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Influence of Mining-Related Activities on Concentrations of Metals in Water and Sediment from Streams of the Black Hills, South Dakota

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Abstract. Water and sediment samples were collected from streams in Spearfish Creek, Whitewood Creek, and Bear Butte Creek watersheds in the Black Hills, SD, an area impacted by gold mining operations. Arsenic concentrations that exceeded the U.S. Environmental Protection Agency's Maximum Concentration Limit of 50 μg/L for drinking water were found in water from Annie Creek, a tributary of Spearfish Creek, and from Whitewood Creek. Gold Run, a tributary of Whitewood Creek, and Annie Creek contained Se concentrations in water that exceeded the EPA Ecotox threshold of 5 μg/L and were classified as a high hazard for Se accumulation from water into the planktonic food chain and for resultant toxicity to fish and aquatic birds. Concentrations of As, Cd, Cu, Hg, Ni, Pb, and Zn in sediment exceeded EPA Ecotox thresholds in one or more of the watersheds suggesting potential adverse ecological effects. Sediment from Rubicon Creek, a tributary of Spearfish Creek, contained Se concentrations high enough (4.0 μg/g) to be a moderate hazard for accumulation from sediments into the benthic food chain, with resultant dietary toxicity to fish and aquatic birds. These results are discussed in light of historical mining activities and recent clean-up and reclamation efforts. Based on the results and comparisons to Ecotox tresholds, further studies of ecological effects are warranted.

The Black Hills is an isolated group of mountains covering an area of about 20,600 km^2 on the southwestern border of South Dakota. The mountains extend about 222 km in a north-south direction and 74 to 93 km in an east-west direction, with elevations ranging from 914 to 2,195 m. Topography is diverse, including forested mountains and hills, canyons, and grasslands, all interlaced with various cold-water streams (Froiland 1990). The drainage basins of Spearfish, Whitewood, and Bear Butte Creeks in the northern Black Hills and Black Hills National Forest (Figure 1) are unique in the state because they are spring-fed cold-water streams supporting sensitive salmonids fish, such as rainbow (*Oncorhynchus mykiss*) and brown (*Salmo trutta*) trout (Modde *et. al.* 1991) as well as longnose dace (*Rhinichthys cataractae*), mountain suckers (*Catostomus platyrhynchus*), white suckers (*Catostomus commersoni*), and longnose suckers (*Catostomus catostomus*) (Newman *et al.* 1999). These streams are primarily gravel-riffle-pool areas with some beaver dams, stock impoundments, hydro dams, and backwater areas. Stream flow is generally north to northeast in these watersheds. Some stream reaches support rich populations of submergent and emergent aquatic vegetation and diverse aquatic invertebrate communities, with 26 genera of invertebrates having been identified in Spearfish Creek alone (Duffy 1994). Sensitive species of invertebrates, such as amphipods (*Gammarus lacustris*, *Gammarus fasciatus*, *Hyalella azteca*) and cladocerans (*Ceriodaphnia reticulata*, *Daphnia pulex*), have been collected in several streams and can likely be found in lentic or lotic water areas (Bureau of Sports Fisheries 1971, 1972; Chadwick and Associates 1993; Duffy 1994; Gable 1991, 1992, 1993, 1994). In addition to the aquatic fauna, the bald eagle is the one federally listed bird species that can be found in this rich habitat. At least 15 rare species also occur (USFWS 1993) along with 62 species of migratory birds, of which 24 are considered rare or infrequent migrants (Froiland 1990) (South Dakota Department of Game, Fish, and Parks National Heritage Database; Nell McPhillips, USFWS, personal communication, Pierre, SD).

In addition to a rich and diverse biological ecosystem, the northern Black Hills contains significant gold-bearing mineral resources. Mining has been an active industry in the Black Hills since gold was discovered in 1874, with most of the mining being associated with gold veins and placers in the northern Black Hills near the towns of Lead and Deadwood (Rahn *et al.* 1996). The mining activity has been particularly heavy in the drainage basins of Spearfish, Whitewood, and Bear Butte Creeks in the northern Black Hills and Black Hills National Forest. The ore mined and milled consisted mostly of silicates, iron and magnesium carbonates, and metallic sulfides, with gold being associated with arsenopyrite in the ore body (Marron 1989). About 100 million tons of finely ground gold-mill tailings were discharged into Whitewood Creek by Homestake Mining Company from 1876 to 1978 (Marron 1992).

