COMPARISON BETWEEN OBSERVED AND MODEL PREDICTED PARTICULATE METAL TRANSPORT IN A MINING-IMPACTED STREAM (NORTH FORK CLEAR CREEK, COLORADO) [1]

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Abstract. Acid-mine drainage (AMD) is an important source of metals to aquatic ecosystems. Once these metals are input to oxygenated stream water of neutral pH, there may be oxidation of metal ions, precipitation of metal oxyhydroxides, and co-precipitation and/or sorption of metals. Understanding the fate and transport of these metals requires knowledge of the distribution of metals between the suspended solid and dissolved phases. Models exist for the prediction of sorption of metals to oxyhydroxides phases, primarily for hydrous iron oxide (HFO). Visual-MINTEQ now includes a database for a second hydrous oxide phase: hydrous manganese oxide (HMO), which may prove to be an important sorbent for some metals in mining-impacted systems. This paper discusses the comparison between model predicted and observed percentage particulate copper and zinc in stream water collected over a two-year study of the North Fork of Clear Creek, Colorado. It was found that the model over-estimated the percentage of particulate copper actually observed, using HFO as the sole sorbent phase, but that the comparison was within a factor of two. Inclusion of HMO for modeling of the zinc improved the prediction of percentage particulate zinc; however, results indicate that there may be another process controlling particulate zinc in the stream.

Additional Key Words: Iron oxyhydroxides, suspended sediment, manganese oxyhydroxides, and adsorption

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Introduction

An important source of metals to aquatic ecosystems is acid-mine drainage (AMD) from active or abandoned sulfidic-ore mining sites. Natural processes and remedial activities both lead to the neutralization of acidity, which results in the removal of dissolved metals from the water column and the production of finely-grained sediments. Partitioning of dissolved metal ions to the particulate phase can involve both precipitation and adsorption processes.

As dissolved free-metal ions are considered more bioavailable (and hence toxic) to aquatic organisms (Sunda and Guillard 1976), understanding the processes by which these metals are sequestered into the particulate phase is of importance. Multiple sorbent phases may be present in AMD systems for sorption of metals. Two of the common ones are hydrous ferric oxyhydroxides (HFO) and hydrous manganese oxyhydroxides (HMO). Models exist for the prediction of particulate associated metals in aquatic environments, such as MINTEQA2 (Allison et al., 1991) and a more recently developed Windows-version, Visual-MINTEQ (Gustafson, 2004). Because AMD systems are so complex, it is desirable to determine if there can be simplification of modeling metal speciation that can still represent accurately what is observed, while limiting or eliminating the need for adjusting model default parameters. For instance, if there is a predominance of one sorbent over another, can the dominant sorbent alone be used to accurately represent what is observed? This paper addresses this question, for copper and zinc, in the North Fork of Clear Creek (NFCC), Colorado.

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 (Cunningham et al., 1994; U.S. EPA, 1999; Wildeman et al., 1974). Due to this past mining activity, a major tributary to Clear Creek, Colorado, the North Fork Clear Creek, does not support fish in locations below AMD inputs (U.S. EPA and Colorado Department of Public Health & Environment, 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 column and in the bed 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 (Schemel et al., 2000; Stumm, 1992). Additionally, some metals may remain in the dissolved phase during transport until conditions are more favorable for sorption and/or precipitation (e.g. higher pH or an alternate sorbent phase).

In NFCC, the predominant sorbent is hydrous iron oxyhydroxides (HFO): the HFO is present in suspended and bed sediments. During some times of the year, a black coating is present on the rocks; it was found that this coating is predominantly comprised of manganese (Harvey et al., 2003). Since the HFO is the dominant sorbent for metal sorption in the stream, the purpose for this research was to compare observed concentrations of particulate copper and zinc, over a two-year period, with Visual-MINTEQ model predictions, based on the use of HFO as the sole sorbent. It was hypothesized that solely HFO would be adequate to represent accurately the

percentage particulate copper and zinc observed in the stream. However, because copper and zinc have been seen to behave differently in the stream (Harvey et al., 2004) and that HMO is known to be a strong sorbent for metals (Jenne, 1968), an additional model run was included for each sample with both HFO and HMO as sorbent phases.

Methods

Field Sampling

Samples were collected biweekly at NCC-SW-3 (Colorado Department of Public Health & Environment designation for North Fork Clear Creek, surface water, location three); the location is identified on Fig. 1. Fig. 1 also shows the primary AMD inputs to NFCC (in bold-italic font), the major tributaries to the stream, and the wastewater treatment plant (NCC-SW-15A). This paper presents results from samples obtained at NCC-SW-3, including replicates, collected between May 21, 2002 and July 15, 2004.
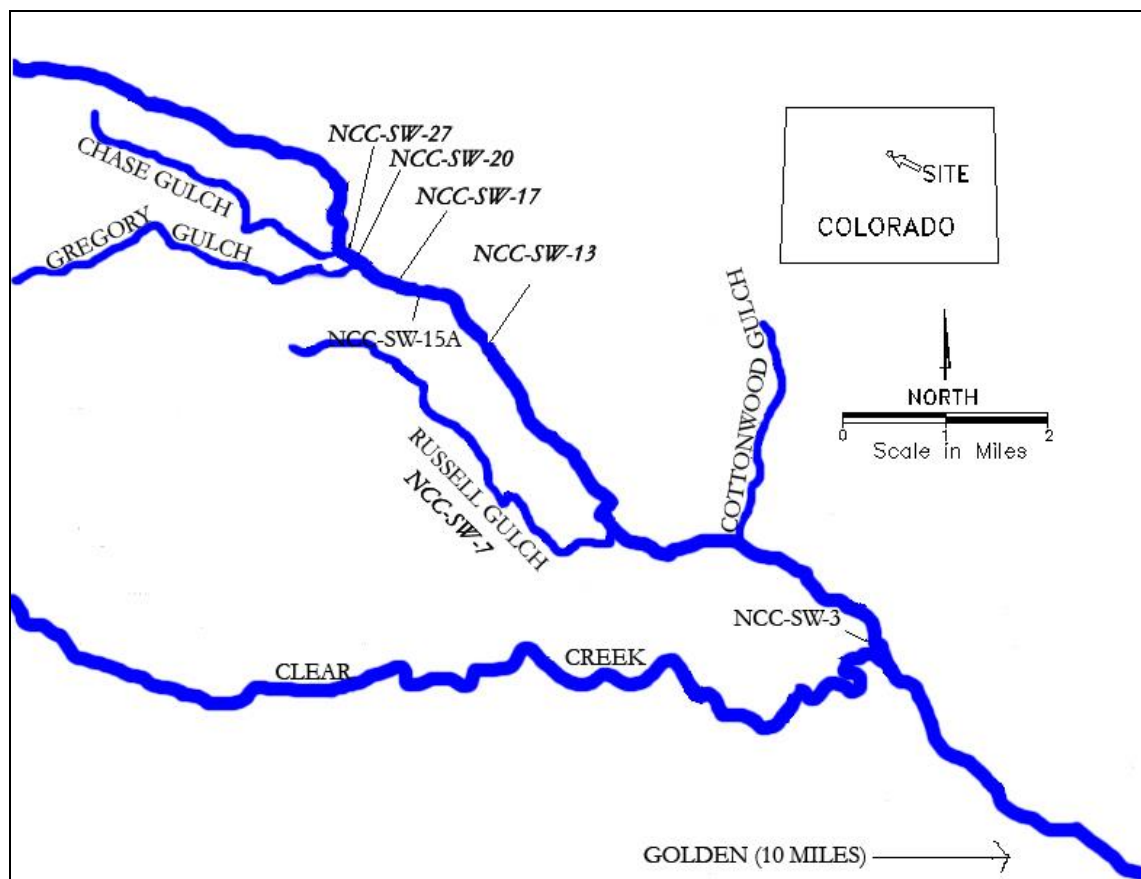
Figure 1. NFCC Study Area (adapted, with permission, from an electronic version of the Clear Creek Watershed Topography map provided by Rocky Mountain Consultants, Longmont, CO).

