Environ. Sci. Technol. **1999**, *33,* 3850−3856

Modeling Removal of Cd, Cu, Pb, and Zn in Acidic Groundwater during Neutralization by Ambient Surface Waters and Groundwaters

ANTHONY J. PAULSON*

James J. Howard Laboratory, NEFSC/National Marine Fisheries Service/NOAA, 74 Magruder Road, Highlands, New Jersey 07732

LAURIE BALISTRIERI

U.S. Geological Survey, University of Washington, School of Oceanography, Box 357940, Seattle, Washington 98195-7940

Removal of Pb, Cu, Zn, and Cd during neutralization of acid rock drainage is examined using model simulations of field conditions and laboratory experiments involving mixing of natural drainage and surface waters or groundwaters. The simulations consider sorption onto hydrous Fe and Al oxides and particulate organic carbon, mineral precipitation, and organic and inorganic solution complexation of metals for two physical systems where newly formed oxides and particulate organic matter are either transported or retained along the chemical pathway. The calculations indicate that metal removal is a strong function of the physical system. Relative to direct discharge of ARD into streams, lower metal removals are observed where ARD enters streamwaters during the latter stages of neutralization by ambient groundwater after most of the Fe has precipitated and been retained in the soils. The mixing experiments, which represent the field simulations, also demonstrated the importance of dissolved metal to particle Fe ratios in controlling dissolved metal removal along the chemical pathway. Finally, model calculations indicate that hydrous Fe oxides and particulate organic carbon are more important than hydrous Al oxides in removing metals and that both inorganic and organic complexation must be considered when modeling metal removal from aquatic systems that are impacted by sulfide oxidation.

Introduction

The natural weathering of rocks rich in sulfide minerals results in the release of dissolved metals, sulfate, and acidity to the environment (*1, 2*). Mining activities increase the exposure of these sulfide minerals to air and, thereby, accelerate the oxidation process and create acid-rock drainage (ARD). The dispersion and fate of dissolved constituents in ARD is a function of physical and biogeochemical processes (*3, 4*). Mixing of ARD with downstream uncontaminated tributaries results in dilution and neutralization. Chemical reactions such as precipitation and adsorption occur during this neutralization process (*5*−*9*). The sequestering of dissolved metals and organic matter by hydrous Fe, Mn, and Al oxides or Fe oxyhydroxy sulfates is ubiquitous in areas impacted by ARD (*5, 6, 10*−*13*).

* Corresponding author phone: (732)872-3012; fax: (732)872-3128; e-mail: Anthony.Paulson@noaa.gov.

The extent to which dissolved metals have been removed in ARD systems has been determined using element−element plots, mass balance calculations, tracer methods, thermodynamic equilibrium calculations coupled with surface complexation models, and direct analyses of precipitates (*7*−*9, 14*−*16*). These and other studies have indicated that metal removal in aquatic environments is a complex function of the relationships between transport processes, chemical kinetics, and biogeochemical processes that control pH (e.g., buffering by dissolution of carbonate minerals, photosynthesis, and mineral precipitation) and the concentrations and identities of dissolved elements and suspended matter (e.g., precipitation and sorption).

In this paper, we build on previous work undertaken to understand the removal and fate of dissolved metals produced by ARD in the Moon Creek watershed of the Coeur d'Alene mining district (*16, 17*). The importance of sorption reactions on the removal of dissolved Cd, Cu, Pb, and Zn along the specific chemical pathway of neutralization of ARD in this watershed is examined using calculations that couple formation of metal oxides during mixing with a surface complexation model. Since fresh metal oxide substrates are formed during ARD neutralization, we attempted to extend the recent successes of substrate assemblage models derived from laboratory adsorption data (*12, 18*) by simulating the geochemical and physical conditions at the Moon Creek site. Parallel changes in metal removal along the chemical pathway of neutralization were determined in mixing experiments with samples of natural drainage collected at the site.

Study Area

The tailings pile from a 1910 jig mill (Figure 1) is the most likely source of an acidic (pH 2.4−3.4), metal-laden groundwater plume at the Moon Creek site (*19*). Well 8 is the sampling location closest to the source (15 m upgradient from well 8), and its groundwater exhibits variations in dilution of the source ARD with ambient groundwater as a function of season. During the spring melt in March 1995, the composition of well 8 resembled undiluted leachate from the tailings and had a pH of 2.86 (*19*). Had this leachate been directly discharged into Moon Creek, significant amounts of hydrous ferric oxide (100 mg Fe/L) would have been available as a substrate for metal adsorption. Significant removal of metals from solution would be expected once the dilution of the ARD was sufficient to allow the buffering capacity of the creek water to raise the pH to values favorable for metal adsorption. Since direct discharge of ARD to the stream does not occur within the study area, we simulated the neutralization of ARD (Table 1) by numerically titrating well 8 groundwater from March 1995 (*19*) with 100 volumes of ambient streamwater using PHREEQE (*20*). In this physical scenario of a stream system, all constituents (total concentrations of solutes, newly formed substrates, and adsorbed metals on these substrates) are transported to the next mixing segment (the upper **bold** values in Figure 2). This "Transported Scenario" simulates the extreme of a high-energy stream system where no ochre or precipitates on stream boulders or other bedforms occur.

The actual acidic groundwater plume flows southward of well 8, where it begins to be neutralized by ambient, oxygenated groundwater and infiltrating surface water (*16, 19*). In March of 1995, partially neutralized groundwater from five wells (not shown in Figure 1) had pHs between 3.13 and 3.77, but much of the dissolved Fe had been removed. Sufficient dilution to raise the pH to values favorable to adsorption (pH 5−6) was observed for three other wells.

