Metals Transport in the Sacramento River, California, 1996–1997. Volume 1: Methods and Data

Charles N. Alpers, Howard E. Taylor, *and* Joseph L. Domagalski, editors

Executive Summary

The overall goal of this study was to determine the significance of contamination from metal sources into the Sacramento River, during a variety of river flow conditions. The main sources investigated were historic mining areas in addition to areas with other land uses including agricultural and urban. Parts of the Sacramento River watershed have been severely affected by historic mining activities. Hard-rock mining of copper, zinc, and lead was done primarily in the vicinity of Shasta Lake, whereas mercury was predominantly mined in the Coast Ranges. Mercury (quicksilver) was used extensively in gold mining and recovery operations, especially at hydraulic placer mines in the Sierra Nevada foothills and the Klamath Mountains but also at mills associated with hardrock mines in both of these areas. This project was funded primarily by the Sacramento Regional County Sanitation District with assistance from a grant administered by the State Water Resources Control Board. Additional funding for the study was made available by the U.S. Environmental Protection Agency, the National Marine Fisheries Service, and the U.S. Geological Survey's Federal–State Cooperative Hydrology Program.

The distribution, fate, and transport of metals in the Sacramento River were studied using a multidisciplinary approach that included water, sediment, and biological sampling. Although the focus of this study was on seven trace metals (aluminum, cadmium, copper, iron, lead, mercury, and zinc), more than 40 additional elements were analyzed in water and sediment samples. Water samples were collected on six occasions during the period July 1996 through June 1997 at up to 19 sites categorized as follows: 11 sites were on the reach of the mainstem Sacramento River between Shasta Dam and Free port; 7 different tributary sites were sampled; and one distributary site, the Yolo Bypass, was sampled during high-flow conditions. Samples of caddisfly (*Hydropsyche californica*) larvae were collected during October 1996 at 5 mainstem sites between Redding and Tehama, and at 1 tributary stream. Streambed sediment samples were collected during October and November 1996 from 9 sites, including each of the 6 sites where caddisfly larvae samples were taken. Water samples were collected and processed using ultraclean techniques necessary for accurate and precise determination of trace metals with concentrations as low as 0.0004 micrograms per liter. Concentrations of metals from an extremely fine filtering technique called "tangential flow ultrafiltration" (0.005 micrometer equivalent pore size) were compared with concentrations from conventional filtration (0.45- and 0.40-micrometer pore sizes) and unfiltered (whole-water) samples. The tangential-flow filtrates, hereinafter referred to as "ultrafiltrates," are a better approximation of truly dissolved metal concentrations than conventional filtrates because they exclude colloidal particles in the size range of about 0.005 to 0.40 (or 0.45) micrometers that pass through conventional filters.

Colloid concentrates were prepared using the solids that were retained from tangential-flow

ultrafiltration of large (100 liter) water samples. The water samples were taken during six sampling periods between July 1996 and June 1997 from the following seven sites: below Shasta Dam, below Keswick Dam, at Bend Bridge, at Colusa, at Verona, and at Freeport, all located on the mainstem of the Sacramento River; and the Yolo Bypass at Interstate 80 located near West Sacramento. The Yolo Bypass is part of a flood-control system and carries water only when the channel capacity of the mainstem of the Sacramento River exceeds, or is expected to exceed, its capacity. All colloid concentrates were analyzed for total metals using a complete dissolution procedure. Some colloid concentrates also were subjected to a sequence of partial dissolution steps to determine the concentrations of metals in three operationally defined parts or fractions: (1) reducible (including hydrous iron and manganese oxides), (2) oxidizable (including organic material and sulfides), and (3) residual (remaining after the previous two steps).

Generally, it was found that using the sum of dissolved and colloidal concentrations from ultrafiltrates and retentate (colloid concentrate) samples, rather than using total recoverable analyses of whole-water samples, provided a more definitive way to estimate total water-column concentrations. The total recoverable analyses were affected by more sources of variation than were the analysis of the dissolved plus colloidal concentrations.

Most of the trace metals transported in the Sacramento River between Shasta Dam and Freeport occurred as colloids (operationally defined as particles with grain size between about 0.005 and 1.0 micrometer). In the water column, colloids appeared to be the dominant form of aluminum, iron, lead, and mercury, and are important in the distribution of other trace metals. The percentage of the load that is colloidal compared with the percentage that is dissolved (operationally defined by concentrations in ultrafiltrates as less than about 0.005 micrometer diameter) was higher for copper than it was for zinc and cadmium. This distinction is significant because the relative amounts of colloidal and dissolved metals may influence the rates and mechanisms of metal bioaccumulation (the accumulation of an environmental compound into an organism).

The influence of metal-laden acidic drainage from the Iron Mountain mine site (via Spring Creek and the Spring Creek arm of Keswick Reservoir) is apparent in water samples from the site below Keswick Dam. Historically, California’s Basin Plan water-quality standards have been exceeded with respect to copper concentrations at this site (the Basin Plan standard for copper in this area is 5.6 micrograms per liter, which is based on a hardness of 40 milligrams per liter). Occasional exceedances of copper concentration standards in the Basin Plan continued during January 1997 despite the ongoing operation of a lime neutralization plant at Iron Mountain, which has removed about 80 percent of copper loads and about 90 percent of zinc and cadmium loads from Spring Creek since July 1994. In mid-December 1996, conventionally filtered samples had copper concentrations that ranged from 4.6 to 5.1 micrograms per liter and zinc concentrations that ranged from 6 to 9 micrograms per liter. During flood conditions in early January 1997, conventional filtered copper concentrations were 4 to 9 micrograms per liter and zinc concentrations were 9 to 16 micrograms per liter. With regard to transport of the these metals below Keswick Dam, copper concentrations in ultrafiltrates were about 40 to 70 percent lower than conventional filtrates (0.40- and 0.45-micrometer) and zinc concentrations were 10 to 50 percent lower, indicating that both copper and zinc are transported as both colloidal and dissolved forms.

Lead isotope data in colloid concentrates and streambed sediments provide a useful fingerprint or natural tracer for lead contamination from Iron Mountain mine drainage via Spring Creek and Keswick Reservoir. Lead isotope data for streambed sediments and suspended colloid samples taken during 1996 and 1997 indicate that contamination from Iron Mountain was (1) a relatively major component of the total lead found at Sacramento River sites at Rodeo Park (in

Redding) and above Churn Creek (near Anderson), (2) less of a component of the lead found at Balls Ferry, and (3) a relatively minor component of the lead in colloids and streambed sediment at Bend Bridge (near Red Bluff) and at sites farther downstream.

The geochemical forms of metals in colloid concentrates from the Sacramento River were evaluated using a sequence of partial dissolution steps. During May–June 1997, cadmium was predominantly associated with the reducible (or iron–manganese oxide) fraction at all mainstem sampling sites, whereas copper and zinc were more or less evenly distributed between reducible and residual (or refractory) fractions at all sites with a small amount present in the oxidizable (or organic plus sulfide) fraction. These results are consistent with the data on caddisfly bioaccumulation, which indicate that cadmium is likely more bioavailable on a relative basis than copper or zinc in the Sacramento River between Redding and Tehama.

In addition to water and sediment concentrations, selected trace elements were examined in relation to their bioavailability. Bioaccumulation of metals in caddisfly larvae was assessed at five sites in the Sacramento River between Redding and Tehama and at one site less impacted by mining (Cottonwood Creek near Cottonwood). Samples were taken in October 1996. Cadmium concentrations in caddisfly larvae at Sacramento River sites were 5 to 36 times greater than concentrations at the Cottonwood Creek site. Cadmium concentrations of the whole body ranged from 0.7 to 2.2 micrograms per gram, dry weight. Of this total, approximately 60 percent (0.4 to 1.3 micrograms cadmium per gram, dry weight) was associated with the cell cytosol, an intracellular fraction that is indicative of metal bioavailability. Concentrations of cadmium in caddisfly larvae from the Sacramento River are comparable with other areas severely impacted by mining. Concentrations of copper and zinc also showed some enrichment in caddisfly whole-body samples and cytosol fractions; copper and zinc concentrations at Sacramento River sites were 1.4 to 3.0 times greater than concentrations at Cottonwood Creek near Cottonwood. The caddisfly data indicate that bioavailable forms of cadmium persist in the Sacramento River downstream of Tehama.

Exceedances of levels of mercury—with respect to the U.S. Environmental Protection Agency (EPA) water-quality criterion (12 nanograms per liter)—are common in northern California during the winter and especially following significant rainfall. The concentrations of total mercury in the Sacramento River increased during storm water runoff and were above the EPA water-quality criterion during high flows in December 1996 and January 1997, from the Bend Bridge site (located near Red Bluff) downstream to Freeport. Dissolved mercury concentrations were low and relatively constant under different flow conditions, but combined concentrations of dissolved and colloidal mercury were found to increase with discharge and with suspended sediment transport. This implies that most mercury transported in the Sacramento River is colloidal in form. Using a sequence of dissolution steps with specific chemical reagents, it was shown that most of the colloidal mercury was in the oxidizable and residual fractions, whereas only a minor component was found in the reducible colloid fraction. The implications of the occurrence of mercury in predominantly oxidizable and colloidal forms are currently unknown and warrant further investigation in the context of mercury methylation processes.

Abstract

Metals transport in the Sacramento River, northern California, was evaluated on the basis of samples of water, suspended colloids, streambed sediment, and caddisfly larvae that were collected on one to six occasions at 19 sites in the Sacramento River Basin from July 1996 to June 1997. Four of the sampling periods (July, September, and November 1996; and May–June 1997) took place during relatively low-flow conditions and two sampling periods (December 1996 and January 1997) took place during high-flow and

flooding conditions; respectively. Tangential-flow ultrafiltration with 10,000 nominal molecular weight limit, or daltons (0.005 micrometer equivalent), pore-size membranes was used to separate metals in streamwater into ultrafiltrate (operationally defined dissolved fraction) and retentate (colloidal fraction) components, respectively. Conventional filtration with capsule filters (0.45 micrometer pore-size) and membrane filters (0.40 micrometer pore-size) and total-recoverable analysis of unfiltered (whole-body) samples were done for comparison at all sites. Because the total-recoverable analysis involves an incomplete digestion of particulate matter, a more reliable measurement of whole-water concentrations is derived from the sum of the dissolved component that is based on the ultrafiltrate plus the suspended component that is based on a total digestion of colloid concentrates from the ultrafiltration retentate. Metals in caddisfly larvae were determined for whole-body samples and cytosol extracts, which are intercellular solutions that provide a more sensitive indication of the metals that have been bioaccumulated.

Trace metals in acidic, metal-rich drainage from abandoned and inactive sulfide mines were observed to enter the Sacramento River system (specifically, into both Shasta Lake and Keswick Reservoir) in predominantly dissolved form, as operationally defined using ultrafiltrates. The predominant source of acid mine drainage to Keswick Reservoir is Spring Creek, which drains the Iron Mountain mine area. Copper concentrations in filtered samples from Spring Creek taken during December 1996, January 1997, and May 1997 ranged from 420 to 560 micrograms per liter. Below Keswick Dam, copper concentrations in conventionally filtered samples ranged from 0.5 micrograms per liter during September 1996 to 9.4 micrograms per liter during January 1997; the latter concentration exceeded the applicable water-quality standard. The proportion of trace metals that was dissolved (versus colloidal) in samples collected at Shasta and Keswick dams decreased in the order cadmium ≈ zinc > copper > aluminum ≈ iron ≈ lead ≈ mercury. At four sampling sites on the Sacramento River at various distances downstream of Keswick Dam (Bend Bridge, 71 kilometers; Colusa, 256 kilometers; Verona, 360 kilometers; and Freeport, 412 kilometers) concentrations of these seven metals were predominantly colloidal during both high- and low-flow conditions.

Because copper compounds are used extensively as algaecides in rice farming, agricultural drainage at the Colusa Basin Drain was sampled in June 1997 during a period shortly after copper applications to newly planted rice fields. Copper concentrations ranged from 1.3 to 3.0 micrograms per liter in filtered samples and from 12 to 13 micrograms per liter in whole-water samples (total recoverable analysis). These results are consistent with earlier work by the U.S. Geological Survey indicating that copper in rice-field drainage likely represents a detectable, but relatively minor source of copper to the Sacramento River.

Lead isotope data from suspended colloids and streambed sediments collected during October and November 1996 indicate that lead from acid mine drainage sources became a relatively minor component of the total lead at the site located 71 kilometers downstream of Keswick Dam and beyond. Cadmium, copper, and zinc concentrations in caddisfly larvae were elevated at several sites downstream of Keswick Dam, but concentrations of aluminum, iron, lead, and mercury were relatively low, especially in the cytosol extracts. Cadmium showed the highest degree of bioaccumulation in whole-body and cytosol analyses, relative to an unmineralized control site (Cottonwood Creek). Cadmium bioaccumulation persisted in samples collected as far as 118 kilometers downstream of Keswick Dam, consistent with transport in a form more bioavailable than lead.

Introduction

Charles N. Alpers

Contamination of surface waters by metals can cause harmful effects to aquatic ecosystems and human health. In the Sacramento River drainage basin of northern California (fig. 1), metal contamination is a major concern, yet the sources, transport, and fate of metals in this basin remain poorly known. Water-quality problems with copper (Cu), cadmium (Cd), and zinc (Zn) have been known for many years near Redding, where large amounts of these metals flow into the Sacramento River system from acid mine drainage associated with inactive mines at Iron Mountain and other sources in the area (U.S. Environmental Protection Agency, 1992). Copper, cadmium, and zinc are also of concern in the San Francisco Bay and Sacramento–San Joaquin Delta (hereinafter referred to as the Bay–Delta), yet the proportion of metals transported to the Bay–Delta by way of the Sacramento River that comes from Iron Mountain Mine and other mineralized areas in the East Shasta and West Shasta mining districts has not been demonstrated. Mercury (Hg) concentrations in water and biota, particularly fish, are major environmental and human health concerns in the lower reaches of the Sacramento River and in the Bay–Delta, however the sources and chemical forms of mercury transported in the Sacramento River remain largely undetermined.

This report presents the results of a U.S. Geological Survey (USGS) study of metals transport in the reach of the Sacramento River between Shasta Dam and Freeport (fig. 1). The study was designed to complement ongoing studies of water quality in the Sacramento River Basin being carried out by the USGS's National Water-Quality Assessment (NAWQA) Program. The overall goals and conceptual design of the NAWQA Program were described by Hirsch and others (1988). Detailed description of the NAWQA Sacramento River Basin study unit is given in the next section of this report. Results of the NAWQA Sacramento River Basin study will be published separately from this report, which is designed to document the results of additional studies of metals transport that were beyond the original scope of the NAWQA investigation.

Routine protocols for sampling and sample processing in the NAWQA Program, and routine laboratory analysis for trace metals at the USGS's National Water Quality Laboratory (NWQL) are designed for a reporting limit of 1 mg/L for most metals. The advent of the USGS "part per billion" protocol for water sampling (Horowitz and others, 1994) represented a significant improvement over previous approaches, however, it was deemed inadequate in addressing critical trace metal issues in the Sacramento Basin. For this study, a more rigorous set of ultratrace protocols were adopted largely on the basis of methods developed by USGS researchers involved with a comprehensive study of trace metal transport in the Mississippi River (Taylor and Shiller, 1995; Taylor and others, 1995; Meade, 1996). Similar protocols also have been used in USGS studies of metals transport in the Arkansas River (Kimball and others, 1995) and elsewhere. Using triple-distilled acids, double-deionized water, precleaned sampling containers, and other precautions combined with state-of-the-art laboratory equipment such as a new generation of inductively coupled plasma–mass spectrometry (ICP–MS) instruments, reporting limits of less than 0.05 mg/L were achieved for many trace metals.

The overall objectives of the Sacramento River metals transport study were to determine the distribution and fate of metals from a known source, namely base-metal mines in the upper part of the watershed near Keswick Dam, and to determine if other sources such as agricultural and urban runoff were major contributors to base-metal loading under different flow conditions. The approach taken was multidisciplinary, involving collection and analysis of water, sediment, and biota. Water samples were taken at 6 to 11 sites during six sampling periods between July 1996 and June 1997, spanning a range of hydrologic conditions. Sample sites were chosen at or near active gaging stations so that discharge data would be available for calculation of metal loads. Streambed sediment and biota (caddisfly larvae) were sampled once at nine and six sites, respectively. To evaluate the importance of colloidal transport of metals, concentrations and loadings of metals were determined from the total recoverable analysis of whole-water samples and the various filtrates and ultrafiltrates of the water. Colloid concentrates were prepared using ultrafiltration and were analyzed for total metals as well as metal speciation using sequential extraction procedures that differentiated three operationally defined geochemical fractions: reducible (iron–manganese oxides), oxidizable (sulfides and organics), and residual (refractory).

This report is organized into several sections, each of which describes a critical aspect of the study. Following this Introduction, the second section contains a description of the Sacramento River Basin, with an overview of surface hydrology, physiography, and land use, plus a summary of the study unit design of the NAWQA Sacramento River Basin investigation. The third section describes the design of the metals transport study, including descriptions of sampling

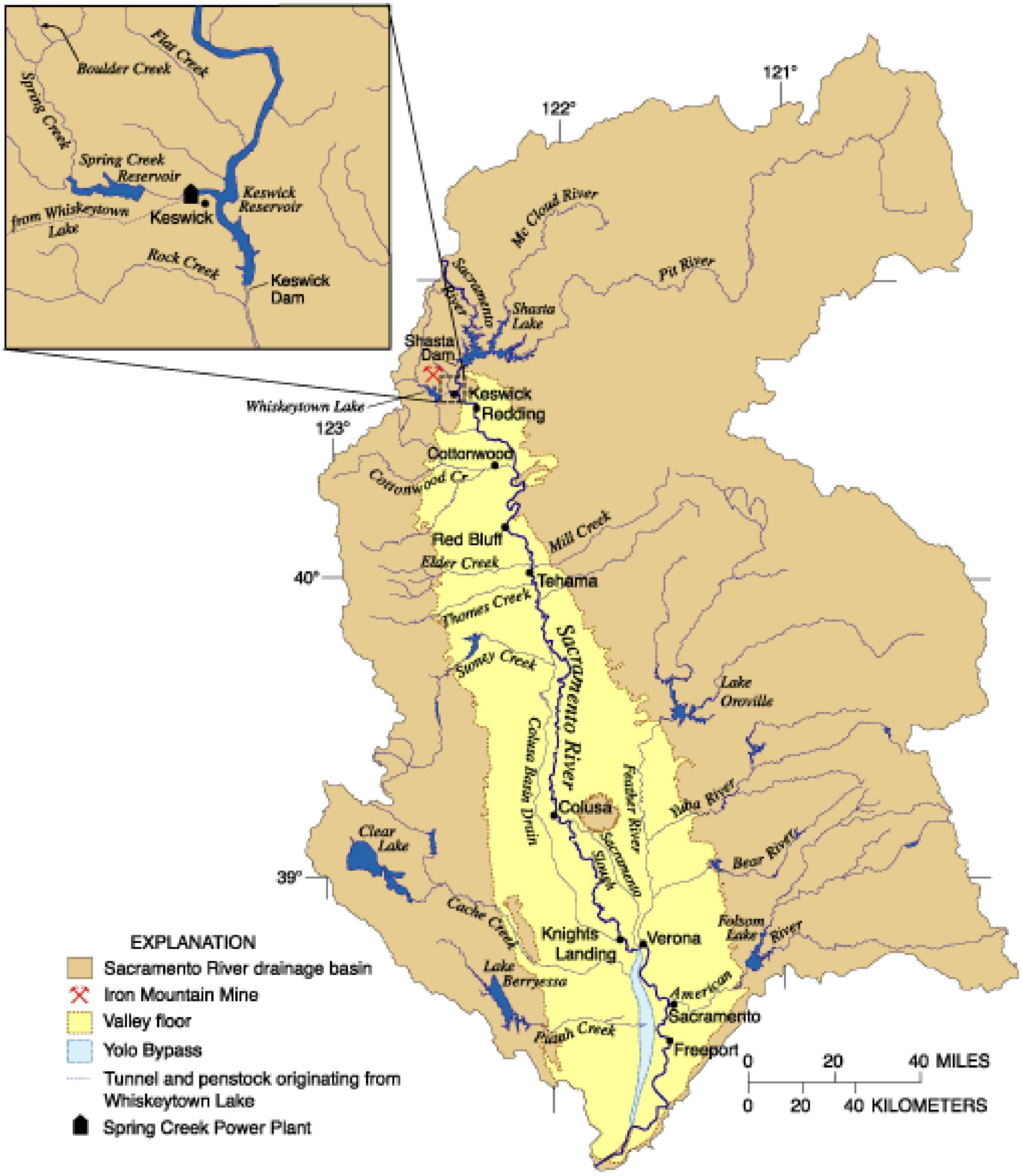

Figure 1. Map of the Sacramento River Basin, California.

methods, analytical procedures, quality assurance and quality control procedures, and data analysis techniques. The fourth section presents a summary of the results of quality assurance and quality control procedures with reference to data quality objectives as described in the Quality Assurance Project Plan, which is included as Appendix 1. The fifth section includes a description of the results of the study, divided into analysis of water, sediment, and biological samples, with emphasis on concentrations of the trace metals of principal concern: cadmium, copper, mercury, lead (Pb), and zinc. The final section of the report presents conclusions based on the results of this study. Metal loadings, sources, and implications of the results of this study to future water-quality management in the Sacramento River Basin are discussed in a companion report (Alpers and others, 2000). The distribution, transport, and loads of mercury in the Sacramento River Basin are discussed in a manuscript by David A. Roth and others (U.S. Geological Survey, written commun., 1999). Results from caddisfly sampling and analysis are described in detail by Cain and others (2000).

Other appendixes to this report include extensive tables of data, including analytical results and supporting quality assurance information. Appendixes 2 through 7 contain tables with the basic data resulting from this study. Appendix 2 contains tables of data relating to quality assurance and quality control for the chemical analyses in this study, including results of analysis of standard reference materials and blanks. Appendix 3 contains tables of data for unstable water-quality indices measured in the field, plus analytical data for major anions, nutrients, and organic carbon and information on sample site locations. Appendix 4 contains tables of metal concentrations in filtered and unfiltered (whole) water samples collected at study sites from July 1996 to June 1997. Appendix 5 presents tables of metal concentrations in sediment and colloids. Appendix 6 contains tables of data showing particulate size distribution in colloid concentrates and streambed sediment samples. Appendix 7 presents tables of trace-element data for caddisfly larvae collected in October 1996. Appendix 8 contains plots of dissolved and colloidal metal concentrations.

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Description of the Sacramento River Basin and Ongoing Studies

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This section provides an overview of the geographic setting in the Sacramento River Basin and a brief description of other ongoing studies in the area. The geographic setting of the basin is described in terms of its surface-water hydrology, physiography, and land use patterns.

Surface-Water Hydrology

The Sacramento River drainage basin (fig. 1) covers approximately 27,000 mi^2 (70,000 km^2) in northern California. The total length of the Sacramento River is 327 mi (526 km). The annual runoff averages 16,960,000 acre-ft/yr (Anderson and others, 1997) making it the largest river in the state of California. The river is of utmost importance to the economy of California, providing irrigation water to farms in the Sacramento and San Joaquin Valleys, drinking water to cities in northern and southern California, and most of the freshwater flow to the San Francisco Bay. The annual discharge of the Sacramento River is partly dependent on the amount of snowpack in the mountainous regions of the basin and stormwater runoff throughout the basin. Because of the variable amounts of snowpack and the destruction caused by floods in low-lying areas, reservoirs have been constructed to store water. These reservoirs were built with the intention of providing a more stable source of water for various uses and for flood control. The largest of these, Shasta Lake (fig. 1), was constructed between 1938 and 1944 by the federal government. The capacity of Shasta Lake is 4,552,000 acre-ft. Lake Oroville (fig. 1) is the second largest reservoir in California with a capacity of 3,537,600 acre-ft. Lake Oroville is on the Feather River and was completed in 1968 by the state of California. Reservoirs have also been constructed on many of the other tributaries to the Sacramento or Feather Rivers, especially within the Sierra Nevada drainage. Nearly all of the major rivers draining the Sierra Nevada and the Coast Ranges on the west side of the basin are regulated by some type of dam or control structure.

Flow on the Sacramento River is affected by reservoir releases, runoff, irrigation drainage, and flood control. Reservoir releases are set by resource managers who need to balance the capacity of reservoirs for flood control and to supply water for irrigation, urban, and environmental needs. The amount of water allocated to irrigation, urban, environmental needs, and other uses is determined in part by reservoir storage. The principal environmental needs involve controlling salinity in the Bay–Delta, meeting temperature requirements for migratory fishes, and controlling metals concentrations below Keswick Dam (fig. 1), which was completed by the federal government in 1950. The principal environmental use of water for wildlife habitat requirements is the discharge of sufficient fresh water to meet salinity criteria within the lower Sacramento River and parts of the San Francisco Bay–Delta estuary. Another important environmental constraint is to provide sufficient water at the proper temperatures for migratory fishes. As an example of the importance of this factor, the Bureau of Reclamation recently completed (in May 1997) construction of a temperature control device on Shasta Dam, at a cost of about $83,000,000, that allows water to be released from different elevations in Shasta Lake (California Department of Water Resources, 1998c).

The principal known input of metals downstream of Shasta Dam is Spring Creek (fig. 1), which receives metal-laden acidic drainage from the inactive copper–zinc mines at Iron Mountain. The Spring Creek Debris Dam (SCDD) was constructed in 1963 by the Bureau of Reclamation for the joint purpose of controlling metal pollution from Spring Creek and to prevent sediment and debris from interfering with the tailrace from the Spring Creek Power Plant (U.S. Environmental Protection Agency, 1992). Water is released from the SCDD in one or two locations depending on the amount of discharge. Discharge less than about 700 ft^3/s is made from gates within the dam; discharge above this amount is made either entirely over the SCDD spillway or in some combination of flow from the gates and over the spillway. The amount of discharge is controlled by the Bureau of Reclamation so that, below Keswick Dam, certain water-quality objectives for metals are met according to a 1980 Memorandum of Understanding between the Bureau of Reclamation (then the U.S. Water and Power Resources Services), the California Department of Fish and Game, and the California State Water Resources Control Board (U.S. Environmental Protection Agency, 1992). When the amount of water in Spring Creek Reservoir exceeds 5,000 acre-ft (or about 86 percent of capacity), there is the potential for an uncontrolled spill. Under those conditions, water may be needed from Shasta Lake or Whiskeytown Lake to dilute metal concentrations. Water from Whiskeytown Lake is supplied through the Spring Creek Power Plant.

The maximum probable impact scenario, insofar as impact on fresh-water resources, is when a wet year follows a dry year. For example, in 1992–1993, dilution water was needed for an early season storm that caused an uncontrolled spill from Spring Creek Reservoir at a time when Shasta Lake was relatively empty. During January 1993, approximately 100,000 acre-ft of water was released from Shasta Lake at a time of year when this water could not be recaptured downstream during a year when farmers did not receive their full allotment of irrigation water (Richard Sugarek, U.S. Environmental Protection Agency, oral commun., 1994). Metal-laden, acidic water from Spring Creek mixes with dilute water from Whiskeytown Lake (released from the Spring Creek Power Plant) in the Spring Creek arm of Keswick Reservoir (fig. 1). Neutralization of the acidic water upon dilution in this mixing zone has caused extensive precipitation of hydrous iron and aluminum oxides, some of which flocculate and settle in the Spring Creek arm (Nordstrom and others, 1999) and some of which remain in suspension and are transported into the main channel of Keswick Reservoir. From Keswick Reservoir, these metals may be transported downstream of Keswick Dam in the Sacramento River.

Agricultural use of water is the highest single category of use in the Sacramento River Basin. In 1990, for example, agriculture accounted for 58 percent of the water use in the basin and environmental needs accounted for 32 percent (California Department of Water Resources, 1993). Urban and other uses accounted for the remaining 10 percent of the allocations. Stormwater runoff or snowmelt takes place in late fall through spring in response to rain in the lowland areas and snowmelt in the mountains. Irrigation water is supplied by reservoir releases or ground water pumping from late March to September. Irrigation runoff is an important component of flow in the summertime. Two drains that discharge a considerable volume of irrigation runoff are the Colusa Basin Drain and the Sacramento Slough (fig. 1).

Flood control efforts have significantly changed the channel morphology and flow characteristics of the Sacramento River. Because of recurring flooding, especially in urbanized areas such as Sacramento, the Sacramento River channel has been modified to accommodate high flow or to divert water out of the main channel. Channel modifications include artificial levees. Flow control is partly accomplished by a series of weirs that remove water from the main channel and divert that flow onto agricultural land. The flow is routed to a region called the Yolo Bypass, at a point just upstream of the Sacramento River at Verona (fig. 1). Water discharges to the Fremont Weir when flow exceeds 55,000 ft^3/s on the Sacramento River at Verona. It is necessary to take water out of the river at that location because of decreasing channel capacity downstream. That water is then diverted to the San Francisco Bay–Delta Estuary. Water may also be taken out of the Sacramento River at Sacramento and diverted to the Yolo Bypass.

In the upper part of the basin, the mean annual discharge of the Sacramento River above Bend Bridge near Red Bluff is 12,790 ft^3/s for the period of record from 1964 to 1996 (Anderson and others, 1997). The mean annual discharge of the Sacramento River at Colusa is 11,460 ft^3/s for the period of record from 1946 to 1996 (Anderson and others, 1997). The mean annual discharge for the Sacramento River at Verona increases to 19,620 ft^3/s for the same period of record. The mean annual discharge of the Sacramento River at Freeport, in the lower part of the basin, is 23,410 ft^3/s for the period of record from 1949 to 1996 (Anderson and others, 1997). The Feather River is the largest tributary to the Sacramento River. The mean annual discharge of the Feather River near Gridley, which is located downstream of Lake Oroville, is 4,852 ft^3/s for the period of record from 1969 to 1996 (after the completion of the dam on Lake Oroville). The Yuba River is the largest tributary to the Feather River and has a mean annual discharge of 2,372 ft^3/s for the site at Marysville for the period of record from 1970 to 1996. The other large tributary to the Sacramento River is the American River, which has a mean annual discharge of 3,715 ft^3/s (just below Folsom Lake) for the period of record from 1956 to 1996. The dam on Folsom Lake was completed in 1955.

Hydrographs during the study period (July 1996–June 1997) for several of the sampling sites used in this study are shown in figure 2*A* through 2*I*. The 1996–1997 water year was characterized by a major flooding event in late December 1996 and early January 1997 that severely affected the Central Valley of California, particularly along the Yuba, Feather, Cosumnes, and Mokelumne Rivers, which experienced numerous (approximately 30) failed levees (Hunrichs and others, 1998). Several feet of snowfall in the Sierra Nevada in mid-to-late December was followed by several inches of warm rain that melted the previously accumulated snow, causing torrential runoff in some areas that experienced events in excess of the “100-year flood.” In the northern end of the Sacramento Valley, the rainfall and streamflow patterns were less anomalous. For example, during

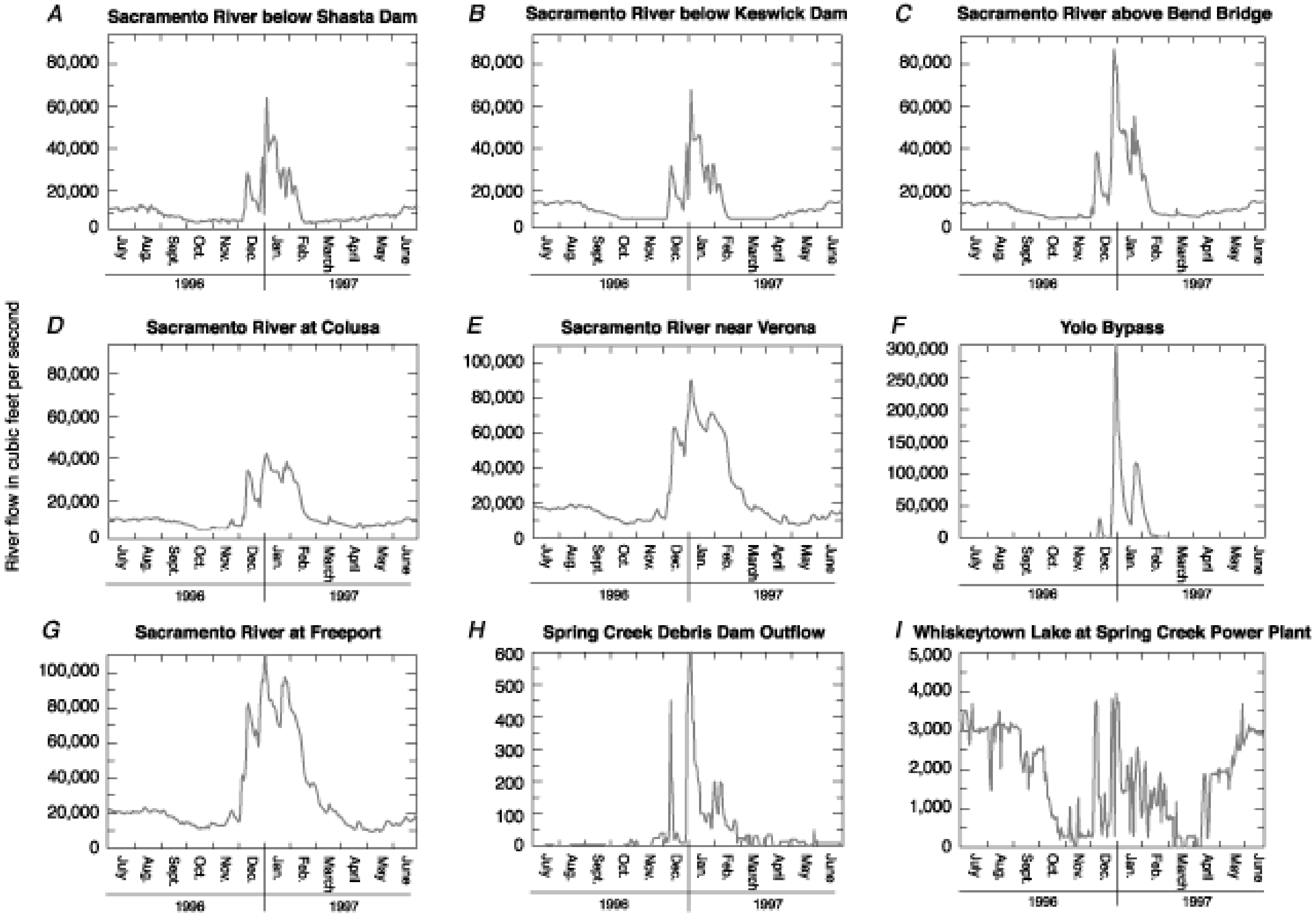


Figure 2. Hydrographs showing daily mean discharge for the period July 1, 1996 to June 30, 1997, for nine sites in the Sacramento River Basin, California. California Department of Water Resources (1998a) for *A*; California Department of Water Resources (1998b) for *B*; U.S. Geological Survey (1998) for *C, D, E, F,* and *G*; and Bureau of Reclamation (1998, written communication) for *H* and *I.*

early January 1997, peak flows at 17 gaged stations on streams in Shasta County and Tehama County had recurrence intervals ranging from 2 to 61 years with a median of 21 years (Hunrichs and others, 1998). In contrast, numerous streams in the southern part of the study area had peak flows corresponding to 1-in-100 year events or more (Hunrichs and others, 1998). For example, 18 gaged streams in El Dorado County (in the American River watershed) had peak flows with recurrence intervals that ranged from 3 to 270 years with a median of 98 years. Flows from Shasta and Keswick dams were held back markedly in early January to minimize downstream flooding.

