Occurrence, transport, and fate of trace elements, Blue River Basin, Summit County, Colorado: An integrated approach

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Abstract Mining activities in the Blue River Basin, Summit County, Colorado, have affected the traceelement chemistry and biota along French Gulch and the Blue River. Elevated concentrations of As, Cd, Cu, Pb, and Zn were present in the bed and suspended sediments. Bed sediment trace-element concentrations were high in the streams in and near mining activities in the basin and remained high as water flowed into Dillon Reservoir about 3.5 km downstream. Bed-sediment $(< 63 \mu m)$ data were useful in assessing the distribution of trace elements in the basin. Suspended-sediment measurements provided information as to the transport of the trace elements. Filtered $(< 0.45$ µm) watercolumn trace-element concentrations were orders of magnitude less than the sediment concentrations. Concentrations of Cd and Zn in the water column at some sites exceeded stream water-quality standards. Elevated trace-element concentrations in the sediment and water column are a source of contamination and must be considered in waterquality management of the Blue River Basin.

Key words Trace-element concentrations · Bed sediment · Suspended sediment · Surface water · Water quality

Introduction

Metal mining in the Upper Colorado River Basin has been an important part of the economy of Colorado since the late 1800s. As a result, many headwater streams in the basin have been affected by mine drainage, which can

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carry heavy metals and other toxic elements that affect stream-water quality. Identifying the effects of mine drainage is important for assessing the quality of water used for drinking, recreation and aquatic life. An investigation of the area surrounding the Breckenridge mining district in Summit County was undertaken to provide a detailed analysis of the stream water and sediments in an area affected by mine drainage. The Breckenridge mining district, encompassing an area of about 115 km^2 , is located near the headwaters of the Blue River, a tributary to the Colorado River (Fig. 1). The study area is mountainous, ranging in altitude from about 3000 to 4055 m, is bounded on the south and east by the Continental

Fig. 1

Location of the Blue River Basin and sampling sites upstream from Dillon Reservoir

Divide, and is located near the town of Breckenridge upstream from Dillon Reservoir, a drinking-water reservoir for the city of Denver. In the study area, tributaries of the Blue River that have been mined or are associated with mining activities include French Gulch, Illinois Gulch, and Swan River (Fig. 1).

In the Blue River Basin, continuous-record streamflowgaging stations used in this study are located at site 7, French Gulch at Breckenridge (installed in October 1995), and site 10, Blue River near Dillon (installed in October 1957; Fig. 1). The annual streamflow in the drainage is dominated by snowmelt in May±July, and peak discharge usually occurs in mid- to late June. For water year 1996 (1 October 1995–30 September 1996), daily mean discharge for French Gulch was $0.36 \text{ m}^3/\text{s}$. At the site where the Blue River discharges into Dillon Reservoir, daily mean discharge was 3.94 m³/s (US Geological Survey 1997). Streams affected by mine drainage, which is usually associated with abandoned mines, are present in much of the Rocky Mountains of Colorado (Moran and Wentz 1974). In studies in which the effects of mine drainage on water quality were examined, some work has been oriented toward identifying the source or sources of trace elements in a watershed (Church and others 1994). In other studies, the effects of mine drainage were investigated to identify the processes that relate to increased trace elements in the water column (Chapman and others 1983; Filipek and others 1987; Davis and others 1991). Bed sediment has been collected to determine the occurrence and distribution of trace elements in certain watersheds (Axtmann and Luoma 1991). Suspended-sediment data have been used to examine short-term and long-term spatial chemical and physical variations as well as transport and fluxes (Horowitz 1995b). Collection of chemical data for bed and suspended sediments and analysis of the filtered phase are important in developing a comprehensive understanding of the effects of trace elements on water quality (Horowitz 1991). Biological studies also are important in assessing the effects of trace elements on a watershed (Crawford and Luoma 1993; Cuffney and others 1993; Clements and Kiffney 1995). Thus, an integrated assessment of trace-element concentrations that affect the water quality in the Blue River Basin requires the collection and analysis of bed and suspended sediments, filtered and unfiltered water-column samples, and biota.

Concerns about the water quality in the Blue River were raised in the late 1980s by the Colorado Department of Public Health and Environment (CDPHE), who observed mortality of newly released fingerlings in the Blue River downstream from French Gulch. The CDPHE initiated surface-water sampling and water-toxicity testing and concluded that during snowmelt, acutely toxic conditions existed in French Gulch from the Wellington-Oro Mine site (Fig. 1) downstream to the Blue River (SAIC 1995). Based on the CDPHE's 1989 sampling results, the Wellington-Oro Mine site was identified as the primary source of metal loading and water-quality effects in the watershed. In the early 1990s, the French Gulch non-