10.1021/es9900454 Not subject to U.S. copyright. Publ. 1999 Am. Chem.Soc.
Published on Web 09/16/1999

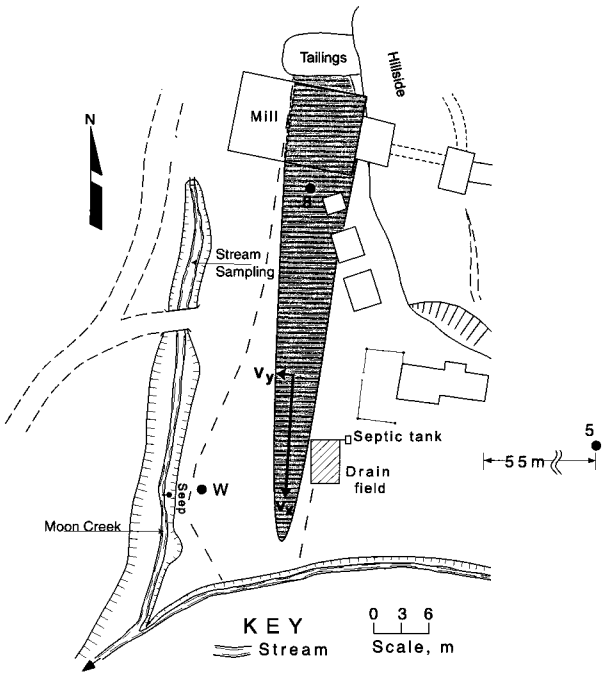

FIGURE 1. Map of the Moon Creek Mill site 5 km NW of Kellogg, Idaho (N47° 33.9′, W116° 01.2′). The locations of the wells (circles) used in the mixing experiments are marked by labels 5, 8, and W. The main flow axis (V_x) of the contaminated groundwater plume (—) is from well 8 southward with lateral dispersive flow toward well W (– – –).

However, the sensitivity of tracer methods for multiple endmembers was not sufficient to determine metal removal in these three wells at these high dilutions. To understand metal removal within this groundwater system, the mixing simulation was manually manipulated to retain new solid phases formed within each segment, along with adsorbed species, and only dissolved solutes are transported to the next mixing segment (lower *italics* values in Figure 2). In this extreme of a groundwater system named the "Retained Scenario", transport of metal hydroxide colloids was precluded.

When the mixing experiments were performed in August 1995, the composition of well 8 was representative of dry conditions and suggested dilution of the leachate by groundwater and removal of dissolved Fe. Direct comparison between the Retained Scenario for the wet season with the composition of wells during the dry season is not exact because of seasonal changes in the composition of both ARD and the neutralizing waters. Because of these seasonal effects, the absolute removal of metals in the mixing experiments will not be directly compared to removals derived from the model simulations. Rather, the changes in metal removal between physical scenarios within a season will be compared. Although the composition of well 8 in August approximates somewhere between steps 2 and 3 of the above Retained Scenario, well 8 is considered the source of ARD flowing into the study area in August. Mixing experiments with contaminated well 8 groundwater and ambient groundwater (well 5) are considered a transported system for the dry season because the maximum amount of hydrous ferric oxides present within the system is available for adsorption. The pathway between well 8 and the stream bank (well W) encompasses the early stages of the Retained Scenario, where most Fe is removed before pH rises significantly. Therefore, mixing experiments with well W groundwater resemble the later stages of the Retained Scenario because the availability of HFO had dramatically decreased.

TABLE 1. Dissolved Concentrations of Solution Used in the Simulation and Mixing Experiments

	simulation (March 1995)		mixing expts (August 1995)			
solution	well 8	Moon Creek	well 8	well 5	well W	Moon Creek
pH	2.86	7.11	3.23	7.39	3.38	6.98
alk, meq		0.51		1.49		1.05
mg/L						
	simulation (March 1995)		mixing expts (August 1995)			
solution	well 8	Moon Creek	well 8	well 5	well W	Moon Creek
Na	6.8	2.2	3.8	8.2	3.6	2.7
K	1.4	NA[b]	0.9	0.6	1.1	0.9
Ca	122	8.3	27.5	17.7	27.9	10.5
Mg	71	3.7	15.5	7.9	16.6	4.6
Si	35	8.8	11	4.3	13.5	6
SO_4	1655	11.7	214	27.6	245	7.5
DOC[a]	1.2	2.35				
μg/L						
	simulation (March 1995)		mixing expts (August 1995)			
solution	well 8	Moon Creek	well 8	well 5	well W	Moon Creek
Pb	300	1.3	58	0.5	360	0.5
Cd	1000	0.75	70	0.03	96	1.3
Cu	33 000	<0.5	1500	0.5	2800	1.3
Zn	154 000	170	11 400	2.8	17 600	250
Fe	103 000	1.8	1420	5	240	1.2
Al	64 000	<5	3350	78	6010	6
Mn	8000	<0.2	845	2	1210	0.5

[a] Assumed. [b] NA: not available.

Groundwater, which has a composition similar to well W, seeps out of the bank just below well W (Figure 1) and is neutralized as it enters Moon Creek. There, natural precipitates formed that scavenged metals. Using multiple tracers (*16*), the mass balances of metals and sulfate within the seep area were determined, and removals of Pb, Cu, Zn, and Cd were estimated for this retained system. The removal within the seep area can be directly compared to removal in the well W mixing experiment. Again, removal for a transported system in the field could not be determined because nowhere within the study area was ARD discharged directly into surface waters.

Methods

Model Simulations. Precipitation of metal hydroxides, carbonates, and basic carbonates is considered in this model using solubility constants and solution complexation constants summarized in Appendix Table 1 (Supporting Information). The computer code MINTEQA2 (*21*) and the Diffuse Double Layer Model are used to determine adsorption of Cd, Cu, Pb, and Zn onto HFO and HAlO. Site densities, intrinsic acidity constants, and intrinsic surface complexation constants for Cd, Cu, Pb, and Zn onto strong and weak HFO sites are taken from Dzombak and Morel (*22*). Since the Pb adsorption constant for the weak HFO sites was thought to be underestimated, a more recent value from Ainsworth et al. (*23*) was used, and the effect of this change can be found in the Supporting Information. A limited set of laboratory data (*24*) and the Diffuse Double Layer Model were used to extract adsorption constants of metals onto HAlO.

