated on Figure 1. Values of pH and concentrations of iron, copper, manganese and zinc, from above Blackhawk to just above the confluence with CC, are shown in Figure 2.

% Copper, Iron, Manganese & Zinc Particulate
May 21, 2002

% Copper, Iron, Manganese, & Zinc Particulate
June 3, 2004
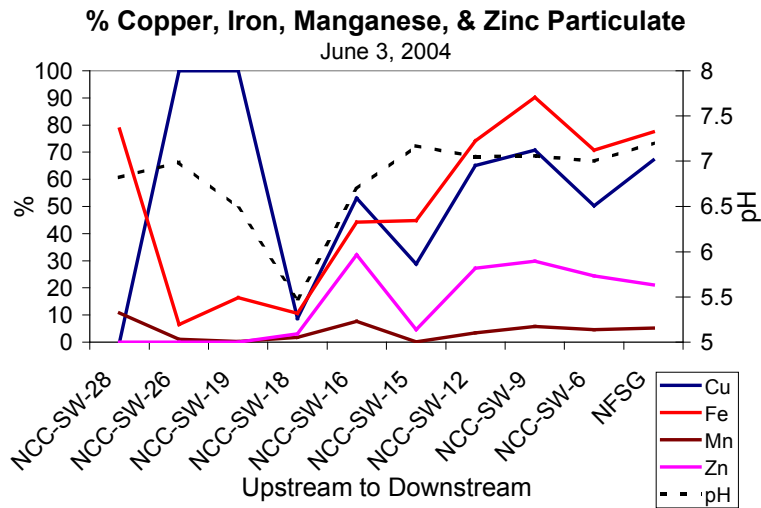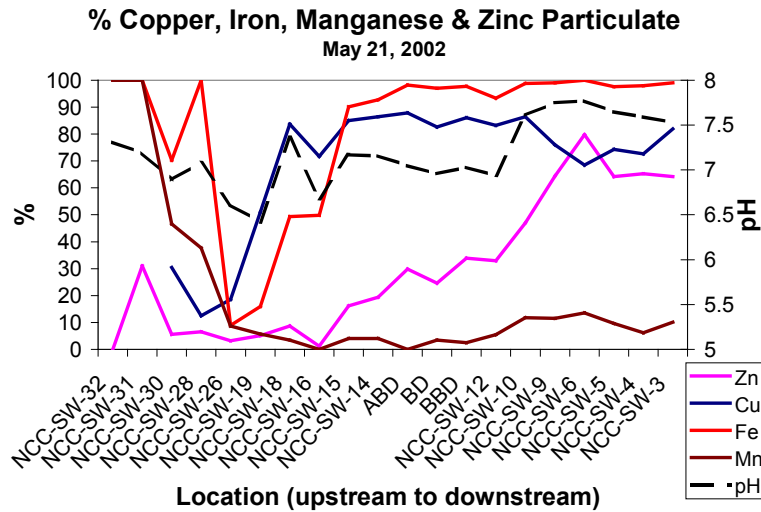
Figure 2. Concentrations of four metals and pH values at North Fork Clear Creek stations in May 202 (upper panel) and June 2004 (lower panel).

Iron oxyhydroxide (HFO) is formed rapidly *in-situ.* Copper is either co-precipitated or quickly adsorbed to the HFO. Iron and copper are transported through the system as suspended particulates.

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There is some loss of iron over distance, primarily due to settling of HFO. Mn is transported in the dissolved phase (> 90%). Some manganese is lost via formation of rock coatings. Zinc is transported in both the dissolved and the particulate phases. Some zinc is lost over distance, possibly associated with the Mn loss. On a mass basis there is more loss of Mn and Zn than of Cu and Fe.

Overall transport behavior of Cu, Fe, Zn, and Mn are similar for the two years. Iron precipitate formation, however, occurs further downstream in 2004 than in 2002.

Temporal Studies:

Flow in NFCC was very low in 2002, with a range from 0.4 to 25 cfs (Figure 3). In 2003 strong storm events resulted in higher flows and thus in increased transport of copper and iron in the watershed. Metal concentrations were diluted during higher flows with the exception of iron at NCC-SW-3 and CC-SW-4, where spring runoff caused scouring of iron-laden sediments that have settled over lower flow months.
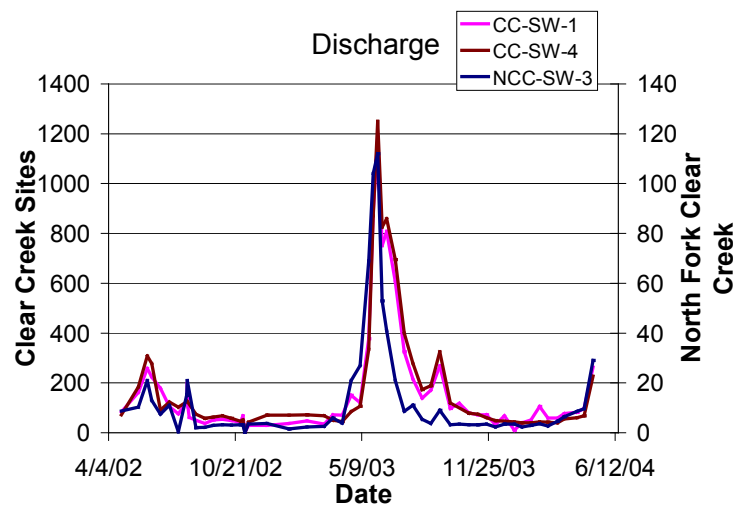
Figure 3.   Flow, sampling dates for Clear Creek and North Fork Clear Creek.

Iron (Figure 4a) and copper (Figure 4b) show increased concentrations during spring flush, but no other seasonal trends are evident. Both Fe and Cu are transported predominantly in the particulate phase in both the main-stem of Clear Creek and in North Fork Clear Creek. This has been seen in other AMD impacted stream systems (Ortiz et al., 1995; Rupert, 2001) and is likely due to flushing of more AMD into the creek during higher flow events. Figure 4a shows that iron is present only in the particulate phase at NFSG during the study period. Elevated levels of particulate iron coincide with the high flows that occur during spring runoff and the summer rainstorm.
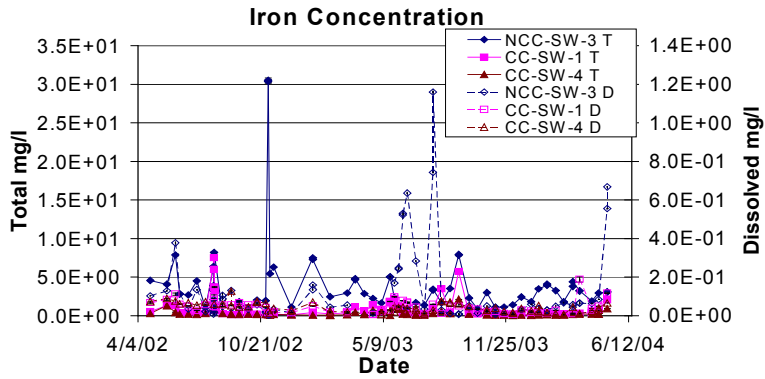
Figure 4a. Seasonal variation in particulate and dissolved iron concentrations in CC and NFCC.
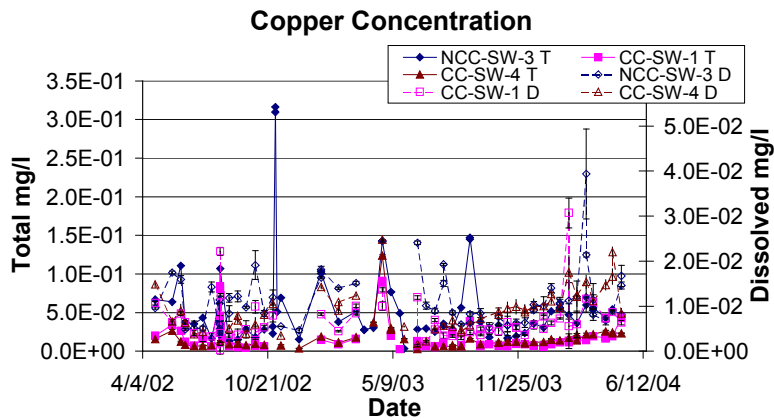
Figure 4b. Seasonal variation in particulate and dissolved copper concentrations in CC and NFCC.

Manganese (Figure 4c) and Zinc (Figure 4d) show seasonal trends with increasing concentrations over summer, fall, and winter and decreases during spring runoff. Both metals are transported predominantly in the dissolved phase in both the main-stem of Clear Creek and in North Fork Clear Creek.

Manganese Concentration
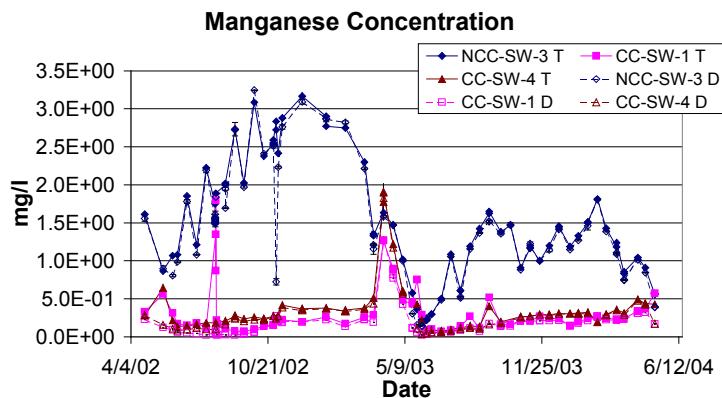
Figure 4c. Seasonal variation in particulate and dissolved manganese concentrations in CC and NFCC.

Manganese Concentration
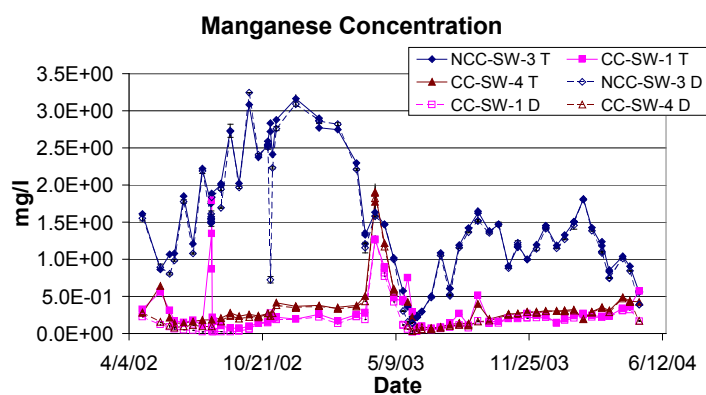
Figure 4d. Seasonal variation in particulate and dissolved zinc concentrations in CC and NFCC.

Metal Partitioning and distribution

We asked the research question, "Can metal transport in our system be modeled with a simple approach or is a more complex model required?" To date we have only applied the simplest approach, distribution coefficients, Kd. Our first approach was to determine Kd's based on Total Suspended Solids (TSS).   Assuming that metals are primarily associated with iron oxides in the TSS, we also normalized Kd's to particulate iron concentrations in the TSS. Figures 5a and 5b show distribution coefficients between dissolved and particulate phases for copper and zinc, respectively. Data are normalized to either (TSS) or Iron in TSS.

Copper Kd
Based on Mass TSS

Copper Kd
Based on Mass of Iron in TSS
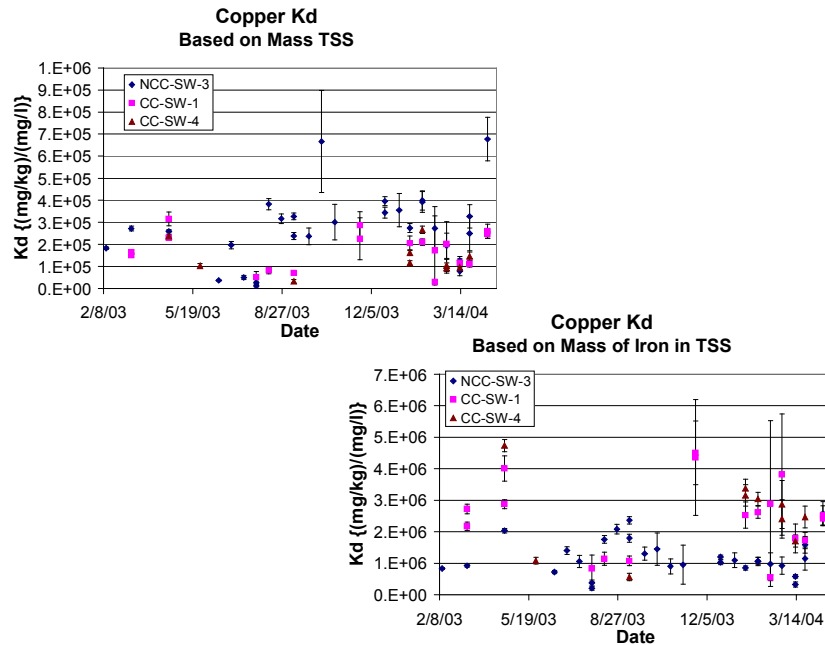
Figure 5a. Distribution coefficients between dissolved and particulate phases for copper. Data are normalized to either Total Suspended Solids (TSS) or Iron in TSS.

The calculated Kd values vary widely over the study period. Copper Kd's are generally larger than those for zinc. Normalization to iron in TSS increases the variability, suggesting that iron oxide is not the only phase responsible for partitioning of copper and zinc into the TSS.

Zinc Kd
Based on Mass TSS

Zinc Kd
Based on Mass Iron in TSS
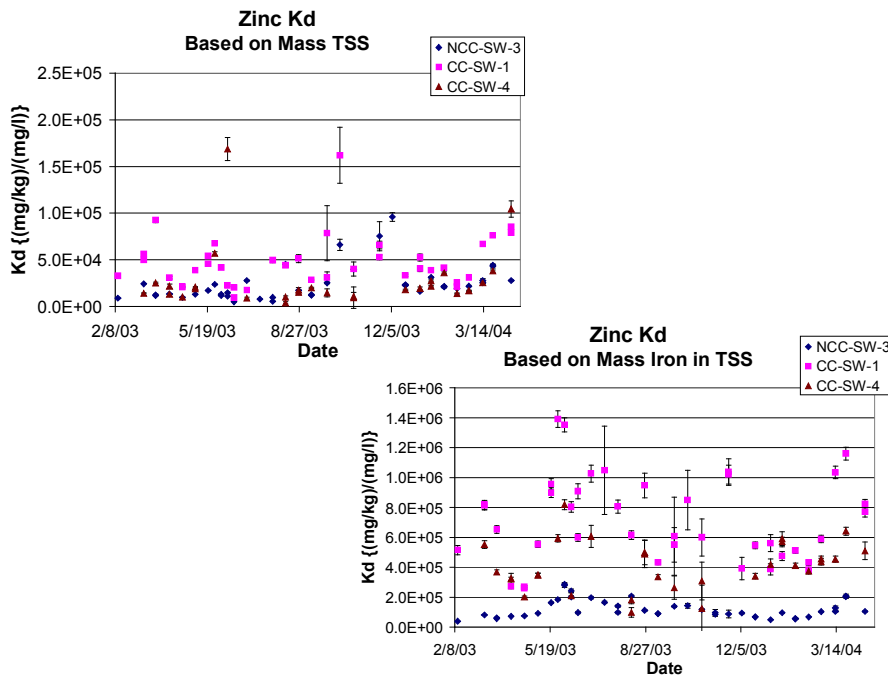
Figure 5b. Distribution coefficients between dissolved and particulate phases for zinc. Data are normalized to either Total Suspended Solids (TSS) or Iron in TSS.

Future Work

Further efforts will be focused on determining whether HFO can be used as the dominant sorbent phase or if another phase must be considered. This will be accomplished by modeling using Visual MinteqA2. Data sets to be modeled include field data (temporal and spatial) and results from laboratory sorption experiments.

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Modeling Cu and Zn Desorption Kinetics from Soil Particles

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Introduction

       Desorption of trace metals from soils is an important process that controls metal bioavailability in the environment. Much of the trace metals entering surface waters are released from contaminated soil particles. Soil particles are transferred by surface waters and trace metals are leached out of these particles into solution thus becoming available to plants and animals. Soils provide an important source of trace metals to rivers, both in the dissolved form through leaching and in the particulate form through erosion (Bergkvist, 1986; McColl and Pohlman, 1986; Rasmussen, 1986). Desorption of metals from soil is a slow process and equilibrium between soil particles and solutions may not be attained (Sparks, 1989), so existing approaches based on equilibrium assumptions are not sufficient to characterize the behavior of trace metals in soil systems. Compared with the extensive study on sorption process of metals on soils, little study has focused on desorption process of trace metals from soils, especially kinetics (Yin et al., 1997; Strawn and Sparks, 2000; Sukreeyapongse et al., 2002). It is therefore necessary to determine the rates of the metals transferring into solutions and to study how these rates are dependent on solution chemistry for the levels of contamination of soils found in the environment.

       The rates of trace metals desorption may be affected by both solution chemistry (pH, dissolved organic matter (DOM), etc.) and soil properties. pH and DOM are among the most important solution parameters affecting the rates of Cu and Zn desorption from soils. pH can strongly affect distribution of trace metals between solid and solution phases (Buchter et al., 1989; Sauvé et al., 2000). At low pH, proton competition will dominate since protons have relatively very strong binding ability with soils, for example, with soil organic matter (SOM). Several equilibrium partitioning models have been developed to predict the effect of pH on the equilibrium distribution of trace metals between soil and solution phases (Impellitteri, 2002). However, the effect of pH on the rates of trace metals release remains unknown.

       DOM also has a significant effect on metal solubility and thus the leaching of metals from soils because metals may form soluble complex with DOM. Soluble organic matter present in surface waters and soil solutions strongly complexes some trace metals (Impellitteti et al., 2002; Martinez et al., 2003). Thus, the mobility and bioavailability of the metals in soils should be affected by the concentration of DOM. Copper is recognized as a metal forming very strong complexes with DOM. So, dissolved Cu correlated with DOM concentration in soil suspensions (Hsu and Lo, 2000; Impellitteri et al., 2002; Romkens et al., 1996; Temminghoff et al., 1997; Yin et al. 2002). Compared with Cu, Zn has lesser tendency to form soluble complexes with DOM.

       Generally, how pH and DOM affect kinetics of Cu and Zn desorption from soils has been little studied. Some models, which were summarized by Sparks (1989), have been used to describe metal sorption and desorpiton kinetics. The rates of the reactions on soil constituents have been described using some models, such as ordered models (zero-, first-, and second-order kinetics equations), parabolic diffusion, two-constant rate, Elovich, and differential rate equations. Kinetics of Zn desorption from soils was described by parabolic diffusion, two-constant rate and Elovich equations (Dang et al., 1994; Kuo and Mikkelsen, 1980; Rupa and Tomar, 1999; Rupa et al., 2000). The Elovich Zn desorption rate constant correlated with clay content and CEC at different pH (Rupa et al., 2000). The rate of pH-dependent release of Cd, Cu and Pb can be described by a proton induced dissolution model (Sukreeyapongse et al., 2002). However, the rate constants obtained in these models were not constant but changed with experimental conditions. Most of their modeling was mainly based on individual curve fitting and then correlation analysis. The mechanisms controlling metal desorption in these models was not explicit and their usefulness is limited.

       Some researchers developed models based on mass balance of flow system to describe adsorption and desorpiton kinetics (Bar-Tal et al., 1990; Hinz and Selim, 1999; Skopp and McCallister, 1986). Rather than using calculated adsorbed/desorbed quantities data, these models treated effluent solution concentration data directly, which thus decreased mathematical errors. Selim and coworkers (Amacher, 1991; Selim, 1992) also proposed a multireaction model which assumes more than 3 reaction

sites in soil matrix to describe reactions in soils. The models which have more than 3 sorption sites, involve so many adjustable parameters that their usefulness is limited. Furthermore, metal speciation was little considered for previous modeling. Metal speciation is dependent on solution conditions and different speciation may result in different partitioning. Thus solrly parameter optimization cannot independently determine an appropriate number of rate coefficients and the model parameters obtained in previous modeling from one experimental condition cannot apply to other conditions. So, in order to set up a model with good prediction functions, we should control different kinetics processes and isolate different variables in the experiment and then carefully handle them in the modeling.

The objectives of this study were (1) to study the effects of pH, DOM, and flow rate on the rates of Cu and Zn desorption from soils and to understand the mechanisms controlling the reaction rates; (2) to develop an adsorption/desorption kinetics model that is based on mass balance and, more importantly, one that explicitly incorporates chemical reactions that occur in the adsorption/desorption process that apply to various solution conditions.

Materials and Methods

The study was carried out on a Matapeake silt loam soil from Delaware and a Codorus clay loam soil from Maryland. The soils were sampled from the 0-20 cm layer. Selected soil properties are present in Table 1. The soil samples were mixed, air-dried, and sieved to pass through a 2-mm screen. Sub-samples of the soils were spiked with $Cu(NO_3)_2$ up to 48 mg Cu/kg or with $Zn(NO_3)_2$ up to 103 mg Zn/kg. Samples were spiked with 500 mL metal solution to 250 g soil samples. The slurry was mixed for 10 min and allowed to settle for another 2 hours before the supernatant was gently decanted. The moist soil was then mixed and air-dried. Dissolved organic matter was separated from the water of the Edisto River in South Carolina with a reverse osmosis system. Properties of this DOM can be found elsewhere (Lu, 2000).

Table 1. Selected soil properties

Soil	pHa	Sand	Silt	Clay	WB-OMb	Cuc	Znc
				%		mg/kg	
Matapeake silt loam	6.38	13	%	24	2.46	21.4	73.5
Codorus clay loam	6.05	27	45	28	2.68	14.2	58.5

[a] H_2O, 1:1
[b] organic matter measured with the Walkley-Black method
[c] measured using microwave digestion (EPA method 3051)

Metals desorption kinetics was studied with a stirred-flow method using a 6.4-mL reaction chamber through which a leaching solution flows (Yin et al., 1997). Soil samples (0.3 g) were leached with 3 mM $Ca(NO_3)_2$ solution as a background electrolyte. Before leaching, samples were pre-equilibrated in the chamber with the leaching solutions for 20 min. Leaching solution was pumped through the stirred-flow chamber with a peristaltic pump at a flow rate 1 mL/min and the breakthrough solution was collected with a fraction collector and analyzed for Cu and Zn (ICP-AES). DOM concentrations in leaching solutions were changed by adding concentrated DOM solution to the background electrolyte. The DOM concentrations used in our study are close to those observed in surface waters (Tipping, 2002). DOM concentration was measured with a DC-190 Rosemount Total Organic Carbon Analyzer. pH was kept at desired value using 1 mM MES buffer which does not complex metal ions (Kandegedara and Rorabacher, 1999).

Results

Effect of pH and DOM on Cu and Zn desorption from soils

Decrease of pH greatly enhanced both Cu and Zn release from spiked soils. This can be attributed to increased proton competition at lower pH. The total amounts of Cu desorbed within 5 hours from spiked Matapeake soil were 6.39 mg/kg at pH 5.5, 4.25 mg/kg at pH 6.0, 2.64 mg/kg at pH 6.4, and 2.33 mg/kg at pH 7.2, which respectively accounted for 13.3%, 8.8%, 5.5%, and 4.8% of total spiked Cu in the soil. Compared with Cu, much more Zn desorbed, 74.36 mg/kg at pH 5.5, 58.97 mg/kg at pH 6.0, 47.51 mg/kg at pH 6.4, and 13.36 mg/kg at pH 7.2, which respectively accounted for 72.0%, 57.1%, 46.0%, and 12.9% of total spiked Zn in the Matapeake soil. Cu and Zn desorption from Codorus soil at different pH is quite similar to Matapeake soil.

DOM significantly enhanced Cu desorption from both soils. At 15 mg/L DOM, the total amount of Cu desorption was about 49% of spiked Cu for Matapeake soil, which is nearly four times the Cu desorption without DOM addition. This demonstrated that, besides pH, DOM is a very important solution parameter affecting Cu release from soils. Copper release from Codorus soil appeared to be similar to that observed for Matapeake soil. However, compared with Cu, Zn desorption was little affected by DOM.

Modeling Zn desorption kinetics

Release of trace metal from soil particles may involve several different processes with different time scales (Sparks, 1989). Our model addresses the relatively short-term adsorption/desorption kinetics that are assumed to be controlled by reactions on the soil surface, and how these kinetics processes are affected by the change of solution chemistry and flow conditions. Although it is not practical to completely separate chemical kinetics from diffusion controlled kinetics, film diffusion and interparticle diffusion were minimized with the vigorous stirring employed in our experiment. The concentrations of metals were below those that cause precipitation.

Since SOM is the dominant phase among soil components that adsorb Cu and Zn (Weng et al., 2001; Gustafsson and Pechova, 2003), SOM was used as the sorption ligand. It is assumed that only the ionic form of the metal, the portion not complexed by organic ligands, can adsorb to soil particles. Since DOM had little effect on Zn, the major form will be free Zn ion in solution.

As shown below, two types of sites in soil particles are required to model Zn adsorption and desorption. We have used mass units in our calculations to avoid the necessity of defining molar quantities for soil and DOM reaction sites. Metal concentrations are low and thus sorption of metal does not significantly affect the concentration of available sites.

The mass balance equations are derived as follows. Let k_{a1} (g^{-1} L min^{-1}), k_{d1} (min^{-1}), and C_{p1} (µg Zn g^{-1}) respectively be the adsorption and desorption rate coefficients and particle Zn concentration for site 1 and C_{ion} (µg Zn L^{-1}) be the solution concentration of ionic Zn. Then, we have the kinetic equation for Zn release from site 1,

$$\frac{dC_{p1}}{dt} = -k_{d1}C_{p1} + k_{a1}C_{ion} \tag{1}$$

and similarly for site 2,

$$\frac{dC_{p2}}{dt} = -k_{d2}C_{p2} + k_{a2}C_{ion} \tag{2}$$

The equation for ionic Zn concentration in the solution follows from mass balance

$$\frac{dC_{ion}}{dt} = -k_{a1}mC_{ion} - k_{a2}mC_{ion} + k_{d1}mC_{p1} + k_{d2}mC_{p2} - \frac{Q(C_{ion} - C_{ion,0})}{V} \qquad (3)$$

where m (g L^{-1}) is soil particle concentration, Q (mL min^{-1}) is the flow rate, and V (mL) is the volume of the stirred-flow chamber. All concentration terms refer to the concentrations in the stirred-flow chamber. Subscript 0 denotes initial concentrations at time 0. Because all Zn concentrations are expressed as the amount of Zn per gram of soil or per liter solution, the above equations still strictly obey the reaction stoichiometry. The pH dependency is dependent on the surface sites and the extent of protonation. We used an empirical expression in which $k_a = k_{a0}[H^+]^{-n}$.

Both one-site and two-site models were used to model kinetics of Zn desorption. The two-site model fits the desorption data for Zn better than the one-site model. More important, the two-site model can reproduce the stop-flow experimental results but one-site model cannot (Figure 1a). This demonstrates the importance of this type of critical test experiment (Bar-Tal et al., 1990) in estimating the parameters of a kinetic model. The model also reproduced the results of different flow rates (Figure 1b). In fact, the observed Zn release kinetics is mainly controlled by the net Zn release from soil particles and dilution due to the flow out of the chamber. Bar-Tal et al. (1990) pointed out that if equilibrium is attained instantaneously, no effect of flow rates can be found when plotting relative concentration vs. effluent volume. A plot of effluent Zn concentrations versus number of flow volumes passing through the chamber in our modeling demonstrates different Zn release behavior at different flow rates (Figure 1c) indicating a kinetics controlled Zn release that is consistent with the stop-flow results.
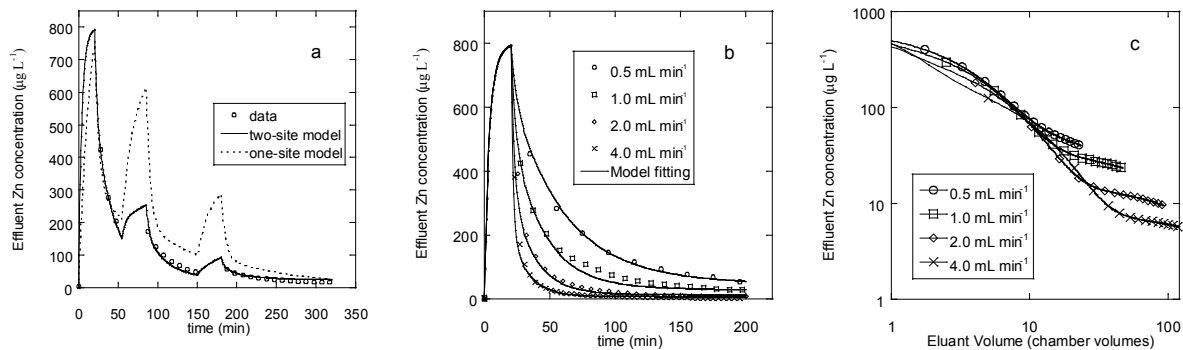
Figure 1. Kinetics of Zn desorption from spiked Matapeake soil at pH 5.5 and [Ca] = 3 mM. (a) Stop-flow experiment; (b) Different flow rates (values are annotated in the figure). (c) Effluent Zn concentration vs. volume of solution passed through the chamber (expressed in chamber volumes). Lines are calculated with the model.

The pH effect model and data are summarized in Figure 2 for both soils. It is assumed that the same pH dependency applies for both sites. The fitted result is n = 1.0 for both soils. Both sites are important for Zn release. The site which has the higher desorption and adsorption rates mainly supplied the Zn release during pre-equilibrium and fast release periods and the other site with the much lower rate coefficients accounted for the slow Zn release. The Zn desorption rate coefficients are reasonably consistent with those obtained by others (Zhang et al., 2004).

Figure 2. Effect of pH (values are annotated in the figure) on the kinetics of Zn desorption from spiked (a) Matapeake soil and (b) Codorus soil ([Ca] = 3 mM). Lines are calculated with the model.

Modeling Cu desorption kinetics

The adsorption-desorption reactions used in the model are the same for Cu as for Zn. The major difference is that free Cu ion concentration in the solution is highly dependent on DOM concentration. In the presence of DOM, the Cu-DOM complex may dominate the solution Cu speciation. Ma et al. (1999) also demonstrated the Cu complexation reaction with DOM is kinetically controlled. Therefore, the model was expanded with the kinetic equations for Cu-DOM complexation and dissociation with rate coefficients k_1 and k_2, respectively.

$$DOM + Cu^{2+} \xrightarrow{\;k_1\;} Cu - DOM \tag{4}$$

$$Cu - DOM \xrightarrow{\;k_2\;} Cu^{2+} + DOM \tag{5}$$

The net Cu-DOM complexation rate can be calculated as follows,

$$\frac{d[Cu-DOM]]}{dt} = k_1[Cu^{2+}][DOM] - k_2[Cu-DOM] \tag{6}$$

Total DOM concentration, C_{DOM} (mg C L^{-1}), is used to represent total reactive ligand concentration. The mass balance equations for ionic Cu concentration, C_{ion} (µg Cu L^{-1}), and Cu-DOM complex concentration, $C_{Cu\text{-}DOM}$ (µg Cu L^{-1}), are

$$\frac{dC_{ion}}{dt} = -k_{a1}mC_{ion} - k_{a2}mC_{ion} + k_{d1}mC_{p1} + k_{d2}mC_{p2} - \frac{Q(C_{ion} - C_{ion,0})}{V}$$
$$- k_1 C_{ion} C_{DOM} + k_2 C_{Cu-DOM} \tag{7}$$

$$\frac{dC_{Cu-DOM}}{dt} = k_1 C_{DOM} C_{ion} - k_2 C_{Cu-DOM} - \frac{Q(C_{Cu-DOM} - C_{Cu-DOM,0})}{V} \tag{8}$$

The measured total soluble Cu concentration equals the sum of the ionic Cu concentration and the Cu-DOM complex concentration. The pH dependency of these reactions was formulated as the same way as the Zn model.

The modeling method is the same as employed for Zn. However, in order to determine the pH dependency for the adsorption coefficients the WHAM VI predicted pH dependency of the partition coefficient K_p was calculated which indicated that $n = 1.3$. This value was used and only k_a was estimated in the model fitting. For Cu-DOM complexation, however, the model was used to estimate both k_1 and n.