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 upside down below the water surface and filled by inverting and moving the bottle

upward 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. Care was taken that the bed sediments were not disturbed during water sampling.

A 50-ml aliquot of each bulk water sample was poured into VWR™ 50-ml polypropylene centrifuge tubes. A second 50-ml aliquot was filtered through a 0.45-micron Sartorius™ Cellulose Acetate (CA) filter, using a Gelman™ 25-mm filter holder and a Norm-Ject™ 50-ml syringe (polypropylene barrel with polyethylene plunger). This water was captured in a 50-ml centrifuge tube. The 50-ml tubes of water were inverted three times, and then 10 to 12 ml of the water from each 50-ml tube (unfiltered and filtered) was poured off into individual 15-ml centrifuge tubes.

Temperature and pH were measured in the stream using a Beckman™ Φ210 pH and temperature meter with a combination VWR™ gel pH-temperature electrode. A three-point calibration was conducted and the calibration was checked using a pH 7.01 check-standard solution. The probe was placed in the flowing water and left until the pH reading stabilized.

Analytical
Alkalinity was measured in the bulk raw water sample in the laboratory, using the Hach™ titration method (available from www.hach.com). A packet of bromocresol-green was added to 100 ml of stream water. The sample was titrated with 0.2 N H_2SO_4 until the color of the solution reached a light pink, indicating the bicarbonate endpoint (pH 4.5). The value on the autotitrator was converted to a concentration of alkalinity in mg/l as calcium carbonate.

Water remaining in the 50-ml centrifuge tubes was archived in a freezer. The water in the 15-ml centrifuge tubes was prepared for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analyses following a modified EPA Method 200.7 (U.S. EPA 1994). Briefly, the water was acidified with several drops of metal-free hydrochloric acid to a pH < 2 and left to equilibrate for a minimum of 24-hours. Prior to analysis on the Perkin Elmer Optima 3000 ICP-AES, the samples were examined for remaining particulate material; if present, additional acid was added to aid in dissolution and the samples were sonicated immediately prior to analysis. No samples had particles larger than would pass through the instrument, so filtration prior to analysis was not necessary.

Data Reduction and QA/QC
ICP-AES data for all samples were compared to instrument detection limits and values determined to be below detection (BDL) were not used for calculation of particulate metal. Particulate metal concentrations were determined by the subtraction of total and dissolved metal concentrations, shown by Equation 1 and percentage particulate by Equation 2.

$$M_T - M_D = M_P \qquad\qquad (1)$$

$$\frac{M_P}{M_T} * 100\% = \% M_P \qquad\qquad (2)$$

Where M equals metal and the subscripts P, T, and D refer to particulate, total, and dissolved, respectively, in each equation. Standard deviations of the total and dissolved metals were determined through three instrument replicates of each sample. Equations 3 and 4 were used to calculate standard deviation propagated through particulate metal calculation steps, addition/subtraction and multiplication/division, respectively (Skoog and Leary 1992). The overall %CV (coefficient of variation) was calculated for both copper and zinc for each sample, using Equation 5.

$$s_P = \sqrt{(s_T)^2 + (s_D)^2} \tag{3}$$

$$s_{\%P} = \%M_P * \sqrt{\left(\frac{s_P}{M_P}\right)^2 + \left(\frac{s_T}{M_T}\right)^2} \tag{4}$$

$$\%CV = 100\% * \frac{S_{\%P}}{\%M_P} \tag{5}$$

Where s is the standard deviation, M equals metal, and the subscripts P, T, and D refer to particulate, total, and dissolved, respectively.

Metal specific (copper and zinc) QA/QC criteria for data included in the comparison between modeled and field results were that: 1) calculated percentage particulate metal was neither zero nor 100; and 2) the %CV for the calculated percentage particulate metal was less than 30%.

Modeling: Visual-MINTEQ

Visual-MINTEQ was downloaded from www.lwr.kth.se/english/OurSoftware/Vminteq (Gustafson, 2004). This model is based on the DOS-version of MINTEQA2, which was developed by the EPA (Allison et al., 1991). MINTEQA2 and Visual-MINTEQ are equilibrium speciation models, meaning that for a given ion that is input to the model, output will include the different forms expected to be in the environment at equilibrium, under the chemical conditions input to the model. For example, at a given temperature, pH, alkalinity, and total copper concentration, copper will be present as Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2{}^0$, $CuCO_3(s)$, etc; the model will output which of these species are present and at what concentration.

