Diurnal Variations in Metal Concentrations in the Alamosa River and Wightman Fork, Southwestern Colorado, 1995–97

By Roderick F. Ortiz and Robert W. Stogner, Sr.

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CONVERSION FACTORS AND ACRONYMS

Multiply	By	To obtain
	Length	
inch	2.54	millimeter
foot	0.3048	meter
mile	1.609	kilometer
square mile	2.590	square kilometer
cubic foot per second	0.02832	cubic meter per second
gallon	3.785	liter

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Acronyms used in this report:

CDPHE	Colorado Department of Public Health and Environment
COC	Constituents of Concern
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
EWI	Equal-width increment

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Abstract

A comprehensive sampling network was implemented in the Alamosa River Basin from 1995 to 1997 to address data gaps identified as part of the ecological risk assessment of the Summitville Superfund site. Aluminum, copper, iron, and zinc were identified as the constituents of concern for the risk assessment. Water-quality samples were collected at six sites on the Alamosa River and Wightman Fork by automatic samplers. Several discrete (instantaneous) samples were collected over 24 hours at each site during periods of high diurnal variations in streamflow (May through September). The discrete samples were analyzed individually and duplicate samples were composited to produce a single sample that represented the daily-mean concentration. The diurnal variations in concentration with respect to the theoretical daily-mean concentration (maximum minus minimum divided by daily mean) are presented.

Diurnal metal concentrations were highly variable in the Alamosa River and Wightman Fork. The concentration of a metal at a single site could change by several hundred percent during one diurnal cycle. The largest percent change in metal concentrations was observed for aluminum and iron. Zinc concentrations varied the least of the four metals. No discernible or predictable pattern was indicated in the timing of the daily mean, maximum, or minimum concentrations. The percentage of discrete sample concentrations that varied from the daily-mean concentration by thresholds of plus or minus 10, 25, and 50 percent was evaluated. Between 50 and 75 percent of discrete-sample concentrations varied from the daily-mean concentration by more than plus or minus 10 percent. The percentage of samples exceeding given thresholds generally was smaller during the summer period than the snowmelt period.

Sampling strategies are critical to accurately define variability in constituent concentration, and conversely, understanding constituent variability is important in determining appropriate sampling strategies. During nonsteady-state periods, considerable errors in estimates of daily-mean concentration are possible if based on one discrete sample. Flow-weighting multiple discrete samples collected over a diurnal cycle provides a better estimate of daily-mean concentrations during nonsteady-state periods.

INTRODUCTION

The upper Alamosa River Basin is a heavily mineralized area in the San Juan Mountains of southwestern Colorado (fig. 1). Metal contamination of streams in the basin from the Summitville Mine site, other smaller mines, and from natural metal-enriched acidic drainage in the basin has occurred for decades. Mining operations have been active intermittently in the Summitville area since the late 1800’s. Large-scale open-pit mining began at the Summitville Mine site in the mid-1980’s and continued until the mine site was abandoned in late 1992. As a result, the U.S. Environmental Protection Agency (USEPA) assumed site-maintenance responsibilities for the site under the emergency response provisions of Superfund. In 1998, the Colorado Department of Public Health and Environment (CDPHE) assumed shared responsibility of the Summitville site with USEPA.

In 1995, the Morrison-Knudsen Corporation and ICF Kaiser Engineers (1995) identified multiple data gaps needed for the ecological risk assessment of the Summitville Superfund site. As a result, the U.S. Geological Survey (USGS) developed a comprehensive data-collection plan for the basin to address these data gaps. The sampling analysis plan included the operation of several streamflow gages, water-quality monitors, and automatic samplers on the Alamosa River and Wightman Fork (Edelmann and Ortiz, U.S. Geological Survey, written commun., 1995 and 1997). Data collected from 1995 through 1997 were used to evaluate the diurnal variations in the water quality of the Alamosa River and Wightman Fork. The data also will be used in the current draft Tier II Summitville ecological risk assessment (Camp Dresser and McKee, Inc., 1999) to help address exposure of aquatic biota to metals in stream water.

Purpose and Scope

The purpose of this report is to characterize the diurnal variations in metal concentrations during periods of nonsteady-state streamflow conditions at selected water-quality sites on the Alamosa River and Wightman Fork. The report addresses the high variability in metal concentrations in the basin and quantifies the extent to which instantaneous sample concentrations vary in comparison to the daily-mean concentration. Additionally, the report addresses the unpredictability of sample concentrations throughout the diurnal discharge cycle and the implications to sampling strategies in the Alamosa River Basin.

Description of Study Area

The upper Alamosa River Basin is located in southwest Colorado (fig. 1). Elevations in the study area range from 8,400 feet to nearly 13,000 feet above sea level. Annual precipitation ranges from approximately 12 inches at the lower elevations to as much as 40 inches at the top of the highest peaks (Miller and McHugh, 1994). Most of the precipitation is in the form of snowfall.