Contrary to the Zn results, a one-site model for Cu fit all data as well as a two-site model. A unique set of rate coefficients fits all the breakthrough curves at different DOM concentrations and flow rates (Figures 3 and 4) indicating that the proposed mechanism for the effect of DOM is not unreasonable. Martino et al. (2003) also found Ni adsorption rate on suspended sediment particles was inversely dependent on the concentration of DOM in the samples. The rate constants for formation and dissociation of the Cu-DOM complex were calculated to be $k_1 = 292$ L s^{-1} mol^{-1} C and $k_2 = 0.018$ s^{-1}. The value of k_2 is within the range $10^{-3.1} - 10^{+1.6}$ s^{-1} found by other researchers, summarized by Tipping (2002). The model fits for the effect of pH on Cu release are presented in Figure 5.
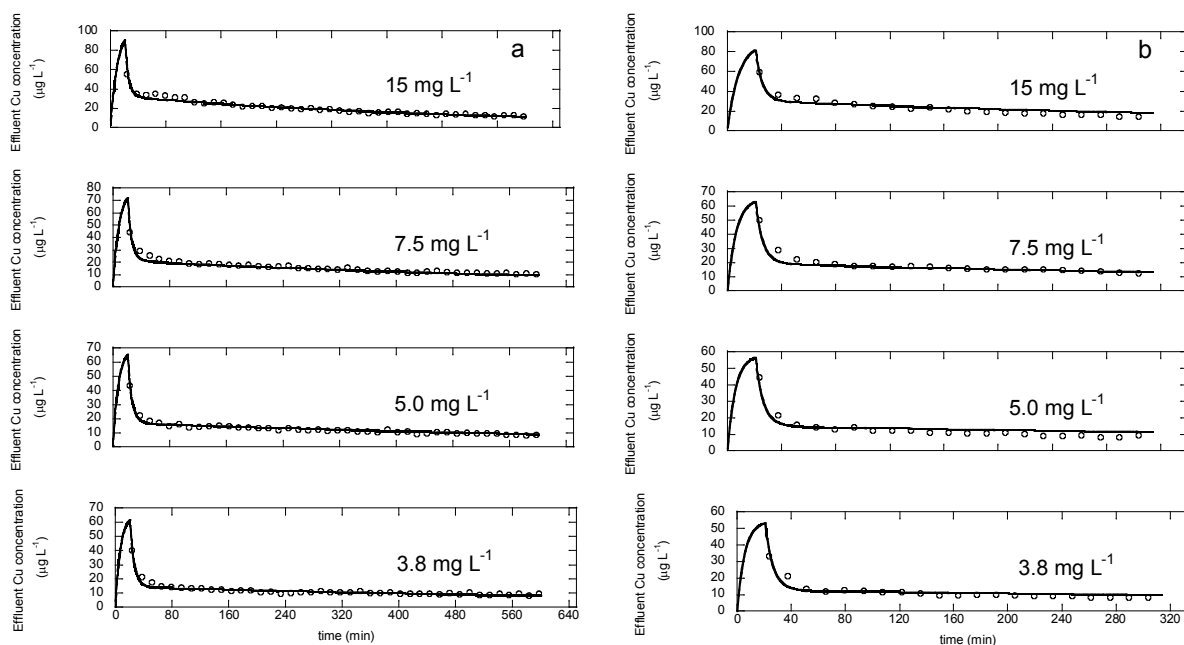
Figure 3. Effect of DOM (values are annotated in the figure) on the kinetics of Cu desorption from spiked (a) Matapeake soil and (b) Codorus soil ([Ca] = 3 mM). Lines are calculated with the model.
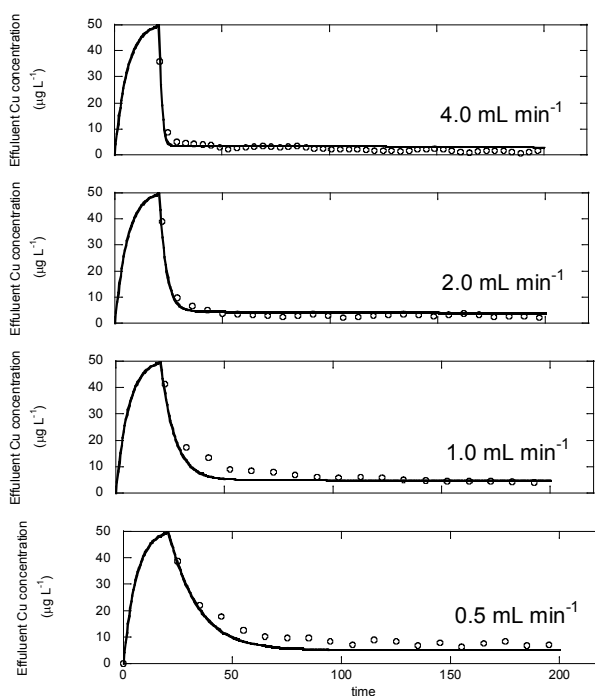
Figure 4.   Effect of flow rates (values are annotated in the figure) on the kinetics of Cu desorption from spiked Matapeake soil ([Ca] = 3 mM). Lines are calculated with the model.
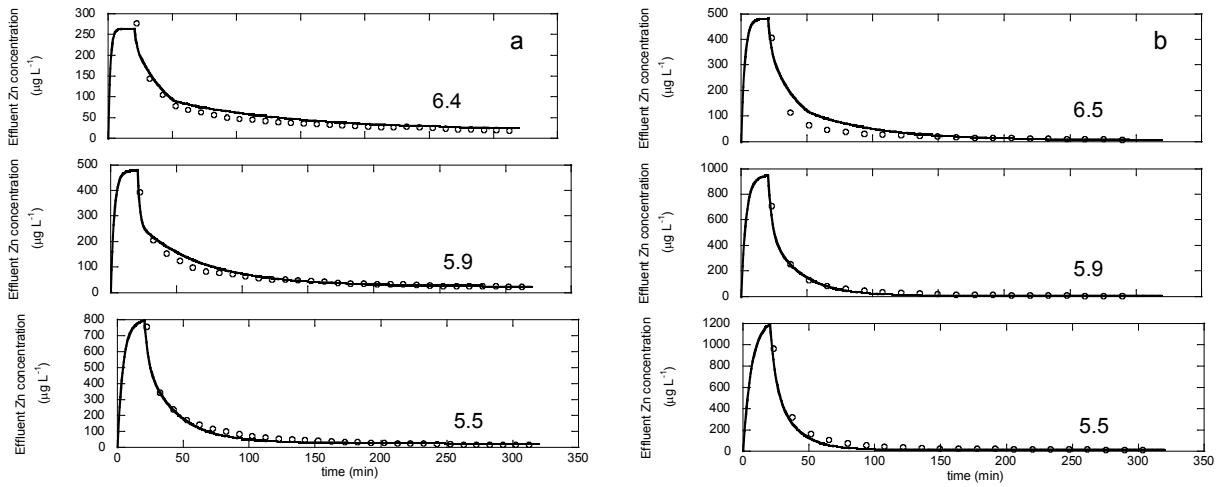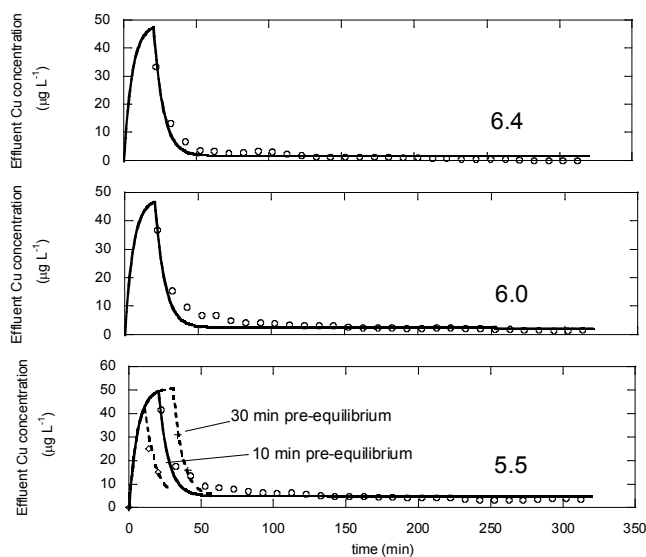

Figure 5.   Effect of pH (values are annotated in the figure) on the kinetics of Cu desorption from spiked Matapeake soil ([Ca] = 3 mM). The effect of different pre-equilibrium times is shown on the plot for pH = 5.5. Lines are calculated with the model.

Future Investigations

   We have successfully developed the kinetics models for describing both Cu and Zn release from soil particles to solutions. Our further efforts will focus on improving the existing models to the general

Cu and Zn kinetics models which can be used to predict Cu and Zn release under different solution chemistry conditions and from different soils (e.g. different soil organic matter contents). We will investigate both Cu and Zn adsorption/desorption kinetics and our experiment will be extended to different soils.

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Metal Speciation in Watersheds

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Summary of Progress

This EPA grant is a study of the speciation of metals in mid-Atlantic watersheds. The overall aim of this proposal is to describe the fluvial fate of metals with respect to their distribution and speciation in the watershed.

Our specific objectives are to:

(1)   Model existing metal data in the coastal watersheds.

(2)   Measure the concentration and speciation of select metals in coastal watersheds

(3)   Compare this experimental data with the distribution and speciation predicted by the models.

During Year 1, we accomplished these objectives as follows:

(1) Previous metal data in the watersheds was modeled using those (e.g. WHAM) available in Environmental Engineering at University of Delaware (D. DiToro). This modeling will supplement additional sampling of waters in both fresh (Potomac) and estuarine (Delaware Inland Bays) environments. These watersheds already have generated abundant data sets under previous EPA and NOAA Sea Grant programs. Initial model runs combined the trace metal data with the other major ions and master variables. In the freshwater system (Potomac), these were sampled during the same period by the USGS (during the NAWQA studies) with whom we are collaborating. The modeling was patterned after the "Unit World" approach in collaboration with others at CSME using these watersheds as metal test beds. Parameters that were measured and used for the model include Cd, Cu, Pb and Zn species as well as other master parameters (e.g. ionic strength/salinity, pH, and TIC/alkalinity, DOC, POC, Chl a, and AVS).

(2) The field program was initiated in both the Potomac River and Delaware Inland Bays in mid-2004. The Potomac sampling was conducted on June 12 and September 16, 2004, at four locations under moderately high flow in the fresh Potomac watershed. Only four stations were chosen for sampling to ensure the large sets of parameters needed for the models and high quality samples for the laborious speciation analyses. The Delaware Inland Bays sampling was conducted in Torquay Canal during May and June 2004.

(3) The preliminary results for the Potomac suggest significant primary production that resulted in high pH, chlorophyll a, and alkalinity in June. The result was a significant distribution of the metals primarily on the particulates for Cd and Zn and equally for Pb and Cu. Although Cu, Zn, Pb and Cd species were targeted in electrochemical measurements, mainly Zn complexes were observed. The results indicated the absence of simple zinc inorganic complexes involving ligands such as hydroxide, chloride and sulfate. Some weak to moderately strong Zn organic complexes were observed. The remaining dissolved Zn was beyond the analysis window of square wave anodic stripping voltammetry (SWASV) and represent very strong organic complexes (involving multi-dentate chelates) and/or stable multinuclear zinc sulfide clusters. The latter is supported by the presence of acid volatile sulfide in samples. Metal sulfur clusters have not been included in current freshwater speciation models, but will be attempted as part of this project. In Torquay Canal, some Zn (in)organic complexes were observed in the surface water. An increase in the numbers and stability of complexes were observed during an algal bloom in Torquay Canal. It was noticed that weak Zn (in)organic complexes were common in Potomac and Torquay Canal samples.

Study and Sample Collection

Potomac River

Water samples were collected on June 12 and September 16, 2004, at four sites along the Potomac River: Chain Bridge, D.C.; Point of Rocks, MD; Handcock, MD and Cumberland, MD (Figure 1). Great care was taken to avoid contamination of samples. All plasticware used for sampling and storage were acid washed with 10% HCl, rinsed with deionized water and triple bagged to ensure that they remained trace metal clean. A Teflon bailer attached to plastic line was lowered from a bridge at

each site to collect 2 L of sample, which was transferred to an acid washed 2 L polyethylene bottle. Samples for determination of metal speciation, alkalinity, and chlorophyll, dissolved and particulate organic carbon were filtered onsite. A portable pH meter (Digi-Sense) was used to determine the pH of filtered samples out in the field.
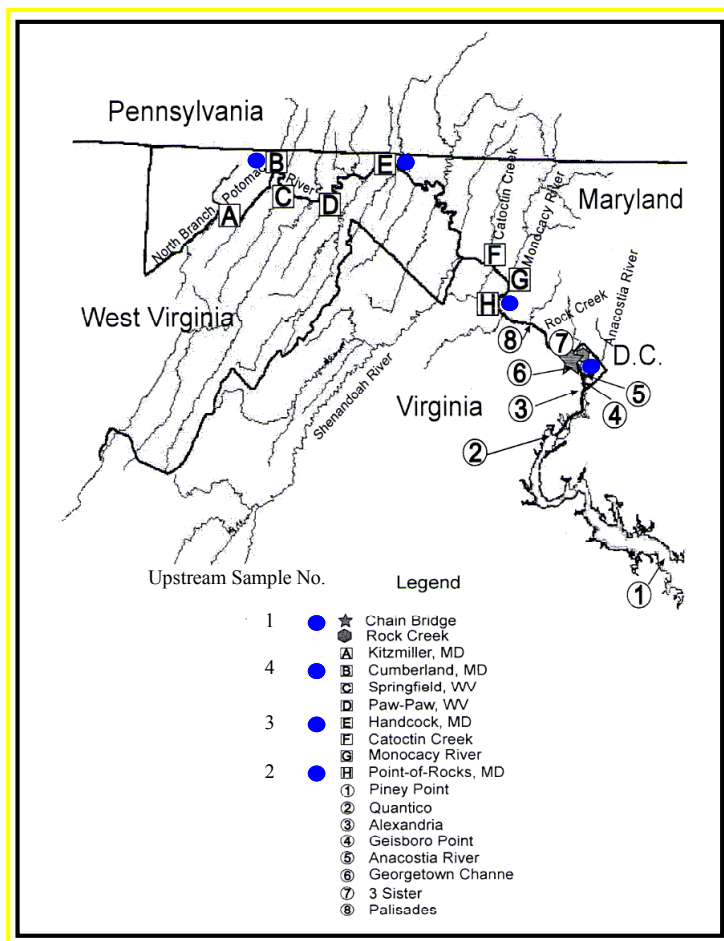
Figure 1.   Potomacwatershed and sampling sites highlighted by filled circles (•).

Two hundred mL of each sample was vacuum filtered through an acid washed 47mm diameter 0.4 μm Isopore polycarbonate membrane filter (Millipore) loaded into a Nalgene filter stack. Filtration of samples was performed in a glove bag onsite out in the field to ensure that metal speciation was not compromised. The filtrate was transferred to a 250 mL low density polyethylene bottle and quick-frozen on dry ice. These frozen filtered samples were retained for electrochemical and alkalinity measurements. Chlorophyll was collected from each site by passing 100 mL of sample through a 25mm glass fiber filter (Whatman); filtration was performed in darkness. The filters were placed into clean vials and stored in a freezer until ready for chlorophyll a analysis. A further 100 mL of sample was passed through baked ($400^{o}C$, 2 hours) 25mm glass fiber filters (Whatman) to separate dissolved and particulate organic carbon. Fifteen mL of filtrate from each site were placed into baked ($450^{o}C$, ~12 hours) glass vials and sealed with caps lined with baked ($450^{o}C$, ~12 hours) aluminum foil. The filters were also stored in baked vials.

The remaining unfiltered samples were taken back to the College of Marine Studies, University of Delaware, Lewes, where suspended particulate matter was collected. This was done by passing samples through pre-weighed, trace metal clean (acid washed) 47mm diameter 0.4 μm Isopore

polycarbonate membrane filters (Millipore) until these were blocked (0.2-0.9 L). Filtration and air drying of filters were performed in a class 100 clean hood. When dried they were weighed again to determine mass of particulate matter (3-19 mg). Filters were weighed in sealed acid washed plastic Petri dishes to prevent contamination. The filtrate from SPM collection was retained for the determination of acid volatile sulfide (AVS) and total dissolved metals (Al, Fe, Zn, Cu, Cd and Pb.

Delaware Inland Bays

Surface water samples were collected from Torquay Canal, Delaware Inland Bays (Figure 2) on May 13, 27 and June 10, 2004. A Van Dorn (Wildco) sampler was used to collect water at 0.2 m below the surface; 250 mL was transferred to an acid washed polyethylene bottle. The sample was placed into a cooler and immediately taken back to the laboratory (College of Marine Studies, University of Delaware, Lewes) and vacuum filtered, as above but in a class 100 clean hood. The filtrate was either analyzed immediately or the following day, in which case the sample was stored frozen until ready for analysis.
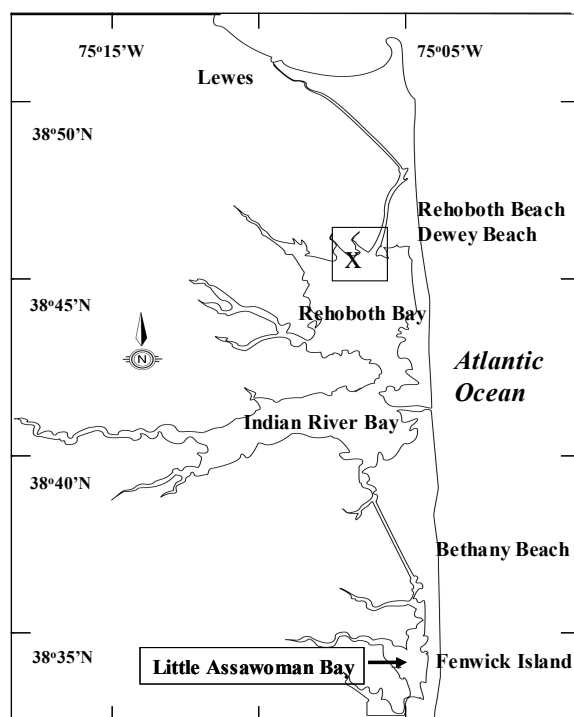
Figure 2. Potomacwatershed and sampling sites highlighted by filled circles (●).

Methods of the Project

Alkalinity

Twenty mL of each Potomac River sample was titrated with 5 mM HCl until the equivalence point was reached. The course of the titration was followed using a digital pH meter (Fisher Scientific, Accumet basic), which was calibrated with standard buffers (Fisher Scientific) prior to use. The volume of HCl required to reach the equivalence point was determined from Gran function plots. The HCl was standardized with a standard solution of Na_2CO_3 prior to alkalinity titrations.

DOC, POC/PN, Chlorophyll a and Major Cations

These parameters, required for modeling, were measured using standard methods employed in analytical laboratories at the College of Marine Studies, Lewes.

Total Dissolved and Particulate Metal Analysis

The total dissolved metals were analyzed by both ICP-OES (Jobin Yvon, model JY70 plus) and GF-AAS (Perkin Elmer 3300). The total particulate samples on the Isopore filters were acid digested and analyzed for a suit of trace metals (Fe, Mn, Cu, Pb, Cd and Zn). Briefly, river SPM along with the whole filter was placed in Teflon vials (15 mL capacity) and treated with a 5 mL mixture of HF (48%) and HNO_3 (70%) in equal proportion. After complete particle dissolution, the leached filter was removed and the solution digest completely evaporated. The residue was re-dissolved in 25 mL of 1 M HNO_3, diluted to a known volume of 0.1 M HNO_3 and analyzed by ICP-OES (Jobin Yvon, model JY70 plus) using externally calibrated multi-element standards (SPC Science Co.). The analytical precision was found to be ±5% (1 sigma) as determined by several repeat measurements of samples and standards.

Metal Speciation

Electrochemical measurements were performed with an EG&G Princeton Applied Research (PAR) model 303A static dropping mercury electrode, in hanging mercury drop mode, coupled to an Analytical Instrumentation Systems, Inc. (AIS) model DLK-100A voltammetric analyzer. Square wave anodic stripping voltammetry (SWASV) was used for all analyses, which were conducted with a scan rate of 100 mVs^{-1} over a potential range of -1.3 to 0 V with a 20 mV pulse height. Pseudovoltammograms (I vs E_{dep} plots) were generated by decreasing the deposition potential from -0.2 to -1.7 V by 50 mV increments. All analyses were performed with 10 mL of sample in an acid washed Teflon polarographic cell. Metals were reduced and deposited on the mercury drop for 10 minutes at each deposition potential. The presence of Cu, Pb, Cd and Zn in natural waters were identified by their specific metal reduction potential of -0.25, -0.45, -0.65 and -1.05 V, respectively. Total dissolved metals were determined from samples that were UV-irradiated for 5 hours and analyzed in the same manner as outlined above, except deposition potentials were performed from -1.2 to -1.7 V. For certain Potomac River samples, metal depositions were performed at -1.7 V for 30 minutes on non-irradiated samples.

Acid Volatile Sulfide (AVS)

To determine the acid volatile sulfide (AVS) content of Potomac River samples, 15 mL of sample from each site was reacted with 0.5 mL 3 M HCl in a sealed test tube filled with Argon. The AVS extractions were performed in duplicates for each site. Any sulfide produced was trapped in 15 mL 0.1 M NaOH. One mL aliquot of this NaOH solution was mixed with 9 mL of, pH 10 adjusted, de-aerated 0.5 M NaCl and analyzed by cyclic voltammetry using the same electrochemical set up described above. These electrochemical measurements were performed with a scan rate of 1000 mVs^{-1} over a potential range of -0.1 to -1.8 V. A holding potential of -0.1 V was applied for 60 seconds before measurements were performed.

Discussion and Results

Potomac River Field and Laboratory Auxiliary Data (June 12, 2004)

There was a minimum in suspended particulates in the middle of the Potomac, with distinct maxima both upstream and downstream at Chain Bridge (data not shown). The upstream maximum was due to the occurrence of intense rainfall (1-2 inches) near Cumberland the day before sampling. Downstream maxima are often observed, presumably due to more soil run off in the coastal plain mobilized by agricultural and suburban activities.

At the same time, there is a marked increase in pH (data not shown) downstream during the warmer sampling season consistent with increasing eutrophication and net photosynthesis. The pH values above 8 are beyond the ZPC for most metals and should lead to trace metal hydrolysis onto the particulate load. This pH trend continued in the laboratory analyses, only increasing slightly which is consistent with some CO_2 degassing and continued growth during storage. The elevated alkalinity

associated with this elevated pH must mean that a substantial amount is supported by both inorganic and organic weak acids in the system from net respiration and degradation of biological debris. There is a slight downstream and marked upstream increase in chlorophyll a and POC, respectively, consistent with chronic increase waste runoff and concurrent eutrophication from rural and suburban activities in the coastal plain and D.C. metropolis. Upstream, these increases are consistent with significant runoff of terrestrial organic debris from the recent large rainfall in the area.

Potomac Major Ion and Total Metal Data

The major cations measured (data not shown) in the Potomac are consistent with previous USGS data and the rock types in this mid-Atlantic watershed. These types consist of low-grade metamorphic shales, gneisses and quartzites. The ratio of Mg/Ca supports this and appears consistent throughout the year according to USGS NAWQA data sets. Thus the elevated levels of alkalinity are due primarily from aerobic respiration and degradation of organic debris in the system, rather than the weathering of carbonate rocks. This debris during the June growing period should consist of both forest and agricultural material.

The total trace metal data are likewise consistent with previous data collected as part of the EPA Chesapeake Bay Program from August 1996 to October 1997. There is very significant particulate distribution of Cd and Zn at all sampling sites (Figures 3a and 3d), which is consistent with their particle reactivity as oxy-anion due to high pH or strong binding onto organic particles. The equivalent distribution of Cu and Pb between the dissolved and particulate phases is consistent with equally strong binding in solution or onto particles (Figures 3b and 3c). Thus generally the low proportion of these particulate metals in the Potomac even at high flow may be attributed to strong dissolved ligands. However, the presence of AVS, much greater than dissolved metal, suggests sulfide complexation in these freshwaters may be comparable to organic complexation. This hypothesis is supported by the metal speciation data presented in the next section.
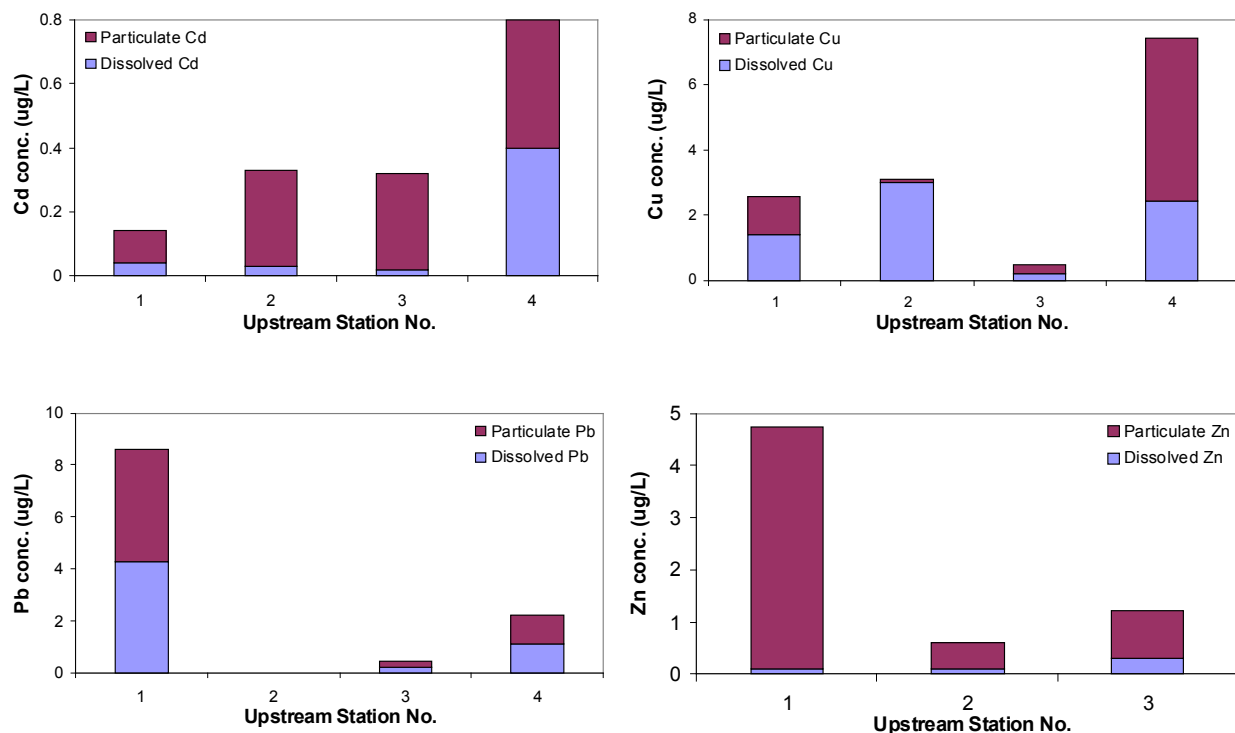
Figure 3. Particulate metal distribution for (a) Cadmium, (b) Copper, (c) Lead and (d) Zinc in Potomac River samples collected on June 12, 2004 (Please refer to Figure 1 for the location of each station number. Note: No reliable data for Pb and Zn at stations 2 and 4, respectively.

Potomac River Metal Speciation

        Square wave anodic stripping voltammetry (SWASV) was used to determine the presence of Cu, Zn, Pb and Cd in unaltered Potomac River samples. However, mainly Zn complexes were observed upon reoxidation of the amalgam (reaction 1) following ten minutes of metal preconcentration onto the mercury drop.

$$ZnL + 2e^- \rightarrow Zn(Hg) + L \qquad\qquad\qquad\qquad\qquad\qquad\qquad (1)$$

        In pseudovoltammograms, the presence of inorganic Zn can be determined by its half wave ($E_{1/2}$) potential of -1.05 V. This is not observed in the Zn pseudovoltammograms for Chain Bridge, Point of Rocks, Handcock and Cumberland (Figure 4), indicating the absence of weak inorganic Zn complexes, involving ligands such as chloride, hydroxide and sulfate. Different zinc complexes will give different $E_{1/2}$ values. The more negative the $E_{1/2}$ value the more strongly bound the metal (in)organic complex is. At the four Potomac River sampling sites, Zn exists in (in)organic complexes that are relatively more stable than simple inorganic Zn complexes, such as those mentioned above. The existence of dissolved Zn organic complexes in all Potomac River samples are likely, owing to the presence of significant levels of dissolved organic carbon (data not shown).
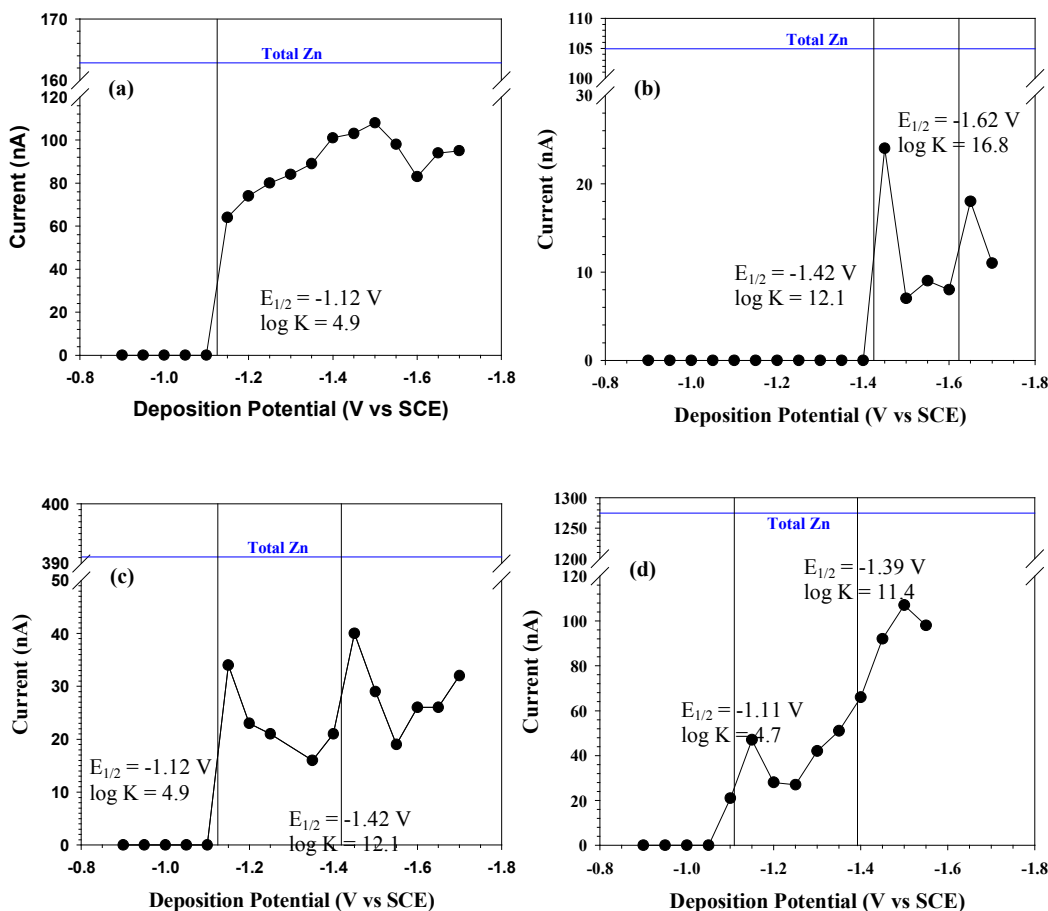
Figure 4. Zinc pseudovoltammograms for samples collected on 06/12/04 at (a) Chain Bridge, (b) Point of Rocks, (c) Handcock and (d) Cumberland. Note: For the Cumberland sample, no reliable data for deposition potentials of -1.6 to -1.7 V.

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The Zn pseudovoltammogram for the sample collected at Chain Bridge illustrates an $E_{1/2}$ of -1.12 V (Figure 4a), which indicates a Zn complex with a log K_{THERM} of 4.9 (where K_{THERM} is the thermodynamic stability constant). This is determined from the Zn chelate scale (Figure 5), which suggests that the complex at Chain Bridge has a thermodynamic stability constant equivalent to a Zn-glycine complex. Figure 4c also indicates a Zn complex with log K_{THERM} of 4.9 exists at the Handcock site. This may indicate that the same ligand exists at both Chain Bridge and Handcock. At the Handcock site, a second Zn complex can be tentatively identified in the Zn pseudovoltammogram at -1.42 V (Figure 4c), which corresponds to a log K_{THERM} of 12.1.
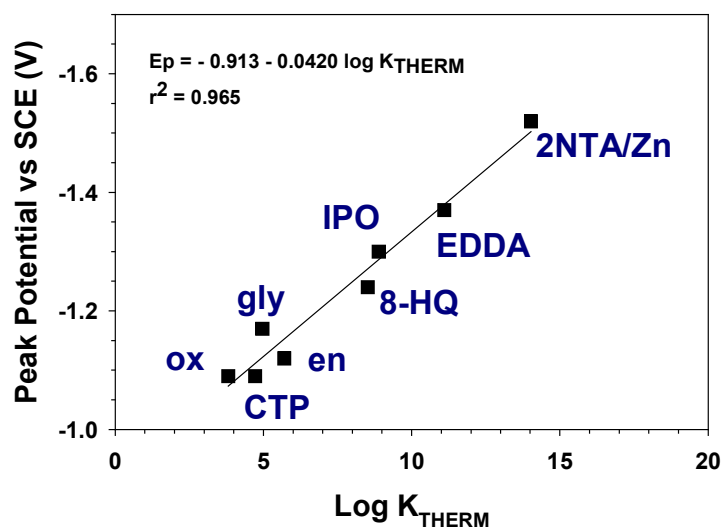
Figure 5. Zinc chelate scale (Lewis et al., 1995 and Luther et al., 2001).