The two models are very similar in capability, with the major exception that the DOS-version cannot be used on computers with operating systems newer than Windows 98® (Langmuir et al., 2003). They each include a linkable database for an HFO sorbent phase developed by Dzombak and Morel (1990), but Visual-MINTEQ contains an additional linkable database with parameters for sorption of metals onto hydrous manganese oxide (HMO), developed by Tonkin et al. (2004). These databases for sorption are based on the double-layer model (DLM), one of several surface complexation models. Briefly, the DLM assumes there are two planes associated with a surface: the surface plane and the diffuse-layer plane. The model assumes 1) the potential measured at the surface-plane and at the diffuse-layer plane are equal, 2) the sum of the surface charge and the diffuse-layer charge is zero, and 3) specific adsorption occurs at the surface-plane (Allison et

al., 1991). For more information on MINTEQA2 and Visual-MINTEQ, including historical development, surface complexation theory, and how to perform model runs, the reader is referred to Allison et al. (1991) and Gustafson (2004), and references therein.

A user may input a variety of data into the model. For this study, the following data were used: pH, temperature, alkalinity, concentrations of total Mg^{2+}, Na^+, K^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, SO_4^{2-}, Al^{3+}, Mn^{2+}, Fe^{3+}, and Ni^{2+} (data are provided as an Appendix). The model will not allow the presence of any input solids if alkalinity is specified; thus, an initial run, using the known alkalinity was done to determine the carbonate concentration for subsequent runs. Particulate iron concentrations were converted to mass of HFO for sorption modeling. HFO was assumed to be $Fe_2O_3 \cdot H_2O$ (MW 177.7 g/mol), having a specific surface area of 600 m^2/g and a site density of 2.31 sites/nm^2, as recommended by Davis and Leckie (1978). Particulate manganese was calculated for each sample and converted to a mass of HMO for sorption modeling. The HMO was assumed to be $MnO_2 \cdot H_2O$ (MW 119 g/mol), having a specific surface area of 765 m^2/g and a site density of 1.695 sites/nm^2, as recommended by Tonkin et al. (2004). The model was run using the instructions available in the program help files (Gustafson, 2004).

Results and Discussion

The first model run (after determining carbonate concentration as discussed previously) was conducted using HFO as the sole sorbent; the second run included both HFO and HMO. Comparison between model and observed percentage particulate, for each of the metals and for each of the model runs is shown in Fig. 2.

Both the model runs with HFO as sole sorbent and the runs with HFO plus HMO greatly over-predict the percentage particulate copper. However, with the exception of four data points, comparison is within a factor of two. Thus, it appears that the use of HFO as the sole sorbent is sufficient to determine percentage particulate copper, accepting an error of plus a factor of two. The majority of zinc data with only HFO as the sorbent phase is under-predicted by the model. There are also far more data points outside of the factor of two range than with the copper, twenty-nine points. Addition of HMO is shown to greatly improve the comparison between the model and observed results, with only twelve of the initial twenty-nine data falling outside of the factor of two range. Thus, it appears that HFO, as the sole sorbent, is not sufficient to predict the observed percentage of particulate zinc.

To more clearly see the deviations from a 1:1 relationship, for each of the model runs, and to determine if there was any seasonal influence in the data falling outside of the factor of two range, data were plotted as shown in Fig. 3 and 4, for copper and zinc, respectively. Data falling below the 1:1 line indicate the model having under-predicted the percentage particulate; data lying above the 1:1 line indicate over-prediction of the model. It appears there is a slight trend in the deviation from model and observed percentage particulate copper, with a somewhat greater over-prediction by the model during spring and summer months. Interestingly, zinc shows the opposite trend with a much greater under-prediction by the model during spring months and summer months. The trend with zinc is much larger when looking only at HFO model results, seeming to indicate a seasonal relationship with HMO.