Discharge data from several gaging stations and dams in the study area are plotted as daily mean discharges in figure 2. The data from Shasta and Keswick dams are from the Bureau of Reclamation, or BOR (California Department of Water Resources, 1998a,b). Hydrographs for the Sacramento River gaging stations at Bend Bridge, Colusa, Verona, and Freeport, and for the Yolo Bypass are based on published data from the USGS (U.S. Geological Survey, 1998). The data for the Spring Creek Debris Dam outflow and the Whiskeytown Lake discharge through the Spring Creek Power Plant were provided by the BOR (Valerie Ungvari, Bureau of Reclamation, written commun., March 12, 1998).

Monthly rainfall data during 1996-1997 at Shasta Dam, Redding, and Sacramento are compared with long-term monthly average rainfall data in figure 3 (National Oceanic and Atmospheric Administration, 1996, 1997a–f). Despite their proximity, there is generally higher annual rainfall at Shasta Dam (61 in./yr) compared with Redding (33.5 in./yr). This difference was even greater in the data from the 1996–1997 water year. For example, in December 1996, Shasta Dam had about three times as much rainfall as Redding. The rainfall data (fig. 3) show that the 1996-1997 water year was characterized by much higher than normal rainfall in the early part of the wet season (December and January), followed by much lower than normal rainfall during February through April. Despite the extensive flooding in many parts of the Sacramento River Basin, the 1996–1997 water year ended up close to average with regard to total precipitation in many areas because there was very little if any rain from mid-January to May, during what is normally a very wet period.

Physiography

The Sacramento River drainage basin can be divided into seven regions that are based on physiography (fig. 4). These physiographic provinces are largely based on geologic factors, including rock types and tectonic setting. The provinces are the Sacramento Valley, the Klamath Mountains, the Coast Ranges, the Modoc Plateau, the Cascade Mountains, the Sierra Nevada, and the Sacramento–San Joaquin Delta. The Sacramento Valley and the Sacramento–San Joaquin Delta are the low-lying parts of the basin. For a more complete description of the geology of these zones, the reader is referred to reports by Bailey (1966) and by Norris and Webb (1990).

Land Use

The major land uses in the Sacramento River Basin are agriculture, forestry, urban development, and mining. Mining is discussed in greatest detail in this report because of the potential for water quality degradation from acid-mine drainage and the potential for mercury transport from mercury and gold (Au) mines.

Mining

Metals have been mined from locations in the Klamath Mountains, the Sierra Nevada, and the Coast Ranges provinces. The West Shasta mining district, located in the Klamath Mountains near Shasta Lake, contains several massive sulfide copper–zinc deposits with historic production. The massive sulfide deposits consist of millions of tons of the minerals chalcopyrite ($CuFeS_2$), sphalerite [(Zn,Fe,Cd)S], and pyrite (FeS_2) hosted by hydrothermally altered volcanic rocks with minimal capacity for neutralization of sulfuric acid (H_2SO_4) solutions formed during weathering. These metal deposits formed during the Devonian Period (approximately 400 million years ago) when sulfide minerals were deposited from sea-floor vents presumably analogous to active “black smokers” found at mid-ocean ridges and in back-arc basins (Morton and others, 1994; Barrie and Hannington, 1999). Mine wastes and acid discharges from historic mining of these massive sulfide deposits has resulted in acid mine drainage that has caused extreme metal contamination in several northern California streams, including Boulder Creek, Slickrock Creek, Spring

Creek, Little Backbone Creek, and West Squaw Creek (Nordstrom and others, 1977).

Gold was also mined in the Klamath Mountains; this province is second only to the Sierra Nevada for gold production in California (Norris and Webb, 1990). Placer gold was recovered from modern and ancient stream deposits both in the Klamath Mountains and the Sierra Nevada. “Lode” gold (or hardrock) also was mined both in the Klamath Mountains and in the Sierra Nevada foothills region, known as the Mother Lode. At least 107 million ounces of gold have been recovered from the Mother Lode (Norris and Webb, 1990). From the 1849 gold rush until the early 1900s, the dominant process used for gold recovery was mercury amalgamation (Bradley, 1918). The mercury used for gold processing was mined in the Coast Ranges of California. Residual mercury from gold processing operations has contaminated streambed sediments within the Sierra Nevada and downstream locations (Hunerlach and others, 1999). Elevated mercury concentrations in benthic invertebrates and fish have been shown in some Sierra Nevada streams (Slotton and others, 1997a) and in the Cache Creek watershed, which is heavily impacted by mercury mining and processing activities (Slotton and others, 1997b).

The location of mines in these different physiographic zones relates to the potential for trace metal transport from past or present mining operations, or from natural sources, such as springs, associated with the mineralized areas. The locations of historic copper, lead, and zinc mines are shown in figure 5, and the locations of gold and mercury mines are shown in figure 6.

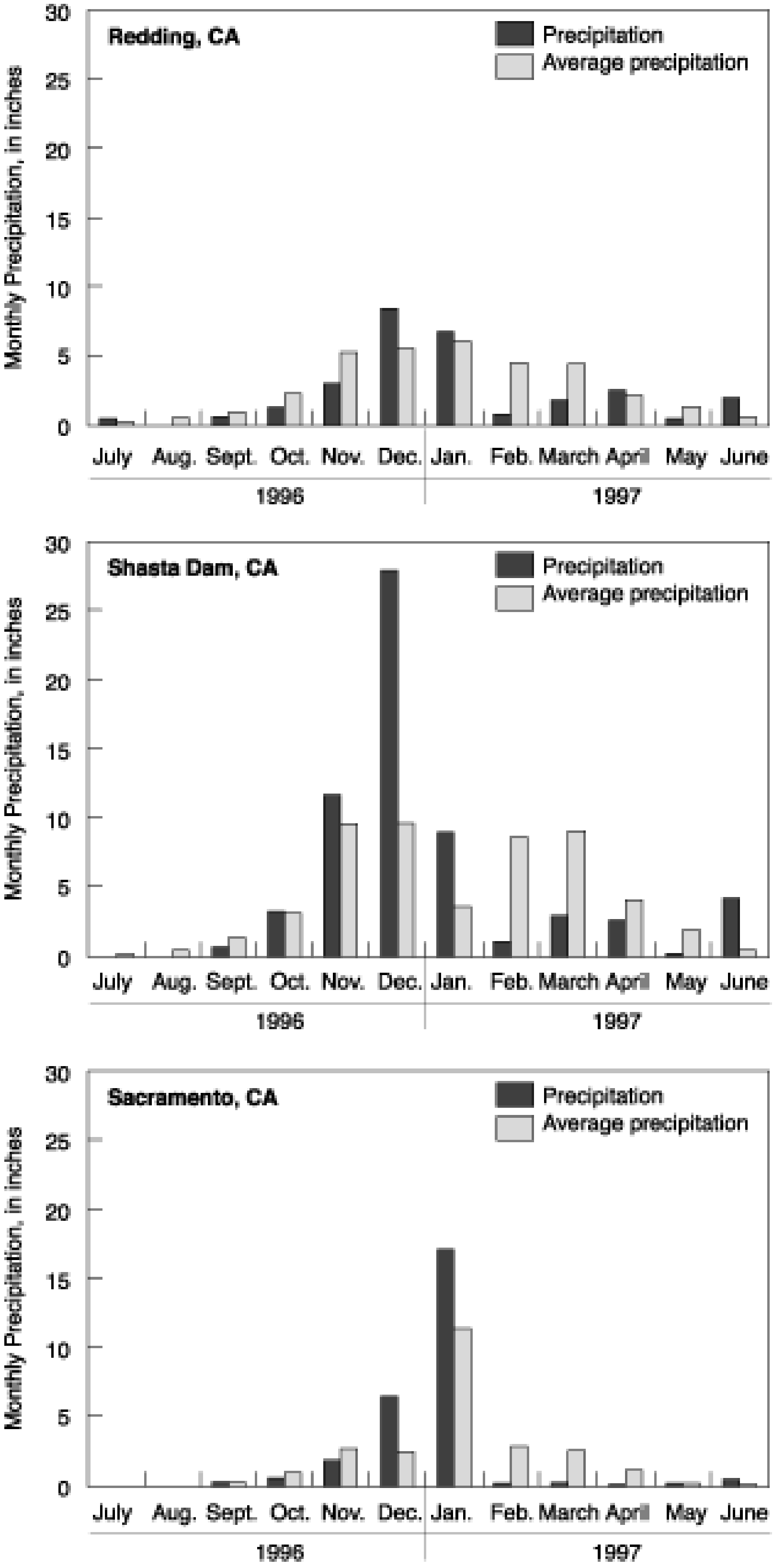


Figure 3. Histograms showing monthly precipitation for the period July 1996 to June 1997 and long-term monthly averages for three sites in the Sacrmento River Basin, California.

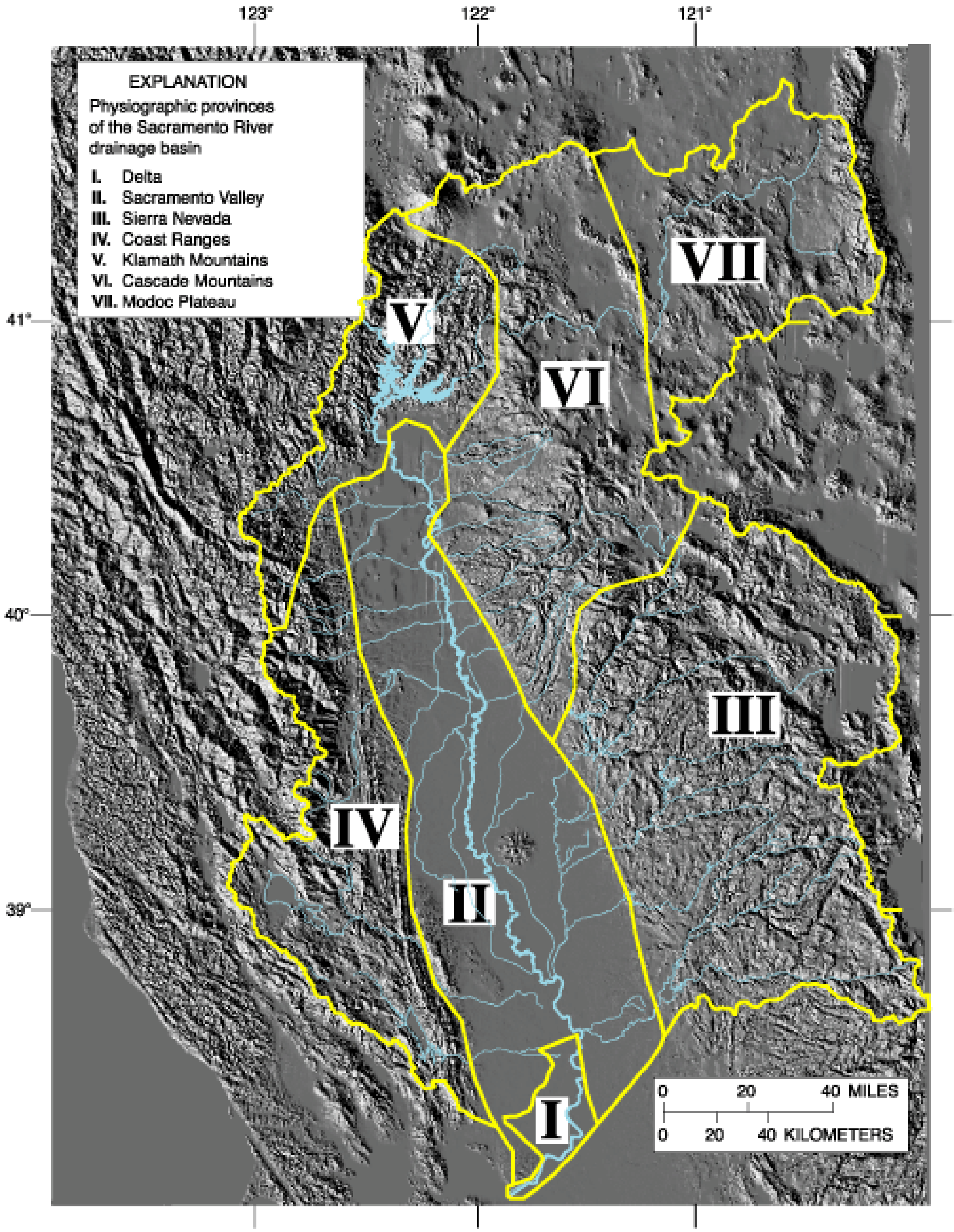
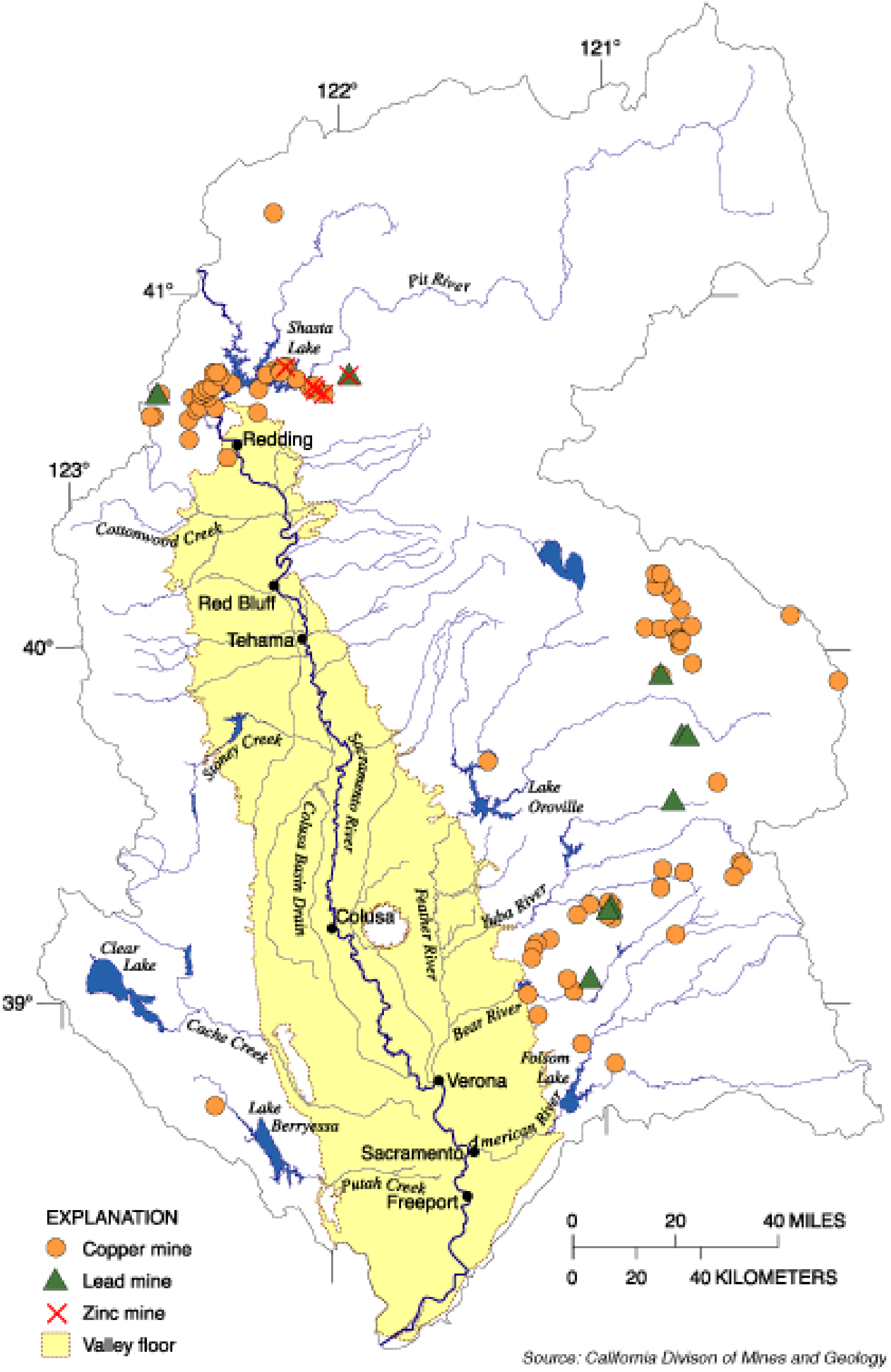
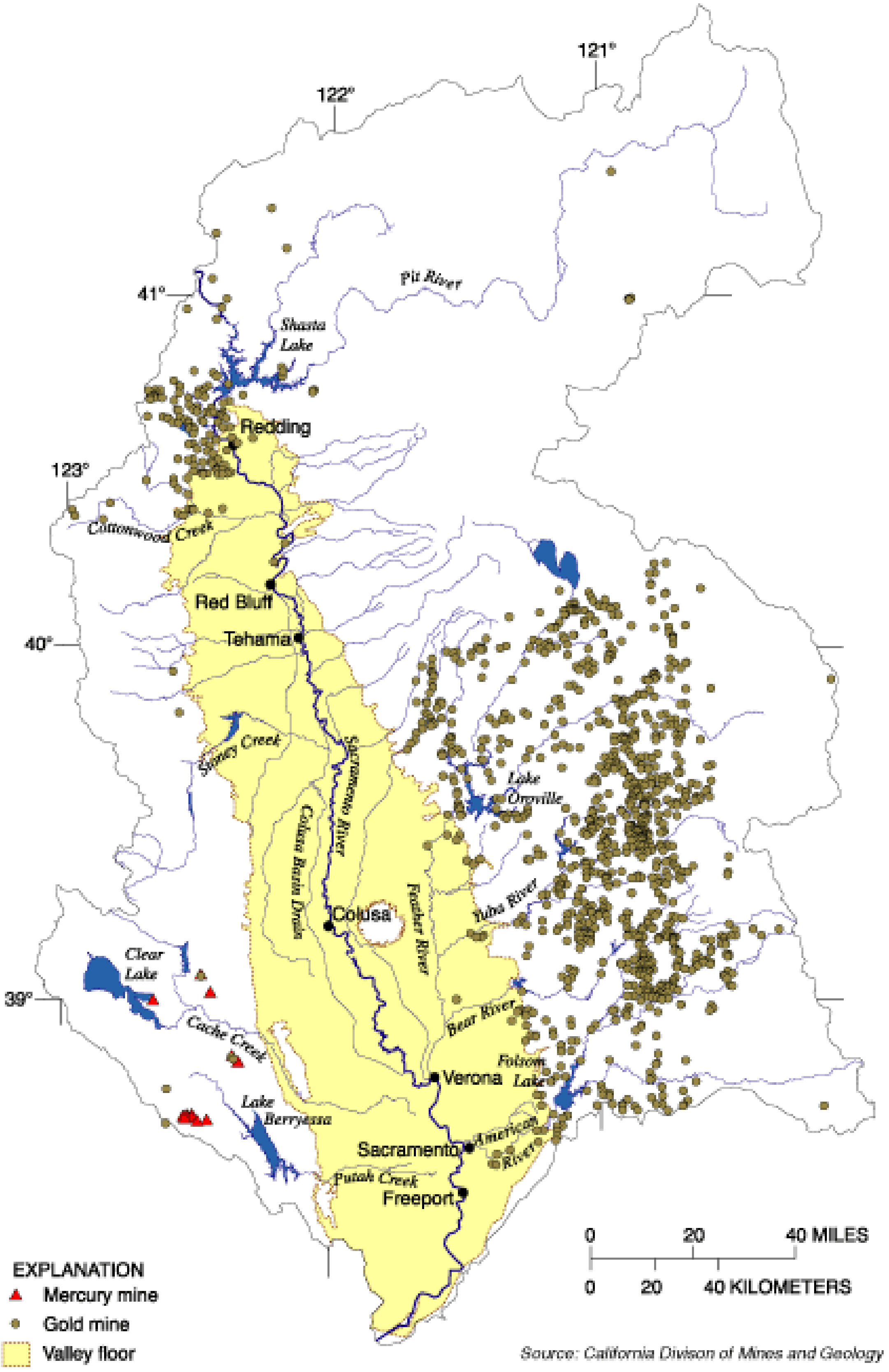


Figure 4. Map of physiographic provinces for the Sacramento River Basin, California.



Source: California Divison of Mines and Geology

Figure 5. Map showing historic copper, lead, and zinc mines in relation to other selected features in the Sacramento River Basin, California.



Source: California Divison of Mines and Geology

Figure 6. Map of historic gold and mercury mines in relation to other selected features in the Sacramento River Basin, California.

Other Land Uses

Other (nonmining) land uses of the Sacramento River Basin are shown in figure 7. The Sacramento Valley floor (figs. 1, 4, and 7) is the major agricultural region of the basin. Row crops are predominant in the southern Sacramento Valley and grazing is an important activity in the northern valley. Rice is one of the most important crops of the Sacramento Valley. Rice production involves the creation of temporary wetlands. Pest control in these temporary wetlands includes the use of cooper compounds, such as copper sulfate, for the control of algae. Land cover in most of the mountainous areas of the basin is principally forest. The types of forests in the various locations were described in detail by Schoenherr (1992).

Ongoing Studies—NAWQA Program

One of the goals of the NAWQA Program is to investigate and describe the status of, and trends in, the water quality of the nation's streams and ground water. Conceptual details of the program were given by Hirsch and others (1988). A total of 59 NAWQA study units throughout the United States are assessing water quality in basins representing more than 75 percent of the nation's water use. The environmental setting and study design of the NAWQA study unit in the Sacramento River Basin are described by Domagalski and others (1998). The study design includes a network of basic fixed sites that are monitored monthly for water quality and a network of sites where streambed sediment and biological tissues are sampled on a less frequent, synoptic basis. The sites selected for these monitoring activities are described in more detail below.

The NAWQA Program is designed to provide continuing documentation of the quality of the rivers and ground water in major basins throughout the United States. Investigations at individual basins are designed for a 10-year cycle. As part of the NAWQA Program, rivers are sampled for a period of 2 years during part of that 10-year cycle. The sampling takes place at predetermined monthly intervals and in response to hydrological conditions such as stormwater runoff. Water-quality samples collected at NAWQA sites are analyzed for a suite of constituents, including major cations and anions, nutrients, dissolved organic carbon, and general water-quality parameters such as pH, dissolved oxygen, specific conductance, temperature, and alkalinity. At a subset of sites, samples are collected for pesticide or volatile organic chemical analyses, or both. Additional samples, such as those for trace metals, are collected if additional funding has been appropriated. Data is aggregated at the national level, where attention is currently directed to the concentrations and trends detected in nutrients, pesticides, ecology, volatile organic chemicals, and trace elements. In the NAWQA Program, sampling sites on rivers are selected on the basis of natural features of the environment, such as physiography, and of anthropogenic factors such as land use. Consideration in sampling site selection also is given to the subsequent data interpretation, including the capability to provide a mass balance for various constituents in the watershed and to complete biological assessments at or near the water-quality sampling sites.

Basic fixed sites

Twelve river sites were chosen as basic fixed sites in the Sacramento River Basin for the NAWQA project. Four sites were chosen on the Sacramento River: the Sacramento River above Bend Bridge near Red Bluff, the Sacramento River at Colusa, the Sacramento River at Verona, and the Sacramento River at Freeport (fig. 8). The Bend Bridge site was selected because it is the northernmost location, below Shasta Lake, that met applicable national NAWQA criteria. It was suspected that impacts of acid mine drainage from Iron Mountain Mine, via Spring Creek, might be detectable at this site. The Colusa site was chosen because it is centrally located in the basin, it is sufficiently downstream of Spring Creek, such that the effects of acid mine drainage are less likely to be detected, and it is upstream of both drainage from the Sierra Nevada and most of the agricultural drainage of the Sacramento Valley. The Verona site is just downstream of the confluence with the Feather River, one of the major streams draining the Sierra Nevada. The site is also just downstream of the location where much of the agricultural drainage of the Sacramento Valley drains to the Sacramento River. The Freeport site was chosen as a basic fixed site because of its downstream location. Water-quality samples at that site provide an overall indication of multiple sources of constituents to the Sacramento River and also provide an indication of the quality of water entering the San Francisco Bay–Delta Estuary.

Three streams draining the Sierra Nevada were selected as basic fixed sites for the NAWQA study

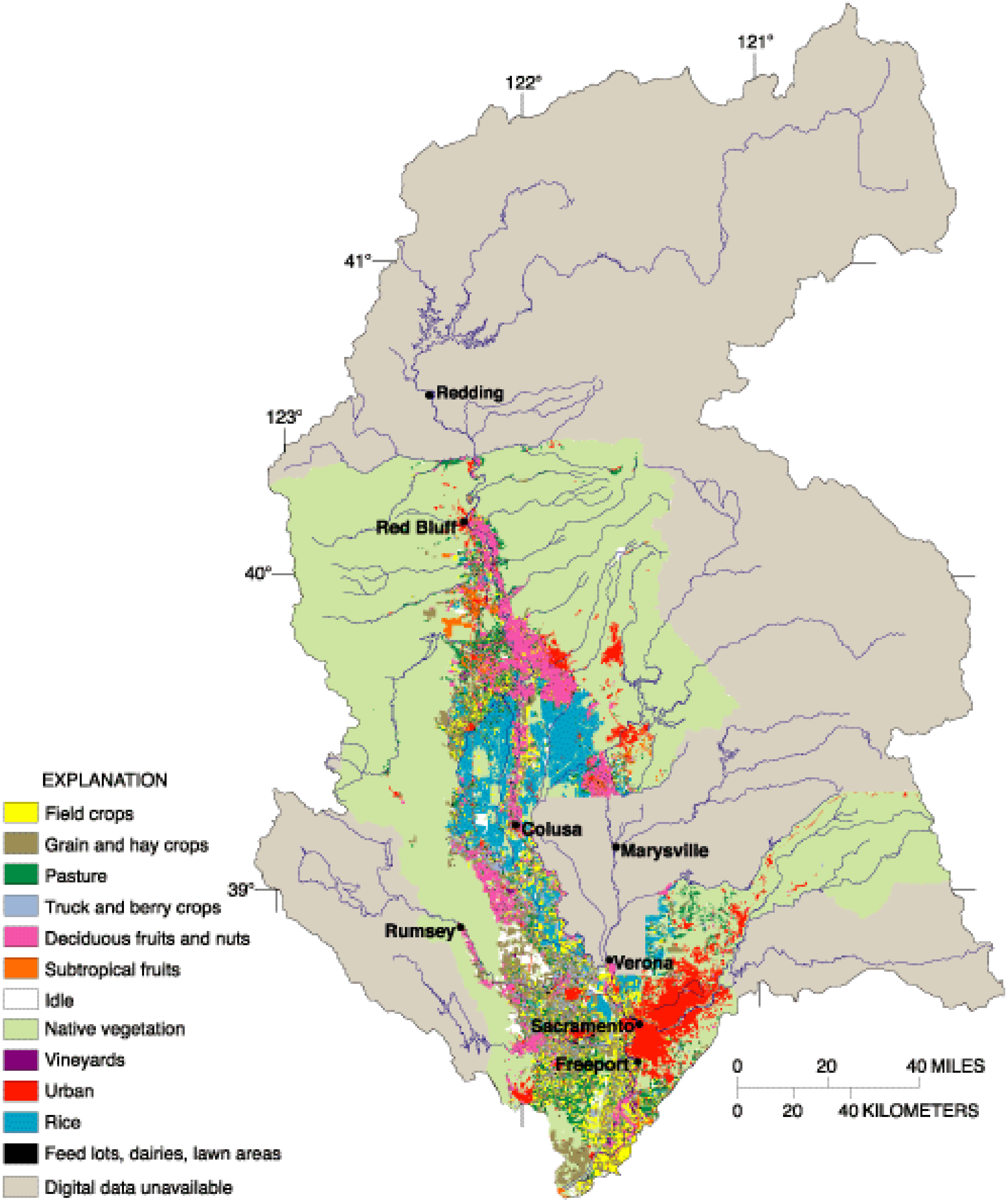


Figure 7. Map showing agricultural and other nonmining land uses in the Sacramento River Basin, California.

unit: the Feather River near Nicolaus, the Yuba River near Marysville, and the American River in Sacramento (Domagalski and others, 1998). The chosen locations on these streams are either near the confluence with the Sacramento River, or in the case of the Yuba River, near the confluence with the Feather River. Two NAWQA basic fixed sites were chosen on streams draining agricultural regions in the Sacramento Valley: the Colusa Basin Drain and the Sacramento Slough. Two additional streams were

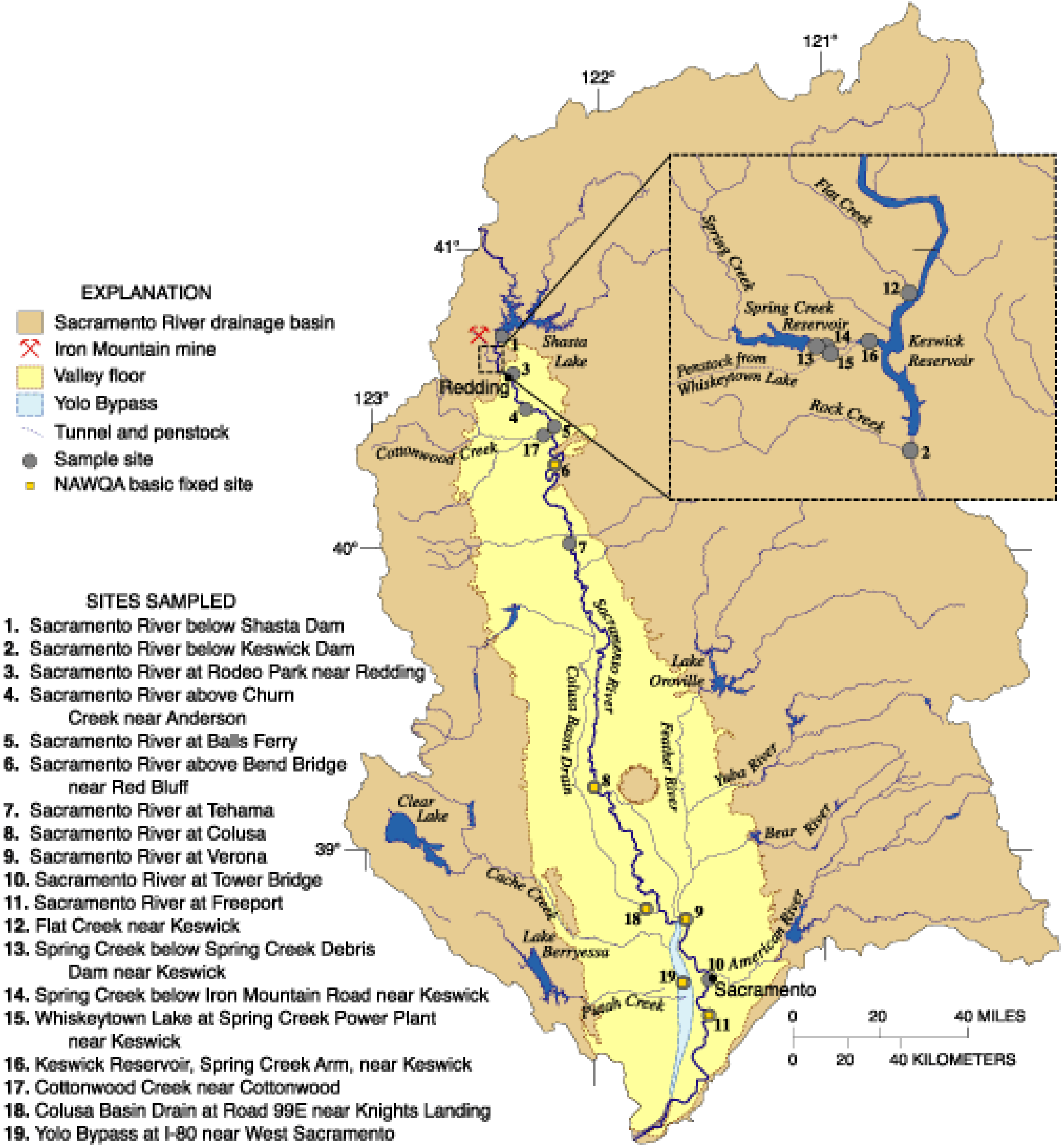


Figure 8. Map showing sampling sites in Sacramento River Basin, California.

selected: Cache Creek, which drains a part of the Coast Ranges with considerable mercury mining, and Arcade Creek near Del Paso Heights, an urban stream.

One distributary site, the Yolo Bypass at Interstate 80 near West Sacramento, also was selected. As discussed previously, water flows in the Yolo Bypass only during wet years and primarily during the winter months. It is necessary to sample the Yolo Bypass at Interstate 80 near West Sacramento to understand the transport of metals and other constituents from the Sacramento River to the Bay–Delta.

Streambed Sediment and Tissue Sites

In addition to the twelve basic fixed sites selected for monthly monitoring of water quality, an additional set of six sites was selected for the sampling of streambed sediment and tissue of aquatic organisms as part of the NAWQA Program. The aquatic organisms collected for tissue analyses were the Asian clam, *Corbicula fluminea*, and bottom feeding fish such as the common carp, *Cyprinus carpio*. The Yolo Bypass at Interstate 80 near West Sacramento (a basic fixed site) was not sampled for streambed sediment or tissue of aquatic organisms because it was dry at the time of sampling. The other 11 basic fixed sites were sampled for streambed sediment and tissue, making a total of 17 sites. These additional sites are the McCloud River, the Cottonwood Creek near Cottonwood, the Deer Creek near Vina, the Jack Slough near Jack Slough Road, and the Stony Creek below Black Butte Dam (Domagalski and others, 1998). Samples of streambed sediment and tissue of select aquatic organisms were collected initially in October 1995 for the determination of trace elements and hydrophobic organic contaminants (MacCoy and Domagalski, 1999). Results of follow-up sampling during 1997 and 1998 will be presented in a subsequent report.