In contrast to the Chain Bridge and Handcock sites, Point of Rocks does not contain a Zn complex with log K_{THERM} of 4.9 (Figure 4b). However, a relatively more stable Zn complex with log K_{THERM} of 12.1 exists at Point of Rocks (Figure 4b). Zinc complexes with the same log K_{THERM} also exists at Handcock (Figure 4c). A relatively more stable second Zn complex can be tentatively identified in the Point of Rocks sample (Figure 4b), which has a log K_{THERM} of 16.8. Two Zn species are also present in the Cumberland sample (Figure 4d). The weaker of the two species has a log K_{THERM} of 4.7, which is comparable to the weak complexes observed at Chain Bridge and Handcock (Figures 4a and 4c). The stronger Zn complex at Cumberland has a log K_{THERM} of 11.4 (Figure 4d).

The total dissolved Zn data at each Potomac River site, determined by electrochemical measurements of UV-irradiated samples, are also shown in the Zn pseudovoltammograms (Figures 4a-d). The results show incomplete recovery of Zn for each Potomac River sample during pseudovoltammetry experiments. This is attributed to the Na^+ reduction that starts at -1.7 V. Hence pseudovoltammograms are limited to a maximum deposition potential of -1.7 V, which equates to log $K_{THERM} < 18.7$ for Zn. Therefore the incomplete recovery of Zn may be attributed to the presence of strong (in)organic complexes with log $K_{THERM} > 18.7$.

Figures 4a-d indicate that 66.3, 22.9, 10.2 and 8.4% of the total Zn exist as weak to moderately stable Zn complexes at Chain Bridge, Point of Rocks, Handcock and Cumberland, respectively. The remainder of the Zn at each site exists in stronger complexes that are not detected by pseudovoltammetry. It is noticeable that the amount of strong Zn complexes progressively increases

upstream from station 1 to 4 (Figure 1). These may be strong organic and/or multinuclear sulfide complexes with log K_{THERM} > 18.7. The latter has been observed by Rozan et al. (2000) in natural oxic waters and have log K_{THERM} > 40. The acid volatile sulfide content for Chain Bridge, Point of Rocks, Handcock and Cumberland samples are 50, 70, 184 and 88 nM, respectively. The presence of sulfides in the Potomac River samples gives credence to the postulate that multinuclear zinc sulfide clusters contribute to Zn species present in the Potomac River.

Lead is not detected in any of the Potomac River samples including those subjected to UV-irradiation. It is possible that Pb in the Potomac River exists in particulate phases that are removed upon filtration and therefore are not detected by SWASV. In contrast, Cd is present in all UV-irradiated samples. However, during pseudovoltammetry, Cd is only observed in non-irradiated samples from Chain Bridge and Point of Rocks. The Cd pseudovoltammogram for the Chain Bridge sample shows two Cd complexes with log K_{THERM} values of 21.5 and 30.6 (Figure 6). No reliable Cd complexes could be determined from the pseudovoltammogram for the Point of Rocks sample as the data is barely above the detection limits of SWASV. Copper was not detected by pseudovoltammetry in any Potomac River sample. However, following UV-irradiation Cu is only present in samples from Handcock and Cumberland. These results are not shown.
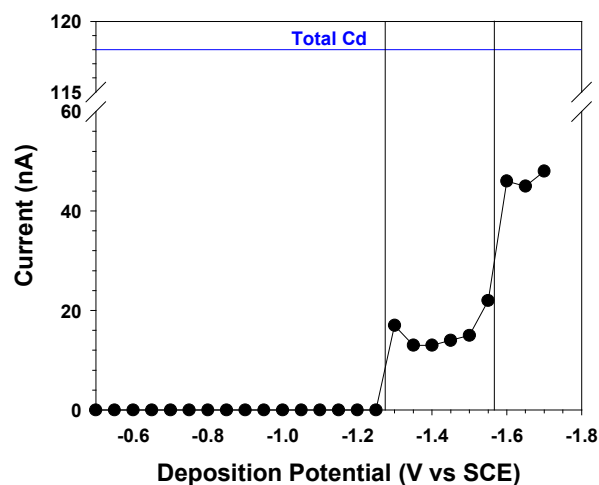
Figure 6. Cd pseudovoltammogram for a sample collected at Chain Bridge on 06/12/04.

The absence of Pb, Cd and Cu in certain samples during pseudovoltammetry may be attributed to the conditions of the electrochemical measurements. Rozan et al. (2003) showed that SWASV could achieve (sub)nanomolar detection limits for Pb when 30 minute depositions were employed. Deposition times at -1.7 V, in this study, were increased from 10 to 30 minutes for samples from Point of Rocks, Handcock and Cumberland. However, the increase in deposition time did not reveal the presence of metals that were absent during 10 minute depositions.

The non-results of the longer deposition experiments support the assumption that the absence of Pb is due to its removal during filtering. Particulate Pb is present in the Potomac River samples (data not shown). In the case where Cd and Cu are observed in UV-irradiated samples and not in non-irradiated samples, the non-result of the increase in deposition time further supports the presence of strong complexes that are electrochemically inert. These may be organic in nature or multinuclear metal sulfide clusters.

Delaware Inland Bays Metal Speciation

Pseudovoltammetry was also employed to determine Zn speciation present in Torquay Canal, Delaware Inland Bays (Figure 2). Surface water samples were collected on three different occasions

spanning a five-week period. One weak Zn complex with log K_{THERM} of 4.9 is observed in the sample collected on May 13, 2004 (Figure 7a). A similar weak complex with log K_{THERM} of 4.0 is observed two weeks later on May 27 at the same site in Torquay Canal (Figure 7b). Two additional moderately strong Zn complexes, with log K_{THERM} of 10.6 and 16.4, are also observed in this sample, which coincided with an algal bloom (Figure 7b). Hence it appears that algal growth and degradation produced new ligands that formed two relatively stronger Zn complexes (Figure 7b) compared to the one present before the bloom (Figure 7a). Two weeks following the bloom event, only one weak Zn complex, with log K_{THERM} of 4.9, is observed in Torquay Canal (Figure 7c). This Zn complex is the same as the one observed before the bloom. It is also noteworthy that Zn complexes with log K_{THERM} of 4.9 are also observed at Chain Bridge and Handcock sites along the Potomac River (Figures 4a and 4c). The same type of complex may also exist at Cumberland (Figure 4d). Moreover, the strongest Zn complex observed during the algal bloom (Figure 7b) is similar to the one tentatively identified in the Point of Rocks sample that has a log K_{THERM} of 16.8 (Figure 4b).

Figure 7. Zinc pseudovoltammograms for surface water samples collected from Torquay Canal on (a) 05/13/04, (b) 05/27/04 and (c) 06/10/04.

Only 66.8 and 63.3% of total Zn exists as weak to moderately strong complexes in samples collected on May 13 and June 10, 2004, respectively (Figures 7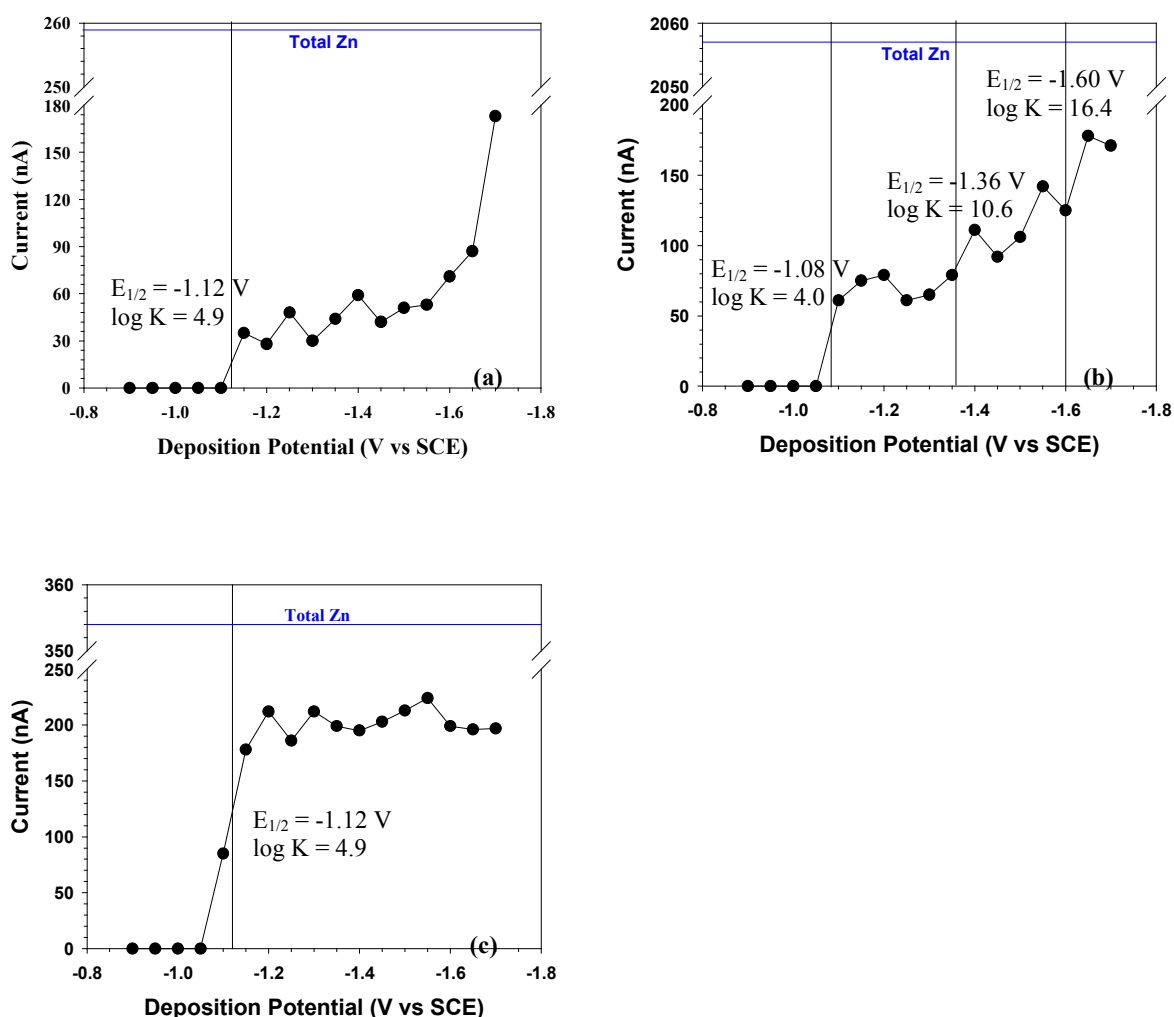a and 7c). However, during the algal bloom only 8.7% of dissolved Zn exists as relatively weak to moderately strong complexes (Figure 7b).

The other 91.3% is in strong complexes (log $K_{THERM} > 18.7$) and are not detected by pseudovoltammetry. An increase in these strong (in)organic complexes is observed during the algal bloom. A number of researchers (Croot et al., 1999 and Luther et al., 2001) have shown that bacterially produced ligands form very strong complexes with metals

Conclusions and Future Work Plan

Potomac Field and Laboratory Results

It is evident that the high particulate inorganic and organic loading during the June sampling period reflected both high flow and vigorous biological productivity. However, this resulted in different distributions between particulate and dissolved phases according to a particular metal and location. The field trips executed on September 16, 2004, collected samples during similar moderate high flow, but presumably lower biological growth. This should have an impact on lowering the pH, alkalinity, DOC, POC, and PN loading, and thus presumably the metal distribution and speciation patterns as it might pertain to the dissolved population of either inorganic (sulfide) or organic ligands. However, it is unlikely that either the major ion proportions, or total metal loadings will change significantly as both the natural weathering or anthropogenic sources are likely to remain consistent even during later period of the growing season.

Metal Speciation in the Potomac River and Delaware Inland Bays

Cadmium mainly existed in strong electrochemically inert complexes at all Potomac River sites. However, two moderately strong Cd species (log K_{THERM} = 21.5 and 30.6) were detected at Chain Bridge by pseudovoltammetry. Copper was only present in Handcock and Cumberland samples as electrochemically inert complexes. Dissolved Pb was not detected in any Potomac River samples. The samples collected on September 16, 2004 will determine if this pattern is consistent during the growing season.

No weak inorganic Zn (chloro, hydroxo, sulfato) complexes were observed in Potomac River samples. Weak to moderately strong Zn (in)organic complexes with $4.7 <$ log $K_{THERM} < 16.8$ were common at different stations along the Potomac River. These complexes only represent 66.3, 22.9, 10.2 and 8.4% of the total dissolved Zn at Chain Bridge, Point of Rocks, Handcock and Cumberland, respectively. The remaining Zn at each site is present as strong electrochemically inert (in)organic complexes, which increased upstream. These might include stable multinuclear zinc sulfide clusters owing to the presence of sulfide in all Potomac River samples. The presence of AVS in oxic Potomac River samples will be confirmed by samples collected on September 16, 2004, which were handled more rigorously than samples collected on June 12, 2004.

Weak complexes with log K_{THERM} of 4.0 to 4.9 were observed in all samples collected from Torquay Canal, Delaware Inland Bays. These are similar to weak complexes detected at Chain Bridge, Handcock and Cumberland sites along the Potomac River. Two additional moderately strong Zn complexes (log K_{THERM} = 10.6 and 16.4) were observed in the Torquay Canal sample collected on May 27, 2004, which coincided with an algal bloom. This also resulted in an increase in strong electrochemically inert complexes compared to that in the absence of the bloom.

Presentations

Church, T.M., Luther G.W. III, Tsang J.J. and Kraiya C. (2004). "Metal speciation in watersheds" Center for Metals in the Environment, 2nd Annual Workshop, July 2004.

Publications

Church, T.M. and Conko K.M. "Trace metals in the greater Potomac I: Riverine concentration, distribution and yields", being submitted to WASP.

Tsang, J.J., Kraiya C., Luther G.W. III, and Rozan, T.F. "Determination of Cd complexation in oxic and sulfidic waters using pseudovoltammetry" In preparation from this report.

Tsang, J.J., Kraiya C., Luther G.W. III, and Church T.M. "Metal organic complexation in freshwater and estuarine environments" In preparation from this report.

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Developing a Unit World Model for Metals in Aquatic Environments

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Introduction

Recently there has been interest in developing methods for evaluating the environmental hazard associated with the release of metals and metal compounds to the environment (Adams et al., 2000). These procedures should include the major processes that affect the fate of metals. However, existing methods (e.g. Mackay, 1992) were developed for organic chemicals and ignore many of the processes that determine the long-term fate of metals in the environment. Furthermore, unlike most organic chemicals, the total metal concentration is not the bioavailable fraction. There is a clear need for a more comprehensive approach to estimating the persistence, bioaccumulation, and toxicity of metals and metal compounds that takes into account these metal specific processes. This purpose of this project is to build such a model – the Unit World Model.

Approach

Environmental fate and transport models have been used to conduct exposure assessments for metals (e.g. O'Connor, 1988; Diamond, 1990; Di Toro et al., 1991). However these models did not address the specific issues of persistence, bioaccumulation, and toxicity of metals. To be useful the model should include the major processes that determine the long term fate of metals in an aquatic environment. These include partitioning to suspended particles, and transport to and from the sediment. The bioaccumulation and toxicological effects of metals in each of these environmental compartments would be addressed by the addition of suitable representations of metal bioavailability and bioaccumulation. This model would represent a standard aquatic environment, a "unit world". The general concept of a unit world modeling approach is not new. It has previously been applied in various forms to pesticides (USEPA, 1986) and industrial organic chemicals (Mackay, 1991; Mackay, D., 1992, European Commission, 1996).

The model would be designed to represent the major processes that determine the fate and transport of metals in the aquatic environment. In the water column these processes include solubilization, complexation with dissolved ligands, and partitioning to suspended particles. The Biotic Ligand Model (BLM) has recently been developed (USEPA, 1999, 2000; Di Toro, et al., 2000; Santore et al., 2000, Paquin et al., 2002) and can be used to compute the complexation of metals to dissolved ligands. A particle sorption model SCAMP (Lofts and Tipping, 1998) has also recently become available as part of the WHAM 6 program (Tipping, 1998). The sorption of metals to particulate matter leads to the transfer of the metal to the bottom sediments. Hence, sediments are the ultimate repository of metals in aquatic settings. It is for this reason that an approach for evaluating the fate, bioavailability, and toxicity of metals in the sediments is important. For metals, EPA has developed sediment quality guidelines that are based on the relative magnitudes of acid volatile sulfide AVS and simultaneously extractable metal SEM, and organic carbon (Di Toro et al., 1990, 1992; Ankley et al., 1993, 1996; USEPA, 2000). A number of sediment models have been developed that successfully predicts levels of AVS and SEM in sediments and resulting fluxes of dissolved metal from the sediments to the overlying water column (Di Toro, 1996; Carbanaro, 1999; Di Toro, 2001). Therefore the frameworks exist, for at least most of the processes in various stages of development, for the water column and sediment compartments.

In order to produce a unit world, it is necessary to synthesize these components into a unified modeling framework, and then to test the model with laboratory and field data for a variety of metals. The initial tasks have been performed in the first year: structure the model and collect data sets from the literature with which to calibrate the various portions (Diamond, 1990; Santschi, 1987; Hesslein, 1980;O'Connor 1988) Data for streams will be generated as part of the Center's research program.

During the first year the Unit World Model (UWM) has been formulated and programmed. An initial calibration of the mesocosm data sets is in progress and results are presented below. In addition progress has been made in testing the partition model to particulate organic carbon. A start has been

made in modeling the sorption of metals to algae. Finally an initial set of stream data collected by other researchers in the Center have been analyzed.

Overview of Fate Controlling Processes of Metals in Aquatic Systems

Metals and inorganic metal compounds enter the aquatic environment via surface runoff, storm water flow, groundwater inflow, atmospheric deposition, and direct discharges of wastewater. Figure 1 provides a conceptual representation of an aquatic system, including both the water column and the underlying sediment. The metal that is in the water column will be present in one of the following three forms:

- Dissolved inorganic metal, including both the ionic form and inorganic complexes of the metal;
- Dissolved organically complexed metal, i.e. metal complexed to DOC;
- Particulate metal, including both sorbed to particles, newly precipitated forms, and any stable mineral phases that may be present.

Tier 1 Model for Lakes
Simple Partitioning Model
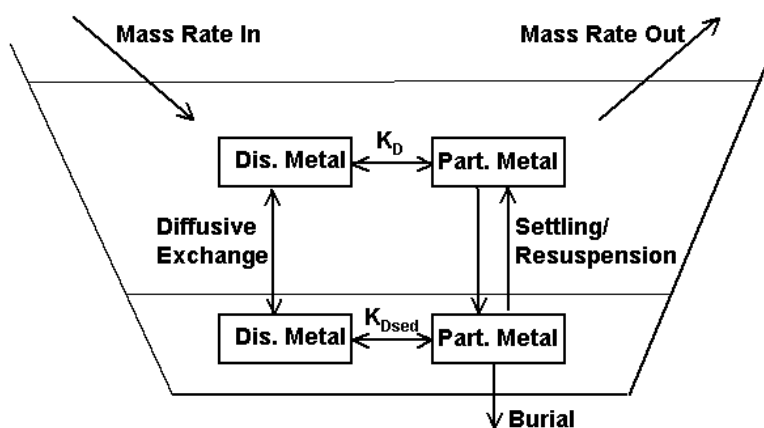
Figure 1.   Tier 1 modeling.

The water column and sediment layer are in direct contact in aquatic systems. This leads to an exchange of constituents, including metals, between these compartments. The metal in the sediment is distributed among the same three phases as in the water column. However, the percentage of the total metal in each phase, as well as the detailed chemical speciation, will differ considerably from that in the water column. For example, the particulate metal in the sediment will typically include significant levels of metal sulfides, a form that may be present in the water column as well, but at much lower concentrations. More generally, the redox conditions in the sediment will control the forms of the metals that are present. Understanding the distribution of the metal among the various phases in both the water column and sediment is of critical importance to assessing the potential for toxicity and persistence.

It should be emphasized that Figure 1 provides only a first order representation of the complex set of reactions and transfer processes that actually occur. For example, the magnitude of the partition coefficient that is used to control sorption to solids is assumed to reflect equilibrium partitioning of the

metal between the water (dissolved metal) and the particles (particulate chemical). It is often evaluated in terms of the organic carbon content of the particles. The pH, hardness, salinity/total dissolved solids, dissolved oxygen concentration, and the presence of sulfides will also impact the complexation reactions. Finally the assumption of equilibrium may not be appropriate.

Fate of Metals in the Water Column

In order for the unit world model to be credible, its is necessary that it be calibrated using field data sets. There exist a number of experimental studies that have evaluated the fate of different metals in various ways. The most common are mesocosm experiments, both freshwater and marine, in which either instantaneous releases or continuous additions of soluble metal compounds have been used. In addition, whole-lake experiments have been conducted. The data from a number of these experiments was presented in the first year's proposal. Two data sets have been modeled so far using the unit world model.

Perch Lake

Using water from Perch Lake (Canada), a mescosm experiment was conducted using seven metals (see Diamond, et al. 1990). The enclosure (0.78 m diameter, 2 m depth) was sealed to prevent inflow of ambient lake water. Figure 2 presents the zinc concentrations versus time normalized to the initial concentration. Results are shown for two replicate experiments. After an initial period of 21 days following the addition of the metals, the enclosures were flushed with lake water to remove residual metals from the overlying water. They were then re-sealed with clean water overlying the sediment to which the metals had previously settled. The subsequent increase in concentration that is shown in the overlying water reflects the release of these metals from the sediments (Figure 2). The model was used to determine the partition coefficients both in the water column and in the sediment.

Figure 2.   Application to Perch Lake.

MELIMEX

The MELIMEX (Metal LIMnological EXperiment) experiment (Gachter 1979) was conducted in Lake Baldegg, Switzerland by the researchers of the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG). The mesocosm is quite large with a diameter of 12 m and a depth of 10 m. Unlike the experiment Perch Lake experiment there was a continuous addition of metals for over one year. The results for copper are shown in Figure 3. The observations for replicate experiments are the open and filled dots. The smooth lines are the results of the UWM using the listed partition coefficients.

Figure 3. Application to MELIMIX.

Modeling the Partition Coefficients

A critical part of the UWM is the prediction of partition coefficients. We intend to use a model based on the WHAM formulation. The initial results for the Perch Lake data set are presented in Figure 4. With the exception of cobalt, the WHAM predictions are is reasonable agreement with the values founds from fitting the Tier 1 UWM to the experimental data.

Perch Lake

- Soft water lake
- Circumneutral pH
- TSS: ca. 2 mg/l
- DOC: ca. 10 mg/L
- Assume $f_{oc} = 0.2$

- POC $\Rightarrow$ Humic Acid
- DOC $\Rightarrow$ Fulvic Acid
- $Co_3O_4(s)$ precipitation?
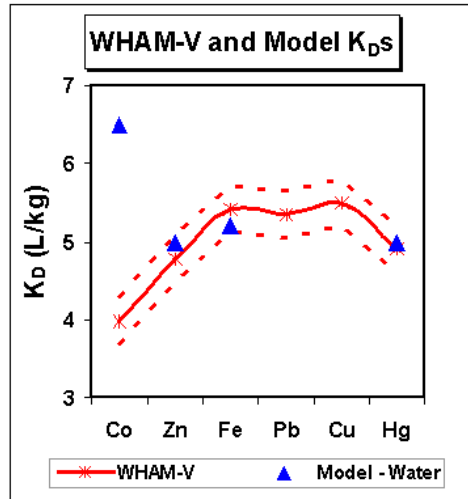
Figure 4.   Partitioning coefficients for Perch Lake.

A similar comparison to the MELIMEX data is shown in Figure 5. There are three metals for which the WHAM predictions are inaccurate. The table to the side of Figure 5 demonstrates that these are the metals that form very insoluble carbonates. It is likely that precipitation is the cause of the large partition coefficients found from the data fitting. Figure 6 presents a summary of the partitioning modeling to date.
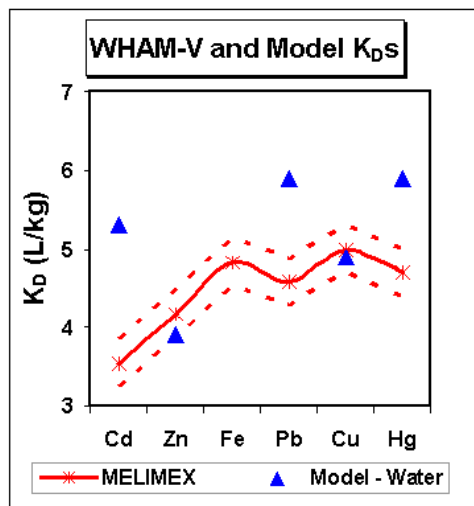
- WHAM-V significantly underpredicts K_Ds for Cd, Pb, and Hg

	log K_{sp}[1]
$HgCO_3(s)$	-16.1
$CdCO_3(s)$	-13.7
$PbCO_3(s)$	-13.1
$ZnCO_3(s)$	-10.0
$CuCO_3(s)$	-9.6
[1]Values from Morel and Hering, 1993	

Figure 5.   Partition coefficients for MELIMIX Lake.

Summary

Comparison of K_Ds

(plot: x-axis "WHAM-V: K_D (L/kg)", y-axis "Part. Model: K_D (L/kg)")
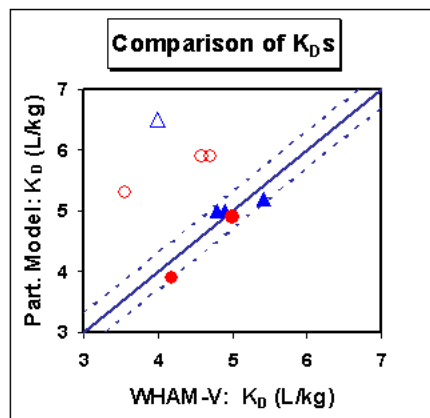
1. Simple K_D Model
2. K_D estimates from WHAM-V
3. Precipitation or coprecipitation reactions?
4. Linear free energy relationships
5. Tier 1 model limitations:
   - POC, DOC, water chemistry vary seasonally
   - No sulfide precipitation

Figure 6.   Summary of partition coefficient.

Modeling Algal Sorption

The WHAM model is intended for modeling metal sorption to humic and fulvic acids. It also appears that it can be applied to non-living particulate organic carbon (POC). However, in many situations the primary form of particulate organic matter in the water column is algal biomass. Therefore, it is necessary to have a modeling framework that can be applied to the algal component of POC.

We have assembled a substantial quantity of algal sorption data from the literature as a starting point for the model development. The usual model applied to algal sorption is a surface complexation model, usually a single site model. Since we have a multi-site model available (WHAM VI), we applied it to the algal sorption data. The algal data is normalized as metal sorbed per unit algal organic carbon, in order to be consistent with the WHAM formulation.

The results are presented in Figure 7. No adjustments have been made to the WHAM VI parameters. The computed lines are the sorption predicted by WHAM VI to humic acid organic carbon. The x axis is metal activity. For the algal data it is either reported by the authors, or is computed from the aqueous chemistry data reported by the authors.

The results are certainly encouraging. For most of the data the WHAM VI model is within an order of magnitude of the observations. There is a marked deviation for Zn sorption. This is likely due to the algal metabolic requirement for Zn.

The next step will be to calibrate the WHAM VI model to the algal data. The fact that it appears to be reproducing the general shape and the correct magnitudes at the higher concentrations suggests that the calibration should not be too difficult.

It is also interesting to note that no low concentration data for Cd, Ni and Pb (not shown) are available. It may be necessary to determine the concentrations at these lower levels if the toxic concentrations of concern are in the range where no data exist.

Figure 7.   Comparison of WHAM VI prediction for humic acid organic carbon and observed metal sorption to algae, normalized by algal organic carbon content.

Application to Stream Data

        The Unit World Model is intended to be used for both lake and stream settings. Since there appears to be very little suitable stream data in the literature, two center projects are sampling metal impacted streams.

An analysis of the results of one of the projects (Colorado School of Mines) is presented in Figure 8. Data from Clear Creek CO are shown.

Data Evaluation for Rivers and Streams
Simple Dilution Calculations

Clear Creek, CO

$$C_{Golden}^{calc.} = \frac{(QC)_{Kermits} + (QC)_{NFSG}}{Q_{Kermits} + Q_{NFSG}}$$
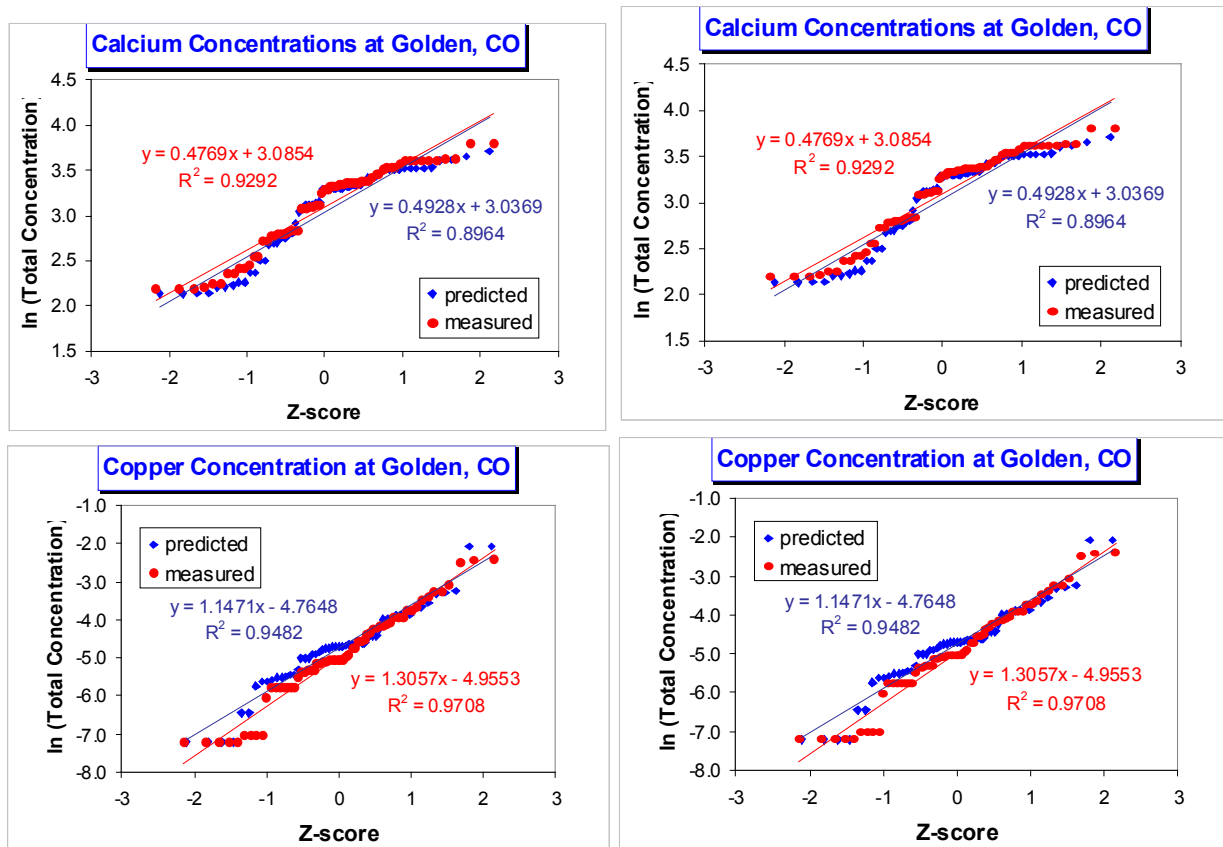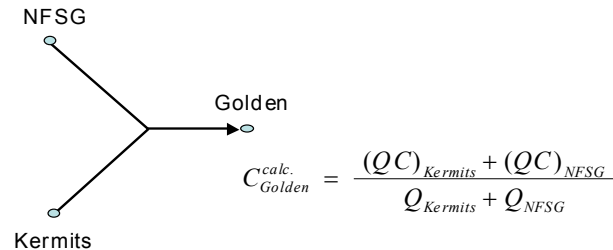
Figure 8. Application to Stream Metals Data. Probability plots of predicted and computed concentrations.