point-source project, which involved characterization of the Wellington-Oro Mine site by the US Environmental Protection Agency and the Colorado Department of Minerals and Geology, was initiated. Surface- and ground-water monitoring was implemented to examine the effects from the mill tailings, roaster fines, waste rock, and other waste piles, which may be major contaminant sources in the watershed. Ground-water seepage from underground workings and also along structural features is another potential source of trace elements that could affect water quality in the watershed (Arthur Morrissey, Consulting Geologist, oral pers. comm. 1997). This study was designed to assess the source(s) and environmental effects of trace elements in the Blue River Basin by collecting and analyzing bed-sediment samples, filtered, unfiltered, and suspended-sediment water-column samples, biological tissue and by assessing fish and macroinvertebrate communities. Because of the strong association of numerous trace elements (e.g. As, Cd, Pb, and Zn) with bed and suspended sediments, an understanding of the distribution, transport, and availability of particular trace elements in a watershed is important (Horowitz 1991). Data that describe sediment concentrations may be useful in examining environmental effects on a regional scale because chemical analyses of the sediment can help identify point or non-point sources of contamination. The relations between bed- and suspended-sediment sampling methods are important because bed sediments that were sampled during low-flow conditions can be a major source for suspended sediment transported during high-flow conditions and/or may provide an integrated picture of the material transported earlier during high-flow conditions. The chemical and hydrologic conditions that exist during low- and highflow conditions are important in defining annual chemical end members (low and high) in a watershed (Horowitz 1995b), and biota are important in understanding the complexities of contaminant fate, distribution, and effects by providing additional lines of evidence for the effects of trace elements in a watershed (Crawford and Luoma 1993).

Specific objectives of this study are to: (1) determine the occurrence and spatial distribution of trace elements in and around the mining district; (2) relate trace-element concentrations to standards and guidelines; (3) assess the transport of trace elements in the Blue River Basin; (4) assess the fate and effect of trace elements on the biota in the watershed; and (5) compare and integrate various phases of trace elements in the basin. This information is important when evaluating the effects or potential effects of mined areas on a watershed.

Mining activities

Most of the mining activities in the Blue River Basin were along French Gulch (part of the Breckenridge mining district), located about 3 km east of Breckenridge

(Fig. 1). From the 1850s to the 1960s, extensive placer and underground lode mining was done in the French Gulch Basin; large amounts of Au, Pb, Ag, and Zn and minor amounts of Cu were produced from the lode deposits (SAIC 1995). Ore deposits in the French Gulch Basin consist of veins and stockworks of Au, Pb, Ag, and Zn, metamorphic replacement deposits, and Ag-Au deposits in the Dakota quartzite described by Lovering (1934). Primary ore mineralogy in the district consists of pyrite, sphalerite, chalcopyrite, galena, gold, and gangue minerals of quartz and ankerite. The predominant alteration type in the district consists of sericitization (phyllic), with accompanying ankerite formation. Silicification also is extensive in the district, but the most widespread alteration is propylitic. Several abandoned mine sites are located along French Gulch. Near the Wellington-Oro Mine site, the largest of the abandoned mine sites (Fig. 1), an estimated 42000 m^3 of mill tailings and 33000 m^3 of roaster fines remain onsite (US Bureau of Reclamation, written comm. 1997). The entire volume of waste at the Wellington-Oro Mine site is approximately 200000±250000 tons (SAIC 1995). Gold dredging in the area has worked many of the deep gravels in the stream channel, and placer tailings occur as 12- to 15-m-high piles, which have altered the natural streamflow and ground-water flow directions.

Sampling and analytical techniques

Bed-sediment, filtered water-column, and suspended-sediment samples for trace-element analyses were collected from six sites in the Blue River Basin during low-flow conditions in October 1995 (Fig. 1). Bed-sediment, filtered and unfiltered (total-recoverable) water-column, and suspended-sediment samples for trace-element analyses were collected from ten sites during high-flow conditions in May 1996 (Fig. 1). Discharge and basic field parameters, which include specific conductance, pH, temperature, dissolved oxygen, and alkalinity, were measured at each site. Bed-sediment samples were collected at the four additional sites in the French Gulch Basin in October 1996. At site 7, the gaging station at the mouth of French Gulch, 15 water-column samples were collected annually and analyzed for trace elements and other constituents beginning in water year 1996. In addition, suspended-sediment samples were collected monthly and sometimes weekly for water years 1996 and 1997 at the French Gulch and Blue River gaging stations to determine suspended-sediment loading. At sites 7 and 8, biological studies, which include biological tissue analysis and fish and macroinvertebrate community analyses, were conducted in August 1996.

Fine-grained bed sediments were collected during lowflow conditions in October 1995 and 1996 from natural deposition zones in the stream channels of French Gulch and the Blue River. The upper $1-2$ cm of sediment were

collected from five or more deposition zones in a stream segment and composited. Bed-sediment composites then were field processed by wet sieving, using native water, through a 0.63-µm nylon mesh (Shelton and Capel 1994). Chemical analyses of bed-sediment material were completed for the $\lt 63$ -µm fraction size, which represents silt/clay-sized particles. Analysis of the fine-grained sediment fraction decreases the biases resulting from the differences in particle-size distribution among samples (Axtmann and Luoma 1991). The bed-sediment samples were analyzed for Al, As, Cd, Cu, Fe, Pb, Mn, and Zn following the techniques described by Horowitz and others (1989).

Water-column samples at each site were collected using depth- and width-integrated sampling techniques along the cross section (Shelton 1994). The filtered fraction of the aqueous phase was obtained by filtering the water sample through a 0.45 -µm filter and preserving the filtrate with ultrapure nitric acid to a $pH < 2$. The methods used for analysis of the filtered major ions and trace elements are described in Fishman (1993) and Garbarino and Taylor (1996), respectively. Analyses were completed at the US Geological Survey National Water Quality Laboratory. Unfiltered (total-recoverable) samples also were collected, and trace elements were determined after a weak acid in-bottle digestion by inductively coupled plasma-atomic emission spectrophotometry at a US Geological Survey laboratory. The suspended-sediment material was obtained by processing the whole-water sample (approximately 200 l for low-flow conditions and 20 l for high-flow conditions) through a continuous-flow or flowthrough centrifuge, which retained the solids and discharged the clarified effluent (Horowitz and others 1989). Dewatered suspended-sediment samples were freeze-dried prior to analysis. The freeze-dried suspended-sediment samples were analyzed for Al, As, Cd, Cu, Fe, Pb, Mn, and Zn following the techniques described by Horowitz and others (1989).

