

Impacts of Historical Mining on Aquatic Ecosystems—An Ecological Risk Assessment

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Chapter D of

Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado

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Chapter D

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Abstract

We evaluated ecological risks of historical mining to the aquatic biota of the Animas River watershed study area, based on a synthesis of studies of the geology, hydrology, water quality, and biology of the watershed. The risk assessment summarizes the spatial and temporal variation of chemical stressors relative to exposure levels associated with acute or chronic toxic effects, with the goal of characterizing risks on the watershed scale to provide guidance for remedial action. We determined that exposure to dissolved or colloidal metals (and acidity) in streams poses the greatest risk to aquatic biota. Exposure to aluminum, cadmium, copper, and zinc was characterized based on synoptic sample collections made during autumn low-flow periods of 1996 to 2000, plus information on seasonal variation of metal concentrations available for a limited number of stations. Toxicity risks associated with ranges of concentrations of each metal were compared with chronic and acute water-quality criteria for protection of sensitive aquatic biota and with chronic and acute toxicity thresholds for brook trout (*Salvelinus fontinalis*), the predominant fish species in the watershed. All of the metals studied occurred at potentially toxic levels in acid (pH<4.5) stream reaches, but the risks posed by these metals in neutral (pH>6.5) stream reaches varied widely. Risks of acute aluminum toxicity to brook trout and other stream biota were limited to acidic stream reaches and to their mixing zones with neutral streams, whereas risks of chronic toxicity associated with aluminum colloids may occur in neutral stream reaches. Zinc, and to a lesser extent cadmium, occurred widely in neutral streams well downstream of source area at levels that pose risks of toxicity to sensitive aquatic biota, but not to brook trout. Copper may pose greater risks of direct toxicity to brook trout, but these risks decrease rapidly downstream from source areas. Toxicity risks from all four metals are greatest during late winter, especially in stream reaches that experience seasonal acidification. The status of fish and benthic invertebrate communities in the watershed generally reflected the toxicity risks for the metals studied, although the status of biota in some stream reaches suggested greater impacts than were evident based on risks determined for the autumn sampling period. Overall risks were characterized for each reach, and reaches were aggregated

into larger stream segments with similar risk levels. Greater detail of sources and severity of risks is included for stream segments in the Moderate Risk category (chronic toxicity of one or two metals) and the Severe Risk category (risks from several metals, including risk of acute toxicity), where remediation of mining impacts may result in noticeable improvement in the productivity and taxonomic richness of stream biotic communities.

Introduction

This chapter presents an assessment of ecological risks posed by historical mining activities to aquatic ecosystems of the Animas River watershed study area. The U.S. Environmental Protection Agency (USEPA, 1998) established a framework for ecological risk assessment that involves three steps: problem formulation; risk analysis (characterization of exposure and ecological effects); and risk characterization. This process is intended to provide a scientific basis for risk-management decisions, based on estimates of exposure to environmental stressors and estimates of stressor levels associated with adverse effects on target biota. The research conducted during this study provides an extensive scientific basis for risk assessment, including:

- Measures of spatial and temporal variation in metal concentrations
- Estimates of premining baselines of water and sediment quality
- Studies of toxic effects of water and sediment from the watershed on aquatic biota
- Estimates of thresholds for toxic effects of metals of concern on resident biota
- Surveys of the status of resident fish and invertebrate communities.

A synthesis of ecological risks in the watershed, based on these studies, provides a basis for decisions about remediation by public and private land managers.

Purpose and Scope

This report summarizes four steps in the ecological risk assessment of mining impacts on biota of the study area:

- Develop a conceptual model of ecosystem stressors and exposure pathways for biota
- Analyze risks by comparing levels of exposure relative to thresholds for toxic effects
- Compare predictions of toxicity with current status of aquatic community
- Summarize ecological risks and prospects for remediation by stream segment.

Ecosystem Stressors and Exposure Pathways

The aquatic ecosystems of the Animas River watershed study area have developed in response to a variety of natural and anthropogenic stressors. Over a geologic time frame, the alteration of volcanic and sedimentary rocks by hydrothermal processes resulted in the formation of orebodies containing economically valuable minerals and development of extensive areas of naturally acidic rocks and soils (Bove and others, this volume, Chapter E3). This geologic setting resulted in elevated background levels of acid and toxic metals in some stream reaches (Mast and others, this volume, Chapter E7) that are incompatible with establishment of diverse and productive aquatic communities. Even in streams less affected by high background levels of acid and metals, the high altitude of the watershed and barriers to colonization by some stream biota contributed to a relatively depauperate aquatic community. Only a very few native fish species occurred upstream from the Animas River canyon before European settlement, including Colorado River cutthroat trout (*Oncorhynchus clarki pleuriticus*) and possibly mottled sculpin (*Cottus bairdi*). After the area was settled by miners in the late 19th century, native stream communities were altered by the introduction of non-native fish species, notably brook trout (*Salvelinus fontinalis*), rainbow trout (*Oncorhynchus mykiss*), and brown trout (*Salmo trutta*).

The development of extensive mining and associated activities in the study area led to substantial alteration of premining aquatic habitat and degradation of water quality, with severe consequences for stream biological communities. Early mining and milling practices involved deposition of large quantities of fine-grained tailings into active stream channels (Jones, this volume, Chapter C; Church, Fey, and Unruh, this volume, Chapter E12), resulting in extensive alteration of in-stream substrata (previously dominated by coarse bed materials) and destruction of riparian habitats (Milhous, this volume, Chapter E21; Vincent and Elliott,

this volume, Chapter E22). During recent decades, improved mining practices and cleanup efforts have led to reduced loadings of tailings and mine wastes into stream habitats.

Mining activities also led to greatly increased acid drainage, the result of weathering of sulfide minerals in mines and in deposits of mine wastes (Nash and Fey, this volume, Chapter E6; Mast and others, this volume). Increased levels of acid and toxic metals, including aluminum, zinc, copper, and cadmium (Wright, Simon, and others, this volume, Chapter E10), have probably eliminated fish from some stream reaches and resulted in reduced productivity and diversity of aquatic communities in almost all stream reaches downstream of mining activities (Besser and Brumbaugh, this volume, Chapter E18; Besser and Leib, this volume, Chapter E19; Anderson, this volume, Chapter E20). Increased loadings of acid and metals also contribute to degradation of physical habitat, as a result of the precipitation of large quantities of aluminum and iron as insoluble hydrous oxides in neutral-pH waters downstream of acid tributaries (Kimball and others, this volume, Chapter E9; Church, Fey, and Unruh, this volume). These precipitates coat stream substrata and fill interstitial spaces in streambeds, smothering biofilm communities and making benthic habitats unavailable for benthic organisms and spawning trout. Although the ecological effects of iron and aluminum precipitates on benthic habitats are important, they are difficult to distinguish from the toxic effects of metals, which typically occur in the same stream reaches. Therefore, this analysis will principally focus on the exposure of biota to metals and linkages between metal exposure and toxicity.

In streams directly affected by metal-rich acid drainage, most toxicity can be attributed to exposure to dissolved metals. Toxicity studies demonstrated that stream water sampled at several gauging stations near Silverton, Colo., was highly toxic to fish and invertebrates in short-term (7–14 days) exposures (Besser and Leib, this volume; Fey and others, 2002; Peter Butler, Robert Owen, and William Simon, Unpublished report to Colorado Water Quality Control Commission, Animas River Stakeholders Group (ARSG), 2001). Results of toxicity tests with stream water were compared to toxicity thresholds derived from laboratory toxicity tests and to data on seasonal dissolved metal concentrations at these gauging stations. Together, these data were used to develop toxicity models that explained much of the observed toxicity at these sites in terms of toxicity of dissolved metals (Besser and Leib, 1999; Besser and Leib, this volume). Studies of other streams affected by metal-rich acid drainage suggest that some metals, notably aluminum, may be most toxic in acid-neutral mixing zones, where aluminum speciation changes rapidly from dissolved metal ions to colloidal particulates (Henry and others, 1999; Verbost and others, 1995; Kimball and others, this volume). Although no on-site toxicity studies have evaluated toxicity in mixing zones in the watershed study area, laboratory studies with brook trout exposed to aluminum found that observed toxicity corresponded closely to concentrations of dissolved (filtered with 0.45 μm (micrometer) filter) aluminum (Besser and others, 2003). In contrast, studies of aluminum-rich colloids collected from the Animas River

(station A72, downstream of Mineral Creek) found no toxicity to a mayfly (*Baetis tricaudatus*) exposed to colloid suspensions that were 15–20 times more concentrated than ambient stream water (Unpublished report to U.S. Department of Agriculture (USDA) Forest Service, San Juan/Rio Grande National Forest, Hydrosphere Resource Consultants, 2001).

Although most toxic effects on stream biota of the study area can be attributed to dissolved metals, particulate metals in sediment and in components of stream food webs may contribute to chronic toxicity in mining-impacted streams. For benthic invertebrates, exposure to metals in periphyton (the layer of algae, microbes, and associated inorganic deposits that develops on surfaces of stream beds) or in streambed sediment may also contribute to overall toxic effects of metals. Studies of mayflies (*B. tricaudatus*) grazing on periphyton from the Animas River at Elk Park found reduced growth rates compared to mayflies fed periphyton from nearby Elk Creek (Unpub. report to USDA Forest Service, Hydrosphere, 2001). Elevated levels of metals occur in fine-grained sediment well downstream of metal loadings associated with mining (Church and others, 1997). Concentrations of several metals (As, Cu, Cd, Zn, Pb) determined in active stream sediments from the Animas River and the Cement and Mineral Creek basins frequently exceeded geochemical baselines, which were established for each basin based on sediment cores collected from premining terrace deposits (Church, Fey, and Unruh, this volume). The percent of stream-sediment samples exceeding baselines was greatest for copper (60–71 percent of samples across the three basins) and lowest for cadmium (10–56 percent). Greatest enrichment ratios (maximum sediment concentration/maximum baseline concentration) occurred in the Mineral Creek basin (enrichment ratios were 7 for zinc and 8 for arsenic and copper) and in the upper Animas River basin (enrichment ratios were 14 for copper and 15 for lead). The frequency of sediment samples exceeding consensus sediment-quality guidelines, which estimate the probability of toxic effects in benthic organisms (MacDonald and others, 2000), was substantially greater for postmining stream sediment than for premining sediment. Toxic effects have been reported for benthic invertebrates exposed to fine-grained streambed sediment from Cement and Mineral Creeks and the Animas River near Silverton (Besser, Allert, and others, 2001). However, toxic effects of sediment exposure were less severe than those resulting from exposure to stream water, and the presence of sediment was found to reduce the toxicity of overlying stream water (Besser and Leib, this volume).