Two upstream locations in the main stem and a tributary (Kermits and NFSG) flow into the downstream station at Golden. The concentration at Golden can be computed as the flow weighted concentrations from the two upstream stations as shown in Figure 8. This computation assumes that there are no sources or sinks of metal in the reaches between the upstream and downstream stations. The four panels in Figure 8 compare the probability distributions of the observed downstream data with that computed from the flow weighted upstream concentrations. For calcium (top left) the two

distributions agree quite nicely as would be expected since the pH of the streams are high enough so that no precipitation of calcium carbonate would be expected. For iron (Figure 8 top right) the data indicate a source at the higher concentrations. By contrast, the concentration of copper (Figure 8 bottom left) seems to show a loss at the lowest concentrations. Finally the concentrations of zinc (Figure 8 bottom right) are always lower than the predicted concentrations, indicating a loss process is active over the entire concentration range.

We will be analyzing the reasons for the source and sink terms for the metals in order to understand the mechanisms that affect the fate of metals in streams. The use of a probabilistic dilution model is quite useful in this regard. We intend to include sorption and scour mechanisms and see whether the model can reproduce the observed probability distributions.

Tier 2 Models

Portions of the unit world model have been constructed in the first year and testing will begin using the data sets described above. The model has been useful at this stage of development. In particular we have reproduced the partitioning in the water column and sediment for one of the mesocosm data sets. Testing against the field data will establish whether the model is sound. The model will continue to be applied in the second and third years to data from contaminated and pristine streams collected by the researchers at the collaborating institutions.

The projected Tier 2 model is presented in Figure 9. We intend to use either a simplified eutrophication model or the necessary inputs, such as primary production, that are required for the metals fate calculation. The design of the Tier 2 model will evolve as we gain more experience with the Tier 1 model calibration in both lake and stream settings.
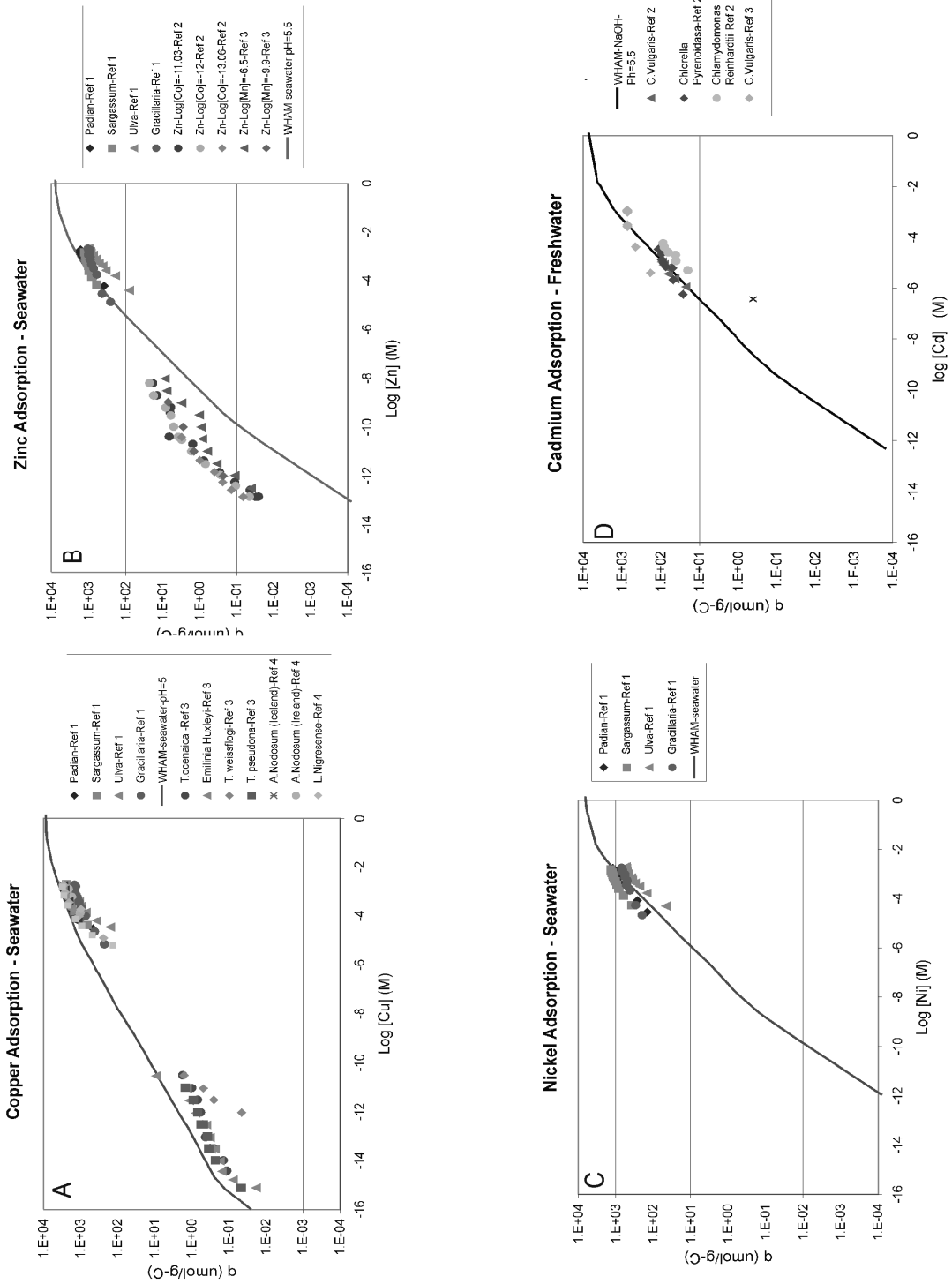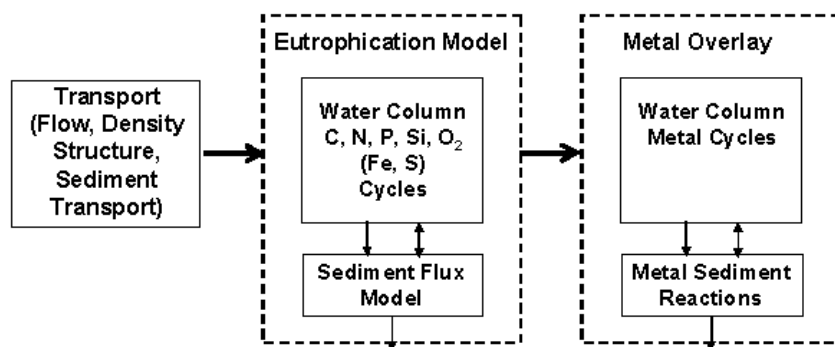

Figure 9. Comparison of WHAM VI prediction for humic acid organic carbon and observed metal sorption to algae, normalized by algal organic carbon content.

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Evaluation of Automobile sources for Metals in Urban Areas

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The primary objective in the first year of this study was to assess metal emissions from automobile brake pads, in particular the amount and rate at which metals dissolve from brake pad wear debris. Two types of brake pad wear debris were collected: *natural wear debris*, from the wheels/hubs of automobiles, and *artificial wear debris,* which were generated by grinding or sanding the brake pads in the laboratory. In Part I of this study, natural wear debris were collected from a 1994 Honda Civic and artificial wear debris were generated by abrading this automobile's brake pads with a die grinder. In Part II of our study four different sets of brake pads and brake pad wear debris were collected from automobiles, with artificial wear debris generated by sanding the brake pads. The leaching solution was synthetic rainwater in Part I and a non metal complexing organic buffer solution in Part II.

The following tasks were completed in year 1.

- A protocol was developed for collecting brake pad wear debris on an intermittent basis from five automobiles known to use brake pads with significant copper content.
- A method for generating artificial brake pad particles from brake pads removed from these automobiles was tested to determine if these particles, which are much easier to collect than natural wear debris, could be used to assess metal emissions.
- Spectroscopy methods were evaluated for characterizing the distribution of Cu and other relevant elements on wear debris surfaces.
- Leaching studies were conducted to evaluate the amount of Cu, Fe, Ba, Ca, and S dissolved from brake pad wear debris from five automobiles using two leaching solutions: synthetic rainwater (varying pH), initial pH = 4.2-4.4; and a non metal complexing organic buffer solution (constant pH), pH = 4.2-4.3.

With the completion of these tasks the following conclusions were drawn.

- Artificially brake wear debris generated using a belt sander (Part II) produced particles of similar size (1-30 $\Box$m) to those collected from the natural brake wear debris. Grinding the brake pads (Part I) generated particles approximately 5 to 10 times larger than natural debris.
- Specific surface areas differed by as little as 30% and up to a factor of 10 between artificial and natural wear debris, depending on the vehicle type. There was no consistent trend with surface areas, i.e., specific surface areas were sometimes larger and sometimes smaller for the artificial versus natural brake pad wear debris.
- Cu content was found to be higher for the artificial particles than the natural particles, with differences ranging from 40% to a factor of 10.
- X-ray energy dispersive spectroscopy data suggest that Cu is distributed differently between the artificial and natural wear debris. For artificial debris Cu was primarily associated with the largest particles, while it was distributed among all particle sizes for natural wear debris.
- Buffered leaching solutions with pH = 4.2-4.3 indicate that 50 to 60% of the Cu in the artificial and natural particles was leached after 3 days for the four automobiles tested, with the exception of the 1997 Nissan Sentra where 80% of Cu was leached.
- In the buffered leaching study, the Cu dissolved at a faster rate from natural particles versus artificial particles, with approximately 50-60% of the Cu leached in the first 26 hours from natural particles. For the artificial particles, the rate of dissolution was slower: 75 hours were required to leach 50-60% of the Cu. Leaching rates were similar for wear debris from the four different automobiles.
- Brake pad wear debris (artificial and natural) from one automobile was leached using the synthetic rainwater. The initial pH = 4.2-4.4 stabilized to 6.8 after 90 hrs and only 8-9% of the Cu leached from the natural particles after 120 hours.

Introduction

Urban stormwater runoff is considered to be a major source of metals to receiving waters. Total and dissolved concentrations of Cu in stormwater runoff have been found to exceed US EPA criteria for fresh and marine waters. For example, studies of runoff samples from an interstate highway showed dissolved event mean concentrations of Cu as high as 380 μg/l, 1-2 orders of magnitude above discharge criteria to surface water (Sansalone and Buchberger, 1997). It is estimated that 53% of all Cu discharged to South San Francisco Bay comes from urban runoff (Santa Clara Valley Runoff Pollution Prevention Program, 1997). A study evaluating metals from urban sources suggested 47% of the Cu and 25% of the Zn released in urban residential neighborhoods in Maryland was released from automobile brake pads and tires respectively (Davis et al., 2001).

Metals are a significant component in brake pad formulations and their use has increased as manufacturers have sought to meet new federal safety regulations and customer safety requirements (Brake Pad Partnership, 2002). For example the use of Cu has increased by 40% since 1998. Oxides, sulfides and metallic alloys of Cu and other metals such as Fe, Ba and Ca are added in many forms to brake pads: as Cu powder to control heat transport, as brass chips to improve wet friction, as $BaSO_4$ to aid in wear resistance, as Fe_2O_3 to improve cold friction (Nicholson, 1995, as cited by Blau, 2001) and as Cu_2S to stabilize the friction coefficient (Gudmand-Hoyer, et al., 1999, as cited by Blau, 2001).

While the significance of metals in urban stormwater runoff is established, the potential amount released from source materials, their speciation, and their dissolution rates from these source materials have not been examined. Understanding and predicting bioavailability, toxicity, reactivity and transport of metals requires knowledge of metal speciation, dynamics of metal sorption, desorption, and dissolution.

In recent studies by Hur et al. (2003 and 2004), brake pad wear debris was generated from a single automobile under simulated city driving conditions. These particles were analyzed for Cu content and Cu leaching using different leaching solutions. Particles were found to contain ~10 % of Cu by mass, and between 13 to 90% of the available Cu was leached after 18 h using different leaching solutions, where the pH ranged from 5.0 to 6.2. This study was limited, though, in that particles were analyzed from only one brake pad and leaching tests were terminated after 18 or 48 h, depending on the type of test. In the first year of our study we attempted to overcome these limitations by conducting leaching tests over extended periods to quantify the total amount leached from the wear debris, and by examining leaching characteristics of wear debris generated from brake pads taken from multiple automobiles.

Material and Analytical Equipment

Artificial and natural wear debris

In Part I of the study brake pad wear debris from a typical automobile (1994 Honda Civic) was collected during a scheduled replacement of the brake pads. In Part II of the study four different sets of brake pads and brake pad wear debris were collected from automobiles known to use semi-metallic brake pads (1997 Nissan Sentra, 1998 Honda Civic, 2000 Honda Accord, 2000 Toyota Camry). Two different sets of brake pad wear debris were collected: natural brake wear debris, which were taken from the wheels/hubs of the automobile; and artificial brake wear debris, which were generated in the laboratory from brake pads removed from these automobiles. The artificial particles were generated using two different procedures: ground particles were collected using a die grinder in Part I, while a belt sander was used to sand particles from the brake pad surface in Part II.

Chemicals and Reagents

Trace metal grade reagents, hydrochloric acid (HCl, 30%, Fisher Scientific), nitric acid (HNO₃, 70%, Fisher Scientific), sodium chloride (NaCl, analytical grade), PIPBS buffer (GFS Chemicals Inc.), copper metal and copper oxide (analytical grade, Fisher Scientific), and hydrogen peroxide (30%,

analytical grade, Fisher Scientific) were used for the study, All solutions were prepared using distilled, deionized water (DDW) having a resistivity > 18 M-ohm cm.

Leaching solution

In Part I of the study synthetic rainwater (SRW) (pH 4.2-4.4) was used as an extracting solution for the leaching experiment. The SRW was prepared using DDW following procedures outlined by Davis et al. (2001). The solution contained 23 μM NaCl, 18 μM HNO_3, and 18 μM H_2SO_4. This rainwater was similar in composition to the rainfall in the Mid Atlantic region (Maxwell and Mann, 1987). A non metal complexing organic buffer solution 10 mM (pH 4.3-4.4, PIPBS buffer, GFS chemicals Inc, Ohio) was used as an extraction solution in Part II of the study.

Analytical Equipment

A microwave digestion unit, mega 1200 (Milestone Inc.), was used to digest all particles. Metal concentrations in digested samples were measured using an inductively coupled plasma emission spectrophotometer (ICP) (Spectro Flame-EOP, Spectro Analytical Instruments). A digital pH meter (Orion Research Inc.) with a glass pH electrode (Orion Research Inc.) was used for the measurement of pH. Surface area measurements were carried out using surface area analyzer Micrometrics-2010.

Microscopy and spectroscopy Analyses

A scanning electron microscope (SEM) (Model JEOL/JXA-840) with an attached X-ray energy dispersive spectroscopy (XEDS) detector was used for microscopic analyses and determining elemental composition of particle surfaces. The SEM was used to obtain the size distribution of the brake pad particles. XEDS analyses were simultaneously performed to obtain the elemental composition of the particle surfaces.

Experimental Design

Total content of metals (Cu, Fe, Ba) and elements (Ca, S)

The particles collected were analyzed for total metals and key elements known to be significant components in brake pad formulations using the microwave assisted acid digestion method. Automated microwave-assisted acid digestion was conducted in a commercial microwave sample preparation system. The brake pad particles were homogenized by gently shaking and tapping them. A subsample (0.10 g) was removed and placed into a Teflon microwave digestion vessel. A digesting solution (HNO_3:HCl:H_2O_2 ::1:3:0.5, by volume) (Schlautman, 2002) was used in place of the conventional nitric acid solution (HNO_3). A controlled volume (10 mL) of digesting solution was then added to the vessel and the contents were gently swirled to ensure complete contact of the brake pad particles and digesting solution. he Teflon vessel was then sealed with its Teflon cover and placed into the microwave for digestion. The digestion times and temperature program were based on EPA Method – 3051 and are shown in the table below.

Temperature	Time
100°C	5 min
120° C	5 min
160° C	5 min
100° C	5 min

After digestion, the digested solution volume was transferred to an appropriate volumetric flask. The digested solution volume was then diluted 1:50 with DDW and analyzed using the ICP. Pure copper metal and copper oxide were digested to verify the efficacy of the digestion procedure.

Dissolution/leaching of metals and elements

The leaching experiments were designed to determine the dissolution of metals and other elements from artificial and natural brake wear debris. In Part I of the study, batch reactors (500 ml) were prepared with CuO particles and natural and artificial brake wear debris. A blank reactor was operated along with the other reactors to serve as control. Each reactor was filled with 500 ml of SRW, initial pH = 4.2 – 4.4. A solid to liquid ratio of 1: $1.4x10^3$ was used in the study. The batch reactors were shaken in a horizontal shaker at a uniform speed (200 RPM) throughout the study. Samples (3 ml) were taken with time and filtered using 0.45 micron filters. The "dissolved" Cu was operationally defined as Cu passing this filter. The filtered solution was diluted using 0.5% HNO_3 and then analyzed for Cu using ICP. The pH of the samples was monitored during the course of the study. Samples were withdrawn from each reactor with time until equilibrium was reached.

In Part II of the study, dissolution tests were conducted with a non metal complexing buffer solution. Experiments were conducted in 250 ml batch reactors using a solid to liquid ratio of 1: $1x10^4$. The reactors were shaken as described above, and 2 ml samples were withdrawn through time until equilibrium was reached. Samples were filtered and analyzed using the same procedure as in Part I.

Particle size and metal element distributions for brake wear debris

Selected artificial and natural wear debris were analyzed using SEM and XEDS to assess particle sizes and distribution of elements on particle surfaces. Standard operating procedures used in electron microscopy and spectroscopy were followed in conducting these analyses.

Results and Discussion

Total content of metals and important elements in brake wear debris

The mean Cu content in brake particles collected in Part I of this study was 2.73 ± 0.075SE% and 8.73 ± 0.068SE% (SE = one estimated standard error, based on three samples) for the natural and artificial brake wear debris, respectively. The smaller Cu content in the natural particles suggests entrainment or contamination from other non-copper sources, or loss of Cu in the airborne fraction. Natural wear debris in this study were fallout particles collected from the wheels/hubs of automobiles.

Illustrative results from Part II of this study are shown in Figure 1 for samples analyzed from a 2000 Honda Accord. A higher fraction of Fe was observed in natural as compared to artificial debris, which was also observed for the other three automobiles in Part II of the study. The larger fraction of Fe is likely a result of abrasion of the brake pad with the steel rotor. The content of selected elements for the other brake pads showed similar trends, as can be seen by the data in Table 1. From these data it is clear that the composition of the brake pads used on these four automobiles varied significantly. The Cu content of the artificial particles ranged from 8 to 33%, while natural particles had Cu contents ranging from 2 to 8%. The Cu content was always larger in the artificial versus the natural wear debris.
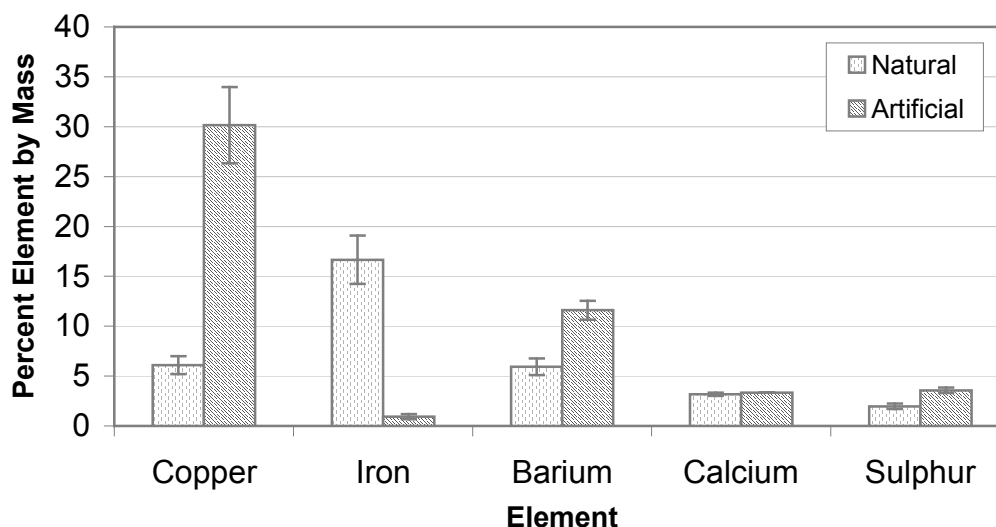
Figure 1. Content of selected elements iartificial and natural brake wear debris from the 2000 Honda Accord.

Table 1.   Total elemental content (percent) in artificial and natural debris.

Element	1998 Honda Civic		2000 Toyota Camry		1997 Nissan Sentra	
	Artificial	**Natural**	**Artificial**	**Natural**	**Artificial**	**Natural**
Iron (Fe)	1.2	3.99 +/- 0.97	13.73 +/- 0.51	38.56	0	23.43 +/- 3.35
Barium (Ba)	10.51 +/- 1.63	2.19 +/- 0.01	11.24 +/- 0.03	6.96	14.19 +/- 0.38	8.38 +/- 0.16
Calcium (Ca)	3.21 + /- 0.47	6.44 +/- 0.07	1.86 +/- 0.04	1.85	2.06 +/- 0.03	1.95 +/- 0.12
Sulphur (S)	3.12 +/- 0.58	0.66 +/- 0.04	3.58 +/- 0.05	2.15	4.29 +/- 0.25	2.53 +/- 0.07
Copper (Cu)	33.38 +/- 4.88	1.12 +/- 0.06	8.42 +/- 0.14	1.68	24.44 +/- 0.54	7.94 +/- 0.03

+/- values are one estimated standard error based on duplicate samples

Specific surface areas of natural and artificial brake wear debris

Specific surface areas were calculated using the linear part of the Brunaure-Emmett-Teller (BET) plot. The specific surface areas differed between the natural and artificial brake wear debris from the 1994 Honda Civic (Part I): 23.01 m^2/g was determined for the natural particles and 2.81 m^2/g for the artificial particles. This result was not unexpected, since the artificial particles generated in Part I of this study were larger than the natural particles. Particles were created by grinding brake pads with a die grinder, while the artificial wear debris generated for Part II were generated by sanding the surfaces of the pads with a belt sander.

Specific surface areas for brake wear debris from the four automobiles in Part II are shown in Figure 2. Specific surface areas differed by as little as 30% and up to a factor of 10 between artificial and natural particles, depending on the vehicle type, with no consistent trend in the data. Sometimes the greater surface area was associated with the artificial particles and sometimes the natural particles.
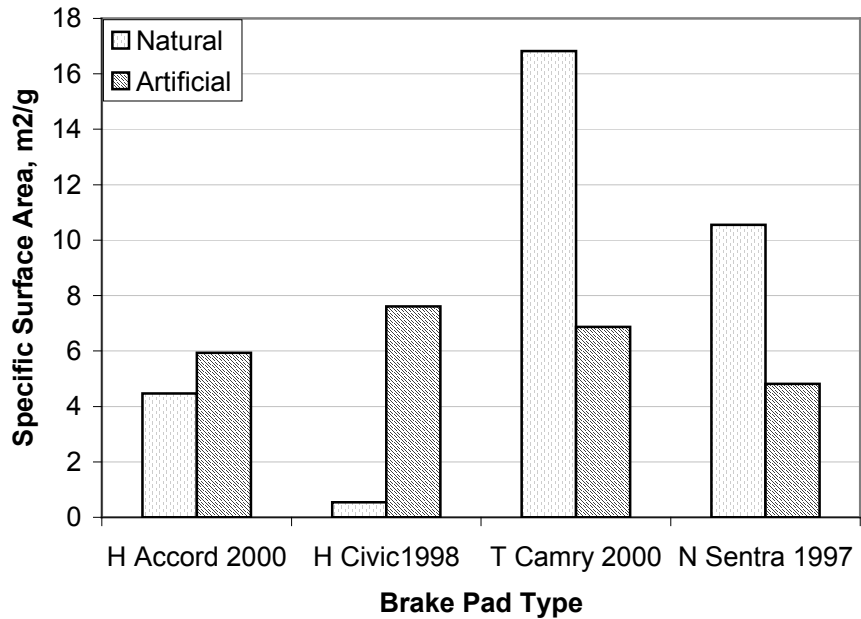
Figure 2. Surface area of artificial and natural brake wear debris.

Particle size and distribution of copper in brake wear debris

Artificial and natural brake wear debris were examined using SEM to determine the average size and morphology of brake wear debris. XEDS was simultaneously used to examine the distribution of Cu and other important elements on debris surfaces. Selected results from natural and artificial wear debris generated from the 2000 Honda Accord are shown in Figures 3 and 4. The SEM images indicate that particles vary in size from 1 to 30 μm for both artificial and natural wear debris. Though similar in size, the natural particles were more spherical than the artificial particles.
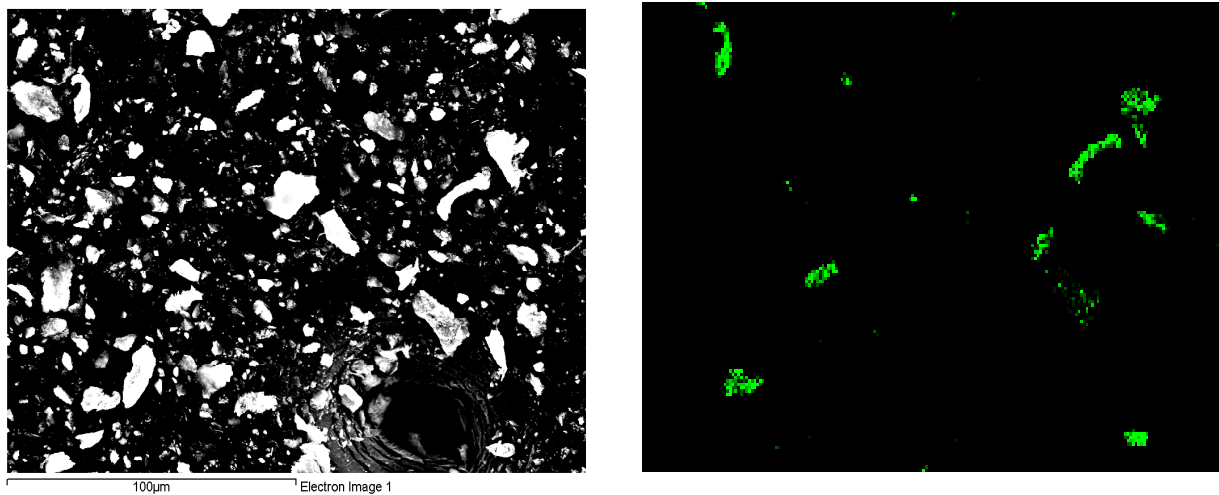
Figure 3. Scanning electron micrograph (left) and Cu distribution (right) for artificial particles collected from a 2000 Honda Accord. The bright spots in the right image indicate Cu on particle surfaces.
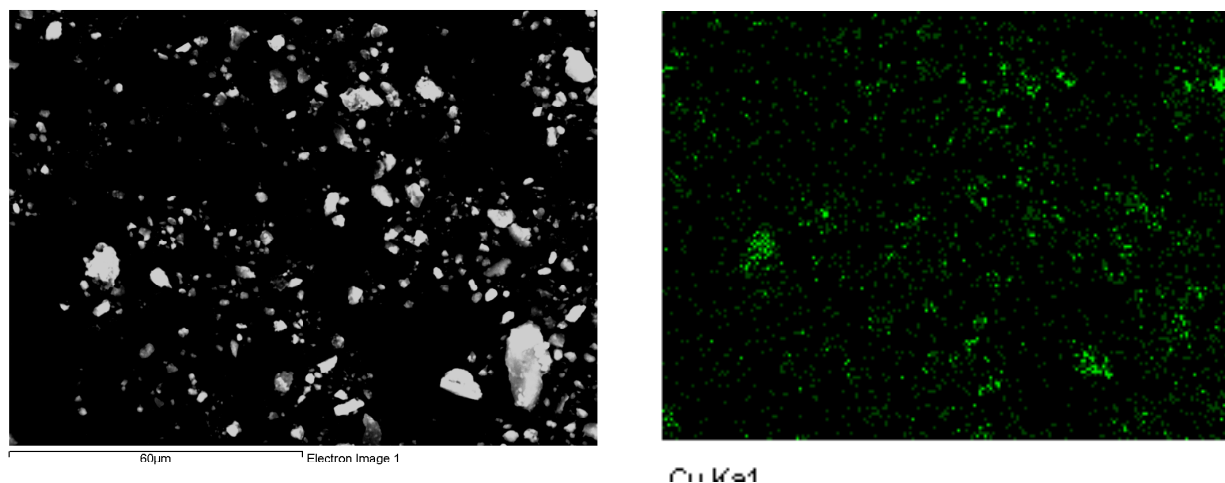
Figure 4. Scanning electron micrograph (left) and Cu distribution (right) for natural particles collected from a 2000 Honda Accord. The bright spots in the right image indicate Cu on particle surfaces.

From the elemental scans Cu is distributed on the surfaces of a few large particles for the artificial wear debris, while it is more uniformly distributed on the surfaces of most natural wear debris. This observation will be used to explain observed Cu leaching rates below.

Dissolution of Cu with SRW and buffered leaching solution:
Brake pad wear debris (artificial and natural) from 1the 994 Honda Civic was leached using SRW in Part I of the study. A pure mineral CuO was also leached simultaneously. The initial pH = 4.2-4.4, but this quickly increased to pH greater than 6.0 after 5 hours, eventually reaching a stable pH = 6.8 after 90 hours for the natural particles. The fraction of Cu leached from artificial and natural wear debris as a function of time is shown in Figure 5. For this leaching solution and set of natural particles from a single vehicle, only 8-9% of the Cu in the natural particles was leached after 120 hours. Only a tiny amount of Cu was leached from the artificial particles generated from the 1994 Honda Civic, likely because of the much smaller surface areas for the artificial particles generated in Part I of this study.
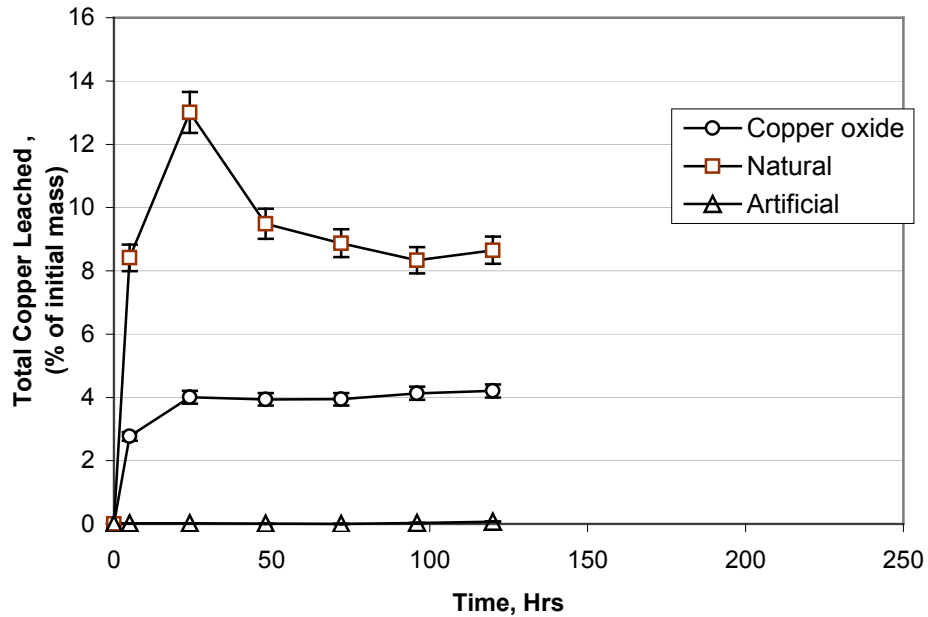
Figure 5. Percent of Cu leached in SRW from 1994 Honda Civic.