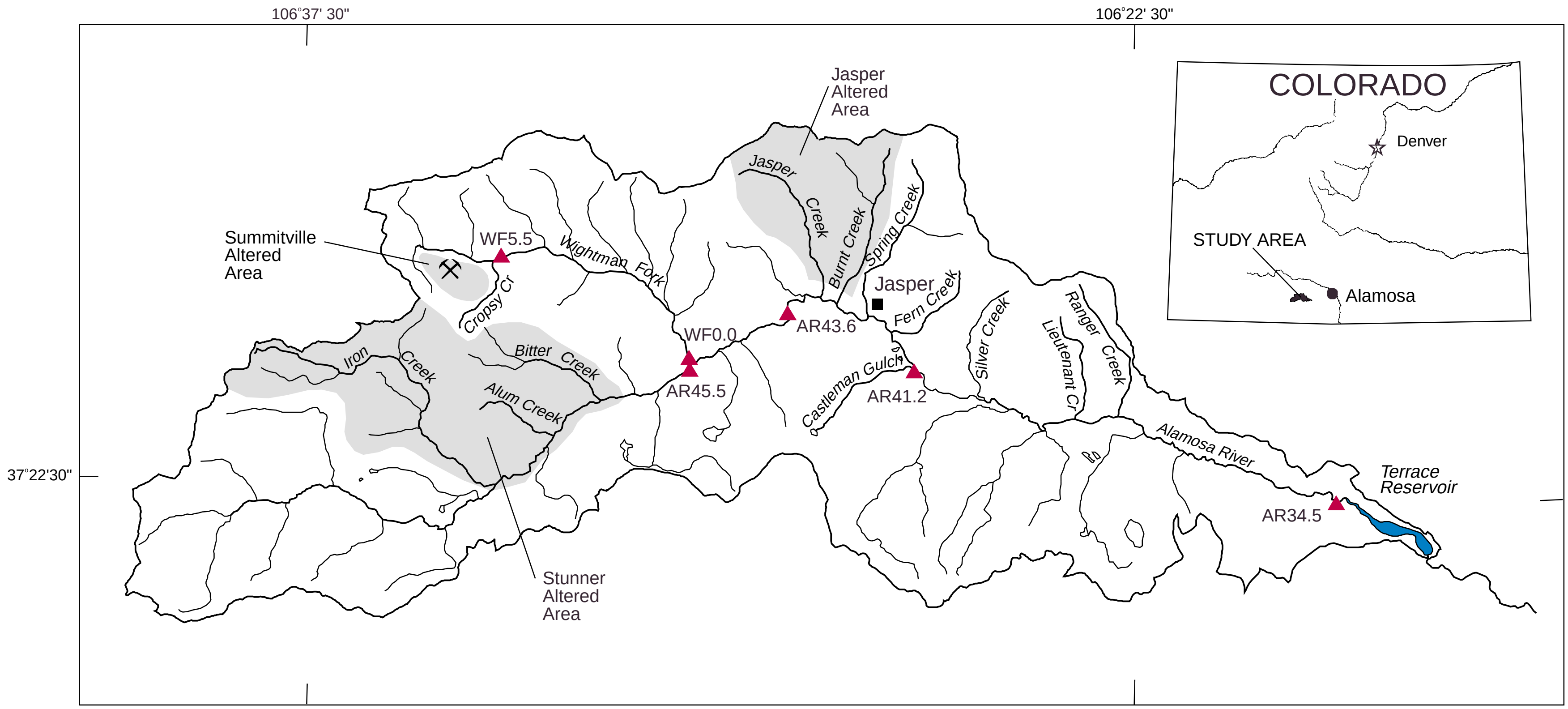
The study area extends from the headwaters of the Alamosa River to just above Terrace Reservoir and has a drainage area of approximately 110 square miles (Stogner, 1996). Several areas in the basin are hydrothermally altered and contain sulfide minerals and precious metals. Runoff from mined areas and unmined areas that are hydrothermally altered can adversely affect the quality of the water in the basin. Low-pH water with high concentrations of trace metals from the Summitville Mine site affects Wightman Fork and the Alamosa River downstream from its confluence with Wightman Fork (fig. 1). Upstream from the confluence, the Alamosa River receives drainage from hydrothermally altered areas. The Alamosa River flows east from the confluence with Wightman Fork through the Alamosa Canyon for 14 miles before reaching Terrace Reservoir. Several small tributaries enter the Alamosa River along this reach.

METHODS OF INVESTIGATION

Six sites were selected for streamflow gaging and water-quality sampling in the Alamosa River Basin (fig. 1). Four sites were located on the Alamosa River: Alamosa River above Terrace Reservoir (AR34.5), Alamosa River below Castleman Gulch (AR41.2), Alamosa River above Jasper (AR43.6), and Alamosa River above Wightman Fork (AR45.5). The remaining two sites were located on Wightman Fork: Wightman Fork at the mouth (WF0.0) and Wightman Fork below Cropsy Creek (WF5.5). Site WF5.5 is located immediately downstream from the Summitville Mine site. Each of the six sites was equipped with instantaneous streamflow-gaging equipment and automatic pumping samplers. With the exception of AR43.6, all the sites were equipped with instantaneous water-quality monitors.

Data-Collection Methods

Streamflow-gaging procedures were conducted in accordance with USGS methods (Rantz and others, 1982). Generally, streamflow-gaging equipment was installed before snowmelt conditions began



Hydrology modified by Denver Water, 1998
From U.S. Geological Survey Digital Line Graphs, 1:100,000, 1982
Universal Transverse Mercator projection, Zone 13, Feet

0 1 2 3 4 5 MILES

0 1 2 3 4 5 KILOMETERS

EXPLANATION

Approximate extent of hydrothermal alteration

Summitville Mine site

WF0.0 Water-quality sampling site with streamflow gage

Figure 1. Location of study area and water-quality sampling sites in the Alamosa River Basin.

(mid-April) and was operated through the summer period (mid-September to early October). Instantaneous streamflow data were recorded every 15 minutes.

Automatic pumping samplers, hereinafter referred to as “samplers,” were installed at all six sites. The automatic samplers were used from mid-April to September when large variations in diurnal flow and, potentially, metal concentrations would be expected. A diurnal cycle began at the low-flow trough of the day and ended on the trough of the following day. Generally, the sampling events occurred once in May, twice in June, and once each in July and August. A sampler may have been used in September if nonsteady-state streamflow conditions existed at that time. The samplers were operated from 1995 through 1997.

Samplers were programmed to collect multiple water-quality samples at each of the sampling sites at predetermined intervals over a 24-hour period. Sampling times were selected to cover the observed diurnal streamflow cycle at each site (fig. 2). Typically, sample sets were collected every 4 hours, which resulted in six sample sets for the day. Each sample set included four instantaneous samples collected in separate 1-liter bottles. Water from two of the instantaneous samples was processed for analysis of total-recoverable and dissolved constituents, one sample was composited using flow-weighted techniques (U.S. Environmental Protection Agency, 1991), and one sample was used for rinsing equipment prior to processing samples (fig. 2). At the end of the 24-hour sample-collection period, the samples were retrieved and transported to a nearby staging area for processing. Discrete samples were processed and submitted for analysis of selected anions and trace metals. The results of chemical analyses on these discrete samples were used to evaluate the variation in concentration at each site over the 24-hour period. Samples designated for compositing were flow-weighted to produce a single composite sample that represented the daily-mean concentration at a particular site (U.S. Environmental Protection Agency, 1991).

