Partitioning of Zinc between Dissolved and Colloidal Phases in the Animas River near Silverton, Colorado

By Laurence E. Schemel, Marisa H. Cox, Briant A. Kimball, and Kenneth E. Bencala

ABSTRACT

Partitioning of zinc (Zn) between dissolved and colloidal phases was studied in the upper Animas River. Most of the Zn was dissolved in the water column, but a variable fraction of the total Zn was associated with aluminum (Al)- and iron (Fe)-rich colloidal particles. Colloids were supplied to the river by tributary creeks that drain areas with natural sulfide mineral deposits and debris from abandoned mines. The fraction of the total Zn that was in the colloidal phase increased with pH in the river, indicating the possibility of adsorption by colloidal Al and Fe. The influence of pH was confirmed in laboratory experiments in which larger fractions of the total Zn were associated with the colloids when pH was increased in samples from the river. The effect of increasing pH was greatest in the sample with the highest concentration of colloidal Al and Fe. The total concentration of colloidal Al and Fe appeared to be a factor limiting the adsorption of Zn during the late summers when the samples were collected. Our results indicate adsorption of Zn would be greater downstream where the pH increases in the river and perhaps during spring when concentrations of colloidal Al and Fe are higher.

INTRODUCTION

Colloidal particles in the water column of the Animas River near Silverton, Colorado, are primarily composed of aluminum (Al) and iron (Fe) precipitates, but also contain zinc (Zn) and other metals (Church and others, 1997). The association of a small, variable fraction of the total Zn with the Al- and Fe-rich colloids possibly indicates adsorption or coprecipitation in the water column (Jenne, 1998). The purpose of this study is to examine factors that influence the partitioning of Zn between dissolved and colloidal phases in the Animas River. Zn is of particular interest in this river system because of its many natural and mining-related sources and its impact on aquatic life (Wright, 1997; Nimmo and others, 1998).

METHODS

Concentrations of total and dissolved Al, Fe, and Zn and pH were measured in Cement Creek (CC) and Mineral Creek (MC) and at sites in the Animas River (fig. 1). Filtrates for dissolved metal analysis were collected from a tangential-flow filtration apparatus using 10k Dalton filters (approx. 0.001 micron pore size). All samples were acidified with nitric acid (1 percent final concentration) and digested at room temperature in polyethylene bottles for two months before analysis. Al, Fe, and Zn were measured by an inductively coupled argon plasma atomic emission spectrometer. Mean particle sizes at all sites were within the colloidal range. Colloid concentrations reported here are the differences between total (unfiltered) and dissolved concentrations.

RESULTS

Zinc was dissolved in the acidic (pH 3.8) waters of Cement Creek, but a fraction of the total Zn was colloidal in the near-neutral-pH waters of the Animas River and Mineral Creek (Table 1.). Little colloidal Al or Fe was present in the

Animas River at AR1, but concentrations increased downstream from the Cement Creek

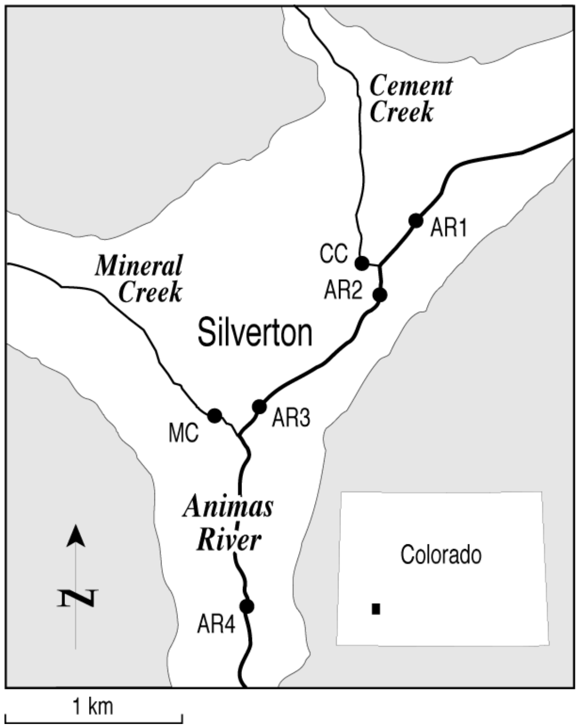

Figure 1. The upper Animas River near Silverton, Colorado.

Table 1. Average concentrations (micromoles per liter) of dissolved (Dis.) Zn and colloidal (Coll.) Zn, Al, and Fe in Cement Creek (CC), Mineral Creek (MC), and the Animas River (AR1-AR4) during September 1996.

Site	Dis. Zn	Coll. Zn	Coll. A1	Coll. Fe
AR1	5.6	0.7	1	2
CC	12	0	5	64
AR3	6.5	1.5	43	28
MC	3.4	0.3	71	21
AR4	5.2	0.7	49	24

confluence. Sources of colloidal Al and Fe were 1) reactions when inflow from Cement Creek mixed with the Animas River, 2) inflow from Mineral Creek, and 3) oxidation in the water column of the Animas River (see Schemel and others, this volume). Aluminum dissolved in Cement Creek formed colloidal Al upon mixing with the Animas River near AR2. Nearly all of the Al in the river downstream of AR2 and in Mineral Creek was in the colloidal phase. Both creeks supplied dissolved and colloidal Fe to the river, and colloidal Fe continued to form in the river as dissolved Fe was oxidized.