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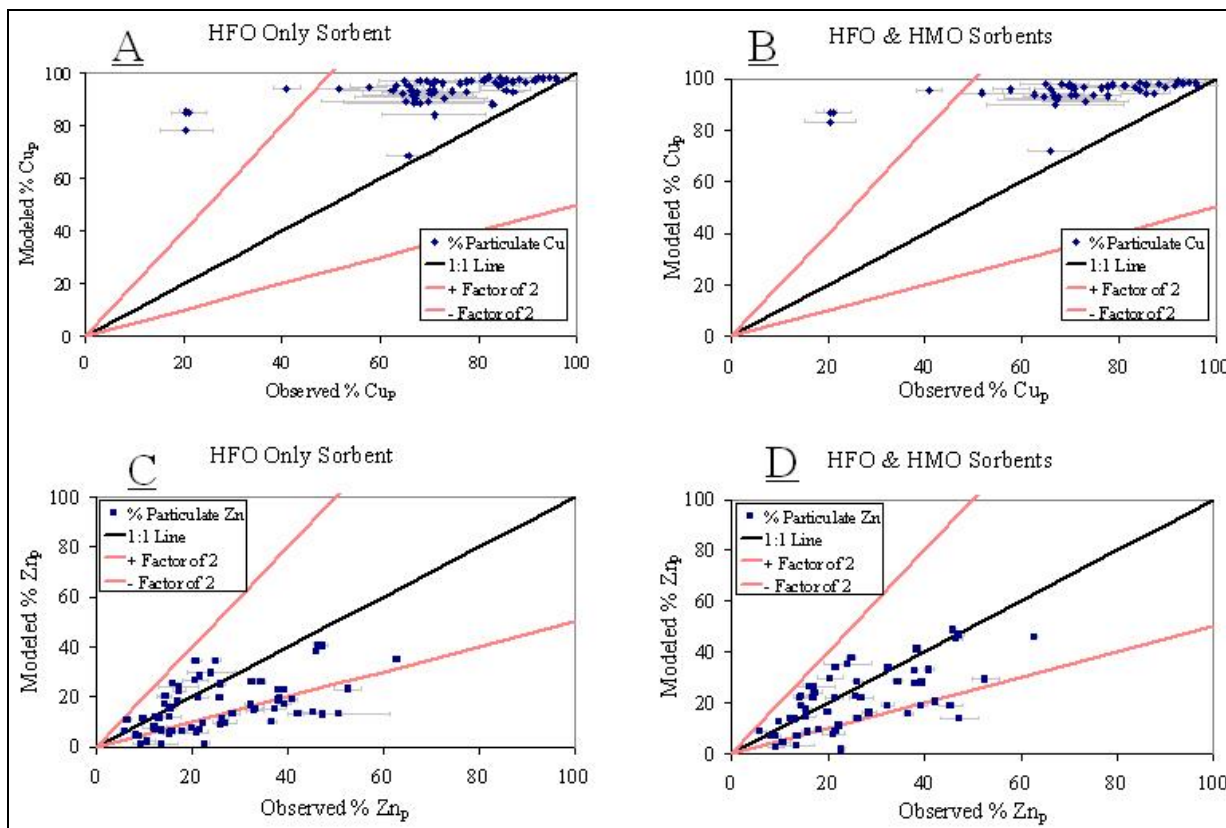
Figure 2. Model % particulate metal versus observed % particulate metal. A) Cu with HFO as sole sorbent; B) Cu with HFO and HMO sorbents; C) Zn with HFO as sole sorbent; and D) Zn with HFO and HMO sorbents. Error bars represent propagated instrument standard deviation.
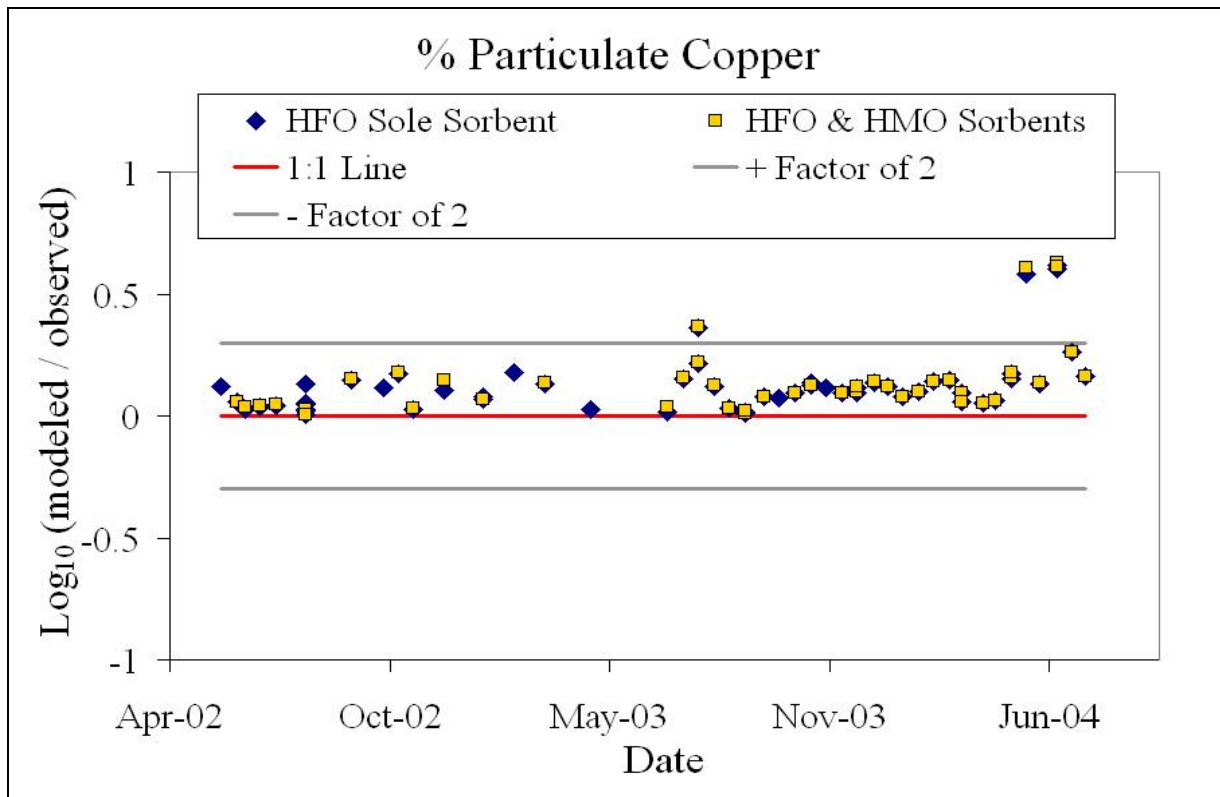
Figure 3. Deviation from 1:1 relationship between model and observed % particulate copper.
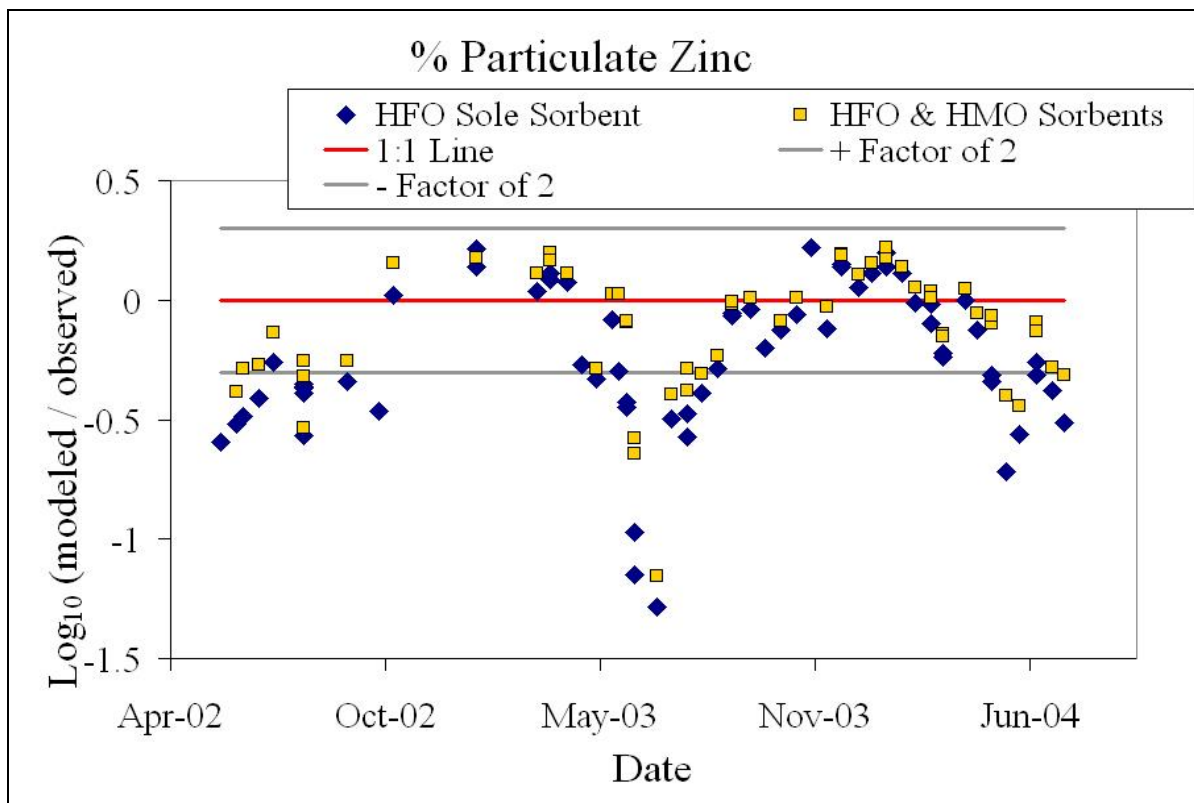

Figure 4. Deviation from 1:1 relationship between model and observed % particulate zinc.