The USGS recommends that samples be retrieved from automatic samplers at the earliest possible time to reduce the chance of chemical and biological alteration of the sample (Shelton, 1994). For the majority of the discrete samples collected from the samplers, the holding times prior to processing was less than 24 hours. However, it was assumed that the longest a discrete sample set might remain unprocessed was about 36 hours. As such, quality-control measures were taken to address the concern that sample degradation could occur during these extended holding times (Edelmann and Ortiz, U.S. Geological Survey, written commun., 1995 and 1997). During each sampling trip, two of the sites were selected for additional sample collection using conventional USGS equal-width increment (EWI) techniques (Edwards and Glysson, 1988); the sites were rotated throughout the study period to represent all six sites. The EWI samples were processed immediately according to USGS techniques for major anions, total-recoverable metals, and dissolved metals (Ward and Harr, 1990). The remaining sample water was set aside for approximately 36 hours before being processed in the same manner for the same analytes. Overall, the percent difference in metal concentrations between the samples processed immediately and the samples held for 36 hours indicated that there was good replication of data. Nearly 90 percent of the total-recoverable metals data from the sample proceeded immediately varied by less than 12 percent from the sample held for 36 hours. Likewise, 80 percent of the dissolved metal data, excluding iron, varied by less than 15 percent.

Data-Analysis Methods

For the purpose of this report, the constituents of concern (COC) were dissolved and total-recoverable aluminum, copper, iron, and zinc. The four metals were identified as COCs in the ecological risk characterization prepared by Morrison-Knudsen Corporation and ICF Kaiser Engineers (1995) and the draft Summitville ecological risk assessment prepared by Camp Dresser and McKee, Inc. (1999). Discrete and flow-weighted composite data were used for the analysis of diurnal variations in metal concentrations. Water-quality data were tabulated and plotted to evaluate variations in water quality associated with diurnal variations in streamflow.

The raw data used in the analyses were not included in the text of this report; however, the data are available from the Colorado Department of Public Health and Environment, Hazardous Materials and Waste Management Division, 4300 Cherry Creek Drive South, Denver, CO 80222–1530. The data

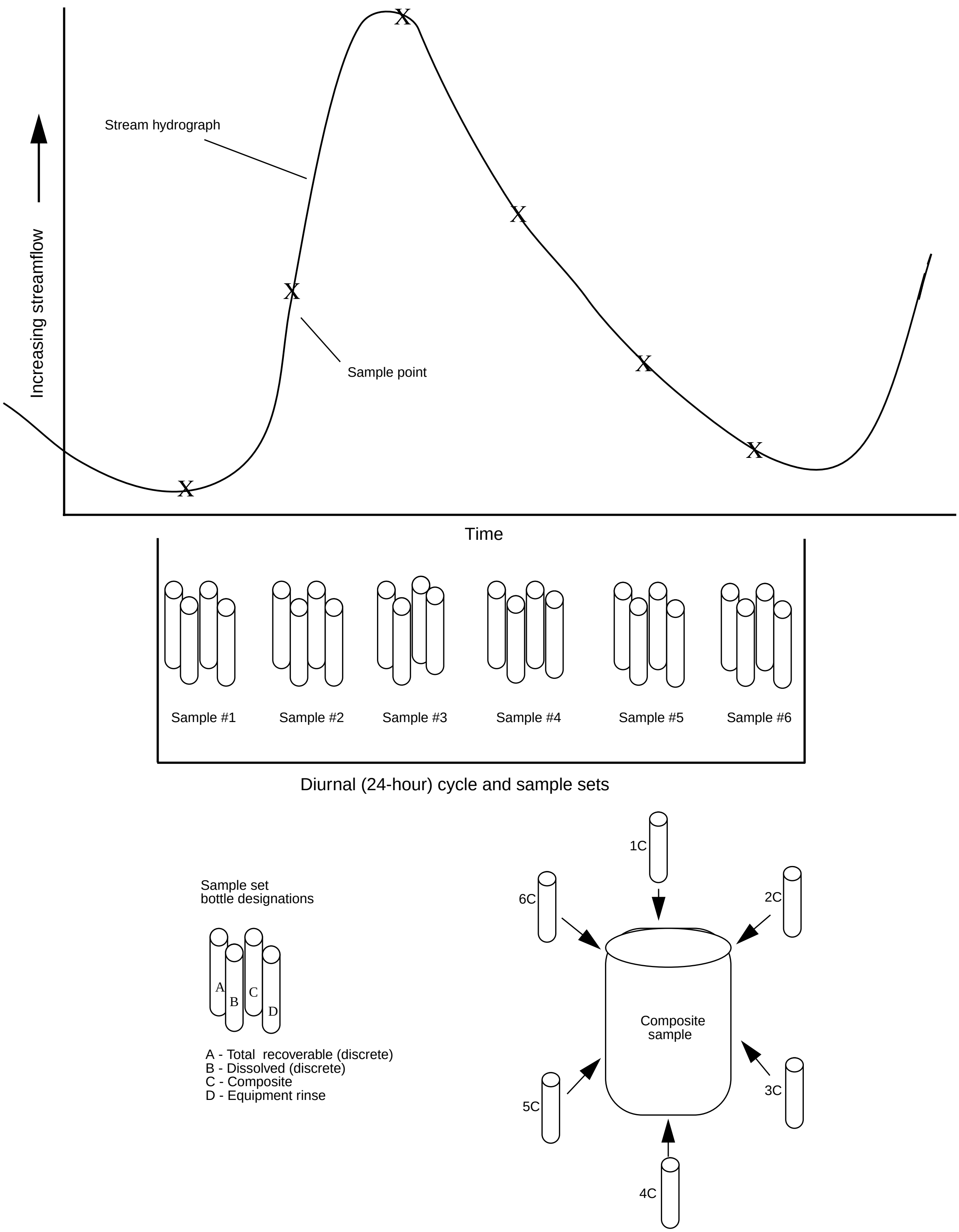


Figure 2. Hypothetical hydrograph showing sample points and graphical depiction of discrete and composite sample sets.

include all dissolved and total-recoverable concentrations for discrete and composite samples collected from 1995 through 1997. Discrete- and composite-sample groups are found in the data base under the general heading of "sample type."