The adsorption of dissolved organic carbon (DOC) onto newly formed HFO and HAlO as well as complexation of

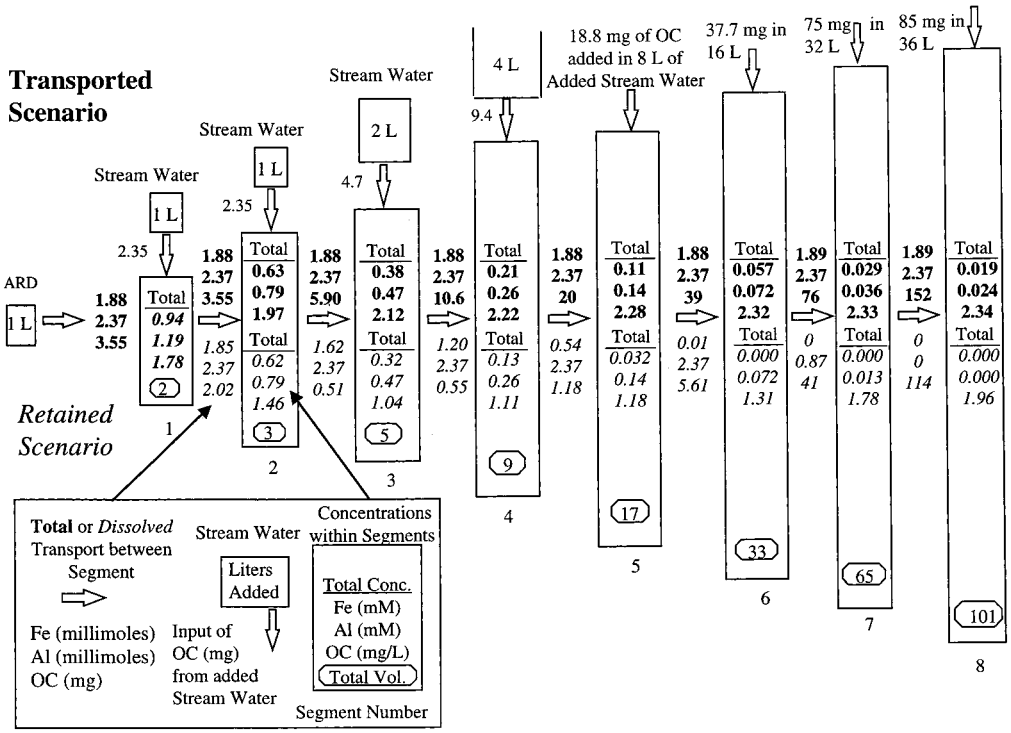

FIGURE 2. Transport of Fe, Al, and organic carbon (OC) between mixing segments of the model simulation (horizontal arrows), addition of OC from streamwater (vertical arrows), and concentrations of total Fe, Al, and OC within each segment (boxes). For the Transported Scenario (upper half), transports of Fe and Al (bold value above arrow *between* segments in milligrams) remain constant because virtually all Fe and Al to the entire system originates from the ARD. Decreases in total Fe and Al concentrations (bold values in upper half *within* the segment box in mg/L) result solely from the dilution by increasing volumes of streamwater. Transport of OC increases as increasing amounts of OC are added from streamwater. In the Retained Scenario (lower half), transport of dissolved Fe and Al (*italicized* value below arrow *between* segments in milligrams) decreases to zero as HFO and HAlO are retained in previous segments. Total Fe and Al concentrations (*italicized* value in lower half *within* segment box in mg/L) decrease due to both dilution by streamwater and decreasing transport of Fe and Al along flowpath.

metals with organic carbon (OC) is considered. Sorption of organic carbon as a function of pH was modeled using the Langmuir isotherms for HFO (*25*) and for HAlO (*26*). Apparent stability constants determined for Cu complexation with surface-bound particulate organic carbon (DOC_{ads}) are used (*27*). The complexation constant for the interaction of Cu with DOC_{ads} at a given pH was estimated to be 0.6 log units greater than that with aqueous DOC (*27*). To include organic complexation for other metals, differences in stability constants between Cu and other metals for fulvic acids were examined. Based on this evaluation, the complexation constants used in the model simulations for Fe, Pb, Zn, and Cd interactions with DOC_{ads} and DOC at a given pH are estimated to be 0.1, 0.43, 1.0, and 1.0 log units, respectively, less than the Cu-organic complexation constants (*28*). DOC concentrations in the streamwater are assumed to be 2.35 mg/L and half that in the ARD (*6*, *11*). Organic matter is assumed to have 1 μmol of sites per milligram of organic carbon (*27*).

Mixing Experiments. The usual measurements of pH, electrical conductivity (EC), and alkalinity for water from each of the three wells and the stream were made in the field on August 3, 1995. Based on the EC measurements, the concentrations of major ions were estimated based upon empirical relationships derived from 14 prior sample collections (*19*). Given the pH, alkalinity, and major ion concentrations, a titration simulation was performed on a laptop computer in the field. The ratio of ARD:ambient water mixed together in the mixing experiments was chosen to produce final pHs between 6 and 7 in the mixtures. The following solutions were mixed in acid-cleaned carboys in the field: [low-dilution well 8] 8.04 L of filtered contaminated groundwater from well 8 with 11.06 L of filtered ambient groundwater (well 5); [high-dilution well 8] 4.54 L of filtered well 8 groundwater with 13.69 L of filtered ambient groundwater; and [well W] 3.35 L of filtered contaminated groundwater from well W with 13.3 L of unfiltered streamwater from Moon Creek. The samples for dissolved metal determinations of the four endmembers and the particulate matter in the streamwater were collected in the field.

