Colloid formation and the transport of Aluminum and Iron in the Animas River near Silverton, Colorado

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ABSTRACT

Flows and concentrations of dissolved and colloidal aluminum (Al) and iron (Fe) were measured in the upper Animas River to identify sources of colloids and quantify their transport. Colloidal Al and Fe are important in this reach of the river near Silverton, Colorado, because of effects on river bed habitat, macroinvertebrates, and fish. The largest sources of Al and Fe to the river were Cement Creek (42 percent of the total load) and Mineral Creek (56 percent of the total load). Acidic inflow from Cement Creek (pH 3.8) supplied dissolved Al that formed colloids as it was neutralized upon mixing in the Animas River. The Al supplied by Mineral Creek was colloidal, and nearly all of the Al in the Animas River was colloidal. Both creeks supplied Fe in dissolved and colloidal form. Some colloidal Fe formed in the mixing zone downstream of Cement Creek, and colloidal Fe continued to form downstream in the river as dissolved Fe was oxidized. Although colloidal Al and Fe accumulated on the river bed, transports measured in this 2.5 km reach of the river showed that losses of Al and Fe from the water column as a result of colloid formation were less than 10 percent of the total transport.

INTRODUCTION

Tributaries of the upper Animas River in the San Juan Mountains of Colorado drain a caldera that is rich in sulfide mineral deposits and contains numerous structures and debris from mining activities over the last century (Wright, 1997). Cement and Mineral creeks join the Animas River near Silverton, contributing substantial loads of dissolved and colloidal metals (Church and others, 1997). Colloidal aluminum (Al) and iron (Fe) are of particular concern because they cement the river bed and affect plant and animal life in the river downstream of the confluences (Owen, 1997). The purpose of this study was to quantify the transport of Al and Fe in this reach of the river and identify the sources colloidal Al and Fe.

METHODS

Streamflows (discharges), pH and concentrations of total and dissolved Al and Fe were measured during September 1996 in Cement and Mineral creeks and at four sites in the Animas River (fig. 1). Streamflows were measured at the

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

sites or estimated from gages on the two creeks and at AR1 and AR4. Samples were collected using the equal-discharge-interval method. Filtrates for dissolved metal analysis were collected from a tangential-flow filtration apparatus using 10k Dalton filters (approx. 0.001 micron pore size). Filtered and unfiltered samples for metal analysis were adicified with nitric acid (1 percent final concentration) and digested in polyethylene bottles for two months before analysis. Al and Fe concentrations were measured using an inductively coupled argon plasma atomic emission spectrometer. Mean particle sizes at all sites were within the colloidal range. Concentrations of colloidal Al and Fe reported here are the differences between total (unfiltered) and dissolved concentrations.

RESULTS

Concentrations in Cement Creek (CC) of dissolved Al and Fe and colloidal Fe were the highest observed in this study, and the pH in Cement Creek was the lowest (Table 1.). Upstream in the Animas River at AR1, Al and Fe concentrations were low, and pH was the highest observed in this study. Discharge from Cement Creek into the Animas River created large gradients in chemical concentrations across the channel in the mixing zone (AR2) because of the large differences in pH (>3 units) and in concentrations of Al and Fe between the two streams. The formation of colloidal particles was visibly apparent in the water column, and precipitates also coated bank and bed materials downstream. The Animas River was well mixed farther downstream at AR3, where colloids accounted for nearly all of the Al and more than half of the total Fe in the water column (Table 1.).

Table 1. Concentrations of dissolved (Dis.) and colloidal (Coll.) Al and Fe in micromoles per liter and pH at sites in Cement Creek (CC), Mineral Creek (MC) and the Animas River (AR1-AR4).

Site	pH	Dis. Al	Coll. A1	Dis. Fe	Coll. Fe
AR1	7.54	1	1	0	2
CC	3.84	192	5	71	64
AR3	6.79	1	40	12	17
MC	6.60	1	71	19	30
AR4	6.72	1	49	10	23

Details of reactions that occurred in the Animas River downstream of Cement Creek were examined in a laboratory experiment, in which unflitered samples from the Animas River (at AR1) and Cement Creek were mixed in varying proportions. The mixtures were processed within a few minutes of their preparation. The mixing plot showed that Al, which was dissolved in the low pH water of Cement Creek, formed colloidal particles as pH increased from about 4.5 to 6.5 (fig. 2). This is illustrated by the large departure in dissolved Al from the conservative mixing line and the value for colloidal Al intersecting the line near pH 6.5. Cement Creek supplied both dissolved and colloidal Fe to the Animas River, but the mixing plot indicated that additional colloidal Fe formed as pH was increased to about pH 5.3 (fig. 3). Major differences between Al and

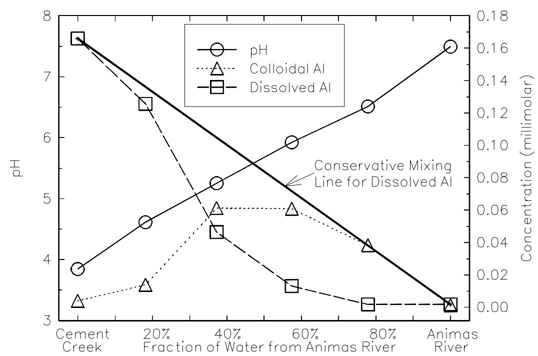

Figure 2. Diagram showing pH and concentrations of dissolved and colloidal Al during mixing of Cement Creek and Animas River (AR1) waters.