Percentage of variation in minimum and maximum discrete concentrations relative to the theoretical daily-mean concentration (the flow-weighted composite concentration) was computed as follows:

$$D_{var} = \frac{C_{max} - C_{min}}{C_{mean}} \times 100$$

where

D_{var} is percent diurnal variation,

C_{max} is maximum concentration observed during the diurnal cycle,

C_{min} is minimum concentration observed during the diurnal cycle, and

C_{mean} is daily-mean concentration.

DIURNAL VARIATIONS IN METAL CONCENTRATIONS

Metal concentrations were highly variable in the Alamosa River and Wightman Fork during a 24-hour period when nonsteady-state streamflow conditions existed. Samples collected at the same site but at different times during a diurnal streamflow cycle could vary several hundred percent. The percent change between the maximum and minimum concentration in 15 percent of the samples collected at an individual site over 24 hours ranged from about 83 percent to about 1,940 percent (table 1). Percent change between maximum and minimum concentrations varied the least for copper, 94 to 344 percent, and zinc, 83 to 226 percent. Iron was the most variable, with variations between the daily maximum and minimum concentration ranging from 185 to 1,940 percent.

In addition, samples collected over a diurnal cycle in the Alamosa River and Wightman Fork were highly variable when compared to the daily-mean concentration as defined by the flow-weighted composite sample (daily mean). The variability of the maximum and minimum concentrations with respect to the theoretical daily-mean concentration provides an estimate of the daily variability relative to the mean concentration at a site. This estimate is particularly important when addressing the question of variability in instantaneous concentration relative to the mean concentration. In other words, how much variation from the mean concentration might be expected from any one sample collected during the day during nonsteady-state streamflow conditions in the basin?

The following sections describe the general tendencies in variation and present boxplots showing the variation around the daily mean for each COC. An example of a boxplot is in figure 3. The descriptor

Table 1. Percent change in metal concentrations over a 24-hour period at six sites in the Alamosa River Basin, 1995–97

Site (*n* = number of sample events)	Percentile	Aluminum		Copper		Iron		Zinc	
		Dissolved	Total recoverable	Dissolved	Total recoverable	Dissolved	Total recoverable	Dissolved	Total recoverable
AR34.5 (*n* = 15)	85th	605	400	139	344	757	305	117	226
AR41.2 (*n* = 14)	85th	190	394	161	125	263	259	98	83
AR43.6 (*n* = 14)	85th	275	228	121	94	185	282	100	83
AR45.5 (*n* = 15)	85th	596	756	173	204	283	284	132	160
WF0.0 (*n* = 15)	85th	311	215	166	146	1,940	355	111	100
WF5.5 (*n* = 14)	85th	154	130	123	142	224	236	108	119

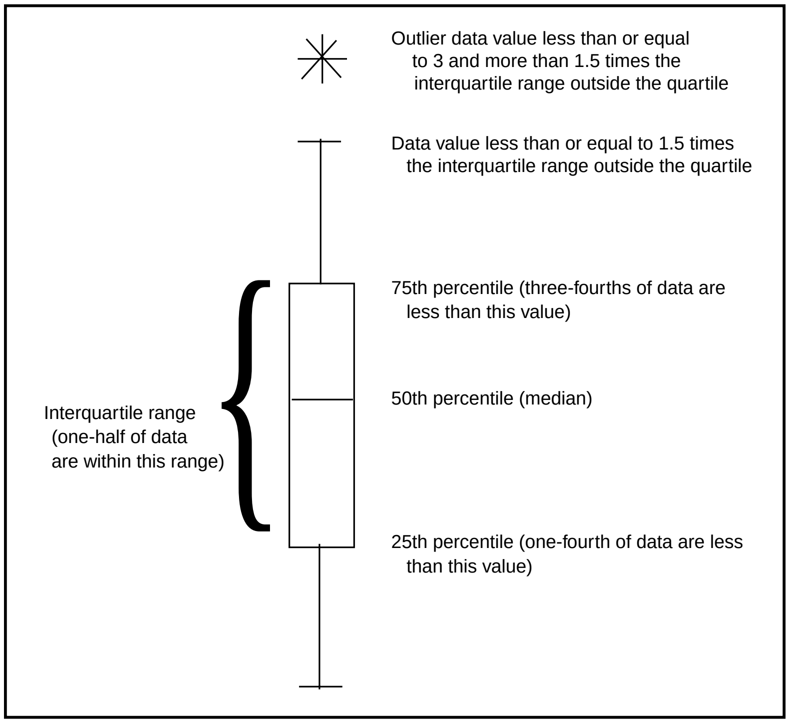


Figure 3. Example diagram of boxplot.

is defined as the difference between the maximum and minimum concentration divided by the daily-mean concentration (a composite sample) expressed as a percentage (see eq. 1). Hereinafter, this descriptor is referred to as the "percent diurnal variation" of the metal concentration.

Aluminum

Large diurnal variations in aluminum concentration occurred in the Alamosa River Basin from 1995 through 1997. The percent diurnal variation was typically less than 160 percent (fig. 4) but exceeded 2,000 percent at various sites. With the exception of AR45.5, more than one-half the reported dissolved aluminum concentrations varied from the daily-mean concentration by 50 percent or more; as much as one-fourth of the concentrations at AR34.5, AR41.2, AR43.6, and WF0.0 varied from the daily-mean concentration by more than 100 percent (fig. 4). The percent diurnal variation for total-recoverable aluminum was less than that for dissolved aluminum; about one-half of the concentrations varied from the composited concentration by more than 35 percent.