The total concentration of Zn was greater than the concentrations of colloidal Al and Fe at AR1. Up to 11 percent of the Zn was colloidal at this site where the concentrations of colloidal Al and Fe were low and pH was high relative to other sites in the river (fig. 2). In the Animas river between AR2 and AR3 downstream of inflow from Cement Creek, the mole ratio of colloidal Al plus Fe to total Zn averaged 9. Up to 22 percent of the total Zn was in the colloidal phase, and an increase in the percent of Zn in the colloidal phase was observed as pH increased. In the mixing zone near AR2, reactions that formed most of the colloidal Al and Fe were largely completed by pH 6.5, although some colloidal Fe continued to form downstream as Fe(II) was oxidized to Fe(III) (see Schemel and others, this volume). The fraction of Zn associated with the colloids between AR2 and AR3 increased most rapidly above pH 6.8, indicating that Zn had adsorbed onto previously formed colloidal Al and Fe. However, coprecipitation or adsorption onto colloidal Fe that was forming in the river might also account for some of the Zn associated with the colloidal phase.

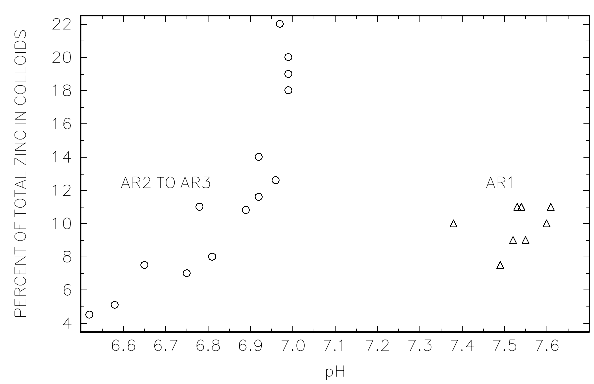

Figure 2. Percentage of total Zn in the colloidal phase versus pH in the water column of the Animas River. Data are from September 1996 and 1997.

The potential for rapid adsorption of Zn by colloidal Al and Fe was tested in the laboratory by increasing the pH of samples collected at MC and AR4 with sodium hydroxide. Samples were removed from the batch reactor when pH became stable, and they were processed within a few minutes. Most of the Al and Fe in these samples was colloidal. As expected, the fraction of Zn associated with the colloids increased with increasing pH in both cases, but a greater fraction of the Zn was associated with the colloids in the sample from MC (fig. 3). The mole ratio of colloidal Al plus Fe to total Zn in the sample from AR4 was 13, whereas that for MC was 32. Therefore, with increasing pH a larger fraction of the total Zn was colloidal in the sample with higher concentrations of Al and Fe colloids and presumably a greater abundance or density of adsorption sites.

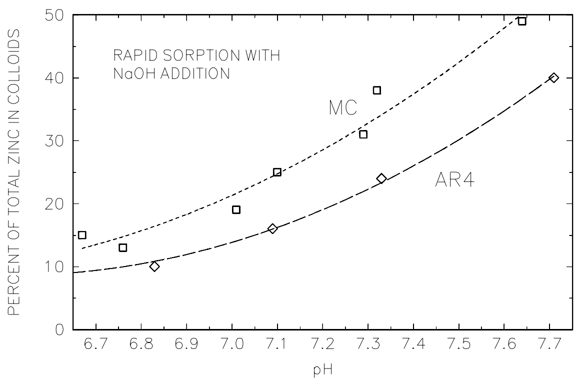

Figure 3. Results of laboratory experiments with samples from Mineral Creek (MC) and the Animas River (AR4) showing the increase in the percentage of total Zn in the colloidal phase with pH increased by the addition of NaOH. Lines are second-order fits to the data.

DISCUSSION

Partitioning of Zn between dissolved and colloidal phases in the water column of the Animas River downstream of AR2 was most likely dependent on two major factors, pH and the abundance of colloidal Al and Fe relative to the concentration of Zn. Most studies that show significant adsorption of Zn over a narrow range of about one pH unit near pH 7 have a large excess of adsorbent, usually Fe or Al hydroxides, relative to the total concentration of Zn (for examples see Duker and others, 1995, and Webster and others, 1998). At the low mole ratios observed in the water column of the Animas River between AR2 and AR4 available sites for adsorption might be limited, and only a small fraction of the total Zn could be adsorbed over the pH range observed in this reach of the river (pH< 7.1).

Results of our laboratory experiment with the sample from AR4 indicated that greater adsorption of Zn might occur downstream of AR4, where pH increases of nearly one-half unit have been measured. Field observations, although limited in number, indicate that one-third or more of the Zn can be associated with the colloidal phase when the pH is higher at AR4 and at locations downstream (Church and others, 1997, and our unpublished data).

Greater adsorption observed in the sample from MC relative to the sample from AR4 indicated that a greater fraction of the total Zn might be colloidal when concentrations of colloidal Al and Fe are higher in the river during spring runoff. This was supported by measurements during the mid- and late-spring runoff period of 1996, when colloidal Zn was a large fraction of the total Zn transport (Church and others, 1997). The very low concentrations of colloidal Al and Fe at AR1 indicated that relatively little Zn could be adsorbed even at the high pH. Consequently, some of the Zn associated with the colloidal fraction at AR1 might not be adsorbed.

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