In the laboratory, the carboys were shaken daily for 5 days. Aliquots from each carboy were then filtered through 25-mm, 0.4-μm Teflon filters and analyzed for dissolved metal and sulfate concentrations. Triplicate particulate samples were collected from each carboy and microwave-digested in aqua regia. Metal concentrations in water and digestion solutions were determined by ICP-AES, ICP-MS, and GFAAS, while sulfate was determined by IC. Large-mass particulate samples for POC were then collected in the following weeks by centrifuging at 10 000 rpm and analyzed by high temperature combustion. Sources of POC in the well 8 solutions were either adsorption of DOC onto the newly formed HFO and HAlO (DOC_{ads}) or biological growth during the mixing experiments. For the well W experiment that was mixed with unfiltered streamwater, POC could also have originated from stream particles. Predictions of the adsorption of Cd, Cu, Pb, and Zn were made using the actual amounts of HFO, HAlO, and POC measured after 5 days and the metal stability and adsorption constants used in the above simulations.

Results

Model Simulations. The model simulations are intended to lay the foundation for a conceptual model of dissolved metal removal during neutralization in natural systems where metal removal is dominated by sorption processes. The amounts

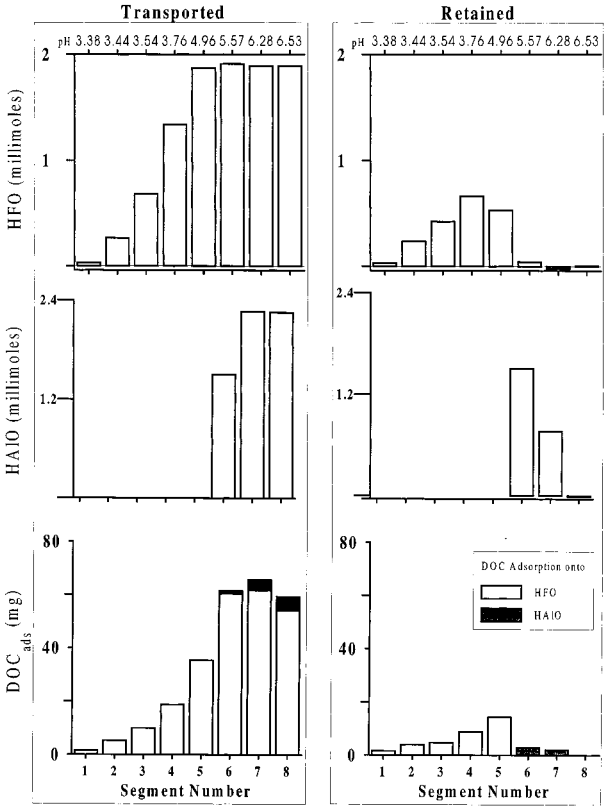

FIGURE 3. Model simulations of hydrous Fe and Al oxides (HFO and HAlO) precipitation and adsorption of dissolved organic matter (DOC_{ads}) during neutralization for the Transported (left) and Retained (right) Scenarios. The values for the Transported Scenario are cumulative amounts, while the values for the Retained Scenario are incremental amounts.

of newly formed HFO, HAlO, and POC that metals encounter for the Transported and Retained Scenarios are presented as total millimoles of HFO or HAlO or as milligrams of DOC_{ads} in each segment (Figure 3). The HFO, HAlO, and DOC_{ads} in each mixing segment of the Transported Scenario are cumulative amounts, while only the incremental amounts that form in each segment are available in the Retained Scenario. The sum of HFO and HAlO in all mixing segments of the Retained Scenario equals the total amounts of these phases in the last segment of the Transported Scenario (Figure 3).

DOC is adsorbed primarily onto HFO rather than by HAlO. DOC_{ads} accounts for 27% of the total organic carbon at the end of neutralization for the Transported Scenario. About 90% of the DOC is adsorbed in segments 2−4 in the Retained Scenario (Figure 2), and very little DOC is transported to the next segment. The equilibrium concentration of DOC only begins to increase above 0.1 mg/L in segment 5 as greater amounts of OC are added from the diluting streamwater. The majority of DOC that is added to the system during the later mixing segments never encounters the major fraction of HFO removed from the system within the earlier mixing segments, and DOC_{ads} is limited to <4% of the total organic carbon of the system.

The micromoles of Pb, Cu, Zn, and Cd adsorbed in each mixing segment under the Transported and Retained Scenarios are shown in Figure 4. The first significant amounts of Pb adsorption onto strong HFO sites are predicted to occur in the fifth mixing segment of the Transported Scenario, where the pH has increased from pH 3.8 to 5.0. Under the Transported Scenario, 77% of the total Pb is adsorbed by the end of the neutralization process. For the Retained Scenario, the most significant Pb adsorption is also predicted to occur within the fifth mixing segment. However, adsorption in the Retained Scenario is much less than in the Transported Scenario because dissolved Pb encounters only 28% of the HFO found in the fifth mixing segment of the Transported Scenario.

Significant Cu adsorption onto weak HFO sites is predicted to occur in the fifth through seventh mixing segments of the Transported Scenario because the Cu adsorption edge occurs at a higher pH than the Pb adsorption edge. Overall Cu adsorption is 38% of the total Cu for the Transported Scenario. HFO precipitation is completed by the latter stages of neutralization in which pH increased to values that are favorable for Cu adsorption, and little HFO is available for Cu adsorption under the Retained Scenario (3.9% removal).