Conclusions

The use of HFO as a sole sorbent phase to predict observed percentage particulate copper seems to be appropriate, within a factor of two, in a stream where HFO is the dominant sorbent. It does appear, however, that something in the stream is causing a portion of the copper to remain in the dissolved form, especially during spring and summer months. This could be due to the system not being at equilibrium during these higher flow seasons, or perhaps due to complexation of the copper with dissolved organic carbon (DOC) present in the stream. An equilibrium study conducted during February 2004 indicated that copper and zinc were at equilibrium in the stream. And it was assumed this would be the case for all seasons, but perhaps this assumption is incorrect for higher flow seasons. Modeling including measured total DOC was not investigated in this paper, but is in progress.

HFO as a sole sorbent for zinc is not sufficient to describe observed zinc behavior, with the model considerably under-predicting percentage particulate zinc, especially during spring and summer months. The addition of another sorbent phase, HMO, greatly improves the comparison between model and observed results, although there are still some dates that remain under-predicted, each being during either spring-runoff or during storm events. This could be due to the system not being at equilibrium during these higher flow seasons, or perhaps due to an additional sorbent phase not considered in modeling.

The presence of HMO does have a seasonal trend, being observed as rock coatings predominantly under lower flow conditions, such as in late summer, fall and winter. The presence of algae is also observed during these times, and it is suspected that the algae are responsible for biogenic production of the HMO. During spring and early summer, with runoff events, scouring of the HMO from the rocks increases its concentration in the suspended sediment. It is likely that during these times, particulate zinc is increased due to its sorption onto the HMO being scoured. It is especially interesting that copper and zinc have opposite trends during spring and summer months. It is possible that this is due to a relationship with algae and/or dissolved organic carbon. Copper is known to complex strongly with dissolved organic carbon species, and zinc to a lesser extent. Perhaps the copper is being complexed with the organic carbon and this allows for more sites available for sorption of zinc onto both HFO and HMO, and perhaps onto algal biomass scoured from the rocks associated with HMO. Future modeling exercises will be conducted to determine the importance of DOC in relation to the observed percentage particulate copper and zinc.

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Appendix

Sample Date	T-Al	T-Ca	T-Cu	T-Fe	T-K	T-Mg	T-Mn	T-Na	T-Ni	T-SO$_4$	T-Zn
5/21/2002	0.227	30.407	0.064	4.097	3.761	9.330	0.865	21.283	0.014	98.012	0.402
6/4/2002	0.897	22.533	0.110	7.895	2.488	7.579	1.066	11.536	0.011	60.615	0.792
6/11/2002	0.175	24.447	0.037	2.859	2.180	7.551	1.079	14.379	0.011	78.220	0.445
6/25/2002	0.134	35.444	0.035	2.705	3.446	10.842	1.852	23.000	0.016	121.686	0.671
7/9/2002	0.306	28.209	0.043	4.513	3.124	8.540	1.210	15.435	0.011	75.334	0.484
8/5/02 14:32	1.150	45.752	0.062	6.400	5.046	14.925	1.752	33.090	0.073	153.692	0.856
8/5/02 16:03	0.613	43.419	0.042	3.899	4.509	14.024	1.549	28.737	0.029	150.495	0.654
8/5/02 16:15	0.372	45.529	0.040	3.468	4.507	14.409	1.486	31.368	0.014	159.725	0.699
8/5/02 16:35	0.337	45.375	0.040	3.360	4.469	14.175	1.503	31.089	0.014	157.596	0.686
8/5/02 17:00	0.375	45.801	0.037	3.274	4.481	14.432	1.554	31.353	0.013	161.944	0.669
8/6/2002	1.029	40.567	0.107	8.201	4.308	13.458	1.887	31.068	0.025	142.797	1.489
9/16/2002	0.170	60.049	0.029	1.842	7.663	18.520	2.023	58.680	0.020	231.927	0.631
10/15/2002	0.053	58.392	0.028	2.018	6.474	18.083	2.376	37.382	0.023	224.891	0.661
10/29/2002	0.058	54.944	0.023	1.953	6.009	16.912	2.589	36.970	0.025	205.460	0.919
11/11/2002	0.302	63.005	0.069	6.287	7.209	20.156	2.879	41.590	0.030	237.470	1.409
12/10/2002	0.044	73.179	0.015	1.127	6.542	22.818	3.165	40.327	0.033	278.932	1.498
1/14/2003 FR1	0.322	66.541	0.103	7.484	6.685	20.476	2.900	56.824	0.029	239.175	1.187
1/14/2003 FR2	0.318	64.251	0.101	7.301	6.291	19.866	2.772	52.564	0.026	225.916	1.135
2/11/2003	0.143	68.095	0.038	2.477	6.758	21.317	2.750	56.452	0.022	263.326	1.172
3/11/2003	0.169	60.586	0.051	2.944	6.255	19.221	2.298	66.775	0.018	226.743	0.969
3/24/2003 FR1	0.605	55.929	0.027	4.684	5.638	17.271	1.352	74.506	BDL	170.166	1.105
3/24/2003 FR2	0.622	55.877	0.028	4.826	5.681	17.249	1.331	75.605	BDL	171.145	1.112
4/8/2003	0.493	58.172	0.030	2.871	5.406	18.539	1.633	54.072	BDL	170.924	1.330
4/22/2003	0.963	31.686	0.143	2.251	2.883	10.412	1.467	19.138	0.006	94.912	1.333
5/6/2003	0.793	25.133	0.077	1.677	2.295	8.170	1.018	14.324	BDL	73.131	1.063
5/20/2003	1.092	12.058	0.049	5.016	1.733	3.925	0.576	7.576	BDL	31.812	0.458
5/27/2003	0.756	8.321	0.003	2.360	1.355	2.698	0.360	5.531	BDL	21.617	0.222
6/3/2003 FR1	0.457	7.761	BDL	1.288	1.222	2.421	0.224	5.375	BDL	19.675	0.163
6/3/2003 FR2	0.379	7.718	BDL	1.079	1.203	2.387	0.207	5.072	BDL	19.741	0.159
6/10/2003 FR1	0.213	10.014	BDL	0.846	1.293	3.023	0.242	6.375	BDL	27.285	0.219
6/10/2003 FR2	0.205	9.892	BDL	0.809	1.294	2.993	0.237	6.445	BDL	27.061	0.208
7/1/2003	0.140	13.511	0.029	1.715	1.547	4.122	0.502	7.151	BDL	41.229	0.301
7/15/2003	0.066	22.511	0.025	1.387	2.486	6.849	1.087	16.398	0.010	76.268	0.485
7/29/2003 FR1	0.953	16.059	0.036	3.337	2.273	5.276	0.605	9.220	0.005	47.149	0.314
7/29/2003 FR2	0.984	16.131	0.033	3.424	2.279	5.227	0.609	10.411	0.005	47.950	0.314
8/12/2003	0.125	30.748	0.029	1.683	3.496	9.314	1.193	24.625	0.012	110.389	0.555
8/26/2003	0.438	35.601	0.056	3.516	3.961	10.902	1.421	27.433	0.013	131.065	0.804
9/9/2003 FR1	3.110	29.599	0.145	7.873	3.615	9.626	1.622	19.498	0.017	103.664	1.152
9/9/2003 FR2	3.090	30.154	0.147	7.947	3.719	9.889	1.649	19.725	0.018	105.646	1.167