For this study, quality-control samples consisted of duplicate analyses and analysis of reference sediment material. The results from the duplicate analyses of bed and suspended sediment indicated a percent difference of less than 10% for most of the trace elements in the samples. The trace elements in the duplicate suspended-sediment samples had more variability than the trace elements in the bed-sediment samples. The percent difference for the reference material was less than 10% for the samples analyzed in water years 1995 and 1996. All equipment used in the collection of the water-column samples was acid rinsed prior to use, and equipment blanks were obtained using water, free of analytes of concern. The equipment blanks indicated no contamination from sample equipment, procedures, or preservation. Fish in the Blue River Basin were collected by electrofishing along a stream length of 150-300 m (Meador and others 1993). If possible, multiple taxa were collected. All fish that were collected along the stream reach were identified, weighed, and released back to the stream, if not used for trace-element analysis. Fish livers were

collected from seven fish, composited, frozen, and analyzed for trace elements. The fish livers were processed on site following US Geological Survey National Water-Quality Assessment Program protocols (Crawford and Luoma 1993). The fish livers were analyzed for trace elements at the US Geological Survey National Water Quality Laboratory. Macroinvertebrates also were sampled in accordance with the sampling protocols outlined in Cuffney and others (1993).

Results and discussion

To determine the occurrence, spatial distribution, and transport of trace elements in and around the Breckenridge mining district, sampling sites were selected to represent background concentrations in mineralized areas, at mining-affected sites, and at sites downstream from the mining-affected sites.

Bed sediment $-$ occurrence and spatial distribution of trace elements

To determine elevated trace-element concentrations in French Gulch and the Blue River, background concentrations for the Blue River Basin needed to be established. The least-affected sites along French Gulch and the Blue River were selected to represent background conditions. Sites 2 and 3 were selected to represent background conditions for mineralized areas along French Gulch (Fig. 1). For the Blue River, site 1 was considered to be the least affected by mining activities. Site 1 is located downstream from Illinois Gulch and upstream from the confluence of

French Gulch with the Blue River (Fig. 1). Along French Gulch, the lowest concentrations of Cd, Cu, Fe, Pb, Mn, and Zn were in samples collected from sites upstream from the Wellington-Oro Mine (sites 2 and 3; Table 1). Along the Blue River, the lowest bed-sediment traceelement concentrations were in samples collected from site 1 (Table 1). Zn concentrations in the bed sediment were lowest at the three background sites. However, the Zn concentrations at these sites exceeded reported average concentrations in igneous and sedimentary rocks of shale and sandstone composition by about 3 orders of magnitude (Hem 1992). In mineralized areas, traceelement concentrations that exceed average host-rock composition are expected.

Bed-sediment trace-element concentrations in samples from sites 2 and 3 also can be compared to trace-element concentrations in the altered host rocks in the Breckenridge mining district. Pride and Robinson (1978) determined the concentrations of Cu, Pb, and Zn (Table 1) in monzonite and quartz-monzonite porphyritic rocks that have undergone propylitic and phyllic alteration in French Gulch at the Wirepatch Mine located near Farncomb Hill (Fig. 1). The concentrations of Pb and Zn in the bed sediment at sites 2 and 3 exceeded the average concentrations in the propylitically altered rocks (Table 1). However, the concentrations of Cu, Pb, and Zn in the bed sediment are near, but less than, the concentrations in the mineralized host rocks that have undergone phyllic alteration (Table 1). The weathering of altered rocks is reflected in the concentrations of Cu, Pb, and Zn in the bed sediment at sites 2 and 3.

An approach to evaluating background trace-element concentrations for the Blue River Basin was to plot the

Table 1

Concentrations of selected trace elements in bed sediment $(< 63 \text{ µm})$; – not available; Dist distance from upstream to downstream along French Gulch and the Blue River (distances in bold reflect upstream to downstream distances along French Gulch)

Sampling site	Dist km	Al wt%	As μ g/g	$Cd \mu g/g$	$Cu \mu g/g$	Fe wt%	$Pb \mu g/g$	$Mn \mu g/g$	$Zn \mu g/g$
Low-flow sampling									
1 Blue River at Adams St. at Breckenridge	4.13	7.8	13	2.8	45	3.6	160	1300	600
2 French Gulch above Farncomb Hill	3.29	7.5	59	5.8	46	3.9	150	1300	630
3 French Gulch above Rich Gulch near Lincoln	2.55	8.0	62	6.1	66	3.8	380	770	780
4 French Gulch at Country Boy Mine	1.24	6.0	180	210	490	6.3	6500	3600	35000
5 French Gulch below Ford Gulch	0.99	6.6	110	91	280	7.1	1800	3300	17000
6 French Gulch above Gibson Gulch	0.68	6.0	110	110	310	10.6	1900	12000	22000
7 French Gulch at Breckenridge	3.49 or 0	7.7	42	18	190	4.6	1900	2700	7500
8 Blue River below French Gulch	3.26	8.5	22	10	83	4.7	520	1700	3200
9 Swan River at mouth	1.99	7.6	23	4.9	60	5.0	180	1600	810
10 Blue River near Dillon	0.19	8.3	24	15	68	4.4	315	1300	2300
Background concentrations this study		6.0	62	18	83	5.0	520	1700	810
^a Sediment guidelines (Soil and Sediment Quality Section Guidelines Division 1995)									
Threshold effect level - TEL			5.9	0.60	36		35.0		123
Probable effect level - PEL			17.0	3.53	197		91.3		315
^a Alteration zones (Pride and Robinson 1978)									
Propylitic alteration zone					18		27	-	174
Phyllic alteration zone					110		239		746