The pH dependence of Zn and Cd removal is predicted to be similar because adsorption is controlled by complexation of these metals with the DOC_{ads} onto HFO, and because the model stability constants of these metals with organic matter obtained from the literature are identical. In the Transported Scenario, Zn complexation by DOC_{ads} occurs in mixing segments five through seven, with up to 94% of the DOC_{ads} sites being complexed by metals. The overall Zn removal is 1.5%, while Cd adsorption is 1.3%. The retention of HFO within the early segments of the Retained Scenario dramatically decreases the formation of DOC_{ads} in the fifth mixing segment, where pH becomes favorable for complexation of Zn and Cd with DOC_{ads}. The smaller amounts of DOC_{ads} in the fifth mixing segment of the Retained Scenario decreases the overall removal of Zn and Cd by 6-fold compared to the Transported Scenario.

Mixing Experiments. Well 8 solutions represented a transported system in which the solid-phase products of neutralization from all the dissolved Fe entering the study area were available for adsorption in the carboys (Appendix Table 2, Supporting Information). The low-dilution well 8 solution (pH = 5.92) was not supersaturated by any Cd, Cu, Pb, or Zn minerals. For all four metals, the observed removal was within 25% of the predicted removal even though the extent of removal and the metal concentrations spanned almost 3 orders of magnitude (Figure 5). Pb adsorbed equally on the strong and weak HFO sites. The predicted Cu removal (6%) was dominated by weak HFO sites (73% of the Cu adsorbed) and was equal to the observed removal. Model predictions attributed most of the Zn and Cd removal to POC complexation. Zn and Cd predictions were comparable to the observed removals (Table 2).

For the high-dilution well 8 solution (pH = 6.93), the predicted Pb adsorption (49% removal) was dominated by strong HFO sites (Table 2) and was about half the observed removal (92%). The high observed removal of Cu (38%) relative to the prediction could possibly have resulted from the supersaturation of the basic copper carbonate, malachite [$Cu_2CO_3(OH)_2$], assuming that precipitation occurred. Model predictions of Zn and Cd removal in the solution indicated that complexation by POC was dominant (73−97%). The observed Zn and Cd removals were within a factor of 2 of the predicted removals (Table 2).

In contrast to the mixing experiments with well 8 water, the well W solution (pH = 7.12) represented a later segment of a retained system in which most of the dissolved Fe had already been removed from the system. The amount of particulate Al increased from 33 to 1300 μg/L upon mixing the streamwater with well W. In contrast, particulate Fe concentrations increased from 64 to 83 μg/L, of which only 32 μg/L was attributed to newly formed HFO phases, with the remainder originating from stream particles. POC (9% dry wt) was within the range found for natural precipitates collected in the stream just below well W (*16*).

The observed Pb removal (49%) in the well W mixing experiment was higher than the predicted removal, which

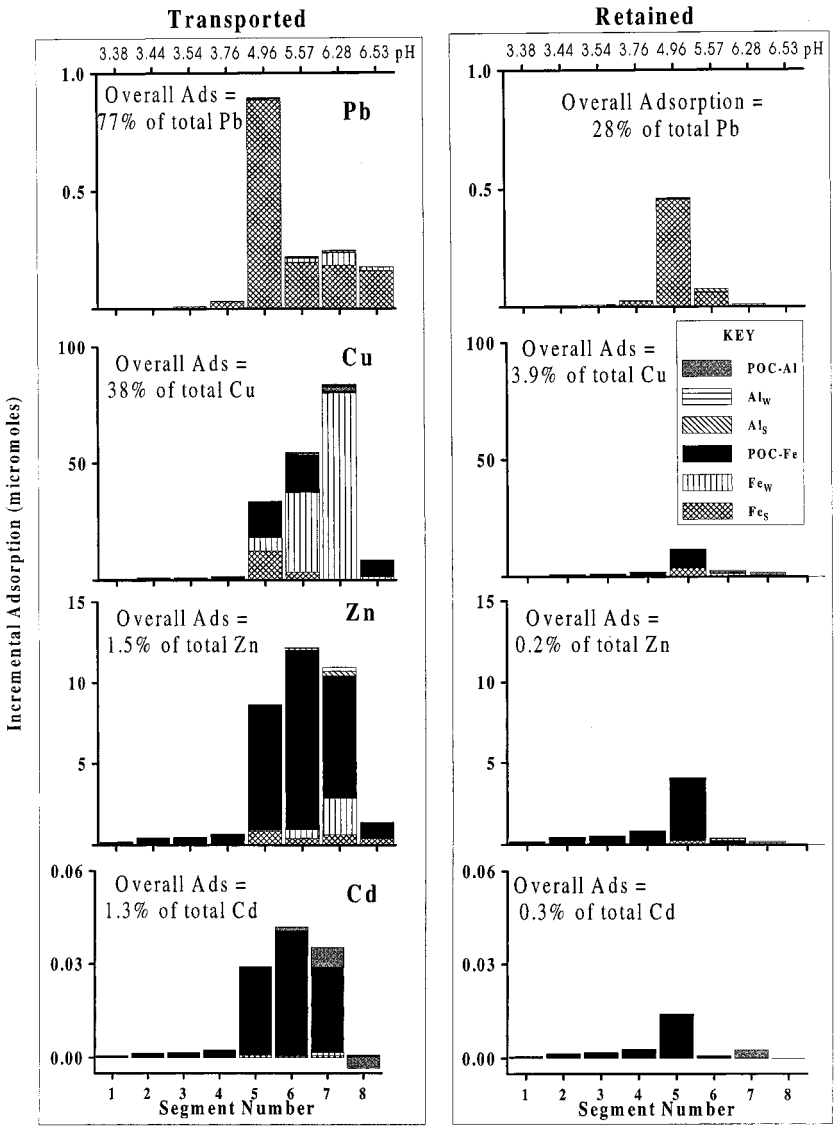

FIGURE 4. Model simulations of the incremental adsorption of Pb, Cu, Zn, and Cd in each mixing segment under the Transported (left) and Retained (right) Scenarios onto Fe_S and Fe_W (the strong and weak HFO sites, respectively), Al_S and Al_W (the strong and weak HAlO sites, respectively), and complexation with organic matter adsorbed onto HAlO (POC−Al) and HFO (POC−Fe).