Studies in other watersheds affected by metal mining have documented toxic effects in trout fed diets of metal-contaminated invertebrates (Woodward and others, 1994; Farag and others, 1999). A survey of metal concentrations in components of stream food webs of the Animas River watershed (Besser, Brumbaugh, and others, 2001; Besser and Brumbaugh, this volume) reported high levels of dietary metal exposure and risks of chronic dietary toxicity. This study noted different patterns of metal bioaccumulation and trophic transfer for different metals. Lead and zinc accumulated predominantly at lower trophic levels (as, invertebrate

grazers and detritivores), reflecting high uptake from water and detritus. Highest concentrations of cadmium and copper occurred in higher order consumers (invertebrate predators and fish), suggesting a greater contribution of trophic transfer. Elevated concentrations of copper in tissues of brook trout and in benthic invertebrates from some reaches of the Animas River suggest that these fish are exposed to metal concentrations (via both water and diet) that are associated with chronic toxicity (Besser, Brumbaugh, and others, 2001; Besser and Brumbaugh, this volume).

Risk Analysis Approach

This analysis assumes that direct toxic effects of metals in stream water are the most important measure of ecological risks associated with mining in the Animas River watershed study area. The most definitive characterization of the toxicity of stream water would be achieved by exposing aquatic organisms (belonging to appropriate taxa) to water from sites of concern. However, direct toxicity testing is not a practical approach for assessing toxicity risks at the watershed scale, as toxicity can be expected to vary widely among locations, through time, and among taxa. We characterized toxicity risks based on a series of synoptic studies of metal concentrations in stream water during autumn low-flow conditions in the years 1996–2000 (Kimball and others, this volume; Sole and others, this volume, Chapter G), which provide data of consistent quality that covers a high proportion of stream reaches in the watershed. Dissolved metal concentrations (concentrations determined in samples filtered through 0.45 μm membranes) were used to evaluate metal toxicity, except in specific cases. To interpret these data, we assumed that dissolved metal concentrations during the autumn low-flow period are typically intermediate between annual minima, which usually occur during spring snowmelt, and annual maxima, usually in late winter (Besser and Leib, this volume; Wright, Simon, and others, this volume). Because autumn is not the period of greatest dissolved metal concentrations, risks estimated for autumn conditions underestimate overall toxicity risk associated with dissolved metals.

Ecological risks posed by dissolved metals are characterized relative to two sets of thresholds for acute and chronic toxicity: (1) national water-quality criteria established by USEPA (1985a, 2002), which are intended to provide protection for 95 percent of aquatic taxa; and (2) thresholds derived from toxicity tests with brook trout, the predominant fish species in the watershed, under water-quality conditions representative of the watershed. Acute toxicity thresholds for brook trout were defined as one-half the median lethal concentration (LC50) and chronic toxicity thresholds for brook trout were defined as the geometric mean of no-observed-effect concentration (NOEC) and lowest-observed-effect concentration (LOEC) for survival or growth. These procedures are based on guidelines for derivation of water-quality criteria (USEPA, 1985a). Because toxicity of cadmium, copper, and zinc is known to vary with differences in water quality, water-quality criteria and brook trout toxicity

thresholds were adjusted for differences in water hardness, using the slopes of empirical hardness/toxicity relationships derived by USEPA (2002) or Robert Andrew and others (unpub. report to U.S. Environmental Protection Agency; Great Lakes Environmental Center, 1998). To simplify the calculation and presentation of toxicity risks, adjustments for hardness were made on typical hardness ranges for major stream segments, rather than for individual sample points (table 1).

Risks posed by acidity and individual metals are summarized in a series of ribbon maps (figs. 1–6). Stream reaches are color coded to represent different degrees of toxicity risk. Break points for stream reaches were based on hydrologic features, such as confluence of tributaries, and on the distribution of sample stations. To increase clarity of the ribbon maps, color coding was extrapolated between available data points, except where data were not available for long stream reaches. However, because of the uneven distribution of sampling points, metal concentrations (and therefore toxicity risks) may vary substantially within reaches designated with the same color code. Color codes for different risk categories, in order of increasing risk, are as follows: blue (no toxicity expected; metal concentration below lowest toxicity threshold), green (exceeds chronic water-quality criterion), yellow (exceeds acute water-quality criterion), orange (exceeds chronic brook trout toxicity threshold), and red (exceeds acute brook trout toxicity threshold). Not all risk levels are defined in table 1 or illustrated on all ribbon maps, if a threshold for a greater risk category for a particular metal was less than or equal to that for a lesser risk category. For example, stream segments would

not be colored yellow if the acute water-quality criterion for a metal (in a particular hardness range) was greater than the chronic toxicity threshold for brook trout.

Risks of Metal Toxicity

Aluminum

Aluminum toxicity is a concern in streams receiving acid drainage because the solubility and toxicity of aluminum are strongly related to pH. The speciation of aluminum is complex, and relationships between measured dissolved or total aluminum concentrations and toxicity are poorly understood. Toxic effects of aluminum and acidity are indistinguishable at very low pH (<4.5; Gensemer and Playle, 1999), and no fish and few macroinvertebrates can tolerate the highly acidic conditions that occur in most of the mainstem of Cement and Mineral Creeks and some of their tributaries (fig. 1). Risk of aluminum toxicity is also great in the moderately acidic pH range, from 4.5 to 6.5, where the speciation of aluminum shifts from free ions to monomeric and polymeric complexes, and eventually to colloidal hydrous oxide precipitates (Gensemer and Playle, 1999). Most published toxicity studies with aluminum in moderately acidic waters are of questionable applicability to streams in the watershed study area because they were conducted in dilute soft waters (for example, Cleveland and others, 1989; Mount and others, 1988; Ingersoll and others, 1990). However, recent

Table 1. Toxicity thresholds used to define risk categories for ribbon maps (figs. 1–6).

[WQC, water-quality criteria (USEPA, 2002, or unpub. report to USEPA, Great Lakes Environmental Center, 1998); hardness expressed in mg/L CaCO₃; toxicity thresholds expressed as dissolved metal except where noted; --, no threshold listed for a category or thresholds were poorly defined or were greater than those for a more severe risk category; *, dissolved aluminum risk category was assumed to be “red” if pH<4.5, regardless of measured aluminum concentrations, due to combined toxic effects of acid and aluminum. See text for derivation of thresholds]

Metal	Water quality	Toxicity threshold (µg/L)				
		Blue (low risk)	Green (Chronic WQC)	Yellow (Acute WQC)	Orange (Brook trout chronic)	Red (Brook trout acute)
Aluminum (dissolved)	pH >4.5*	<83	--	--	83	122*
Aluminum (total)	pH = 4.5–6.5	<87	87	--	110	218
	pH >6.5	<87	87	--	122	1,800
Cadmium	Hardness = 50	<0.15	0.15	1.0	--	2.2
	Hardness = 90	<0.23	0.23	1.8	--	3.3
	Hardness = 140	<0.23	0.31	2.8	4.6	5.0
	Hardness = 400	<0.64	0.65	7.7	10	15
Copper	Hardness = 50	<2.7	2.7	--	--	7.0
	Hardness = 90	<3.0	3.0	--	7.8	9.8
	Hardness = 140	<3.3	3.3	--	8.4	15
	Hardness = 400	<3.9	3.9	--	10	41
Zinc	Hardness = 50	<65	--	65	698	912
	Hardness = 90	<107	--	107	1,148	1,500
	Hardness = 140	<156	--	156	1,670	2,182
	Hardness = 400	<379	--	379	4,060	5,311

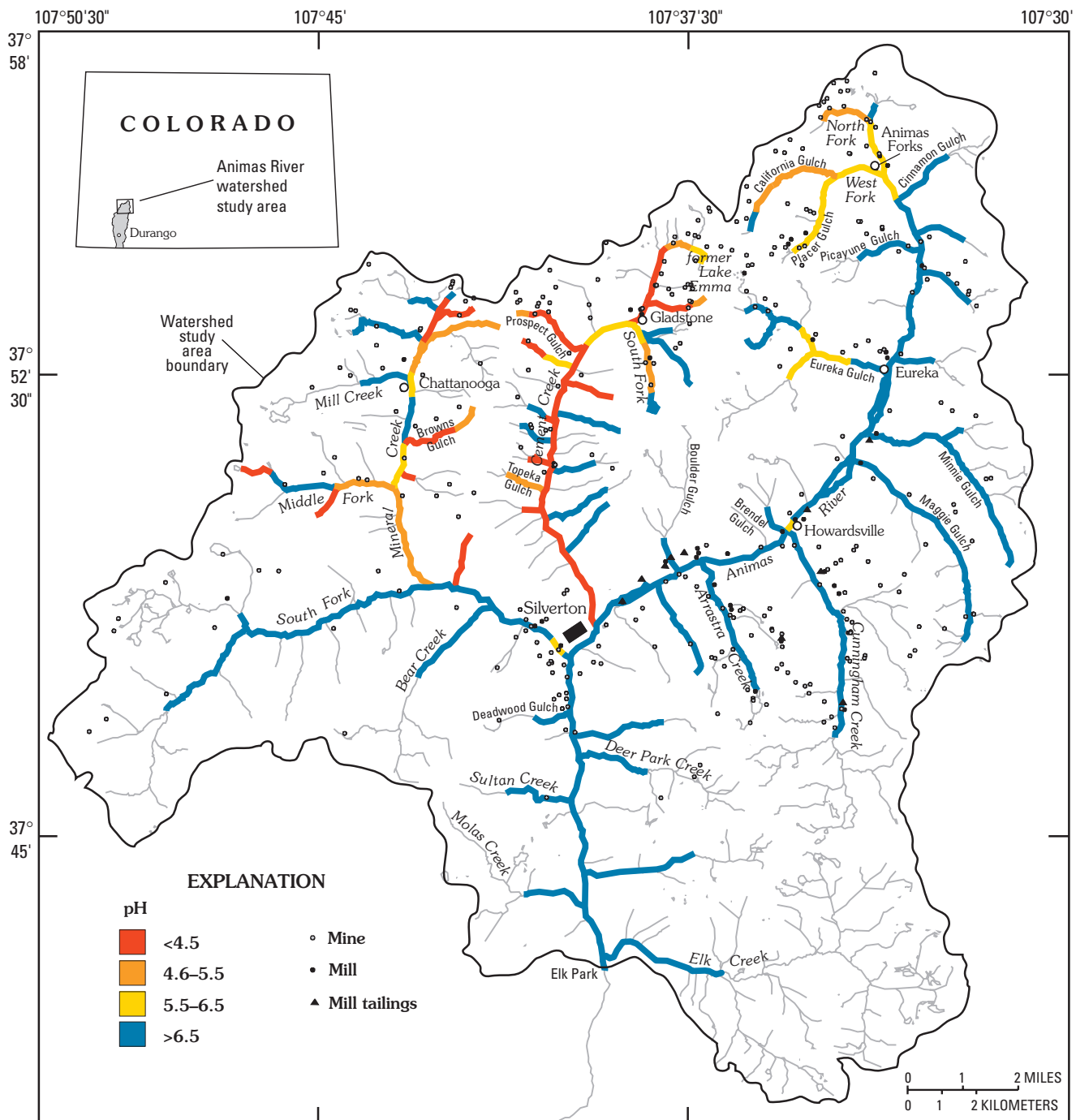


Figure 1. pH in streams, Animas River watershed study area, at autumn low flow.