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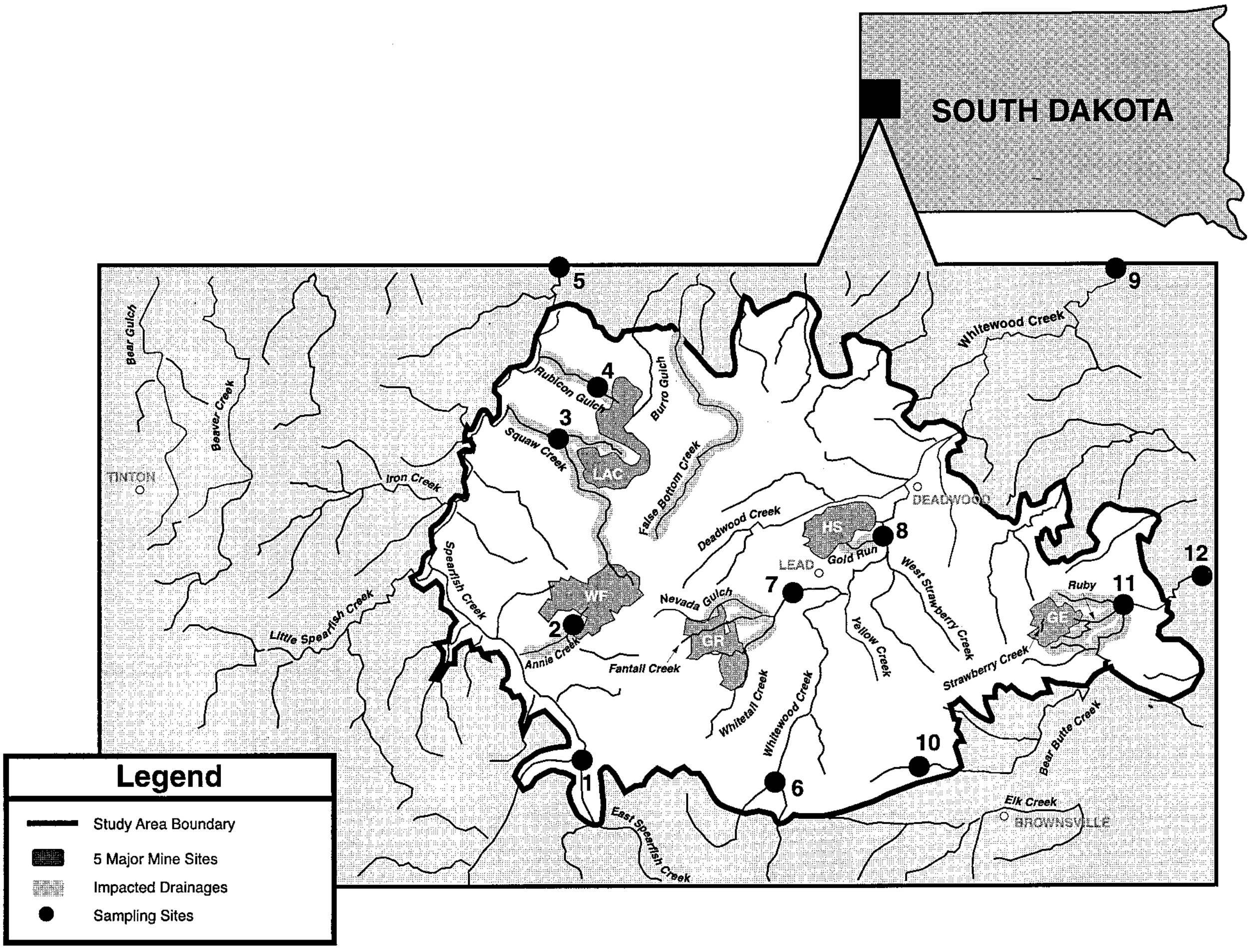

Fig. 1. Map of four watersheds in the study area indicating locations of major streams, sampling sites, and active mines

Gold recovery from lode mines was originally accomplished through mercury amalgamation (Hesse *et al.* 1975), through which an esimated 15 kg of mercury was lost daily to Whitewood Creek (Rahn *et al.* 1996). Although the use of mercury was discontinued in 1971 and replaced with processes relying on cyanide solutions, historic mercury discharge has resulted in elevated mercury levels in fish and fish-eating birds as far downstream as Lake Oahe (Figure 2; Hesse *et al.* 1975). In addition to mercury, daily averages of 140 kg of cyanide, 100 kg of zinc, and 10 tons of arsenopyrite were also released into Whitewood Creek, and mine tailings rest in the alluvium along Whitewood Creek, the Belle Fourche River, and the Cheyenne River (Figure 2; Marron 1992; Rahn *et al.* 1996). Numerous tributaries on the eastern flank of Spearfish Creek are in a mineralized area with a long history of gold-mining activity. A number of streams draining this area are noted for elevated concentrations of metals, particularly arsenic. Annie Creek, a tributary of Spearfish Creek, has received arsenic-bearing tailings from mining operations and at least one site on the creek was proposed for inclusion on the National Priorities List by the U.S. Environmental Protection Agency in 1991 (Driscoll and Hayes 1995). Besides contamination from leeching processes and tailings, many abandoned gold mines in these basins contribute acid and heavy metals to streams, with potentially severe impacts in areas of high sulfide mineralization due to the production of acid-mine drainage when the sulfides are exposed to the atmosphere and as water leaches through the rock. Elements frequently associated with acid-mine drainage from gold mining in the Black Hills include Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn (Goddard 1989b; Ruelle *et al.* 1993). Rahn *et al.* (1996) reported five large mines involving 800 ha still operating (Figure 1), which were mostly open-pit operations using cyanide leaching treatment of low-grade ores. It is the objective of this study to ascertain whether area streams in the vicinity of these five large-scale gold mines (LAC Resources [LAC], Homestake [HS], Wharf [WF], Golden Reward [GR], and Gilt Edge [GE]) show evidence of metal contamination in both water and sediment that may represent a hazard to biological resources.

Materials and Methods

Area of Study

Twelve sites were established throughout three watersheds: Spearfish Creek, Whitewood Creek, and Bear Butte Creek (Figure 1). For each