TABLE 2. Observed and Predicted Removal of Metals during Mixing Experiments[a]

	low-dilution well 8 (pH = 5.92)			high-dilution well 8 (pH = 6.93)			well W (pH = 7.12)		
	observed	predicted		observed	predicted		observed	predicted	
	% removal	% removal	dominant site	% removal	% removal	dominant site	% removal	% removal	dominant site
Pb	38	30	Fe_W,[b] Fe_S	92	49	Fe_S	49	20	Fe_S
Cu	5.6	5.7	Fe_W	38	12	Fe_W[c]	18	57	Fe_W[c]
Zn	0.13	0.15	POC	1.6	1.0	POC	0.3	1.0	POC
Cd	0.12	0.11	POC	0.9	0.7	POC	0.02	1.1	POC

[a] Details of predicted results are given in Appendix Table 3 of Supporting Information. [b] Fe_S = strong HFO site, Fe_W = weak HFO site, and POC = particulate organic matter [c] Speciation modeling indicate supersaturation with respect to malachite. No mineralogical analysis was performed on these solid samples.

was dominated by adsorption onto the weak HFO sites (Table 2). The observed Pb removal in the mixing experiment was only slightly higher than the Pb removal (36%) by natural precipitates formed within the stream. The observed removal of Cu during the mixing experiment was three times higher than the predicted removal and 1.5 times greater than that removed by the natural precipitates. The high observed Cu removal in this mixing experiment may have possibly been a result of precipitation of malachite, which was supersaturated in this solution. Predicted Zn removal amounted to 1.0%, which was three times the observed removal, and was dominated by complexation with POC (85% of total metal adsorption). The very low Cd removal that was observed in the mixing experiment (0.02%) was not predicted.

Discussion

Importance of the Physical System in Metal Removal. Differences in metal removal under the Transported and

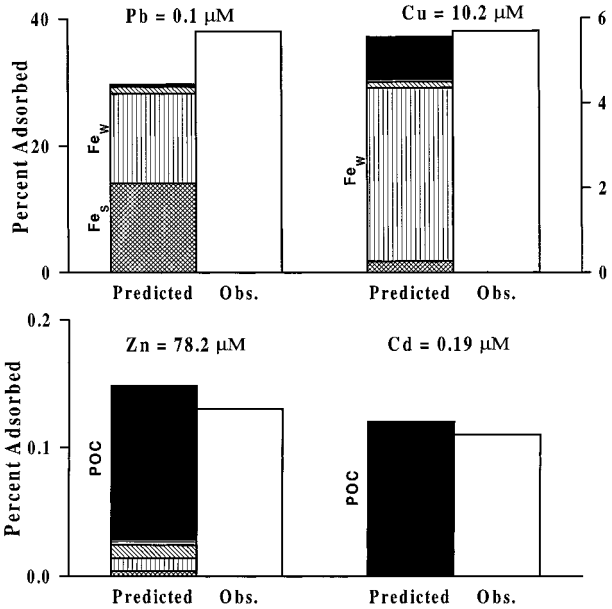

FIGURE 5. Comparison of model predictions and observed removal in the low-dilution well 8 solution (pH = 5.92). Legend for bars are same as in Figure 4.

Retained Scenarios are based upon the dominance of HFO adsorption and organic carbon complexation. For the Transported Scenario and the well 8 mixing experiments, the HFO formed during the early stages of neutralization was available for significant metal adsorption during the later stages of neutralization, where pH had increased to circumneutral values. In the Retained Scenario, the zone of precipitation and the retention of HFO along the chemical pathway is separated from the zone where pH increases to the adsorption edge of specific metals, resulting in significant decreases in overall metal adsorption (Figure 6). For a steady-state system, the separation along the chemical pathway represents a separation in space along the flow path (e.g., between wells 8 and W at the Moon Creek site).

The model simulations and mixing experiments with contaminated groundwater provide insight into the removal processes occurring in the aquifer at the Moon Creek site, as ARD is neutralized by ambient waters. The stage along the chemical pathway of acid neutralization at which groundwater enters surface waters significantly affects the dissolved metal to particulate Fe ratio downstream, a key parameter that determines the fate of metals in surface waters contaminated by ARD. The particulate Fe not only provides the adsorption sites for Cu and Pb but also enhances Zn and Cd removal by the adsorbing organic carbon that in turn complexes Zn and Cd. Thus, the physical characteristics of the environment play an important role in determining the extent of metal removal downstream. Metals are transported over long distances (10−100 km) within surface waters in mining districts where the majority of the metals are derived from fluvially deposited tailings and tailings impoundments, such as in Coeur d'Alene (ID) and Clarks Fork (MT). The removal of the majority of the Fe within the oxic interstitial waters of tailings or soils can explain the conservative nature of tailings-derived Zn and Cd from some acidic discharges, even after the acid is neutralized by surface waters. Since contaminated groundwater entered Moon Creek after a majority of the dissolved Fe had been removed from the groundwater, little particulate Fe (0.02−0.05 mg/L) was available for metal adsorption (*16*).