toxicity studies with brook trout, conducted at relevant pH and water quality (pH=5.3, calcium=40 mg/L) demonstrated lethal effects of low concentrations of dissolved aluminum (96-hr LC50=243 µg/L; 7-day LC50=166 µg/L; Besser and others, 2003). In the watershed study area, dissolved aluminum concentrations exceed these thresholds in almost all stream reaches with pH <6.5, suggesting that risks of aluminum toxicity to brook trout are high in virtually all of Cement Creek, in Mineral Creek upstream of the South Fork, and in the Animas River upstream of Cinnamon Gulch (fig. 2).

In neutral-pH reaches, dissolved aluminum concentrations are low and virtually all aluminum occurs in the suspended particulate phase, except in localized reaches, such as the braided reach of the Animas River downstream from Eureka and in the Animas River near the mill tailings ponds at Howardsville. Colloidal aluminum particles persist in suspension for long distances downstream of mixing zones (Kimball and others, 1995; Kimball and others, this volume), although the toxicity of colloidal aluminum to biota has been little studied. USEPA (1988, 2002) established

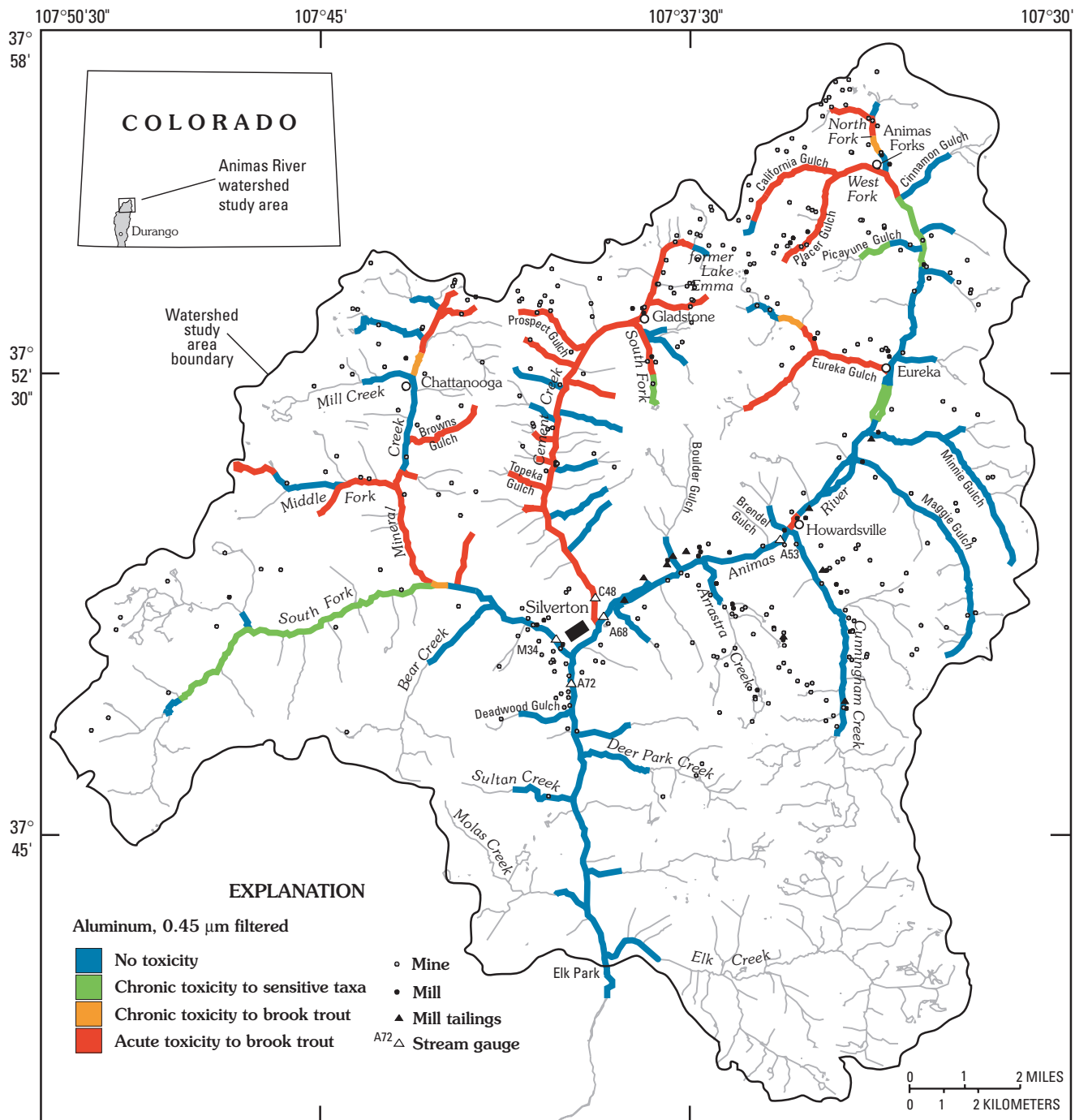


Figure 2. Toxicity risk from dissolved (0.45 μm filter) aluminum in streams, at autumn low flow.

water-quality criteria for total (unfiltered) aluminum in waters with $\text{pH} > 6.5$ (table 1) for protection of sensitive aquatic biota, but few studies have reported the toxicity of aluminum in unfiltered water to brook trout at neutral pH . Cleveland and others (1989) reported significant (24 percent) reductions in growth in larval brook trout exposed to 169 $\mu\text{g/L}$ total aluminum at pH 6.5 for 60 days, and Freeman and Everhart (1971) reported severe growth reductions in brook trout during chronic exposures to 514 $\mu\text{g/L}$ total aluminum

at pH 7.0. In contrast, Decker and Menendez (1974) reported low acute toxicity of aluminum to juvenile brook trout at neutral pH (96-hr $\text{LC}_{50} = 3,600 \mu\text{g/L}$ total aluminum). These limited data suggest that significant risks of chronic aluminum toxicity to brook trout occur for several neutral- pH reaches, including South Fork Mineral Creek, lower Mineral Creek, the reach of the Animas River downstream of Eureka, and the Animas River downstream of Mineral Creek (fig. 3).

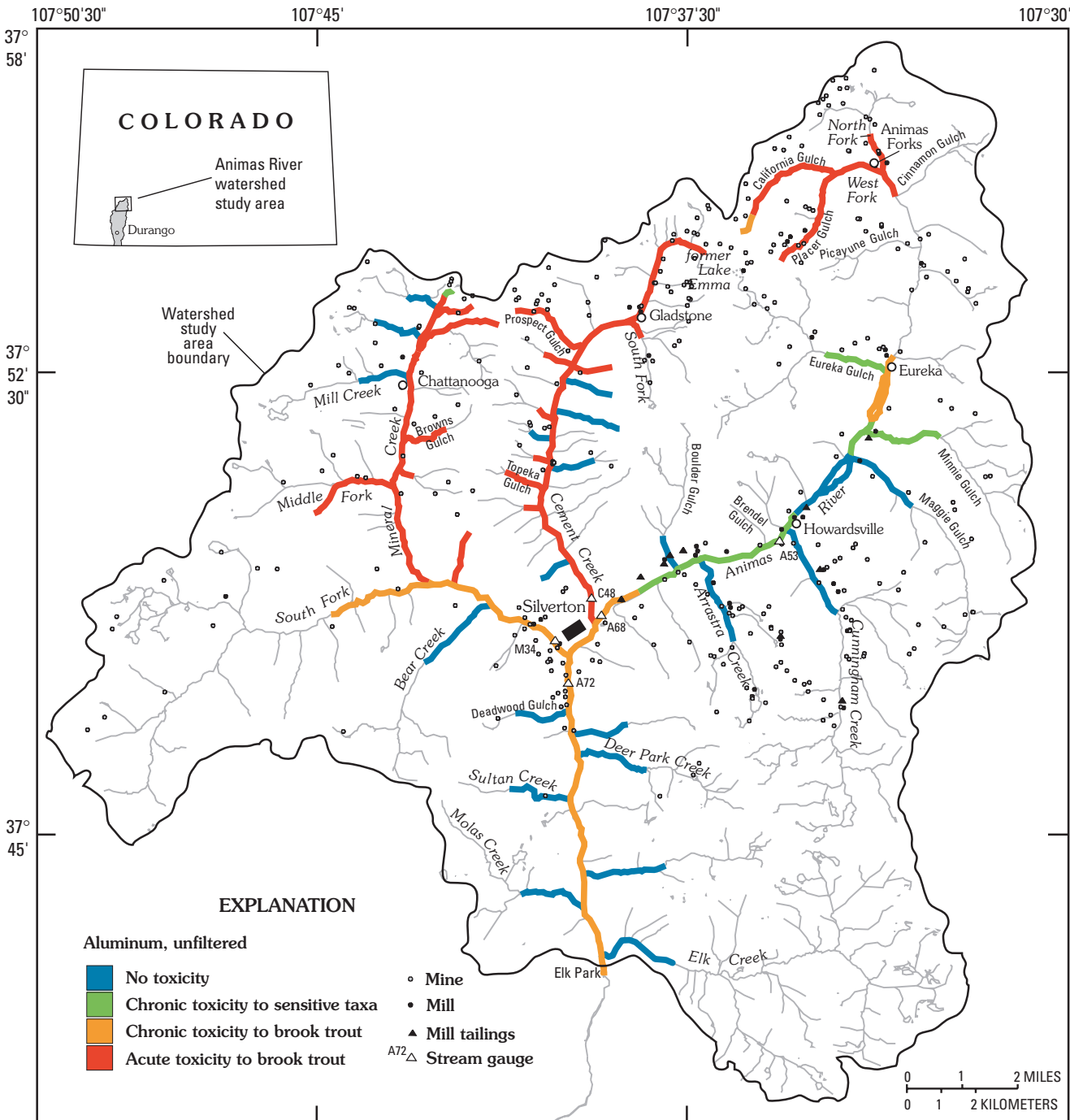


Figure 3. Toxicity risk from total (unfiltered) aluminum in streams, at autumn low flow.