Sample Date	T-Al	T-Ca	T-Cu	T-Fe	T-K	T-Mg	T-Mn	T-Na	T-Ni	T-SO$_4$	T-Zn
9/26/2003	0.310	38.538	0.038	2.304	4.778	11.761	1.381	32.211	BDL	135.190	0.634
10/10/2003	0.071	40.836	0.018	0.901	4.293	12.069	1.467	32.797	BDL	144.540	0.525
10/25/2003	0.189	25.150	0.034	3.014	3.170	7.635	0.910	17.036	BDL	73.020	0.500
11/8/2003 FR1	0.040	37.834	0.017	1.064	3.525	11.724	1.164	32.089	0.009	142.278	0.566
11/8/2003 FR2	0.049	38.600	0.017	1.119	3.962	11.987	1.198	32.848	0.010	145.462	0.583
11/22/2003	0.054	39.310	0.019	1.125	3.498	12.089	0.997	30.934	0.010	145.213	0.649
12/6/2003	0.050	45.721	0.023	1.409	5.217	14.078	1.197	38.998	0.012	174.456	0.716
12/20/2003 FR1	0.081	49.596	0.036	2.414	5.273	15.288	1.452	40.669	0.018	187.921	0.854
12/20/2003 FR2	0.078	49.740	0.036	2.440	5.261	15.091	1.452	40.883	0.017	186.192	0.850
1/5/2004	0.054	51.441	0.031	1.827	5.500	15.647	1.186	42.667	0.015	193.827	0.912
1/17/2004	0.132	49.308	0.051	3.511	5.513	15.181	1.329	42.298	0.016	188.285	0.847
1/31/2004 FR1	0.144	50.285	0.055	3.951	5.135	15.378	1.498	42.447	0.018	191.344	0.895
1/31/2004 FR2	0.159	50.451	0.057	4.120	5.161	15.351	1.509	42.376	0.018	193.648	0.910
2/14/2004	0.062	51.503	0.047	3.265	5.920	16.125	1.812	54.373	0.026	198.477	0.833
2/27/2004	0.078	51.509	0.036	1.803	5.816	15.933	1.425	50.934	0.024	185.796	0.736
3/13/2004 FR1	0.258	42.875	0.060	3.799	4.840	13.289	1.181	39.628	0.026	154.948	0.744
3/13/2004 FR2	0.335	42.843	0.070	4.412	4.852	13.306	1.238	39.587	0.015	155.630	0.779
3/24/2004 FR1	0.248	32.225	0.053	3.207	3.521	9.969	0.833	24.390	0.010	113.058	0.509
3/24/2004 FR2	0.236	32.374	0.056	3.224	3.502	9.994	0.854	24.289	0.009	112.889	0.508
4/13/2004	0.232	31.356	0.043	1.893	3.238	9.866	1.040	26.368	0.010	92.585	0.625
4/24/2004	0.396	25.340	0.054	2.949	2.849	8.000	0.908	21.845	0.017	80.661	0.558
5/8/2004 FR1	0.406	13.766	0.046	3.065	1.743	4.274	0.557	8.643	0.007	39.830	0.334
5/8/2004 FR2	0.417	13.672	0.048	3.105	1.692	4.218	0.567	8.369	0.005	39.348	0.335
5/22/2004	0.146	12.555	0.026	1.449	1.725	3.834	0.404	8.793	0.005	37.478	0.248
6/3/2004	0.107	13.669	0.024	1.458	1.727	4.146	0.462	8.942	0.006	43.251	0.237
6/19/2004 FR1	0.197	12.778	0.025	1.798	1.613	3.958	0.430	8.582	0.006	38.840	0.265
6/19/2004 FR2	0.175	12.836	0.027	1.807	1.641	3.973	0.433	8.646	0.005	39.297	0.270
7/3/2004	0.203	17.070	0.032	1.810	2.186	5.305	0.600	13.449	0.007	49.484	0.296
7/15/2004	0.196	19.694	0.036	1.922	2.721	6.146	0.835	15.355	0.007	63.507	0.325