Copper

The percent diurnal variation for copper was less extreme than the diurnal variation for aluminum. Typically, the diurnal variation was less than 80 percent (fig. 5), but variations as much as 600 percent were observed. With the exception of dissolved copper at AR45.5 and total-recoverable copper at WF0.0, more than one-half the reported dissolved and total-recoverable copper concentrations varied from the daily-mean concentration by more than 40 percent (fig. 5). As many as one-fourth of the dissolved copper concentrations at AR34.5, AR41.2, AR43.6, WF0.0, and WF5.5 varied from the daily-mean concentration by more than 80 percent.

Iron

Large diurnal variations in iron concentration occurred in the Alamosa River Basin (fig. 6). The percent diurnal variation was typically less than 140 percent but exceeded 1,000 percent for various sites. More than one-half of the reported dissolved iron

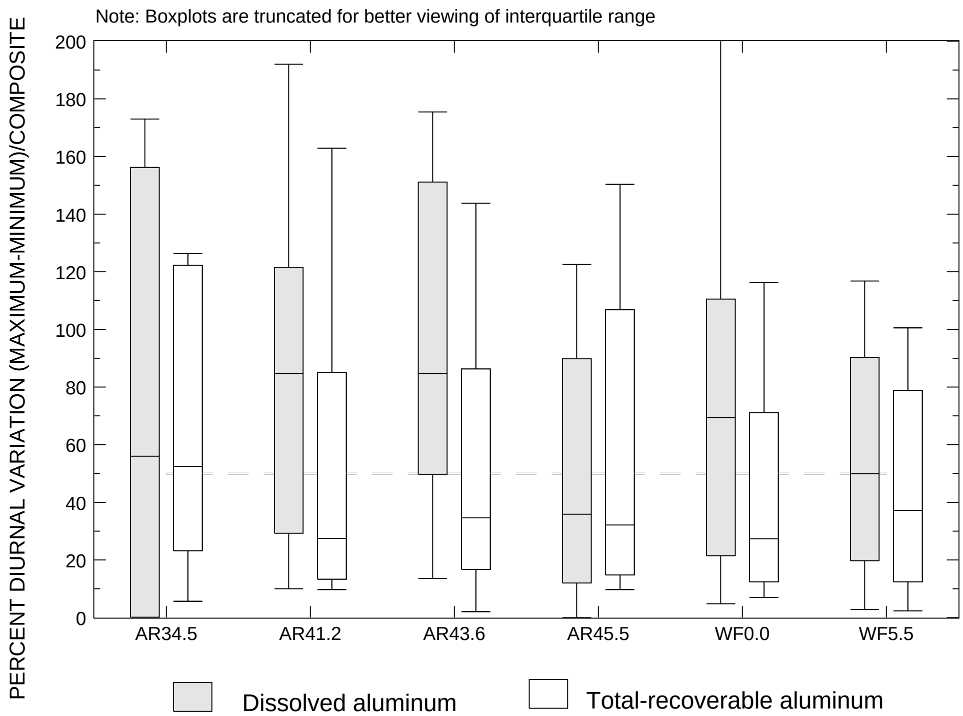


Figure 4. Variations in dissolved and total-recoverable aluminum concentrations in relation to daily-mean concentration.

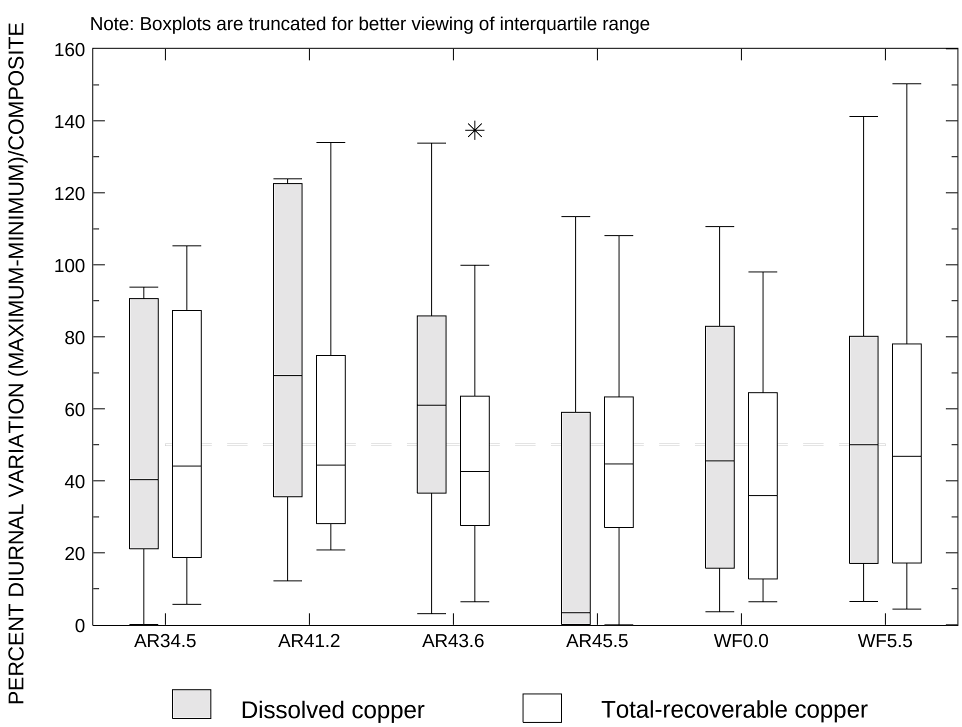


Figure 5. Variations in dissolved and total-recoverable copper concentrations in relation to daily-mean concentration.

concentrations varied more than 60 percent when compared to the daily-mean concentration. At least one-fourth of the dissolved concentrations at all the sites varied from the daily-mean concentration by about 100 percent. The percent diurnal variation for total-recoverable iron was generally less than that for dissolved iron; about one-half of the concentrations varied from the daily-mean concentration by more than 25 percent.

Zinc

The percent diurnal variations for zinc concentrations were the least variable of the four constituents of concern (fig. 7). Typically, the diurnal variation was less than 80 percent, but variations as much as 290 percent were observed. At least one-fourth of the dissolved and total-recoverable zinc concentrations varied more than 50 percent when compared to the daily-mean concentration. The percent diurnal variation for total-recoverable zinc was similar to that for dissolved zinc.