Study design: Field and Laboratory Methods

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This section describes the design of the Sacramento River metals transport study and the field and laboratory methods used. The site selection and sampling schedule are discussed, including methods used for the collection and processing of water, sediment, and biological samples. The analytical procedures that were used in the field and the laboratory are also discussed.

Site Selection and Sampling Schedule

Samples of water, colloids, streambed sediment, and caddisfly larvae were taken at 19 different sites for this study (fig. 8), though each type of sample was not necessarily taken at each site. Table 1 shows the dates of sampling for each type of sample at the various sample sites, along with distance from the river mouth.

Water Sampling

Water sampling sites for this study included six principal sites along the mainstem Sacramento River, plus the Yolo Bypass, a distributary site that receives water from mainstem Sacramento River for flood control during high-flow conditions (fig. 8). On one sampling trip during extreme high-flow conditions, an alternate site was chosen at one of the mainstem locations for logistics reasons. Six tributaries to the Sacramento River also were sampled, focusing on the Spring Creek area near Keswick Reservoir. The individual water sampling sites and the rationale for their selection are discussed in the following sections.

Sacramento River and Yolo Bypass Sites

One of the principal objectives of this study was to assess metal loads along the mainstem of the Sacramento River from Shasta Dam to Freeport (fig. 1). The four mainstem basic fixed sites from the NAWQA study—Sacramento River above Bend Bridge near Red Bluff, at Colusa, at Verona, and at Freeport (fig. 8, table 1, sites 6, 8, 9, and 11, respectively)—were selected for detailed trace-metal analysis. In addition, two other mainstem sites on the Sacramento River upstream from the Bend Bridge site were chosen for detailed sampling of water and colloids: the Sacramento River below Shasta Dam and below Keswick Dam (fig. 8, table 1, sites 1 and 2). All six of these mainstem sites were sampled during five of the six sampling periods (July, September, November, and December 1996, and May–June 1997).

Water samples also were taken from mainstem Sacramento River sites below Keswick Dam, above Bend Bridge, and at Colusa during the sixth (fifth chronologically) sampling period, which corresponded

Table 1. Sampling sites along the Sacramento River showing distance from river mouth and dates of sampling for various media

[Dist., distance from river mouth. DD, Debris Dam; PP Power Plant; Jan., May, and June samples taken in 1997; all other months in 1996. **Bold** denotes field replicate samples taken and analyzed; *italics* denote sequential extraction analysis for speciation of colloids; blank cells indicate no samples taken]

	Dist. River Mile (kilometer)	Media Sampled			
		Water	Colloids (speciation in italics)	Streambed Sediment	Hydropsyche Larvae
SACRAMENTO RIVER SITES					
1. Sacramento River below Shasta Dam	311 (500)	**July, Sept., Nov., Dec., May**	July, Nov., Dec., *May*		
2. Sacramento River below Keswick Dam	302 (486)	**July, Sept., Nov., Dec., Jan., May**	July, Nov., Dec., *Jan.*, *May*		
3. Sacramento River at Rodeo Park near Redding	298 (479)			Oct.	Oct.
4. Sacramento River above Churn Creek near Anderson	285 (459)			Oct.	Oct.
5. Sacramento River at Balls Ferry	276 (444)			Oct.	Oct.
6. Sacramento River above Bend Bridge near Red Bluff	258 (415)	**July, Sept., Nov., Dec., Jan., May**	July, Sept., Nov., Dec., *Jan.*, *May*	Oct.	Oct.
7. Sacramento River at Tehama	229 (368)			Oct.	Oct.
8. Sacramento River at Colusa	143 (230)	**July, Sept., Nov., Dec., Jan., June**	July, Sept., Nov., Dec., *Jan.*, *June*	Nov.	
9. Sacramento River at Verona	78 (126)	**July, Sept., Nov., Dec., June**	July, Sept., Nov., Dec., *June*	Nov.	
10. Sacramento River at Tower Bridge	59 (95)	**Jan.**	Jan.		
11. Sacramento River at Freeport	46 (74)	**July, Sept., Nov., Dec., June**	July, Sept., Nov., Dec., *June*	Nov.	
TRIBUTARY SITES					
12. Flat Creek near Keswick	304 (489)	**Dec., May**			
13. Spring Creek below Spring Creek DD near Keswick	303 (488)	**Dec., May**	Dec., *May*		
14. Spring Creek below Iron Mountain Road near Keswick	303 (488)	**Jan.**	Jan.		
15. Whiskeytown Lake at Spring Creek PP near Keswick	303 (488)	**Dec., May**			
16. Keswick Reservoir, Spring Creek arm, near Keswick	303 (488)	**July, Sept., Nov., Dec., May**	July, Nov., Dec., *May*		
17. Cottonwood Creek near Cottonwood	273 (439)			Oct., June	Oct.
18. Colusa Basin Drain at Road 99E near Knights Landing	90 (145)	**June**	*June*		
DISTRIBUTARY SITE					
19. Yolo Bypass at I-80 near West Sacramento	83 (134)	**Jan.**	Jan.		

to extremely high flows associated with the New Year's flood event of early January 1997. No extreme high-flow samples were taken at the sites below Shasta Dam, at Verona, or at Freeport for logistic reasons, such as limited boat access and unsafe river conditions.

During the flood conditions of early January 1997, the flow regime of the Sacramento River near Sacramento was sufficiently different that sampling in the lower part of the river was done at different locations. Because of the magnitude of the flow, a large part of the river flow was diverted to the Yolo Bypass by way of the Fremont weir (fig. 8). Therefore, a composite sample consisting of thirty vertical intervals was collected from the Yolo Bypass at Interstate 80 (fig. 8, table 1, site 19). Also during this extremely high-flow period, the Sacramento River, south of its confluence with the American River, consisted mainly of water from the American River because most of the flow from the mainstem Sacramento River was diverted to the Yolo Bypass. During these conditions, boat access to certain parts of the Sacramento River was limited or deemed unsafe. In lower-flow conditions, the Freeport site is routinely sampled by boat; the nearby bridge has been deemed unsafe for bridge-based sampling because of narrow traffic and pedestrian lanes. In January 1997, boat access at Freeport was not possible; therefore, the mainstem Sacramento River was sampled at Tower Bridge, near downtown Sacramento, located 21 km (13 mi) upstream (fig. 8, table 1, site 10).

Tributary Sites

The tributary best known as a source of metals to the Sacramento River is Spring Creek (figs. 1 and 8). During five of the six sampling periods for this study (all except January 1997), a sample was taken in the Spring Creek arm of Keswick Reservoir (fig. 8, table 1, site 16). The sampling point for site 16 was approximately 100 m downstream of the mixing zone of Spring Creek and the tailrace from the Spring Creek Power Plant (SCPP) (water from Whiskeytown Lake) (figs. 1 and 8). At this site, the flow from these tributaries was relatively well mixed horizontally, in a constricted part of the Spring Creek arm where the influence from water released at Shasta Dam was extremely unlikely. It was assumed that the dissolved and colloidal fractions of the water column were well mixed vertically at this location.

Spring Creek was sampled on three occasions (December 1996, January 1997, and May 1997) between the SCDD and the discharge point to the Spring Creek arm of Keswick Reservoir. The site named "Spring Creek below Spring Creek Debris Dam near Keswick" (fig. 8, table 1, site 13) corresponds to the concrete weir that receives water from the outlet works of SCDD. This was the sampling location in December 1996 and May 1997. During January 1997, the Spring Creek samples were taken at the site named "Spring Creek below Iron Mountain Road near Keswick" (fig. 8, table 1, site 14) so that the discharge from the SCDD spillway and other runoff from areas near the SCDD would be included.

Samples were taken of Whiskeytown Lake water from the SCPP near Keswick in December 1996 and May 1997. Under some conditions, the discharge from the SCPP represents most of the flow in the Spring Creek arm of Keswick Reservoir. The water samples were taken from a spigot off a turbine housing on the lowest level of the power plant. No sample was taken during early January 1997 because discharge through the SCPP was minimal at that time.

The Flat Creek near Keswick site is located near the confluence of Flat Creek and Keswick Reservoir. Flat Creek is a tributary to Keswick Reservoir approximately 1.5 km upstream from the Spring Creek arm of Keswick Reservoir (fig. 8, table 1, site 12). Construction of a diversion of upper Spring Creek into Flat Creek was completed in December 1990 (U.S. Environmental Protection Agency, 1992). This diversion carries up to 600 ft^3/s of relatively uncontaminated water from upper Spring Creek to reduce the flow into Spring Creek Reservoir. It is known that metals contaminate upper Spring Creek because of the Stowell Mine, a copper-zinc mine similar in geology to Iron Mountain; but because the mine is considerably smaller in terms of deposit size and production, the contamination is relatively insignificant (Kinkel and others, 1956).

The Flat Creek drainage also includes the Minnesota Flats site, which was a disposal area for high-pyrite mill tailings from the Minnesota copper flotation mill, which operated from about 1914 to 1942 (U.S. Environmental Protection Agency, 1992). During 1988, the tailings (approximately 28,000 yd^3) were excavated and deposited in the Brick Flat Pit near the top of Iron Mountain, effectively eliminating this source of pollution (U.S. Environmental Protection Agency, 1992). Also, since 1994, a lime neutralization plant has been located at the Minnesota Flats site. This plant treats drainage from the Richmond and Lawson portals on the Boulder Creek side of Iron Mountain, as well as water pumped from the Old mine and Number 8 mine workings on the Slickrock Creek side of Iron Mountain. The treated water is discharged to Spring Creek so that, under normal operating conditions, there is no metal loading to Flat Creek associated with operation of the treatment plant. Nevertheless, Flat Creek carries the second largest metal loading to Keswick Reservoir, behind Spring Creek (John Spitzley, CH2M Hill, Redding, California, written commun. to Richard Sugarek, U.S. Environmental Protection Agency, 1997).

Flat Creek was sampled near its confluence with Keswick Reservoir during December 1996 and May 1997 (table 1). During early January 1997, flood conditions had caused scouring of a bridge where Iron Mountain Road crosses Flat Creek. The upper Spring Creek Diversion was temporarily shut down while the bridge was repaired. Although there was some flow in Flat Creek associated with its original watershed, the metal loadings were probably much lower than would have been the case if the diversion had been operating. Therefore, Flat Creek was not sampled during the January 1997 sampling period.

The Colusa Basin Drain was sampled to represent agricultural drainage from an area with active rice production. Substantial amounts of copper sulfate are added to rice fields periodically to suppress algae and other pests. This site was sampled monthly during 1996 as a basic fixed site in the NAWQA Program, and showed elevated copper concentrations during June of that year, a period when the rice fields were draining. The Colusa Basin Drain site was sampled with the additional trace metal protocols for this study in June 1997 to evaluate the potential occurrence of metals and their manner of transport at this location during drainage of the rice fields.

Streambed Sediment and Caddisfly Larvae Sampling

Streambed sediment was sampled (table 1) at each of the four basic fixed sites on the Sacramento River (Bend Bridge, Colusa, Verona, and Freeport). Four additional sites on the mainstem Sacramento River between Redding and Tehama (Rodeo Park, Churn Creek, Balls Ferry, and Tehama; fig. 8, sites 3, 4, 5, and 7) and one tributary (Cottonwood Creek, fig. 8, site 17) also were sampled for streambed sediment in conjunction with sampling for caddisfly larvae (table 1). The purpose of sediment sampling was to investigate possible correlations of trace metal chemistry between sediment, water, and biota at selected sites.

Additional suitable sites for caddisfly larvae collection could not be found between Keswick Dam and Shasta Dam (namely, in Keswick Reservoir) or in the Sacramento River downstream of Tehama because of the lack of a suitable habitat, such as riffle zones. In addition, an attempt to collect additional caddisfly samples in June 1997 was unsuccessful in the mainstem Sacramento River at the sites sampled previously in October 1996 because of relatively high-flow conditions.

Methods for Sample Collection and Field Measurements

This section describes the methods of collection for samples of water, sediment, and caddisfly larvae. Also discussed are methods used for field measurements, including pH, specific conductance, and dissolved oxygen.

Water Sampling

The Sacramento River metals transport study and the concurrent NAWQA study used somewhat different procedures for the collection and processing of water samples. The metals transport study used protocols developed by the USGS's National Research Program (NRP) in water resources, under the direction of Dr. Howard E. Taylor. Both the NAWQA and the NRP procedures are described in this report, although much of the NAWQA data will be reported elsewhere. The water sampling collection methods are described in this section, and the processing methods are described in a later section.

NAWQA Protocols

At the four basic fixed sites on the mainstem Sacramento River (Bend Bridge, Colusa, Verona, and Freeport), the NAWQA Program collected monthly samples using a D-77 depth-integrating sampler (Horowitz and others, 1994) with the equal-width-increment method (Edwards and Glysson, 1988). The D-77 sampler (see sketch in fig. 3 in Appendix 1) is suspended from a boat or bridge using a pulley and winch with hand crank. The sampler consists of a 3-L polytetrafluoroethylene (PTFE, a variety of Teflon) bottle with a PTFE nozzle that is designed to transmit water in an isokinetic manner. (Note that two varieties of Teflon were used in this study, PTFE and perfluoroalkoxy, or PFA.) In isokinetic sampling, the water enters the sampler at the same velocity as the water flowing near the sampler to ensure that concentrations of suspended sediment particles are representative of concentrations in the water sampled. The 3-L bottle is housed in the bronze body of the D-77; the bronze is coated with epoxy paint to eliminate potential contamination. The D-77 is considered to be rated as isokinetic to a depth of 15 ft, and to a maximum river velocity of about 4 ft/s (Shelton, 1994).

The D-77 sampler was raised and lowered at a constant rate, sufficiently fast to ensure that the 3-L bottle did not completely fill. Several equally spaced locations were sampled in a cross-section of the river and the volume collected in each vertical pass was recorded. For the purposes of the NAWQA Program, a total volume of about 9 L was generally collected in three separate 3-L PTFE bottles, which were processed using a PTFE cone splitter, as described in the following section on Sample Processing.

The NAWQA project used a grab method for the collection of water samples for mercury, dissolved organic carbon, and suspended organic carbon analyses. A single 3-L PTFE bottle and D-77 nozzle was dedicated to collection of the grab samples, which were taken generally from a single depth-integrated vertical interval located near the center of the river. The mercury grab samples were transferred immediately to acid-cleaned PTFE bottles, preserved with approximately 5 mL of 50 percent hydrochloric acid (HCl), and then closed tightly with a wrench, chilled, and shipped to a USGS laboratory in Madison, Wisconsin for analysis of total mercury. In some cases, water samples for monomethylmercury (MMHg) were taken also. Results for mercury and monomethylmercury from the NAWQA project will be presented in a separate report.

Measurements were made of field water-quality parameters according to NAWQA protocols (Shelton, 1994). Temperature was measured in place using an ASTM-calibrated thermometer (Cole Parmer model number 90201-10) that was placed about 10 cm below the water surface; temperature readings are considered accurate to within 0.2°C. Dissolved oxygen was determined in place using a probe with a thin permeable membrane. The dissolved oxygen meter (YSI model number 57) was calibrated at 100 percent saturation using the air-calibration-in-water method (Shelton, 1994). Barometric pressure was measured with a hand-held barometer at the time of each dissolved oxygen measurement so that the saturation value could be computed. Field values of specific conductance and pH were determined using raw (unfiltered) subsamples from the cone splitter. Specific conductance was determined using a Cole Parmer conductivity meter (model number 1481-60). Field values of pH were measured using an Orion meter (model number 250A) with a liquid-filled Triode electrode. Specific conductance and pH standards in the range of the unknown samples were used to calibrate the meters (Shelton, 1994). Laboratory determinations of specific conductance and pH were also made by similar methods on separate raw subsamples. Alkalinity determinations made on 50-mL subsamples of filtered (0.45-mm capsule filter) water from the cone splitter were based on titrations performed with a digital titrator and 0.16 Normal (*N*) sulfuric acid. In general, two separate alkalinity titrations were done for each sample, each using 50 mL of filtered water. The titration results were computed using the Gran titration method (Butler, 1982).

USGS's NRP Ultratrace Element Protocol

At the four basic fixed NAWQA sites on the Sacramento River, water sample collection for the concurrent metal transport study was also performed using equal-width increment methods. In cases where the D-77 sampler was used, either from a boat or a bridge, the additional samples were taken in a similar manner as in the NAWQA study. During July 1996, a modified D-77 sampler was used, in which a collapsible PTFE bag was inserted into a perforated 3-L polyethylene bottle (Kelly and Taylor, 1996). During the July 1996 sampling period, trace metal samples were composited in acid-washed 8-L PTFE-lined stainless-steel churns. Details of the water (composite water and grab water) and colloid sample collection for each sample taken in this study are given in tables 2–4. For all other sampling periods (September 1996 through May–June 1997), water samples for the metal transport study were collected by using either the standard D-77 sampler or PTFE tubing with a peristaltic pump.

Samples taken from September 1996 to June 1997 generally were composited in an acid-washed 20-L PTFE-lined stainless-steel churn. At the four basic fixed NAWQA sites, the pumping was done at the same equal-width stations at which concurrent NAWQA samples were taken. Volumes yielded by the D-77 sampler during the NAWQA sampling were used to determine the volume needed from each station to achieve a width-integrated sample. At the Spring Creek arm site, horizontal integration was achieved by moving the boat from side to side across the full width of the flow channel (about 10 m). Some degree of vertical integration for pumped samples was achieved in the upper 0.2 to 2.5 m of the river by placing the PTFE tubing inside a 3-m length of 5-cm-diameter rigid polyvinyl chloride (PVC) pipe. The PTFE tubing was taped in place using nonmetallic, white duct tape so that it protruded about 30 cm beyond the end of the PVC pipe. The tubing-pipe assembly was moved vertically in the river from the bow of the boat with the tubing pointed upstream, so that the water collected had minimal (if any) contact with the PVC pipe. Field and equipment blanks were performed on these materials; results are described in the section on Quality Assurance and Quality Control.

At most other sites, water samples were also collected by pumping with PTFE tubing. At sites where boat access was not available or deemed unsafe, pumping through PTFE tubing with a peristaltic pump was done from the shoreline. Three such sites were located immediately downstream of dams (Shasta Dam, Keswick Dam, and Spring Creek Debris Dam), where the flow was considered to be well mixed and width-integrated sampling was considered unnecessary.

At the sampling site below Shasta Dam, lateral differences in water quality are possible under certain flow conditions, such as when water is drawn from more than one depth in Shasta Lake and is partly diverted through the turbines and partly through the spillway. During July 1996, a horizontal traverse of the river was performed from a bridge using a Hydrolab instrument to determine lateral heterogeneities with respect to pH, temperature, and specific conductance. No such heterogeneity was found, and samples were taken from the right bank (facing downstream), about 30 m downstream from the bridge (a sampling point used on occasion by other agencies). This shoreline sampling point was also used in September and November 1996; however, the water level was higher in December 1996, and for safety reasons, a width-integrated sample was collected from the bridge using a D-77 sampler. In May 1997, the sample from below Shasta Dam was also taken from the bridge using a D-77 sampler (table 2).

The sampling point for the site below Keswick Dam also was on the right bank at a point about 100 m from the dam, a location that is also used routinely for sample collection by the BOR. During January 1997, the USGS sample was taken concurrently with one by the BOR for comparative purposes.

The sampling from Spring Creek also was accomplished using PTFE tubing from the shoreline. At the site “below SCDD,” samples were pumped from a point on the right bank, about 10 m upstream from the concrete V-notch weir. At the Spring Creek site “below Iron Mountain Road,” samples were pumped from a point on the right bank about 50 m downstream from the culvert that passes under Iron Mountain Road.

The water sample taken from the Yolo Bypass at Interstate 80 in January 1997 was collected using a D-77 sampler. The extreme width of this water body (about 5 km) and its potential lateral heterogeneity required that 30 separate width increments be taken, spaced at an interval of about 150 m. A composite sample using a 20-L churn was taken concurrently with a NAWQA Program sample that was split with the cone splitter. Flow measurements were taken at each of the sampling stations along the Yolo Bypass to derive an estimate of total discharge.

In addition to the composite (churn) sample taken at all sampling sites in the study, a separate grab sample also was taken at each site (table 3), specifically for the analysis of lead in whole water and various filtrates. A grab sample is defined as a sample taken from a single location in a water body; it is preferred in some studies of ultratrace elements because of lower potential for contamination. A single 3-L PTFE bottle was dedicated to collection of the grab samples. At sites where multiple vertical intervals were sampled, the grab sample was taken from the centermost station, similar to the NAWQA mercury grab samples. At sites where water was pumped from the shoreline, the grab sample represents a replicate sample of the composite; this situation is indicated in tables 2 and 3 as sites with one collection point for both “composite” and grab samples.

Streambed Sediment Sampling

Streambed sediment samples were collected using NAWQA protocols (Shelton and Capel, 1994). Relatively fine-grained sediment from three to six

Table 2. Sampling methods used for composite water samples

[Site numbers correspond to figure 8 and table 1 (no composite water samples were taken at sites 3, 4, 5, 7, and 17); DD, Debris Dam; PP, Power Plant; NS, no sample taken; initial number in cells (1–30) denotes number of sampling points composited (parentheses denote estimate); *, composited from samples collected continuously while passing boat horizontally across water body; Bo, boat; Br, bridge; Sh, shoreline; Sp, spigot in power plant; D-77M, D-77 sampler modified with Teflon bag; PPTT, peristaltic pump with Teflon tubing; Dip-1L, dipped 1-liter Teflon bottle near surface; Dip-2L, dipped 2-liter Teflon bottle near surface; 8L, 8-liter Teflon-lined churn; 20L, 20-liter Teflon-lined churn; JC, 13-liter Teflon-lined high-density polyethylene jerrican; CS, Teflon cone splitter used to split sample for USGS's National Water-Quality Assessment Program. L, liter]

	Sampling Period					
	July 1966	**September 1996**	**November 1996**	**December 1996**	**January 1997**	**May/June 1997**
SACRAMENTO RIVER SITES						
1. Sacramento River below Shasta Dam	1, Sh, PPTT, 8L	1, Sh, PPTT, 20L	1, Sh, PPTT, 20L	3, Br, D-77, 20L	NS	4, Br, D-77, 20L
2. Sacramento River below Keswick Dam	1, Sh, PPTT 8L	1, Sh, PPTT, 20L	1, Sh, PPTT, 20L	1, Sh, PPTT, 20L	1, Sh, PPTT, 20L	1, Sh, PPTT, 20L
6. Sacramento River above Bend Bridge near Red Bluff	5, Br, D-77M, 8L	5, Bo, PPTT, 20L	4, Bo, PPTT, 20L	1, Sh, PPTT, 20L	5, Bo, PPTT, 20L	5, Bo, PPTT, 20L
8. Sacramento River at Colusa	5, Bo, D-77M, 8L	5, Bo, Dip-2L, 20L	(4), Bo, PPTT, 20L	4, Bo, PPTT, 20L	5, Bo, PPTT, 20L	5, Bo, PPTT, 20L
9. Sacramento River at Verona	6, Bo, D-77M, 8L	6, Bo, PPTT, 20L	(6), Bo, PPTT, 20L	8, Bo, PPTT, 20L	NS	5, Bo, PPTT, 20L
10. Sacramento River at Tower Bridge	NS	NS	NS	NS	(4), Br, D-77, 20L	NS
11. Sacramento River at Freeport	5, Bo, D-77M, 8L	5, Bo, PPTT, 20L	(5), Bo, PPTT, 20L	4, Bo, PPTT, 20L	NS	5, Bo, PPTT, 20L
TRIBUTARY SITES						
12. Flat Creek near Keswick	NS	NS	NS	1, Sh, 20L	NS	1, Sh, Dip-1L, JC
13. Spring Creek below Spring Creek DD near Keswick	NS	NS	NS	1, Sh, PPTT, 20L	NS	1, Sh, PPTT, 20L
14. Spring Creek below Iron Mountain Road near Keswick	NS	NS	NS	NS	1, Sh, PPTT, 20L	NS
15. Whiskeytown Lake at Spring Creek PP near Keswick	NS	NS	NS	1,Sp, 20L	NS	1,Sp, 20L
16. Keswick Reservoir, Spring Creek arm, near Keswick	*, Bo, PPTT, 8L	*, Bo, PPTT	*, Bo, PPTT	*, Bo, PPTT	NS	*, Bo, PPTT
18. Colusa Basin Drain at Road 99E near Knights Landing	NS	NS	NS	NS	NS	Br, 20L
DISTRIBUTARY SITE						
19. Yolo Bypass at I-80 Near West Sacramento	NS	NS	NS	NS	30, Br, D-77, CS, 20L	NS

Table 3. Sampling methods used for grab water samples

[Site numbers correspond to figure 8 and table 1 (no grab water samples were taken at sites 3, 4, 5, 7, and 17); DD, Debris Dam; PP, Power Plant; NS, no sample taken; initial number in cells (1) denotes number of samling points composited; *, composited from samples collected continuously while passing boat horizontally across water body; Bo, boat; Br, bridge; Sh, shoreline; Sp, spigot in power plant; D-77M, D-77 sampler modified with Teflon bag; PPTT, peristaltic pump with Teflon tubing; Dip-2 L, dipped 2-liter Teflon bottle near surface; Dip-1L, dipped 1-liter Teflon bottle near surface; 3L, 3-liter Teflon bottle; L, liter]

	July 1966	September 1996	November 1996	December 1996	January 1997	May/June 1997
SACRAMENTO RIVER SITES						
1. Sacramento River below Shasta Dam	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L	1, Br, D-77, 3L	NS	1, Br, D-77, 3L
2. Sacramento River below Keswick Dam	1, Sh, PPTT 3L	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L	1, Sh, PPTT, 3L
6. Sacramento River above Bend Bridge near Red Bluff	1, Br, D-77M, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	1, Sh, PPTT, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L
8. Sacramento River at Colusa	1, Bo, D-77M, 3L	1, Bo, Dip-2L, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L
9. Sacramento River at Verona	1, Bo, D-77M, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	NS	1, Bo, PPTT, 3L
10. Sacramento River at Tower Bridge	NS	NS	NS	NS	1, Bo, PPTT, 3L	NS
11. Sacramento River at Freeport	1, Bo, D-77M, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	1, Bo, PPTT, 3L	NS	1, Bo, PPTT, 3L
TRIBUTARY SITES						
12. Flat Creek near Keswick	NS	NS	NS	1, Sh, 3L	NS	1, Sh, Dip-1L, 3L
13. Spring Creek below Spring Creek DD near Keswick	NS	NS	NS	1, Sh, PPTT, 3L	NS	1, Sh, PPTT, 3L
14. Spring Creek below Iron Mountain Road near Keswick	NS	NS	NS	NS	1, Sh, PPTT, 20L	NS
15. Whiskeytown Lake at Spring Creek PP near Keswick	NS	NS	NS	1, Sp, 3L	NS	1, Sp, 3L
16. Keswick Reservoir, Spring Creek arm, near Keswick	*, Bo, PPTT 3L	*, Bo, PPTT, 3L	*, Bo, PPTT, 3L	*, Bo, PPTT, 3L	NS	*, Bo, PPTT 3L
18. Colusa Basin Drain at Road 99E near Knights Landing	NS	NS	NS	NS	NS	Br, 20L
DISTRIBUTARY SITE						
19. Yolo Bypass at I-80 Near West Sacramento	NS	NS	NS	NS	1, Br, D-77, 3L	NS

locations within 100 m of the water sampling site was collected from shallow-water areas with acid-washed, plastic spoons and spatulas, and composited in an acid-cleaned, 8-L glass container. The sediment and associated river water was homogenized, and a split (about 100 mL, or roughly 200 g) of the whole sediment was taken for grain-size analysis. The remaining sample was then screened through a 62-μm nylon mesh; the coarse fraction was discarded. The fine-grained material (clay plus silt size fractions) was placed in acid-washed plastic jars and chilled.

Caddisfly Sampling

Samples of *Hydropsyche* larvae were collected at five stations (fig. 8, table 1, sites 3, 4, 5, 6, and 7) in the Sacramento River between Redding and Tehama during October 21–23, 1996, a period of low-flow conditions. In addition, a sample was collected from Cottonwood Creek (fig. 8, table 1, site 17); this sample was used for comparison with metal levels in samples from the Sacramento River. Caddisfly samples were not collected upstream of Keswick Reservoir, nor downstream of Tehama, nor during other times of the year because of the scarcity of habitat that could be sampled using the methods employed. *Hydropsyche* larvae were collected with large kick nets, and by hand, from a single, wadeable (approximately 0.3-m deep) riffle at each site. Specimens were picked from the net with nylon forceps and placed into plastic trays with stream water (forceps and trays were previously acid washed). Water in the trays was freshened every few minutes. Specimens were transferred from the trays to sealed, plastic bags and then frozen on dry ice in a small volume of river water within 1 hour of collection. The samples were moved to the laboratory where they were stored at –70°C until analysis. Specimens for taxonomic identification were preserved in 10 percent formalin in the field and transferred to 75 percent ethanol in the laboratory.

Sample Processing Methods

This section contains descriptions of methods used for sample processing in this study. The types of samples include water, sediment, and biological samples.

Water Sample Processing

Two approaches for the processing of water samples were used in this study. The “part-per-billion” protocol adopted by the NAWQA Program (Horowitz and others, 1994) was used for subsamples analyzed for anions, nutrients, and organic carbon at the basic fixed sites. For the second approach, subsamples analyzed for cations, trace elements, and iron redox speciation were processed using a protocol for ultra-trace constituents developed by the USGS’s NRP in water resources, under the direction of Dr. Howard E. Taylor. Both processing approaches are described in this subsection.

NAWQA Protocols

Water samples collected for the NAWQA study were processed to make subsamples using a Teflon (PTFE) cone splitter (see sketch in fig. 4 in Appendix 1). The use and precision of the cone splitter have been described by Ward and Harr (1990) and Capel and others (1995). Raw subsamples from the cone splitter were collected for analysis of suspended sediment concentration and certain nutrient constituents. A raw subsample was used for measurement of pH and specific conductance. Additional raw subsamples from the cone splitter were used as input to filtration processes. A disposable 0.45-μm capsule filter (Gelman 12175) was used to filter samples for major and trace element analyses. The capsule filters were preconditioned by passing 1 L of deionized water through, prior to any sample. A minimum of 50 mL of sample was passed through the capsule filter prior to rinsing and filling the sample bottles with filtrate.

A raw subsample of 100 mL, taken from the 3-L PTFE bottle used to collect the grab sample for mercury, was processed for dissolved and suspended organic carbon analysis. It was filtered through a 47-mm-diameter silver membrane filter (pore diameter of 0.45-μm, manufactured by the Poretics Products Division of Osmonics). The silver filters were heated to 300°C for 4 hours and then mounted in a multistage PTFE filter holder. A clean amber glass bottle was placed in a sealed PTFE canister. The canister is equipped with a fitting that allows for an airtight connection, using PTFE tubing, between the PTFE filter holder and the amber glass bottle. Water was drawn through the filter under a vacuum, with an oil-free vacuum pump attached to the PTFE canister. The filtrate samples were collected in the precleaned 100-mL amber glass bottles and immediately chilled.

The silver filters were retained in plastic petri dishes for analysis of suspended organic matter.

Both raw (unfiltered) and filtered water subsamples were taken for analysis of nutrients. Filtration was done using the same 0.45-µm capsule filter (manufactured by Gelman) as used for the major and trace element subsample. The unfiltered subsamples that were used for nutrient analysis were acidified with sulfuric acid, whereas the filtered samples were not preserved other than chilling on ice immediately after collection and processing and keeping refrigerated until analyzed. Samples for analysis of nutrients and organic carbon were shipped on ice within 24 hours of collection to the USGS's NWQL in Arvada, Colorado.

USGS's NRP Ultratrace Element Protocol

After compositing streamwater in PTFE-lined churns, the composite raw water samples were mixed using conventional churn-splitting techniques (Leenheer and others, 1989) and processed as necessary to obtain representative subsamples for whole-water analysis, subsequent filtration, and suspended sediment concentration determinations (see table 5, which has been modified from the Quality Assurance Project Plan, table 4 in Appendix 1). Whole-water and filtered subsamples for analysis of cations and trace metals were collected in acid-soaked, screw-cap 250-mL polyethylene bottles and were immediately preserved with high-purity nitric acid (HNO_3) (table 5). The nitric acid was purified in the laboratory using a distillation procedure described by Kuehner and others (1972).

Whole-water samples intended for analysis of major cations and trace metals were preserved in the field using 2 mL of concentrated, distilled nitric acid per 250-mL subsample, and were then subjected to an in-bottle digestion using 5 mL of concentrated hydrochloric acid per 200 mL of sample in a water bath at near-boiling conditions (see method I-3485-85 in Fishman and Friedman, 1989). Results from this method are considered "total" if greater than 95 percent of a substance is solubilized and are considered "total recoverable" if less than 95 percent of a substance is solubilized (Fishman and Friedman, 1989). The addition of nitric acid in the field was necessary to avoid metal precipitation in iron-bearing samples. The net result was a more rigorous digestion than that which would be obtained using only hydrochloric acid.

The whole-water samples intended for iron redox analysis were preserved in the field using 2 mL of concentrated, distilled hydrochloric acid per 250-mL subsample. Nitric acid, a weak oxidant, was not added to these samples because it likely would have changed the proportion of ferrous iron [Fe(II)] and ferric iron [Fe(III)]. Because bacteria were not excluded from these unfiltered samples, and some iron-oxidizing bacteria are known to survive in extremely acid conditions (Nordstrom and Southam, 1997), some oxidation of Fe(II) to Fe(III) may have occurred after sample preservation. This effect is less likely to have occurred in the filtered subsamples preserved in a similar manner for iron redox determinations.

Filtration for analysis of cations (including trace metals), mercury, anions, iron redox, and nutrients was performed in a mobile laboratory using a 0.45-µm capsule filter (Gelman) and peristaltic pump. Subsamples for replicate analysis, and in-bottle spikes, if required, were taken from the churn and processed in a manner similar to that described earlier. Containers and preservatives were used in accordance with quality assurance protocols (see table 5 and Appendix 1). A diagram showing the procedure for the processing of composite samples is shown in figure 9.

A subsample of the 3-L grab sample was also filtered (in the mobile lab) using a separate 0.45-µm capsule filter (Gelman) for lead analysis (fig. 10). With the exception of PTFE bottles, which were used in place of polyethylene bottles, the handling procedures for the grab samples were the same as those used for the composite samples and related subsamples that were prepared for analysis of cations and trace elements.

Water remaining in the churn and in the grab sample bottle, as well as the 100-L sample for colloid isolation, were transported to a processing laboratory as quickly as logistics permitted (generally within 2 to 24 hours). There, subsamples from the composited sample and the grab sample were filtered using a Nuclepore 0.40-µm membrane in an all-PTFE filter holder, under vacuum (Kelly and Taylor, 1996). Replicate filtered subsamples were obtained in this manner for the analyses of cations and mercury (see second column of table 5; fig. 9).