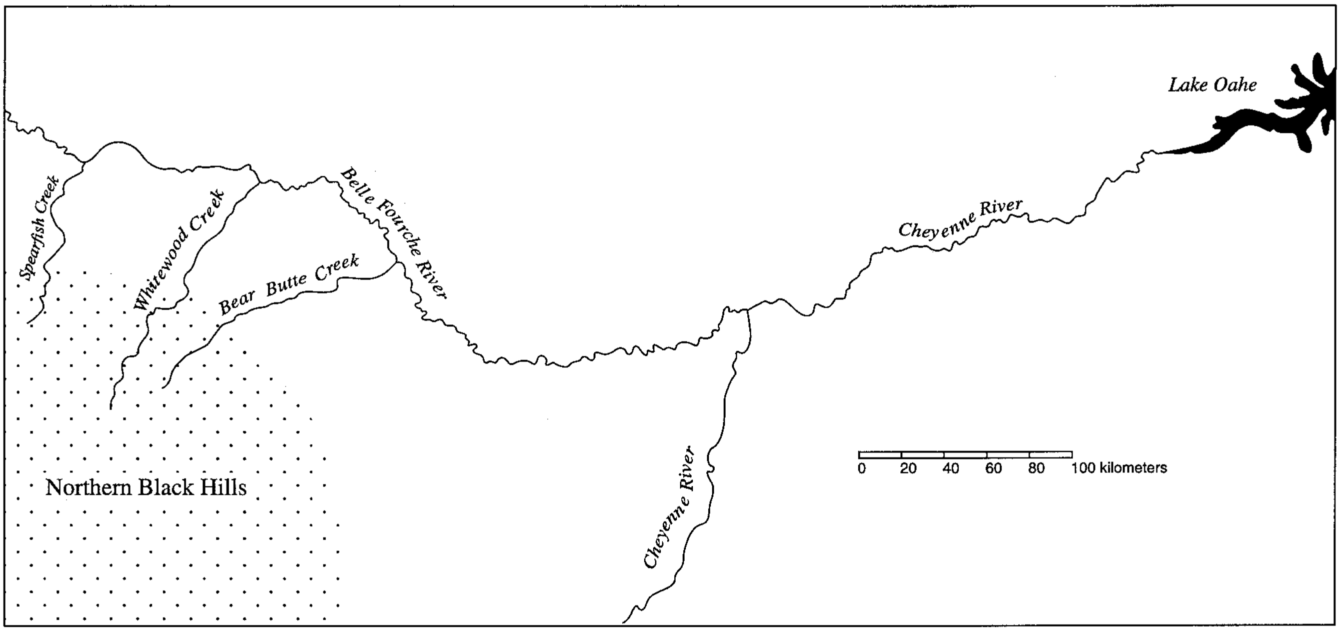

Fig. 2. Location and components of Cheyenne River System receiving drainage from the northern Black Hills

watershed, an upstream site above any active mines provided a reference site: (Site 1) east fork of Spearfish headwaters at Hanna Dam above active mines; (Site 6) Whitewood Creek headwaters; (Site 10) Bear Butte Creek headwaters. The nine experimental sites were located either just downstream of the active mining areas or farther downstream, well below all mining activities (designated "plains"). These experimental sites for each watershed were as follows: *Spearfish Creek Watershed* (Site 2) Annie Creek below WF; (Site 3) Squaw Creek at old Cleopatra Mine downstream from LAC and WF; (Site 4) Rubicon Gulch downstream from LAC; (Site 5) Spearfish Creek downstream on plains; *Whitewood Creek Watershed* (Site 7) Whitetail Creek below GR and Nevada Gulch; (Site 8) Gold Run below HS discharge; (Site 9) Whitewood Creek downstream on plains at USBR siphon; *Bear Butte Creek Watershed* (Site 11) Ruby Gulch below GE and just before confluence with Bear Butte Creek; (Site 12) Bear Butte Creek downstream on plains.

Sample Collections

Water: Filtered and unfiltered water samples were collected from each site according to techniques described by U.S. Fish and Wildlife Service (1996) and by the U.S. Geological Survey (CERC 1996). Two grab samples of water were collected at each site. One precleaned 250-ml Nalgene® polyethylene bottle was rinsed with water from the stream and used to collect stream water, with the bottle opening pointing downstream. The water was filtered through a disposable 0.45-micron polycarbonate portable filtration unit into a second bottle and acidified with two 2-ml ampules of 70% nitric acid (I-CHEMpules®, I-CHEM, New Castle, DE). The original bottle was then used to collect a second grab sample from the stream, which was not filtered but was acidified with two I-CHEMpules®. Four field blanks were also collected (two filtered and two unfiltered). Identical field procedures were followed for the collection of blanks using deionized water instead of stream water. Samples were immediately placed on ice and shipped within 1 week to the analytical laboratory.

Sediment: Equal quantities of sediments were collected from areas of sediment deposition at each site. Samples were collected from a sediment depth of 0–5 cm with a clean stainless steel spoon. Sediment samples for a given cross-section were mixed in a stainless steel bowl and placed in a precleaned 250-ml glass jar leaving about 2–3 cm of headspace. All stainless steel implements were cleaned with Alconex® detergent and rinsed with deionized water following their use at each site. Samples were immediately placed on ice and shipped within a week to the analytical laboratory.

Laboratory Preparation: Water

Water samples were digested in two ways depending on analytes of interest. For elements to be determined by inductively coupled plasma-mass spectrometry (ICP-MS; As, Cd, Cr, Cu, Ni, Pb, Ag, Zn), filtered samples were analyzed as received, but an aliquot of each unfiltered sample (20 ml) was digested with nitric acid and hydrogen peroxide while slowly evaporating down to 1 ml in Zymark TurboVap® tubes (Zymark Corp., Hopkinton, MA) in a CEM microwave oven (CEM Corp., Matthews, NC). After cooling, digestates were transferred and diluted to 100 ml final volume (~ 1% HNO_3 final acid matrix). For mercury and selenium determinations in both unfiltered and filtered water samples, aliquots (20 ml each) were subjected to potassium persulfate oxidation followed by hydrochloric acid reduction in beakers on a hot plate (~ 8% HCl final acid matrix).

Laboratory Preparation: Sediment

An aliquot of each sediment sample was lyophilized in a VirTis 20-SRC lyophilizer (VirTis Co. Gardiner, NY). In conjunction with the process of freeze drying, percent moisture determinations were also conducted gravimetrically. Once dried, sediments were placed in plastic Ziploc® bags and crushed by moving a roller pin from the bottom of the bag to the top until a uniform powder was produced.