Temporal Variations in Maximum and Minimum Concentrations

The timing of maximum and minimum concentrations was evaluated. The 24-hour sampling periods were subdivided into 6-hour periods. The occurrence of maximum and minimum COC concentrations were then tabulated. Analysis indicated no discernible pattern in the timing of maximum or minimum concentrations during a diurnal cycle (fig. 8). In general, maximum and minimum dissolved and total-recoverable COC concentrations were fairly evenly distributed throughout the 6-hour periods, with the exception of dissolved iron. Maximum dissolved iron concentrations were more likely to occur (about 75 percent) between 0600 hours and 1800 hours and least likely to occur between midnight and 0600 hours. Minimum dissolved iron concentrations were least likely to occur between 0600 hours and 1200 hours and more like to occur between 1800 hours and midnight. Therefore, determining the likely time of day when COC concentrations might represent a daily mean, minimum, or maximum concentration is generally unpredictable.

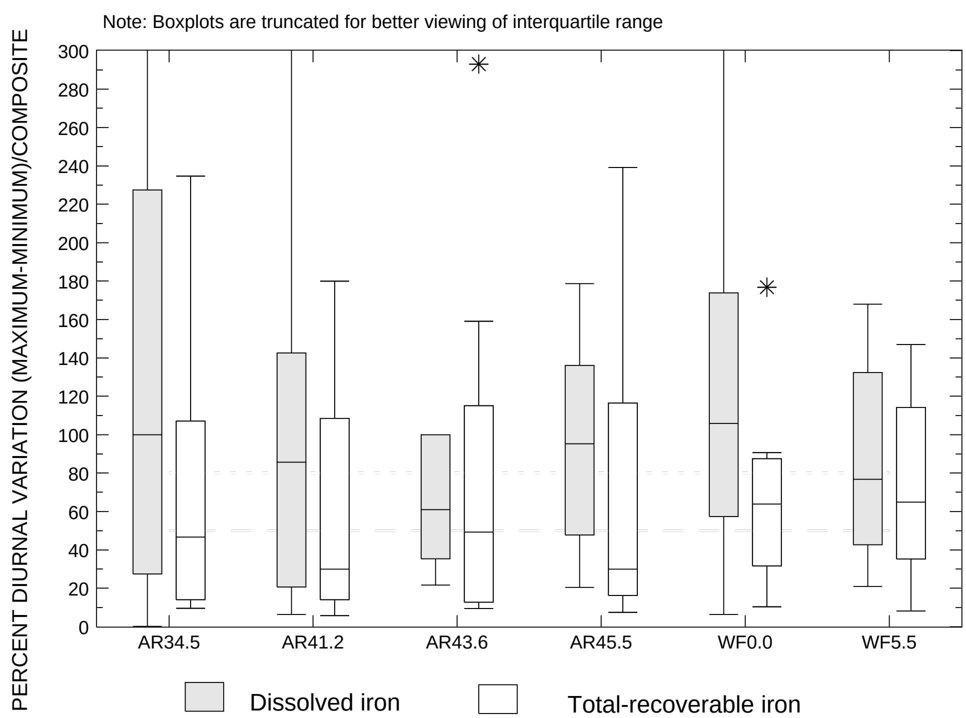


Figure 6. Variations in dissolved and total-recoverable iron concentrations in relation to daily-mean concentration.

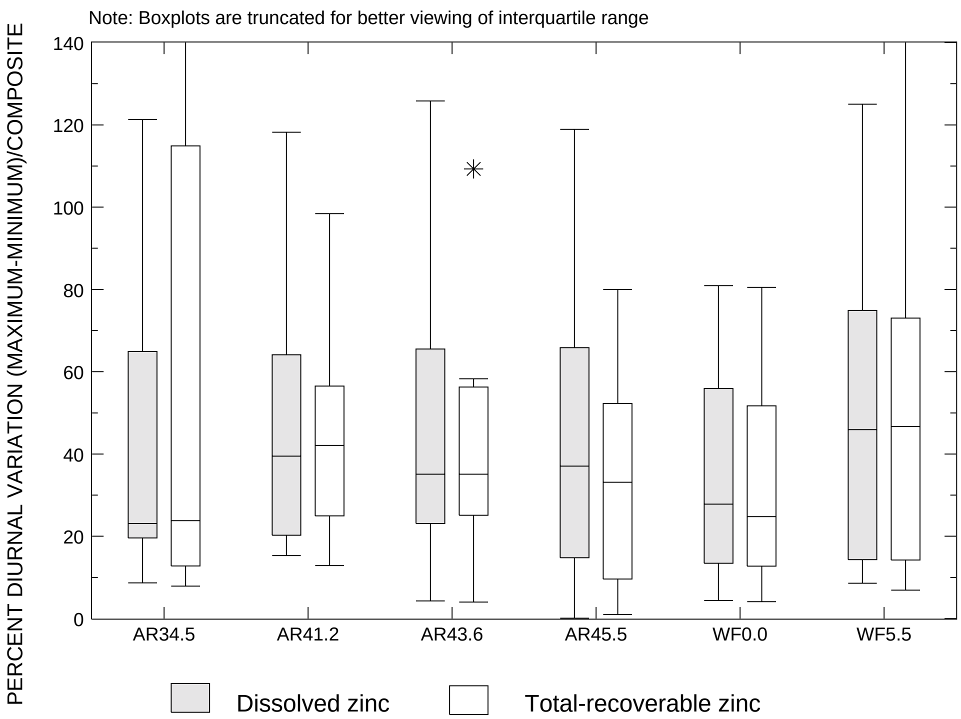


Figure 7. Variations in dissolved and total-recoverable zinc concentrations in relation to daily-mean concentration.