The results of Cu dissolution from the four automobiles in Part II of this study are shown below in Figures 6 and 7. Here, the leaching solutions were buffered solutions with pH = 4.2-4.3. Varying amounts of Cu were leached from the artificial and natural brake wear debris from different automobiles.
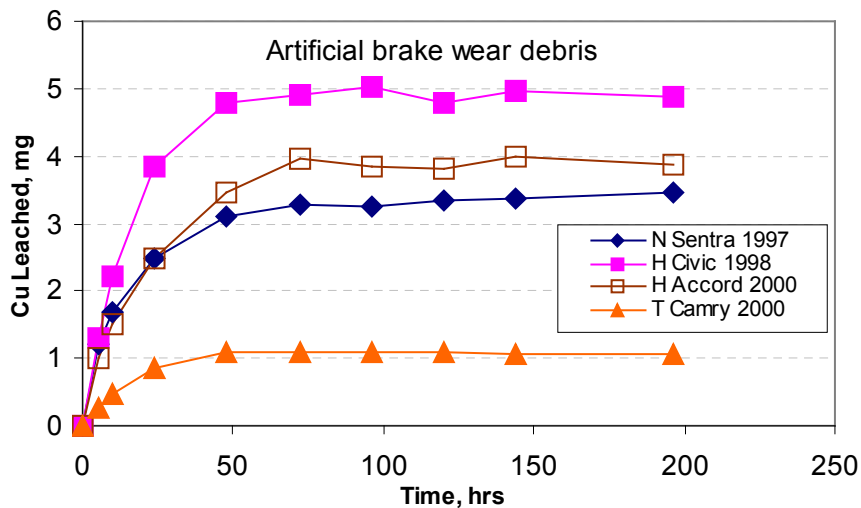
Figure 6. Cu leached from artificial brake wear debris from four automobiles in Part II of the study.
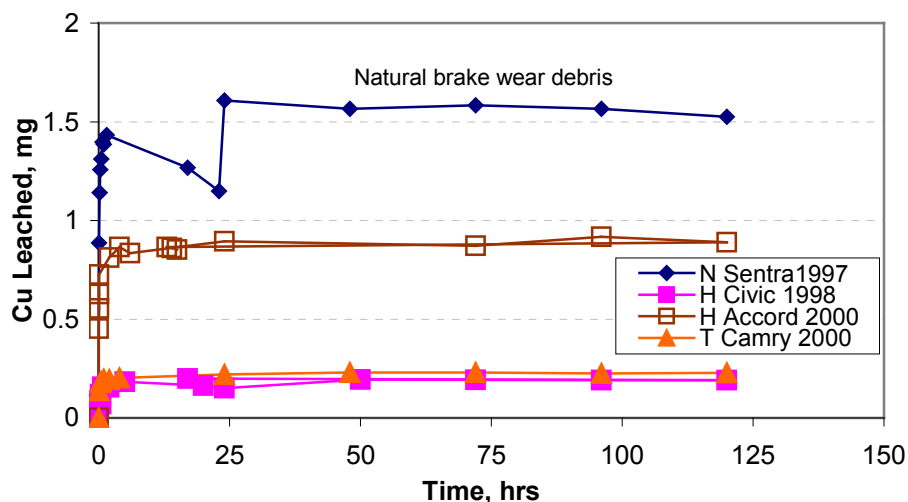
Figure 7. Cu leached from artificial brake wear debris from four automobiles in Part II of the study.

The rates of Cu dissolution are markedly different between the artificial and natural brake wear debris in Part II. Cu dissolved at a much faster rate from natural debris collected from all four automobiles, with all of it leached in 26 hrs. On the other hand, it took approximately 75 hrs for the Cu to leach from the artificial particles. The high rate of dissolution in natural brake wear debris is likely due to the more uniform distribution of Cu on debris surfaces (Figure 4).

Though the rates and amounts of Cu leached are dramatically different between particles, the dissolution data normalized with the total Cu content in the particles agrees well with each other, as shown in Figures 8 and 9. With the exception of the 1997 Nissan Sentra data, when normalized by the total Cu in the particles approximately 50-60% of the Cu is leached from all natural and artificial particles collected from these four automobiles. These data suggest that the natural and artificial wear debris from these automobiles contain similar fractions of Cu that is insoluble with this leaching solution.
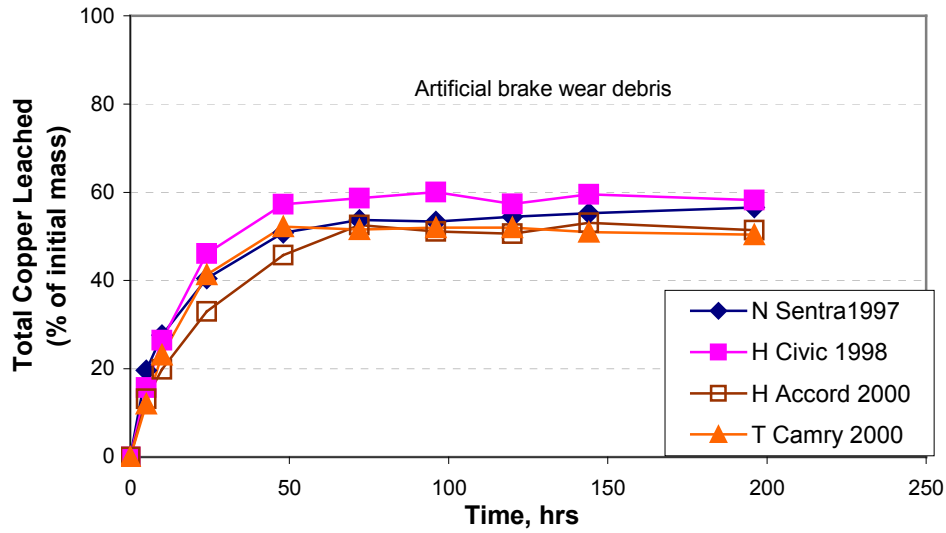
Figure 8. Percent Cu leached from artificial brake wear debris collected from four automobiles in Part II of this study.
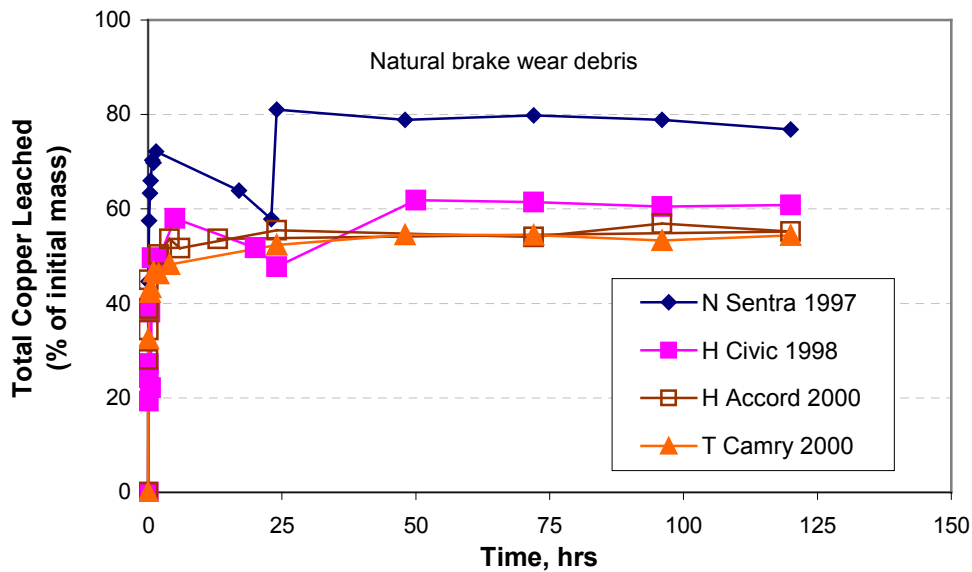
Figure 9. Percent Cu leached from natural brake wear debris collected from four automobiles in Part II of this study.

A comparison of the dissolution of Cu from brake wear debris in Part I and Part II of this study indicates that smaller amounts of Cu were leached in SRW versus the buffered solution with pH = 4.2-4.3: 8 to 9% of Cu leached in Part I, but 50 to 60% of Cu leached in Part II. This is due to differences in the final pH in the two systems.

Conclusions: Year 1

- Significant variations in the amount of metals and other key elements were observed in the wear debris from the semi-metallic brake pads collected from five automobiles in this study.
- An appreciable amount of copper was in the natural wear debris and was associated with particles that ranged from 1 to 30 μm.
- Leaching studies demonstrate significantly different leaching rates between natural and artificial particles, which are consistent with the results obtained from spectroscopy. Cu leached at a faster rate in the natural versus artificial particles, since the Cu was distributed more uniformly on the particle surfaces.
- Leaching studies indicate that while the rate of Cu dissolution is dramatically different between artificial and natural particles, the total fraction of Cu leached is similar for all but one automobile. This suggests that the Cu that was insoluble in the buffered leaching solution (pH = 4.2-4.4) is in a similar form in the artificial and natural particles.
- Leaching studies also indicate that the amount of Cu leached is a strong function of pH, consistent with the findings of Hur et al. (2004).

Future Research

The data collected on Cu dissolution from brake pad wear debris is consistent with that recently reported by Professor Mark Schlautman's group at Clemson University (Hur et al., 2004). They also found Cu dissolution to be a strong function of pH, with near 90% of the Cu in brake wear debris dissolving during 48 hour leaching experiments for solutions with pH < 4.0, but with less than 20% leached from solutions with pH > 6.5. While Schlautman's group used wear debris collected from a single automobile, in our study wear debris was collected from five different automobile types. Thus, our analyses complement Schlautman's work and provide a more complete picture of Cu emissions from brake wear debris.

In year 2 we will complete leaching studies of Cu and other important elements from brake wear debris. Using information on the composition of brake pad materials, thermodynamic modeling (using FactSage 5.2) will be used to predict the change in composition of brake pad materials during braking, which should provide insight into the forms of Cu that might exist in wear debris. This analysis, when combined with our spectroscopy data and leaching studies, may provide us with a means to predict the forms of Cu in brake pad wear debris for brake pad formulations that are not a part of our testing materials, and the corresponding Cu leaching characteristics associated with these wear debris.

Beginning in year 2 and continuing in year 3, we will conduct a similar analysis of metal leaching from tire particles, focusing primarily on Zn leaching. Protocols will be developed for collecting representative tire particles and then experiments designed to assess the amount of total and free metal ions leached under different environmental conditions.

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Sondhi, A., Imhoff, P.T., Allen, H.E., and S.K. Dentel., "Dissolution of metals from brake pad wear debris under conditions simulating leaching in urban areas," accepted for the SETAC- 25th Annual Meeting 2004 Oregon.

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The Impact of Surface Precipitation on Sequestrian and Bioavailability of Metals in Soils

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Objectives and Background Information

The objectives of this study are to investigate the formation and residence time of metal precipitate phases, particularly metal hydroxides, in contaminated soils under a range of environmental conditions and the effect this formation has on metal availability and sequestration in field contaminated soils. Sorption, sequestration, and precipitation of metals within the soil matrix are critical processes affecting contaminant speciation, toxicity, transport and bioavailability. Unfortunately, there is a lack of fundamental understanding of these processes in natural soil systems at a molecular, mechanistic level. In order to improve the decision making process for metal contaminated sites and develop reliable risk assessment methods, it is necessary to acquire a more thorough understanding of the processes controlling metal mobility, speciation and bioavailability in contaminated soils.

An important sorption mechanism for metal retention in natural system is the formation of polynuclear metal hydroxide complexes and surface precipitates. A number of investigators, using in-situ x-ray absorption fine structure spectroscopy (XAFS), have shown that metal (Co, Cr, Cu, Ni, Pb, and Zn) hydroxide complexes and surface precipitates can form on the surfaces of important soil components such as clay minerals and metal oxides (Chisholm-Brause et al., 1990; Charlet and Manceau, 1992; Fendorf et al., 1994; O'Day et al., 1994; Scheidegger et al., 1997; Towle et al., 1997; Scheidegger et al., 1998; Ford et al., 1999; Thompson et al., 1999; Ford and Sparks, 2000). The formation of these precipitates occurs at pHs undersaturated with respect to pure metal hydroxide solubility and at submonolayer surface loadings. In many cases, the surface precipitates occur on time scales of minutes (Scheidegger et al., 1998; Roberts et al., 1999). Moreover, research from our group at the University of Delaware, using X-ray absorption fine structure spectroscopy (XAFS) and diffuse reflectance spectroscopy (DRS), has precisely shown that metal (Ni and Zn) sorption on Al-bearing clay minerals, metal oxides, and soils results in the formation of mixed metal-Al hydroxide precipitates while metal hydroxide precipitates form on non-Al bearing minerals (Ford et al., 1999; Roberts et al., 1999; Scheinost et al., 1999). Co-Al hydroxide surface precipitates have been noted by Towle et al. (1997) and Thompson et al.(1999). These precipitate phases share structural features common to the hydrotalcite group of minerals and the layered double hydroxides (LDH) observed in catalyst synthesis. The LDH structure is built up of stacked sheets of edge-sharing metal octahedra containing divalent (e.g., Mg(II), Ni(II), Co(II), Zn(II), Mn(II)) and trivalent (e.g., Al(III), Fe(III), and Cr(III)) metal ions separated by anions between the interlayer spaces. The LDH structure exhibits a net positive charge, x, per formula unit (e.g., when Al(III) would substitute for a divalent metal in the octahedral layer) which is balanced by an equal negative charge from interlayer anions. While mixed Co-Al, Ni-Al and Zn-Al hydroxide surface precipitates form on Al-bearing metal oxides and phyllosilicates, which appears to be related to the similar size of Co(II), Ni(II), and Zn(II) to Al(III) such that substitutions could occur, such phases have not been observed with Pb(II). This could be related to the mismatch in size between Pb(II) and Al(III), preventing substitution.

As these surface precipitates age, metal retention is greatly enhanced. Several studies document that, as LDH-type precipitates that have formed on a pyrophyllite clay mineral substrate age, Ni release is greatly impeded (Scheckel et al., 2000; Scheckel and Sparks, 2001). With increased aging time the mixed Ni-Al surface precipitate on the pyrophyllite surface was transformed to a precursor mixed Ni-Al phyllosilicate surface precipitate phase, greatly enhancing the stability of Ni. The increased stability is due to a combination of factors, depending on sorbent structure, but includes enhanced silication of the interlayers of the LDH phases and Ostwald ripening (Ford et al., 1999; Scheckel et al., 2000). In short, the formation of metal hydroxide surface precipitates could be an important way that metals could be sequestered in soils, greatly diminishing their mobility and bioavailabilty.

However, questions remain as to whether such phases occur in soils, what environmental conditions (e.g., pH, time, metal loadings, competitive ions and sorbents) affect metal precipitate formation, and how precipitate formation and residence time affects metal sequestration/release from field contaminated soils. Some preliminary data collected by our group suggests that metal hydroxide

surface precipitates can form in soils. Studies by Roberts et al. (1999) found that mixed metal-Al surface precipitates formed on the clay fraction of a Matapeake silt loam soil from Delaware and the whole soil when reacted with Ni in the laboratory (a Ni concentration of 3 mM and a reaction pH of 7.5). The intensity of the precipitate formation was enhanced as time increased. Precipitates also formed at pH 6.8, but not at pH 6 under similar reaction conditions. It is hypothesized that under soil pH conditions of 6.5 and higher and at relatively high metal loadings, which would be the case for some contaminated soils, that metal surface precipitates form and they could significantly sequester the metal so that it is less mobile and bioavailable. More recently, Nachtegaal et al. (2004, unpublished data) have shown that both mixed metal-Al and metal phyllosilicate phases occur in Zn-contaminated and remediated soils, respectively, from Belgium. In order to establish the importance of these soils under field contamination conditions and to develop predictive models incorporating these phases where appropriate, a better understanding of precipitate formation and stability under field soil conditions is required.

Approach

The specific hypotheses being tested in this research are:

- 1. The formation of polynuclear metal hydroxide complexes and surface precipitates, particularly layered double hydroxides, could play a significant role in trace metal speciation and sequestration in contaminated soils with pH levels $\geq$ 6.5.
- 2. Formation of these precipitates sequesters metals into stable phases of low bioavailability, reducing their toxicity to the surrounding ecosystem.

Testing of the first hypothesis involves a two-step approach. In the first step, metal speciation studies of laboratory contaminated soils will be used to determine the parameters controlling the formation of layered double hydroxide (LDH) phases. The role of environmental variables such as pH, organic matter and aluminum solubilization from the underlying clay substrates will be carefully examined. The results of these initial experiments will be used to screen our database of approximately 40 contaminated soils for those which can potentially support the formation of these LDH phases. Soils meeting these criteria will then be examined to determine whether these phases are actually present, and whether they contribute substantially to the overall speciation of the contaminant metal. In both steps of this project, speciation information will be obtained primarily through the use of x-ray absorption spectroscopy. BIOMET analysis of metal bioavailability in these soils will be carried out to determine the effect of precipitate formation on metal sequestration and toxicity. Further details on experiments carried out so far are given below.

Precipitate formation in Ni amended laboratory soils

In order to investigate the role of organic matter and soil mineralogical properties on metal precipitate formation under more controlled circumstances, three distinct soils will be reacted with Ni in the laboratory under conditions identical to those used in previous studies (Roberts et al., 1999), i.e. 3 mM Ni and 0.1 M $NaNO_3$, at pH 6, 7 and 7.5. The three soils include a Matapeake silt loam (1-2 % soil organic matter (SOM), 12 % clay, primarily kaolinite) and a Berryland loamy sand (8-9% SOM, 6% clay, primarily kaolinite), both typical Delaware soils, and a Fort Ellis clay loam (5 % SOM, 37 % clay, primarily montmorillonite), a reference Wyoming soil with higher clay content and different mineralogy. Soil samples will be reacted with the aqueous Ni solution for 30 days with constant stirring, and then analyzed for solid phase Ni speciation by XAFS and tested for Ni desorption using replenishment and stirred flow studies. A portion of the soils will be aged for up to one year in contact with the Ni solution to examine the effects of precipitate aging on Ni release.

Metal speciation

Metal speciation of the soils to determine what phases (adsorbed, metal precipitates, mineral) are present in the soils will be carried out using XAFS analyses. Bulk XAS analyses will be determined on X-11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Samples will be run under ambient conditions using an unfocussed beam under conditions described in previous papers published by our research group (Ford et al., 1999; Roberts et al., 2002). Data will be collected in fluorescence mode using a Stern-Heald type (Lytle) detector filled with Ar gas and equipped with a filter. Depending on metal concentrations in the soils, multiple scans will be collected until satisfactory signal-to-noise ratios are achieved. Spatially resolved micro-XANES and micro–EXAFS (extended x-ray absorption fine structure) and micro-X-ray fluorescence (XRF) spectroscopic analyses of the metal-contaminated soils will be determined at beamline X-26A at NSLS, at beamline 13-1D-C at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), and beamline 10.3.2 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). EXAFS data will be extracted from the raw spectra using the Sixpack suite of programs for background removal and χ extraction. Determination of the identity of metal precipitate phases will be accomplished using comparisons to spectra of reference mineral and sorbed metal phases collected under identical conditions.

Metal desorption/dissolution studies

To determine the effect of residence time, pH, metal speciation and precipitate formation on metal sequestration and release, desorption/dissolution studies at the pH of unamended and amended soils will be conducted using an ion exchange resin as an infinite sink for solution metal (Strawn et al., 1998). Organic buffers (MES and HEPES) will be used to control the pH in the resin studies. Preliminary experiments have shown no significant interactions with metals such as Ni, Cu or Zn. For the resin method, our primary objective will be to quantify the labile fraction of the sorbed metal. Assessment of changes in the stability of a less labile fraction of the metals will be achieved using a stirred-flow technique (Sparks, 1995; Strawn and Sparks, 2000) and 0.01 M $NaNO_3$ at pH 3 as the desorptive agent. Other desorptive agents such as EDTA and nitric acid may also be employed to examine metal sequestration/release from the contaminated and amended soils. Selected samples will be examined by XAS and BIOMET tests after desorption at various times to determine metal speciation and bioavailability changes that might have taken place.

Thermodynamic analysis

In order to develop models of metal speciation that incorporate the potential formation of LDH-type surface precipitates, thermodynamic information on the formation and stability of these phases must be obtained. A number of model Ni-LDH phases will be prepared at environmentally relevant conditions (25 °C and pH 6.9) from solutions containing 2:1 and 10:1 aqueous Ni to Al ratios with a range of interlayer anions (NO_3^-, SO_4^{2-}, CO_3^{2-}). These phases will be prepared by titration of a Ni- Al solution to pH 6.9 following the method described by Taylor (1984), and their identities confirmed by both XRD and EXAFS analysis. Enthalpies of formation for these compounds will be determined using high temperature oxide-melt calorimetry as described in Navrostsky (1997). From this information, it will be possible to calculate solubility product constants for the analogous surface precipitate phases.

Results
Precipitate formation on laboratory contaminated soils

Nickel sorption onto the three laboratory contaminated soils is primarily dependent on three parameters: solution pH, soil clay content, and % soil organic matter. The Fort Ellis soil showed the greatest Ni loading after one month, at 16,000 mg/kg at pH 7.5, followed by the Berryland (13,000 mg/kg) and Matapeake (9,000 mg/kg) soils. In all three cases, the amount of nickel sorbed onto the

solid phase increased substantially as pH increased. At each pH tested, the Fort Ellis soil had the highest Ni loading, a result of the very high clay fraction in this soil. The elevated levels of soil organic matter in the Berryland soil resulted in greater nickel loading on this soil when compared with the Matapeake soil at each pH, although the difference lessened as pH increased.

Previous research has shown that the presence of LDH type Ni precipitate phases on clay substrates can be identified by a characteristic dampening in the chi-transformed EXAFS data at 7.5-8 $Å^{-1}$ when compared with $Ni(OH)_2$ or Ni phyllosilicate phases (Scheinost and Sparks, 2000). For the soils examined in this study, EXAFS results at one month definitely indicates the presence of Ni-Al hydroxide phases in the Matapeake and Berryland soils after one month at pH 7.5 (Figure 1). At pH 7, LDH precipitates are also present in both soils, although less strongly in the Berryland soil, suggesting that Ni complexation by SOM may play a more significant role in Ni speciation at this pH. The LDH finger print signature is not evident in any of the spectra collected from either soil at pH 6, or from the Fort Ellis soil at any pH.
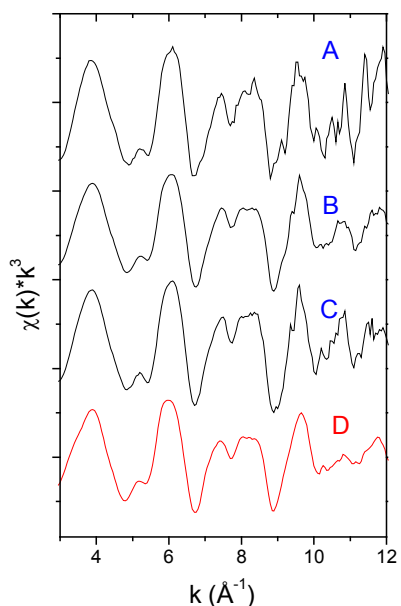
Figure 1. EXAFS spectra of pH 7.5 soils at 1 month. A) Fort Ellis B) Berryland C) Matapeake D) reference Ni layered double hydroxide phase.

Empirical fitting of EXAFS spectra from these three soils was performed with the SixPack software using a set of reference standards including Ni-LDH phases, α and β-$Ni(OH)_2$, $Ni_3Si_4O_{10}(OH)_2$ (a nickel-phyllosilicate phase), $NiCO_3$, $Ni(H_2O)_6^{2+}$, Ni complexed with humic acid, and Ni sorbed onto a variety of clay substrates. Non-negative least squares fitting results for the Matapeake soils at pH $\geq$ 7 suggest that approximately 70% of the sorbed Ni is accounted for by LDH precipitate formation. The Berryland soil shows more of a pH effect, with 50% of the Ni associated with LDH phases at pH7 and 75 % at pH 7.5. Ni speciation in the Fort Ellis soils at pH $\geq$ 7 is composed primarily of non-LDH precipitate phases, most likely α-$Ni(OH)_2$ or Ni-phyllosilicate phases, which have very similar EXAFS spectra. At pH 6, Ni in the Matapeake and Fort Ellis soils is present only as sorbed Ni species (both inner and outer sphere complexes), while the Berryland soil also shows the influence of Ni-humic acid complexes.

Previous researchers have suggested that the observed lack of LDH formation on 2:1 clay substrates such as montmorillonite may be due to the lower solubility of Al from these phases (Scheinost and Sparks, 2000). Data on aluminum release from the three soils suggest that this may be the reason for the different behavior of the Fort Ellis soil in these spiking experiments. Without Ni present, aluminum release from the Fort Ellis soil after 24 hours in the spiking solution is 2-3 times lower than both of the other soils even without accounting for the higher clay content in this soil. When Ni is added, aluminum concentrations in the bulk solution drop to almost zero in the Berryland and Matapeake slurries above pH 7, but not at pH 6, suggesting that solubilized aluminum is being taken up into surface precipitates. In the Fort Ellis soil, Ni addition has little effect on dissolved aluminum concentration, further establishing that LDH precipitate phases do not form in this soil.

From these results, the primary factors affecting LDH precipitate formation appear to be the soil pH and the total solulizable aluminum present in the soil matrix. The role of soil organic matter in enhancing or inhibiting LDH precipitate formation, however, is not yet fully established. While the soil with higher organic matter content had less Ni-LDH formation at pH 7, a slightly higher percentage of sorbed Ni was associated with LDH phases at pH 7.5. This may be due to the much higher concentrations of dissolved aluminum seen in this soil at pH 7.5, most likely due to stabilization of the aluminum ions by complexation with the SOM, but further research is needed to determine the extent of this effect.

Kinetics of Precipitate Formation

We investigated the speciation of Ni in the Matapeake and Berryland soils within the first 72 hours after Ni addition using a continuous scanning XAS technique that allowed us to gain time-resolved EXAFS spectra at 1.5-2 hour intervals. At pH 7.5, both soils showed the onset of LDH precipitate formation within 9-12 hours after Ni addition, and LDH phases were the dominant Ni species by 24 hours. At pH 7, Ni speciation in the Matapeake soil followed a similar pattern, but the Berryland soil showed much less precipitate formation by the end of the 72 hour experiment. These results suggest that soil organic matter can retard the formation of surface precipitate phases, most likely by forming organic Ni complexes. We did not observe the inhibitory effect seen in previous studies (Nachtegaal and Sparks, 2003), however, as Ni precipitates did eventually form at longer times. This is most likely due to differences in the structure of the organic matter present in the system, as the previous experiments used more reactive humic acid fractions.

Stability of Ni LDH Precipitate Phases

Model LDH phases created from starting solutions with 2:1 and 10:1 Ni to Al ratios resulted in precipitate phases with soil Ni to Al ration of 1.8 to 3.3. The substitution of carbonate into the anion interlayers proved to be strongly favored- phases formed in the presence of excess sulfate and nitrate anions still had 10-20% substitution of carbonate into the anion interlayer. Standard enthalpies of formation (ΔH_f^0) for Ni LDH phases containing sulfate, carbonate and nitrate anion interlayers ranged from -800 to -1020 kJ/mol. Phases with carbonate interlayers had the lowest enthalpies, while higher Al substitution showed no consistent trend with regards to enthalpy. Calculation of solubility product constant (K_{sp}) values from these enthalpies revealed that LDH solubilities are six to eight orders of magnitude less soluble than pure phase nickel hydroxides. Substitution of silicate ions into the interlayer of a carbonate-LDH phase resulted in a further decrease in standard enthalpy (to -1100 kJ/mol) and solubility when compared with the original LDH phase.

Desorption studies carried out on all three Ni spiked soils after one and six months of reaction time indicate that Ni LDH precipitate phases become increasingly stable as the age. After one month desorption time, replenishment studies using a 1 mM EDTA solution adjusted to pH 7.5 (a reagent which is capable of dissolving LDH precipitates) resulted in the release of 95-100% of sorbed Ni from the Berryland and Matapeake soils originally reacted at pH 7.5 (Table 1), while at six months, 17% of

the Ni was retained on both soils. The Fort Ellis soil did not show any decrease in Ni solubility with aging in this study. Similar experiments using a weak nitric acid solution designed to remove only sorbed and complexed Ni did not show any change in Ni release between the one and six month samples, suggesting that there is not continued incorporation of Ni into the LDH precipitates after one month. Ni speciation results from the Matapeake and Berryland soils also show no significant change in the LDH fraction for either soil between one and six months. Based on the thermodynamic results presented above, the most likely explanation for this change in desorption behavior is the substitution of dissolved silica from the clay substrate into the LDH interlayer, resulting in increased precipitate stability. This change would not be observable by EXAFS analysis, since the immediate local environment of the Ni ions in the LDH structure remains essentially unchanged.

Table 1. % Ni retained in soils originally spiked at pH 7.5 after1 and 6 month reaction times. Values are for 10 replenishments using a weak nitric acid solution (pH 4.0) or a 1 mM EDTA solution (pH 7.5).

	HNO3 pH 4.0		1m M EDTA pH 7.5	
	1 month	6 month	1 month	6 month
Matapeake	77 %	76 %	0 %	17 %
Berryland	85 %	84 %	6 %	17%
Fort Ellis	96 %	98 %	33 %	29 %

Ongoing Research

Based on the data collected from the Ni-amended soils during the first year of the project, we will screen the University of Delaware's database of approximately 40 contaminated soils to find soils where the formation of LDH phases could be expected. We will concentrate on soils contaminated with Ni, Zn and Cr as metal surface precipitates have been shown to form with these metals, and effective biosensors are available to assess bioavailability of these metals. The soils will be fully characterized including determination of pH, cation exchange capacity, cold acid extractable metal concentrations, organic matter and metal oxide contents, surface area, and clay mineralogical suites using standard techniques (Sparks, 1996). Contaminant metal speciation in the candidate soils will be examined using both bulk and micro-XAS and micro-XRF techniques in order to determine whether the formation of LDH phases has occurred in these soils under natural conditions. Other soils may be pH amended to determine whether it is possible to induce LDH formation in soils where contaminants are already present. Metal dissolution/desorption from these whole soils will also be examined using a combination of replenishment and stirred-flow desorption techniques in order to assess the effect of LDH formation on reducing contaminant mobility and availability. Continued experiments on the Ni- amended test soils are also planned to further isolate the effects of organic matter content on LDH formation.

Samples of the Ni-amended soils used for the first year's experiments are currently being prepared for BIOMET analysis of metal bioavailability. The bioavailability of LDH-containing natural and pH amended soils from the University of Delaware database will also be determined and, as much as possible, compared to metal bioavailability from soils with similar contaminant loadings where LDH phases are not present. These experiments will answer the second hypothesis that LDH phase formation may help to reduce metal bioavailability in whole soils.

Presentations

Sparks, D. L. 2003. Frontiers in contaminant fate and speciation. The role of synchrotron radiation Keynote presentation. IUPAC, Canadian Chemical Society, Canadian Light Source, Ottawa, Canada, August 10-14.

Sparks, D. L. 2003. Frontiers in basic soil science research: grand challenges and opportunities. 26th Congress of the Polish Society of Soil Science, Plenary Presentation, Krakow, Poland. September 8-10.

Peltier, E. F. and Sparks, D. L. 2003. Factors Affecting Ni and Zn Hydroxide Precipitate Formation in Soils. 2003 ASA-CSA-SSSA International Meetings, Denvern, Colorado November 1-5.

Sparks, D. L., 2004. Shedding Light on Soil Contamination and Remediation: The Role of Synchrotron Radiation, Roscoe Ellis, Jr. Lecturer, Kansas State University, Manhattan, Kansas, March 17.

Sparks, D.L. 2004. It's About Scale and Interfaces: Soil Chemistry from the Landscape to the Molecular. Kansas State University, Manhattan, Kansas, March 18.

Peltier, E.F. and Sparks, D.L. 2004. Kinetics of Nickel Precipitate Formation in Soils. 227th ACS National Meeting, Anaheim, California March 28-April 1.

Sparks, D. L. 2004. Kinetics and mechanisms of metal sorption at the soil mineral/water interface. The continuum from adsorption to precipitation. Keynote Lecture, in "Chemistry of Metals in Terrestrial Aquatic Systems" symposium. 227th ACS National Meeting, Anaheim, California March 28 - April 1.

Sparks, D.L. 2004. The role of synchrotron radiation in advancing the frontiers of water-rock interactions. Proceedings of the Eleventh International Symposium on Water-Rock Interaction WRI-11. Saratoga Springs, New York. June 27 - July 2.

Peltier, E.F., Allada, R. A., Navrotsky, A. and Sparks, D. L. Formation and Stability of Nickel Soil Precipitates. 228th ACS National Meeting, Philadelphia, PA August 22-26.