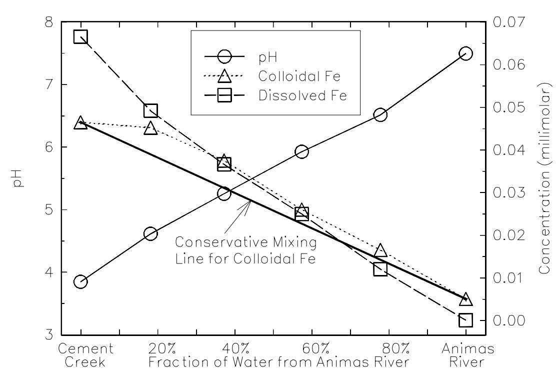

Figure 3. Diagram showing pH and concentrations of dissolved and colloidal Fe during mixing of Cement Creek and Animas River (AR1) waters.

Fe were that colloidal Al had formed at a higher pH, and only about 17 percent of the dissolved Fe had precipitated during mixing.

Nearly all of the Al and about 61 percent of the Fe supplied to the Animas River from Mineral Creek was colloidal (Table 1.). The pH of Mineral Creek was similar to the pH upstream in the Animas River (AR3), and mixing resulted in a small change in pH and no change in the partitioning of Al between colloidal and dissolved forms downstream at AR4. However, a larger fraction of the total Fe was colloidal at AR4 compared to MC and AR3, indicating the formation of additional colloidal Fe downstream of the confluence.

Table 2. Flow in cubic feet per second and transport of total Al and Fe in kilograms per day at sites in Cement Creek (CC), Mineral Creek (MC), and the Animas River (AR1-AR4). Total inputs to the confluences (Sum) are compared to measurements downstream.

Site	Flow	Al transport	Fe transport
AR1	63	10	19
CC	17	221	313
Sum	80	231	332
AR2	80	239	345
AR3	82	224	328
MC	61	291	408
Sum	143	515	736
AR4	147	483	686

Cement and Mineral Creeks were the dominant sources of Al and Fe to the Animas River (Table 2.). Mineral Creek was the larger source, accounting for about 56 percent of the transport of total Al and total Fe in the water column of the Animas River at AR4, compared to about 42 percent for Cement Creek. Transports of total Al and total Fe showed small losses (<10 percent) over the approximately 2.5 km reach of the Animas River. Even though coatings and accumulations of Al- and Fe-rich precipitates were visible in the Animas River between AR2 and AR4, our results show that losses were a small fraction of the total transport under low flow conditions.

DISCUSSION

The formation of colloidal Al and Fe hydroxides or hydrous oxides as acid mine waters are neutralized has been shown in numerous field and laboratory studies (see Nordstom and Ball, 1986; Stumm and Morgan, 1996, and references therein). Nearly half of the colloidal Al in this study reach of the Animas River was formed in the mixing zone near AR2. The formation of colloids in the river might be detrimental to fish and other organisms. Colloidal Al that is freshly formed in the water column can be particularly toxic to fish (Witters and others, 1996). In addition, the Al and Fe colloids contain zinc and copper, which could contribute to the toxic effects observed near AR4 (Nimmo and others, 1998). Aggregates of these colloids accumulate on the stream bed and enter the food chain through benthic invertebrates that are consumed by fish (Woodward and others, 1995).

Transformations of Al and Fe between dissolved and colloidal forms were not apparent within the mixing zone of Mineral Creek with the Animas River, which might be expected by the similar pH values in these two streams. Nearly all of the Al already was in colloidal form in both streams before they mixed, but both the transport and the concentration of colloidal Al were increased in the Animas River downstream of the confluence. Iron was present in dissolved and colloidal forms in both Mineral Creek and at AR3. The formation of additional colloidal Fe downstream from the confluence appeared to result from oxidation of dissolved Fe(II) to Fe(III), which probably was occurring in both streams before they mixed.

Our results showed that more than 90 percent of the input of total Al and Fe was transported past AR4. All of the Al and 70 percent of the Fe was colloidal at AR4, and the dissolved iron would eventually form additional colloidal Fe downstream. Other studies have shown that the colloids supplied by or formed from the Al and Fe discharged by Cement and Mineral creeks affect the riverbed for at least 60 km downstream of AR4 (Owen, 1997).

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