Sediment samples were digested by two different procedures depending on the analytes of interest. For all elements except Se, a dried aliquant of each sample (~ 0.25 g) was digested with nitric acid, hydrochloric acid, and hydrogen peroxide in a sealed Teflon® FEP vessel using a CEM microwave oven. After cooling, samples were transferred to polyethylene bottles and diluted to 100 ml final volume. The final acid matrix was 5% nitric acid, 1% hydrochloric acid. For selenium, and to cross-check ICP-MS arsenic results, ~ 0.25 g of each sample was subjected to a combination nitric acid wet digestion and magnesium nitrate dry ash procedure. After dry ashing at 500°C, the ashed residue was subjected to a hot hydrochloric acid reduction procedure to reduce selenium to the required oxidation state for analysis. Digestates were transferred and diluted to 100 ml in polyethylene bottles, with a final acid matrix of 10% hydrochloric acid.

Instrumental Analyses

Water samples and water and sediment digestates were analyzed for selected metals with a Perkin-Elmer Sciex ELAN 6000 ICP-MS (Perkin-Elmer Corp., Norwalk, CT) equipped with platinum sampling and skimmer cones. Samples were pumped by a Gilson peristaltic pump (Gilson Inc., Middleton, WI) from tubes arranged on an AS-90 autosampler to a glass cyclonic spray chamber containing a Meinhard® TR-30-C3 nebulizer (J. E. Meinhard Associates Inc., Santa Ana, CA). The resulting spray was delivered into the plasma with a nebulizer argon gas flow of approximately 1 L/min. The instrument was mass calibrated (tuned) with a 10 ppb solution of Be, Mg, Co, Rh, Cs, and Pb; peak resolutions were adjusted to approximately 0.7 amu. Optimization of analog and pulse voltages, dual-detector calibration, and lens voltages (auto-lens) were performed according to the manufacturer's specifications. Prior to each analytical run, instrument performance characteristics were adjusted through changes in the nebulizer flow rate to result in net intensities exceeding the manufacturer's specifications for Mg, Rh, and Pb. Adjustments were made to result in Ba^{++}/Ba^{+} and $CeO^{+}/Ce^{+} < 3\%$. Germanium (30 ppb), Rh (10 ppb), and Bi (10 ppb) were used as internal standards. Instrumental runs and quality control parameters analyzed with the sample sets were patterned after EPA Method 6020 (U.S. Environmental Protection Agency 1994) and included a continuing calibration blank, independent calibration verification standard, reference water solutions (laboratory control samples), replicate sample analyses, and sample spikes. Preliminary scans of the samples were conducted to determine optimal dilution factors based on the widely varying analyte concentrations. The presence of a suspect interferent was evaluated by the dilution percent difference test, in which the concentration from a selected sample or sample digestate analyzed full strength is compared with the concentration achieved from a 5× dilution. A synthetic interference check solution was also analyzed as an indication of instrument performance in correcting for interferences. Elemental masses monitored included Cr^{52}, Cr^{53}, Ni^{60}, CU^{63}, Zn^{66}, Zn^{68}, As^{75}, Ag^{107}, Ag^{109}, Cd^{111}, and Cd^{114}. Lead was determined from the summation of three isotopes: Pb^{206}, Pb^{207}, and Pb^{208}. Because large solution concentration differences observed between the Cr masses in some samples determined by ICP-MS indicated the presence of interferences, all samples were cross-checked for Cr by Zeeman furnace atomic absorption to determine which Cr mass showed best agreement. Arsenic concentrations determined by ICP-MS were cross-checked by flow injection hydride generation atomic absorption spectroscopy as a further check on accuracy of ICP-MS results for this element. Mercury was determined in water and sediment by cold vapor atomic absorption using a Perkin-Elmer FIAS -200 flow injection system and a Perkin-Elmer Model 3100 atomic absorption spectrophotometer. Stannous chloride reductant varied from 5% (water) to 10% (sediment) in 10% HCl, with a 10% HCl carrier. The phase separator, reaction coil, absorption cell, and pump tubing were set up according to the manufacturer's specifications. Se and As were determined in the same matrices by hydride generation atomic absorption using the same flow injection system and spectrophotometer as described for mercury. The reductant was 0.2% $NaBH_4$ in 0.05% NaOH with a carrier of 10% HCl for water and 50% HCl for sediment. The phase separator, reaction coil, heated absorption cell, and pump tubing to the absorption cell were set up and operated according to the manufacturer's specifications.

Statistical Analysis

For each watershed, the distance of each experimental site from the reference site was determined. A simple linear regression was performed to test for a relationship (significant positive slope, $p < 0.05$) between analyte concentrations at an experimental site and distance (km) of that site from the reference site (Snedecor and Davis 1972).

U.S. EPA Ecotox Thresholds and Aquatic Hazard Assessment of Selenium

Ecotox thresholds (ETs) were developed by the U.S. Environmental Protection Agency (US EPA) to identify media-specific contaminant concentrations above which there is sufficient concern regarding adverse ecological effects to warrant further site investigation (US EPA 1996). ETs are used for screening purposes only as a tool to efficiently identify contaminants that may pose a threat to ecological receptors and represent a measure of direct toxicity to exposed organisms based on studies reported in the literature. Surface water ETs, expressed as dissolved concentrations (filtered), are the chronic Ambient Water Quality Criteria, whereas the Effects Range—Low value is used for sediment. Concentrations of elements in dissolved water and sediment in this study were compared to existing ET values for these media. Water concentrations of Se (μg/L) were also evaluated using a published protocol for an aquatic hazard assessment for this element (Lemly 1995): < 1, no hazard; 1–2, minimal hazard; 2–3, low hazard; 3–5, moderate hazard; > 5 high hazard. Sediment concentrations of Se (μg/g dry weight) were similarly evaluated (Lemly 1995): < 1, no hazard; 1–2, minimal hazard; 2–3, low hazard; 3–4 moderate hazard; > 4, high hazard.