Sparks, D.L., 2004. Multi-scale assessment of ion sorption kinetics at the mineral/water interface. 228th ACS National Meeting, Philadelphia, PA August 22-26.

Sparks, D.L. 2004. Shedding light on metal speciation at mineral surfaces: The role of synchrotron-based spectroscopic techniques. 228th ACS National Meeting, Philadelphia, PA. August 22-26.

Publications

Two papers are in preparation as a result of the research to date. The first treats the results of the thermodynamic studies of model LDH phases and the implications for precipitate stability, while the second covers the kinetic studies on short term LDH formation in the Matapeake and Berryland soils. These papers will be submitted to refereed journals in the autumn of 2004.

Acknowledgements

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Quantitative Structure Activity Relationships for Toxicity and Fate Parameters of Metals and Metal Compounds

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Introduction

The purpose of this research project to develop quantitative structure activity relationships (QSARs) for metals for which little or no experimental information exists. The parameters of interest are those required for hazard ranking and ultimately for evaluation using modeling approaches such as the Unit World Model. There are many metal and metalloid compounds for which there is concern with the environmental hazard associated with their release to the environment. It is important that rational methods of evaluating the potential for harm be employed. Ranking methods have been suggested for this purpose. Unlike the most studied metals, Cd, Cu, Ni, Pb, and Zn, or metals that have recently been of concern, for example Ag, most of the other metals are not well studied, particularly the transition metals in the third and fourth rows and the lanthanides.

It is not only toxicity that needs to be estimated. Basic environmental chemical parameters are also required. For example the WHAM model has been used to evaluate the extent of metal complexation to dissolved organic carbon. It is part of the Biotic Ligand Model of metal toxicity and is used in the Unit World Model. It requires complexation constants to the strong and weak sites of dissolved organic carbon. It has been shown that there is a correlation between metal-DOC binding constants used in WHAM and the metal binding constant to lactate. It would be very useful if such a relationship could be established for the untested metals and perhaps improved using other predictors. Sorption to particles is also important and data from mesocosm experiments for a variety of metals is available. A QSAR for this parameter would be quite useful as well.

Approach

We intend to use modern quantum chemical methods in the development of QSARs. The energetics of gas phase species including main row elements and, to less an extent, transition metals can be evaluated with reasonable accuracy. Until recently, processes in aqueous solution were not as completely addressed since solvent effects complicate reaction energetics and dynamics. But recent advances, particularly the development of continuum solvation models (Schuurmann, 1998; Klamt et al., 1998) and the use of explicit water clusters (Feller et al., 1994; Kallies and Meier, 2001) have remedied this situation to some extent. Also significant progress has been made in solving the technical problems with quantum chemical computations of transition metals. New computational methods (Vacek et al., 1999) and empirical core potentials for heavy atoms (Cundari et al.,1997) have made these calculations feasible. Thus the tools are available for computing properties of aqueous ions for use in QSARs.

QSARs for inorganic ions have been developed in the past (Kaiser, 1980; McCloskey et al., 1996; Newman et al.,1996, 1998; Tatara, et al., 1997, 1998). Figures 1 and 2 present two examples. However the molecular descriptors available at the time were quite limited. In fact the electronic descriptors: electronegativity, ionization potential, and softness index are either for isolated atoms or gas phase ions. With modern quantum chemistry methods, it is possible to compute these indices for hydrated ions. Since ion hydration is a fundamental feature of metal chemistry in aqueous systems, its explicit consideration should greatly improve the applicability of the descriptors. This should make for a much more realistic set of descriptors of ionic reactivity than the atomic or gas phase properties. The descriptors will include dipole and higher moments, the energy of the highest molecular orbital (HOMO), the energy of the lowest unoccupied molecular orbital (LUMO), the Mulliken electronegativity, and a powerful new concept: the molecular hardness (Pearson, 1997) of the hydrated ions. We will then use the standard tools for developing QSAR relationships: multiple linear regression, and perhaps neural networks and genetic algorithms to develop QSAR equations for the parameters with reasonably large data sets (Kaiser, 1997).
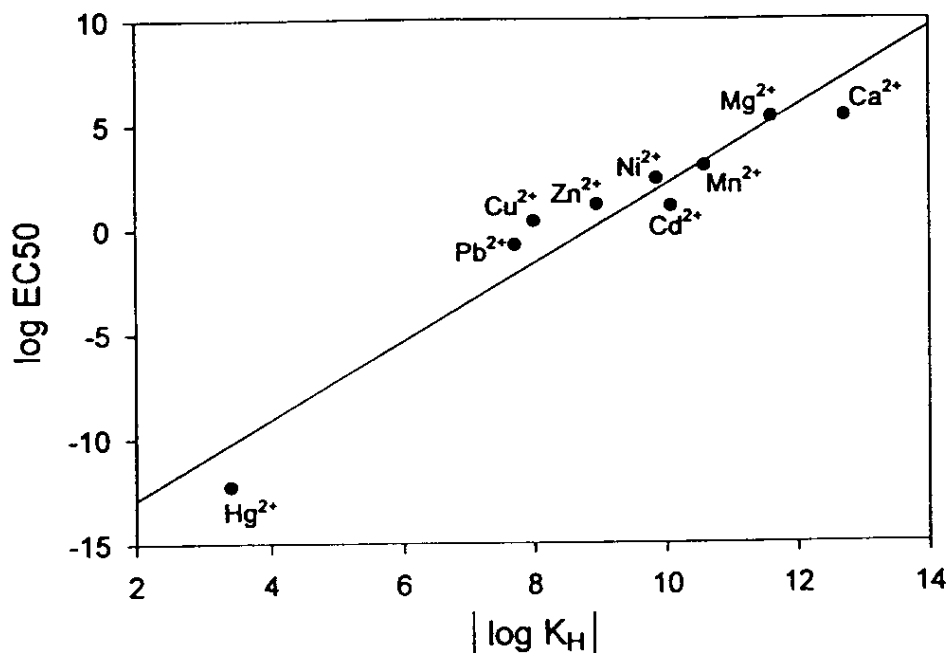
Figure 1.   The model for log EC50 (free ion) and [log K_H] for nine metals.
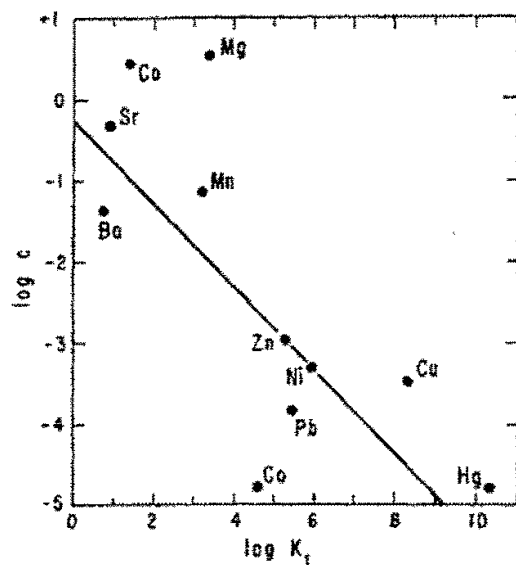
Figure 2.   Toxicity of Daphnia magna.   Log LC50 versus glycine binding constants of the cations. (toxicity data from Biesinger and Christensen, 1972).

In order to test our methods, we will use well understood parameters with large data sets, for example the first hydrolysis constant and the binding constant to lactate, for which data for the lanthanides are available.   We will develop the QSAR on a subset of the data and then predict the remaining values.   In this way we can develop some confidence that our descriptors and methods are

reliable. In order to make reliable QSARs, the first step is to be able to compute reliable thermodynamic properties. The available methods and their accuracy are assessed in the next section.

Results

We have been investigating QSARs for the WHAM V proton-metal exchange constants for humic acid K_{M-HA} and fulvic acid K_{M-FA} (Tipping, 1998). Figure 3 presents the correlation to the lactic acid proton-metal exchange constant K_{M-LA} (Smith and Martell 1993). There is a reasonable relationship with the exception of the most strongly bound cation (Th^{4+}) there is a reasonably linear relationship. Figure 4 presents the correlation to the hydroxide-metal binding constant K_{M-OH} (Smith and Martell 1993). The trivalent cations are the flat portion of the relationship. This suggests that the relationships need to be valence specific. However, these correlations suggest that if we can compute the first hydrolysis constant for the other cations of interest, then we can predict the binding constants to organic carbon.
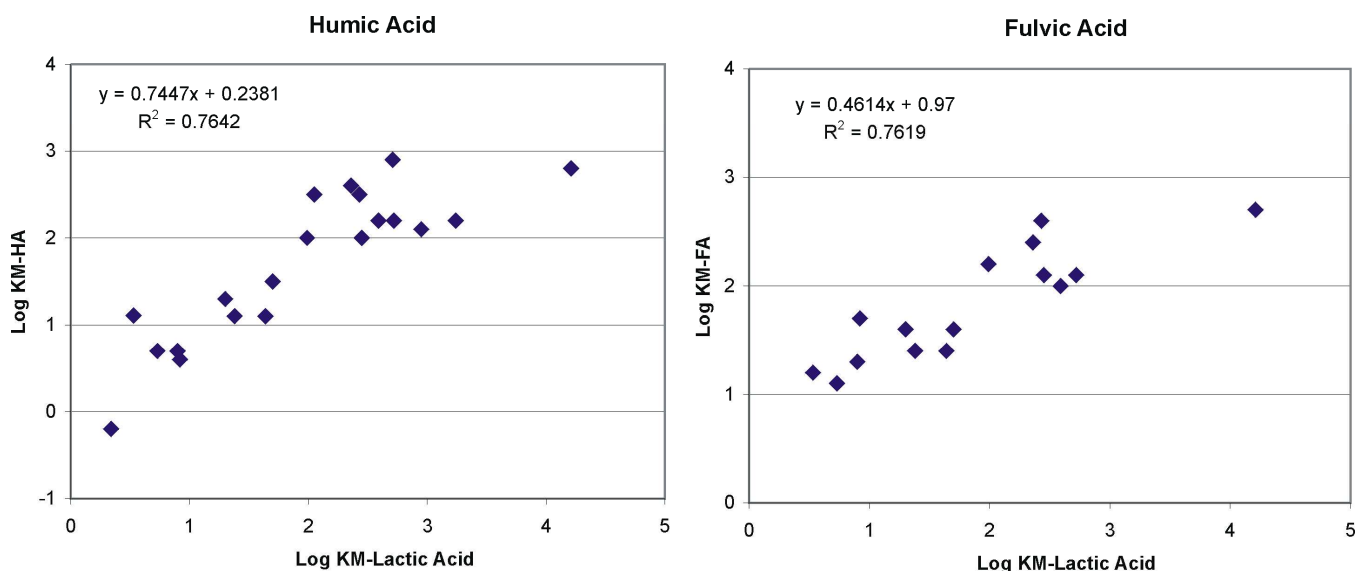

Figure 3.   Humic acid and fulvic acid binding constants vs lactic acid binding constant.
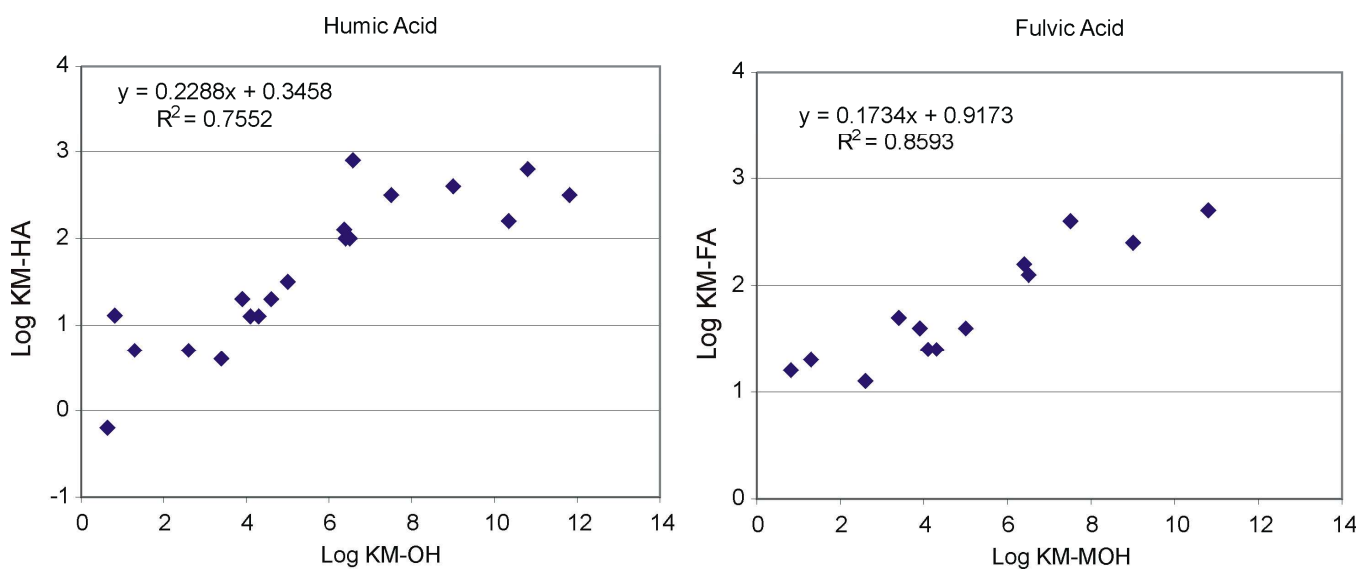

Figure 4.   Humic acid and fulvic acid binding constants vs hydroxide binding constant.

The method we have been investigating is based on computing the gas phase proton affinity of the hydrated cation using quantum chemistry methods. Figures 5 and 6 present an example of the calculation. The structures of the hydrated cation $Al(H_2O)_6^{3+}$ and the first hydroxide complex $Al(H_2O)_5(OH)^{2+}$ are shown in Figure 5. The energies of the necessary species and the final reaction energies are listed in Figure 6. These are computed using Gaussian 98 and Gaussian 03 quantum chemical computational packages. (Frisch et al., 1998).

$$Al(H_2O)_6^{3+} \qquad\qquad Al(H_2O)_5(OH)^{2+}$$
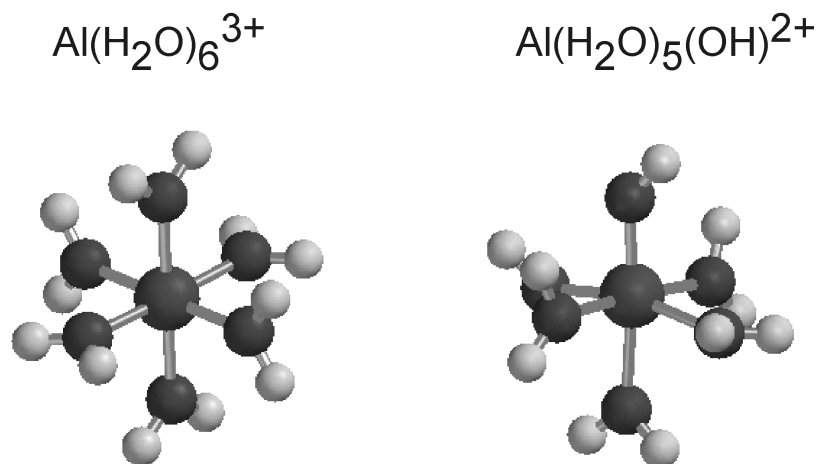
Figure 5. Structure of hydrated aluminum cation and hydrated aluminum monohydroxide.

Gas Phase Energy of Formation (0 K) (1 hartree = 628 kcal/mol)

Metal	$M^{3+}(H_2O)_6$ ΔE (0K) (hartrees)	OH- ΔE (0K) (hartrees)	$M^{2+}OH(H_2O)_5$ ΔE (0K) (hartrees)	H_2O ΔE (0K) (hartrees)
Mn^{3+}	-561.443	-75.726	-561.410	-76.420
Al^{3+}	-700.098	-75.726	-700.023	-76.420

Zero Point Energy

	ZPE (kcal/mol)	ZPE (kcal/mol)	ZPE (kcal/mol)	ZPE (kcal/mol)
Mn^{3+}	94.949	5.011	87.222	13.409
Al^{3+}	97.806	5.011	87.894	13.409

Reaction Energy

	ΔE (0K) (hartrees)	+ZPE (hartrees)	ΔE_{H+} (kcal/mol)
Mn^{3+}	0.0328	0.020	12.836
Al^{3+}	0.0748	0.059	37.008

Figure 6. Example calculation of gas phase proton affinity for Al^{3+} and Mn^{3+}.

These computed gas phase proton affinities are compared to the measured first hydrolysis constants in Figure 7, for trivalent cations, and Figure 8 for divalent cations. The results are quite encouraging. We intend to continue this method by including monovalent cations M^+ and first

hydrolysis species themselves $M(OH)^+$. We will also be examining the use of gas phase complexation to lactic acid in order to estimate $K_{M-LA,}$ as well as other quantum chemical descriptors described above.

Regression Analysis

Figure 7. Regression analysis of the first hydrolysis binding constant of the metal cation versus the gas phase proton binding energy, computed using quantum chemistry methods. Rustad, J., D. Dixon, et al. (1999). "Trivalent Ion Hydrolysis Reactions: A Linear Free-Energy Relationship Based on Density Functional Electronic Structure Calculations." J Am. Chem. Soc. **121**: 3234-3235..
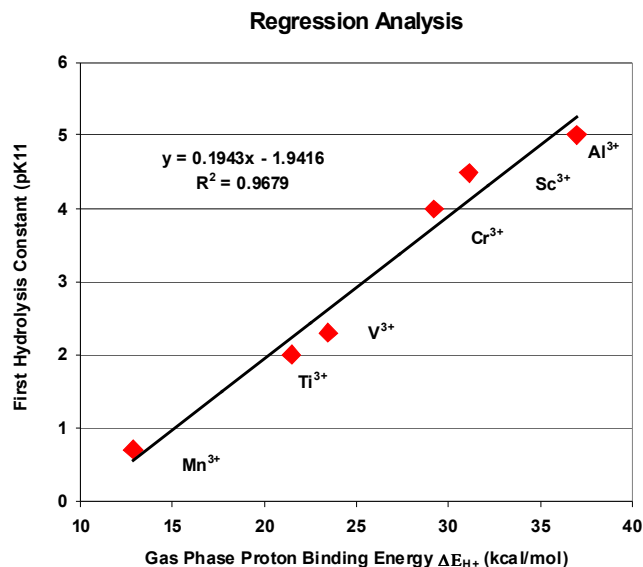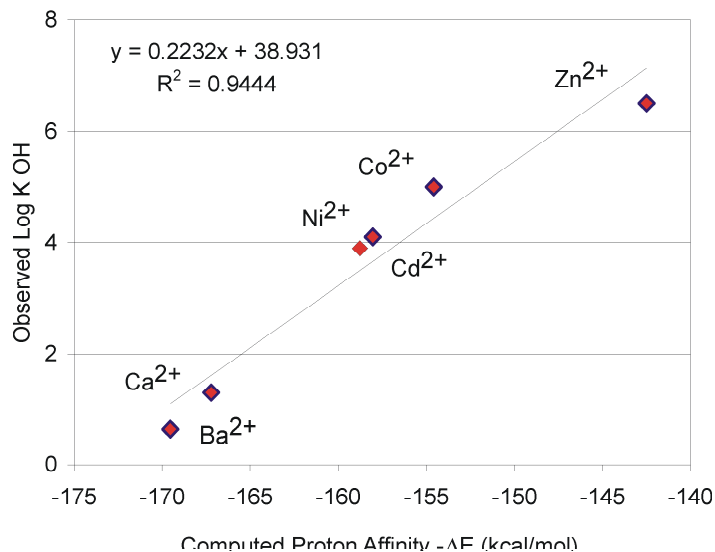

Figure 8. Regression analysis of the first hydrolysis binding constant of the metal cation versus the gas phase proton binding energy, computed using quantum chemistry methods.

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Transport Processes of Mining Related Metals in the Black River of Missouri's New Lead Belt

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Introduction
Objectives

Researchers at the University of Missouri - Rolla are conducting a metals fate and transport study on two adjacent river systems in of southeastern Missouri; the Big River and the West Fork of the Black River. Both watersheds are located in the St. Francois Mountains Region, approximately 50 to 80 miles (80 to 130 km.) south-southwest of Saint Louis. Each river transects a world-class sized lead-zinc mining district with ores that are hosted in carbonate bedrock. This study is being jointly conducted by faculty researchers from the Departments of 1) Geology and Geophysics (G&G) (D.J. Wronkiewicz) and 2) Environmental Engineering (EE) (C.D. Adams and C. Mendoza). Current student researchers include Gary Krizanich (Ph.D. G&G), Anne Faeth (recent M.S. graduate EE/G&G), Josh McBurnett (M.S.G&G), and Graeme Stroker (G&G undergraduate)..

It is the goal of this project to acquire data that can be used for the calibration and validation of comprehensive fate and transport models for heavy metals. Data sets that will be collected include water column and bed load metal concentrations, particle size distribution, mineralogy, particle density, acid leachability, specific surface area, and other key parameters. The heavy metals that are focus of this research are Pb, Zn, Cu, Cd, Co, and Ni. The specific objectives of the proposal are to:

- Characterize segments of the Big and Black Rivers with respect to hydraulics, metal inputs, and metal sinks.
- Develop hydrographs for the study reach of the Black River. USGS gauge records will be used for the Big River.
- Measure the bed load metal concentrations and their temporal and spatial variability within the study systems.
- Measure the water column metal concentrations (including both "dissolved" and "particulate" fractions) and their temporal and spatial variability in relation to hydraulic flows within the study system during various hydraulic events.
- Assess the bioavailability of heavy metals within the study system through determination of acid extractability and speciation.
- Develop, calibrate and validate a transport model for heavy metals to provide guidance for implementation of sampling regimes.
- Coordinate the sample collection, chemical analysis, and other methods with collaborators within the CSME to provide comparable data for varied aquatic systems, and to provide appropriate data for calibration of a Unit World Model.
- Characterize metal transport for two distinct hydraulic events: 1) a slow rise and fall (i.e. "spring melt"), and 2) a steep rise and fall (i.e. "summer storm event"). These two events may be significantly different with respect metal transport properties and hydraulics, with both of these factors significantly impacting the complexation and transport of metals through the system.

The Old Lead Belt Study Area

Three centuries of mining in the "Old Lead Belt" of Missouri has resulted in the accumulation of over 250 million tons of waste tailings that serve as a potential source for metal contaminants in the Big River Watershed. Small-scale mining began in the region in 1701, while larger scale industrial mining techniques began in 1860 and continued nearly uninterrupted until the last mines were closed in 1972. The Big River drainage basin also includes within its confines the Washington County barite (BaSO$_4$) district and numerous smaller historic mining and smelting operations. The Old Lead Belt ores were composed primarily of the Pb, Zn, and Cu-Fe sulfide minerals. Variable, though sometimes economically recoverable amounts of Co, Ni and Ag also occurred, as well as non-economic concentrations of Cd and As. All ore zones of the district were hosted in carbonate-rich bedrock. Waste metals are being released from the tailings piles and into the river drainage system waters during

weathering processes. Weathering processes include both physical erosion by wind and water, as well as chemical corrosion and dissolution of sulfide particles within the tailings pile.

The Big River watershed encompasses a region of approximately 955 square miles (2473 km^2). The river flows approximately 138 nautical miles northward from its headwaters in the St. Francois Mountains until it merges with the Meramec River near St. Louis. Stream gradients are gentile, ranging from a drop of approximately four feet per mile in the mining district to two feet per mile in the lower stretches near the Brynesville sampling location. Major tributaries of the Big River include the Flat River Creek, Mineral Fork, Cedar Creek, and Terre Bleue Creek systems. The sediments of the Big River reflect their low stream gradient, being dominated by sand- and silt-sized particles. Land usage and geological features in the Big River Watershed change over the course of the river with the upper portions being primarily forested wilderness on a bedrock geology of middle-Precambrian aged high alkali-silica granite and rhyolite. The lower reaches (where our samples were collected) are characterized by increasing agricultural usage, including pasture and row cropping. Small urban centers are located within the Old Lead Belt Mining District including the adjoining communities of Park Hills, Bonne Terre, Leadville, Desloge, and Leadington. These cities have a combined population of approximately 18,000 (2000 census figures). Paleozoic-aged dolomites and calcareous shales dominate the bedrock geology in the lower watershed, except in the extreme lower reaches where sandstones become more prevalent. These rock units exert a considerable influence on the chemistry of the river waters, especially in maintaining a slightly alkaline pH and high bicarbonate content.

The New Lead Belt (Viburnum Trend) Study Area

The "New Lead Belt" or "Viburnum Trend" ore district rivals the size and productivity of the "Old Lead Belt" district. Initial discoveries of the present-day ore horizons were made in 1955. Ore production began in 1960 and continues today. Ore processing in the New Lead Belt has resulted in the accumulation of over 235 million tons of waste tailings to date.

The mineralogy and host rock lithology of the New Lead Belt ores are similar to those of the Old Lead Belt, although local differences in trace metal compositions and mineralogy are noted both within and between mining districts. Improved metallurgical processing of the ores in this newer mining district has resulted in greater metal sulfide recoveries in the New relative to the Old Lead Belt. Thus, metal contents are likely to be lower in the New Lead Belt tailings piles relative to the Old Lead Belt. All of the major ore horizons of the New Lead Belt are confined to strata located below the land surface and all mining activity takes place in underground operations.

The West Fork of the Black River is located in Reynolds County Missouri (location maps provided in the 2003 annual report). The river emerges from its headwaters near the Reynolds-Dent County line and flows approximately 45 nautical miles in an easterly direction until it merges with both the Center and East Forks of the Black River near Lesterville, Missouri. A stretch of the river approximately 18 miles in length is being characterized in the present study. Five of the six sampling sites from this study lie within a 4.6 nautical mile east flowing stretch of the river that transects the north-south trending Viburnum ore trend. The sixth sample location is located an additional 13.2 miles downstream. The West Fork watershed receives run off drainage from three large mining operations in the region, the Brushy Creek, the West Fork, and Fletcher mines.   Over the course of the sampling region the river falls approximately 11.2 feet per nautical mile. Major tributary creeks that join the West Fork over this segment include Toms Creek, Bills Creek, and Bee Fork, with the latter two also including mines within their drainage basins. The character of the sediments in the West Fork reflect their high stream gradient, being dominated by cobble, pebble, and sand-sized particles.

Land usage features of the West Fork of the Black River are limited to livestock grazing. Grazing activities are minor in extent, but are concentrated along the Black river valley. The majority of the watershed above the study area is forested wilderness. Reynolds County has a total population of approximately 6700 and there are no major urbanized centers that affect the drainage within our study

segment of the river. The surface bedrock geology is characterized by Paleozoic-aged dolomites, with lesser calcareous shales and sandstones. As with the Big River system, these rock units maintain a slightly alkaline pH and high bicarbonate content of the river waters.

Experimental Procedures

Eight sampling sites were selected on the Big River system and six on the West Fork of the Black River. These sites were selected to fulfill several criteria including ease of accessibility, proximity to known mining operations, and correspondence to sampling locations from previous environmental studies.

Sampling Dates and Locations – Big River

Water column and bed load sediment samples were collected from the Big River and associated tributaries during four successive sampling events spaced approximately three months apart. Sampling dates were on March 9th, June 9th, September 8th, and December 19th in the year of 2002. These sampling events allowed for a preliminary evaluation of metal transport parameters as a function of differing river flow conditions and seasonal variability. Details of the sampling protocol and locations were provided in the 2003 report and will not be repeated here, however, river flow conditions on the sampling dates are given in Table 1. Approximately 20 additional panned concentrate sediment samples were collected in 2004. These samples are being used to characterize the longevity of contaminant sulfide minerals in fluvial systems, determine what alteration phased may form, and identify potential sorptive phases for metals that may exist in the stream bed sediments.

Table 1.   Flow conditions of the Big River during sampling events.

Date	Conditions	USGS Gage Richwoods	River Water Temp. ^{o}C
3/09/02	-Moderate flood stage high turbidity water	4040 ft^3/sec 8.77	10.4 – 11.5
6/09/02	Water slightly above normal seasonal flow	440 ft^3/sec 3.57′	22.9 – 24.5
9/08/02	Water slightly above normal seasonal flow	188 ft^3/sec 2.77	24.8 – 26.2
12/19/02	-Minor flooding of Flat River Creek	1050 ft^3/sec	8.4 – 10.6

Sampling Dates and Locations – West Fork of the Black River

Water column samples were collected in May, August, and November of 2002; February, June, and September of 2003; and February of 2004. In addition to the regularly scheduled sampling, researchers also collected samples during two disturbance events. The first recorded a 2.75 inch rise in river levels resulting from a rainstorm event which occurred directly following the June of 2003 regular quarterly sampling, and the second was due to a sediment disturbance event upstream caused by low water bridge construction and gravel mining in August of 2002. Black River flow conditions on the sampling dates are given in Table 2. Sediment samples were also collected on all dates except the September 2003 and February 2004 sampling trips.

Table 2. Flow conditions of the Black River during sampling events.

Date	Conditions	Calculated Flow Site D	River Water Temp. $^{\circ}$C
5/28/02	low flow, high water clarity	135 ft^3/s	17.3 - 18.6
8/23/02	low flow, high water clarity County gravel operation disturbance	57 ft^3/s	24.1 - 26.1
11/23/02	low flow, high water clarity	35 ft^3/s	6.9 - 11.3
2/21/03	water high from previous rain light rain throughout the day	293 ft^3/s	5.1 - 6.7
6/11/03	Flood rise and increasing turbidity multiple samples collected during rise	28 ft^3/s (low)	17.7 - 19.5
9/16/03	low flow, high water clarity	40 ft^3/s	19.6 - 23.7
02/04	low flow, high water clarity	92 ft^3/s	0.4 - 4.0

Samples were collected from six primary sites on the West Fork during each sampling trip. Site A lies just above Bills Creek and was chosen to represent the control site as its located is upstream of all known mining activities. Site B lies further downstream, below the confluence with Bills Creek, which receives drainage from the Brushy Creek Mine. Site C lies just to the west (upstream) of the Highway KK Bridge and is located above both Toms Creek and the West Fork mine. Site D and E are located further downstream, just below the drainage of the West Fork mine. Sites A through E span a collective distance of 4.6 nautical miles. Site F lies a further 13.2 miles downstream from site E at the Centerville Public Fishing Access. This last site receives distal drainage from the Brushy Creek, West Fork, and Fletcher Mines.

Experimental Modeling

All collection vessels and equipment apparatus were thoroughly cleaned prior to use. Water column samples were collected by submerging 1000 ml polyethylene bottle just below the water surface of the rivers. Four different aliquots were segregated in the field for cation analysis including an unfiltered water sample and filtered water samples that had passed through 5.0, 0.45, or 0.02 syringe filters. Sediment samples were wet sieved in the field using native river water, stainless steel sampling pans, and stainless steel sieves to collect a –10 to +80 mesh (coarse to medium sand), –80 to +230 mesh (medium to fine sand), and a –230 mesh fraction (silt + clay) sediment fraction. The >10 mesh size fraction was discarded. Additional sediment samples were panned concentrated to collect the high density and presumably heavy metal-bearing particles. Water hardness, alkalinity, conductivity, pH, Eh, and temperature readings were also measured in the field for each sampling location and sampling date. Further details on the sampling procedures can be found in the 2003 annual report.

Results and Discussion
Big River Results
Big River Water Column

Analytical results for lead, zinc, and other metals in the Big River water column samples were reported in the 2003 annual summary. No new samples were collected during the past year due to budgetary constraints. Previous investigations indicate that many of the metals are being released from

the tailings piles in a soluble or colloidal form, in solutions that have yet to approach equilibrium with their surrounding environment. As an example, zinc concentrations in waters seeping from the base of the tailings piles were found to be 30-fold greater that what would be expected for a solution in equilibrium with smithsonite ($ZnCO_3$).

Metal concentrations in the main channel of the Big River differ between high and low water events. Low-water events are characterized by zinc values that range from <1 to 219 μg/L, with values progressively decreasing with distance downstream.   The March 2002 flood event samples still progressively decreased downstream, while overall zinc concentrations were elevated relative to low water events (between 144-227 μg/L). Lead concentrations ranged between 16 to 82 μg/L during low water events, while levels during flood stage were between 197 to 286 μg/L. Unlike zinc, however, lead levels often increased with distance downstream, possibly reflecting resuspension of lead bearing bottom sediments or additive contributions from multiple point sources (e.g., additional mine sites down river). The water turbidity also increased dramatically during flooding, indicating that metal-bearing particles could have been easily be resuspended from the bed load sediments during high flow stage and thus have contributed to the overall metal transport process. The maximum total metal concentration and percent passing through a 0.45 μm filter from the Big River waters during the March 9th flood event are: Ba-317 μg/L -33%; Cd-4.1 μg/L -10%; Cu-17.7 μg/L -15%; Ni-11.4 μg/L -15%; Co-11.0 μg/L -6%; As-5 μg/L -100%; with silver at 0.22 μg/L which was below the detection limit.