Zinc

Zinc toxicity has been a principal concern in planning for remediation of mining effects in the study area (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001). Existing water-quality criteria for zinc are based on toxicity tests with many aquatic taxa, across a wide range of water-quality conditions (USEPA, 1987, 1996). In addition, we derived toxicity thresholds for brook trout based on acute and

chronic toxicity studies in test water representative of conditions in the Animas River near Silverton (Besser, Allert, and others, 2001; Besser and Leib, this volume). High concentrations of zinc are acutely toxic to aquatic biota, but chronic toxicity is typically not a concern, because fish and other organisms can regulate concentrations of this essential element at sublethal concentrations (table 1). Zinc is highly soluble in stream water, as reflected in the occurrence of dissolved zinc concentrations greater than water-quality criteria in all mainstem reaches of the

Animas River, Mineral Creek, and Cement Creek in the study area (fig. 4). Exceedances of these criteria indicate a substantial risk of zinc toxicity to sensitive taxa throughout much of the study area. In contrast, zinc toxicity is not a significant concern in streams that drain subbasins with less acidic water and less mining activity. Because brook trout are relatively insensitive to zinc toxicity (Besser and Leib, this volume), zinc concentrations during the autumn low-flow period are generally below thresholds for direct toxic effects on brook trout, except in a few acid stream reaches. Models of seasonal variation of

dissolved zinc concentrations at three gauging stations near Silverton found that concentrations peaked in March or April, before the onset of substantial snowmelt runoff, at levels two to three times greater than those in September (Besser and Leib, this volume). However, modeled dissolved zinc concentrations marginally exceeded this threshold at gauging station A68, Animas River at Silverton, during early spring, but remained below chronic toxicity thresholds for brook trout year-round at stations M34, Mineral Creek at Silverton, and A72, Animas River downstream of Mineral Creek.

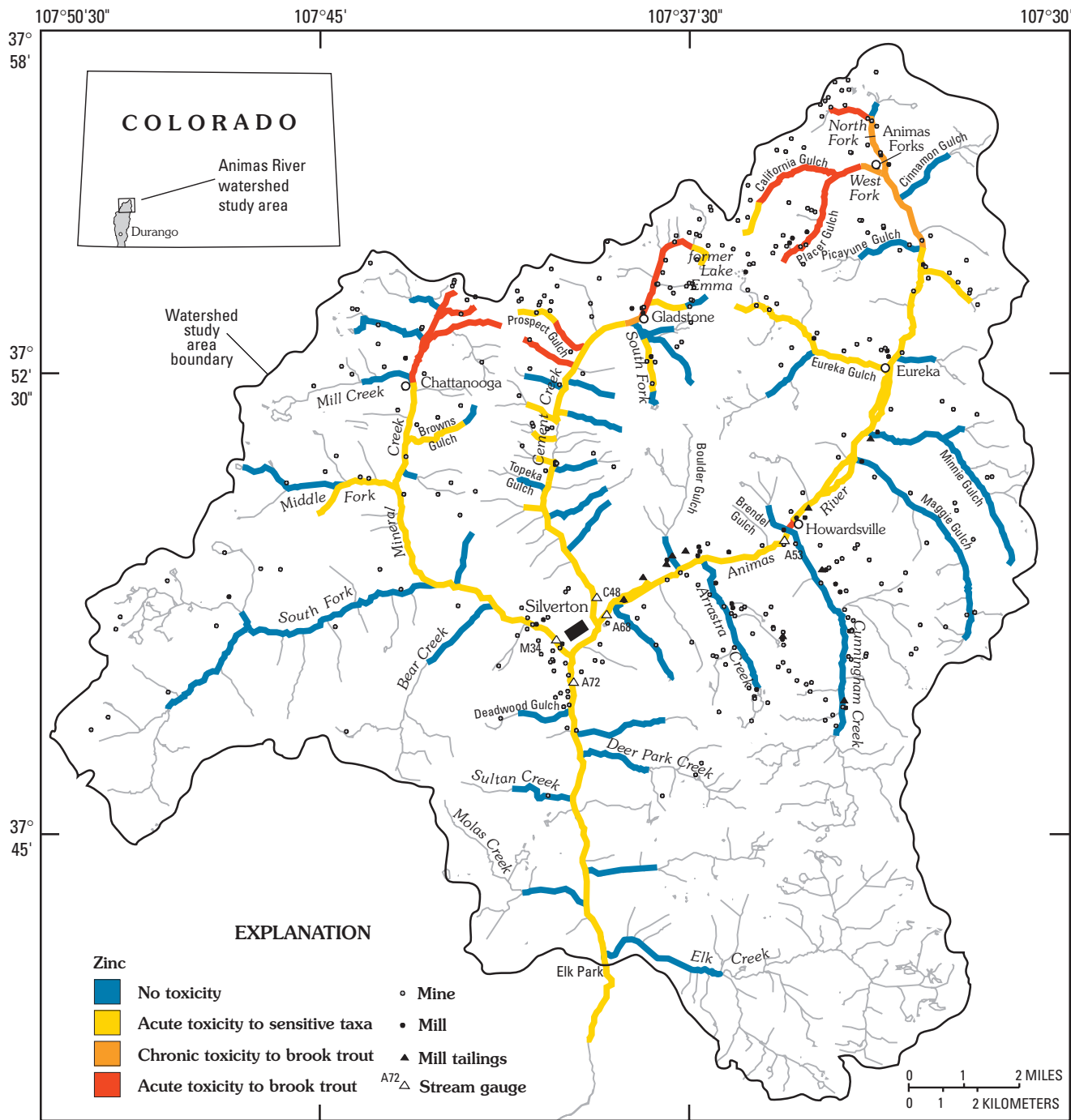


Figure 4. Toxicity risk from dissolved (0.45 µm filter) zinc in streams, at autumn low flow.

Copper

Risks of copper toxicity in streams of the study area tend to be more localized and more seasonal in nature than those for zinc. Water-quality criteria for copper are well established, based on a substantial toxicity literature (USEPA, 1985b, 1996), although more conservative criteria have been proposed recently (Robert Andrew and others, unpub. report to U.S. Environmental Protection Agency, Great Lakes Environmental Center, 1998) and are used here to estimate risks (table 1). Outside of acidic stream reaches, dissolved copper concentrations exceeded criteria in relatively few reaches during autumn, with exceedances occurring in lower Mineral Creek, in the Animas River upstream of Minnie Gulch, and in the Animas River between Cement and Mineral Creeks (fig. 5). Toxicity studies conducted in test water representative of the upper Animas River indicated that brook trout are relatively sensitive to copper toxicity (Besser and Leib, this volume; table 1). Risks of copper toxicity to brook trout during autumn conditions were only indicated for short reaches of Mineral Creek, downstream from South Fork Mineral Creek and near Silverton, and for the Animas River near Eureka. However, modeled dissolved copper concentrations exceeded chronic water-quality criteria and chronic toxicity thresholds for brook trout during part or all of the year at all three gauging stations studied (Besser and Leib, 1999; Besser and Leib, this volume). For the Animas River at Silverton (A68), copper concentrations exceeded chronic risk thresholds for brook trout for a brief period during early summer, but copper concentrations in the Animas River downstream from the Mineral Creek confluence (A72) exceeded this threshold from early winter through early summer, and copper concentrations in Mineral Creek at Silverton (M34) exceeded acute toxicity thresholds for brook trout year-round. These seasonal trends suggest that copper toxicity during the critical winter low-flow period is likely to limit brook trout populations in substantial portions of the Animas River. Areas subject to greatest risks of copper toxicity include most of the fishless neutral-pH reaches: lower Mineral Creek, the Animas River downstream from Cement Creek, and probably the Animas River upstream from Minnie Gulch.

Cadmium

Cadmium is highly toxic to aquatic biota, but dissolved cadmium occurs at much lower concentrations than zinc or copper in streams of the study area, and risks of cadmium toxicity are more uncertain. Water-quality criteria for cadmium, based on extensive laboratory testing, indicate that acute and chronic effects on sensitive biota can occur at very low dissolved cadmium concentrations (USEPA, 1985c, 1996, 2002; table 1). Based on these criteria, risks of chronic or acute cadmium toxicity during autumn conditions are predicted for most neutral-pH stream reaches in the study area, except the Animas River between Howardsville and Silverton and the reach of Mineral Creek immediately downstream of

South Fork Mineral Creek (fig. 6). No site-specific toxicity tests were performed with cadmium. A threshold for chronic cadmium toxicity to brook trout was estimated from several published toxicity studies (Benoit and others, 1976; Sauter and others, 1976; Eaton and others, 1974; table 1), but available studies did not distinguish reliable acute thresholds that were consistently greater than the chronic threshold (Benoit and others, 1976; Carroll and others, 1979; Hamilton and others, 1987). No stream reaches in the study area exceeded the chronic brook trout criterion during autumn conditions.

Risks of cadmium toxicity based on autumn conditions (fig. 6) may underestimate overall risk due to seasonal variation of dissolved cadmium concentrations. Dissolved cadmium concentrations vary seasonally at most locations studied in the Mineral Creek and upper Animas River basins, as well as the Animas River downstream of Cement and Mineral Creeks (Leib and others, this volume, Chapter E11). At most sites where significant seasonal trends were documented, cadmium concentrations varied inversely with streamflow, reaching seasonal maxima in late winter. The opposite trend was observed for the Animas River at Howardsville, where dissolved cadmium varied positively with streamflow and reached seasonal maxima during spring runoff periods. This atypical seasonal trend may reflect release of dissolved cadmium from tailings deposits in stream gravels in this reach. Under either of these seasonal patterns, the risk categories for autumn conditions in figure 6 underestimate the overall severity of effects of cadmium on stream biota. Cadmium tends to remain in dissolved form under prevailing water-quality conditions in the watershed, as indicated by the persistence of elevated risks of chronic cadmium toxicity through the entire study reach of the Animas River downstream of the Mineral Creek confluence (fig. 6). Studies of other watersheds affected by mining have also reported that cadmium remained biologically available farther downstream from source areas than other metals (Moore and others, 1991). In addition, chronic toxicity of cadmium may be facilitated by efficient transfer of cadmium in stream food webs (Besser, Brumbaugh, and others, 2001; Besser and Brumbaugh, this volume).