^a Sediment guidelines and alteration zones concentrations reflect total trace-element concentrations

Sample of a cumulative frequency curve used to determine background trace-element concentrations

trace-element data from all sampling sites in the basin on a probability plot (Velz 1984). Differences between the background concentrations for mineralized areas and the elevated concentrations for mining-affected sites show a two-stage distribution in the data (a point at which a substantial change in concentration occurs; Fig. 2). Concentrations of Al, As, Cd, Cu, Fe, Pb, Mn, and Zn plotted on probability plots showed a two-stage distribution. Background concentrations determined for the Blue River Basin were as follows: $Al = 6.0$ wt%; $As = 62 \mu g/g$; Cd = 18 μ g/g; Cu = 83 μ g/g; Fe = 5.0 wt%; Pb = 520 μ g/g; $Mn = 1700 \mu g/g$; and $Zn = 810 \mu g/g$. The concentrations of As, Cd, Cu, Pb, and Zn are substantially higher than those in fine-grained bed sediments in nonmineralized areas. Concentrations in the fine-grained sediments were as follows: $As = 7 \mu g/g$; $Cd = 1 \mu g/g$; $Cu = 20-30 \mu g/g$; Pb = 20-40 μ g/g; and Zn = 80-160 μ g/g (Arthur Horowitz, US Geological Survey, pers. comm. 1998). The environmental effects of bed-sediment trace-element concentrations can be assessed by comparing the concentrations with guidelines that have been established to evaluate water-quality conditions. Sediment-quality guidelines for the protection of aquatic life have been developed in Canada and have been divided into two assessment values (Soil and Sediment Quality Section Guidelines Division 1995). The low value is the threshold effect level (TEL), which is the level at which adverse effects are expected to occur rarely. The high value is the probable effect level (PEL), which is the level at which adverse effects are expected to occur frequently. Values that plot between the TEL and the PEL are expected to be associated occasionally with adverse biological effects. The values listed in Table 1 refer to the total concentration of an element in surficial sediments on a dry weight basis (Soil and Sediment Quality Section Guidelines Division 1995). Guidelines are not available for concentrations of Al, Fe, and Mn in sediment. When comparing bed-sediment trace-element concentrations to the sediment-quality guidelines, it is important to remember

that the bed-sediment concentrations reflect the $\langle 63-\mu m\rangle$ fraction size particles, which generally contain higher trace-element concentrations than the total fraction. Background concentrations in the Blue River Basin that were determined for As (62 μ g/g), Cd (18 μ g/g), Pb (520 μ g/g), and Zn (810 μ g/g) exceeded the PEL guideline for these elements (Table 1). The background Cu concentration (83 μ g/g) plotted between the TEL and PEL guidelines. In this study, sites 4–7 along French Gulch have concentrations that exceeded the PEL guidelines for As, Cd, Pb, and Zn (Table 1). Cu concentrations for sites 4±6, which are located at the most intensely affected sites along French Gulch, exceeded the PEL guideline. Downstream trends indicate that concentrations of As, Cd, Cu, Pb, and Zn increased, by an order of magnitude, at the affected sites along French Gulch and then slightly decreased at the mouth of French Gulch (site 7), except for Pb (Fig. 3a). Downstream from French Gulch on the Blue River (sites 8 and 10) and on the Swan River (site 9), concentrations of As, Cd, Pb, and Zn exceeded the PEL guidelines for these elements (Table 1). Cu concentrations for these sites plotted between the TEL and PEL guidelines. The downstream trend in concentrations of

Selected bed-sediment trace-element concentrations along (a) French Gulch and (b) Blue River

As, Cd, Pb, and Zn indicated that, after French Gulch discharges into the Blue River, concentrations in the Blue River bed sediment became elevated and remained high, indicating that mining activities along French Gulch affect bed-sediment trace-element concentrations in the Blue River to its mouth at Dillon Reservoir (Fig. 3b).

Water column - occurrence of major ions and trace elements - filtered phase

Stream waters in the Blue River Basin have an almost neutral pH, ranging from 7.5 to 8.1, and consist predominantly of Ca, HCO_3 , and SO_4 type waters (Table 2). Major-ion data for the Blue River Basin indicate that the specific conductance and SO_4 concentrations increase, and pH slightly decreases at the mining-affected sites during low- and high-flow conditions (Figs. 4a,b). Seasonal variations in specific conductance and concentrations of Ca, Na, and SO_4 indicate a decrease due to dilution by snowmelt throughout the basin, as shown for site 7 during water year 1996 (Fig. 5). However, stream water becomes more acidic during high flow because of the acidic contributions of the ground water (pH values for affected ground-water sites ranged from 4.2 to 5.8) from the mine site.