In the laboratory, another portion (about 3 L) of the composited sample was filtered with a Minitan (Millipore Corporation) tangential-flow ultrafiltration procedure to remove suspended particulate matter,

Table 4. Sampling methods used for colloid samples

[Site numbers correspond to figure 8 and table 1 (no colloid samples were taken at sites 3, 4, 5, 7, and 17); DD, Debris Dam; PP, Power Plant; NS, no sample taken; initial number in cells (1–30) denotes number of samling points composited (parentheses denote estimate); *, composited from samples collected continuously while passing boat horizontally across water body; Bo, boat; Br, bridge; Sh, shoreline; Sp, spigot in power plant; D-77M, D-77 sampler modified with Teflon bag; PPTT, peristaltic pump with Teflon tubing; Dip-1L, dipped 1-liter Teflon bottle near surface; Dip-2L, dipped 2-liter Teflon bottle near surface; volumes (for example, 92.1 L) denote total volume of water processed through Pellicon tangential-flow ultrafilter; samples colllected in 25-liter high-density polyethylene carboys; *italics* indicate duplicate sample; CS, Teflon cone splitter used to split sample for USGS's National Water-Quality Assessment Program. L, liter]

	July 1966	September 1996	November 1996	December 1996	January 1997	May/June 1997
SACRAMENTO RIVER SITES						
1. Sacramento River below Shasta Dam	1, Sh, PPTT, 92.1 L	1, Sh, PPTT, 99.9 L	1, Sh, PPTT, 98.4 L	3, Br, D-77, 72.7 L	NS	4, Br, D-77, 98.6 L
2. Sacramento River below Keswick Dam	1, Sh, PPTT 46.8 L	1, Sh, PPTT, 93.8 L	1, Sh, PPTT, 100.5 L	1, Sh, PPTT, 90.8 L	1, Sh, PPTT, 93.2 L	1, Sh, PPTT, 96.9 L
6. Sacramento River above Bend Bridge near Red Bluff	5, Br, D-77M, 46.6 L	5, Bo, PPTT, 95.5 L	4, Bo, PPTT, 96.0 L	1, Sh, PPTT, 90.9 L	5, Bo, PPTT, 102.2 L	5, Bo, PPTT, 98.2 L, *98.2 L*
8. Sacramento River at Colusa	5, Bo, D-77M, 94.5 L	5, Bo, Dip-2L, 93.8 L	(4), Bo, PPTT, 104.3 L	4, Bo, PPTT, 93.8 L	5, Bo, PPTT, 45.4 L	5, Bo, PPTT, 98.0 L
9. Sacramento River at Verona	6, Bo, D-77M, 100.5 L	6, Bo, PPTT, 98.3 L	(6), Bo, PPTT, 102.0 L	8, Bo, PPTT, 95.2 L	NS	5, Bo, PPTT, 101.8 L
10. Sacramento River at Tower Bridge	NS	NS	NS	NS	(4), Br, D-77, 49.1 L, 49.1 L	NS
11. Sacramento River at Freeport	5, Bo, D-77M, 101.4 L	5, Bo, PPTT, 98.0 L	(5), Bo, PPTT, 95.3 L	4, Bo, PPTT, 94.5 L	NS	5, Bo, PPTT, 76.8 L, *74.5 L*
TRIBUTARY SITES						
12. Flat Creek near Keswick	NS	NS	NS	NS	NS	NS
13. Spring Creek below Spring Creek DD near Keswick	NS	NS	NS	1, Sh, PPTT, 72.9 L	NS	1, Sh, PPTT, 93.7 L
14. Spring Creek below Iron Mountain Road near Keswick	NS	NS	NS	NS	1, Sh, PPTT, 77.6 L	NS
15. Whiskeytown Lake at Spring Creek PP near Keswick	NS	NS	NS	NS	NS	NS
16. Keswick Reservoir, Spring Creek arm, near Keswick	*, Bo, PPTT 95.3 L	*, Bo, PPTT, 97.5 L	*, Bo, PPTT, 99.6 L	*, Bo, PPTT, 96.3 L	NS	*, Bo, PPTT 95.6 L
18. Colusa Basin Drain at Road 99E near Knights Landing	NS	NS	NS	NS	NS	(4), Br, 80.9 L
DISTRIBUTARY SITE						
19. Yolo Bypass at I-80 Near West Sacramento	NS	NS	NS	NS	30, Br, D-77, CS, 49.7 L	NS

Table 5. Subsamples of water and quality assurance protocols for sample preservation for various analyses

[$K_2Cr_2O_7$, potassium dichromate; HNO_3, nitric acid; HCl, hydrochloric acid. *, triple-distilled HNO_3 for ultratrace element preservation; (a), split sample held for archive purposes; CA, California; CO, Colorado; conc., concentration; poly, polyethylene or polypropylene; PTFE, polytetrafluoroethylene (Teflon); USGS, U.S. Geological Survey; μm, micrometer; mL, milliliter]

Matrix / Filtration	Analysis	Preservation	Bottle Type, Volume	Laboratory
Whole water	Mercury	$K_2Cr_2O_7$, HNO_3*	Glass, 125 mL (a)	USGS–Boulder, CO
	Major & trace elements (cations)	Acidify (HNO_3)*	Poly, 250 mL (a)	USGS–Boulder, CO
	Iron, redox speciation	Acidify (HCl)	Poly, amber, 125 mL	USGS–Boulder, CO
	Nutrients	Chill	Poly, amber, 125 mL	USGS–Arvada, CO
	Suspended sediment conc.	None	Poly, 1,000 mL	USGS–Salinas, CA
0.45 μm filtrate (silver filter)	Organic carbon, dissolved	Chill	Glass, amber, 125 mL	USGS–Arvada, CO
Silver filter retentate	Organic carbon suspended	Chill	petri dish	USGS–Arvada, CO
0.45 μm filtrate (capsule filter)	Mercury	$K_2Cr_2O_7$, HNO_3*	Glass, 125 mL (a)	USGS–Boulder, CO
	Major & trace elements (cations)	Acidify (HNO_3)*	Poly, 250 mL (a)	USGS–Boulder, CO
	Major elements (anions)	Chill	Poly, 250 mL (a)	USGS–Arvada, CO
	Iron, redox speciation	Acidify (HCl)	Poly, amber, 125 mL	USGS–Boulder, CO
	Nutrients	Chill	Poly, amber, 125 mL	USGS–Arvada, CO
0.45 μm filtrate (membrane filter)	Mercury	$K_2Cr_2O_7$, HNO_3*	Glass, 125 mL (a)	USGS–Boulder, CO
	Major & trace elements (cations)	Acidify (HNO_3)*	Poly, 250 mL (a)	USGS–Boulder, CO
	Iron, redox speciation	Acidify (HCl)	Poly, amber, 125 mL	USGS–Boulder, CO
10,000 daltons ultrafiltrate (tangential-flow, 0.005 μm equivalent)	Mercury	$K_2Cr_2O_7$, HNO_3*	Glass, 125 mL (a)	USGS–Boulder, CO
	Major & trace elements (cations)	Acidify (HNO_3)*	Poly, 250 mL (a)	USGS–Boulder, CO
	Iron, redox speciation	Acidify (HCl), chill	Poly, 250 mL	USGS–Boulder, CO
Colloid concentrate, 10,000 daltons ultrafiltrate (tangential-flow, 0.005 μm equivalent)	Major & trace elements (cations) –total digestion and sequential-extractions	Chill, freeze dry	PTFE, 500 mL or 1,000 mL	USGS–Boulder, CO
	Lead isotopes	Chill, freeze dry	PTFE, 30 mL	USGS–Denver, CO
	Particle size distribution (photon correlation spectrometry)	Chill, freeze dry	Poly, 100 mL	USGS–Boulder, CO

including most of the colloidal material, from the water. A separate set of four (in a stack) 10,000 nominal molecular weight limit (NMWL), or daltons, low-binding, regenerated cellulose tangential-flow membranes were used for each sampling site to reduce cross-contamination problems. The 10,000 NMWL regenerated cellulose membranes retain particles in the range of 0.0035 to 0.0055 μm (Millipore Corporation, 1993). In this report, we refer to the pore size of these membranes as “0.005-μm equivalent

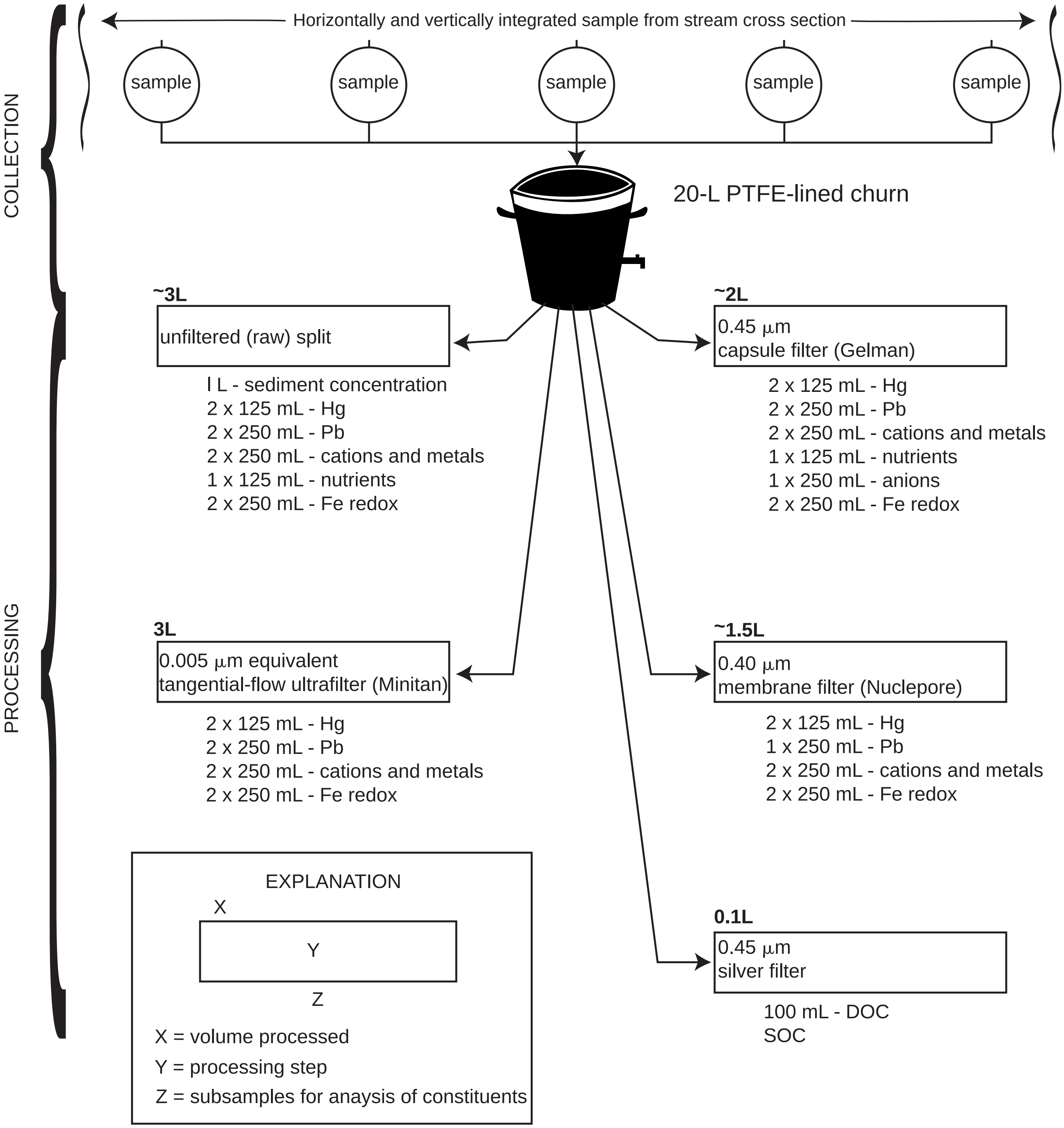

Figure 9. Diagram showing the procedure for the collection and processing of composite water samples in the Sacramento River Basin, California. DOC, dissolved organic carbon; SOC, suspended organic carbon. PTFE, polytetrafluoroethylene; Hg, Mercury; Pb, lead; Fe, iron; ~, approximately; µm micrometer; mL, milliliter; L, liter.

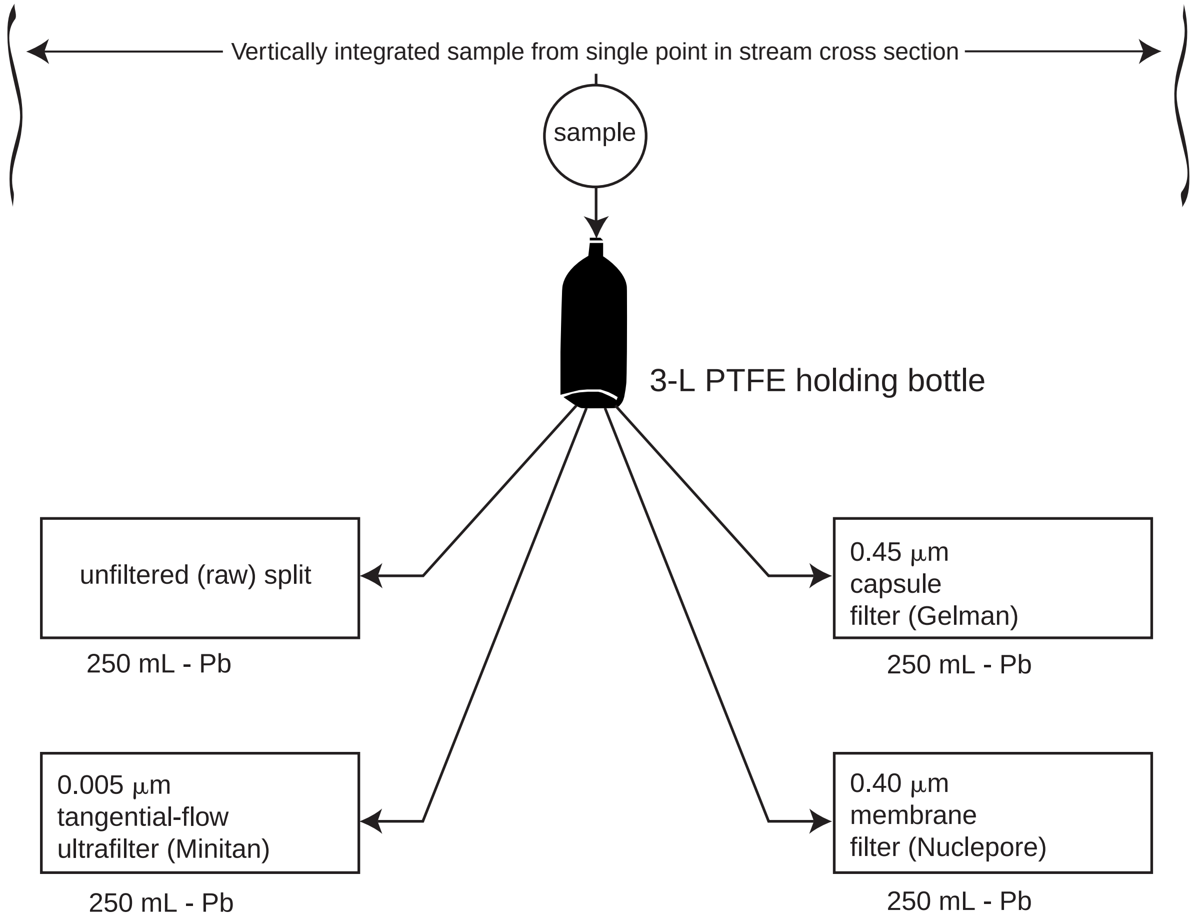

Figure 10. Diagram showing the procedure for the collection and processing of grab water samples in the Sacramento River Basin, California. PTFE, polytetrafluoroethylene; Pb, lead; µm micrometer; mL, milliliter; L, liter.

pore-size diameter." Ultrafiltrates produced by tangential-flow ultrafiltration with 10,000 NMWL membranes are the best available approximation to truly dissolved concentrations. Prior to filtration, the membranes and filter apparatus were acid-rinsed with a 1 percent (by volume) solution of high-purity, distilled nitric acid (Kuehner and others, 1972) to remove potential metal contamination on the filters, followed by a thorough rinsing with deionized water (type 1, 18 MΩ-cm).

Whole-water and filtered subsamples for total mercury analysis were collected in duplicate as 125-mL sample aliquots in acid-cleaned borosilicate glass bottles. All water subsamples for mercury analysis were preserved by the addition of 5 mL of a 1:100 mixture of high-purity potassium dichromate and nitric acid (w:v,g $K_2Cr_2O_7$:mL HNO_3) (table 5).

Large water samples totalling approximately 100 L were collected than split in four acid-cleaned 25-L high density polyethylene (HDPE) carboys for the recovery of suspended colloids (fig. 11). The water contents, undisturbed in the original carboys, were allowed to settle for 1 hour at room temperature to separate the material greater than about 1 µm in diameter. After settling, the supernatant phase was filtered with a Pellicon, model OM-141, tangential-flow ultrafilter (Millipore Corporation) using a stack of 8 individual 10,000 NMWL (0.005-µm equivalent pore-size diameter) regenerated cellulose membrane filters. The Pellicon, rather than the Minitan, was used to isolate a concentrate of colloidal-size particulate material because of the larger surface area of the filters (7,440 cm^2 for the Pellicon as opposed to 240 cm^2 for the Minitan). This larger surface area (30:1) greatly increased the efficiency of processing the 100-L sample. Pellicon filter membranes were rinsed with dilute nitric acid and then rinsed with deionized water prior to filtration as described previously for the Minitan membranes. During sample processing with the Pellicon unit, most of the ultrafiltrate was discarded and the "retentate," or residual solids, were retained. After the original volume of approximately

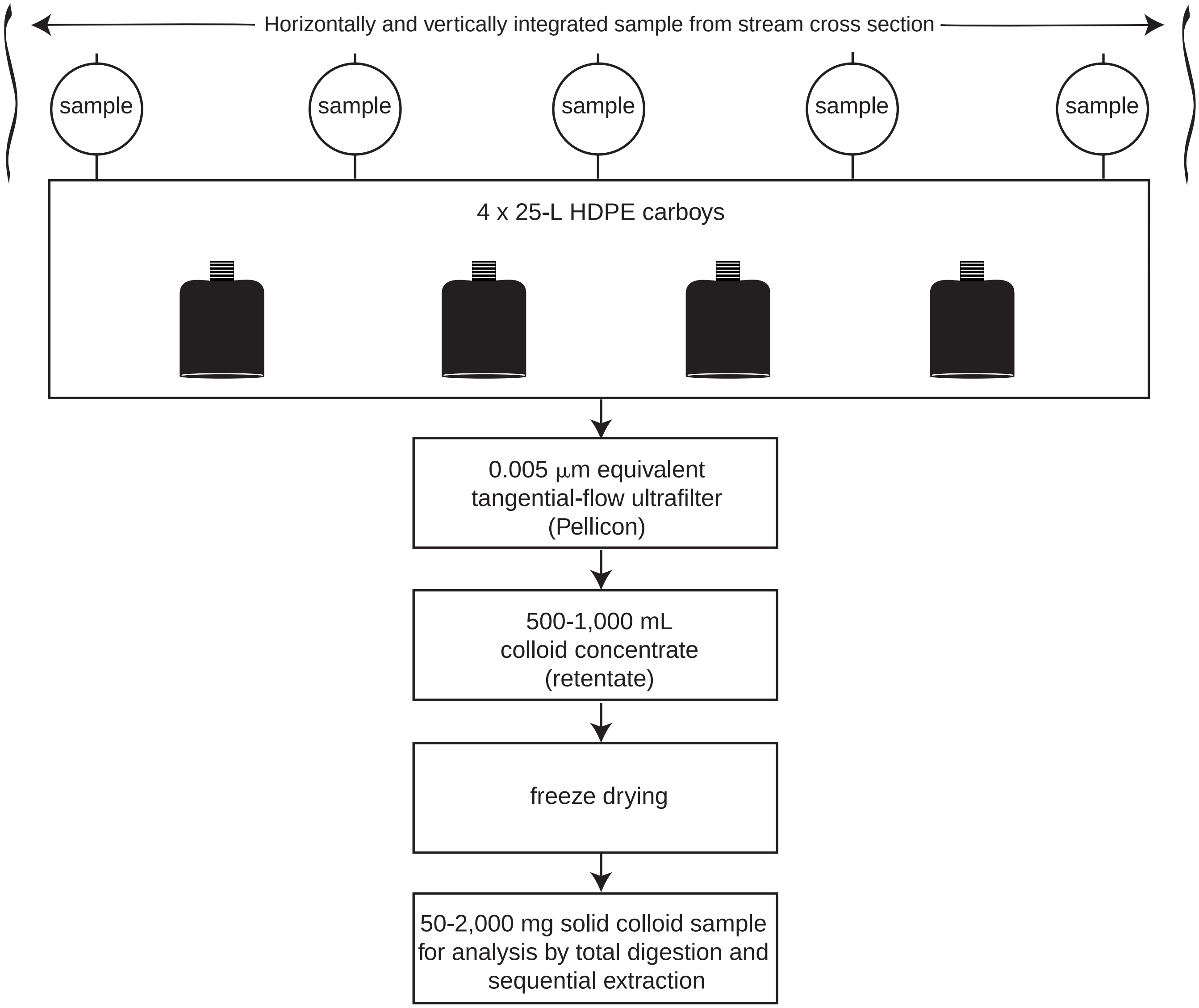

Figure 11. Diagram showing the procedure for the collection and processing of colloid samples in the Sacramento River Basin, California. HDPE, high density polyethylene; µm, micrometer; mL, milliliter; mg, milligram; L, liter.

100 L was reduced to about 0.5 L, the Pellicon filter unit was disassembled and the residual solids on the filter plates were recovered into a Teflon bag using a squeeze bottle filled with ultrafiltrate. The final colloid concentrate was stored in a 1 L PTFE bottle and refrigerated.

The colloid concentrate was dewatered by spinning successive 50-mL quantities in a polycarbonate centrifuge tube at 12,000 revolutions per minute and 10°C using a Sorval model RC-5B refrigerated centrifuge. As each aliquot was centrifuged, the supernatant liquid was carefully decanted to waste. When dewatering by centrifugation was completed, the residue was freeze-dried for 24 hours to remove the residual moisture. Subsamples of the freeze-dried material were microwave digested (Milestone, Model mls 1200 “mega” microwave oven) using a combination of distilled nitric acid, hydrochloric acid, and hydrofluoric acid (HF) in PTFE closed-digestion vessels (Hayes, 1993). Following the digestion and before the analysis, boric acid was added to the solutions to reduce the activity of the excess fluoride, thereby reducing deleterious impact on glassware and plasma torches. The digested samples were diluted to an appropriate concentration and stabilized with the same preservative solutions used for the preservation of similar water samples (table 5); namely, nitric acid was added to subsamples intended for analysis of cations and trace metals, and potassium dichromate ($K_2Cr_2O_7$) plus nitric acid were added to subsamples intended for analysis of mercury. Subsamples of freeze-dried colloid solids for particulate size distribution were preserved with sodium azide (NaN_3, to a final concentration of 0.01 percent) to inhibit bacterial growth, then refrigerated until analyzed.

Sequential chemical extractions (Hayes, 1993) were performed on the colloid samples that had a sufficient amount of material, approximately greater than 200 mg. A 100-mg sample was first extracted in a 30-mL PTFE screw-capped tube in a reducing environment with acidified hydroxylamine hydrochloride to remove metals weakly bound to the sediment and those associated with any iron or manganese oxide coatings. This fraction is referred to as the “reducible” phase. The residue from this extraction was treated with a potassium persulfate solution to oxidize any organic coatings or organic and sulfide particles. This fraction is referred to as the “oxidizable” phase. Finally, an $HCl–HNO_3–HF$ acid microwave digestion, identical to that used for total digestions, was performed on the residue from the oxidizable phase extraction. This fraction is termed the “residual” phase. All chemical extractions were carried out in closed containers, and sample aliquots were preserved immediately (as with water samples in table 5) to minimize contamination or loss of volatile constituents such as mercury.

Streambed Sediment Sample Preparation

Streambed sediment samples were chilled on ice immediately after collection and stored at 5°C until further processing. A subsample for particulate size distribution was chilled until analysis. The remaining sediment samples were freeze dried for 24 hours to remove the residual moisture.

Dissolution of subsamples of streambed sediments was performed using a total $HCl–HNO_3–HF$ acid microwave digestion procedure identical to that used for suspended sediments (Hayes, 1993). The digested samples were diluted to an appropriate concentration range for analysis by inductively coupled plasma methods and stabilized with the same reagents used for the preservation of the water samples (table 5).

Caddisfly Sample Preparation

Specimens were partially thawed in batches, rinsed with cold deionized water (type 1, 18 MΩ-cm) to remove sediment and detritus, and then transferred to a glass sorting dish that was placed on a bed of ice. Individual animals were immersed using tweezers in a small amount of water and viewed under a stereomicroscope for identification and further cleaning. Instars of *Hydropsyche californica* were not sorted, although smaller specimens that could not be clearly identified were discarded. Identified and cleaned specimens then were transferred to a second container and put on ice. When the sample had been sorted and cleaned, the animals were blotted dry with tissue paper, pooled into replicate subsamples of caddisfly larvae of approximately the same wet weight, and temporarily refrigerated.

Cold 0.05 Molar (*M*) Tris-hydrochloride buffer [pH 7.4, previously degassed to remove carbon dioxide (CO_2) with nitrogen gas (N_2)] was added to each subsample at a ratio of 8:1 (mL Tris-hydrochloride:g wet sample). Subsamples were homogenized with a stainless-steel, high-speed tissue homogenizer under a nitrogen (N_2) atmosphere for 1 minute. The homogenate was split into two fractions: one for the whole-body metal analysis and the other for the cytosolic metals. The cytosol was isolated by centrifuging the homogenate at 100,000 *g* for 1 hour at 5°C. The supernatant (cytosol) and pellet were collected and transferred to separate screw-cap glass vials. Samples were kept cold throughout the procedure. Sample fractions were frozen at –20°C as they were prepared. Later, they were freeze dried, weighed, digested by reflux in hot, isopiestically distilled (Kuehner and others, 1972) 16 *N* nitric acid. When the digestion was complete, the sample residues were evaporated to dryness. Before analysis, sample residues were reconstituted by the addition of 10 mL of 1 percent distilled nitric acid. For the trace metal analysis, 5 mL of this solution was diluted to 50 mL.

All plastic and glassware used for the preparation and digestion were cleaned by soaking overnight in a Micro-90 solution (available from International Products Corp., Burlington, New Jersey), rinsed with deionized water, then washed in 5 percent hydrochloric acid and rinsed with deionized water. The tissue homogenizer was cleaned by soaking it overnight in a solution of RBS 35 detergent (available from Pierce, Rockford, Illinois) and rinsing it in deionized water.

Analytical Procedures

This section presents information on analytical procedures used in this study. In cases where USGS-approved methods are used, such as the determinations made by the USGS's NWQL, relatively little information is given and the reader is referred to published sources. More detailed information is given in this section for research methods that are not officially approved by the USGS as "production methods."

Major Cations and Trace Elements

Inductively Coupled Plasma Spectrometry

Major elements that were present in samples at high concentration levels, including calcium (Ca), magnesium (Mg), sodium (Na), and silica (Si, reported as SiO_2), respectively, were determined by inductively coupled plasma-atomic emission spectrometry (ICP–AES) techniques utilizing a Jarrell–Ash Atomcomp 975, multichannel emission spectrometer. A description of the analysis conditions and procedures was reported by Garbarino and Taylor (1979). Potassium (K) also was determined by ICP–AES using a Varian Liberty 150AX Turbo axial-view sequential spectrometer. A modified flow-injection, pneumatic-nebulization sample introduction technique (Varian SPS5 Sample Prep Station) was employed to perform this determination (Antweiler and Taylor, 1998).

Except for mercury, trace-element determinations were performed by inductively coupled plasma-mass spectrometry (ICP-MS), using a Perkin Elmer Elan Model 5000. Aerosols of acidified aqueous samples were introduced into the spectrometer with a cone-spray pneumatic nebulizer. Multiple internal standards (indium [In], iridium [Ir], rhodium [Rh], and thorium [Th], respectively), which covered the mass range, were used to normalize the system for drift. Details of the specific analysis techniques, procedures, and instrumental settings were described by Garbarino and Taylor (1995).

Multielement instrument calibration standards for ICP–AES determinations were matrix-matched with comparable concentrations of reagents used in the digestion procedure. This was simulated by the composition of the digest, which reduced interelement suppression interference effects. Because of the higher sensitivity of ICP–MS relative to ICP–AES, 10:1 dilutions of the digest solutions were used for ICP–MS determinations to avoid interelement interferences.

Atomic Fluorescence Spectrometry

Mercury stock and standard solutions were made from Puratronic grade (99.9995 percent) mercuric chloride ($HgCl_2$) salt (Johnson Mathey) and preserved in a solution of high-purity nitric acid and primary-standard grade potassium dichromate using the same reagents and concentrations as those used to preserve samples (table 5). Deionized water (type 1, 18 MΩ-cm) was used for preparing all standards and reagent solutions. A 2 percent stannous chloride ($SnCl_2$) solution (wt:volume, stannous chloride:3 percent hydrochloric acid) in 3 percent hydrochloric acid (volume:volume, hydrochloric acid:type 1, 18 MΩ-cm deionized water) was used for the reduction of mercury to its elemental form in the cold vapor reactor.

Trace concentration levels of mercury were measured using an automated, cold vapor-atomic fluorescence spectrometer or CV–AFS (PS Analytical) using methods described previously by Roth (1994) and by David A. Roth and others (U.S. Geological Survey, written commun., 1999). Instrumental parameters for the atomic fluorescence mercury analysis are listed in table 6.

The procedure involves reduction of mercury in the sample with excess stannous chloride to produce elemental mercury vapor. The vapor is transported to the detector with a stream of argon gas. Peak height intensities of unknown samples are compared to a six-point calibration curve prepared from aqueous

Table 6. Operational settings for analysis of mercury with the cold vapor–atomic fluorescence spectrometer

[s, second]

Characteristics	Settings
Cold-vapor reactor timing	
Delay	15 s
Rise	30 s
Analysis	30 s
Memory	60 s
Argon flow rates	
Sample	0.30 liter per minute
Shield	0.25 liter per minute
Backflow	2.7 liter per minute
Fluorescence spectrometer settings	
Coarse gain	1,000
Fine gain	optimized
Integration time	0.25 s
Damping	32 readings (8 s)

standards ranging in concentration from 0 to 50 ng/L, preserved with potassium dichromate and nitric acid in a similar manner as with the samples.

Iron Redox Speciation

Total iron (Fe) and Fe(II) were determined using a modification of the FerroZine colorimetric technique proposed by Stookey (1970). For Fe(II) determination, an adequate volume of acidified sample (as much as 20 mL) to give 0.1–40 μg iron per 25 mL, was transferred by pipet into a 25-mL volumetric flask. Then, 0.5 mL FerroZine reagent was added and the contents of the flask were mixed. Next, 1.25 mL of an ammonium-acetate buffer solution was added, the flask was shaken, and at least 5 minutes were allowed for full color development. The solution in each flask was then diluted to the mark and shaken well. Absorbance was measured within 2 hours at 562 nm using an ultraviolet–visible (UV–vis) spectrometer.

For total iron, the same procedure was used as for Fe(II), except for the addition of 0.25 mL hydroxylamine hydrochloride, a reducing agent, to the samples before the addition of 0.5 mL of FerroZine reagent. The procedure for all blanks and standards was similar to that described for total iron analysis, including the hydroxylamine hydrochloride step. A linear regression of absorbance versus iron concentration was developed on the basis of at least five standards.

Double-distilled water was used in the preparation of all solutions. Ammonium acetate buffer solution was prepared by mixing appropriate volumes of high-purity acetic acid and ammonium hydroxide. Traces of iron were removed from a solution of reagent grade hydroxylamine hydrochloride by solvent extraction with isoamyl alcohol.

Lead Isotopic Analysis

Isotopic compositions of lead from selected freeze-dried samples of suspended colloids and streambed sediments were determined by chemical separation of lead followed by thermal-ionization mass spectrometry. Samples weighing 3 to 10 mg (containing 80 to 100 ng of lead) were decomposed overnight in a 4:1 mixture of 24*M* hydrofluoric acid and 16*M* nitric acid in screw-cap PFA-Teflon vials at 50°C. Lead was separated using anion exchange with analytical grade Dowex-1 X8 resin in 1.2*M* hydrobromic acid (HBr) medium and was eluted from the anion-exchange columns with 1.0*M* nitric acid, following the procedures of Unruh (1982). The purified lead separate was loaded onto a rhenium filament for mass spectrometry analyses using the conventional phosphoric acid–silica gel method (Cameron and others, 1969). Lead blanks for the chemical procedure were less than 0.1 ng.

Lead isotopic data were initially measured using a VG Elemental model Sector 54 seven-collector mass spectrometer operated in "static" mode. However, during the course of this work, an electrical malfunction in this mass spectrometer made it necessary to complete the analyses using a VG Elemental model 54R single-collector mass spectrometer. Mass fractionation during analyses with both mass spectrometers was monitored by analyses of National Institute of Standards and Technology (NIST) lead isotope standard SRM-981, using the values for this standard reported by Todt and others (1993). Analytical uncertainties in the fractionation-corrected data were calculated in the manner prescribed by Ludwig (1979) and reflect both the internal precision of each individual run, as well as the uncertainties induced by the mass-fractionation corrections.

Anions

The determination of major anions in water, including chloride (Cl^-), fluoride (F^-), and sulfate (SO_4^{2-}), was done on filtered samples by ion-exchange chromatography following procedures described by Fishman and Friedman (1989). The anion determinations were made at the USGS's NWQL in Arvada, Colorado.

Nutrients

A standard suite of nutrient analyses was done for each water sample taken in this study, using both raw (unfiltered) and filtered samples. Samples that required filtration were filtered with a 0.45-μm capsule filter (Gelman) in accordance with standard NAWQA protocols (Shelton, 1994) and analyzed at the USGS's NWQL.

A total of eight nutrient determinations are reported for each water sample—three analyses of phosphorus (P) forms and five analyses of nitrogen (N) forms (table 7). The phosphorus determinations included orthophosphate in filtered water, plus total phosphorus in both raw and filtered water. Orthophosphate was determined using an automated, colorimetric, phosphomolybdate blue procedure with antimony (Sb) added to increase the reduction rate (Patton and Truitt, 1992; Fishman, 1993). Total phosphorus was determined colorimetrically as orthophosphate after Kjeldahl digestion (Patton and Truitt, 1992).