Status of Stream Biota Relative to Toxicity Risks

Fish

Trout have a patchy distribution in the Animas River watershed study area (fig. 7). Fish populations were characterized by a series of surveys conducted by the State of Colorado and the USDA Forest Service since 1991 (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001; Besser and Brumbaugh, this volume), together with recent and historical anecdotal reports. Results of these surveys indicate that trout are currently absent from the mainstems of Cement and Mineral Creeks, and from the mainstem of

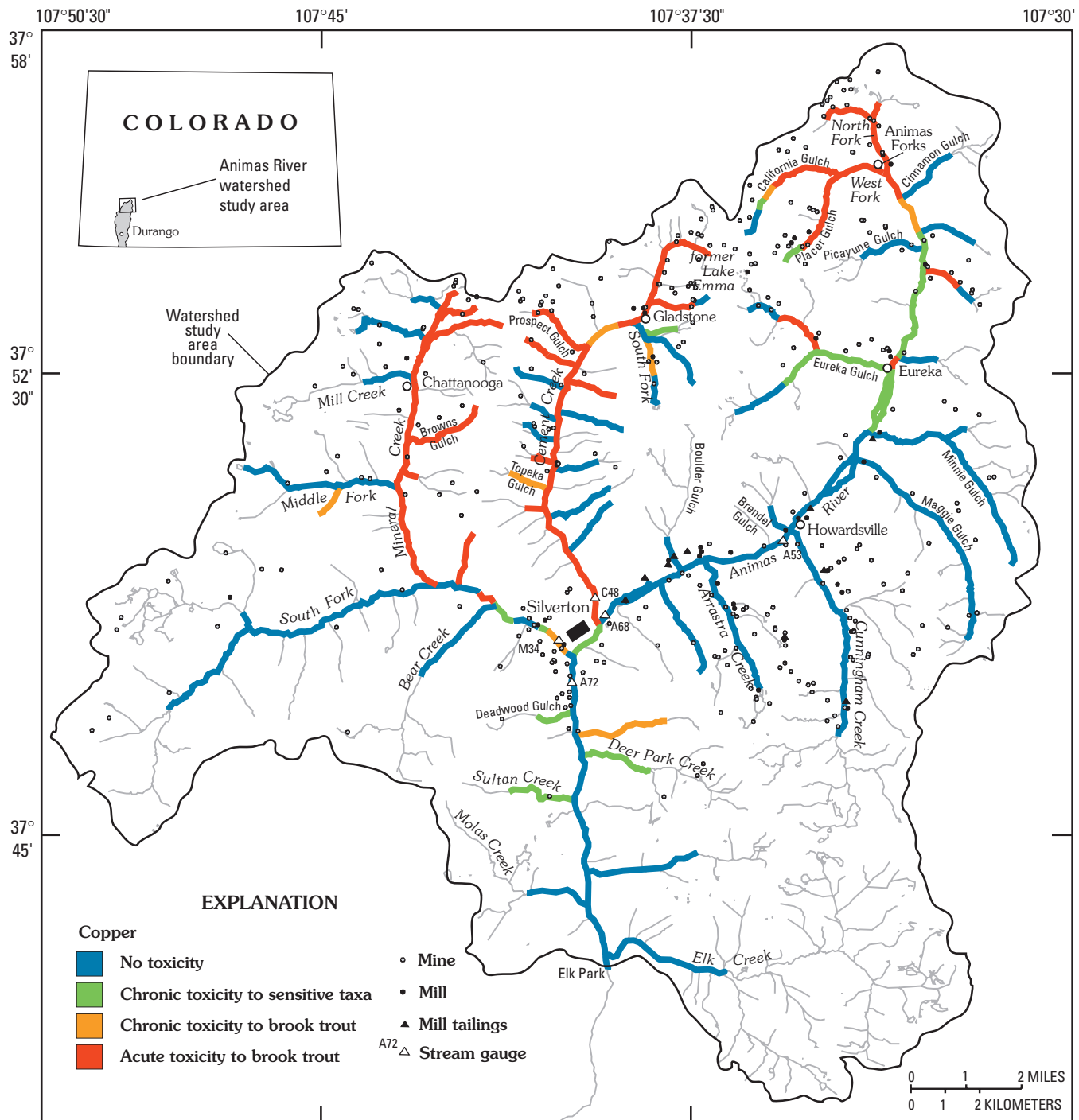


Figure 5. Toxicity risk from dissolved (0.45 µm filter) copper in streams, at autumn low flow.

the Animas River upstream from Minnie Gulch, and that fish have not occurred in these reaches in the recent past. The native Colorado River cutthroat trout has been largely eliminated from the study area, except for a few tributary streams, including Minnie Gulch and Cunningham and Deer Park Creeks. Mottled sculpin were reported historically from South Fork Mineral Creek but have not been reported in recent surveys. Currently, the only widespread fish species in the study area is brook trout, which occurs in South Fork Mineral Creek, in the reach of the

Animas River upstream of Cement Creek to Minnie Gulch, and in several tributaries entering the Animas River downstream from Eureka. Trout are absent from Arrastra Creek and from virtually all tributaries of upper Mineral Creek, Cement Creek, and the Animas River upstream of Eureka, except possibly the North Fork of the Animas River. Populations of brook trout in South Fork Mineral Creek and in the Animas River and its tributaries upstream from Silverton are separated from the population farther downstream in the Animas River

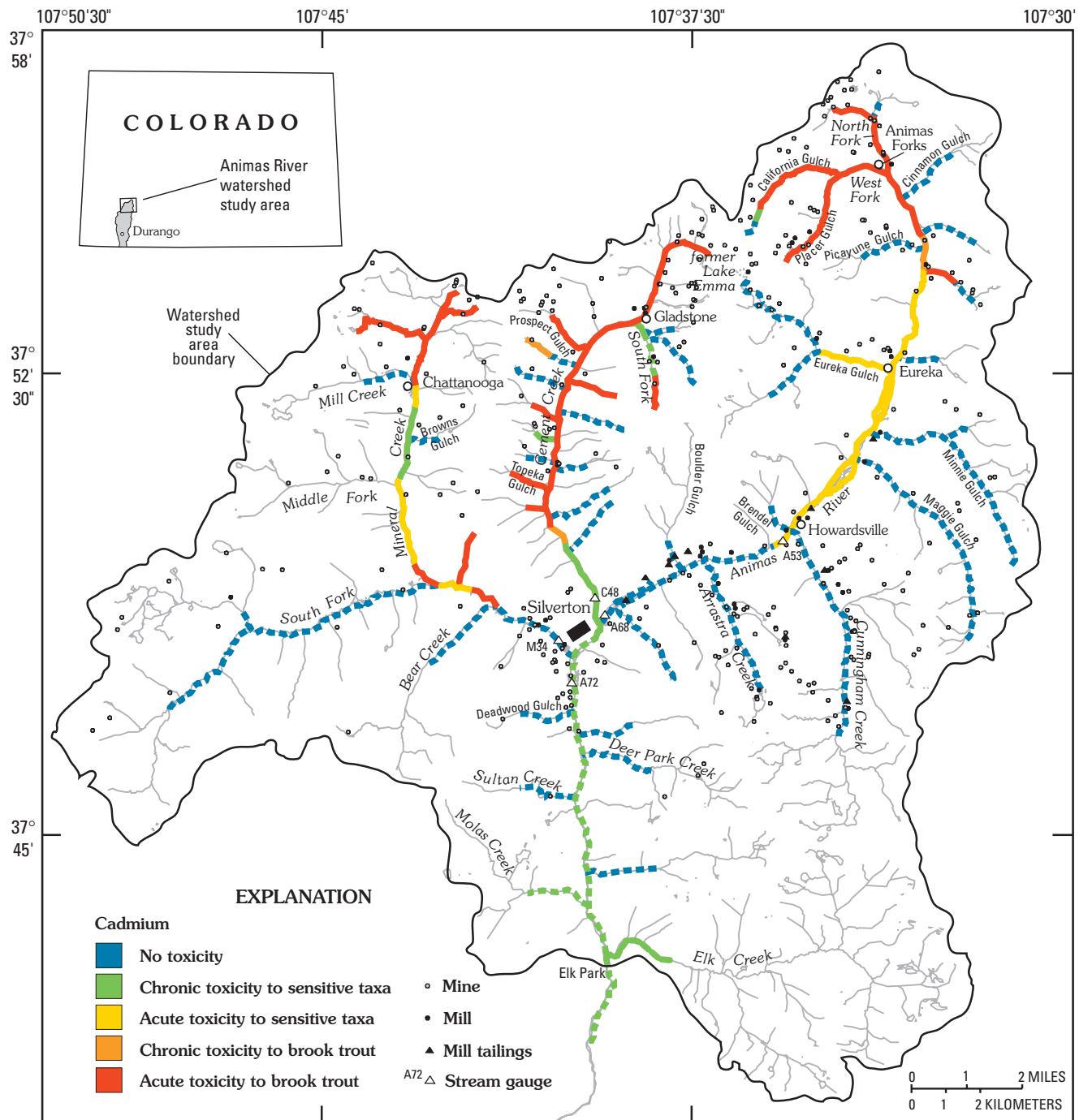


Figure 6. Toxicity risks from dissolved (0.45 μm) cadmium in streams, at autumn low flow. Dashed lines indicate one or more measurements of dissolved cadmium less than limit of detection (LOD; 1.4 or 2.0 μg/L); blue dashed line, all values less than LOD; green dashed line, one or more values greater than LOD.

canyon by fishless reaches of lower Mineral Creek and of the Animas River downstream of Cement Creek. Although brook trout have been collected in the Animas River immediately downstream of Cement Creek, they were found in the plume of unmixed Animas River water that persists along the east bank. Brook trout occur in the Animas River canyon as far upstream as Molas Creek in recent surveys, but whether the population extends farther upstream is unclear.