High-flow stream-water analyses along (a) French Gulch and (b) Blue River

Table 2

Fig. 5

Annual stream-water analyses at the French Gulch at Breckenridge site

As with the bed-sediment trace-element concentrations, the chemistry of the filtered water column indicates the water is affected by mine drainage and mill tailings piles along French Gulch (Table 2; Fig. 6). Concentrations of Cd and Zn in the filtered phase for some sites exceeded stream water-quality standards (Colorado Water Quality Control Commission 1996). Concentrations of Al, Fe, and Mn were detected at all sampling sites. As concentrations in the filtered phase were less than the detection limit at all sites. Concentrations of Cu and Pb were near or less than the detection limit for most of the sites. Because remediation objectives frequently are based on water-quality criteria for aquatic life and human health, trace-element concentrations in filtered water-column samples need to be compared to established, State, stream-water quality criteria and drinking-water stand-

Fig. 6 Stream-water analyses for Zn at the French Gulch at Breckenridge site

ards. The Colorado Water Quality Control Commission (1996) has established temporary stream water-quality standards for French Gulch. The temporary chronic value for Cd for French Gulch (2.4-km upstream from the confluence with the Blue River) is 4.0 μ g/l, and the temporary chronic value for the main stem of the Blue River from French Gulch to near the Swan River is 4.3 µg/l. Along French Gulch, Cd concentrations in the water column were less than the detection limit $(< 1 \mu g/l)$ except in areas affected by mining, where concentrations ranged from 6 to 8 µg/l (Table 2). The temporary chronic value for French Gulch was exceeded at sites 5-7 (Table 2). Site 8 on the Blue River had Cd concentrations of 4 μ g/l during low-flow conditions and 2 μ g/l during high-flow conditions. These concentrations were high but did not exceed the temporary chronic value. For sites where concentrations exceeded the temporary chronic value, the drinking-water standard for Cd of $5 \mu g/l$ MCL (maximum contaminant level; US Environmental Protection Agency 1996) also was exceeded.

Zn concentrations in the filtered phase ranged from 4 to 3100 mg/l during low-flow conditions. During high-flow conditions, the Zn concentrations ranged from 2 to 2300 mg/l. The temporary chronic value for Zn for French Gulch is 1980 μ g/l, and the temporary chronic value for the Blue River is 1700 μg/l (Colorado Water Quality Control Commission 1996). The highest Zn concentration in the water column within the study area is from the French Gulch at Breckenridge site (site 7; Table 2). The concentration at that site exceeded the temporary chronic value during both low- $(3100 \mu g/l)$ and high-flow (2300 μ g/l) conditions. Zn concentrations at site 7 for water year 1996 fluctuated throughout the year, and the largest decrease occurred during the snowmelt (Fig. 6). The fluctuations in the Zn concentration may be a result of the contribution of groundwater to the streamflow. Drinking-water standards for Zn are not established, but human health advisories for an adult during a lifetime are at 2000 µg/l (US Environmental Protection Agency 1996). Concentrations in samples collected at site 7 during low- and high-flow conditions exceeded the human health advisory.

Fe concentrations in the water column were less than the temporary chronic values established for French Gulch of 1000 μg/l and for the Blue River of 300 μg/l (Colorado Water Quality Control Commission 1996). Mn concentrations were less than the established temporary chronic values for French Gulch (1000 mg/l) and the Blue River (50 mg/l), except at site 8 (Table 2; Fig. 1; Colorado Water Quality Control Commission 1996). The highest Mn concentrations were in French Gulch at sites 5-7.

Water column $-$ occurrence of trace elements $$ suspended-sediment phase

Suspended-sediment samples were collected during lowand high-flow conditions in the Blue River Basin to evaluate changes in the associated chemical concentrations and loads. The suspended-sediment concentrations in the basin during this study ranged from 0.1 to 4.0 mg/l dur-

Table 3

Selected trace-element concentrations in the suspended-sediment phase; Q instantaneous discharge, Sed sediment concentration, no data

ing low-flow conditions and from 2.0 to 11.0 mg/l during high-flow conditions (Table 3). In addition, suspendedsediment trace-element concentrations varied between low- and high-flow conditions (Table 3). Decreased traceelement concentrations during high-flow conditions can result from an increase in the percentage of sediment particles of the > 63 -µm fraction size in the sediment load; nevertheless, the > 63 -µm fraction is important to the overall suspended-sediment concentration and affects the trace-element transport (Horowitz 1995b). Throughout the study area, concentrations of As, Cd, Pb, and Zn in the suspended sediment generally exceeded the PEL guidelines for the protection of aquatic life (Soil and Sediment Quality Section Guidelines Division 1995; Tables 1 and 3). Cu concentrations in the suspended sediment exceeded the PEL guideline at site 8 during lowflow conditions and at sites 5 and 7 during high-flow conditions (Tables 1 and 3).

Generally, suspended-sediment trace-element concentrations (As, Cd, Cu, Pb, Mn, and Zn) were higher than bedsediment concentrations for the Blue River Basin as indicated by the Zn concentrations. For example, Zn concentrations in suspended sediment at the mouth of French Gulch (site 7) was about 1.5 (low flow) to 3 (high flow) times greater than Zn concentration in the bed sediment (Tables 1 and 3). The higher suspended-sediment trace-element concentrations may be a result of finer grained sediment that is being transported (Horowitz 1995b). However, higher bed-sediment concentrations were measured along French Gulch at sites 4–6 near the most mining-affected area of the basin. The higher bedsediment concentrations probably are a result of the trace-element source material (mill tailings and roaster fines) being nearby, whereas the suspended sediment has a mixture of sediment sources. Although each of these

sampling media varied in trace-element concentrations, the concentrations of As, Cd, Cu, Pb, and Zn in the bed and suspended sediment were elevated and exceeded the PEL guidelines for the protection of aquatic life for many sites (Soil and Sediment Quality Section Guidelines Division 1995).