Filtered water samples were analyzed for nitrogen in the following forms: (1) nitrite (NO_2^-), (2) nitrite plus nitrate (NO_3^-), (3) ammonia (NH_3), and (4) ammonia plus organic nitrogen. Ammonia plus organic nitrogen was also determined in raw water samples. The method used for nitrite determination was diazotization using sulfanilamide and N-1-naphthylethylenediamine under acidic conditions to form a red compound, the absorbance of which was determined colorimetrically using an automated-segment flow procedure (Fishman, 1993). Nitrite plus nitrate determinations were made by reducing nitrate to nitrite using cadmium metal, followed by nitrite analysis by diazotization (Fishman, 1993). Ammonia determinations were performed using a salicylate-hypochlorite method, in the presence of ferricyanide ions, that produces the salicylic acid analog of indophenol blue, which was analyzed colorimetrically using an automated-segmented flow procedure (Fishman, 1993). The determinations of ammonia plus organic nitrogen in raw and filtered samples were made using the same Kjeldahl digestion as that used for total phosphorus, in which the organic nitrogen is reduced to the ammonium ion, followed by determination of the ammonium ion by the colorimetric salicylate-hypochlorite method (Fishman and Friedman, 1989; Patton and Truitt, 1992).

Organic Carbon

Dissolved organic carbon (DOC) concentrations were determined on 100-mL filtered water samples (0.45-µm silver membrane filter). The filtrates were first acidified to remove dissolved and colloidal carbonates and bicarbonates, then the organic carbon was oxidized to carbon dioxide with persulfate and ultraviolet light. The carbon dioxide was then measured by infrared spectrometry using a Dorhmann carbon analyzer (Brenton and Arnett, 1993).

Suspended organic carbon (SOC) concentrations were determined with the residual material that was collected on the silver membrane filters used to prepare DOC samples. The silver membrane filters were treated with acid to dissolve inorganic forms of carbon, then were reacted with potassium persulfate in glass ampules for 4 hours at 116° to 130°C. The ampules were then broken in the carbon analyzer, releasing carbon dioxide which was measured by infrared spectrometry using an Oceanography International carbon analyzer (Wershaw and others, 1987).

Particulate Size Distribution

Colloids

The size distribution of colloids was determined from subsamples of the residual colloid concentrates collected from tangential-flow ultrafiltration procedure (Pellicon, discussed earlier in this report). Samples for colloid particulate size distribution analysis were subsampled from the colloid concentrate and preserved to inhibit bacterial growth with sodium azide, to a final concentration of 0.01 percent, and refrigerated until analyzed. Before analysis, samples were warmed to room temperature and were shaken to homogenize the contents, and a few milligrams were removed by Pasteur pipette. Three drops of a nonionic surfactant, FL-70 (Fisher Scientific) at a concentration of 2.5 percent (volume:volume, FL-70 type 1

Table 7. Types of nutrient analyses and analytical methods

Nutrient	Sample type		Analytical Method
	Unfiltered	Filtered	
Phosphorous			
Orthophosphate	No	Yes	Phosphomolybdate blue
Total phosphorous	Yes	Yes	Kjeldahl digestion with phosphomolybdate blue
Nitrogen			
Nitrite	No	Yes	Diazotization
Nitrite plus nitrate	No	Yes	Reduction using cadmium with diazotization
Ammonia	No	Yes	Salicylate–hypochlorite
Ammonia plus organic nitrogen	Yes	Yes	Kjeldahl digestion with salicylate–hypochlorite

deionized water, 18 MΩ-cm) were added to the sample cuvette followed by three drops of sample. The sample-surfactant mixture was diluted (5 mL of type 1 deionized water, 18 MΩ-cm, prefiltered through a 0.45-μm Gelman capsule filter) and mixed, and suspended particulates were dispersed by ultrasonication (with a Horiba Ultrasonic Disrupter, model HA40) at 20 watts and 20 kHz for at least 60 seconds.

Sample transmittance, at 632.8 nm, was measured with a Milton-Roy, Spectronic Mini20 spectrophotometer, to confirm it was in a suitable range for analysis (60 to 90 percent). The sample was placed in the cell holder of a Brookhaven Photon Correlation Spectrometer and particle size determinations were performed at goniometer angles of 45°, 90°, and 120° measured parallel to an incident laser beam. Particle distributions were calculated using an exponential sampling routine. Instrumentation and calculation parameters used in the colloid particulate size distribution analysis are listed in table 8.

The scattering source of the photon correlation spectrometer used a 10 mW helium-neon laser at a wavelength of 632.8 nm. Slit widths ranging from 100 to 200 μm were used with an optical filter designed for 632.8 nm. Voltage bias on the detector was –1,800 volts (direct current). Toluene (98.8 percent, HPLC grade, Sigma Aldrich) was used as the index matching liquid in the cell holding device to reduce scattered light originating from the liquid-glass interfaces. Temperature of the sample and index matching solutions were maintained at 20.0 °C with a recirculating cooler.

Streambed Sediments

Particulate size distribution in streambed sediment samples was determined by wet sieve and X-ray adsorption methods. Wet sieve methods were used to determine the percentage of the mass of each sample less than standard sieve openings of 16, 8, 4, 2, 1, 0.5, 0.25, 0.125, and 0.062 mm (Allen, 1990). The SediGraph 5100 X-ray absorption analyzer manufactured by Micrometrics (Syvitski, 1991) was used to determine the percentage of mass finer than the following sizes in millimeters: 0.031, 0.016, 0.008, 0.004, 0.002, 0.001, 0.00050, and 0.00025.

Quality Assurance and Quality Control

Howard E. Taylor, Ronald C. Antweiler, Charles N. Alpers, David A. Roth, Terry I. Brinton, Daniel J. Cain, James W. Ball, Daniel M. Unruh, *and* Peter D. Dileanis

A variety of measurements and analyses were used to determine the quality of the data produced in this study. Precision and accuracy criteria were evaluated by the analysis of numerous field and laboratory blank samples, standard reference materials, spike recoveries, and replicate samples. Data quality objectives, as described in the Quality Assurance Project Plan (QAPP, Appendix 1), were met in nearly all respects for dissolved data (ultrafilter effluent), whole-water data (unfiltered samples), colloids, total sediment, and sequential extraction sediment analyses. Quantitative analysis for data quality was not made for capsule filter and membrane filter effluents because these data were not used in quantitative interpretations outlined in a companion report by Alpers and others (2000).

Data Quality Objectives

Accuracy is defined in this study as the measure of the degree of conformance of values generated by a specific method with the true or expected value of that measurement. The accuracy of field measurements

Table 8. Instrumentation and calculation parameters used in the colloid particulate size-distribution analysis

[cP, centipoise; I_m, imaginary part of the measurement calculation of the refractive index; R_c, real part of the measurement calculation of the refractive index; nm, nanometer; °C, degree Celsius]

Parameter	Setting	Parameter	Setting
Prescale (gain)	0	Viscosity	1.002 Cp
Sampling time	30–250 milliseconds (optimized)	Wavelength	632.8 nm
Sample duration	6 seconds	Refractive index	
Acquisition angle	45°, 90°, and 120°C	of liquid	1.4903
First channel used	Channel 2[1]	of particle (R_c)	1.59
Temperature	20°C	of particle (I_m)	0

[1] Channel 1 was omitted because it had excessive errors.

was established by the use of standard methods of analysis with the appropriate calibration standards. The accuracy of laboratory analytical data for trace metals and major cations was assessed by analyzing standard reference materials (SRM) and the recovery of known concentrations of analytes in spiked samples. For the SRMs, the percentage recovery (REC) was computed as:

$$REC_{SRM} = \frac{\text{measured value}}{\text{certified or most probable value}} \times 100 \quad (1)$$

For the spiked samples, the REC was computed as:

$$REC_{SPIKE} = \frac{\text{measured value}}{\text{expected value}} \times 100 \quad (2)$$

For all analytes discussed in the QAPP, the data quality objective with regard to accuracy was to have REC values equal to 100 ± 25 percent for concentrations greater than 10 times the detection limit, and 100 ± 50 percent for concentrations less than 10 times the detection limit.

Precision (or variability) is defined in this study as the degree of similarity among independent measurements of the same quantity. The precision of laboratory analytical data was evaluated by randomly submitted split samples and evaluated in terms of relative percentage difference (RPD), where

$$RPD = \frac{\text{difference between reported values}}{\text{average reported value}} \times 100 \quad (3)$$

For all analytes discussed in the QAPP, data were considered sufficiently precise when the RPD values were less than 25 percent for concentrations greater than 10 times the detection limit, or less than 50 percent for concentrations less than 10 times the detection limit. Concentrations in water and solid samples were determined for numerous additional elements not specifically mentioned in the QAPP, such as rare earth elements and other trace elements. For these analytes, precision was evaluated using percentage Relative Standard Deviation (RSD), defined in a later section of this report.

Completeness (a term specified by the EPA to conform to their preferred QAPP) was considered in this study as the percentage of analyses meeting the accuracy and precision objectives. In all, 48 water samples were taken at various sites during six sampling periods (table 1). Therefore, to achieve the goal of 90 percent completeness described in the QAPP (Appendix 1), 44 of 48 samples needed to meet the data quality objectives. Colloid concentrates were prepared from 41 water samples of which 37 samples needed to meet the accuracy and precision objectives to satisfy the 90 percent completeness goal. Speciation analysis was carried out on 17 of the colloid concentrates of which 16 needed to meet data quality objectives to exceed 90 percent completeness. Accuracy, precision, and completeness are discussed in turn for each of the analytical procedures, if appropriate, in the remainder of this section.

Major Cations and Trace Elements

Accuracy

The levels of accuracy for the determinations of major cations and trace element concentrations performed in this study were evaluated by three specific techniques: (1) measurement of natural-matrix SRMs, (2) determination of spike recovery information for selected elements, and (3) measurement of blanks, both in the field and in the laboratory. These approaches provide information regarding the proximity of reported analytical results to the best known values of various analytes in the measured samples. This information was used during data interpretation to evaluate bias or systematic error in the measured concentrations of major cations and trace elements in the samples collected during the study.

Standard Reference Materials

Two types of SRMs were used for evaluation in this study: (1) natural-matrix certified SRMs produced by the NIST, and (2) natural-matrix noncertified standard reference water samples (SRWS) produced by the USGS. SRMs were analyzed with each group of water samples analyzed in the laboratory at a frequency of about 30 percent of the total number. For sediment analysis, about 15 percent of the total samples analyzed consisted of reference materials.

The NIST standards used in this study included: SRM 1643a Trace Elements in Water, SRM 1643b Trace Elements in Water, SRM 1643d Trace Elements in Water, SRM 1645 River Sediment, and SRM 2704 Buffalo River Sediment. NIST standards SRM 1643a, b, and d, were also diluted 1:10 to approximate the concentration range anticipated in the samples from this study. USGS standards used in this study included: SRWSs T-99, T-101, T-103, T-105, T-107, T-111, T-113, T-117, T-119, T-125, T-129, T-131, T-133, T-135, T-137, T-143, and T-145 for trace elements, and Hg7, Hg10, Hg12, Hg15 and Hg24 (diluted 1:100 to approximate the concentration range for study samples) for trace mercury determinations. Certified values, or "most probable values" (MPV), for selected elements in each of these standards are tabulated elsewhere (Peart and others, 1998). Results of repeated analysis of these standards are tabulated in Appendix 2 of this report.

Summary data obtained from the analysis of dissolved constituent SRMs (table 9), which were processed with every suite of samples throughout the study, demonstrate conformance to the criteria specified in the QAPP (Appendix 1) for the specified "critical" elements. Namely, for each constituent listed, at least 90 percent of the observed values (n) occurred within 25 percent of the certified value or MPV, depending on the SRM (table 1 in Appendix 1). Calculation of REC equals the observed (measured) value divided by either the certified value or MPV (depending on the SRM) multiplied by 100 (to convert to percentage). Table 9 uses a frequency calculation, expressing the percentage of observations at various intervals of various percentage REC levels. Table 9 shows that all determinations of the specified elements for the SRMs were within the stated data quality objective criteria in QAPP (table 1 in Appendix 1). Note that two entries are provided for mercury in table 9: (1) accumulated data for all mercury standards included in the study, and (2) only those standards whose values exceeded the detection limit for mercury by a factor of 10. By definition, when the reported value of the determination approaches the detection limit, the precision deteriorates accordingly (see the section on Precision).

Similar data on accuracy were developed for all other elements that we report (table 10), but that were not specified in the QAPP. For elements that do not have a certified value or MPV in the SRMs, we compare our observations to data reported by NIST as "for informational purposes." These data are provided to assist in the interpretation of other determinations included in this study. Nevertheless, 21 of 24 elements satisfy the criterion that at least 90 percent of analyses are within 25 percent of the certified or most probable values. Only silver (Ag), boron (B), and tellurium (Te) do not meet this criterion.

Several figures summarize the results of the analyses of SRMs and SRWSs. Figures 12 through 16 consist of correlation plots of SRMs for dissolved determinations. Figure 12 shows the correlation between MPV and observed (measured) values for four major elements in the concentration range of 2 mg/L to about 300 mg/L. Figures 13 and 14 show elements in the range of greater than 1.5 μg/L to 3,000 μg/L. Figures 15 and 16 display data for elements with concentrations in the range of 0.6 μg/L to 60 μg/L. Each plot includes a dotted line demonstrating perfect agreement (not a regression line) and lines representing 99 percent confidence bands.

For the establishment of accuracy in sediment analysis, tables are presented showing the data for the determination of NIST SRM 2704–Buffalo River Sediment, which was analyzed with each laboratory analysis group of suspended and streambed sediment samples. A listing of REC data is shown in table 11 for

Table 9. Percentage of determinations for critical elements within the stated percentage recovery for the certified or most probable value for the National Institute of Standard and Technology's standard reference materials (waters) or the U.S. Geological Survey's standard reference water samples

[REC_{SRM}, percentage recovery with respect to standard reference materials; n, number of observations. %, percent]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125[1]	85–115	90–110	95–105
Aluminum	1,917	100	100	99	97	93	72
Cadmium	2,275	99	98	95	88	81	62
Copper	2,275	100	99	97	89	78	59
Iron	881	100	98	90	76	65	41
Lead	1,984	100	100	99	97	92	74
Mercury[2]	605	100	98	81	70	58	38
Mercury[3]	303	100	100	94	88	79	53
Zinc	2,275	100	100	93	89	83	64

[1] Data quality objective was at least 90% completeness in the 75–125% range of REC_{SRM}.

[2] All mercury standards.

[3] Mercury standards with concentrations greater than 10 times the detection limit.

Table 10. Percentage of determinations of noncritical elements within the stated percentage recovery for the certified or most probable value for the National Institute of Standards and Technology's standard reference materials (waters) or the U.S. Geological Survey's standard reference water samples

[REC_{SRM}, percentage recovery with respect to standard reference material; n, number of observations. *, "for informational purposes" value]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125	85–115	90–110	95–105
Antimony	886	100	100	99	97	85	66
Arsenic	1,187	100	100	98	96	85	56
Barium	1,221	100	100	98	96	92	71
Beryllium	1,087	100	99	98	95	89	65
Bismuth	419	100	99	94	93	90	74
Boron	1,021	100	99	89	78	63	41
Calcium	1,025	100	100	99	91	81	55
Chromium	1,258	100	98	92	84	72	47
Cobalt	1,626	100	100	99	95	90	74
Lithium	1,360	100	99	97	96	90	70
Magnesium	1,025	100	100	99	94	88	68
Manganese	1,655	100	100	98	89	82	64
Molybdenum	1,263	100	100	98	91	80	54
Nickel	1,891	100	100	98	94	84	64
Rubidium*	260	100	97	95	93	93	83
Selenium	1,839	100	98	90	76	64	45
Silica[1]	1,007	100	100	98	92	85	65
Silver	1,183	98	83	69	55	44	30
Sodium	1,025	100	100	96	82	71	51
Strontium	1,222	100	100	98	96	93	79
Tellurium*	235	100	95	73	49	37	18
Thallium	508	100	100	96	95	93	78
Uranium	101	100	100	100	100	97	76
Vanadium	1,243	100	100	98	95	80	66

[1] Silica was the only substance reported as an oxide.

the total determination of elements specified in the QAPP (table 2 in Appendix 1); and table 12 is a tabulation of all other major and trace elements determined on a total basis, but not mentioned specifically in the QAPP. For the elements listed in the QAPP, the REC data in table 11 indicate that accuracy was within the specified data quality objectives. Table 12 includes REC data for 28 elements not listed in the QAPP. For the 16 elements listed in table 12 for which certified values are available for SRM 2704, 11 elements met the criterion of at least 90 percent of SRM analyses in the range of 75–125 percent REC. Three of the other elements (magnesium, nickel [Ni], and silica [SiO_2]) had 89 percent of REC values in this range and 2 of the 16 elements (sodium and potassium) had only 58 percent of REC values in the 75–125 percent range.

Figures 17 through 21 show correlation plots for the analysis of NIST SRM 2704 with regard to total digestions and the sum of sequential digestions. Figure 17 is for five major elements at concentrations within the range from about 2 to 32 percent by weight (wt percent). Figure 18 shows five elements at concentrations within the range of 100 to 30,000 μg/g. Figures 19 and 20 show elements in the range of 3 to 800 μg/g. Finally, figure 21 shows concentration data for trace element standards that range from about 1 to 3 μg/g. On figures 17 through 21, dotted lines represent perfect agreement between observed and certified, or MPV, concentrations, and lines represent 95 percent confidence bands. Because no SRMs are available for sequential extraction data, the sum of the three components (oxidizable, reducible, and residual) are compared with the total values certified in the respective SRM. The data points for these determinations are noted in the legends. Figure 21 shows that the mercury value for NIST SRM 2704 falls at the edge of the 95 percent confidence band on the low side. This is expected, because the procedure for sequential extraction involves several steps that could result in loss of mercury because of its volatility.

Spike Addition Recovery

Selected water samples ($36 \leq n \leq 50$) were spiked in the field, immediately after processing, for elements: Ag, arsenic (As), Cd, cobalt (Co), chromium (Cr), Cu, Hg, Ni, Pb, selenium (Se), uranium (U), and Zn. For each of these elements in each sample, the REC_{SPIKE} was calculated, as indicated earlier in this report, using the theoretical value (calculated from known amount of spike added) as the basis for recovery. The expected concentration for each spiked element is listed along with the number of spiked samples and a frequency distribution (percentage of observations within a range of percentage recoveries) of REC_{SPIKE} in table 13. Specific quantities of the spike addition will vary slightly from sample to sample depending on its final volume; however, this variation is well within the experimental error of the measurements. Similar to the SRMs, REC_{SPIKE} is calculated by dividing the measured value of the spike by the expected recovered value, multiplied by 100 to convert to percentage recovery. Beryllium was added to the spike solution to serve as an internal standard to compensate for volume variations in samples. All trace elements listed in table 13 that are specified in the QAPP (table 1 in Appendix 1) are within the listed data quality objectives. No spiked additions were performed on sediment samples.

Figure 22 shows a distribution diagram of the REC_{SPIKE} of spiked additions for cadmium, copper, mercury, lead, and zinc versus the percentage of

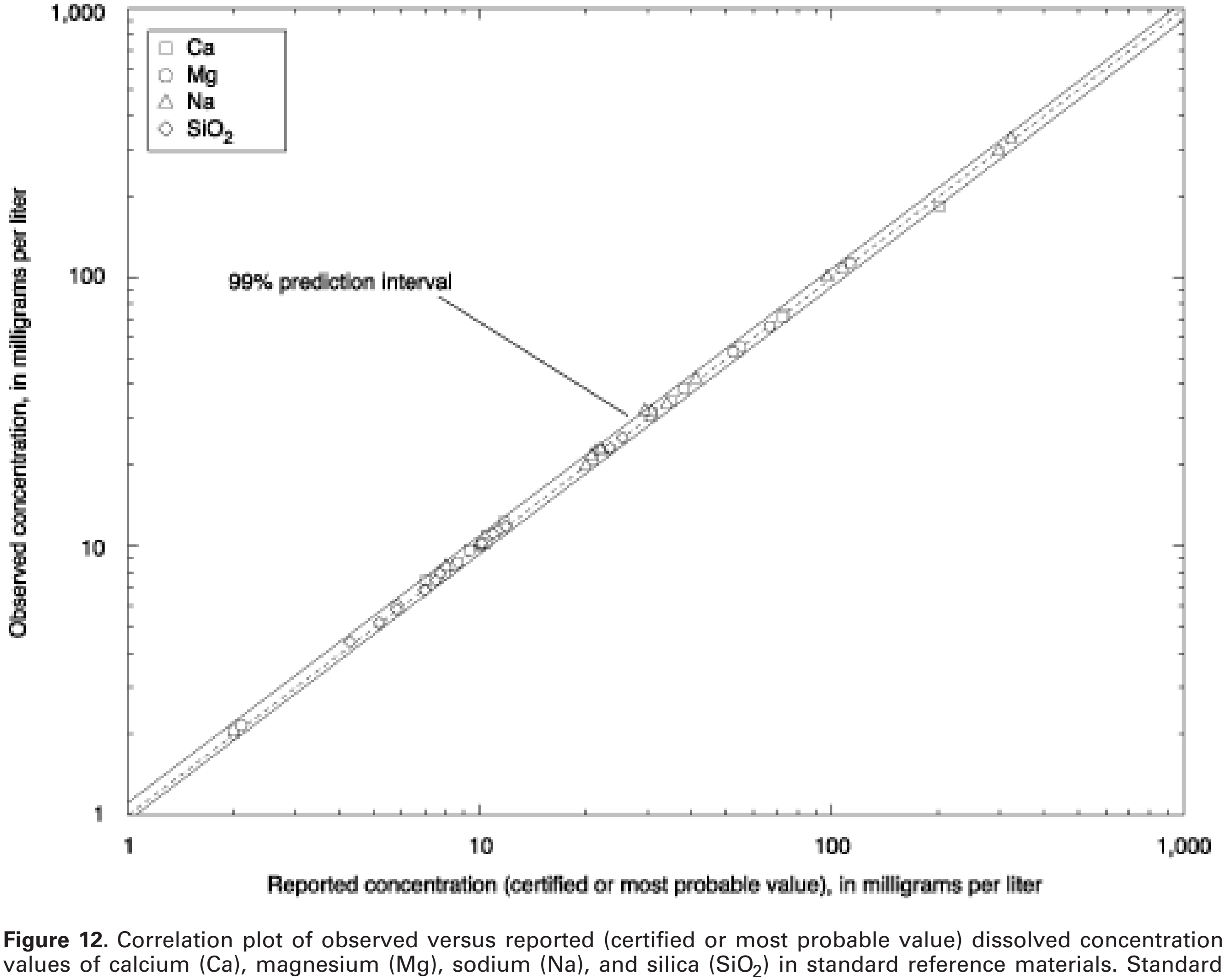

Figure 12. Correlation plot of observed versus reported (certified or most probable value) dissolved concentration values of calcium (Ca), magnesium (Mg), sodium (Na), and silica (SiO_2) in standard reference materials. Standard reference materials tested were National Institute of Standards and Technology's standard reference material 1643b and U.S. Geological Survey's standard reference water samples T99, T101, T103, T105, T107, T117, T125, T131, T133, T135, T137, T143, and T145. Error band represents the 99 percent (%) prediction interval.

samples observed. Dashed lines specifying limits of compliance (from the QAPP) are shown on the diagram.

Because no SRMs are available for the evaluation of sequential chemical extraction of sediments, the only determination of accuracy is the comparison of the sum of each phase of the extraction to the total certified values for a sediment reference material. This approach provides indirect information regarding the confidence in the sequential extraction process. Table 14 shows the REC_{SRM} values for the sum of the sequential extraction of multiple aliquots of NIST SRM 2704–Buffalo River Sediment, for all elements specified in the QAPP (table 2 in Appendix 1). Similarly, table 15 shows the REC_{SRM} sediment data for all other elements not mentioned in the QAPP that were determined in the sequential extraction of multiple aliquots of NIST SRM 2704–Buffalo River Sediment, compared with the total certified or "informational purposes" values in the reference material. The data in table 15 shows good conformance to the QAPP criteria for all elements except aluminum (Al).

Blanks

Analytical laboratory reagent blank and deionized water blank data were used to correct analyte determinations in concurrently measured samples. Reagent blanks were analyzed at a minimum

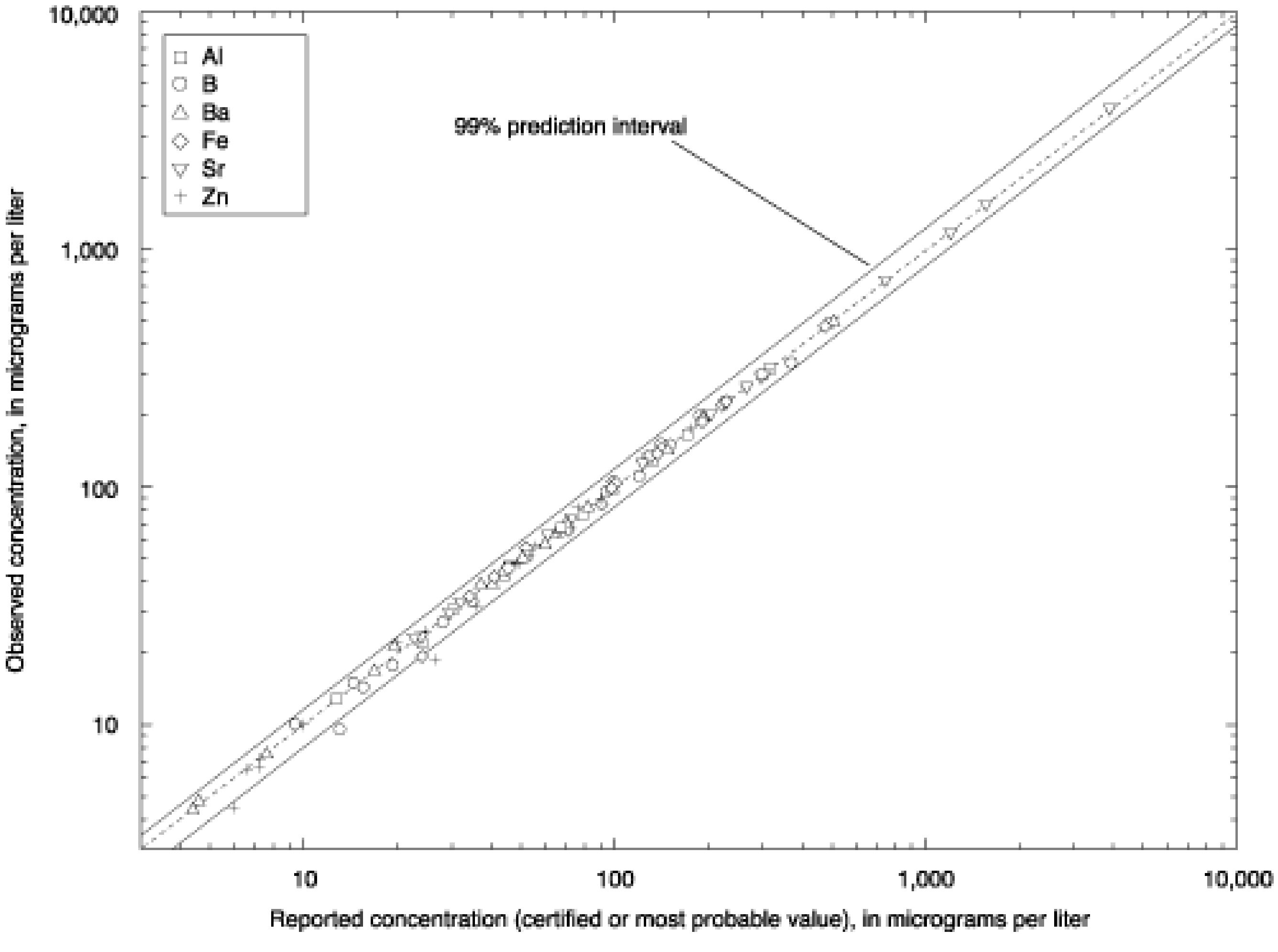

Figure 13. Correlation plot of observed versus reported (certified or most probable value) dissolved concentration values of aluminum (Al), boron (B), barium (Ba), iron (Fe), strontium (Sr), and zinc (Zn) in standard reference materials. Standard reference materials tested were National Institute of Standards and Technology's standard reference materials 1643a, 1643b, and 1643d; and U.S. Geological Survey's standard reference water samples T99, T101, T103, T105, T107, T113, T117, T119, T125, T131, T133, T135, T137, T143, and T145. Error band represents the 99 percent (%) prediction interval.

of 10 percent frequency of total samples with each group of laboratory analyses performed. Field process blanks for each step of sampling and processing of samples were analyzed at a minimum of 10 percent frequency of all samples collected (dissolved and sediment analyses). The purpose of the field and process blanks was to monitor potential contamination of sample collection and handling processes. No analytical data corrections were made for positive concentration values observed for field or process blanks. Because the dissolved concentrations of trace metals, for interpretation purposes, was focused on data collected by tangential-flow filtration, only blank data related to this process were evaluated. These included tangential-flow filter blanks, deionized water blanks, and churn blanks.

Analytical results of all blank determinations (with appropriate error terms) are tabulated in Appendix 2 (table A2-2). Blank data obtained to evaluate contamination problems are element specific and are focused on the trace elements of primary interest (critical elements) in this study. Results of blank data for these elements are evaluated individually.

Figures 23 through 28 show box plots comparing different types of blank sample concentration data with Sacramento River mainstem dissolved (ultrafiltrate) concentration data for the elements Al, Cd, Cu, Fe, Pb and Zn, respectively. No apparent significant blank problems for the elements aluminum, cadmium, and copper are shown in figures 23–25, respectively. With the exception of an occasional

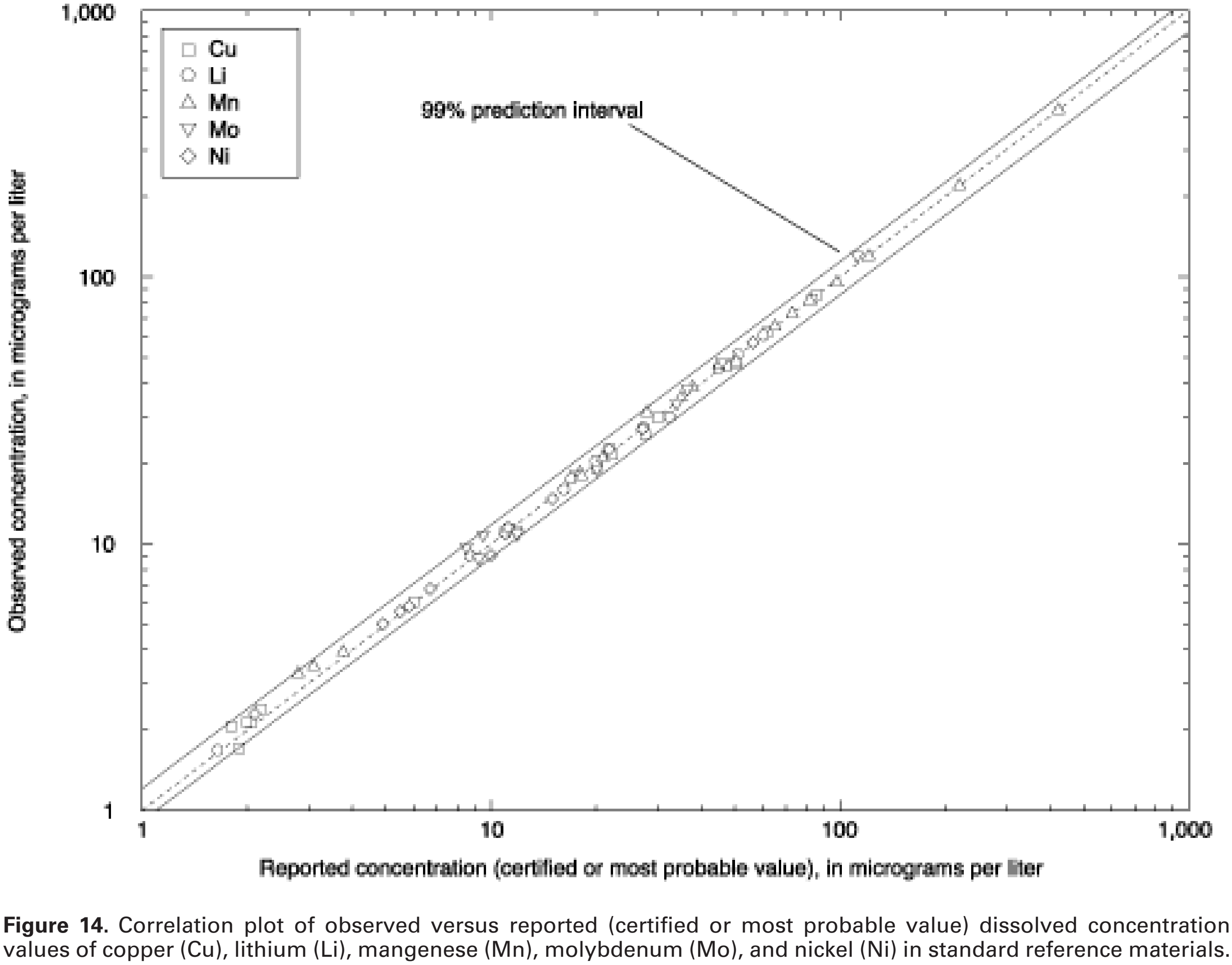

Figure 14. Correlation plot of observed versus reported (certified or most probable value) dissolved concentration values of copper (Cu), lithium (Li), mangenese (Mn), molybdenum (Mo), and nickel (Ni) in standard reference materials. Standard reference materials tested were National Institute of Standards and Technology's standard reference materials 1643a, 1643b, and 1643d; and U.S. Geological Survey's standard reference water samples T101, T103, T105, T107, T113, T117, T119, T125, T131, T133, T135, T137, T143, T144, and T145. Error band represents the 99 percent (%) prediction interval.

outlier, the mean and median of the blanks for these three elements are significantly smaller than the values observed in the mainstem of the river, which are used for the study and interpretation of the distribution of these elements in the hydrologic system.