Quality Control

Percent recovery of elements in reference solutions analyzed as laboratory control samples averaged 102 ± 14 (SD) for all water and sediment analytical runs. Elements spiked into unfiltered water and digested averaged 97 ± 6% recovery, whereas digested sediment spikes averaged 101 ± 6%. Recoveries of elements spiked into samples or digestates at the instrument as a check on signal enhancement or suppression averaged 100 ± 8% for water and 100 ± 5% for sediment. A synthetic interference check solution containing high concentrations of Al, C, Ca, Cl, Fe, K, Mg, Mo, Na, P, S, and Ti was analyzed to determine how well the ICP-MS was correcting for these elemental interferences on analytes of interest; recoveries of Ag, As, Cd, Cr, Cu, Ni, Pb, and Zn averaged 96 ± 18%, indicating adequate correction for interferences. The dilution percent difference test, which measures the percent difference between a 1× and 5× dilution of a sample as an indication of matrix interference, ranged from 0.2% (As) to 17.2% (Zn) for water samples, with an elemental average of 6.4 ± 4.5%, and 0.1% (As) to 5.9% (Zn) for sediment, with an elemental average of 3.3 ± 2.1%. Zinc in unfiltered water was the only case where the dilution percent difference was > 10, which suggested possible interferents for the element in that matrix. Method precision was determined by duplicate analysis of filtered water samples (relative percent difference, RPD), and triplicate digestion and analysis of unfiltered water and sediments (% relative standard deviation, %RSD). The duplicate analysis of filtered water samples produced acceptable RPD values ranging from 0 (Cu) to 12 (Zn). The %RSD for unfiltered water was excellent (< 5) for all analytes except Pb (41) and Zn (64). For sediment, the %RSD was also good (< 7) for all analytes except Hg, which was 31. The poorer precision results for Pb in unfiltered water and Hg in sediment were largely due to sample concentrations in the replicates approaching the method limit of detection (MLOD) for each element. The poor precision for Zn in unfiltered water was presumably caused by contamination of one of the three replicates during digestion. Chromium concentrations determined by Zeeman furnace atomic absorption spectroscopy for each sample agreed well with ICP-MS results of Cr^{52} for filtered water and sediment but Cr^{53} for unfiltered water. Thus, Cr data for these particular masses were reported for each matrix. Arsenic concentrations determined by flow injection hydride generation atomic absorption spectroscopy agreed well with ICP-MS values, confirming the accuracy of ICP-MS results for this element. MLODs were calculated as $3 \times [(SD_b)2 + (SD_s)^2]^{1/2}$, where SD_b and SD_s were the standard deviations of the blanks and a triplicate analysis of a low level sample or spiked sample. Selected masses and MLODs (μg/L) for unfiltered and filtered water were as follows: Cr^{53}, 1.4; Cr^{52}, 0.51; Ni^{60}, 0.21 and 0.074; Cu^{63}, 0.24 and 0.13; Zn^{66}, 0.42 and 1.0; As^{75}, 0.11 and 0.29; Ag^{109}, 0.19 and 0.044; Cd^{114}, 0.17 and 0.037; and Pb, 0.050 and 0.092. The MLOD (μg/L) for Hg in both filtered and unfiltered water was 1.4, and for Se 0.59 and 0.80. For the sediment matrix, selected masses and MLODs (μg/g dry weight) were as follows: Cr^{52}, 0.18; Ni^{60}, 0.024; Cu^{63}, 0.037; Zn^{66}, 0.12; As^{75}, 0.21; Ag^{109}, 0.011; Cd^{114}, 0.008; and Pb, 0.034. MLODs for Hg and Se in the sediment matrix (μg/g dry weight) were 0.044 and 0.028. Overall, the quality control results were considered to be within the acceptance criteria specified by the analytical laboratory.

Results and Discussion

Water Analyses

Concentrations of selected elements in Black Hills unfiltered and filtered water samples were comparable, with the unfiltered value usually being slightly higher (Table 1). In some cases, unfiltered concentrations for some analytes were substantially higher, as indicated by As concentrations from Site 9 and As and Cu concentrations from Site 8. Silver, Cd, Cr, and Hg concentrations were below the MLOD for most samples. In the Spearfish Creek watershed (Table 1), As concentrations were about 1 μg/L at the Hanna Dam reference site (Site 1), but drainage from WF (Annie Creek, Site 2) showed increased As (51 and 55 μg/L) and Se (5.8 and 6.1 μg/L) concentrations. Selenium concentrations exceeded the EPA ET for this element in water (Se, 5.0 μg/L) and were also classified as a “high hazard” ($>$ 5 μg/L) for Se accumulation into the planktonic food chain with resultant dietary toxicity to fish and aquatic birds (Lemly 1995). The high As concentrations exceeded the Maximum Concentration Limit (MCL) of 50 μg/L in drinking water established by the US EPA. Earlier work conducted in 1989–1991 on Spearfish Creek also indicated As concentrations in water from Annie Creek to be approaching the MCL of 50 μg/L (Driscoll and Hayes 1995). Arsenic concentrations ranged from 4.6 to 9.0 μg/L at sites 3 and 4. These levels are comparable with those found earlier (1989–1991) by Driscoll and Hayes (1995), who described in-stream concentrations of As from Squaw Creek at the “moderate level,” or generally approaching 5 μg/L. Downstream where Spearfish Creek traverses onto plains, As concentrations were at reduced levels, but still greater than those at the reference site. Previous work (Driscoll and Hayes 1995) indicated comparable As concentrations from 1 to 5 μg/L for this downstream area. Cu, Pb (unfiltered), and Ni concentrations showed a slight input from all sites downstream of Hanna Dam. These results suggest contamination of Spearfish Creek waters with As and Se emanating from WF mining operations, and to a lesser extent As from LAC.