When examining trace elements, it is important to consider the association of trace elements in the bed sediment and in the suspended sediment because certain associations probably indicate a similar source and/or concentrating mechanism. The most significant traceelement correlations in the bed sediment and in the suspended sediment were for Cd-Cu (0.92), Cd-Zn (0.97), Cu-Zn (0.94), and Cu-Pb (0.94), with associated p-values of < 0.005. For sites only along French Gulch, the most significant trace-element correlations in the bed and suspended sediments again were for Cd-Cu (0.93), Cd-Zn (0.97), and Cu-Zn (0.96), with associated p-values of < 0.005. Overall, for the Blue River Basin, bed sediment provided more useful information than suspended sediment for determining trace-element concentrations because of the extremely low suspended-sediment values $(< 0.1$ mg/l at some sampling sites during this study). However, bed sediment only provided information on the source and occurrence of trace elements, whereas suspended sediment provided valuable information on the transport of trace elements.

Transport

In addition to chemical analysis of the suspended-sediment material, discharge and suspended-sediment data for water years 1996 and 1997 were collected at the French Gulch and Blue River gaging stations (approximately once a month during low-flow conditions and weekly to biweekly during high-flow conditions) to deter-

mine the suspended-sediment and associated trace-element loading on an annual basis. Suspended-sediment and trace-element concentrations can have marked spatial and temporal variability (Horowitz 1995b). Spatial variability in the suspended-sediment concentrations was accounted for by using depth- and width-integrated sampling techniques. Temporal variability can be accounted for by changing the sampling frequencies, which may not be apparent from the sampling efforts completed in water years 1996 and 1997.

For the Blue River Basin, suspended-sediment transport was calculated on an annual basis and was dependent on the sampling frequency. A discussion on determining annual sediment transport is given in Horowitz (1995a). The data for discharge and suspended-sediment concentrations were not normally distributed in water years 1996 and 1997, but the range, mean, and median values for discharge were similar between these water years (Table 4). Calculations of the suspended-sediment transport for French Gulch (site 7) in water year 1996 indicated that 94% of the suspended sediment was transported during 86% of the total discharge and during 28% of the time. For water year 1997, 85% of the suspended sediment was transported during 68% of the total discharge and during 11% of the time. For French Gulch, the average daily suspended-sediment transport was within 10% for water years 1996 and 1997. Suspendedsediment transport for the Blue River (site 10) is very similar to that for French Gulch for water years 1996 and 1997. For water year 1996, 89% of the suspended sediment was transported during 66% of the total discharge and during 15% of the time. For water year 1997, 91% of the suspended sediment was transported during 62% of the total discharge and during 11% of the time. Average daily suspended-sediment transport was within 5% for water years 1996 and 1997. On an annual basis, most of the suspended-sediment transport in French Gulch and the Blue River occurred during May and June. The hydrograph for water year 1996 for the gaging station at the mouth of French Gulch indicated several increases in discharge during May from a base line of about 0.05 m³/s to a peak of about 2.3 m³/s (Fig. 6). However, high suspended-sediment concentrations also were measured in March. Inputs from stored ground water during these low-flow conditions may be affecting the suspended-sediment concentrations because ground water is considered to be the principal source of water in French Gulch during low-flow conditions (Art Morrissey, Consulting Geologist, pers. comm. 1997). The frequency of sampling during this time of year may need to be increased to determine if the increased suspended-sediment loading is occurring annually. Also, increased sampling at various times of the year may be useful in determining if short-term events (such as storms) represent a significant part of the annual hydrograph. The two years of discharge monitoring and suspended-sediment sampling in the Blue River Basin have provided initial results of suspended sediment and associated trace-element loading. The results indicate that the determination of annual trace-element loading may be possible by monitoring

only discharge and suspended-sediment concentrations in the basin.

Using the annual discharge and suspended-sediment data along with the chemical data obtained during low- and high-flow conditions, annual trace-element transport in French Gulch and the Blue River can be estimated. Chemical sediment transport was obtained by multiplying the chemical sediment concentrations, in milligrams per liter, by the discharge, in cubic meters per second, and then converting to tons per day (Horowitz 1995a, Table 3). Because suspended-sediment chemical concentrations were determined on a whole-water sample using a total-recoverable procedure, the values for daily transport result in an underestimate of the total trace-element transport (Horowitz 1991). For site 7, a mean chemical concentration can be obtained for the trace elements using the low- and high-flow data (Table 3). However, for site 10, only high-flow data are available, and, thus, only a minimal estimate of the mean chemical concentration can be obtained because low-flow concentrations tend to be higher (Table 3). The average chemical loading is calculated using the assumptions that discharge and suspended-sediment concentrations determined at the time of sampling were constant for the sampling interval and the mean chemical concentration represents the traceelement composition of the suspended sediment. In French Gulch and the Blue River, most of the traceelement loading associated with the suspended sediment predominantly was for Al, Fe, Pb, Mn, and Zn (Table 4). Along French Gulch trace-element loading increases from site 3 to site 7 (Fig. 1) as indicated by the average of the low- and high-flow data. Loading along French Gulch, in tons per day, increases from upstream to downstream at about 5% for Al, 22% for Fe, 77% for Pb, 66% for Mn, and 93% for Zn during water years 1996 and 1997. This indicates that, along French Gulch, the mining activities near the Wellington-Oro Mine site (Fig. 1) significantly affect the trace-element loading. An accurate determination of the trace-element loading into Dillon Reservoir cannot be determined because low-flow suspended-sediment trace-element concentrations, which tend to be higher, are not available. A more detailed chemical analysis of the suspended sediment is needed to determine more accurate mean/median suspended-sediment chemical data for the Blue River Basin, thus allowing for determination of the annual trace-element loading by monitoring discharge and suspended-sediment data (Horowitz 1995a).