Blank concentration data for zinc may demonstrate a minor problem on the basis of the apparent marginal overlap of box plots with concentration data shown for the mainstem of the Sacramento River (fig. 28). Two specific deionized water blank outliers, which were known to be contaminated (independently from the deionized water system), were removed from the data set. From this plot it is clear that the source of the overlap is most prevalent from blank samples taken from the churns. In evaluating these data, one must consider the procedure that was used to collect and process the blank samples—namely, the deionized water from the deionizer column was sampled (without filtration) and immediately transferred to the precleaned churn. A subsample from the churn was collected (without filtration) and the remainder was processed through the tangential-flow filtration system, where (after ultrafiltration) a sample was taken for blank analysis ("filter" blank). The only logical explanation for churn blank samples being higher in trace element concentration than either the original deionized water or the tangential flow ultrafiltrate is that particulate matter containing trace elements, from a poorly cleaned churn, was analyzed in these churn blank samples. These constituents would necessarily be removed from the filter blank samples by the nature of the filtration process. In summary, this situation

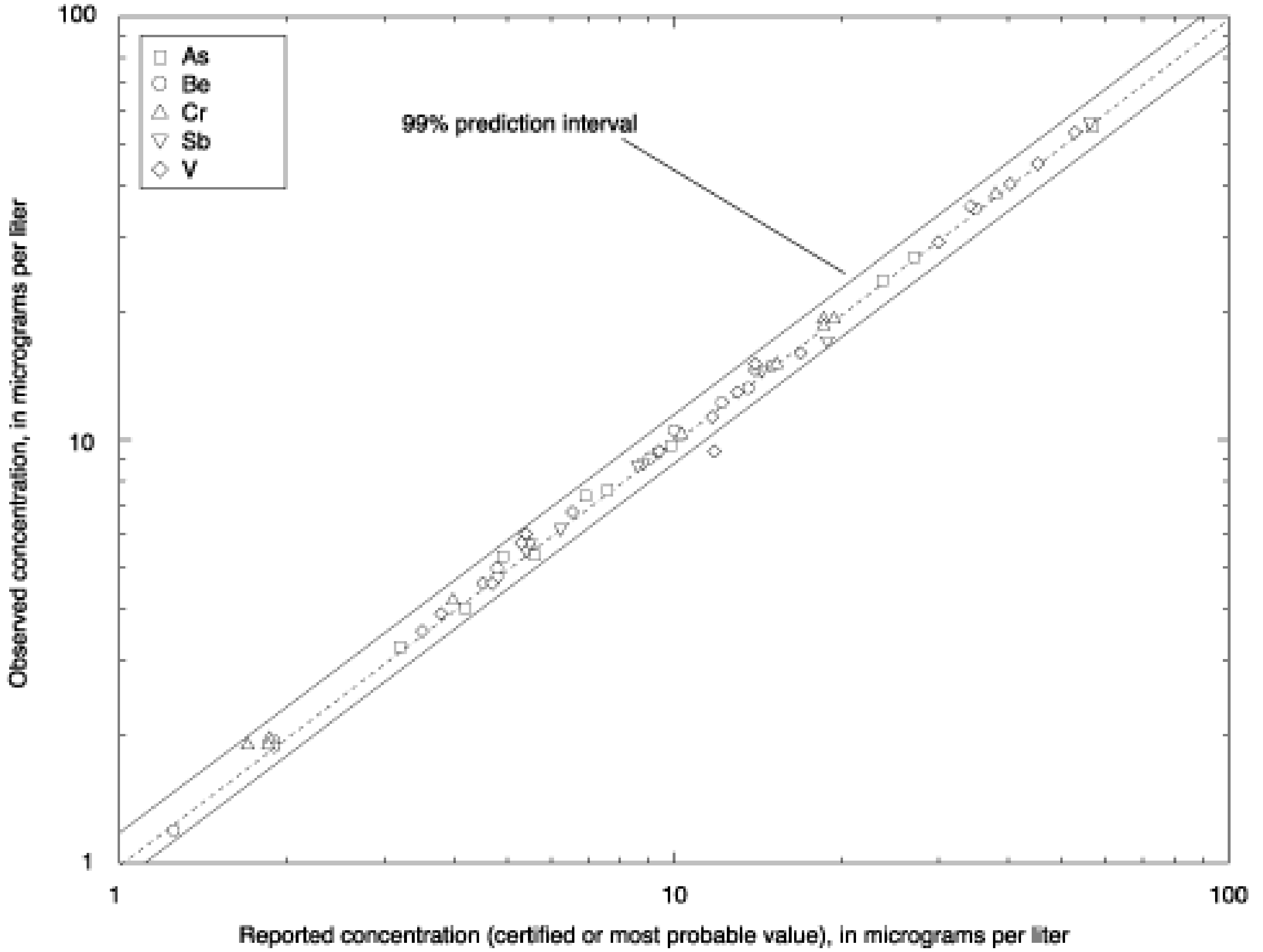

Figure 15. Correlation plot of observed versus reported (certified or most probable value) dissolved concentration values of arsenic (As), beryllium (Be), chromium (Cr), antimony (Sb), and vanadium (V) in standard reference materials. Standard reference materials tested were National Institute of Standards and Technology's standard reference materials 1643a, 1643b, and 1643d; and U.S. Geological Survey's standard reference water samples T99, T101, T103, T105, T107, T113, T117, T119, T125, T131, T133, T135, T137, T143, and T145. Error band represents the 99 percent (%) prediction interval.

does not reflect a problem that will impact sample determinations for zinc in ultrafiltrates or hinder the interpretation of such data for zinc.

The filter blanks from Minitan ultrafilters (U1 and U2 in table A2-2, Appendix 2) have zinc concentration values ranging from the detection limit (usually <0.3 µg/L) to 0.57 µg/L. The highest filter blanks for zinc were collected during the first sampling trip. Remedial action was taken (field processing facilities were moved to a more suitable location) to ameliorate these high blanks. The mainstem river samples have a median dissolved zinc value of 0.8 µg/L, and less than 25 percent of the mainstem river samples have concentrations less than 0.4 µg/L; indeed less than 5 percent of the mainstem river samples have lower concentrations than that of the median filter blank samples. These considerations lead to the conclusion that in the samples, zinc data are at most only marginally affected by contamination, and contamination is insignificant in the interpretation of dissolved zinc concentrations in river water samples.

The data for lead concentrations in blank samples show some overlap with ultrafiltrate concentrations in mainstem Sacramento River samples (fig, 27). As with zinc, the most commonly observed blanks with elevated lead concentrations were the churn blanks, which had a mean value of 5 ng/L. The mean and median concentration values of the mainstem

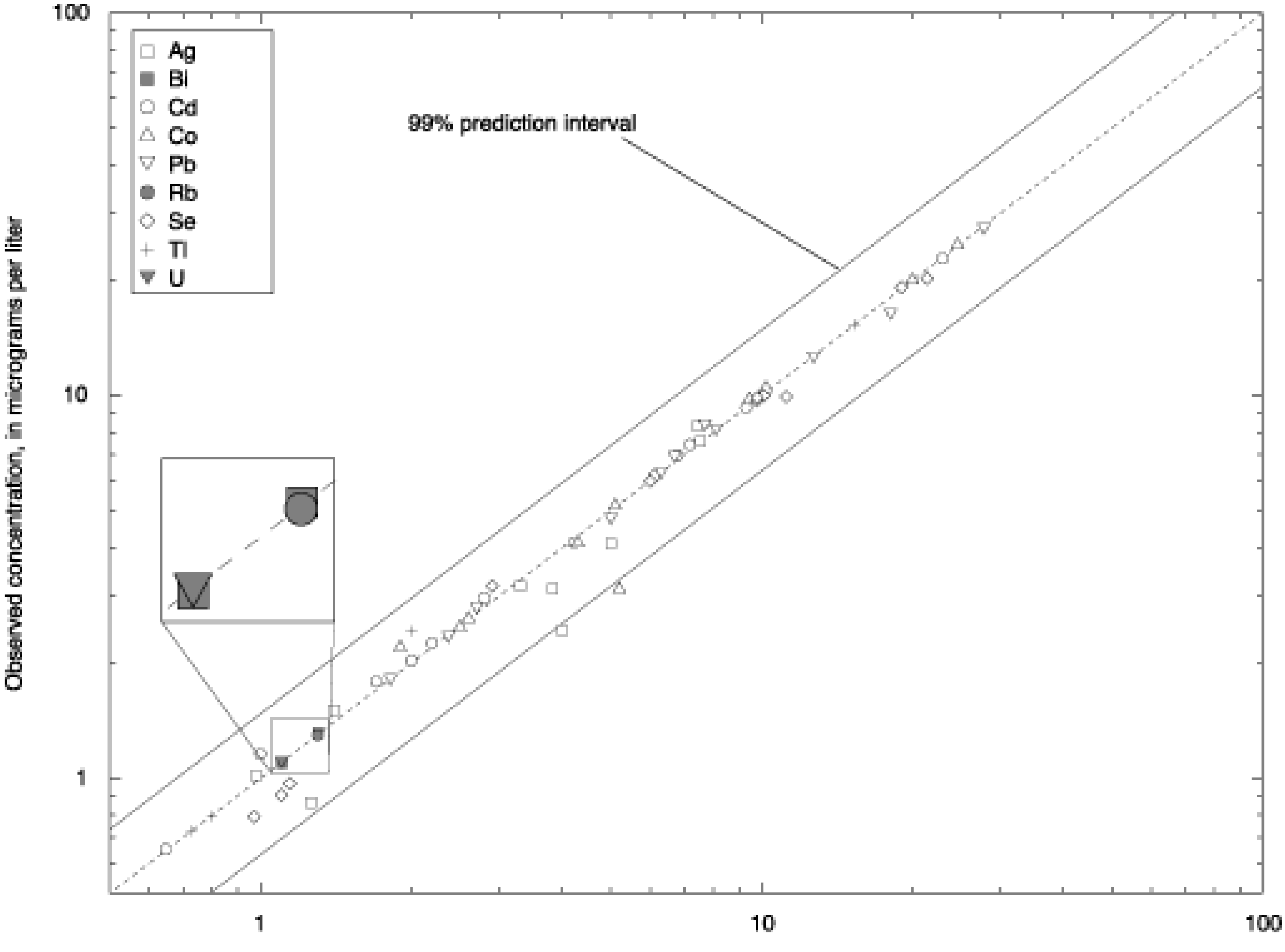

Figure 16. Correlation plot of observed versus reported (certified or most probable value) dissolved concentration values of silver (Ag), bismuth (Bi), cadmium (Cd), cobolt (Co), lead (Pb), rubidium (Rb), selenium (Se), thallium (Ti), and uranium (U) in standard reference materials. Standard reference materials tested were National Institute of Standards and Technology's standard reference materials 1643a, 1643b, and 1643d; and U.S. Geological Survey's standard reference water samples T103, T113, T117, T119, T125, T131, T133, T137, and T145. Error band represents the 99 percent (%) prediction interval.

samples are also about 5 ng/L. In addition, a few concentration values greater than 5 ng/L were observed for deionized water and the filter blanks, suggesting that 5 ng/L is a reasonable reporting limit for dissolved lead for this study.

The data for iron concentrations in blanks show significant overlap with the iron data obtained for the Sacramento River mainstem samples (fig. 26). Therefore, the dissolved iron data for the Sacramento River samples cannot be distinguished from the blank

Table 11. Percentage of determinations for critical elements within the stated percentage recovery for the certified value for the National Institute of Standards and Technology’s standard reference material SRM 2704–Buffalo River Sediment

[REC_{SRM}, percentage recovery with respect to standard reference materials; n, number of observations. %, percent]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125[1]	85–115	90–110	95–105
Aluminum	19	100	100	100	95	68	32
Cadmium	19	100	100	100	95	84	42
Copper	19	100	100	95	89	68	37
Iron	19	100	100	100	100	100	89
Lead	19	100	100	100	100	100	26
Mercury	18	100	100	100	83	83	39
Zinc	19	100	100	100	100	100	89

[1] Data quality objective was at least 90% completeness in the 75–125% range of REC_{SRM}.

Table 12. Percentage of determinations of noncritical elements within the stated relative percentage recovery for the certified or “informational purposes” value for the National Institute of Standards and Technology’s standard reference material SRM 2704–Buffalo River Sediment

[REC_{SRM}, percentage recovery with respect to standard reference materials; n, number of observations. *, “informational purposes” value]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125	85–115	90–110	95–105
Antimony	19	100	100	100	89	84	74
Barium	19	100	100	100	79	63	53
Calcium	19	100	100	100	100	100	89
Cerium*	19	100	100	53	26	11	0
Cesium*	19	100	100	100	84	68	53
Chromium	19	100	100	100	100	79	79
Cobalt	19	100	100	100	100	100	37
Dysprosium*	19	100	100	58	0	0	0
Europium*	19	100	100	84	26	26	11
Lanthanum*	19	100	100	58	42	21	5
Lithium	19	100	100	100	100	89	11
Lutetium*	19	100	100	11	0	0	0
Magnesium	19	100	100	89	63	63	32
Manganese	19	100	100	100	100	100	79
Nickel	19	100	100	89	84	58	37
Potassium	19	100	100	58	5	0	0
Rubidium*	19	100	58	5	5	5	5
Samarium	19	100	100	79	58	37	5
Silica[1]	19	100	100	89	84	74	47
Sodium	19	89	89	58	53	42	21
Strontium*	19	100	100	100	74	74	32
Thallium	19	100	100	100	100	89	16
Thulium*	19	100	100	84	58	47	16
Titanium	19	100	100	100	100	100	100
Uranium	19	100	100	100	100	100	68
Vanadium	19	100	100	100	100	89	32
Ytterbium*	19	100	100	100	95	58	47
Zirconium*	19	100	95	79	42	37	21

[1] Silica was the only substance reported as an oxide.

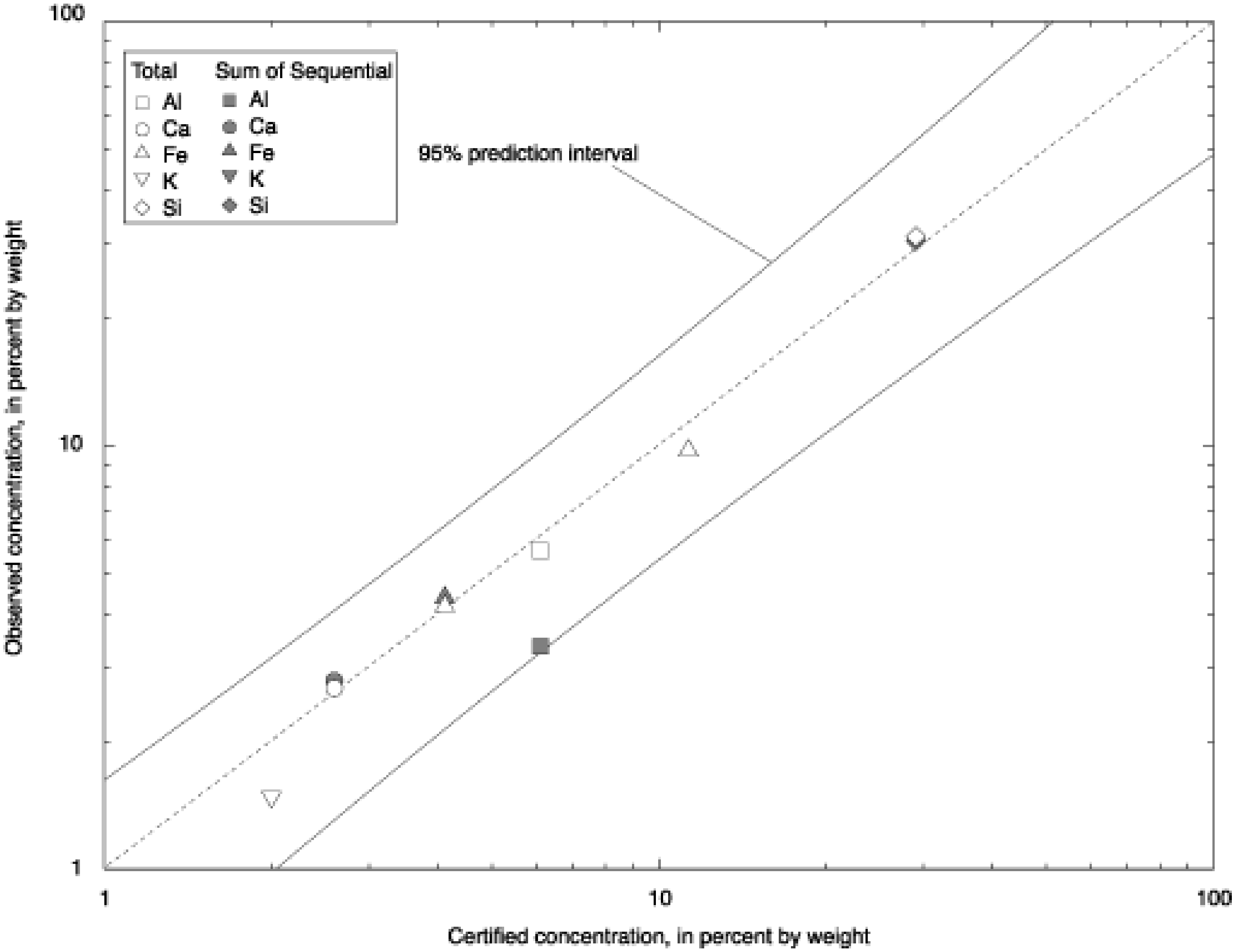

Figure 17. Correlation plot of observed concentration values in total digestions and in the sum of sequential digestions versus certified concentrations of aluminum (Al), calcium (Ca), iron (Fe), potassium (K), and silicon (Si) in standard reference material. The standard reference material tested was National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment. Error band represents the 95 percent (%) prediction interval.

data resulting in an inability to interpret low level, dissolved iron concentrations.

Precision

Each duplicate sample for dissolved constituents (ultrafilter effluent) was analyzed three times. Because of the limited quantities of the freeze-dried colloidal material that were available, single digestions were performed. The solutions from the colloid total digestions, however, were also analyzed in triplicate. Results (for the trace elements listed in table 1 of the QAPP, Appendix 1) for the analyses of field duplicate dissolved samples, expressed as the percentage of sample values whose RPD was below the specified value, are shown in table 16. This table uses the calculation of RPD as specified in the QAPP, which is the difference between the measured value (mean of triplicate determinations) of each of the field duplicates, divided by the mean value of the two duplicates, multiplied by 100 to convert to percentage (as follows):

$$\mathrm{RPD} = \frac{X_{\mathrm{D1}} - X_{\mathrm{D2}}}{X(\mathrm{D}_1 + \mathrm{D}_2)} \times 100 \qquad (4)$$

where, X_{D1} and X_{D2} are the mean values of the triplicate laboratory analysis of each of the field duplicates and $X(_{\mathrm{D1}}+_{\mathrm{D2}})$ is the mean of X_{D1} and X_{D2}.

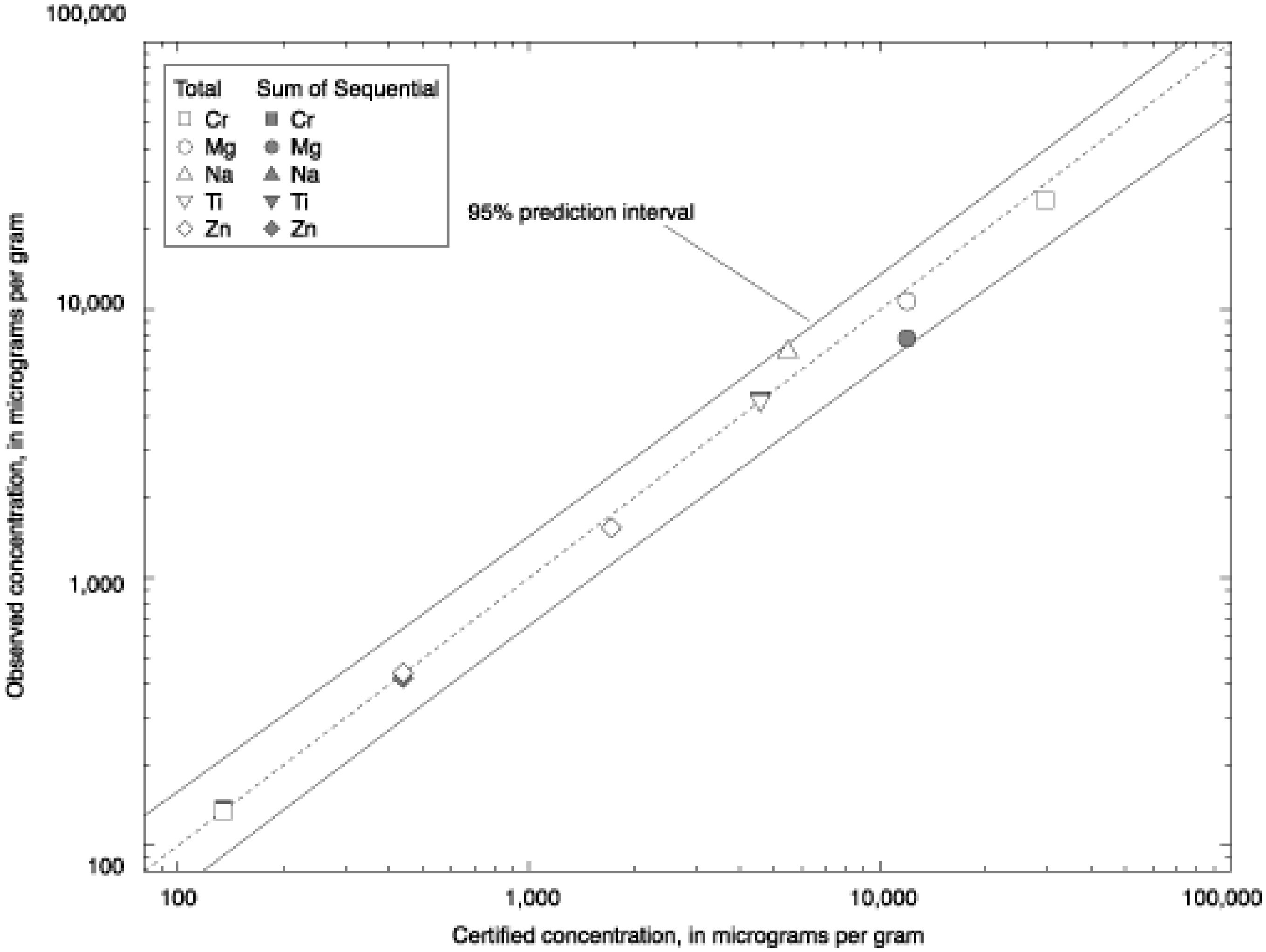

Figure 18. Correlation plot of observed concentration values in total digestions and in the sum of sequential digestions versus certified concentrations of chromium (Cr), magnesium (Mg), sodium (Na), titanium (Ti), and zinc (Zn) in standard reference material. The standard reference material tested was National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment. Error band represents the 95 percent (%) prediction interval.

Field duplicate agreement specifies the worst-case situation for repeatability of determinations because it incorporates all sources of variance, including sampling precision, processing precision, and laboratory analysis precision. Figure 29 provides correlation plots between field replicate samples for six elements: Al, Cd, Cu, Fe, Pb and Zn. Error bars on the correlation plots represent the standard deviation of multiple laboratory determinations on each of the replicates. The range of concentration varies significantly from element to element on the plots. The dotted lines are not regression fits, but the theoretical lines of perfect agreement.

As observed concentrations approach the detection limit for specific elements, the precision of determination decreases. Figures 30 through 33 show how the percentage relative standard deviation increases as dissolved (ultrafiltrate) concentrations decrease for aluminum, cadmium, copper, and mercury, respectively. The RSD is calculated as follows: (1) the overall standard deviation is calculated by pooling the standard deviations of the individual determinations (analysis precisions); (2) the mean of the individual determinations is computed; and finally, (3) the RSD is calculated by dividing the standard deviation by the mean value and multiplying by 100.

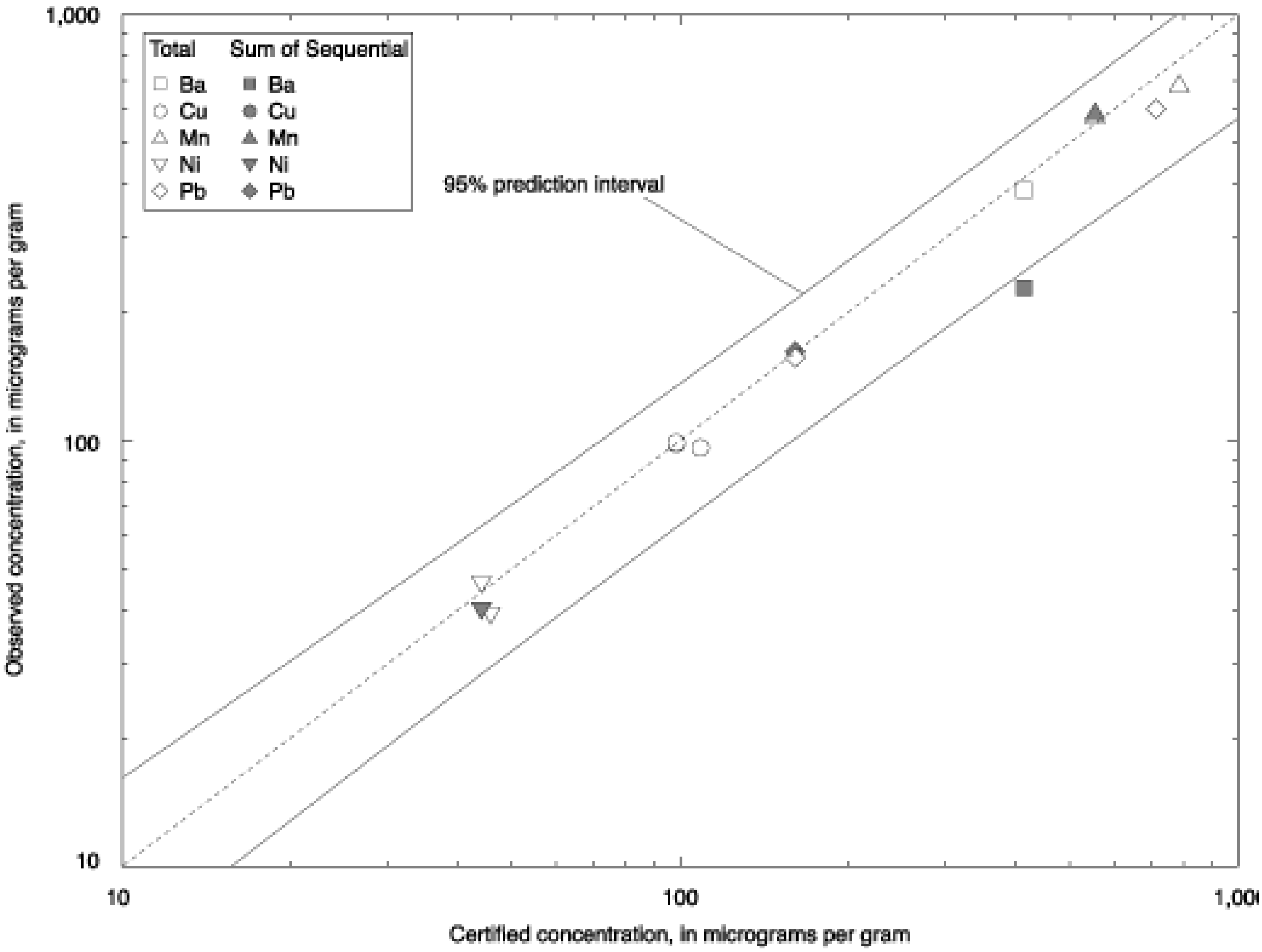

Figure 19. Correlation plot of observed concentration values in total digestions and in the sum of sequential digestions versus certified concentrations of barium (Ba), copper (Cu), manganese (Mn), nickel (Ni), and lead (Pb) in standard reference material. The standard reference material tested was National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment. Error band represents the 95 percent (%) prediction interval.

This calculation provides a more definitive evaluation of the overall precision than the RPD specified in the QAPP. Figures 30 through 33 show vertical lines that represent both the detection limit and 10 times the detection limit. For aluminum and cadmium (figs. 30 and 31), the RSD increases exponentially with the decrease in concentration. For copper (fig. 32), an exponential relationship is suggested for the data in the range of 0.3 to 9 μg/L, although somewhat higher values of RSD were observed for two of three samples from Spring Creek, with copper concentrations in the range of 429 to 535 μg/L. A similar relationship is not clear in figure 33 for mercury, probably because all observed values are very low compared with a value of 10 times the detection limit.

Table 16 provides a summary of the precision of field duplicate dissolved samples. The information is presented in terms of the percentage of samples for which the RPD was less than the specified values. Data quality objectives for this study (QAPP, Appendix 1) were that RPD values for at least 90 percent of the samples should be less than 25 percent. The data in table 16 indicate that this objective was achieved for all of the critical elements in this study with the exception of mercury (74 percent completeness at RPD less than 25 percent) and zinc (78 percent completeness at RPD less than 25 percent).

Table 17 summarizes the percentage of replicate dissolved samples whose percentage RSD occurred below the specified values listed. Table 17 presents

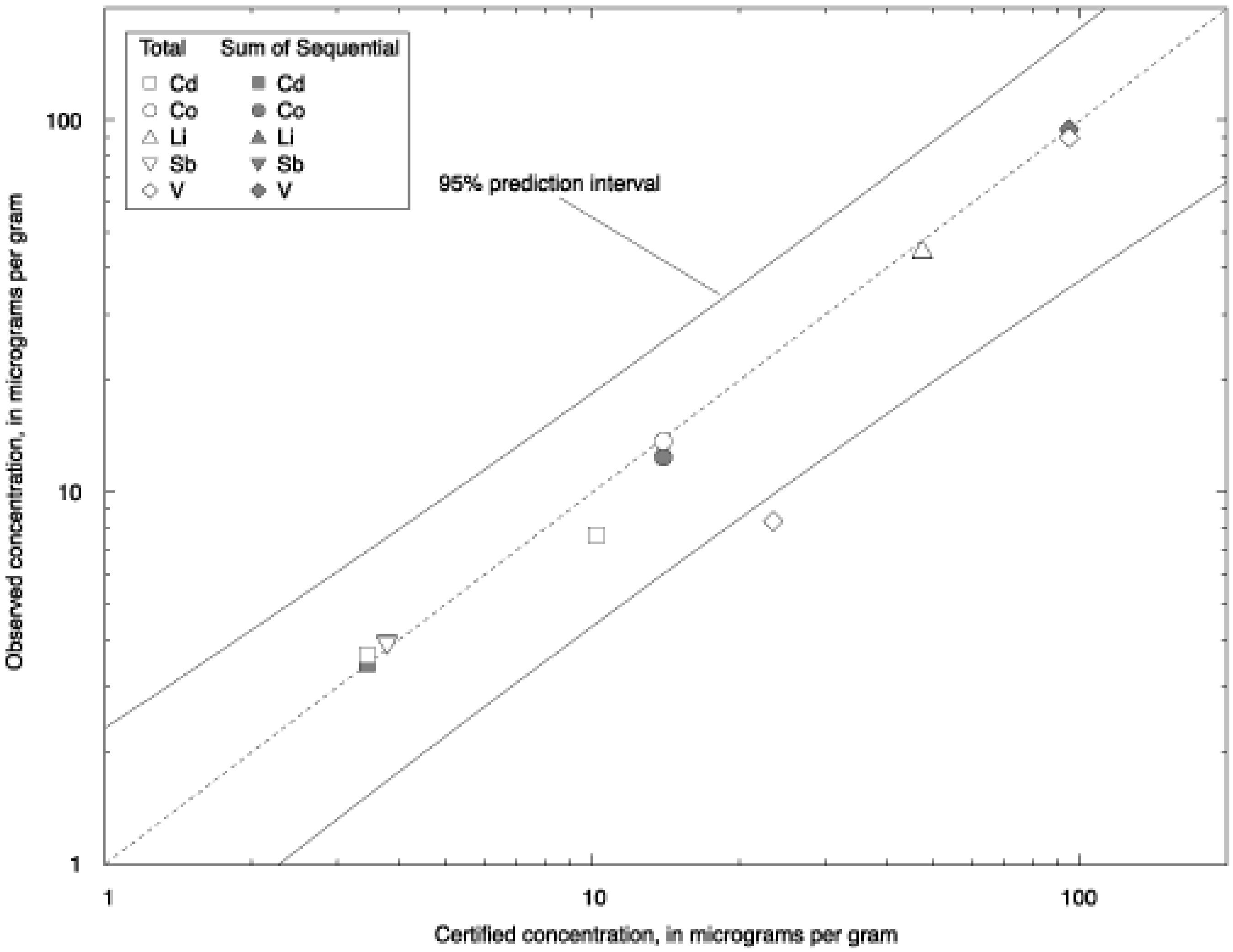

Figure 20. Correlation plot of observed concentration values in total digestions and in the sum of sequential digestions versus certified concentrations of cadmium (Cd), cobalt (Co), lithium (Li), antimony (Sb), and vanadium (V) in standard reference material. The standard reference material tested was National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment. Error band represents the 95 percent (%) prediction interval.

data for all elements determined in this study. Also, table 17 provides average detection limit data computed from the actual analytical determinations, rather than the estimated values presented in the QAPP (tables 1 and 2 in Appendix 1).

For colloid samples, table 18 summarizes the RPD of the elements listed in the QAPP (table 2 in Appendix 1). The table shows the percentage of field duplicate samples for which the RPD value was below the designated levels for each of the critical elements. Field duplicate agreement specifies the worst case situation for repeatability of determinations because it incorporates all sources of variance, including sampling precision, processing precision, and laboratory analysis precision. Since limited field duplicate samples were analyzed because of the limited amount of colloid material recovered, the samples (n=4) for tables 18 and 19 are relatively low.

Table 19 summarizes the percentage of replicate colloid sediment samples whose percentage RSDs (see section on dissolved constituents) are below the specified values listed. This table presents data for all elements determined in this study.