Concentrations of As in Annie Creek waters exceeding the MCL of 50 μg/L were unexpected considering the recent 2.5-year clean-up of Annie Creek conducted by WF. This project began in 1992 in agreement with EPA and under the auspices of the Clean Water Act. The clean-up program was a pilot project initiated by WF and EPA in an effort to avoid the substantial costs and 7–10-year clean-up period required under Superfund National Priority List sites (Long and Hagan 1995). WF conducted an extensive study of the Annie Creek area during 1992–1993, including the collection and analysis of surface water, groundwater, sediment, alluvial soils, aquatic biota, and terrestrial biota. Additional studies included identification of uses and users of water along the site, air quality analysis, and rock stability tests. As a result of these studies, it was concluded that natural vegetation and restoration over 80 years had significantly reduced human health and environmental risks. Additional regrading and reclamation work was done in unvegetated areas where As soil concentrations were still between 2,000 and 3,000 ppm. Site engineers expected the vegetation, soil removal, and drainage control measures to naturally decrease concentrations of As in the water from the 50–60 μg/L level (Long and Hagan 1995). The data found in this study indicate that such reduction has not yet occurred. EPA has recently proposed reducing the current As MCL in drinking water from 50 μg/L to 5 μg/L (US EPA 2000a).

In the Whitewood Creek watershed, water collected from Gold Run Creek (Site 8, Table 1), which drains treated effluent from the HS mining facility, indicated substantial increases in As (36 and 49 μg/L), Cu (11 and 28 μg/L), Ni (15 and 20 μg/L), Se (17 μg/L), and Zn (16 and 18 μg/L) concentrations compared to the Whitewood Creek reference site (Site 6). Selenium concentrations exceeded the EPA ET for this element (5.0 μg/L) and were also classified as a “high hazard” ($>$ 5 μg/L) using Lemly’s hazard profile for Se accumulation into the planktonic food chain with resultant dietary toxicity to fish and aquatic birds (Lemly 1995). Arsenic concentrations were also elevated at Site 7 (14 and 16 μg/L) where Whitetail Creek drains GR facilities, and concentrations were even higher at the downstream plains site (Site 9, 30 and 54 μg/L). Cu, Se, and Zn (unfiltered) concentrations showed slight elevation at Site 7, which was also still evident far downstream for Cu and Se (Site 9). These data suggest contamination of Whitewood Creek watershed streams with As, Cu, Ni, and Se possibly from effluent and entrained streambed tailings from previous mining operations at HS. As and Zn and to a lesser extent Cu and Se contamination was also apparent from GR mining operations,

Although elemental concentrations are normally low at downstream plains sites far removed from the mining source, such is not the case for As in Whitewood Creek waters. For a 100-year period from 1876 to 1977, Whitewood Creek was subjected to massive discharges of mine tailings, estimated at

Table 1. Concentrations (μg/L) of silver, arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium, and zinc in Black Hills water samples

Site Description	Site #	Sample Type	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	Hardness (ppm $CaCO_3$)
Spearfish Creek watershed													
Hanna Dam (ref)	1	Unfiltered water	< 0.19	1.2	< 0.16	< 1.4	< 0.24	< 1.4	1.5	< 0.05	< 0.80	4.7	172
		Filtered water	< 0.04	0.9	< 0.04	< 0.51	0.19	< 1.4	1.6	< 0.09	< 0.60	6.4	—
Annie	2	Unfiltered water	< 0.19	55	< 0.16	< 1.4	0.87	1.7	3.1	0.17	5.8	30	320
		Filtered water	< 0.04	51	< 0.04	0.75	0.85	< 1.4	2.9	< 0.09	6.1[ab]	21	—
Squaw	3	Unfiltered water	0.27	6.8	< 0.16	< 1.4	1.4	< 1.4	1.9	0.80	< 0.80	7.3	160
		Filtered water	< 0.04	4.6	< 0.04	0.65	0.72	< 1.4	1.3	< 0.09	< 0.60	5.3	—
Rubicon	4	Unfiltered water	< 0.19	9.0	< 0.16	1.6	3.2	< 1.4	3.8	3.5	0.95	8.9	252
		Filtered water	< 0.04	7.3	0.05	1.2	1.5	< 1.4	3.3	0.16	1.5	11	—
Spearfish (plains)	5	Unfiltered water	< 0.19	3.3	< 0.16	< 1.4	1.3	< 1.4	2.7	0.42	< 0.80	16	340
		Filtered water	< 0.04	2.9	< 0.04	0.70	0.25	< 1.4	2.4	< 0.09	0.65	4.8	—
Whitewood Creek watershed													
Whitewood (ref)	6	Unfiltered water	< 0.19	1.1	< 0.16	< 1.4	< 0.24	< 1.4	1.4	3.6	< 0.80	4.5	248
		Filtered water	< 0.04	1.0	< 0.04	< 0.51	0.26	< 1.4	1.5	< 0.09	< 0.60	2.4	—
Whitetail	7	Unfiltered water	< 0.19	16	< 0.16	< 1.4	1.2	< 1.4	2.0	< 0.71	1.7	22	224
		Filtered water	< 0.04	14	0.14	< 0.51	1.4	< 1.4	2.0	< 0.09	2.0	6.6	—
Gold Run	8	Unfiltered water	0.27	49	< 0.16	< 1.4	28	< 1.4	20	0.77	17	18	1,160
		Filtered water	< 0.04	36	0.28	< 0.51	11[a]	< 1.4	15	< 0.09	17[ab]	16	—
Whitewood (plains)	9	Unfiltered water	< 0.19	54	< 0.16	< 1.4	3.7	< 1.4	7.5	0.13	1.8	3.8	760
		Filtered water	< 0.04	30	< 0.04	0.59	2.5	< 1.4	6.7	< 0.09	2.3	6.4	—
Bear Butte Creek watershed													
Bear Butte (ref)	10	Unfiltered water	< 0.19	3.4	< 0.16	< 1.4	1.0	< 1.4	2.8	0.21	< 0.80*	22	100
		Filtered water	0.09	1.9	0.09	< 0.51	0.94	< 1.4	2.3	< 0.09	< 0.60	13	—
Ruby	11	Unfiltered water	< 0.19	2.5	< 0.16	< 1.4	5.4	< 1.4	4.2	0.32	< 0.80	8.1	200
		Filtered water	0.05	1.7	0.21	< 0.51	3.6	< 1.4	3.4	< 0.09	< 0.60	11	—
Bear Butte (plains)	12	Unfiltered water	< 0.19	3.0	< 0.16	< 1.4	1.7	< 1.4	7.6	1.3	3.0	9.2	760
		Filtered water	< 0.04	2.4	< 0.04	0.85	1.4	< 1.4	6.4	0.13	2.9	2.6	—
Ecotox threshold		Filtered water	—	190	1.0[c]	10[c]	11[c]	1.3	160[c]	2.5[c]	5.0	100[c]	