Relative Importance of Hydrous Oxides and Organic Matter in Metal Removal. The field simulations and predictions from the mixing experiments simultaneously considered

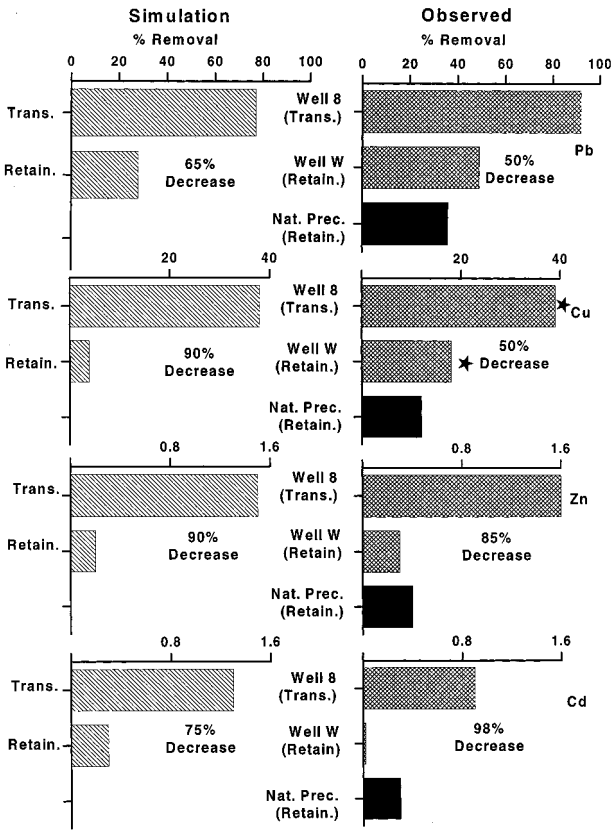

FIGURE 6. Left side: Comparison of metal removal for the retained versus transported simulations (hatched), both at pH 6.53. Right side: Comparison of observed metal removals (crosshatched) in the high-dilution well 8 solution at pH = 6.93 (which represents a Transported Scenario), in the well W solution at pH = 7.12 (which represents a Retained Scenario), and for natural precipitates collected from Moon Creek (solid) when pH = 6.92, which is a retained field system (*16*). Supersaturation with respect to the basic copper carbonate, malachite, is indicated by a star.

adsorption of metals onto both HFO and HAlO, and complexation of metals by organic matter adsorbed onto both oxides. The application of this competitive, assemblage adsorption model to the physical and chemical conditions in Moon Creek clearly demonstrated the dominance of HFO and organic carbon in controlling metal removal (Figures 4 and 5), even when HAlO is present in much higher concentrations. This dominance of HFO over HAlO in removing metals is due to generally stronger affinities for metals and higher site densities for HFO than for HAlO.

In pristine systems, Cu is the dominant trace metal associated with particulate organic matter (*29*). Yet, our modeling results in Moon Creek indicate that sorption of Zn and Cd rather than Cu is dominated by particulate organic carbon (POC) and that Cu sorption is dominated by HFO. The most important factors responsible for these observations are the pH-dependent binding constants of the metals for the particulate phases, the pH of the system, and the relative abundance of POC as compared to HFO sites. For example, for the low-dilution well 8 solution where pH = 5.92 (Figure 5), the logs of the pH-dependent complexation constants for Cu, Zn, and Cd with POC were 6.85, 5.85, and 5.85, respectively, while those for the weak HFO sites were 6.5, 3.9, and 2.9, respectively. The higher concentration of weak HFO sites (1.8 μM) compared to POC (0.2 μM) sites in this mixing experiment and the similar Cu complexation constants for POC and HFO favored the association of Cu with HFO relative to POC. However, the 9-fold greater amounts of HFO sites relative to POC sites did not offset the factors

of 90 to about 900 in the weaker interaction of Zn and Cd with HFO as compared to POC. Thus, POC dominated the removal of Zn and Cd in this system.

Comparisons of Predicted and Observed Metal Removals. In general, the competitive, assemblage adsorption model predicted the removal of Cd, Cu, Pb, and Zn in mixing experiments within a factor of 3 when complexation of Zn and Cd by particulate organic matter was considered. For the low-dilution well 8 mixing experiment, metal removals were predicted within 25% for all four metals (see Figure 5). This agreement between the model and observed results is remarkable considering that both the metal concentrations (0.030−15 μM) and observed removal (0.1−97%) varied over 3 orders of magnitude. Well W mixing experiments simulated the neutralization of groundwater as it mixed with Moon Creek water in the seep area. The removals of Pb, Cu, and Zn for the mixing experiment were similar to those found in natural precipitates (Figure 6) and comparable to the predicted values of the mixing experiments (Table 2). These results suggest that both the inorganic and organic carbon systems must be well defined if metal removals are to be accurately modeled in aquatic systems, even in streams highly contaminated by acidic drainage.

Multisubstrate adsorption assemblage models using empirical binding data have been applied to a variety of sediments in freshwater and marine systems (*30*, *31*). Recently, surface complexation models derived from laboratory data for idealized oxyhydroxide phases were used to describe the association of metals with organic matter in acidic freshwater sediments and with Fe and Mn oxyhydroxides in freshwater sediments at circumneutral pH (*12*). The addition of a surface complexation model containing Fe, Al, Mn oxyhydroxides and solid-phase organic matter sites to an acid-volatile sulfur model may provide a better description of metal behavior in marine and some freshwater sediments (*32*, *33*). Our work in Moon Creek strongly suggests that multisubstrate surface complexation models coupled with models simulating physical processes are capable of simulating dissolved metal removal in natural systems.

Acknowledgments

The authors wish to acknowledge Pam Drake, who performed the ICP and IC analyses, and Dr. Mohammed Ikramuddin, who performed the ICP-MS analyses. The senior author wishes to express his gratitude to Dr. Mark Benjamin for providing instruction into the finer details of adsorption modeling. This manuscript was improved by critical reviews by Kathy Smith and Rich Wanty. The mixing experiments and the resulting chemical analyses were conducted as part of the Contaminant Fate project within the Department of Interior.