Data for the RPD of sequential extraction determinations on colloidal suspended sediments for the critical elements are presented in table 20. Finally, table 21 summarizes the percentage of duplicate sequential extraction determinations on colloid sediment samples whose RSDs are below the specified

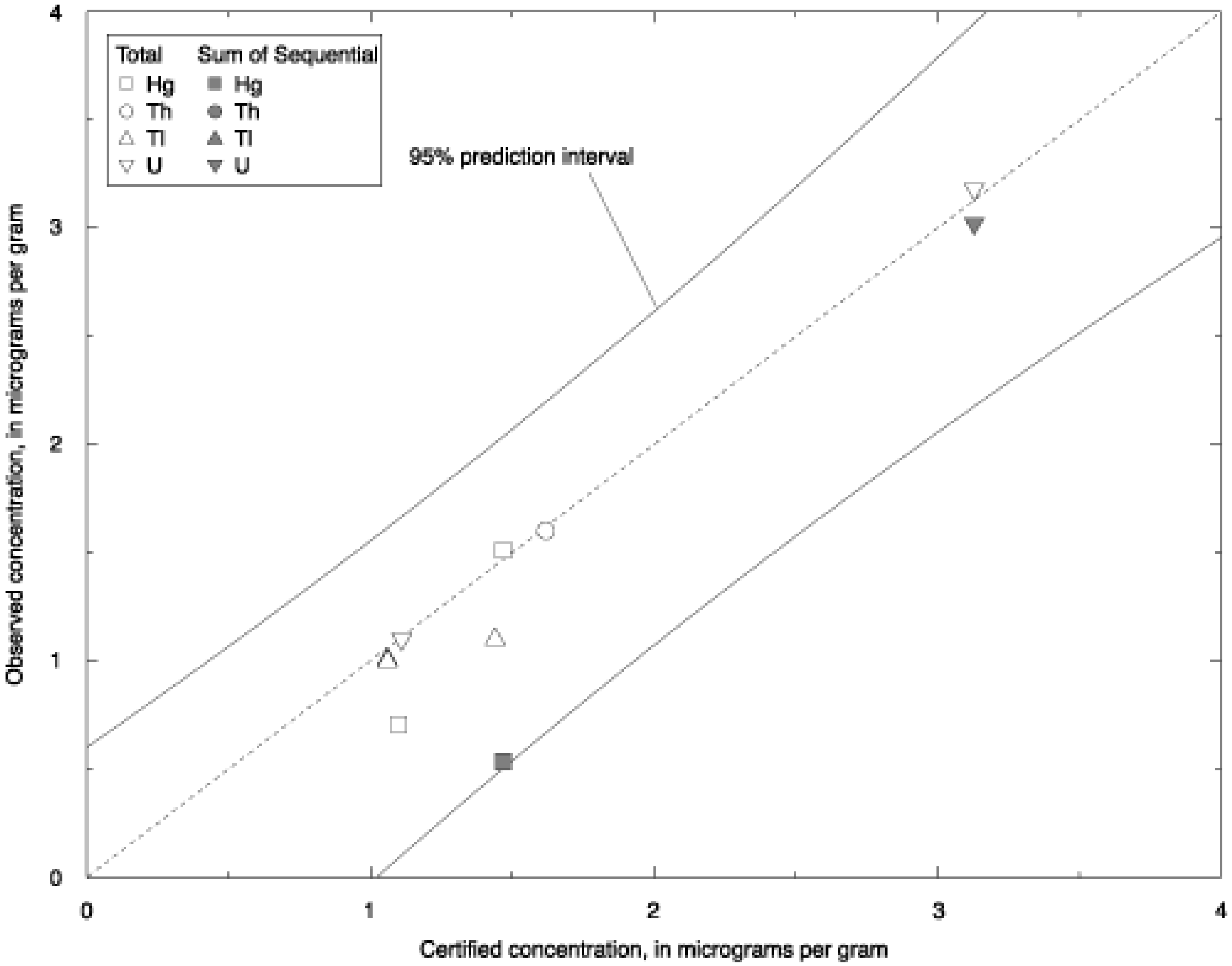

Figure 21. Correlation plot of observed concentration values in total digestions and in the sum of sequential digestions versus certified concentrations of mercury (Hg), thorium (Th), thallium (Tl), and uranium (U) in standard reference material. The standard reference material tested was National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment. Error band represents the 95 percent (%) prediction interval.

values listed. This table presents data for all elements determined in this study.

Trace Elements in Caddisfly Larvae

Standard Reference Materials

Two SRMs were digested along with caddisfly larvae: NIST SRM 1566a oyster tissue, and SRM 50 albacore tuna. No certified values for aluminum, cadmium, copper, or iron were available for SRM 50; only lead and zinc are reported (table 22). With the exception of aluminum, observed values are within 10 percent of certified values.

Spike addition recovery

Spike additions on caddisfly larvae extracts were done on 14 subsamples from 4 sampling sites. Spike recovery percentages for cadmium, copper, lead, and zinc are shown in table 23. The overall range for cadmium was 95–102 percent, for copper was 82–100 percent, for lead was 87–98 percent, and for zinc was 93–108 percent.

Iron Redox

No SRMs exist for iron redox species because of the poor long-term stability of Fe(II) and Fe(III) in

Table 13. Percentage of determinations for each selected element that fell within the specified range of the percentage recovery for the calculated theoretical value of the spike addition in water samples

[REC_{SPIKE}, percentage recovery with respect to spiked samples; n, number of observations; Conc., spiked concentration; QAPP, Quality Assurance Project Plan. %, percent; µg/L, microgram per liter]

REC_{SPIKE} Range (%)	Percentage of spiked samples within the specified REC_{SPIKE} range											
	Arsenic	Cadmium[1]	Chromium	Cobalt	Copper[1]	Lead[1]	Mercury[1]	Nickel	Selenium	Silver	Uranium	Zinc[1]
0–200	100	100	100	100	100	100	100	100	100	98	100	100
50–150	100	100	100	100	100	98	100	100	100	92	100	98
75–125	98	100	98	100	98	98	100	100	100	78	98	98
85–115	92	94	98	100	98	96	89	100	98	58	80	91
90–110	78	88	88	98	85	82	69	96	94	44	62	83
95–105	58	69	52	69	60	56	44	70	70	16	42	55
n	50	48	50	49	47	50	36	50	50	50	50	47
Conc. (µg/L)	10	1	50	5	10	50	0.004	10	20	10	10	10

[1] Data quality objective was at least 90 percent completeness in the 75–125 range of REC_{SPIKE} for indicated elements listed in the QAPP (Appendix 1).

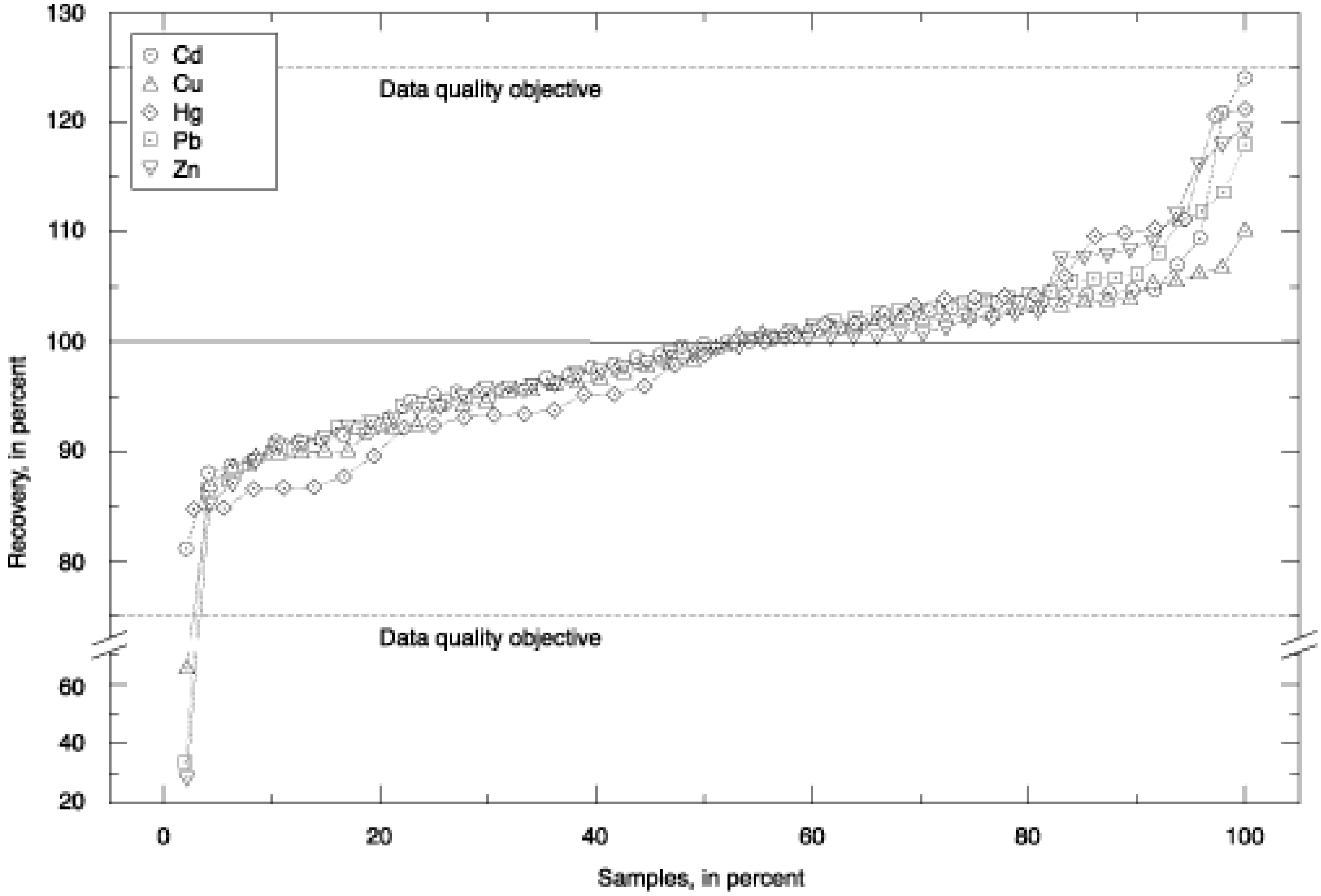

Figure 22. Distribution diagram of the percentage recovery of dissolved spike addition determinations for cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) versus the percentage of samples observed in the Sacramento River Basin, California, including the data quality objective (represented by horizontal lines).

Table 14. Percentage of determinations of critical elements within the stated percentage recovery for the certified or critical value compared with the sum of the sequential extraction phases of the National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment

[REC_{SRM}, percentage recovery with respect to standard reference materials; n, number of observations]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125	85–115	90–110	95–105
Aluminum	5	100	80	0	0	0	0
Cadmium	5	100	100	100	100	80	60
Copper	5	100	100	100	80	60	40
Iron	5	100	100	100	100	80	40
Lead	5	100	100	100	100	80	80
Mercury	5	100	100	100	100	100	80
Zinc	5	100	100	100	100	100	40

Table 15. Percentage determinations of noncritical elements within the stated percentage recovery for the certified or "informational purposes" value compared with the sum of the sequential extraction phases of the National Institute of Standards and Technology's standard reference material SRM 2704–Buffalo River Sediment

[REC_{SRM}, percentage recovery with respect to standard reference materials; n, number of observations. *, "informational purposes" value]

Element	n	Range REC_{SRM} (percent)					
		0–200	50–150	75–125	85–115	90–110	95–105
Antimony	5	100	100	100	80	80	60
Barium	5	100	80	20	0	0	0
Calcium	5	100	100	100	80	80	40
Cerium*	5	100	0	0	0	0	0
Cesium*	5	100	100	100	80	60	40
Chromium	5	100	100	100	100	60	40
Cobalt	5	100	100	100	60	40	20
Dysprosium*	5	100	40	0	0	0	0
Europium*	5	100	80	0	0	0	0
Lanthanum*	5	100	0	0	0	0	0
Lithium	5	100	100	100	80	80	40
Lutetium*	5	100	0	0	0	0	0
Magnesium	5	100	100	0	0	0	0
Manganese	5	100	100	100	100	80	60
Nickel	5	100	100	80	20	20	20
Rubidium*	5	100	0	0	0	0	0
Samarium	5	100	60	0	0	0	0
Silica[1]	5	100	100	100	100	80	20
Strontium	5	100	100	20	20	0	0
Titanium	5	100	100	100	100	80	80
Thallium	5	100	100	100	80	80	60
Thorium*	5	100	40	0	0	0	0
Uranium	5	100	100	100	100	100	40
Vanadium	5	100	100	100	100	100	100
Ytterbium*	5	100	40	0	0	0	0
Zirconium*	5	100	100	80	80	80	60

[1] Silica was the only substance reported as an oxide.

aqueous solution. Therefore, the quality of analytical results for iron redox determinations by ultraviolet–visible (UV–vis) spectroscopy using FerroZine as the complexing agent were evaluated by replicate analysis, by comparison of total iron determinations to those made by another method (ICP–AES), and by comparing the proximity of a given analytical result with the method detection limit. At the method detection limit, by definition the precision of the analytical result is ± 100 percent. Precision improves exponentially with increasing concentration until it is ± 5 percent or less at about

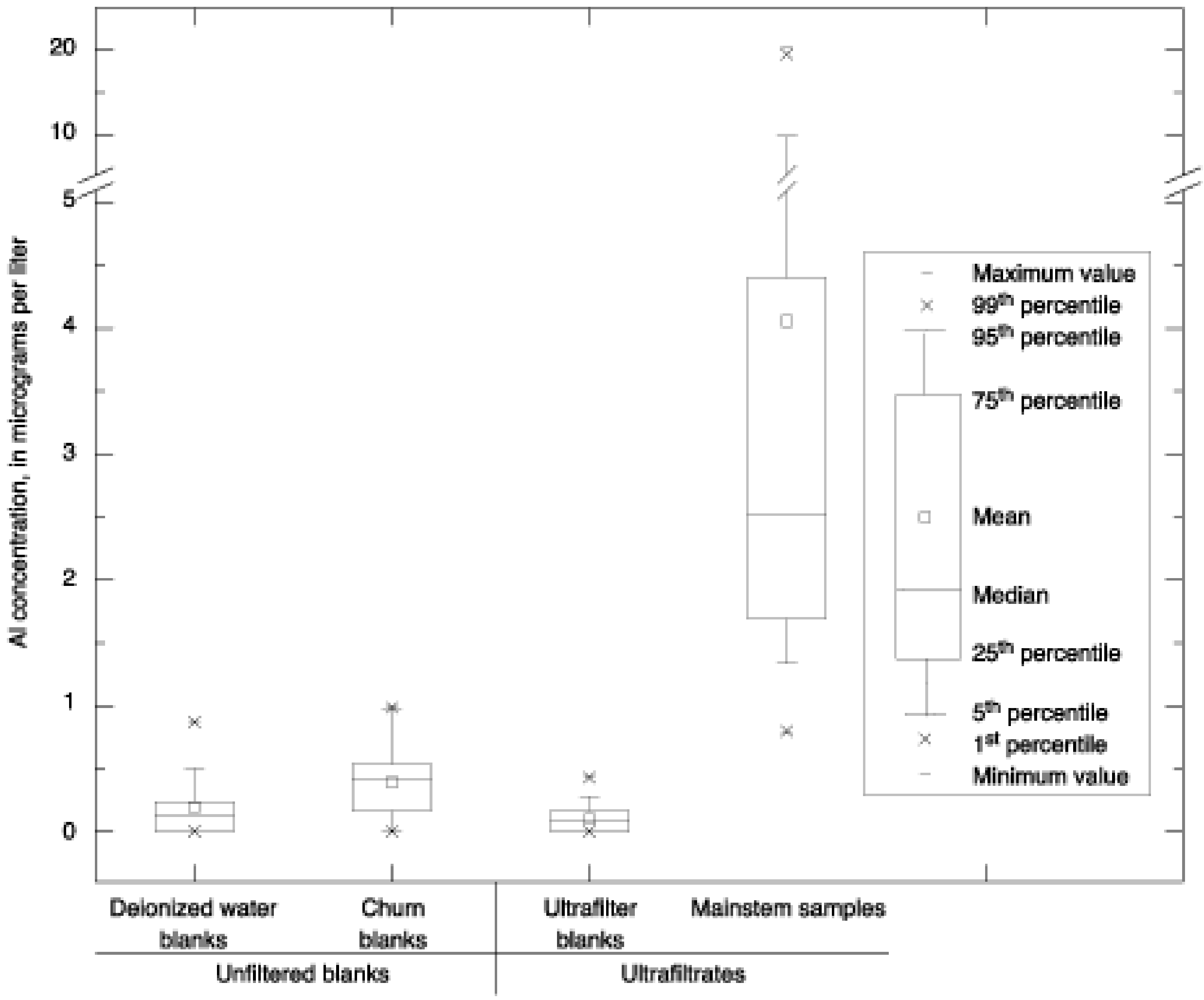

Figure 23. Box plots showing concentration ranges for aluminum (Al) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

10 to 20 times the detection limit. Iron redox samples were analyzed routinely in duplicate, with additional analyses performed for instances where precision between replicates was judged poorer than that expected for the concentration range represented by the analyses.

Concentrations of total iron in filtered water samples determined by UV–vis spectroscopy can be compared with total iron determined by ICP–AES on split subsamples. Comparing results from all six sampling events (table A4-1) indicates a slight bias toward higher iron concentrations with UV–vis spectroscopy than with ICP–AES, especially in the concentration range of about 8 to 80 μg/L. Blanks for the iron redox subsplits for the July and September 1996 sampling trips showed elevated iron in this approximate concentration range (table A2-2), indicating a probable laboratory contamination problem. The source of the iron contamination could have been the bottle washing procedure, the hydrochloric acid used for sample preservation, the pipette used to transfer the acid, or perhaps the environmental conditions in the laboratory used to process and preserve these samples. Sample processing was relocated from the BOR laboratory near Keswick Dam to the USGS laboratory in Sacramento beginning in November 1996. Significantly lower blank levels were observed beginning in November 1996, and the agreement between the data from the two methods of iron determination was also improved beginning with samples from that time. The agreement between the two methods for total iron is especially good above concentrations of 10 μg/L, a value less than 10 times the detection limit of both methods.

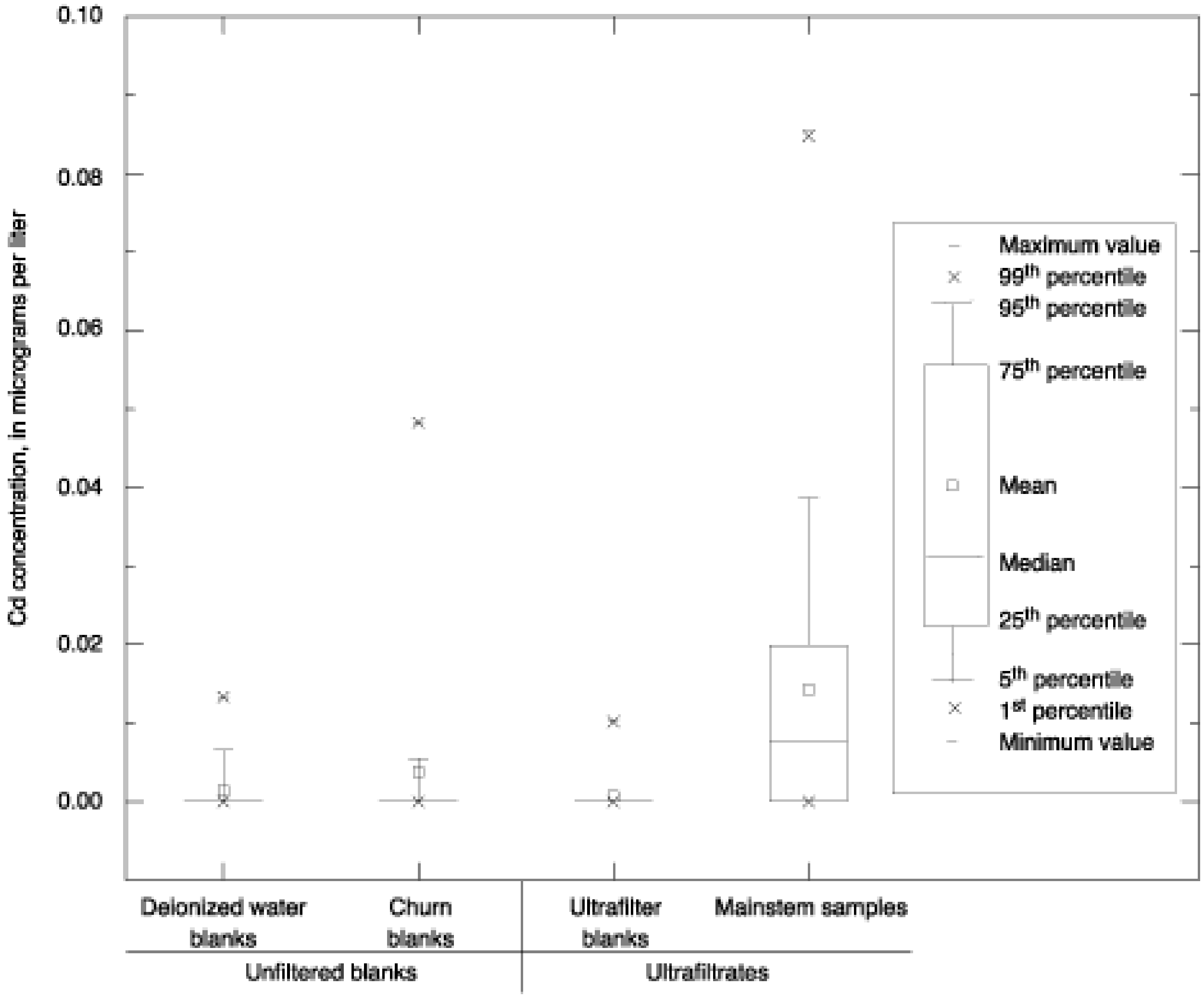

Figure 24. Box plots showing concentration ranges for cadmium (Cd) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

Lead Isotopes

The total chemistry lead blank for the lead procedure is approximately 0.1 ng. In the worst case scenario (83 ng of lead in the sample) the blank contributes 0.12 percent of the total lead. However, because the isotopic composition of the lead blank (^{206}Pb/^{204}Pb = 18.9) is similar to that of the samples (^{206}Pb/^{204}Pb = 18.1–19.1), the blank effect on the isotopic composition of the sample is less than 0.006 percent. This contribution is insignificant relative to the precision of the mass spectrometric analyses (0.05–0.1 percent).

Mass spectrometric data for lead were collected from at least three blocks of 10 ratio sets. When the VG Sector 54 seven-collector mass spectrometer was used in static mode, all lead isotopes were measured simultaneously. Differences in collector efficiencies were routinely measured and corrected mathematically as a part of the general operating software. When lead was measured on the VG 54R single-collector mass spectrometer, data were measured as pairs using peak switching and ^{206}Pb as the reference isotope. Data are considered to be of acceptable quality if the internal precision for a given run is better than 0.1 percent for ^{206}Pb/^{204}Pb and better than 0.05 percent for ^{207}Pb/^{206}Pb and ^{207}Pb/^{208}Pb.

The principal cause of uncertainty in mass spectrometric analyses for lead is mass-dependent fractionation induced during thermal ionization of the sample. The level of accuracy for the mass spectrometric determinations performed in this study was

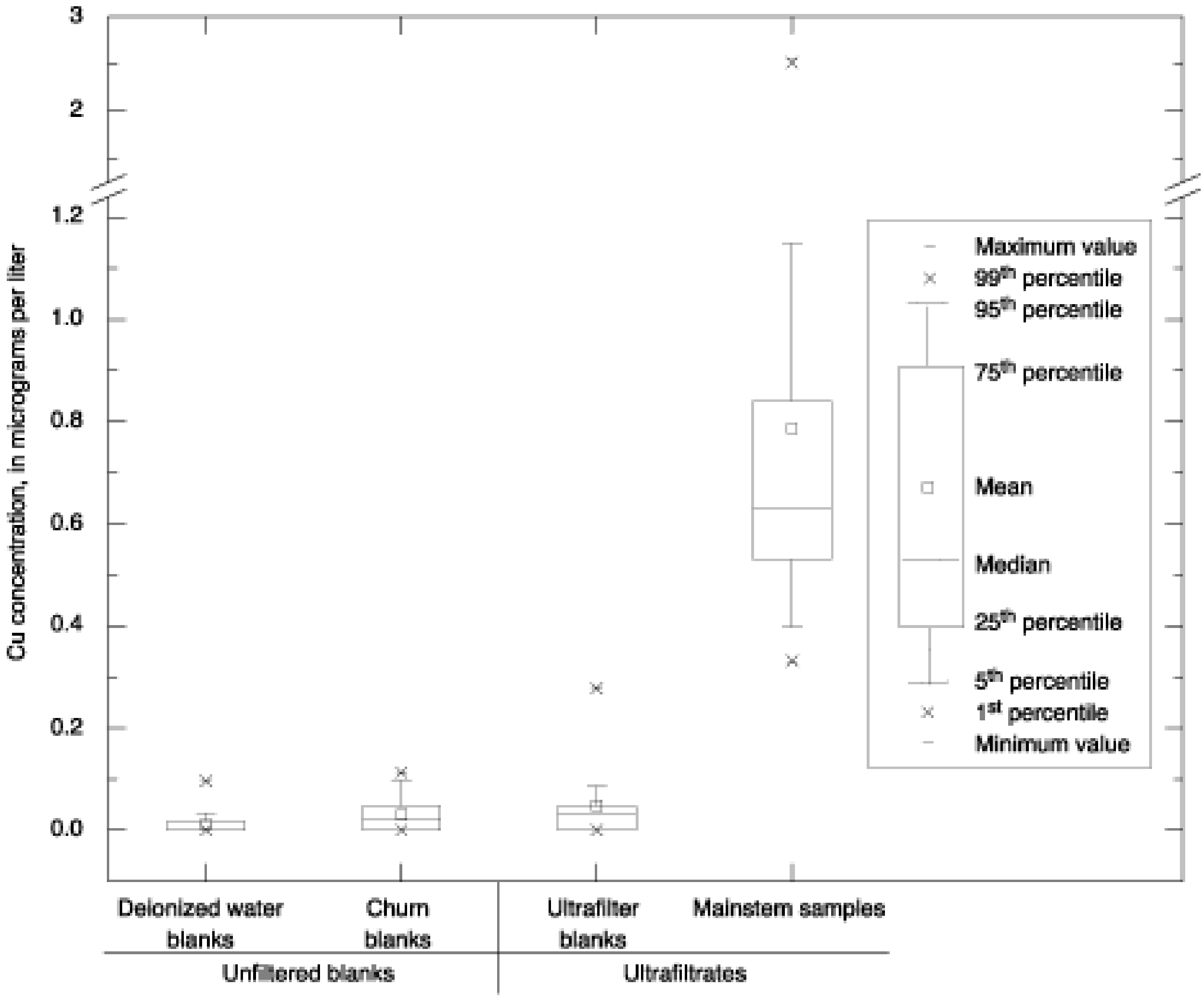

Figure 25. Box plots showing concentration ranges for copper (Cu) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

evaluated by performing concurrent analyses of NIST lead isotopic standard SRM-981 (Todt and others, 1993). One standard analysis was performed for every 10 or fewer sample analyses. A fractionation factor (*F*) that is calculated from the standard data represents the correction in percentage per atomic mass unit that must be applied to a given isotopic ratio as follows:

$$\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{C}} = \frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{M}}(1 + 0.02F) \qquad (5)$$

$$\frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}_\mathrm{C}} = \frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}_\mathrm{M}}(1 + 0.01F) \qquad (6)$$

$$\frac{^{208}\mathrm{Pb}}{^{206}\mathrm{Pb}_\mathrm{C}} = \frac{^{208}\mathrm{Pb}}{^{206}\mathrm{Pb}_\mathrm{M}}(1 + 0.02F) \qquad (7)$$

$$\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{C}} = \frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{M}}(1 + 0.03F) \qquad (8)$$

$$\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{C}} = \frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}_\mathrm{M}}(1 + 0.04F) \qquad (9)$$

where the subscripts C and M refer to the corrected and measured isotopic ratios, respectively.

Lead isotopic data were measured at filament temperatures ranging from approximately 1,200° to 1,300°C. There is a small but measurable effect of filament temperature on mass fractionation as outlined in table 24. Fractionation corrections were applied to the data for individual samples on the basis of the mass spectrometer used and the filament temperature. The uncertainties are calculated after the manner in

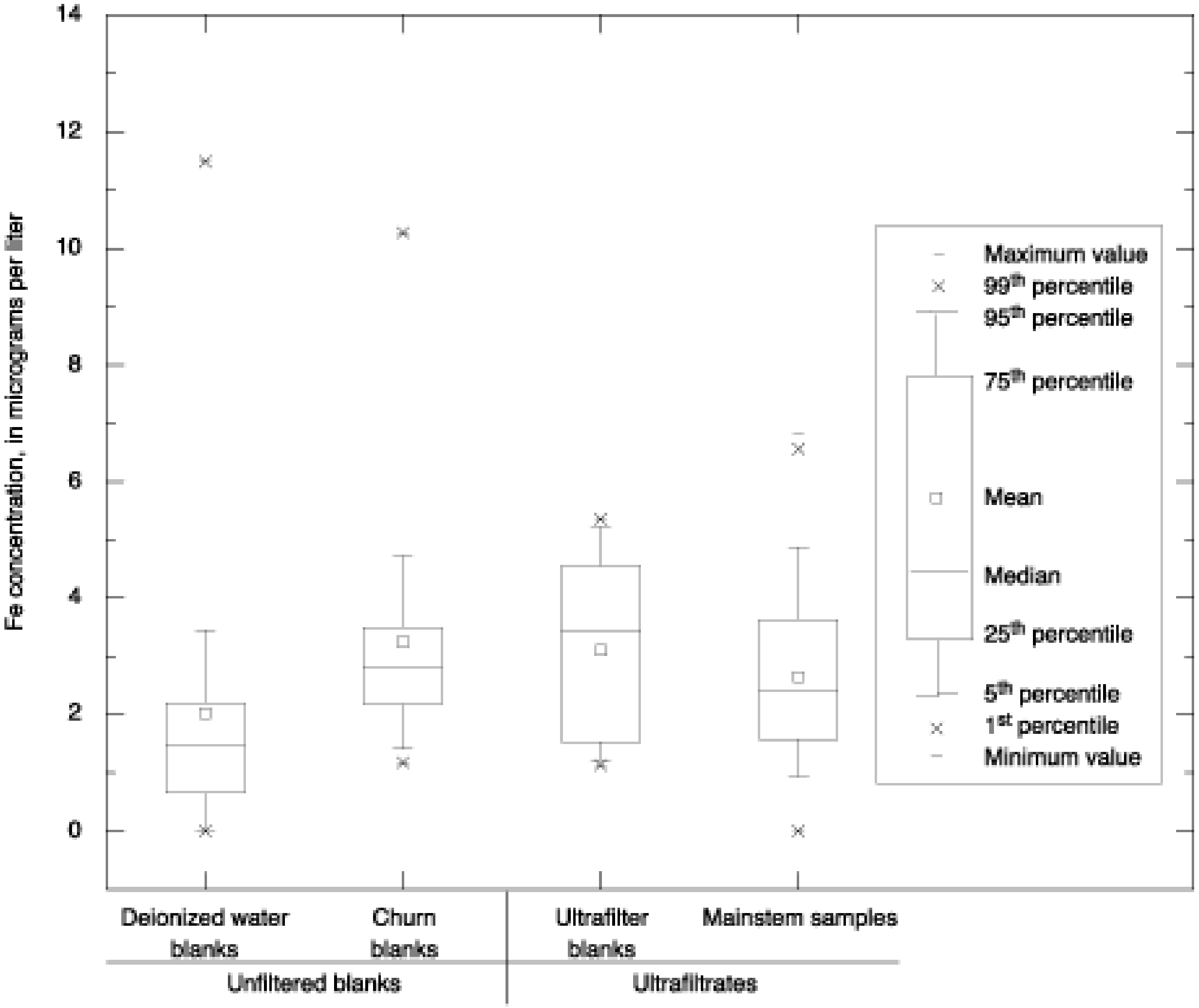

Figure 26. Box plots showing concentration ranges for iron (Fe) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

Ludwig (1979) and are at the 95 percent confidence interval, or 2 sigma (2σ).

As an independent check of the mass spectrometric procedures used in this study, one of the colloid samples (below Shasta Dam) was analyzed on both mass spectrometers. The fractionation-corrected data on this comparison are presented in table 25, showing essentially identical agreement between both mass spectrometers.

Anions, Nutrients, and Organic Carbon

Analyses of anions, nutrients, and organic carbon were done by USGS personnel at the NWQL in Arvada, Colorado. Quality assurance and quality control (QAQC) activities at the NWQL are documented in reports by Friedman and Erdmann (1982) and by Pritt and Raese (1995). Method performance evaluations were based on the analysis of SRMs, laboratory replicates, and analysis of blank samples. A minimum of 10 percent of analyzed samples were reference materials.

In addition to internal QAQC assessments, NWQL participates in numerous external performance evaluation programs, including the EPA’s Water Pollution Performance Evaluation Study (WPPES) and its Water Supply Performance Evaluation Study (WSPES). These studies are made by the EPA's Environmental Monitoring Systems Laboratory and are used to evaluate the performances of EPA, state, and other selected laboratories for 80 water pollution constituents. The NWQL also participates in the

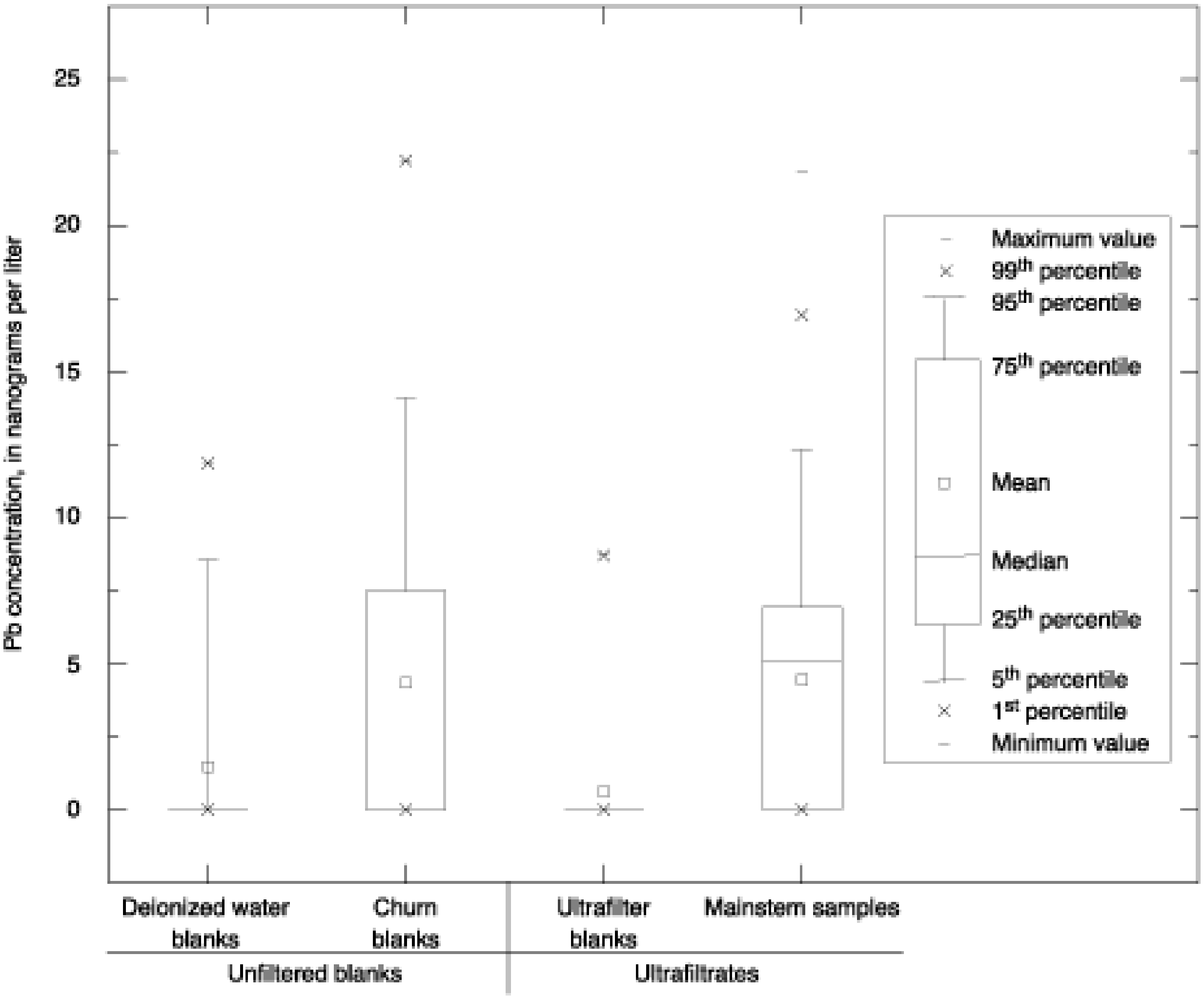

Figure 27. Box plots showing concentration ranges for lead (Pb) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

spring Canadian Federal–Provincial water performance evaluation study. This study includes low-ionic strength, trace metals, and major ion determinations. Additionally, the NWQL participates in the USGS Water Resources Division, Branch of Technical Development and Quality Systems (BTD&QS) round-robin performance evaluation program, which biannually sends standard reference water samples to more than 150 laboratories for comparative analysis. The NWQL also takes part in the BTD&QS blind sample program on an ongoing basis.