[a] Concentration equals or exceeds EPA Ecotox threshold

[b] Concentration exceeds high hazard profile for selenium accumulation from water into the planktonic food chain and resultant dietary toxicity to fish and aquatic birds

[c] Hardness-dependent ambient water quality criterion (100 mg/L as $CaCO_3$ used)

* Elemental concentrations significantly increasing with distance from the reference site ($p < 0.05$)

100 million metric tons, which contained arsenopyrite and other metallic sulfide minerals (Fuller *et al.* 1989). About 13% of the mine tailings were deposited along the Whitewood Creek floodplain, and about 29% of tailings delivered by Whitewood Creek were deposited along the Belle Fourche River floodplain (Figure 2; Marron 1992). Because the sediments were deposited by natural flow, they are very susceptible to resuspension and downstream movement during periods of high discharge when sediment enters the flow from streambed scouring, bank collapse, or by input from overland runoff. The source of the relatively high concentrations of the element at Site 9 was due to the slow release of As from flood plain deposits of finely ground mill tailings into ground and surface waters (Fuller *et al.* 1989). Stream input of As results from the seepage of As- and Fe-bearing reducing ground water out of the flood-plain aquifers following periods of high stream discharge. The As release occurs through oxidation of FeAsS and/or by dissolution of or desorption from As-rich ferrihydrite. The dissolved As derived from seepage of ground water and desorbed from streambed material has reached levels of 130 μg/L in Whitewood Creek (Goddard 1989b).

Concentrations of elements in streams of Bear Butte Creek watershed are indicated in Table 1. In contrast to the other two watersheds, As concentrations at downstream experimental sites are comparable to those found at the reference site. Some Cu contamination is evident in water from Site 11, just before Ruby Gulch confluences with Bear Butte Creek. Ni and Se were slightly elevated at the downstream plains site (Site 12). Linear regression statistics indicated that only Se concentrations at Site 12 were increased significantly ($p < 0.05$) with distance from the reference site (Site 10). The data suggest contamination of Bear Butte watershed streams with Cu, Se, and Ni from GE mining operations.

Sediment Analyses

At each site, a sample of sediment was also collected, and concentrations of acid-extractable elements in these samples are indicated in Table 2. Although a one-time sampling event of water from streams of Spearfish Creek watershed suggested little or no contamination from mining activities regarding Ag, Cd, Cr, Hg, Ni, and Pb, the analyses of correlated sediment

Table 2. Concentrations (µg/g dry weight) of elements in sediments from the Black Hills

Site Description	Site #	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
Spearfish Creek watershed											
Hanna Dam (ref)	1	0.09	10[a]	0.23	9.0	11	0.09	10	8.5	1.5	38
Annie	2	0.60	1,951[a]	0.58	9.2	13	0.38[a]	14	35	2.0	202[a]
Squaw	3	2.3	211[a]	3.2[a]	42	114[a]	0.33[a]	57[a]	55[a]	2.2	231[a]
Rubicon	4	1.7	41[a]	2.6[a]	17	32	0.21[a]	40[a]	176[a]	4.0[b]	157[a]
Spearfish (plains)	5	0.18	24[a]	0.35	7.8	7.8	0.09	11	25	0.79	50
Whitewood Creek watershed											
Whitewood (ref)	6	0.13	10[a]*	0.27	10	13.3	0.05	11	16	1.2**	50
Whitetail	7	2.1	777[a]	1.2[a]	22	41[a]	0.45[a]	35[a]	77[a]	1.4	250[a]
Gold Run	8	1.4	417[a]	0.73	30	90[a]	1.0[a]	37[a]	130[a]	1.9	221[a]
Whitewood (plains)	9	0.67	1,083[a]	0.59	14	43[a]	0.59[a]	27[a]	18	2.9	83
Bear Butte Creek watershed											
Bear Butte (ref)	10	0.44	58[a]	0.46	19	45[a]	0.07	64[a]	12	1.4	97
Ruby	11	0.57	62[a]	1.4[a]	13	159[a]	0.28[a]	33[a]	72[a]	0.68	120
Bear Butte (plains)	12	0.57	23[a]	1.1	12	36[a]	0.25[a]	17	47[a]	1.4	110
Ecotox threshold		—	8.2	1.2	81	34	0.15	21	47	—	150

[a] Concentration equals or exceeds EPA Ecotox threshold (effects range—low value)

[b] Concentration moderate hazard for selenium accumulation from sediments into the benthic food chain and resultant dietary toxicity to fish and aquatic birds

* Elemental concentrations significantly increasing with distance from the reference site ($p < 0.05$)

** Elemental concentrations significantly increasing with distance from the reference site ($p < 0.01$)

samples indicated otherwise. There was a trend in elemental concentrations in sediment which ranged from lowest at the reference site, gradually increasing to a maximum at one of the experimental sites, and then decreasing again at the downstream plains site (Table 2). Highest concentrations of Ag, Cd, Cr, Cu, Ni, and Zn were observed in sediment from Squaw Creek (Site 3). Lead and Se concentrations were most elevated in sediment from Site 4 (Rubicon Gulch), whereas As and Hg were highest in sediment from Annie Creek (Site 2). Whereas the Site 1 As concentration just exceeded the ET of 8.2, concentrations at all experimental sites were markedly above this value. Concentrations of Cd, Cu, Hg, Ni, Pb, and Zn at various experimental sites also exceeded the ET values for these elements. The concentration of Se in sediment from Rubicon was classified as a "moderate hazard" for Se accumulation into the benthic food chain with resultant dietary toxicity to fish and aquatic birds (Lemly 1995). These results suggest contamination of sediment in Rubicon Gulch, Squaw Creek, and Annie Creek from mining-related activities at LAC and WF. The movement of such sediment during hydrologic events, *i.e.*, flooding, scouring, etc., is expected to provide contaminated sediment to Spearfish Creek.