Supporting Information Available

Appendix Table 1 contains all the site densities and equilibrium and adsorption constants used in the model, and Appendix Tables 2 and 3 contain the concentrations of metals on particles and the details of the model predictions for the mixing experiment solutions, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Nordstrom, D. K.; Jenne, E. A.; Ball, J. W. In *Chemical Modeling in Aqueous Systems*; Jenne, E. A., Ed.; American Chemical Society: Washington, DC, 1979; pp 51−79.
(2) Langmuir, D. Aqueous Environmental Geochemistry. *Aqueous Environmental Geochemistry*; Prentice Hall: New Jersey, 1997; p 600.
(3) Kimball, B. A.; Broshears, R. E.; Bencala, K. E.; McKnight, D. M. *Environ. Sci. Technol.* **1994,** *28*, 2065−2073.
(4) Broshears, R. E.; Runkel, R. L.; Kimball, B. A.; McKnight, D. M.; Bencala, K. E. *Environ. Sci. Technol.* **1996**, *30*, 3016−3024.
(5) Chapman, B. M.; Jones, D. R.; Jung, R. F. *Geochim. Cosmochim. Acta* **1983**, *47*, 1957−1973.
(6) Johnson, C. A. *Geochim. Cosmochim. Acta* **1986,** 50, 2433−2438.
(7) Filipek, L. H.; Nordstrom, D. K.; Ficklin, W. H. *Environ. Sci. Technol.* **1987**, *21*, 388−396.
(8) Davis, A.; Olsen, R. L.; Walker, D. R. *Appl. Geochem.* **1991**, *6*, 333−348.
(9) Kimball, B. A.; Callender, E.; Axtmann, E. V. *Appl. Geochem.* **1995**, *10*, 285−306.
(10) Karlsson, S.; Allard, B.; Hakansson, K. *Appl. Geochem.* **1988**, *3*, 345−356.
(11) McKnight, D. M.; Bencala, K. E.; Zellweger, G. W.; Aiken, G. R.; Feder, G. L.; Thorn, K. A. *Environ. Sci. Technol.* **1992**, *26*, 1388−1396.
(12) Tessier, A.; Fortin, D.; Belzile, N.; DeVitre, R. R.; Leppard, G. G. *Geochim. Cosmochim. Acta* **1996**, *60*, 387−404.
(13) Webster, J. G.; Swedlund, P. J.; Webster, K. S. *Environ. Sci. Technol.* **1998,** *32*, 1361−1368.
(14) Smith, K. S.; Ficklin, W. H.; Plumlee, G. S.; Meier, A. L. In *Water-Rock Interactions;* Kharaka, Y. K., Maest, A. S., Eds.; A. A. Balkema: Rotterdam, 1992; pp 443−447.
(15) Webster, J. G.; Nordstrom, D. K.; Smith, K. S. In *Environmental Geochemistry of Sulfide Oxidation*; Alpers, C. N., Blowes, D. W., Eds.; American Chemical Society: Washington, DC, 1994; pp 244−260.
(16) Paulson, A. J. *Appl. Geochem.* **1997**, *12*, 447−464.
(17) Paulson, A. J. Fate of metals in surface waters of the Coeur d'Alene Basin, Idaho. *Report of Invest. (U.S. Bureau Mines) No. 9620;* 1996; p 75.
(18) Lofts, S.; Tipping, E. *Geochim. Cosmochim. Acta* **1998**, *15*, 2609−2625.
(19) Paulson, A. J.; Girard, J. M. Groundwater data from the Silver Crescent Millsite, East Fork of Moon Creek, Idaho. *Report of Invest. (U.S. Department of Energy) No. 9628*; 1996; p 64.
(20) Parkhurst, D. L.; Thorestenson, D. C.; Plummer, N. L. MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual. *Water Resour. Invest. (U.S. Geological Survey) No. 80-96*; 1980; p 83.
(21) Allison, J. D.; Brown, D. S.; Novo-Gradac, K. J. Report EPA/600/3-91/021; U.S. EPA: Washington, DC, 1991; p 106.
(22) Dzombak, D. A.; Morel, F. M. M. *Surface Complexation Modeling-Hydrous Ferric Oxide*; John Wiley and Sons: New York, 1990; p 393.
(23) Ainsworth, C. C.; Pilon, J. L.; Gassman, P. L.; Van Der Sluys, W. G. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1615−1623.
(24) Benjamin, M. M. Ph.D. Dissertation, Stanford University, Palo Alto, 1978; p 228.
(25) Tipping, E. *Geochim. Cosmochim. Acta* **1981**, *45*, 191−199.
(26) Davis, J. A. *Geochim. Cosmochim. Acta* **1982**, *46*, 2381−2393.
(27) Davis, J. A. *Geochim. Cosmochim. Acta* **1984**, *48*, 679−691.
(28) Tipping, E.; Hurley, M. A. *Geochim. Cosmochim. Acta* **1992**, *56*, 3627−3641.
(29) Paulson, A. J.; Feely, R. A.; Curl, H. C., Jr.; Crecelius, E. A.; Geiselman, T. *Geochim. Cosmochim. Acta* **1988**, *52*, 1765−1779.
(30) Oakley, S. M.; Nelson, P. O.; Williamson, K. J. *Environ. Sci. Technol.* **1981**, *15*, 474−480.
(31) Luoma, S. N.; Davis, J. A. *Mar. Chem.* **1983**, *12*, 159−181.
(32) Cooper, D. C.; Morse, J. W. *Environ. Sci. Technol.* **1998**, *32*, 327−330.
(33) Huerta-Diaz, M. A.; Tessier, A.; Carignan, R. *Appl. Geochem.* **1998**, *13*, 213−233.

Received for review January 14, 1999. Revised manuscript received July 12, 1999. Accepted July 14, 1999.

ES9900454