The distribution of brook trout in the study area reflects the range of toxicity risks from acidity and metals. Brook trout populations cannot persist in highly acidic streams such as Cement Creek and several tributaries of Cement and Mineral Creeks, and some of these stream reaches were probably acidic and fishless before the onset of mining in the watershed (Mast and others, this volume; Church and others, 1999). Severe toxic effects of most or all of the metals discussed in

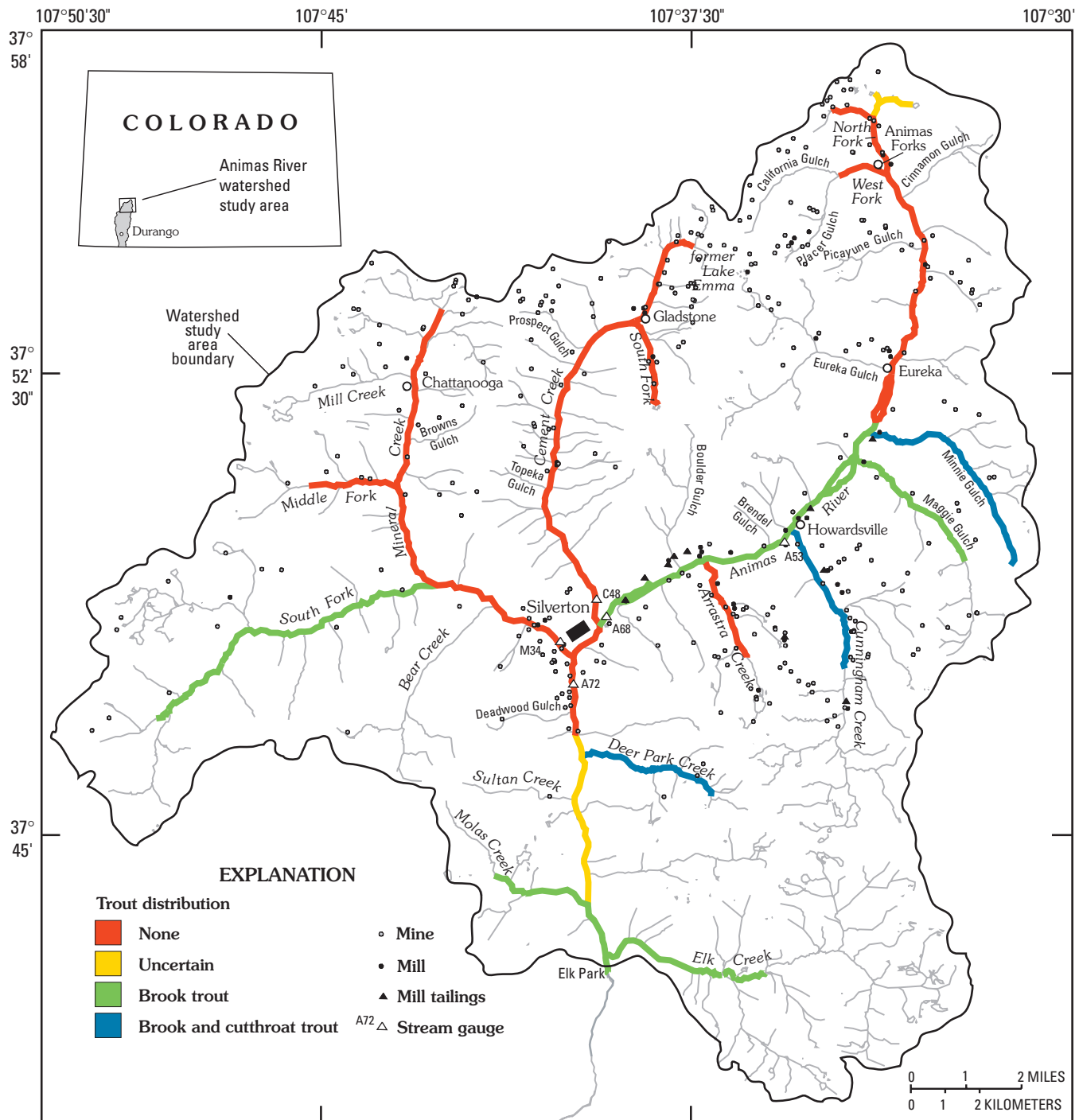


Figure 7. Approximate distribution of trout in streams.

this chapter could explain the absence of fish from less acidic stream reaches in the upper portions of the watershed, including upper Mineral Creek, Middle Fork Mineral Creek, and the Animas River above Eureka. Metal concentrations measured in several other stream reaches that do not currently support fish, including lower Mineral Creek, the Animas River between Eureka and Minnie Gulches, and the Animas River downstream of Mineral Creek, suggest less severe toxicity risks. In these reaches, only dissolved copper concentrations

(in portions of lower Mineral Creek) and total aluminum concentrations clearly exceed brook trout toxicity thresholds during autumn. Elevated concentrations of aluminum colloids may reduce trout growth during much of the year (Freeman and Everhart, 1971), and both dissolved copper and dissolved aluminum may be toxic to brook trout during winter. During winter, copper concentrations exceed brook trout toxicity thresholds in lower Mineral Creek, in the Animas River at Eureka, and in the Animas River below Mineral Creek

(Besser and Leib, this volume; Leib and others, this volume). Concentrations of zinc and cadmium also increase in these reaches during winter, although dissolved concentrations of these metals rarely if ever reach chronic toxicity thresholds for brook trout. Aluminum may also limit trout distribution during winter, as decreases in pH and increases in dissolved aluminum during low-flow conditions (Wright, Simon, and others, this volume) both result in increased aluminum toxicity. This phenomenon may affect reaches of the Animas River upstream of Eureka and downstream of Mineral Creek.

Macroinvertebrates

Data on benthic invertebrate communities during autumn 1997 (Anderson, this volume) were used to develop an index of invertebrate community status to simplify comparisons among stream reaches. Barbour and others (1999) recommended the use of composite scores derived from multiple metrics of community status as the basis for an integrated bioassessment. A composite invertebrate community index for streams in the study area was developed from three metrics of invertebrate abundance and taxa richness: average density of organisms per unit area; average number of taxa per sample; and total number of mayfly, stonefly, and caddis-fly taxa per site. Individual metrics were averaged for sites within each stream reach, and values within five percentile ranges (0–20, 21–40, 41–60, 61–80, 81–100) were converted into scores ranging from 1 (lowest community quality) to 5 (highest community quality). Finally, the scores for the three metrics were averaged to produce a composite score for each segment, which was converted to a color code for presentation in ribbon map format (fig. 8).

The status of benthic macroinvertebrate communities in the watershed followed patterns similar to those of trout distribution. However, in several stream reaches, the status of the benthic invertebrate community provided information on the status of aquatic communities (different trends or additional resolution) that was not evident from patterns of trout distribution. Even stream reaches that supported substantial brook trout populations, such as South Fork Mineral Creek and the Animas River upstream of Silverton, had invertebrate community scores that suggested slight impairment, relative to more pristine tributaries. In contrast, invertebrate community scores in the reach of the Animas River downstream of Mineral Creek do not reflect the trends for impact and recovery that are evident in trout populations. The greater number of sampling points in the invertebrate survey allowed greater resolution of longitudinal trends in water quality at a few locations, such as improvements in Mineral Creek downstream from South Fork Mineral Creek, and degradation in the Animas River downstream from Eureka and downstream from Molas Creek, although these small-scale changes are not evident in figure 8.

These differences reflect the broader range of metal tolerance among the many invertebrate taxa present in the Animas River watershed, compared to the single fish species, brook

trout. Some highly sensitive taxa may be eliminated from stream reaches experiencing low levels of metal stress with little or no apparent effects on trout populations. Conversely, a few metal-tolerant taxa may persist in highly contaminated reaches where trout are absent. The presence of small numbers of several invertebrate taxa in habitats that periodically undergo severe metal stress may also reflect the ability of aquatic insects to rapidly colonize marginal habitats during periods of relatively low metal toxicity.

The gradual nature of the recovery of the invertebrate community in the Animas River canyon downstream of Mineral Creek is of special interest, because little or no additional mining impact would be expected in this reach (Kimball and others, this volume). The composite invertebrate scores used for figure 8 suggest fair to poor community quality throughout this reach, although examination of the original data (Anderson, this volume) indicates differences in the responses of density and taxa richness. Despite substantial site-to-site variation, density of invertebrates remained low throughout the entire Animas River canyon reach, whereas taxa richness showed a general increasing trend with distance downstream from Cement Creek. This increase in taxa richness suggests an amelioration of metal toxicity, although the presence of additional taxa may be biased by short-term colonization from uncontaminated tributaries. However, the generally low densities of invertebrates indicate that overall water quality and habitat conditions in this reach have not recovered to the level observed in the Animas River upstream of Silverton. One possible explanation for these lingering impacts, despite decreases in concentrations in toxic metals, would be persistent impacts on habitat quality, such as those associated with iron oxyhydroxide precipitates. Substantial levels of these orange precipitates were visible on stream substrata of the Animas River from Cement Creek downstream to the confluence with Elk Creek during the period of the invertebrate study (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001). Courtney and Clements (2002) documented reduced colonization of invertebrates into trays of stream substrate transplanted from the Animas River into Elk Creek. These observations suggest that physical limitation of benthic habitat for invertebrates may contribute to persistent depression of invertebrate densities in this reach.

Summary of Risks by Stream Segment

Ecological risks for stream reaches were categorized based on a synthesis of available information on risks of toxicity of several metals and on the current status of trout and invertebrate communities (table 2). The 30 stream reaches listed in table 2 were assigned to one of four risk categories, ranging from A (Lowest risk) through D (Extreme risk). In some cases, reaches were assigned to intermediate categories or, if existing data were inadequate or equivocal, assigned to category U (Uncertain). Characteristics used to assign risk categories were as follows:

- A (Lowest Risk). Self-sustaining brook trout populations and relatively diverse and abundant invertebrate communities. Little evidence that metal toxicity substantially limits current biologic communities.
- B (Moderate Risk). Stable or increasing brook trout populations (which may be sustained by migration) and fair to good invertebrate communities. Metal toxicity risks can be attributed to one or two metals and tend to be chronic and seasonal in nature.
- C (High Risk). Does not support trout, except perhaps seasonal or transient visitors, and has reduced invertebrate diversity and abundance. Risks to biota can be attributed to several metals, and acute toxicity probably occurs, at least on a seasonal or episodic basis.
- D (Extreme Risk). Trout are absent and invertebrate communities are greatly reduced or absent. May never have supported fish because of elevated background metal concentrations. Acute toxicity of multiple metals and (or) acid probably occurs year-round.

The remainder of this discussion focuses on stream reaches in the Moderate and High Risk categories, based on our assumption that reaches in these categories have the best prospects for biological recovery after remediation. The Moderate Risk category was assigned predominantly to two segments of the upper Animas River: from Minnie Gulch downstream to Cement Creek, and from Deer Park Creek downstream into the Animas River canyon. The High Risk category includes two segments of the Animas River: from upstream of Eureka Gulch to Minnie Gulch and from Cement Creek to Deer Park Creek, and one reach of Mineral Creek, from the confluence of South Fork Mineral Creek to the Animas River. The following discussion summarizes metal toxicity risks for each of these stream segments, with the intent to identify the principal factors limiting the recovery of aquatic biota.