The distribution patterns for Mn tend to correlate fairly well with zinc and lead, suggesting that these two contaminant metals may be strongly coupled to the transport of manganese oxides and/or oxyhydroxides in the river system (Figure 1). Weak, though still positive correlations were noted with Fe and Al suggesting that iron-bearing phases iron and aluminum-clays may also play a more limited role in influencing the transport properties of contaminant metals. Organic carbon contents have yet to be measured in this river system but are planned in future studies.

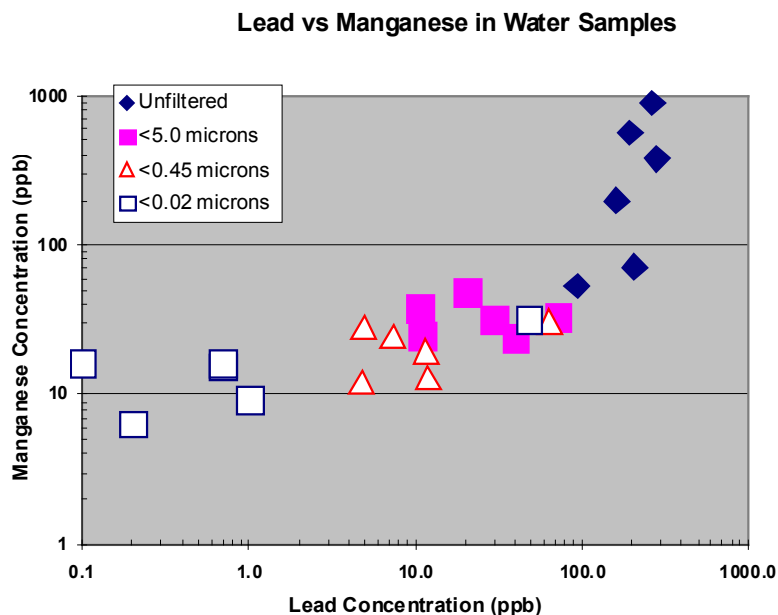**Lead vs Manganese in Water Samples**

Figure 1.   Log concentration of manganese versus log concentration of lead in water samples from the Big River. Samples are segregated into the four different filter size fractions that were collected in the field.

Bed-Load Sediments of the Big River and Associated Tailings Piles

Concentrations of Zn were greatest in the silt- to clay-sized sediment fraction, ranging up to 1600 and 26,400 µg/g for Big River channel and tailings pile sediments, respectively. Distributions of Cd closely paralleled those of Zn, although overall concentrations were considerably lower. Lead concentrations in sediments were also highest in the finer fractions with concentrations ranging up to 2800 and 24,800 µg/g for Big River and tailings pile sediments, respectively.

X-ray diffraction analysis of the various sieve-sized sediment fractions from the tributary creeks indicate that the sediments are dominated by dolomite ($(CaMg)(CO_3)_2$). This composition reflects the host rock mineralogy of the ore zones. By contrast, sediments from the Big River are dominated by quartz. Panned concentrate sediments were collected every 0.5 miles along the Big River from a site at the southeastern edge of the Desloge Tailings Pile in order to more fully characterize the transport properties of sulfide minerals in a fluvial setting. The Desloge Pile was the site of a catastrophic overflow of the retaining dam in 1977, when 450,000 ft^3 of tailings piles were released directly into the Big River. While this tailings pile does not represent the only potential source for sulfide grains in the region, it is considered likely to represent a dominant source due to the amount of material that was released in the 1977 dam failure. Sulfide particles were detected the entire 7.0 mile stretch from the Desloge pile that has been sampled to date, but none were detected at the St. Francois Park site located 11.9 downstream from the Desloge Pile. The additional contribution of sulfide minerals from the Flat River tributary (located 2.5 miles downstream from the Desloge Pile) is also evident from an increase in the abundance and range in the degree of weathering of sulfide particles below the confluence of the Big and Flat River. Sulfide grains have also been recovered in panned concentrates from the Flat River Creek. The sulfide grains included sand to silt sized galena (PbS), pyrite-marcasite (FeS_2 polymorphs), and sphalerite (ZnS). The sulfide grains generally decreased in size and increased in degree of roundness with transport distance down river. The particles also reveal increasing surface dissolution features downstream (Figure 2). Iron oxide-oxyhydroxide, manganese oxide-oxyhydroxide, lead carbonate, and zinc carbonate minerals were also detected in the sediments by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM/EDS) analysis. Fe-Mn oxyhydroxides particles containing Pb, Zn, and Cu were readily identifiable with Mn bearing particles containing up to 7.35 wt% Pb. Iron oxides visually appear to be more predominant than manganese oxides. A chemical analysis of the bulk sediment material corroborates this observation. Partial digestion of sedimentary particles using an *aqua regia* technique indicates that concentrations of both Fe and Mn are also highest in sediments more proximate to the tailings piles and that Fe is present at levels that are approximately 10-fold higher than Mn. Both elements are being liberated into solution by chemical corrosion processes occurring in the tailings piles and then are precipitating onto sedimentary particles short distances after the tailings pile waters are exposed to the atmosphere. Overall sediment Mn concentrations ranged from 0.20 to 0.38% at sites near the tailings piles and 0.11 to 0.23 at sites distal to the piles. Sedimentary iron concentrations ranged from 2.05 to 2.93% at sites proximate to the piles and 1.17 to 2.07% at more distal locations.
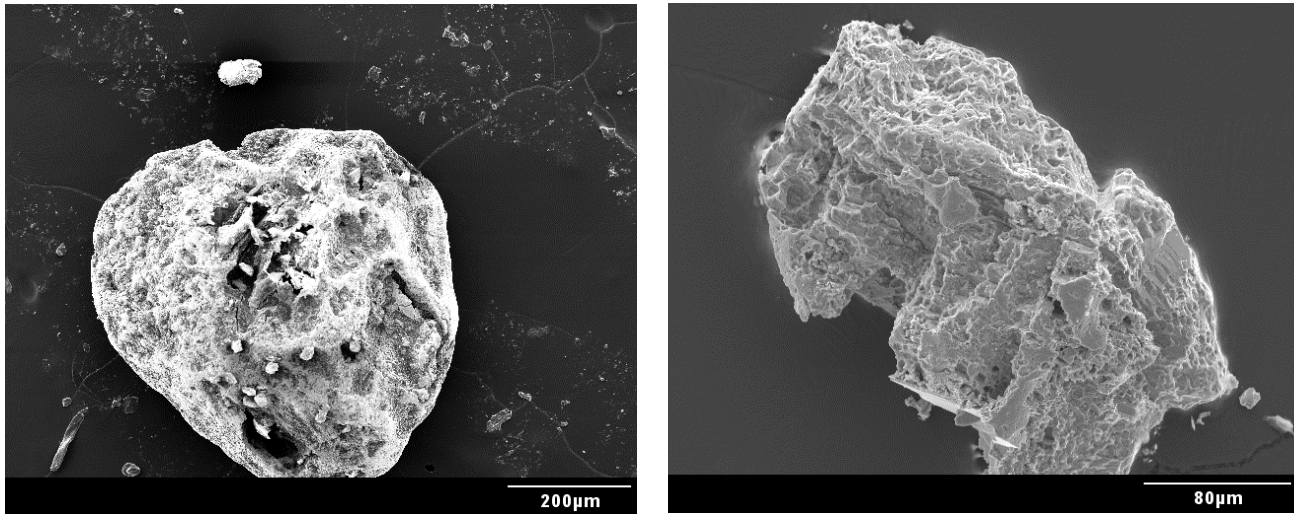
Figure 2. Scanning Electron Microscopy- secondary electron images of panned concentrate river sediment material collected from the Big River at 7.0 nautical miles distance downstream from the Desloge tailings pile site. a) Highly rounded galena (PbS) grain showing minor pitting. Very fine grained cerussite ($PbCO_3$) particles have formed in the pits. b) Sub-rounded sphalerite grain displaying extensively pitted surface indicative of relatively rapid chemical weathering.

West Fork Black River Results

West Fork Black River Water Column Studies

Metal concentrations were generally lower for most water column samples collected from the Black River relative to the Big River. A comparison of total metal concentrations between the West Fork versus the relatively high concentrations noted previously for the Big River attests to the improved environmental management practices employed by the mining companies in the New Lead Belt area. For the West Fork, Pb concentrations were typically lowest at sites A, C, and F, all three of which are also located either upstream or the furthest downstream from known mining operations. Lead concentrations increased at site B, which receives effluent from the Brushy Creek Mine *via* Bills Creek; and at sites D and E, which are located in close proximity downstream of the West Fork Mine. The higher lead concentrations at sites D and E, relative to B, probably reflect this close proximity of the West Fork mining operation rather than any notable difference in metal release. Lead distributions in the water column appear to be dominated by particulate material > 0.45 µm in size. Zinc concentrations roughly parallel those of lead with the highest concentrations occurring at sites D and E and the lowest concentrations occurring at sites A, C, and F.

Five of the seven sampling periods exhibited normal flow conditions (no precipitation or disturbance events during sampling). Average flows on the West Fork of the Black River were estimated to vary between 28 and 293 cubic feet per second (cfs) at Site D, which is located directly below the influx point for drainage from the West Fork Mine. Average estimated flow was calculated using data taken at 12:00 Noon at the Lesterville and Annapolis USGS gauging stations (downstream from our sampling sites), along with considering relative watershed sizes for the two gauging station locations and for the sampling sites along the West Fork. The period of highest flow where we collected samples was in February 2003, and the period of lowest flow was in November 2002. River water pH, alkalinity, and hardness values ranged from 7.6 - 8.2, 100-186 mg/L as $CaCO_3$, and 109-213 mg/L as $CaCO_3$ respectively. Turbidity values that were measured during low flow sampling events were very low, ranging from 0.2 to 2.1 Nephelometric turbidity units (ntu). Turbidity values increased during high

flow, peaked during storm sampling at 17.7 ntu. In general, water clarity on the West Fork was very high with very low suspended solids. DOC was measured during the 2/04 sampling trip and values ranged from 4.15 to 5.02 mg/L.

    All water samples collected during normal flow periods had lead concentrations below the EPA drinking water action level (15 µg/L). Lead and zinc concentrations ranged from <0.15 to 6.7 and <0.15 to 163.0 µg/L respectively for samples taken during normal flow conditions (all sampling periods except 8/02 and 6/03). Since the West Fork is a slightly alkaline bicarbonate dominated system, lead, zinc, and other contaminant metals are expected to be present at low dissolved concentrations. This is confirmed by the lower values of metals seen in the 0.45 µm filtered fraction of water samples. Manganese and iron did not exhibit the same characteristics as contaminant metals, but rather a comparison with both the unfiltered and filtered water fractions indicates that most of the Mn and Fe in water samples is the dissolved or colloidal state (<0.02 µm filtered). As an example, samples from site D taken in 9/03 had 129, 127, 124, and 119 µg/L Mn and 628, 616, 550 and 556 µg/L Fe in the unfiltered, 5.0, 0.45, and 0.02 µm filtered samples respectively.

    Higher lead concentrations were noted at the control site during the highest flow period in 2/03, relative to normal flow sampling events (Figure 3). Lead concentrations downstream from the input point for West Fork Mine effluent did not show any correlation with river flow as the higher lead concentrations were seen for periods of low, moderate and high flow at site D. Zinc concentrations exhibited a closer correlation with river flow. Concentrations of zinc at sites A and D increased during low and moderate flow events, but then decreased again during a period of high flow (2/03). The lower concentrations for zinc during the high flow conditions are believed to be caused by dilution effects.
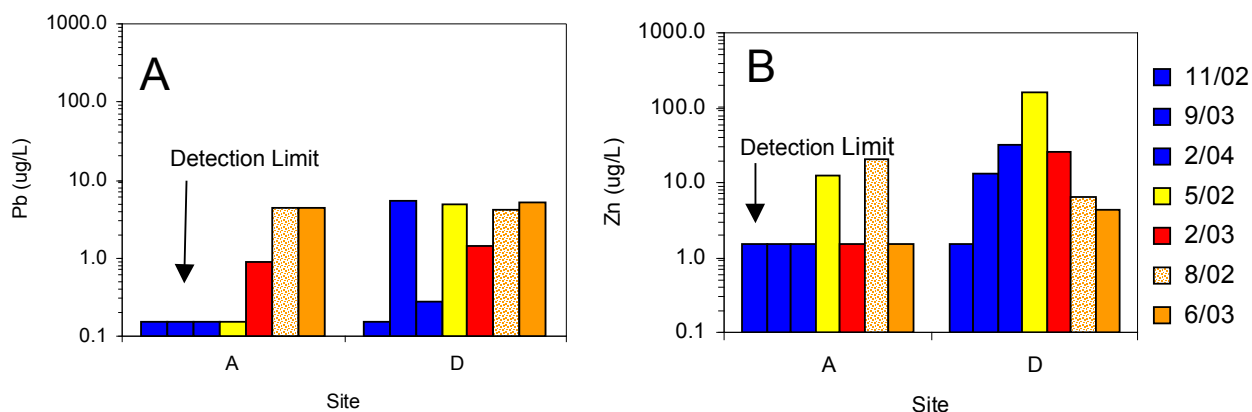

Figure 3. a) Lead and b) zinc concentrations in unfiltered water samples at sites A and D of the West Fork of the Black River. Location A is the control site, located upstream of all surface drainage features of the mining district while site D is located directly downstream from the effluent input location for the West Fork Mine. The blue color pattern indicates relatively low flow river events, yellow - moderate flow, red – high flow, orange – storm induced river rise, and stippled pattern – gravel removal disturbance event upstream of site A.

    Our sampling on 6/03 was conducted during a period of summer rains and a corresponding increase in river flow. Three sets of samples were taken from sites C and D throughout the day and night. The first set was taken late morning (11:20 AM), after rainfall events from the previous night, but before the rainfall event began that day, the second set was taken later that evening (5:51 PM), after rainfall had caused the water to rise two inches at site C, and the third was taken several hours later (10:20 PM) after the water level had risen an additional 0.75 inches. One sample taken during the

second round of sampling had a total Pb concentration of 65.5 µg/L in the unfiltered fraction. This was the highest lead concentration detected during all sampling events. The corresponding concentrations in the 5.0, 0.45, and 0.02 µm filtered fractions were 36.8, 30.4, and 4.7 µg/L, respectively. This distribution suggests that the particulate distribution of lead is a bimodal, with a significant contribution of lead occurring in two particle size ranges; 0.02 to 0.45 µm (39% of total Pb) and >5.0 µm (44% of total Pb). Increasing flow rates and associated turbulence most likely had suspended the particulate matter from the river bed and into the water column, leading to increased metal concentrations in the unfiltered and larger filtered size fractions of water samples at site D. A "Wash-in" of contaminant soil particles from the surrounding forest soil may also play a role in this increased concentration. Concentrations of both Pb and Zn were lower in the third set of samples relative to the second. A "washing-out" of fine materials downstream during high flow or settling of contaminant particles from the water column may have led to this result.

The 8/02 sampling trip unintentionally coincided with a period of low water bridge construction and gravel removal upstream from the sampling reach. Figure 4 shows Pb and Zn concentrations throughout the sampling reach during the 8/02 sampling trip versus the 9/03 sampling trip, which had a similar flow (47 and 52 cfs respectively) but was not affected by any gravel disturbance.. The gravel removal and bridge construction upstream from the sampling trip most likely suspended sediments which normally would only been activated to the water column by scouring events associated during high flood stage conditions. The river bed disturbance during the gravel bed removal operation thus allowed us to examine potential effects that may be associated with a flood event, but without the dilution effects associated with increased runoff into the river system. Higher lead concentrations were seen at the control site (A) and these elevated levels remained relatively constant throughout the sampling reach (A through F), masking any contribution from the mining effluent. Zinc concentrations were higher at the control site (A), dropped off by Site C, and then increased again below the mining effluent input at Site D. The differences between Pb and Zn behavior suggest that the transport of these two contaminant metals is being influenced by different types of sedimentary particles. The preferential retention of Pb in the water column suggests that its transport is more closely associated with low-density (e.g., organics) and/or finer grained particulate material that easily remains suspended in the water column. Alternatively, Zn transport appears to be dominated by larger and/or higher density particles that are removed from the water column more rapidly. Differential scavenging of soluble metals by particulate material may also play a role in these variations.
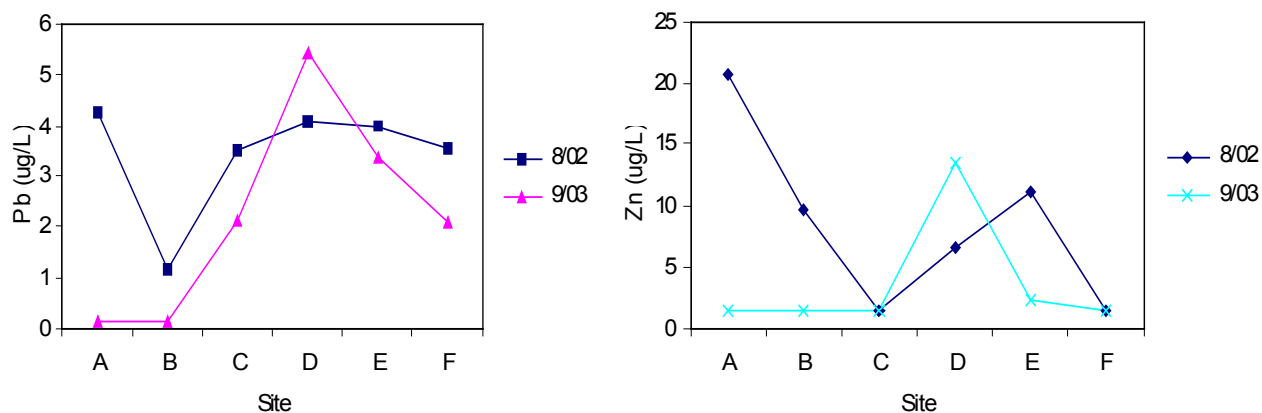

Figure 4.   Lead and zinc concentrations in unfiltered river water from the West Fork of the Black River collected during a period of bridge construction and gravel removal upstream of the sampling reach (Sample collected on 8/02) versus samples collected during a period of similar river flow conditions, but without any sediment disturbance (9/03)..

<u>Bed Load Sediments of the West Fork Black River</u>

Metal concentrations were notably elevated in many of the sediment samples located downstream of the tailings piles along the Black River. Metal concentrations were typically greatest in the two smaller mesh size sediment fractions (80- to +230 and -230 mesh; Figure 5) indicating that the metals are either being emitted into the river as small particles, adsorbed from the water column onto small particles, and/or are converted into small particles by mechanical river processes. Lead and zinc concentrations in all sediment fractions ranged from 2.4 to 960 and 4.3 to 2489 μg/g, respectively. The highest lead and zinc concentrations were seen at sites D and E, which are the two sites located directly downstream from the input point for the West Fork Mine effluent. Overall Zn concentrations are higher than Pb although the two elements display similar distribution patterns.
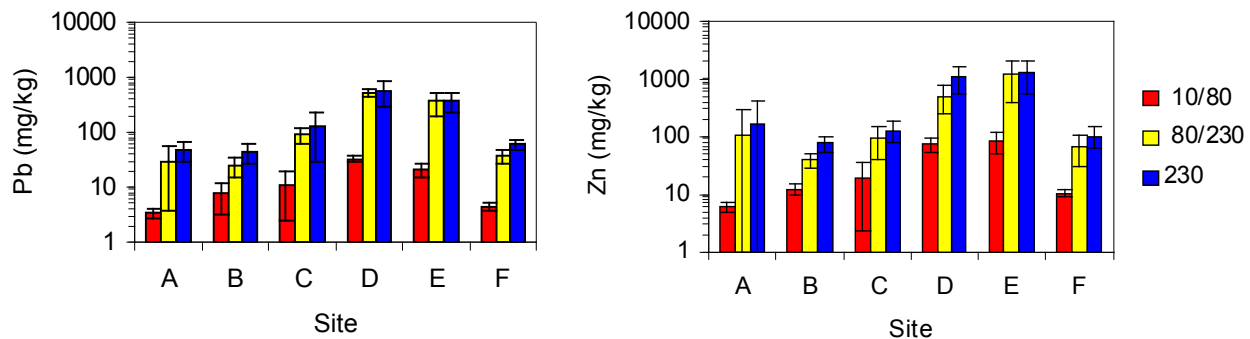

Figure 5.   a) Lead and b) zinc concentrations in three sediment size fractions from the West Fork of the Black River, sites A through F. (10/80 represents sediments which passed through the #10 mesh and were retained in the #80 mesh (coarse to fine sand), 80/230 passed through the #80 mesh and were retained in the #230 mesh (fine to very fine sand), and 230 passed through the #230 mesh (silt and clay sized). Error bars represent one standard deviation from the average values shown.

Panned concentrate sediments were examined using a combination of X-ray Diffraction (XRD), optical microscopy, and SEM-EDS techniques in order to determine the mineral phase(s) that contaminant metals were associated with. An XRD analysis of the bulk sediment indicates that the mineralogic composition of all size fractions is dominated by quartz. SEM/EDS techniques confirmed this by showing high silicon and oxygen peaks in most grains. Dolomite grains were occasionally detected, reflecting minor contributions from the surrounding carbonate bedrock geology and/or contributions from mine waste tailings which are usually dominated by dolomite.

The character of the sediments was visibly changed as they passed through input points for the mine effluent waters. Sediment samples from site A appeared as clean light-colored quartz sand with few grains being coated with secondary minerals. By contrast, sediments from site D were darker in color and showed quartz grains coated with Fe and Mn oxyhydroxide coatings (Figure 6). Small isolated grains of solid Mn and Fe oxyhydroxides were also seen during optical microscopy, these grains crumbled when probed revealing their solid oxyhydroxide cores. In both sediment and water samples, Mn concentrations are relatively low upstream of the mining effluent input, but significantly increase downstream. Iron, on the other hand, does not change appreciably throughout the study reach in both sediment and the water column, so input from mining effluent is not as noticeable for Fe. The ratio of Mn to Fe in sediment also increased dramatically at sites D and E for the smaller two sediment size

fractions (Figure 7). Sulfide minerals were not noted from any of the sampling sites. Their absence suggests that the direct transfer of particulate material from the tailings piles into the streams is minimal to non-existent.

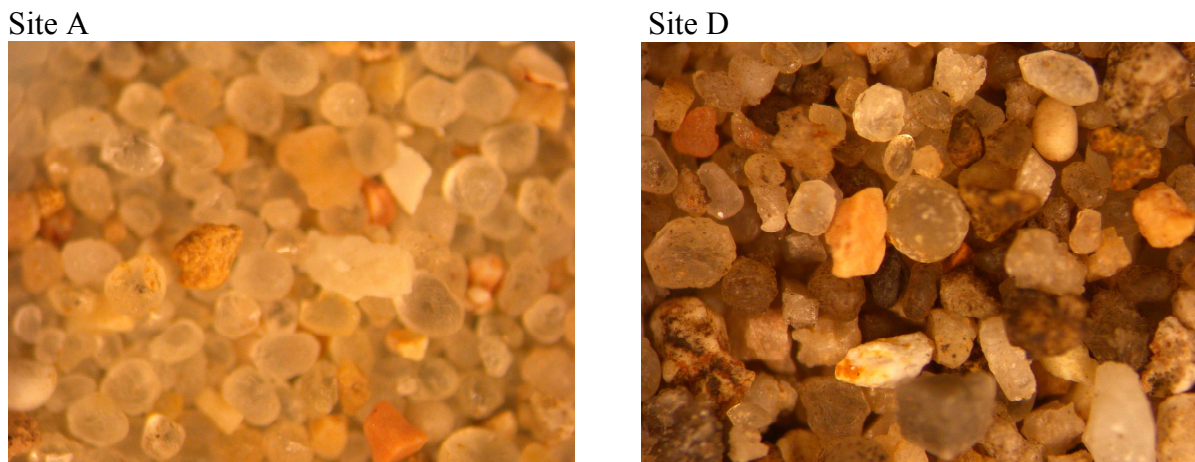Site A   Site D

Figure 6.   Optical microscopy images of panned concentrated sediments from the West Fork of the Black River, sites A and D. Sediments from site D are visibly noted to have more Mn and Fe oxyhydroxides coatings. Scanning Electron Microscopy – Energy Dispersive Spectroscopy analyses for the Mn and Fe oxyhydroxide particles (not shown) also indicate a higher contaminant metal content. The base of each photo is approximately 7.5 mm in length.
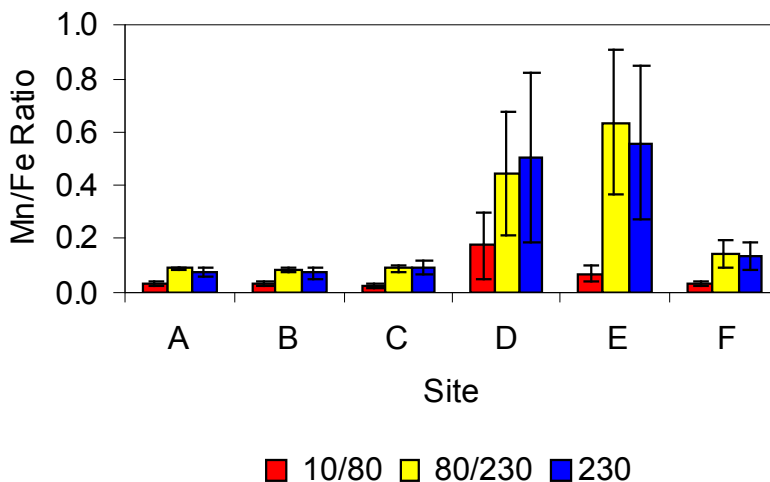

Figure 7.   Average Mn/Fe Ratios in sediment samples from the West Fork of the Black River at sites A through F (Error bars represent one standard deviation). Site D is located just downstream of the point at which effluent water from the West Fork tailings pile enters the river system.

An examination of the SEM-EDS spectra from the sedimentary particles indicates that Pb, Cu, Co, Ni, and Zn are associated with the Mn and Fe-rich precipitate material. Two possibilities exist for the incorporation of metals into Mn and Fe oxyhydroxide coatings and grains. The contaminant metals may either be adsorbing onto pre-existing oxyhydroxide coatings or are being co-precipitated as particles or surface coatings at the same time as the Mn and Fe. The exact mechanism for the inclusion

of metals in these secondary minerals is not known, but optical microscopy and SEM analyses have showed that in West Fork sediment they definitely act as a sink for contaminant metals. Significant correlations for Pb and Zn, with both Mn and Fe are noted in all sediment samples. Manganese, however, displays greater r^2 values with both Pb and Zn than does Fe (Figure 8). The higher correlation coefficients suggest that manganese oxyhydroxides have a greater affinity for inclusion of contaminant metals than do the iron oxyhydroxides. Studies of sediments in other regions have shown that many iron and manganese minerals have high sorption capacities for lead, but manganese oxides are more efficient adsorbents than iron oxides due to their more reactive crystal structures (O'Reilly, 2002).
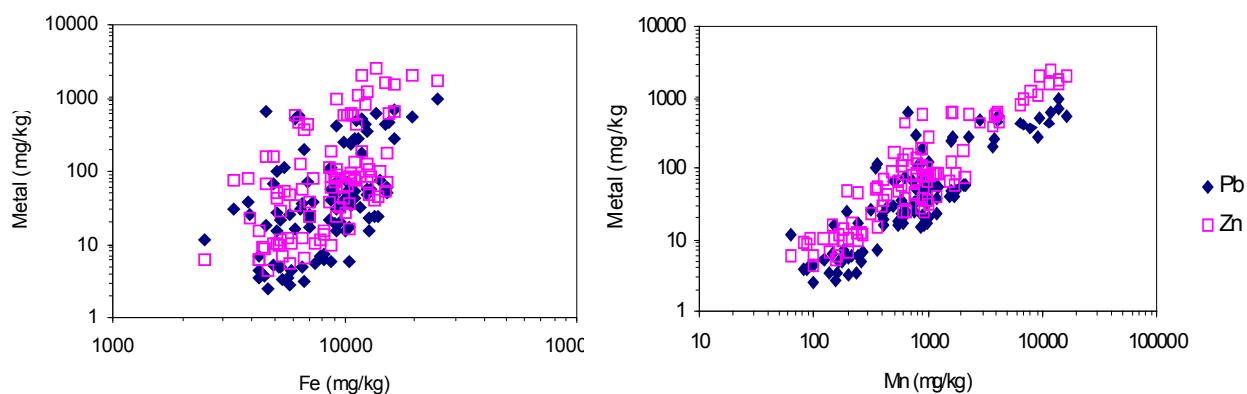

Figure 8.   Elemental correlations in sediments from the West Fork – Black River. a) Iron correlations with Pb and Zn, calculated r^2 values are Pb-Mn 0.8299, Zn-Mn 0.9431, b) Manganese correlations with Pb and Zn, calculated r^2 values are Pb-Fe 0.5132, Zn-Fe 0.5568 . All correlation coefficient calculations were determined to be significant (p<0.001).

Other possible sinks for contaminant metals in sediment are clay minerals and organics. Clay minerals were not detected during XRD analyses of the -230 mesh sediment fraction (silt and clay sized) despite using gravity flotation techniques that are designed to isolate and recover clay-sized particles. The XRD identification technique is relatively insensitive to detecting small quantities of minerals (<5%). The absence of any clay spectral peaks in the gravity separated samples suggests that the proportion of clay present in the West Fork sediment will probably be less than 1%. Total Organic Content (TOC) analyses were performed on a limited number of sediment samples (Figure 9). These correlation evaluations did not indicate significant p values for Pb or Zn with the organics, but this could be due to the limited number of samples that we have analyzed. An earlier Missouri Lead Team study conducted in the region noted that organics were evenly distributed between different sediment size fractions, and since their study indicated that metals seemed to display the same distribution pattern, they suggested the metals could be occurring as metal-organic complexes (Bolter et al., 1977). By contrast, a previous study by the US Fish and Wildlife Service study indicated that only about 20 percent of the lead and a minimal amount of Zn were associated with the organic fraction in sediments at a site on the main fork of the Black River approximately 10 miles south of the confluence with the West Fork (Schmitt and Finger, 1982). It is possible that organics could be an important factor for metals accumulation in the sediment, future studies will focus on interactions between contaminant metals and organics in West Fork sediment.
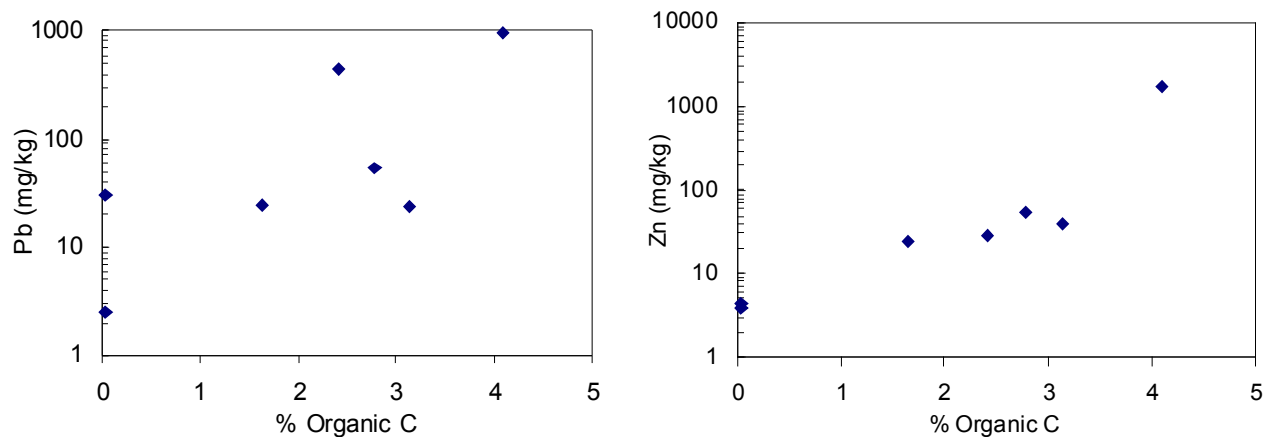
Figure 9.   Elemental correlations in sediments from the West Fork – Black River. a) Lead correlation with organic carbon, n = 7, r^2 = 0.6640, p = 0.119; b) zinc correlation organic carbon, n = 7, r^2 = 0.6125, p = 0.144.