Sample Date	D-Al	D-Ca	D-Cu	D-Fe	D-K	D-Mg	D-Mn	D-Na	D-Ni	D-SO$_4$	D-Zn
5/21/2002	BDL	34.331	0.017	0.129	4.317	11.040	0.896	25.464	0.010	114.279	0.198
6/4/2002	BDL	23.158	0.016	0.377	2.447	7.592	0.804	12.045	0.009	63.035	0.432
6/11/2002	0.014	24.495	0.005	0.112	2.202	7.624	0.985	14.585	0.008	78.170	0.365
6/25/2002	BDL	35.573	0.005	0.036	3.376	10.879	1.778	23.085	0.016	122.395	0.565
7/9/2002	0.021	28.616	0.005	0.136	3.086	8.636	1.078	15.690	0.009	77.196	0.180
8/5/02 14:32	0.056	47.222	0.004	0.031	4.672	15.174	1.535	32.815	0.010	156.943	0.405
8/5/02 16:03	0.161	46.161	0.004	0.063	4.363	14.672	1.514	29.863	0.013	160.338	0.397
8/5/02 16:15	0.041	45.241	0.011	0.043	4.359	14.302	1.493	29.488	0.013	154.730	0.438
8/5/02 16:35	0.044	48.194	0.006	0.084	4.555	15.390	1.614	31.286	0.015	167.473	0.459
8/5/02 17:00	0.031	47.202	0.005	0.008	4.363	14.808	1.574	30.204	0.012	163.806	0.446
8/6/2002	0.022	44.204	0.004	0.019	4.361	14.412	1.837	33.927	0.015	154.829	0.784
9/16/2002	0.023	60.246	0.010	0.040	7.686	18.546	1.970	58.969	0.018	232.866	0.451
10/15/2002	BDL	60.288	0.008	0.057	6.573	18.581	2.406	39.482	0.024	229.409	0.561
10/29/2002	BDL	54.023	BDL	0.016	5.813	16.691	2.513	34.480	0.024	202.037	0.864
11/11/2002	BDL	62.888	0.006	0.034	7.249	20.054	2.763	42.130	0.028	237.330	1.542
12/10/2002	BDL	72.852	0.005	0.014	6.251	22.405	3.093	38.475	0.031	272.104	1.435
1/14/2003 FR1	0.014	67.813	0.016	0.135	6.731	21.104	2.872	56.718	0.027	239.809	0.891
1/14/2003 FR2	0.013	67.876	0.018	0.160	6.774	20.843	2.864	57.560	0.026	240.348	0.898
2/11/2003	BDL	69.674	0.014	0.045	7.057	21.792	2.822	58.363	0.022	272.577	1.111
3/11/2003	BDL	58.874	0.015	0.055	6.059	18.750	2.211	62.062	0.017	222.372	0.805
3/24/2003 FR1	BDL	55.070	BDL	BDL	5.504	16.944	1.207	75.181	BDL	169.436	0.866
3/24/2003 FR2	0.011	52.580	BDL	BDL	6.138	16.185	1.157	73.268	BDL	162.828	0.843
4/8/2003	0.017	58.347	BDL	BDL	5.370	18.569	1.583	54.092	BDL	169.419	1.138
4/22/2003	0.037	32.492	0.024	0.014	3.065	10.667	1.474	20.056	0.005	97.468	1.167
5/6/2003	0.033	25.150	BDL	BDL	2.283	8.157	0.997	15.171	BDL	73.614	0.918
5/20/2003	0.060	11.999	BDL	0.203	1.782	3.645	0.302	7.691	BDL	32.045	0.248
5/27/2003	0.052	8.010	BDL	0.170	1.489	2.410	0.157	6.002	BDL	21.157	0.136
6/3/2003 FR1	0.078	7.416	BDL	0.248	1.132	2.217	0.137	4.939	BDL	19.347	0.119
6/3/2003 FR2	0.065	7.878	BDL	0.242	1.164	2.332	0.147	5.200	BDL	20.235	0.127
6/10/2003 FR1	0.096	9.814	BDL	0.523	1.280	2.947	0.219	6.844	BDL	26.754	0.189
6/10/2003 FR2	0.103	9.874	BDL	0.531	1.732	2.965	0.222	6.735	BDL	27.215	0.189
7/1/2003	0.031	13.358	0.010	0.284	1.537	4.103	0.483	7.110	BDL	41.211	0.233
7/15/2003	BDL	22.518	0.009	0.035	2.523	6.871	1.053	16.630	0.008	76.459	0.380
7/29/2003 FR1	0.032	15.553	0.015	0.743	2.019	4.816	0.508	9.254	0.003	46.632	0.199
7/29/2003 FR2	0.065	16.175	0.019	1.160	1.933	4.896	0.527	10.280	0.004	48.562	0.232
8/12/2003	BDL	30.597	0.009	0.030	3.462	9.267	1.157	24.641	0.011	109.196	0.432
8/26/2003	BDL	35.420	0.006	0.013	3.819	10.711	1.365	27.524	0.012	132.332	0.543
9/9/2003 FR1	0.019	30.039	0.006	0.007	2.750	9.309	1.517	19.887	0.013	106.180	0.615
9/9/2003 FR2	0.020	30.046	0.008	0.011	2.864	9.295	1.518	19.957	0.012	105.746	0.615