Mineral Creek—South Fork Mineral Creek to Animas River (High Risk). The mixing zone of Mineral Creek with South Fork Mineral Creek creates a zone of acute toxicity of aluminum (and probably other metals) at the upstream end of the segment. High levels of colloidal aluminum that persist throughout the segment may be chronically toxic to trout. Below the mixing zone, Mineral Creek has near-neutral pH most of the year, but significant pH depression (pH<5.0) can extend downstream all the way to the Animas River during late winter, at least during drought years (Fey and others, 2002). Even during periods of neutral pH, water of lower Mineral Creek contains relatively high levels of copper, relative to the Animas River upstream of the confluence of Mineral Creek. Levels of dissolved copper exceed chronic toxicity thresholds for brook trout for much of the year, and exceed thresholds for acute lethality for brook trout during late winter.

Animas River—from upstream of Eureka Gulch to Minnie Gulch (High to Moderate Risks). Although water-quality data are sparse for the upper portion of this segment, risk of metal toxicity decreases from High Risk, downstream of Animas Forks, to Moderate Risk, downstream of Eureka Gulch. Concentrations of dissolved zinc and cadmium remain above levels toxic to sensitive invertebrate taxa throughout the reach. Despite heavy upstream loadings, dissolved aluminum concentrations in this reach remain below toxic levels during the autumn sampling season, but elevated levels of total aluminum persist throughout the reach and may have chronic effects on fish and invertebrates. In the braided reach between Eureka and Minnie Gulch, colonization from downstream brook trout populations may be limited by low habitat quality as well as metal toxicity (Milhous, this volume).

Animas River—Minnie Gulch to Cement Creek (Moderate Risk). Zinc is the only metal that poses substantial risk to aquatic biota in this reach. Zinc levels throughout this segment exceed toxicity threshold for sensitive invertebrates year-round. Zinc concentrations are greatest in the reach downstream of Arrastra Creek, and dissolved zinc concentrations at station A68 approach chronic toxicity thresholds for brook trout during late winter. Toxicity of dissolved aluminum may occur in a short reach adjacent to tailings ponds at Howardsville.

Animas River—Cement Creek to Deer Park Creek (High Risk). Inflows from Cement and Mineral Creeks substantially increase risks of metal toxicity, compared to the upstream segment of the Animas River. Although risks of zinc toxicity are reduced somewhat downstream of Cement and Mineral Creeks, these tributaries contribute increased concentrations of aluminum, cadmium, and copper. The mixing of acidic, aluminum-rich waters from Cement Creek with the neutral waters of the Animas River produces a toxic mixing zone (USGS, this volume, Chapter A, fig. 4) and a plume of colloidal aluminum that persists throughout the reach and is augmented by loadings of colloidal aluminum contributed by Mineral Creek. High levels of colloidal aluminum may have chronic toxic effects on brook trout. Downstream of the Cement Creek mixing zone, dissolved aluminum concentrations remain below toxic levels during much of the year, but risks of acute toxicity of aluminum may be significant during periods of pH depression in late winter. For example, during late March 2002, stream water at station A72 had pH ranging from 4.88 to 5.30 and total aluminum concentrations from 2,600 to 3,500 µg/L and was acutely toxic to fish and invertebrates in laboratory tests (Fey and others, 2002). Substantial loadings of copper from Cement and Mineral Creeks do not produce substantial risks of copper toxicity during most of the year, but dissolved copper concentrations also increase markedly in late winter, resulting in risks of chronic toxicity to early life stages of brook trout (Besser, Allert, and others, 2001).

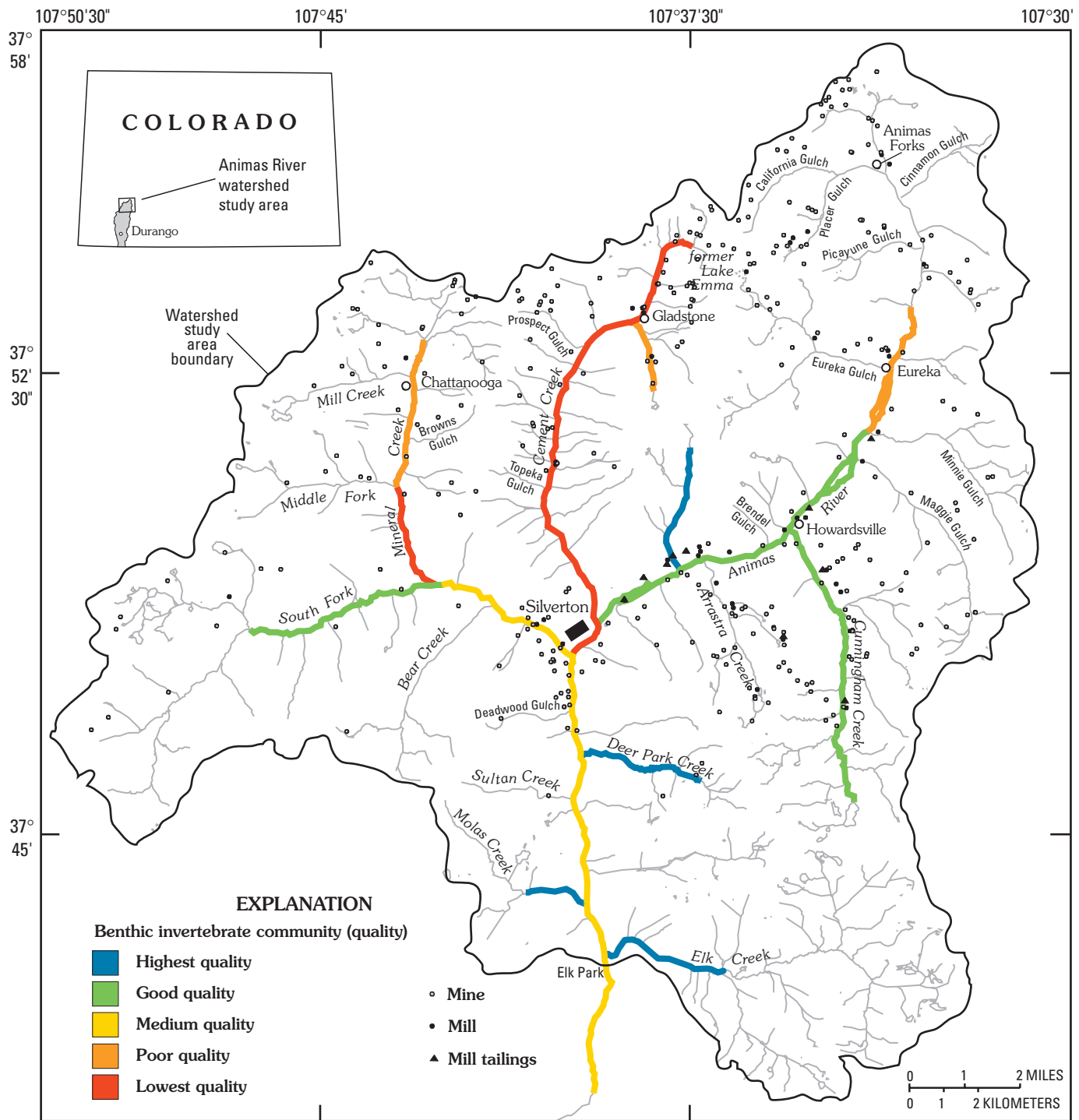


Figure 8. Status of benthic invertebrate communities in streams. Benthic invertebrate communities were evaluated based on three metrics: average density of organisms per unit area; average number of taxa per sample; and total number of mayfly, stonefly, and caddis-fly taxa per site. Quintile ranges for each metric were converted to scores from 1 to 5 and average scores were rounded to nearest integer and converted to color codes: 1, red; 2, orange; 3, yellow; 4, green; 5, blue.

Table 2. Summary of risk categories, status of stream biota, and risk categories for each metal, by stream reach.

[Toxicity risk categories explained in text and table 1; WQC=water quality criterion]

Stream	Reach	Risk category	Status of biota		Toxicity risk				
			Fish	Inverts.	Al (diss.)	Al (total)	Zn	Cu	Cd
Animas River	North Fk.	D	Yellow	White	White	Red	Red	Orange	Red
	West Fk.	D	Red	White	Red	Red	Red	Orange	Red
	Above Eureka	C	Red	Orange	Blue	White	Yellow	Green	Yellow
	Eureka - Minnie	CB	Red	Orange	Green	Orange	Yellow	Green	Yellow
	Minnie - Arrastra	B	Green	Green	Blue	Blue	Yellow	Blue	Yellow
	Arrastra - Cement	B	Green	Green	Blue	Blue	Yellow	Blue	Yellow
	Cement - Mineral	CD	Red	Red	Blue	Red	Yellow	Green	Yellow
	Mineral - Deer Park	CB	Red	Yellow	Blue	Orange	Yellow	Blue	Green
	Deer Park - Molas	B	Yellow	Yellow	Blue	Orange	Yellow	Blue	Green
	Molas-Elk	B	Green	Yellow	Blue	Orange	Yellow	Blue	Green
Cement Creek	Above Gladstone	D	Red	Red	Red	Red	Red	Red	Red
	South Fork	D	Red	Orange	White	Red	Yellow	White	Green
	Prospect Gulch	D	Yellow	White	Red	Red	Red	Red	Red
	Below Gladstone	D	Red	Red	Red	Red	Yellow	Red	Red
Mineral Creek	Above Mill Cr.	D	Red	Orange	Red	Red	Red	Red	Red
	Mill - Middle Fk.	D	Red	Orange	Blue	Red	Yellow	Red	Green
	Middle Fk.	D	Red	White	Red	Red	Yellow	Blue	White
	Middle Fk. - South Fk.	D	Red	Red	Red	Red	Yellow	Red	Yellow
	Upper South Fk.	A	Green	White	Green	White	Blue	Blue	Blue
	Lower South Fk.	B	Green	Green	Green	Orange	White	Blue	Blue
	Below South Fk.	CD	Red	Yellow	Blue	Orange	Yellow	Orange	Blue
Other tributaries	Eureka	U	Yellow	White	Green	White	Yellow	Green	Yellow
	Minnie	A	Blue	White	Blue	Green	Blue	Blue	Blue
	Maggie	A	Green	White	Blue	Blue	Blue	Blue	Blue
	Cunningham	A	Blue	Green	Blue	Blue	Blue	Blue	Blue
	Arrastra	U	Red	White	Blue	Blue	Blue	Blue	Blue
	Boulder	U	Yellow	Blue	Blue	Blue	Blue	Blue	Blue
	Deer Park	A	Blue	Blue	Blue	Blue	Blue	Green	Blue
	Molas	A	Green	Blue	Blue	Blue	Blue	Blue	Green
	Elk	A	Green	Blue	Blue	Blue	Blue	Blue	Green