Hydrologic Characterization of the West Fork of the Black River

Because geometric and site-specific hydrologic data are not available for the West Fork of the Black River, measurements of stream cross sections, stage and discharge have been undertaken to characterize hydraulically the reach of the West Fork under study.   One hundred and forty stream cross sections were measured at selected stations between sites X (furthest upstream site) and E (furthest downstream site). Eighty-five of these sections were located between sites A and E, at interval spacings of 200 to 300 feet. The remaining 55 cross sections were located between Sites X and A at interval spacings of 200 to 400 ft. Traditional surveying techniques were used. A Sokkia total station and prism pole were used to transverse and measure the cross-sections. Sites have also been selected for the location of three gauging stations on the West Fork. The furthest upstream Station will be located at Site A, an intermediate Station near Site B (downstream from Bill's Creek), and the furthest downstream station near Site E. The selection was based on the comparative examination of the hydrologic records of the U.S. Geological Survey gauging stations that exist downstream of the study area, project needs, stability of cross sections and accessibility.   Three Stevens Axsys MPU MultiLoggers and the corresponding Pressure Sensors (Model 210) are being refurbished for future deployment at the selected sites for the gauging stations. These instruments will allow monitoring of the flood waves passing through the gauging sites. Measurements of discharge (velocity area method) and stage at low flows have also been made to develop the appropriate rating curve of each gauging station.

Conclusions

Second year samples of bed load sediment and water column samples were collected from the West Fork of the Black River. Additional sediments were collected from the Big River for microscopic examination.

- Contaminant metal concentrations in waters being emitted from the tailings piles are very high with a significant contribution from soluble and colloidal sized materials. The high metal concentrations occur despite the neutral to moderately alkaline nature of the water (buffered by carbonate bedrock material). Generation of an acidic microenvironment on the surfaces of sulfide minerals located within the tailings piles must be occurring, as it is the only satisfactory explanation that explains the high metal contents observed in the tailings waters. Higher metal concentrations are also associated with the Old Lead Belt (Big River area) tailings piles relative

to the New Lead Belt (Black River area). This difference reflects the less advanced metallurgical processing capacities of the earlier Old Lead Belt operations.

- Sulfide minerals containing lead, zinc, and iron have been recovered from the bed load sediment material in the Big River at sites approximately seven nautical miles downstream of tailings piles. These trends suggest that sulfides may survive transport distances on the order of ten(s) of miles and time spans of at least decades in fluvial river systems where the chemistries of the water are buffered by carbonate host rocks. Sulfides have not been recovered from the West Fork of the Black River. The absence of sulfides in this system may be attributed to better environmental containment practices in the New Lead Belt.

- Contaminant metal concentrations decrease from the tributary creeks adjacent to the tailings piles to the Big River system. Decreases may result from dilution, adsorption onto sediment particles, or both. Metal concentrations also decrease with distance from the tailings piles on the West Fork of the Black River.

- Storm surges (or gravel mining disturbance events) in both rivers resulted in increased contaminant metal concentrations in the water column samples and an increase in the proportion of metals contained on particulate material. Zinc and lead appear to behave in a different manner during sediment disturbance events with lead remaining suspended for longer periods of time. This difference may reflect a higher proportion of lead being contained on lower density organic particles.

- Contaminant metals in both the water column and bed sediments show the strongest correlations with manganese, suggesting that manganese oxides or hydroxides are acting as adsorbents for metals in the river systems. Correlations are also noted with iron and organic carbon, however, these correlations are not as strong as those exhibited by manganese.

- Both iron and manganese occur naturally as discrete particles and as surface coatings on grains in the river sediments. Both elements are also being released from the tailings piles as concentrations of these elements are noted to increase in sediments located downstream of the tailings piles. The Mn/Fe ratio increases appreciably in the sediments as they pass the West Fork Mine in the West Fork – Black River.

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A Test of the Biotic Ligand Model: Fish Exposed to Time-varying Concentrations of Copper and Zinc

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Major Accomplishments
- In Year 1 of this three-year project, we continued to conduct acute toxicity tests with larval fathead minnows (FHM; *Pimephales promelas*) exposed to Zn in the presence of (1) elevated concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K+ (each associated with elevated concentrations of Cl^-, NO_3^- or SO_4^{2-}) or (2) elevated concentrations of dissolved organic matter (DOM) from several sources. Ca and DOM protected larval FHM against acute toxicity of Zn; however, within the ranges of concentrations tested, Mg and Na did not protect against acute Zn toxicity. These preliminary toxicity tests were needed to help parameterize a biotic ligand model (BLM) for Zn, so we can use that model in subsequent years of our current study of the toxicity of Cu and Zn in time-variable water quality conditions.
- Based in part on the results of the Zn toxicity tests we have conducted during the past several years (including Year 1), the preliminary biotic ligand model (BLM) prepared for Zn by Dr. Robert Santore (HydroQual Inc.) was modified.
- We reported results of the Zn toxicity tests in two platform presentations at the Society of Environmental Toxicology and Chemistry's annual meeting in Austin, Texas in November 2003. Draft manuscripts reporting those results have been prepared for submission to scientific journals.

Introduction

The biotic ligand model (BLM) provides a useful tool for regulating aqueous discharges of metals (Di Toro et al. 2001). Although the BLM is based on data from toxicity tests conducted under constant-exposure conditions (Santore et al. 2001), concentrations of metals and routine water quality parameters often vary through time in real-world situations. In concept, the BLM is designed to account for variations in concentrations of total metal and free metal ions by accounting for variations in the amount of metal accumulated at the biotic ligand over time (Di Toro et al. 2001). However, appropriate experiments are needed to test this concept. A major focus of the current three-year research project will be to (1) conduct acute toxicity tests with larvae of the fathead minnow (FHM -- *Pimephales promelas*) exposed to Cu or Zn under time-variable water quality conditions and (2) compare those results to predictions using models of time-variable toxicity (e.g., Meyer et al. 1995) that will be modified to incorporate the BLM.

Before we can use the models of toxicity under time-variable water quality conditions, we need reliable BLMs for Cu and Zn. Although a reliable Cu BLM has been available for several years (Santore et al. 2001) and is being incorporated into an upcoming revision of the U.S. Environmental Protection Agency's (USEPA's) water quality criteria for Cu (USEPA 2003), only a preliminary Zn BLM (Santore et al. 2002) was available when the current research project was initiated. That preliminary Zn BLM had been parameterized for fish solely using information published until 2000, and the available studies did not include tests of the protective effects of specific major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and dissolved organic matter (DOM) against Zn toxicity to fish. Therefore, conducting appropriate fish toxicity tests to fill those data gaps and improve the parameterization of the preliminary Zn BLM became a high priority before we could address the main focus of our research.

In this report, we present results of acute toxicity tests in which we exposed larval FHM to Zn in the presence of elevated concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+ and several types of DOM.

Methods
Toxicity Tests

We conducted a series of continuous-exposure toxicity tests in which we exposed larval FHM to Zn in the presence of elevated concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+ and several types of DOM. We performed all toxicity tests according to standard procedures (ASTM 1993, Weber 1993).

Initially, we used flow-through tests to study the effects of the nitrate salts of Ca, Mg and Na on Zn toxicity in a series of experiments conducted from April 2002 through January 2003. After that, we conducted static-renewal tests for side-by-side comparisons of the effects of the nitrate and chloride salts of Ca and Mg in a series of experiments conducted in April and May 2003. All of those tests were funded in part by the International Lead Zinc Research Organization and initial funding from the Center for the Study of Metals in the Environment. For the current project, we conducted additional Zn toxicity tests in the presence of elevated concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ (added as the salts of various anions, including Cl^-, NO_3^- or SO_4^{2-}) and DOM from four sources (Cypress Swamp, Delaware; Edisto River, South Carolina; Suwanee River, Georgia; and Wastewater Treatment Plant (WWTP), Wilmington, Delaware) from June 2003 through February 2004. Personnel from the University of Delaware concentrated the DOM from those source waters using reverse osmosis (RO).

The duration of all of the toxicity tests was 96 h. The basewater to which the Ca, Mg, Na and K salts and the DOM were added was a mixture of well water and RO/deionized water (nominal water quality: 22°C; pH 7.5; alkalinity of 0.5 mEq/L; hardness of 1 mEq/L; dissolved organic carbon (DOC) concentration of <0.5 mg/L).

We used larval FHM (≤24 h old) produced by a stock population of adults maintained at the University of Wyoming (originating from the U.S. EPA's Midcontinent Ecology Division in Duluth, Minnesota, USA) for all of the tests. The FHM adult brood stock was reared in well water (pH 8, alkalinity and hardness of 4 mEq/L, and DOC concentration of <0.3 mg/L), but each batch of FHM eggs was hatched in the basewater quality in which they were tested. To avoid complications associated with the sorption of metals onto food, the larvae were not fed.

Physical and Chemical Analyses

Extensive water quality analyses, including temperature (by hand-held thermometer), pH (by meter), dissolved oxygen (by meter), alkalinity (by titration), major inorganic anions (by ion chromatography),major inorganic cations (by flame atomic absorption spectrophotometry), dissolved organic carbon (DOC; by combustion), and dissolved (0.45-μm filtered) and total Zn (by flame atomic absorption spectrophotometry), were conducted on all exposure waters in each test using standard methods (USEPA 1979, APHA et al. 1995). These analytical techniques are described in more detail in the UW QAPP for this research project.

Statistical Analyses

We calculated LC50s (median lethal concentrations) for the Zn toxicity tests using the trimmed Spearman-Karber procedure in TOXSTAT Version 3.4 (WEST and Gulley 1994).

Results and Discussion

Analyzed water quality and calculated LC50s for the Zn toxicity tests are listed in Table 1 (elevated concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+) and Table 2 (elevated concentrations of DOM). Dissolved oxygen concentrations in all of the tests were ≥6.0 mg/L (not shown in those tables).

In toxicity tests with elevated concentrations of the major cations, 96-h LC50s for FHM larvae exposed to Zn increased in the presence of elevated Ca^{2+} concentrations but did not increase in the presence of elevated Mg^{2+}, Na^+ and K^+ concentrations (Figure 1). However, the 96-h Zn LC50 was only 1.5- to 1.8-fold higher in the presence of a ~10-fold higher Ca concentration (~5-fold higher hardness), whereas a ~4-fold higher LC50 would be expected using the hardness-adjustment equation in the USEPA criteria document for Zn (USEPA 2002). That lower-than-expected protective effect of Ca suggests that water hardness in the USEPA hardness-adjustment equation was also a surrogate for other water quality parameters (e.g., pH, DOM) that protect against Zn toxicity.

Table 1. Physical and chemical parameters, and calculated median lethal concentrations (LC50s) during 96-h toxicity tests in which larval fathead minnows (*Pimephales promelas*) were exposed to Zn in the presence of elevated Ca^{2+}, Mg^{2+}, Na^+ or K^+. Reference toxicity tests conducted in basewater to which salts of the major cations were added. Physical and chemical parameters are reported as mean $\pm$ 1 standard deviation (samples size in parentheses); LC50s are reported as the mean with 95% confidence interval in parentheses (n = 4 replicate beakers per Zn concentration).

Test # and date	Temperature (°C)	pH	Alkalinity (mEq/L)	DOC (mg/L)	Ion concentration (mM)							Zn_{total} LC50 (μM)	$Zn_{dissolved}$ LC50 (μM)
					Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}		
11Zn 6/2/03	21.2 ± 0.7 (18)	7.50 ± 0.06 (18)	0.44 ± 0.06 (4)	0.9 ± 0.20 (10)	0.27 ± 0.001 (6)	0.27 ± 0.001 (6)	1.58 ± 0.003 (6)	0.116 ± 0.006 (6)	0.145 ± 0.006 (6)	1.36 ± 0.009 (6)	0.48 ± 0.013 (6)	7.5 (6.5-8.4)	6.8 (5.9-7.8)
12Zn 6/2/03	21.6 ± 0.8 (18)	7.46 ± 0.04 (18)	0.43 ± 0.02 (4)	0.6 ± 0.08 (10)	0.27 ± 0.001 (6)	0.27 ± 0.002 (6)	1.69 ± 0.068 (6)	0.031 ± 0.002 (6)	0.054 ± 0.001 (6)	1.46 ± 0.020 (6)	0.47 ± 0.010 (6)	6.7 (6.0-7.3)	6.2 (5.5-6.8)
13Zn 6/2/03	21.2 ± 0.4 (18)	7.47 ± 0.04 (18)	0.35 ± 0.12 (18)	0.8 ± 0.26 (10)	0.27 ± 0.001 (6)	0.28 ± 0.001 (6)	1.66 ± 0.006 (6)	0.024 ± 0.000 (6)	1.46 ± 0.034 (6)	0.028 ± 0.006 (6)	0.46 ± 0.010 (6)	8.1 (7.3-8.9)	7.4 (6.6-8.2)
14Zn 6/2/03 (reference)	21.9 ± 0.4 (18)	7.49 ± 0.04 (18)	0.37 ± 0.12 (18)	0.8 ± 0.09 (10)	0.27 ± 0.001 (6)	0.28 ± 0.002 (6)	0.22 ± 0.001 (6)	0.016 ± 0.000 (6)	0.043 ± 0.001 (6)	0.029 ± 0.004 (6)	0.43 ± 0.015 (6)	7.7 (6.9-8.5)	7.3 (6.5-8.0)
15Zn 7/03	22.0 ± 0.0 (6)	7.37 ± 0.04 (6)	0.35 ± 0.0 (1)	---a	0.24 ± 0.001 (6)	0.29 ± 0.001 (6)	0.26 ± 0.261 (6)	4.45 ± 0.372 (6)	0.033 ± 0.001 (6)	4.88 ± 0.125 (6)	0.48 ± 0.016 (6)	NA (all dead)	NA (all dead)
16Zn 7/03	23.0 ± 0.0 (6)	7.46 ± 0.07 (6)	0.39 ± 0.0 (1)	---a	0.24 ± 0.001 (6)	0.29 ± 0.001 (6)	0.26 ± 0.004 (6)	4.49 ± 0.467 (6)	---a	---a	---a	NA (all dead)	NA (all dead)
17Zn 7/03	22.0 ± 0.0 (6)	7.48 ± 0.05 (6)	0.39 ± 0.0 (1)	---a	0.25 ± 0.001 (6)	0.29 ± 0.001 (6)	0.27 ± 0.003 (6)	4.62 ± 0.470 (6)	---a	---a	---a	NA (all dead)	NA (all dead)
18Zn 7/03 (reference)	22.2 ± 0.4 (6)	7.50 ± 0.06 (6)	0.39 ± 0.0 (1)	---a	0.25 ± 0.002 (6)	0.29 ± 0.001 (6)	0.23 ± 0.002 (6)	0.056 ± 0.011 (6)	---a	---a	---a	NA	NA
22Zn 9/5/03	21.0 ± 0.0 (21)	7.49 ± 0.08 (21)	0.55 ± 0.16 (4)	0.4 ± 0.10 (6)	2.43 ± 0.012 (6)	0.28 ± 0.001 (6)	0.24 ± .003 (6)	0.018 ± 0.001 (6)	0.031 ± 0.001 (6)	4.33 ± 0.031 (6)	0.29 ± 0.016 (6)	22.9 (19.9-25.9)	21.8 (18.9-24.7)
23Zn 9/5/03	21.3 ± 0.4 (23)	7.50 ± 0.08 (23)	0.67 ± 0.07 (4)	0.4 ± 0.16 (6)	2.40 ± 0.008 (6)	0.28 ± 0.000 (6)	0.24 ± 0.001 (6)	0.031 ± 0.002 (6)	4.59 ± 0.219 (6)	0.018 ± 0.001 (6)	0.34 ± 0.016 (6)	20.4 (15.5-25.4)	19.5 (14.7-24.2)
24Zn 9/5/03	21.0 ± 0.0 (24)	7.48 ± 0.06 (24)	0.67 ± 0.06 (4)	0.6 ± 052 (6)	2.46 ± 0.008 (6)	0.28 ± 0.001 (6)	0.24 ± 0.002 (6)	0.015 ± 0.001 (6)	0.028 ± 0.001 (6)	0.020 ± 0.004 (6)	2.54 ± 0.016 (6)	24.1 (19.2-29.0)	22.9 (18.2-27.6)
25Zn 9/5/03 (reference)	21.0 ± 0.0 (21)	7.57 ± 0.06 (21)	0.70 ± 0.05 (21)	0.6 ± 0.54 (6)	0.23 ± 0.002 (6)	0.28 ± 0.001 (6)	0.25 ± 0.002 (6)	0.041 ± 0.001 (6)	0.055 ± 0.003 (6)	0.015 ± 0.001 (6)	0.31 ± 0.015 (6)	13.4 (11.4-15.4)	12.7 (10.8-14.6)
26Zn 9/17/03	21.2 ± 0.4 (18)	7.56 ± 0.09 (18)	0.34 ± 0.21 (4)	0.6 ± 0.13 (6)	0.23 ± 0.001 (6)	2.91 ± 0.015 (6)	0.24 ± 0.001 (6)	0.013 ± 0.001 (6)	0.028 ± 0.002 (6)	5.10 ± 0.143 (6)	0.41 ± 0.012 (6)	6.4 (5.3-7.5)	6.1 (5.0-7.2)
27Zn 9/17/03	21.2 ± 0.4 (21)	7.50 ± 0.07 (21)	0.55 ± 0.04 (4)	0.7 ± 0.13 (6)	0.23 ± 0.001 (6)	2.94 ± 0.007 (6)	0.24 ± 0.002 (6)	0.011 ± 0.001 (6)	5.15 ± 0.061 (6)	0.023 ± 0.003 (6)	0.40 ± 0.008 (6)	8.4 (6.9-10.0)	8.0 (6.5-9.5)
28Zn 9/17/03	21.4 ± 0.5 (18)	7.52 ± 0.08 (18)	0.55 ± 0.02 (4)	0.8 ± 0.20 (6)	0.23 ± 0.001 (6)	3.02 ± 0.012 (6)	0.24 ± 0.002 (6)	0.013 ± 0.000 (6)	0.026 ± 0.000 (6)	0.016 ± 0.001 (6)	3.08 ± 0.025 (6)	6.7 (5.8-7.6)	6.4 (5.5-7.2)
29Zn 9/17/03 (reference)	21.4 ± 0.5 (18)	7.55 ± 0.07 (18)	0.52 ± 0.06 (4)	0.9 ± 0.17 (6)	0.23 ± 0.001 (6)	0.28 ± 0.001 (6)	0.25 ± 0.002 (6)	0.012 ± 0.001 (6)	0.026 ± 0.001 (6)	0.016 ± 0.001 (6)	0.40 ± 0.011 (6)	9.1 (7.8-10.4)	8.5 (7.3-9.8)
33Zn 1/20/04	22.0 ± 0.2 (21)	7.48 ± 0.11 (21)	0.37 ± 0.08 (4)	6.7 ± 0.61 (21)	2.38 ± 0.026 (6)	0.27 ± 0.003 (6)	0.24 ± 0.010 (6)	0.012 ± 0.001 (6)	0.120 ± 0.002 (6)	4.58 ± 0.041 (6)	0.28 ± 0.025 (6)	25.4 (23.0-27.8)	24.5 (22.3-26.8)
34Zn 1/20/04	22.0 ± 0.0 (20)	7.56 ± 0.05 (20)	0.54 ± 0.03 (4)	6.9 ± 0.6 (20)	2.34 ± 0.023 (6)	0.27 ± 0.003 (6)	0.23 ± 0.001 (6)	0.012 ± 0.000 (6)	4.48 ± 0.052 (6)	0.020 ± 0.001 (6)	0.28 ± 0.029 (6)	28.9 (27.9-30.0)	28.5 (27.5-29.4)
35Zn 1/20/04 (reference)	22.0 ± 0.0 (20)	7.57 ± 0.07 (20)	0.85 ± 0.21 (4)	0.9 ± 0.41 (20)	0.23 ± 0.006 (6)	0.27 ± 0.001 (6)	0.24 ± 0.001 (6)	0.012 ± 0.000 (6)	0.025 ± 0.000 (6)	0.021 ± 0.003 (6)	0.20 ± 0.017 (6)	11.2 (9.8-12.6)	10.5 (9.1-11.8)
36Zn 2/15/04	22.5 ± 0.5 (20)	7.47 ± 0.09 (20)	0.46 ± 0.13 (4)	0.8 ± 0.16 (6)	0.27 ± 0.005 (6)	0.27 ± 0.005 (6)	0.27 ± 0.003 (6)	2.26 ± 0.031 (6)	0.033 ± 0.001 (6)	2.61 ± 0.034 (6)	0.43 ± 0.015 (6)	7.8 (7.6-8.0)	7.3 (7.1-7.5)

Table 2. Physical and chemical parameters, and calculated median lethal concentrations (LC50s) during 96-h toxicity tests in which larval fathead minnows (*Pimephales promelas*) were exposed to Zn in the presence of elevated dissolved organic matter (DOM). DOM sources: Cypress Swamp, Delaware (CS); Edisto River, South Carolina (ER); Wilmington Wastewater Treatment Facility effluent (WW), Delaware; and Suwannee River, Georgia (SR). Reference toxicity tests conducted in basewater are designated as "Ref." Physical and chemical parameters are reported as mean $\pm$ 1 standard deviation (samples size in parentheses); LC50s are reported as mean $\pm$ 95% confidence interval (n = 4 replicate beakers per Zn concentration).

DOM test and date	Temperature (°C)	pH	Alkalinity (mEq/L)	DOC (mg/L)	Ion concentration (mM)							Zn_{total} LC50 (µM)
					Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	
CS 12/02	20.4 ± 0.08 (12)	7.46 ± 0.12 (11)	---a	14.0 ± 0.91 (16)	0.30 ± 0.001 (6)	0.34 ± 0.001 (6)	0.21 ± 0.010 (6)	0.014 ± 0.001 (6)	0.28 ± 0.005 (6)	0.019 ± 0.001 (6)	0.10 ± 0.020 (6)	19.1 ± 3.1
ER 12/02	22.2 ± 0.1 (18)	7.79 ± 0.06 (18)	1.13 ± 0.00 (4)	11.3 ± 0.60 (11)	0.22 ± 0.001 (6)	0.26 ± 0.001 (6)	4.77 ± 0.097 (6)	0.041 ± 0.002 (6)	4.02 ± 0.057 (6)	0.25 ± 0.006 (6)	0.09 ± 0.019 (6)	14.6 ± 1.4
WW 12/02	22.6 ± 0.1 (21)	7.77 ± 0.04 (21)	0.98 ± 0.01 (5)	11.7 ± 0.38 (11)	0.35 ± 0.004 (6)	0.76 ± 0.007 (6)	22.1 ± 0.428 (6)	0.709 ± 0.010 (6)	18.4 ± 0.101 (6)	1.32 ± 0.024 (6)	1.92 ± 0.030 (6)	15.1 ± 2.6
Ref 12/02	21.3 ± 0.22 (21)	7.58 ± 0.06 (21)	1.02 ± 0.02 (4)	---a	0.31 ± 0.002 (6)	0.36 ± 0.002 (6)	0.21 ± 0.001 (6)	0.016 ± 0.001 (6)	0.03 ± 0.001 (6)	0.027 ± 0.003 (6)	0.06 ± 0.013 (6)	13.4 ± 2.2
CS 9/03	22.0 ± 0.0 (18)	7.64 ± 0.11 (18)	0.62 ± 0.17 (4)	17.7 ± 0.52 (18)	0.22 ± 0.000 (6)	0.28 ± 0.001 (6)	0.25 ± 0.001 (6)	0.020 ± 0.013 (6)	0.33 ± 0.016 (6)	0.014 ± 0.004 (6)	0.11 ± 0.037 (6)	17.4 ± 1.4
CS + NaCl 9/03	22.0 ± 0.0 (18)	7.60 ± 0.12 (18)	0.77 ± 0.01 (4)	16.7 ± 4.13 (18)	0.22 ± 0.001 (6)	0.28 ± 0.001 (6)	7.52 ± 0.078 (6)	0.018 ± 0.003 (6)	7.60 ± 0.090 (6)	0.018 ± 0.005 (6)	0.12 ± 0.036 (6)	17.0 ± 1.7
Ref 9/03	22.2 ± 0.5 (19)	7.48 ± 0.10 (19)	0.38 ± 0.04 (4)	0.5 ± 0.08 (5)	0.24 ± 0.001 (6)	0.30 ± 0.001 (6)	0.26 ± 0.008 (6)	0.019 ± 0.000 (6)	0.03 ± 0.000 (6)	0.011 ± 0.001 (6)	0.53 ± 0.016 (6)	11.4 ± 1.4
SR 10/03	21.9 ± 0.32 (18)	7.44 ± 0.23 (18)	0.49 ± 0.12 (4)	19.3 ± 0.85 (18)	0.22 ± 0.001 (6)	0.26 ± 0.002 (6)	0.22 ± 0.047 (6)	0.014 ± 0.008 (6)	0.20 ± 0.012 (6)	0.026 ± 0.001 (6)	0.43 ± 0.028 (6)	20.4 ± 2.4
SR + NaCl 10/03	21.9 ± 0.58 (18)	7.44 ± 0.16 (18)	0.58 ± 0.23 (4)	20.3 ± 0.65 (18)	0.21 ± 0.003 (6)	0.26 ± 0.003 (6)	18.3 ± 0.189 (6)	0.016 ± 0.003 (6)	19.9 ± 0.282 (6)	0.026 ± 0.001 (6)	0.42 ± 0.037 (6)	20.5 ± 2.7
Ref 10/03	23.2 ± 1.30 (18)	7.50 ± 0.08 (18)	0.48 ± 0.19 (4)	0.9 ± 0.42 (18)	0.22 ± 0.002 (6)	0.27 ± 0.001 (6)	0.25 ± 0.003 (6)	0.012 ± 0.000 (6)	0.03 ± 0.001 (6)	0.026 ± 0.001 (6)	0.41 ± 0.175 (6)	7.4 ± 0.5
SR + Ca^{2+} 1/04	22.0 ± 0.2 (21)	7.48 ± 0.11 (21)	0.37 ± 0.08 (4)	6.7 ± 0.61 (21)	2.38 ± 0.026 (6)	0.27 ± 0.003 (6)	0.24 ± 0.010 (6)	0.012 ± 0.001 (6)	0.12 ± 0.002 (6)	4.58 ± 0.041 (6)	0.28 ± 0.025 (6)	25.4 ± 2.3
SR + Ca^{2+} 1/04	22.0 ± 0.0 (20)	7.56 ± 0.05 (20)	0.54 ± 0.03 (4)	6.9 ± 0.59 (20)	2.34 ± 0.023 (6)	0.27 ± 0.003 (6)	0.23 ± 0.001 (6)	0.012 ± 0.000 (6)	4.48 ± 0.052 (6)	0.020 ± 0.001 (6)	0.28 ± 0.029 (6)	28.9 ± 1.0
Ref 1/04	22.0 ± 0.0 (20)	7.57 ± 0.07 (20)	0.85 ± 0.21 (4)	0.9 ± 0.41 (20)	0.23 ± 0.006 (6)	0.27 ± 0.001 (6)	0.24 ± 0.001 (6)	0.012 ± 0.000 (6)	0.02 ± 0.000 (6)	0.021 ± 0.003 (6)	0.20 ± 0.017 (6)	11.2 ± 1.4
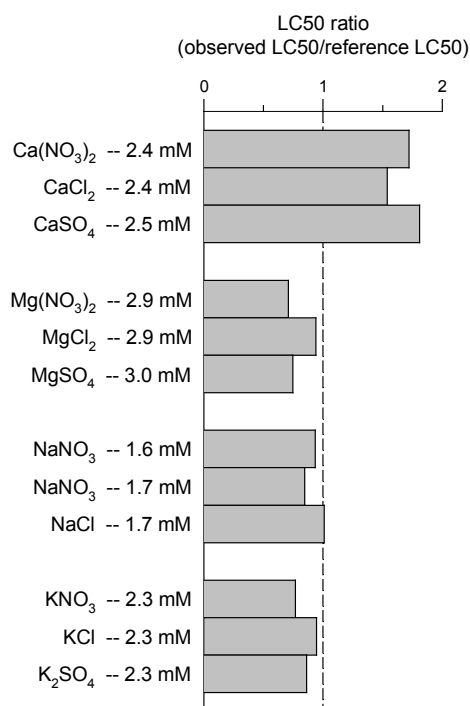
Figure 1. Protective effects of Ca^{2+}, Mg^{2+}, Na^+ and K^+ (when added as their Cl^-, NO_3^-, and SO_4^{2-} salts) on the toxicity of Zn to larval fathead minnows (*Pimephales promelas*), as indicated by the LC50 ratio (i.e., 96-h LC50 observed in reference water to which the salt was added at the indicated concentration, divided by 96-h LC50 in reference water). An LC50 ratio equal to 1.0 indicates no protective effect, and an LC50 ratio >1 indicates a protective effect.

In toxicity tests with elevated concentrations of DOM, 96-h LC50s for FHM larvae exposed to Zn increased as DOM concentration increased when the DOC concentration was greater than ~10 mg/L (Figure 2). That apparent threshold DOC concentration suggests relatively low binding affinity and/or capacity of DOM for Zn.
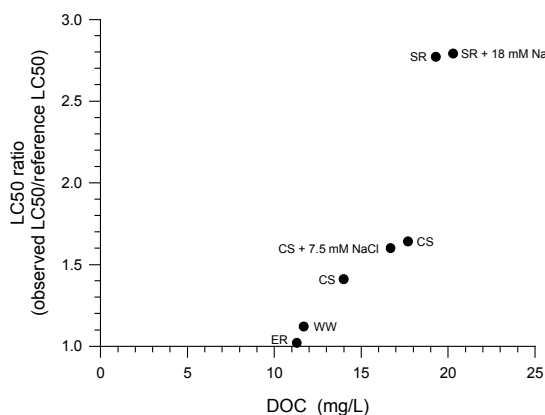

Figure 2. Protective effect of dissolved organic matter (DOM) on the toxicity of Zn to larval fathead minnows (*Pimephales promelas*), as indicated by the LC50 ratio (i.e., 96-h LC50 observed in reference water to which DOM was added at various dissolved organic carbon (DOC) concentrations, divided by 96-h LC50 in reference water). An LC50 ratio equal to 1.0 indicates no protective effect, and an LC50 ratio >1 indicates a protective effect.

Sources of DOM were: Cypress Swamp, Delaware (CS); Edisto River, South Carolina (ER); Wilmington Wastewater Treatment Facility effluent (WW), Delaware; and Suwannee River, Georgia (SR). NaCl was added in some tests with CS and SR DOM to test for effects of addition of NaCl (via Na ion exchangers) before isolation of some of the DOM samples by reverse osmosis.

Based in part on these toxicity results, Dr. Robert Santore of HyrdoQual Inc. has modified the preliminary Zn BLM to (1) decrease the binding-site density of DOM for Zn and (2) decrease the affinity of the FHM "gill" for Na^+. We will use that revised Zn BLM in the next two years of this research project, to help predict Zn toxicity in time-variable water quality conditions.

Anticipated Year 3 Efforts

We will conduct acute toxicity tests needed to calibrate the Cu and Zn BLMs and a model of time-varying toxicity to the larval FHM we are using in this study. Then we begin conducting exposures of larval FHM to Cu under time-variable water quality conditions. Similar exposures to Zn will be conducted during Year 3 of the study.

Publications and Presentations

Bringolf, R.B., B.A. Morris, S.A. Collyard, C.J. Boese, R.C. Santore, H.E. Allen and J.S. Meyer. 2003. Effects of pH and dissolved organic matter on acute toxicity of zinc to larval fathead minnows. Presented at the Twenty-fourth Annual Meeting of the Society of Environmental Toxicology and Chemistry. Austin, TX. 9-13 November.

Morris, B.A., R.B. Bringolf, C.J. Boese and J.S. Meyer. 2003. Protective effects of inorganic salts against zinc toxicity to larval fathead ninnows. Presented at the Twenty-fourth Annual Meeting of the Society of Environmental Toxicology and Chemistry. Austin, TX. 9-13 November.

Bringolf, R.B., B.A. Morris, C.J. Boese, R.C. Santore, H.E. Allen and J.S. Meyer. Influence of dissolved organic matter on zinc toxicity to larval fathead minnows (*Pimephales promelas*). To be submitted to *Comparative Biochemistry and Physiology, Part C, Toxicology and Pharmacology*. (In preparation)

Morris, B.A., R.B. Bringolf, C.J. Boese, R.C. Santore, and J.S. Meyer. Influence of pH, calcium, magnesium, sodium and potassium on zinc toxicity to larval fathead minnows (*Pimephales promelas*). To be submitted to *Aquatic Toxicology*. (In preparation)

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