To determine how trace elements are transported in the Blue River Basin, the magnitude of material transported in the filtered, unfiltered, and suspended-sediment phases needs to be examined. Loads for the filtered, unfiltered, and suspended-sediment phases are calculated by multiplying the trace-element concentration by instantaneous discharge. The discharge measurements for this study were considered minimum discharges because of the cobble stream substrates, which allowed water to flow through the cobbles of the streambed; thus, discharge was not measured by the flow meter.

Fig. 7 Variations in high-flow Zn loading along (a) French Gulch and (b) Blue River

Trace-element concentrations in the filtered phase could be compared to concentrations in other sampling phases because most trace-element concentrations in the filtered phase, with the exception of Zn, were either very low or less than the detection limit. Zn loads in the Blue River Basin during high-flow conditions were higher in the filtered phase than in the suspended-sediment phase for French Gulch and the Blue River (Figs. 7a,b). Although Zn concentrations in the suspended sediment were high in the basin, transport of Zn by suspended sediment was low due to the low suspended-sediment concentrations in the water column (2.0-11 mg/l). Nevertheless, suspendedsediment chemical loading was significantly higher at site 7 during high-flow conditions (5.19 tons per day) than during low-flow conditions (0.01 tons per day). Increased loading during high-flow conditions is not unexpected because of the increased discharge and suspended-sediment concentrations during high-flow conditions. Zn in the filtered, unfiltered, and suspended-sediment phases had increased loads at the most-affected mining sites (sites $5-7$ in Fig. 7a and sites 7 and 8 in Fig. 7b). For the Blue River Basin, Zn in the filtered phase comprises between 57% and 95% of the unfiltered phase.

Fate of trace elements in the biota

In examining the water-quality conditions in the Blue River Basin, biological studies were completed that included the analysis of fish livers for trace elements and the assessment of fish and benthic communities. Biological data are helpful in understanding the fate of trace elements in the biota because tissue analysis is a direct measurement of contaminants that accumulate in biological organisms (Crawford and Luoma 1993). Fish livers from brown trout were collected at site 8 in August 1996 and analyzed for trace elements (Fig. 1). Trace-element concentrations in the fish livers in μ g/g on a dry weight basis, are as follows: $As = 0.2$; $Cd = 81.3$; $Cu = 482$; $Pb = 1.0$; and $Zn = 138$. Concentrations of Cd and Cu in the fish livers exceeded concentrations in the bed and suspended sediment at site 8 (Tables 1 and 3). The concentrations of Cd and Zn were the highest concentrations in brown trout livers in the Upper Colorado River Basin (Deacon and Stephens 1998).

In the study area, fish communities were assessed in August 1996 at sites 7 and 8 (Fig. 1). Fish communities can be useful indicators of the health of an ecosystem, which, in turn, is a reflection of the local water quality. At site 7, no fish were present, probably because of a combination of high trace-element concentrations and degraded stream habitat; however, cutthroat trout (Onchorhynchus clarki), which are indicative of a healthy stream, were present upstream from the mined area on French Gulch (Jay Skinner, Colorado Division of Wildlife, oral comm. 1997). In the Blue River at site 8, the abundance and type of fish species were low compared to those at other sites in the Upper Colorado River Basin (Fig. 1; Deacon and Mize 1997). At site 8, only two species of fish were identified: brook trout (Salvelinus fontinalis), which were the most abundant, and a few brown trout (Salmo trutta; Deacon and Mize 1997). Brook trout are less sensitive to elevated Zn concentrations than brown trout (Woodling and Dorsch 1997). Macroinvertebrates also are useful indicators of water quality because they are directly exposed to varying water-quality conditions and, therefore, integrate effects from contaminants over time (Clements and Kiffney 1995). Results from macroinvertebrate sampling at sites 7 and 8 indicated that the benthic community at site 7 along French Gulch was less abundant and less diverse than that at site 8 on the Blue River (Fig. 1). Taxa ranged from 20 at site 7 to 29 at site 8, and macroinvertebrate abundances ranged from 783 individuals per $m²$ at site 7 and 5800 individuals per $m²$ at site 8 (Jeffrey Deacon, US Geological Survey, pers. comm. 1997). The benthic community at these two sites was dominated by midges (Chironomids), which generally are considered tolerant to contaminants (Clements and Kiffney 1995). Mayflies (Ephemeroptera) and stoneflies (Plecoptera) were present at each site; however, only two to three species from each group were present at site 7. Caddisflies (Trichoptera) were present at each site, but only one genus was collected (Jeffrey Deacon, US Geological Survey, pers comm. 1997). The data indicated that site 7, which is located

Cd concentrations in the Blue River Basin for various sampling media

closest to the mining activities, had fewer organisms and species than site 8, which is located farther downstream from the mining activities. Total abundance and species richness at these sites can be a useful indicator of metal pollution, and results indicate that site 7 along French Gulch is more affected by the mining activities. The occurrence and transport of trace elements in the Blue River Basin are reflected in the biota. The lack of fish and a limited benthic community at the mouth of French Gulch (site 7) might be a result of elevated traceelement concentrations and the condition of the stream habitat. High concentrations of Cd and Zn were detected in the filtered water-column samples and in fish livers from fish obtained downstream from the confluence of French Gulch with the Blue River. Also, the importance of analyzing various sampling

media is reflected in the trace-element concentrations of Cd. Variations in the Cd concentrations at site 8 are illustrated in Fig. 8 for bed sediment, filtered watercolumn samples, suspended sediment, and fish livers. Along the Blue River, Cd concentrations in the filtered water-column samples are orders of magnitude lower than those in the sediment and fish livers. Most waterquality studies include only filtered and unfiltered water samples. If only filtered and unfiltered water samples had been collected in this study, the importance of the occurrence, transport, and fate of Cd in this basin would have been overlooked.