Frequency of Exceeding Daily-Mean Concentration Threshold

The probability that a discrete (instantaneous) sample concentration will vary from the daily-mean (composite) concentration by selected thresholds was evaluated for each COC. Two seasonal periods, snowmelt and summer flow, also were evaluated. The percentage of discrete sample concentrations within thresholds of plus or minus 10, 25, and 50 percent of the daily-mean sample concentration was determined (fig. 9). Analysis indicated that, depending on the COC and flow period, about 50 to 75 percent of discrete sample concentrations varied from the daily-mean concentration by more than plus or minus 10 percent. About 20 to 50 percent of discrete sample concentrations varied from daily-mean sample concentrations by more than plus or minus 25 percent. Finally, between about 5 and 25 percent of discrete sample concentrations varied from the daily-mean sample concentration by more than plus or minus 50 percent. The percentage of variations between discrete and daily-mean sample concentrations during the summer period generally were smaller than percentage of variations between discrete and daily-mean sample concentrations during the snowmelt period for most COCs.

IMPLICATIONS FOR SAMPLING STRATEGIES

Sampling strategies need to accurately represent variations and trends in metal concentrations and loads in the Alamosa River Basin in order to evaluate the effectiveness of remediation efforts on the water quality of the basin. Given the variability and lack of predictable temporal patterns of COC concentrations during a diurnal cycle in the Alamosa River Basin, one discrete sample collected during a diurnal cycle may not accurately represent the daily-mean concentration. On the basis of data collected from 1995 through 1997, during nonsteady-state periods in the Alamosa River Basin, flow-weighting multiple discrete samples collected over a diurnal cycle provides a better estimate of a representative daily-mean concentration as compared to a single discrete sample collected at any one time during the day.

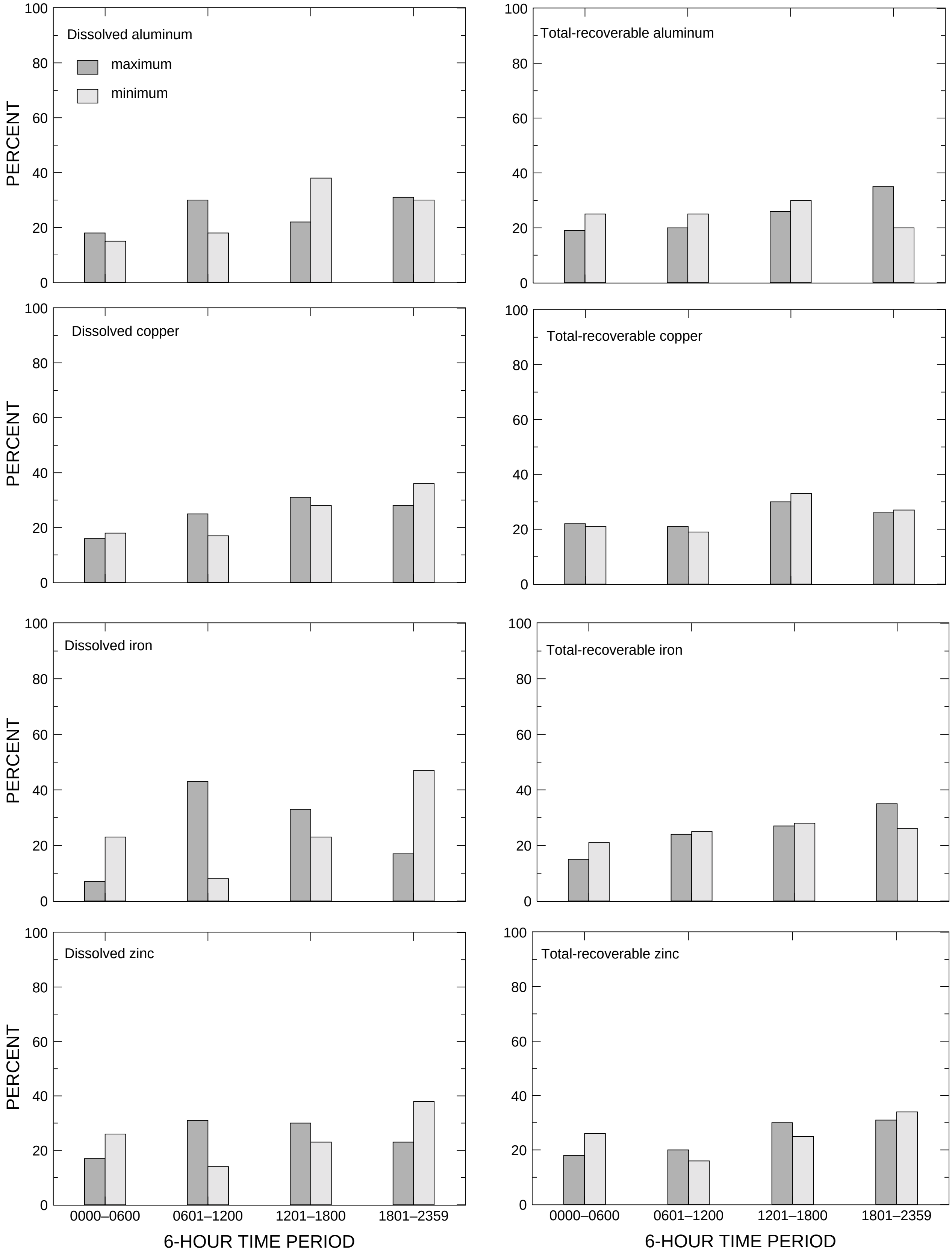


Figure 8. Percentage of days that daily-maximum and daily-minimum concentration occurred during a given 6-hour time period.