Color Code	Fish (Presence/absence)	Invertebrates (Percentile range)	Metals (Toxicity threshold)
Red	No fish	Lowest quality	Brook trout acute
Orange	(not used)	Poor quality	Brook trout chronic
Yellow	Uncertain	Medium quality	Acute WQC
Green	Brook Trout	Good quality	Chronic WQC
Blue	Cutthroat Trout	Highest quality	No toxicity
White	No data	No data	Mixed scores

Animas River—Deer Park Creek to lower Animas River canyon (Moderate Risk). Risks of metal toxicity apparently decrease with distance downstream in this segment, as indicated by the regular occurrence of brook trout at least as far upstream as Elk Park. However, risks of toxicity of dissolved zinc and cadmium to sensitive taxa do not decrease significantly from upstream to downstream during the autumn low-flow period, and this persistent toxicity risk is consistent with the depression of invertebrate abundance throughout the segment. Although risks of metal toxicity to

brook trout during summer and autumn are not high enough to explain the absence of brook trout upstream of Molas Creek, risks of metal toxicity are probably greater during winter, when monitoring water quality in this reach is difficult. Based on winter conditions documented in the Animas River downstream of Mineral Creek, we can hypothesize that the reach of the Animas River downstream of Deer Park Creek also experiences winter pH depression, along with increased risks of toxicity of dissolved metals to brook trout.

References Cited

- Barbour, M.T., Gerritsen, Jeroen, Snyder, B.D., and Stribling, J.B., 1999, Rapid bioassessment protocols for use in streams and wadeable rivers—Periphyton, benthic macroinvertebrates and fish, Second Edition: Report EPA 841-B-99-002, various paginations.
- Benoit, D.A., Leonard, E.N., Christenson, G.M., and Fiannt, J.T., 1976, Toxic effects of cadmium on three generations of brook trout (*Salvelinus fontinalis*): Transactions of the American Fisheries Society, v. 105, p. 550–560.
- Besser, J.M., Allert, A.L., Hardesty, Douglas, Ingersoll, C.G., May, T.W., Wang, Ning, and Leib, K.J., 2001, Evaluation of metal toxicity in streams of the upper Animas River watershed, Colorado: U.S. Geological Survey Biological Science Report 2001-001, 72 p.
- Besser, J.M., Brumbaugh, W.G., Ivey, C.D., Buckler, D.R., and Ingersoll, C.G., 2003, Effects of calcium and equilibration time on toxicity of aluminum to brook trout and rainbow trout: Abstracts, 24th Annual Meeting of SETAC in North America, Austin, Texas, November 9–13, Pensacola, Fla.: Society of Environmental Toxicology and Chemistry, p. 64–65.
- Besser, J.M., Brumbaugh, W.G., May, T.W., Church, S.E., and Kimball, B.A., 2001, Bioavailability of metals in stream food webs and hazards to brook trout (*Salvelinus fontinalis*) in the upper Animas River watershed, Colorado: Archives of Environmental Contamination and Toxicology, v. 40, p. 48–59.
- Besser, J.M., and Leib, K.J., 1999, Modeling frequency of occurrence of toxic concentrations of zinc and copper in the upper Animas River, in Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8–12, 1999, Volume 1, Contamination from hard-rock mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, p. 75–81.
- Carroll, J.J., Ellis, S.J., and Oliver, W.S., 1979, Influences of hardness constituents on the acute toxicity of cadmium to brook trout (*Salvelinus fontinalis*): Bulletin of Environmental Contamination and Toxicology, v. 22, p. 575–581.
- Church, S.E., Fey, D.L., Brouwers, E.M., Holmes, C.W., and Blair, Robert, 1999, Determination of pre-mining geochemical conditions and paleoecology in the Animas River watershed, Colorado, in Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8–12, 1999, Volume 1, Contamination from hard-rock mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, p. 19–30.
- Church, S.E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J., and Vaughn, R.B., 1997, Source, transport, and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado: U.S. Geological Survey Open-File Report 97-151, 135 p.
- Courtney, L.A., and Clements, W.H., 2002, Assessing the influence of water and substratum quality on benthic macroinvertebrate communities in a metal-polluted stream—An experimental approach: Freshwater Biology, v. 47, p. 1766–1778.
- Cleveland, Laverne, Little, E.E., Hamilton, S.J., Wiedmeyer, R.H., and Buckler, D.R., 1989, Chronic no-observed-effect concentrations of aluminum for brook trout exposed in low-calcium, dilute acidic water, in Lewis, T.E., ed., Environmental chemistry and toxicology of aluminum: Chelsea, Mich., Lewis Publishers, p. 229–245.
- Decker, C., and Menendez, R., 1974, Acute toxicity of iron and aluminum to brook trout: Proceedings, West Virginia Academy of Science, Biology Section, p. 159–167.
- Eaton, J.G., McKim, J.G., and Holcombe, G.W., 1974, Metal toxicity to embryos and larvae of seven freshwater fish species—I, Cadmium: Bulletin of Environmental Contamination and Toxicology, v. 19, p. 95–103.
- Farag, A.M., Woodward, D.F., Brumbaugh, W.G., Goldstein, J.N., MacConnell, Elizabeth, and Hogstrand, Christer, 1999, Dietary effects of metals-contaminated invertebrates from the Coeur d'Alene River, Idaho, on cutthroat trout: Transactions of the American Fisheries Society, v. 128, p. 578–592.
- Fey, D.L., Wirt, Laurie, Besser, J.M., and Wright, W.G., 2002, Water quality and aquatic toxicity data of 2002 spring thaw conditions in the upper Animas River watershed, Silverton, Colorado: U.S. Geological Survey Open File Report 02-488, 25 p.
- Freeman, R.A., and Everhart, W.H., 1971, Toxicity of aluminum hydroxide complexes in neutral and basic media to rainbow trout: Transactions of the American Fisheries Society, v. 100, p. 644–658.

- Gensemer, R., and Playle, R., 1999, The bioavailability and toxicity of aluminum in aquatic environments: Critical Reviews in Environmental Science and Technology, v. 29, p. 315–450.
- Hamilton, S.J., Mehrle, P.M., and Jones, S.B., 1987, Evaluation of metallothionein measurement as a biological indicator of stress from cadmium in brook trout: Transactions of the American Fisheries Society, v. 115, p. 551–560.
- Henry, T.B., Irwin, E.R., Grizzle, J.M., Wildhaber, M.L., and Brumbaugh, W.G., 1999, Acute toxicity of an acid mine drainage mixing zone to juvenile bluegill and largemouth bass: Transactions of the American Fisheries Society, v. 128, p. 919–928.
- Ingersoll, C.G., Mount, D.R., Gulley, D., La Point, T.W., and Bergman, H.L., 1990, Effects of pH, aluminum, and calcium on survival and growth of eggs and fry of brook trout (*Salvelinus fontinalis*): Canadian Journal of Fisheries and Aquatic Sciences, v. 47, p. 1580–1592.
- Kimball, B.A., Callendar, E., and Axtmann, E.V., 1995, Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, U.S.A.: Applied Geochemistry, v. 10, p. 285–306.
- MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: Archives of Environmental Contamination and Toxicology, v. 39, p. 20–31.
- Moore, J.N., Luoma, S.N., and Peters, D., 1991, Downstream effects of mine effluent on an intermontane riparian system: Canadian Journal of Fisheries and Aquatic Sciences, v. 48, p. 222–232.
- Mount, D.R., Ingersoll, C.G., Gulley, D., Fernandez, J., La Point, T.W., and Bergman, H.L., 1988, Effect of long-term exposure to acid, aluminum, and low calcium on adult brook trout (*Salvelinus fontinalis*)—1, Survival, growth, fecundity and progeny survival: Canadian Journal of Fisheries and Aquatic Sciences, v. 45, p. 1623–1632.
- Sauter, S., Buxton, K.S., Macek, K.J., and Petrocelli, S.R., 1976, Effects of exposure to heavy metals on selected freshwater fish—Toxicity of copper, cadmium, chromium, and lead to eggs and fry of seven fish species: Report, U.S. Environmental Protection Agency, Duluth, Minn., 75 p.
- USEPA (U.S. Environmental Protection Agency), 1985a, Guidelines for deriving numerical water quality criteria for the protection of aquatic organisms and their uses: Report EPA 822/R–85–100, 61 p.
- USEPA, 1985b, Ambient water quality criteria for copper—1984: Report EPA 440/5–84–031, 142 p.
- USEPA, 1985c, Ambient water quality criteria for cadmium—1984: Report EPA44/5–84–032, 127 p.
- USEPA, 1987, Ambient water quality criteria for zinc—1986: Report EPA–440/5–87–003, 207 p.
- USEPA, 1988, Ambient water quality for aluminum—1988: Report EPA 440/5–88–008, 47 p.
- USEPA, 1996, 1995 updates—Water quality criteria for the protection of aquatic life in ambient water: Report EPA–820–B–96–001, 104 p.
- USEPA, 1998, Guidelines for ecological risk assessment: Report EPA/630/R095/002F, 188 p.
- USEPA, 2002, National recommended water quality criteria—2002: Report EPA 822–R–02–047, 31 p.
- USEPA, 2003, Notice of availability of draft aquatic life criteria document for copper and request for scientific views: Federal Register, v. 68, no. 250, p. 75552–75555.
- Verboost, P., Berntssen, M., Kroglund, F., Lyderson, E., Witters, H., Rosseland, B., Salbu, B., and Bonga, W.S., 1995, The toxic mixing zone of neutral and acidic river water—Acute aluminum toxicity in brown trout (*Salmo trutta* L.): Water, Air, and Soil Pollution, v. 85, p. 341–346.
- Woodward, D.F., Brumbaugh, W.G., DeLonay, A.J., Little, E.E., and Smith, C.E., 1994, Effects on rainbow trout fry of a metals-contaminated diet of benthic invertebrates from the Clark Fork River, Montana: Transactions of the American Fisheries Society, v. 123, p. 51–62.