Conclusion

In water-quality studies of mining-affected sites, traceelement data from a variety of sampling media need to be collected to determine the occurrence, transport, and fate of these constituents. Bed-sediment data provide

insights on the occurrence and source of trace elements; filtered and unfiltered water-column data are needed to assess compliance with State stream water-quality criteria and drinking-water standards; filtered, unfiltered, and suspended-sediment water-quality data are needed to estimate the transport of trace elements; and selected tissue-sample data, in conjunction with fish community analyses, are needed to evaluate the effects of trace elements on the biological system.

In the Blue River Basin, analyses of bed sediment in the background areas indicate that concentrations of As, Cd, Cu, Pb, and Zn are elevated when compared to average concentrations in igneous and sedimentary rocks. The background Zn concentrations are about 3 orders of magnitude greater than the average concentrations in the igneous and sedimentary rocks. Background conditions for mineralized areas, which are a result of weathering of altered rock in the region and are not greatly affected by mining activities, reflect background conditions for the basin. The highest bed-sediment trace-element concentrations were in the mining-affected areas along French Gulch and directly downstream from the confluence of French Gulch with the Blue River. At site 10 at the mouth of the Blue River as it flows into Lake Dillon, which is a drinking-water reservoir for the city of Denver, the bedsediment trace-element concentrations were similar to those at the three background sites; nevertheless, concentrations of Pb and Zn at site 10 exceeded guidelines for the protection of aquatic life. Drinking-water standards were not exceeded at this site; however, the reservoir also is used for fishing and other recreational activities. Concentrations of Cd and Zn in the water column exceeded State stream water-quality standards indicating potential harm to aquatic life at several sites downstream from the mining areas. Concentrations of Cd and Zn were orders of magnitude less than the sediment concentrations. In the water column, other trace-element concentrations generally were less than the detection limit. Concentrations of As, Cd, Cu, Pb, and Zn in the bed and suspended sediments exceeded the probable effect level (PEL) guidelines for the protection of aquatic life at most of the sites sampled in the Blue River Basin. Traceelement concentrations increased at the mining-affected sites and slightly decreased downstream, but still exceeded the guidelines for sediment. Fishing is a popular recreational use of the Blue River, and remediation efforts need to consider the adverse effects of trace elements on the aquatic life.

The suspended-sediment loads during high-flow conditions were higher than those during low-flow conditions; at the mouth of French Gulch, the suspendedsediment load was 3 orders of magnitude greater during high-flow conditions than during low-flow conditions. Most of the suspended-sediment transport in the Blue River Basin occurred during snowmelt in May and June. If any remediation efforts are inititated, it is important to address the amount of loading that occurs during highflow conditions. For water years 1996 and 1997, measurements of discharge and suspended sediment indicated

similarities in the discharge and the percentage of sediment transported, particularly for the Blue River. The results were within the range of $5-10\%$ for water years 1996 and 1997. Along French Gulch trace-element loading increased from upstream to downstream at about 5% for Al, 22% for Fe, 77% for Pb, 66% for Mn, and 93% for Zn. Mining activities near the Wellington-Oro Mine site affect the trace-element loading.

The limited numbers or absence of fish species in the Blue River Basin probably are a result of elevated traceelement concentrations and degraded stream habitat. The concentrations of Cd and Zn were highest in brown trout livers in the Upper Colorado River Basin. The two sites sampled for macroinvertebrates in the basin were dominated by macroinvertebrate species tolerant to contaminants. Limited numbers and species diversity in benthic communities also appear to reflect trace-element effects on water quality.

Zn loading in the filtered, unfiltered, and suspended-sediment phases indicates that most of the Zn is being transported in the water column. Therefore, remediation efforts for the mined areas need to focus on methods to remove Zn in the water column rather than the sediment phase. In the Blue River Basin, most of the trace elements are associated with the sediment, however, the trace elements in the various phases at some point in time may become available to the biota (Church and others 1997). Bed sediment provided the most useful information for determining trace-element concentrations in the Blue River Basin. Concentrations in the filtered phase were lower than concentrations in the sediment phase and frequently were less than the detection limit. Therefore, concentrations in the filtered phase provided less information on the effects of trace elements on stream-water quality. Because As, Cd, Cu, and Pb were detected at high concentrations in the sediments and at concentrations less than the detection limit in the filtered water-column samples, remediation approaches should include some methods that would remove particles smaller than 63 μ m from the system. Suspended-sediment data also are important in evaluating the fate and transport of trace elements; however, the small volume of suspended-sediment material in the Blue River Basin made it difficult to obtain chemical results of the suspended-sediment fraction. The macroinvertebrate, fish-community, and fish-liver analyses generally support the findings in other sampling media. This integrated approach to determine the occurrence, transport, and fate of trace elements in the Blue River Basin addressed more water-qualitymanagement issues than would a typical water-chemistry study.

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