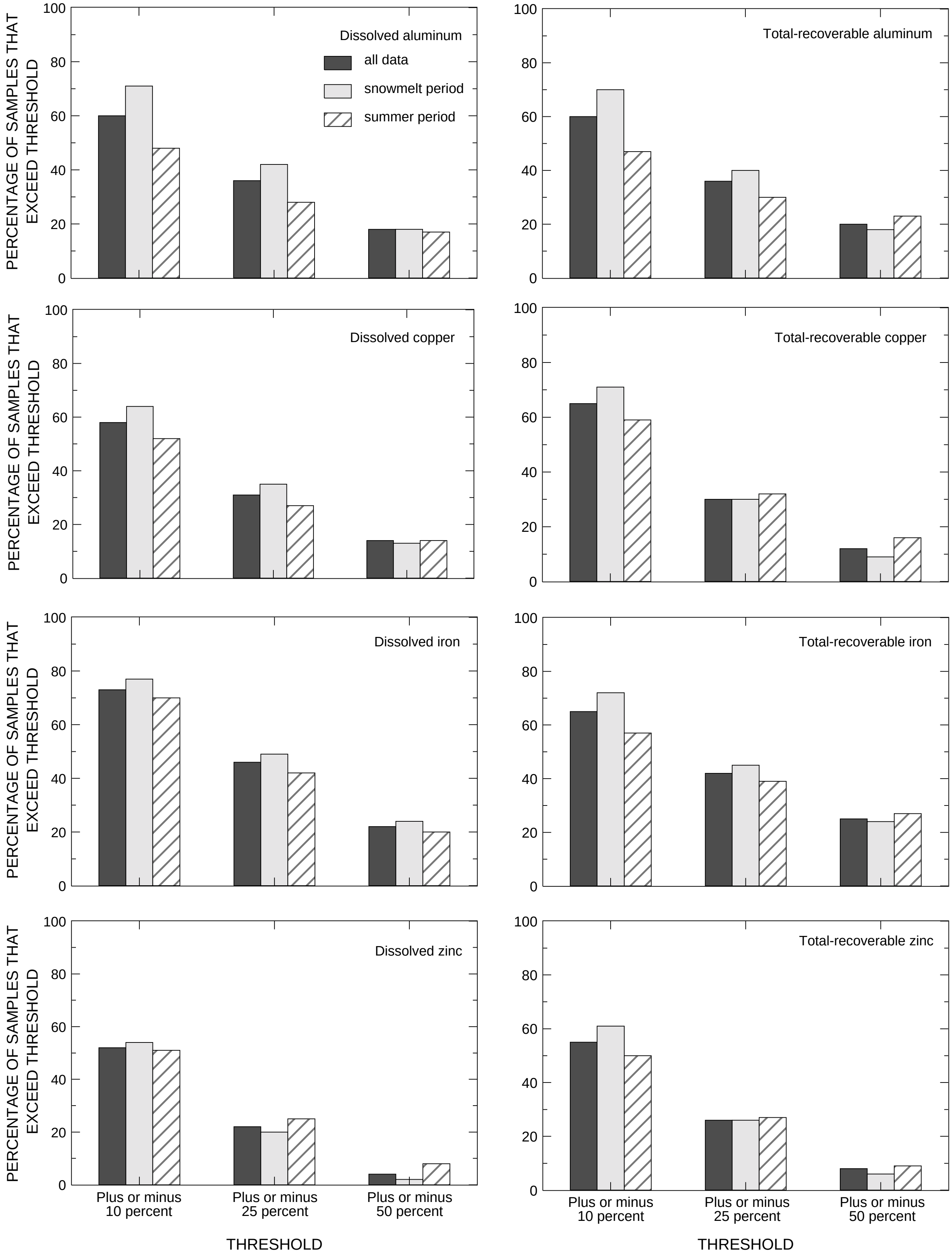


Figure 9. Percentage of discrete sample concentrations that exceeded the daily-mean concentration by a given threshold.

SUMMARY

From 1995 to 1997, a comprehensive sampling network was implemented in the Alamosa River Basin to address data gaps identified as part of the Summitville Superfund site ecological risk assessment. Aluminum, copper, iron, and zinc were identified as the constituents of concern for the risk assessment. Water-quality samples were collected at six locations where automatic samplers were installed on the Alamosa River and Wightman Fork. Several discrete samples were collected over 24 hours at each site during periods of high diurnal variations in streamflow (May through September). The diurnal variations in concentration (maximum minus minimum divided by composite) with respect to the theoretical daily-mean concentration are presented.

Diurnal metal concentrations were highly variable in the Alamosa River and Wightman Fork. The concentration of a metal at a single site could vary by several hundred percent during one diurnal cycle. Diurnal variations with respect to the daily-mean concentration (composited sample concentration) also were large. The percentage of diurnal variation for aluminum was typically less than 160 percent but exceeded 2,000 percent at various sites. More than one-half the dissolved aluminum concentrations varied by at least 50 percent from the daily-mean concentration, and about one-fourth of the concentrations varied by as much as 100 percent. The variation for total-recoverable aluminum was not as large. The percent diurnal variation for copper was generally less than 80 percent, but variations of as much as 600 percent were determined. Generally, about one-half the dissolved and total-recoverable copper concentrations varied from the daily-mean concentration by more than 40 percent. Large diurnal variations in iron concentration occurred in the basin. Typically, the percentage of diurnal variation was less than 140 percent but could exceed 1,000 percent. More than one-half the dissolved iron concentrations varied by more than 60 percent when compared to the daily-mean concentration; one-fourth of the concentrations varied by as much as 100 percent. The variation for total-recoverable iron was not as large. Percent diurnal variation for zinc was the least variable of the constituents of concern. Typically, the variations were less than 80 percent but did exceed 290 percent. At least one-fourth of the dissolved and total-recoverable zinc concentrations varied from the daily-mean concentration by more than 50 percent.

Except for dissolved iron, maximum and minimum dissolved and total-recoverable COC concentrations were fairly evenly distributed throughout a 24-hour period. Therefore, predicting the timing of the daily mean, minimum, or maximum concentration is not feasible.

Percentage of sample concentrations that varied from the daily-mean concentration by more than plus or minus 10 percent ranged from 50 to 75 percent. About 20 to 50 percent of samples exceeded the daily-mean concentration by plus or minus 25 percent, and about 5 to 25 percent of samples exceeded the mean daily concentration by plus or minus 50 percent. The percentage of samples exceeding given thresholds generally was smaller during the summer period than the snowmelt period.

Sampling strategies are critical to accurately define variability in constituent concentration; and conversely, understanding constituent variability is important in determining appropriate sampling strategies. During nonsteady-state periods, considerable errors in estimates of daily-mean concentration are possible if based on one discrete sample. Flow-weighting multiple discrete samples collected over a diurnal cycle provides a better estimate of daily-mean concentrations during nonsteady-state periods.

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