Sample Date	D-Al	D-Ca	D-Cu	D-Fe	D-K	D-Mg	D-Mn	D-Na	D-Ni	D-SO$_4$	D-Zn
9/26/2003	BDL	38.940	0.008	0.054	4.814	11.791	1.355	32.765	BDL	138.356	0.498
10/10/2003	BDL	41.346	0.005	0.013	4.458	12.335	1.475	33.369	BDL	146.788	0.461
10/25/2003	BDL	25.792	0.008	0.051	3.293	7.832	0.882	17.702	BDL	75.599	0.327
11/8/2003 FR1	BDL	40.374	0.006	0.006	4.432	12.424	1.226	34.476	0.010	152.812	0.527
11/8/2003 FR2	BDL	38.471	0.006	0.017	3.916	11.998	1.171	32.809	0.009	145.028	0.506
11/22/2003	BDL	40.261	0.006	0.012	4.476	12.356	1.000	32.027	0.009	150.176	0.607
12/6/2003	BDL	44.369	0.006	0.005	4.264	13.782	1.141	37.721	0.009	169.488	0.606
12/20/2003 FR1	BDL	48.865	0.009	0.030	5.181	14.982	1.411	40.100	0.016	187.930	0.730
12/20/2003 FR2	BDL	50.420	0.010	0.034	5.275	15.306	1.427	41.466	0.017	190.294	0.729
1/5/2004	BDL	50.762	0.010	0.060	5.384	15.566	1.149	41.906	0.016	191.785	0.822
1/17/2004	BDL	48.046	0.014	0.038	5.379	14.776	1.269	41.316	0.013	181.776	0.673
1/31/2004 FR1	BDL	49.801	0.010	0.029	5.076	15.301	1.459	42.042	0.017	190.735	0.741
1/31/2004 FR2	BDL	51.329	0.011	0.030	5.232	15.811	1.504	43.369	0.017	197.133	0.764
2/14/2004	BDL	51.948	0.011	0.049	5.969	16.289	1.804	54.954	0.025	199.847	0.689
2/27/2004	BDL	50.403	0.012	0.068	5.682	15.605	1.387	49.526	0.021	186.074	0.645
3/13/2004 FR1	BDL	42.703	0.039	0.057	4.760	13.225	1.107	39.407	0.034	156.214	0.550
3/13/2004 FR2	BDL	42.229	0.021	0.046	4.697	13.058	1.087	39.707	0.021	153.545	0.525
3/24/2004 FR1	BDL	32.061	0.011	0.065	3.513	10.045	0.743	25.010	0.009	113.362	0.315
3/24/2004 FR2	BDL	32.095	0.008	0.067	3.562	9.886	0.750	24.515	0.009	112.589	0.308
4/13/2004	BDL	31.196	0.007	0.064	3.237	9.855	1.013	26.225	0.011	92.128	0.528
4/24/2004	BDL	25.151	0.009	0.085	2.786	7.825	0.845	21.918	0.015	79.317	0.414
5/8/2004 FR1	0.063	13.613	0.015	0.556	1.620	4.130	0.391	8.563	0.004	39.393	0.197
5/8/2004 FR2	0.069	13.585	0.017	0.668	1.755	4.148	0.390	8.756	0.004	39.357	0.208
5/22/2004	0.074	12.420	0.020	1.002	1.718	3.750	0.366	8.665	0.006	37.637	0.221
6/3/2004	BDL	13.752	0.008	0.329	1.789	4.179	0.438	9.037	0.006	44.438	0.187
6/19/2004 FR1	0.044	12.815	0.020	1.310	1.629	3.956	0.405	8.655	0.005	39.491	0.243
6/19/2004 FR2	0.052	12.784	0.021	1.307	1.674	3.943	0.405	8.629	0.004	39.200	0.246
7/3/2004	0.038	17.065	0.015	0.385	2.192	5.258	0.566	13.360	0.007	49.153	0.217
7/15/2004	BDL	19.784	0.012	0.137	2.711	6.148	0.775	15.632	0.006	62.975	0.187

Sample Date	pH	Alk (mg/l CaCO$_3$)	Temp (°C)	Sample Date	pH	Alk (mg/l CaCO$_3$)	Temp (°C)
5/21/2002	7.07	17.3	15.9	9/26/2003	7.94	33.2	8
6/4/2002	6.92	15.5	7.8	10/10/2003	7.8	35	8.3
6/11/2002	6.89	10.5	13.0	10/25/2003	7.65	33.3	3.1
6/25/2002	6.97	9.8	17.2	11/8/2003 FR1	8.03	26.7	2.8
7/9/2002	7.64	27.2	14.3	11/8/2003 FR2	8.03	27.4	2.8
8/5/02 14:32	7.29	19.4	16 (est.)	11/22/2003	8.03	28.3	0.0
8/5/02 16:03	7.31	17.6	16 (est.)	12/6/2003	7.93	31.6	0.7
8/5/02 16:15	7.3	16.8	16 (est.)	12/20/2003 FR1	8.22	27.5	0.5
8/5/02 16:35	7.3	17.2	16 (est.)	12/20/2003 FR2	8.22	27.8	0.5
8/5/02 17:00	7.32	16.1	16 (est.)	1/5/2004	7.81	26.5	-0.2
8/6/2002	6.96	17.2	15.9	1/17/2004	7.99	29.9	0.1
9/16/2002	7.63	29.2	13.6	1/31/2004 FR1	7.74	28.2	0.6
10/15/2002	7.07	19.7	7.8	1/31/2004 FR2	7.74	27.7	0.6
10/29/2002	7.19	18.1	1.3	2/14/2004	7.82	32.5	0.2
11/11/2002	7.66	18.7	0.4	2/27/2004	7.82	31.9	1.4
12/10/2002	7.82	14.8	1.4	3/13/2004 FR1	7.68	29.5	9.9
1/14/2003 FR1	7.74	24.9	0.0	3/13/2004 FR2	7.68	29.9	10.2
1/14/2003 FR2	7.74	23.2	0.0	3/24/2004 FR1	7.55	20	10.3
2/11/2003	7.83	22.6	0.0	3/24/2004 FR2	7.55	19.1	10.3
3/11/2003	7.84	23	2.5	4/13/2004	7.81	22.2	3.8
3/24/2003 FR1	7.81	29.6	1.7	4/24/2004	7.6	22.5	3.6
3/24/2003 FR2	7.81	28.8	1.7	5/8/2004 FR1	7.46	16.8	7.3
4/8/2003	7.93	28.4	2.0	5/8/2004 FR2	7.46	16.6	7.3
4/22/2003	7.73	20.6	3.8	5/22/2004	7.17	14.9	8
5/6/2003	7.6	15.4	3.8	6/3/2004	7.2	13.4	14.1
5/20/2003	7.58	17.6	3.4	6/19/2004 FR1	7.6	14.3	7.6
5/27/2003	7.35	8.1	6.9	6/19/2004 FR2	7.6	14.1	7.6
6/3/2003 FR1	7.24	7.6	6.5	7/3/2004	7.47	18.1	9.6
6/3/2003 FR2	7.24	10.5	6.5	7/15/2004	7.38	19.2	13
6/10/2003 FR1	6.8	11.3	7.8				
6/10/2003 FR2	6.8	13.9	7.8				
7/1/2003	6.5	7	10.3				
7/15/2003	7.29	15.5	14.9				
7/29/2003 FR1	7.1	15	15 (est.)				
7/29/2003 FR2	7.1	14.4	15 (est.)				
8/12/2003	7.38	21	13.4				
8/26/2003	7.41	20.1	13.5				
9/9/2003 FR1	7.88	16.2	11.4				
9/9/2003 FR2	7.88	16	11.4				

Notes: Elemental concentrations are in mg/l; T indicates total; D indicates dissolved; BDL means below the instrument detection limit; est. means the value was not measured, but was estimated; FR indicates the sampe is a field replicate.