The trend in concentrations of elements in the sediment being minimal at the reference site, maximized at an experimental site, and decreasing out to the plains site, which was observed for Spearfish Creek watershed, was also apparent for some elements in the Whitewood Creek watershed (Table 2). Although the water data from Whitewood Creek suggested contamination from just four elements, the sediment results indicated contamination from all elements studied. Highest concentrations (µg/g) of Cr (30), Cu (90), Hg (1.0), Ni (37), and Pb(130) were observed in sediment from Gold Run Creek (Site 8). Cd (1.2 µg/g), Zn (250 µg/g), and Ag (2.1 µg/g) concentrations were most elevated in sediment from Whitetail Creek (Site 7), whereas As and Se concentrations (1,083 and 2.9 µg/g) were observed highest at the Site 9 plains location (Whitewood at plains). The high concentration of As in sediment far downstream from mine sources is likely due to the discharge of some 100 million metric tons of mining and milling wastes into Whitewood Creek between 1876 and 1977 (Fuller *et al.* 1989). Goddard (1989a) found that As concentrations were still about 400 µg/g near the mouth of Whitewood Creek, as compared to 9.2 µg/g for sediments from an uncontaminated area. Linear regression statistics indicated that only As and Se concentrations at experimental sites in Whitewood Creek Watershed were increasing significantly ($p < 0.05$, Table 2) with distance from the reference site (Site 6). Table 2 indicates sediment concentrations of numerous metals (As, Cu, Hg, Ni, Pb, and Zn) that exceeded EPA ET values. The data suggest that sediment in Whitewood Creek is contaminated with elements from mining-related activities occurring at both GR and HS. Sediment contamination on the plains is expected to be the result of historical mine tailing discharge.

Of the three watersheds in this study, the Bear Butte Creek watershed indicated the least contamination of water and sediment with elements related to mining activities. Sediment data from Ruby Creek (Site 11, Table 2) indicated little or no apparent contribution from As, Ag, Cr, Ni, Se, or Zn, as the reference site concentrations (Site 10) of these elements were equal to or greater than the Site 11 concentrations. However, Site 10 concentrations of As, Cu, and Ni were unexpectedly much higher ($> 4\times$) compared to levels of these elements at the other reference sites (Sites 1 and 6). The arsenic concentration of 58 µg/g is well beyond the 9.2 µg/g concentration given by Goddard (1989a) for sediment from a noncontaminated area. In retrospect, Site 10 was probably not a good selection as a reference site for these elements; possible sources of these contaminants to the sediment have not been identified. Cu and Pb from GE mining operations were the major sources of elemental contamination in Ruby Creek sediment, and to a lesser extent Cd and Hg. These results suggest possible influx of these elements into Bear Butte Creek as they are carried in sediment being moved in association with hydrologic events. As with the Whitewood Creek watershed, there were numerous instances where sediment concentrations of As, Cd, Cu, Hg, Ni, and Pb exceeded EPA ETs (Table 2).

In the late 1990s the Brohm Mining Corporation planned additional mining activities in the Bear Butte Creek Watershed by proposing an expansion of the Anchor Hill gold mining operations at the Gilt Edge Mine (U.S. Dept. Agriculture 1997). However, the mining company was closed prior to starting the expansion. The Gilt Edge Mine site is presently under the jurisdiction of the State of South Dakota and has been placed on the US EPA Superfund National Priorities List for consideration as a Superfund site (US EPA 2000b).

Conclusions

Analysis of water and sediment from Spearfish Creek, Whitewood Creek, and to a lesser extent Bear Butte Creek indicated contamination from various elements associated with gold mining operations in the Black Hills when compared to reference sites. As still appears to be a major contaminant problem in water and sediment from Annie Creek and Whitewood Creek, despite substantial clean-up and reclamation efforts. Concentrations of numerous elements in sediment (As, Cd, Cu, Hg, Ni, Pb, Zn) were found to exceed EPA ETs, indicating the possibility of adverse ecological affects. Another indication of adverse ecological affects was indicated from concentrations of Se in water from Annie Creek and Gold Run that exceeded the EPA ET and were classified as a high hazard for dietary toxicity and reproductive failure in fish and birds. Similarly, one sediment from Rubicon Creek indicated a moderate hazard for Se accumulation into the benthic food chain and resultant dietary toxicity to fish and aquatic birds. Such indications of adverse ecological affects point to the need for future research that addresses the downstream biological impacts of metals contamination from mining operations. Examples of such research are: (1) an evaluation of the presence, movement, and bioaccumulation of metals contamination in all compartments of the food web through a field survey and laboratory analysis of all trophic level components; (2) an evaluation of the bioavailability of metal residues and the toxicity of contaminated sediment to sensitive benthic invertebrates typical of subject streams through laboratory exposure studies; and (3) an evaluation of the effects of invertebrate diet contaminated with metals on salmonid and other fishes typical of subject area streams through laboratory exposure studies. Data from these studies would help formulate a more accurate ecological risk assessment for each watershed in the study area, thus providing useful information for resource managers.

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