Satisfactory results of the three WPPES evaluations (WP036, WP037, and WP038) that were completed during the time period of this study are included in Appendix 2 (tables A2-1a, A2-1b, and A2-1c). The acceptance limits defined by the EPA (Appendix 2) are the 99 percent confidence interval or, effectively, ± 3 standard deviations (3σ). Warning limits are defined as the 95 percent confidence interval, or ± 2σ. The number of decimal places reported in the EPA performance evaluations (Appendix 2) is not necessarily reflective of the precision of the analytical method.

Particulate Size Determinations

Replicate split samples were analyzed for size distribution of both suspended colloid and streambed sediment but are not reported. Similar size distributions were observed in replicate samples analyzed by either of the methods described earlier in this report;

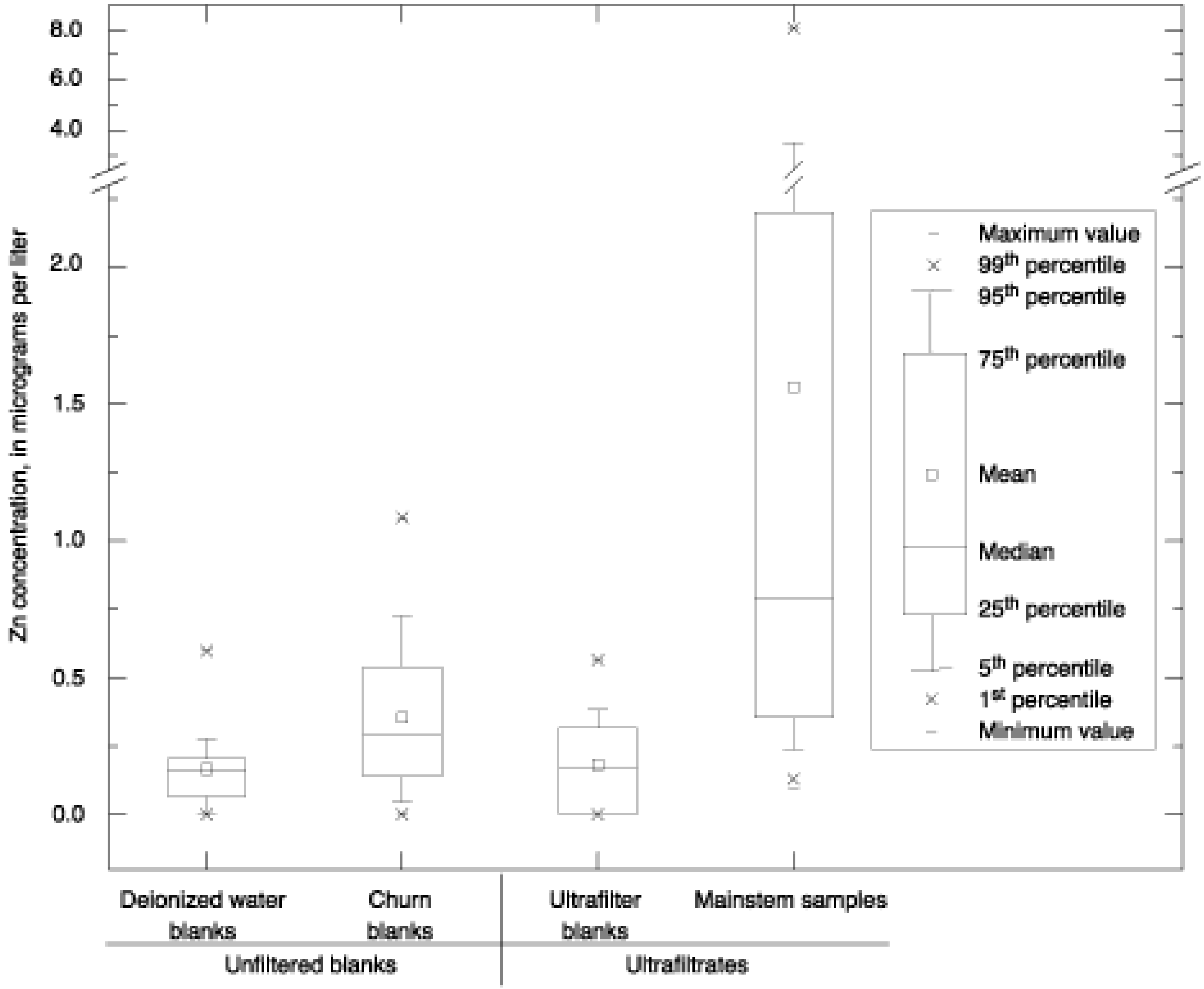

Figure 28. Box plots showing concentration ranges for zinc (Zn) in selected blank water samples and dissolved (ultrafiltrate) subsamples from the mainstem Sacramento River, California.

Table 16. Percentage of field duplicate dissolved samples whose relative percentage difference was below specified values for critical elements

[RPD, relative percentage difference; DL, detection limit; values in table represent the total of those less than detection limit and those which meet the criteria; n, number of duplicate samples. %, percent; <, less than; >, greater than]

RPD	Percentage of duplicate sample results whose RPD fell below the given value						
	Aluminum	Cadmium	Copper	Iron	Lead	Mercury	Zinc
% < 100%	100	100	98	100	100	100	98
% < 50%	100	100	98	100	100	100	96
% < 25%[1]	98	100	98	91	100	74	78
% < 15%	96	100	96	91	100	57	57
% < 10%	85	96	85	91	100	49	46
% < 5%	63	96	59	89	100	28	30
n > Dl	46	9	46	8	3	37	46
Total n	46	46	46	46	46	47	46

[1] Data quality objective was at least 90% completeness for RPD values < 25%.

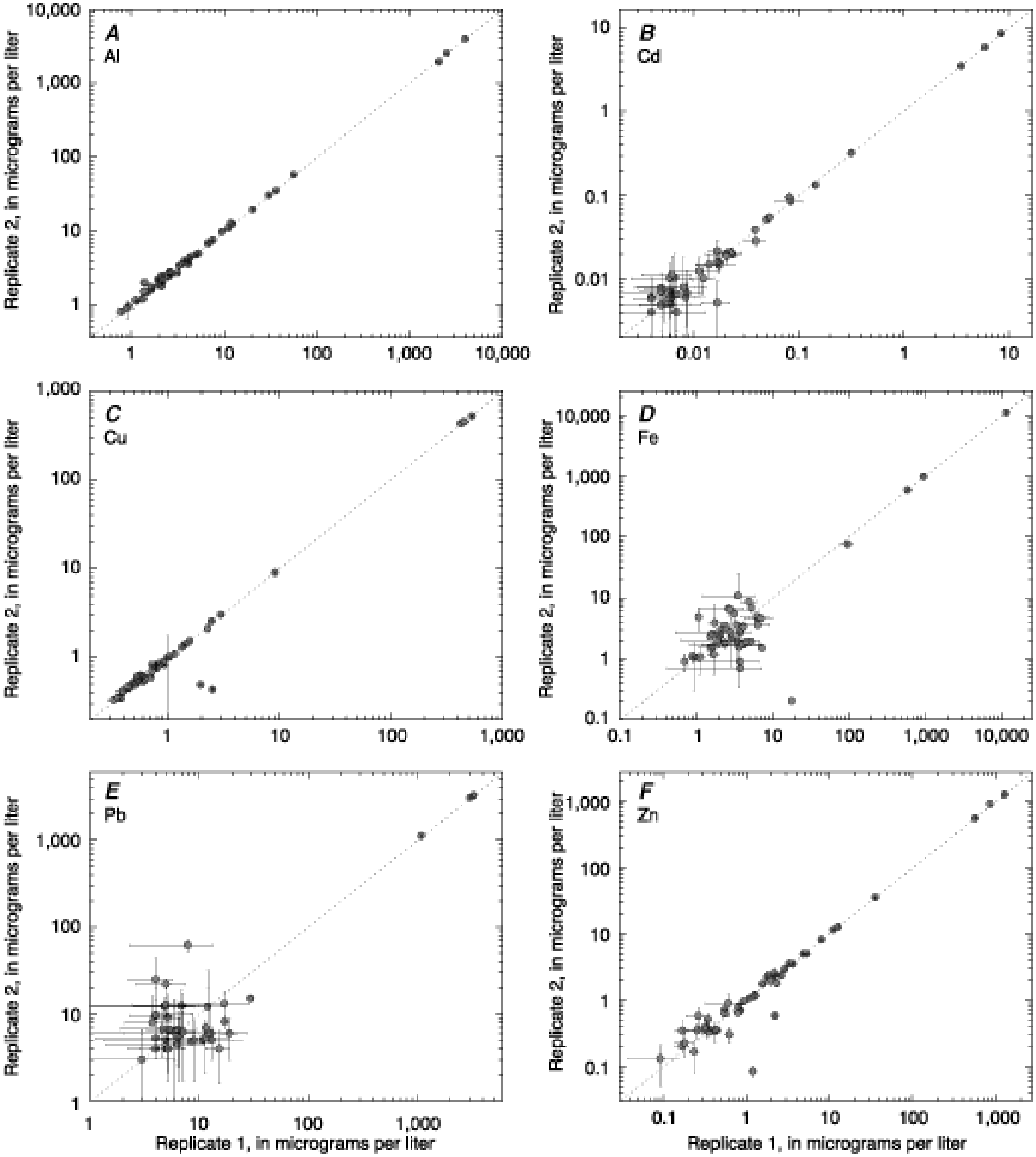

Figure 29. Correlation plots of field replicates for dissolved *A*. aluminum (Al), *B*. cadmium (Cd), *C*. copper (Cu), *D*. iron (Fe), *E*. lead (Pb), and *F*. zinc (Zn) in the Sacramento River Basin, California, with error bars representing laboratory analytical precision.

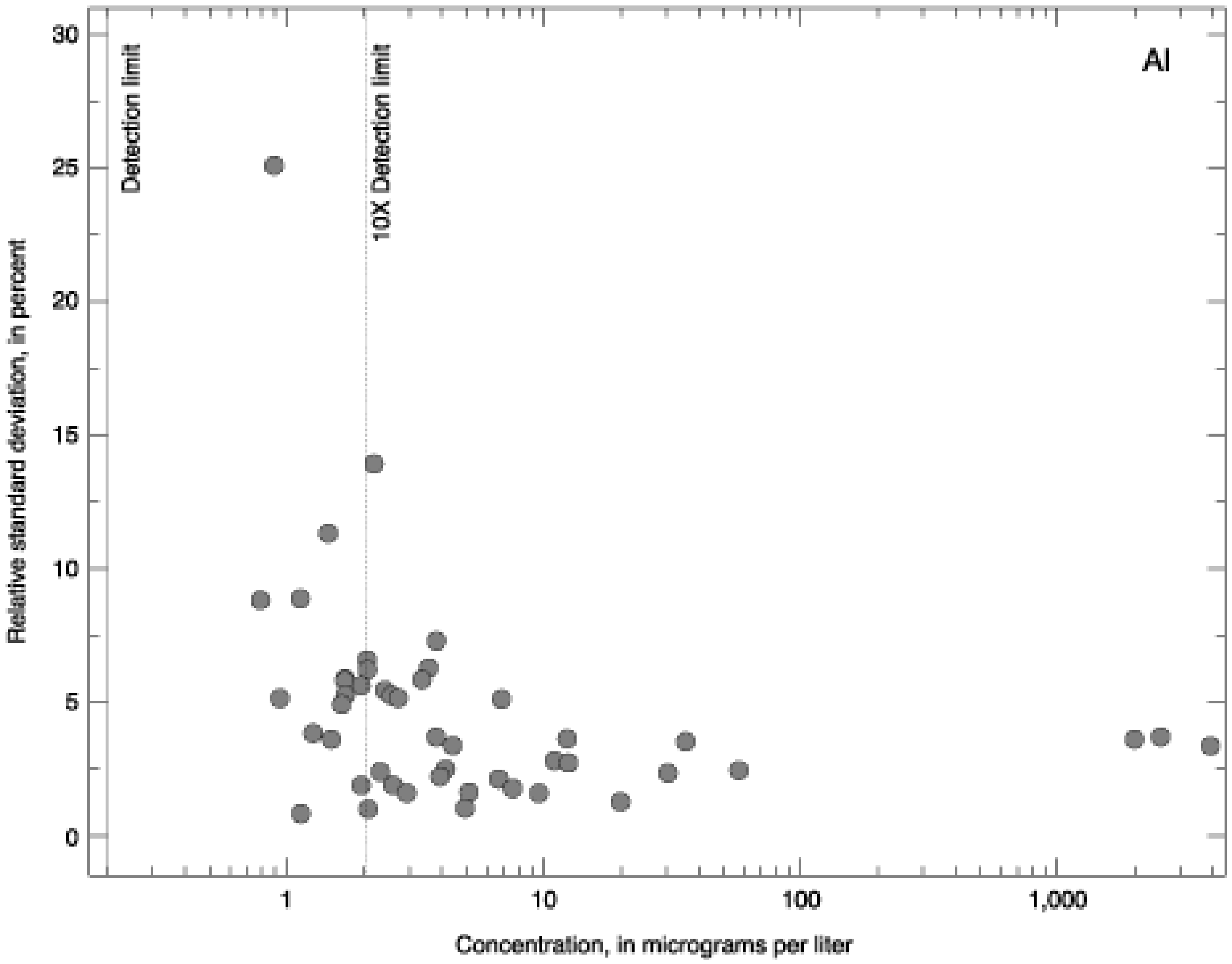

Figure 30. Plot of relative standard deviation for replicate determinations of aluminum (Al) versus dissolved (ultrafiltrate) concentration in the Sacramento River Basin, California, including solid and dashed vertical lines that represent the reported detection limit and 10 times the detection limit, respectively.

however, no quantitative comparative size determinations were performed.

Results

Ronald C. Antweiler, Peter D. Dileanis, Charles N. Alpers, Howard E. Taylor, *and* Joseph L. Domagalski

Metal Concentrations in Water

Raw data for metal analyses in water samples are provided in Appendix 4 (tables A4-1 and A4-2) in the following order: (1) by sampling site in downriver order with tributaries following mainstem sites, (2) within a site by sampling date, and (3) within a date by filter type. Concentration data for various filtrates includes the 0.45-µm pore-size capsule filtrate, the 0.40-µm pore-size membrane filtrate, and the 10,000 NMWL (0.005-µm equivalent pore size) tangential-flow ultrafiltrate (table A4-1). Data are also provided on unfiltered (whole water) samples (table A4-2).

Dissolved Constituents from Tangential-Flow Ultrafiltration

Box plots (figs. 34 and 35) demonstrate average dissolved (from the tangential-flow ultrafiltrates) concentrations (Al, Cd, cerium [Ce], Cu, Fe, manganese [Mn], Pb, and Zn] at various sites along the Sacramento River and for some tributaries in the Keswick Reservoir area. They also provide a direct comparison of the range and median concentrations.

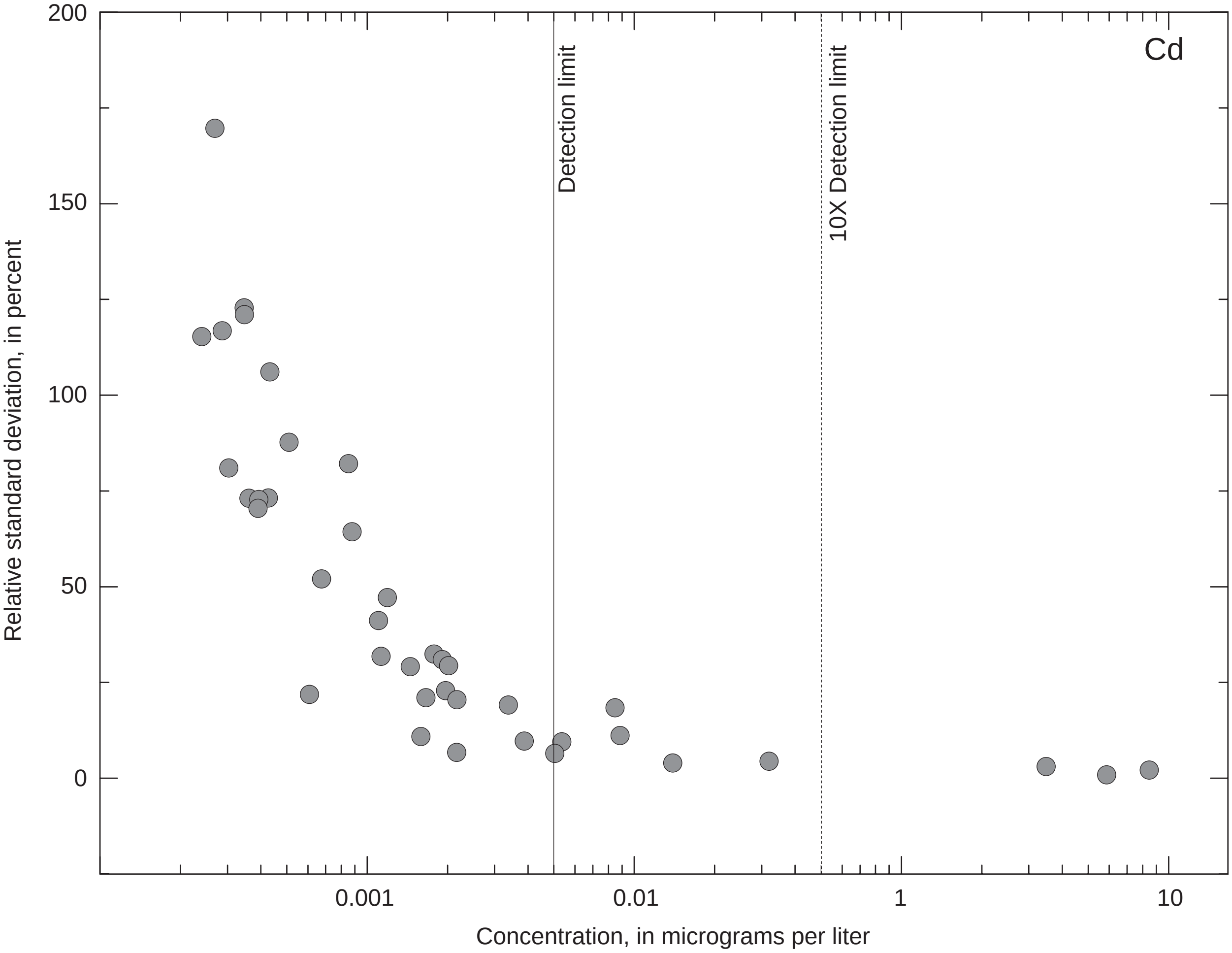

Figure 31. Plot of relative standard deviation for replicate determinations of cadmium (Cd) versus dissolved (ultrafiltrate) concentration in the Sacramento River Basin, California, including solid and dashed vertical lines that represent the reported detection limit and 10 times the detection limit, respectively.

Values in Spring Creek, a tributary, are commonly more than 1,000 times higher than at any other site studied along the Sacramento River.

Concentration data from the mainstem sites on the Sacramento River from tangential-flow ultrafiltration subsamples for selected elements (Al, Cd, Cu, Fe, Pb, and Zn) are plotted as a function of distance in figures 36 through 41, respectively. Similar plots for 14 additional elements are in Appendix 8 (figs. A8-1 through A8-14). On each of these graphs, the vertical axis represents the dissolved concentration of the analyte in question, and the horizontal axis represents distance in kilometers from the mouth of the Sacramento River (table 1; U.S. Army Corps of Engineers, 1991). Because several sampling sites are near Redding and Keswick Dam (near river kilometer 480), and sites are more widely spaced in the lower reaches of the river, the horizontal axis is divided into two parts with different scales that provide the reader with a way to discriminate between the various upriver sites. For most trace metals, the dissolved concentration was fairly uniform in the lower 250 km of the river and varied little from season to season. In the upstream part of the study area, several elements are at higher concentrations in the Spring Creek arm of Keswick Reservoir and below Keswick Dam, including aluminum, cadmium, copper, zinc, nickel, and some rare-earth elements, such as cerium. Dissolved concentrations for these same elements also appear to have varied seasonally, with the highest concentrations having occurred generally in December 1996 or January 1997.

A comparison was made between the analysis of composite-collected lead samples and separate

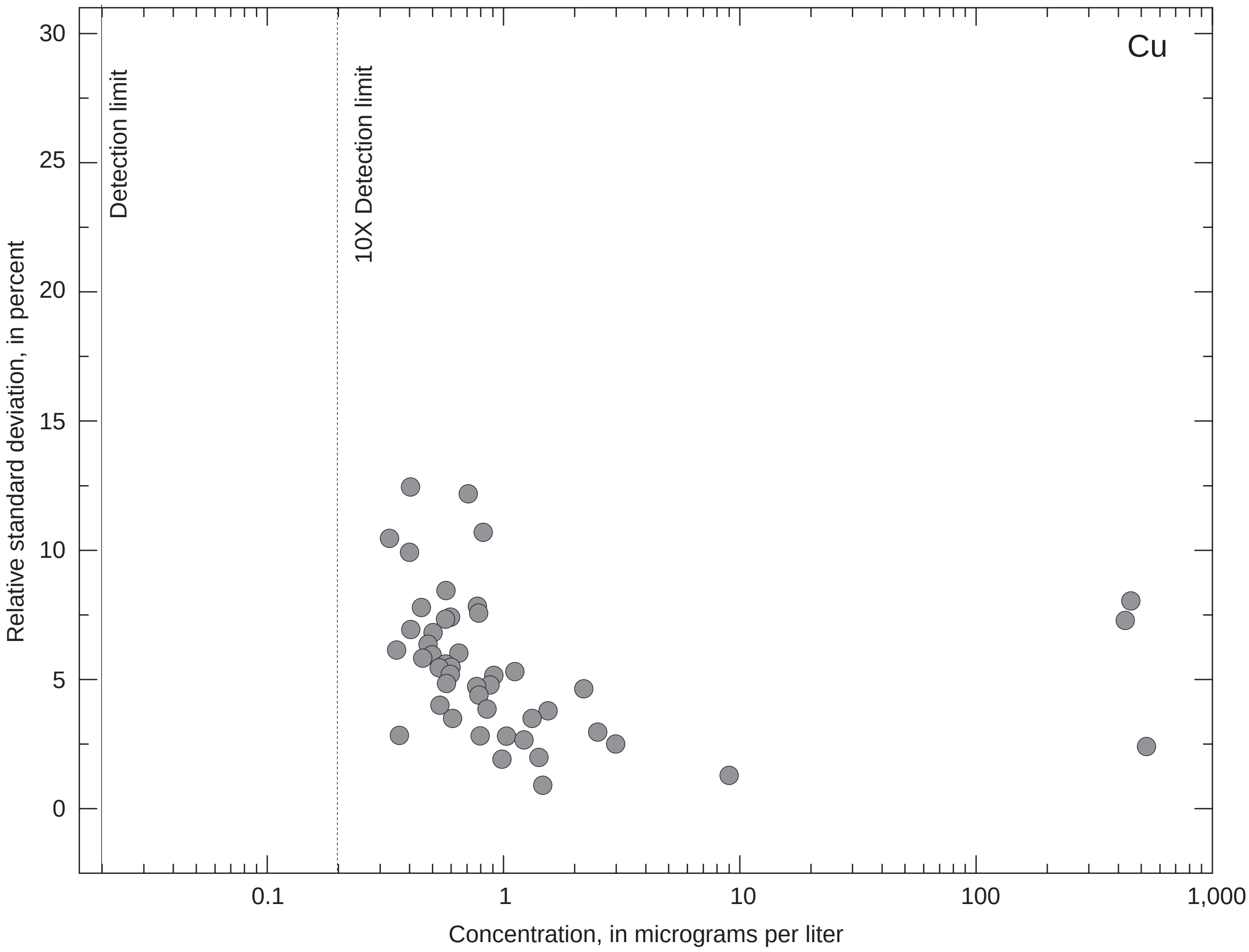

Figure 32. Plot of relative standard deviation for replicate determinations of copper (Cu) versus dissolved (ultrafiltrate) concentration in the Sacramento River Basin, California, including solid and dashed vertical lines that represent the reported detection limit and 10 times the detection limit, respectively.

grab-collected lead samples concurrently collected (fig. 42; tables A4-3 and A4-4 in Appendix 4 contain the corresponding data). Most dissolved lead concentrations were less than 10 times the analytical detection limit, indicating there was practically no dissolved lead present. Composite samples, however, did tend to have lower dissolved lead concentrations than their grab sample counterparts; also, three outlying data points indicate that probable contaminants of unknown origin were present in these grab samples. These results would tend to imply that there is no benefit to the collection of grab samples for dissolved lead from the standpoint of contamination for the methods employed in this study.

Isolated Colloidal Material

Suspended colloids were subjected to two types of analysis: a total digestion in which all colloid material was dissolved and analyzed, and a sequential extraction in which the colloids were subjected sequentially to three distinct digestions. The details of these digestions are described earlier in this report.

Total Digestions

The analytical results from the total digestion of the colloids are presented in Appendix 5, table A5-2. These data—called the “elemental concentrations of the colloids”— are presented as micrograms of analyte per gram of freeze-dried colloid (micrograms per gram), and therefore represent the variation in the suspended sediment chemistry. The product of this quantity (in micrograms per gram), and the concentration of the colloid in the river at the time the sample was collected (in grams per liter) is defined as the “equivalent concentration” in micrograms per liter of the analyte in the river associated with the colloid.

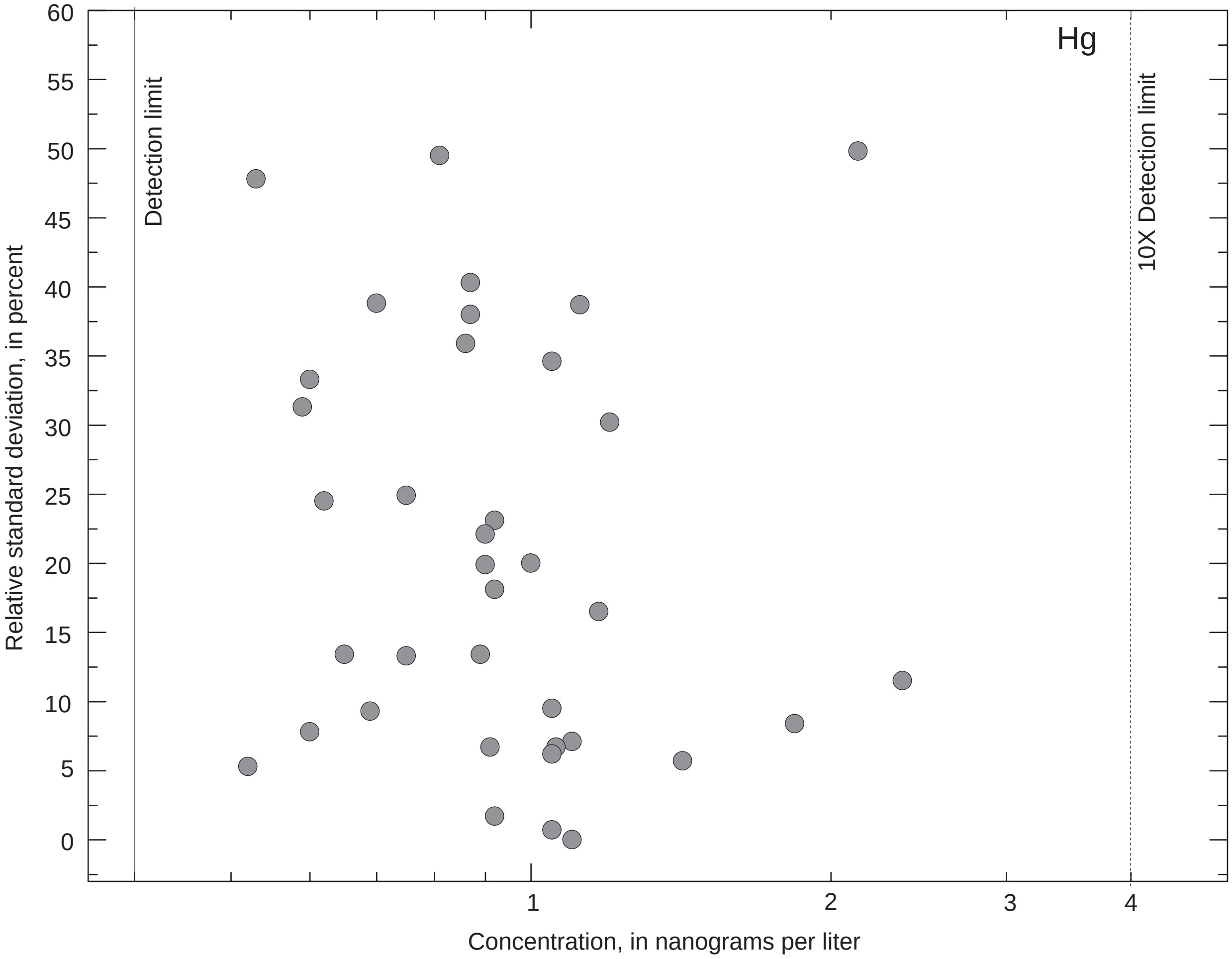

Figure 33. Plot of relative standard deviation for replicate determinations of mercury (Hg) versus dissolved (ultrafiltrate) concentration in the Sacramento River Basin, California, including solid and dashed vertical lines that represent the reported detection limit and 10 times the detection limit, respectively.

Expressed another way, the equivalent concentration of element X represents the amount of X being carried with colloids in the river per liter of river water, and is, therefore, the analogue of the dissolved concentration, with which it can be directly compared. The top figure *A* of figures 36 through 41 are plots of the equivalent concentrations of selected elements (Al, Cd, Cu, Fe, Pb, and Zn, respectively) in the Sacramento River, just as the lower figure *B* of figures 36 to 41 contain the dissolved concentrations of these same elements. Appendix 8 contains similar plots for an additional 14 elements. By comparing the vertical axes on the A panel with those of the B panel on figures 36 through 41 and A8-1 through A8-14, the relative amount of each element that is being carried on colloids can be compared with the relative amount being carried in solution. On all of these figures, the horizontal axis is broken to provide the reader with a way to discriminate between the various upriver sites. For example, in the case of aluminum (fig. 36), roughly 1,000 times more of this element is carried colloidally than in solution. Cadmium, on the other hand (fig. 37), exists in roughly equal amounts in colloidal form and in solution. As noted previously with dissolved (ultrafiltrate) data, the equivalent concentration of most analytes is more or less constant in the lower 250 km of the river. There is, however, a distinct difference in effective concentration seasonally; high-flow periods (December 1996 and January 1997) showed much higher equivalent concentrations than did low-flow periods.

Sequential Extractions

Results from sequential extractions (reducible, oxidizable, and residual) from selected samples

Table 17. Percentage of replicate dissolved samples whose relative standard deviation fell below the specified values for all elements analyzed

[DL, detection limit; µg/L, microgram per liter; RSD, relative standard deviation; n, number of duplicate samples. The range values in the table represent the total of those less than the detection limit and those that meet the criteria. %, percent; <, less than]

Element	Avg. DL (µg/L)	n	Range (%RSD)						
			% < DL	% < 100%	% < 50%	% < 25%	% < 15%	% < 10%	% < 5%
Aluminum	0.05	46	0	100	100	100	98	89	76
Antimony	0.02	46	9	100	100	91	80	72	46
Arsenic	0.04	46	0	100	100	98	93	89	72
Barium	0.01	46	0	100	100	100	100	98	89
Beryllium	0.02	46	93	100	100	100	96	93	93
Bismuth	0.01	46	100	100	100	100	100	100	100
Boron	4	46	4	100	100	98	98	91	76
Cadmium	0.006	46	41	100	98	93	89	80	70
Calcium	20	46	0	100	100	100	100	98	93
Cerium	0.001	46	2	100	98	85	67	54	37
Cesium	0.06	46	67	96	93	91	85	76	67
Chromium	0.2	46	26	100	100	93	80	65	43
Cobalt	0.01	46	52	100	100	96	91	89	83
Copper	0.02	46	0	100	98	98	98	96	74
Dysprosium	0.002	46	59	100	100	91	89	85	72
Erbium	0.002	46	59	100	98	96	87	85	70
Europium	0.001	46	72	98	96	89	85	80	76
Gadolinium	0.003	46	43	100	100	91	74	65	61
Holmium	0.0005	46	52	102	100	91	85	78	70
Iron	0.7	46	11	100	74	57	41	35	33
Lanthanum	0.0005	46	0	100	98	93	70	61	35
Lead	0.006	46	57	98	89	74	70	67	65
Lithium	0.1	46	4	100	100	100	100	100	80
Lutetium	0.0005	46	74	100	96	91	85	83	80
Magnesium	15	46	0	100	100	100	100	98	91
Manganese	0.02	46	0	100	100	98	98	96	89
Mercury	0.0004	47	19	100	100	74	60	55	36
Molybdenum	0.03	46	7	100	100	98	85	72	50
Neodymium	0.003	46	26	100	96	87	74	61	48
Nickel	0.02	46	0	100	100	98	93	87	70
Potassium	10	46	0	100	100	98	98	96	93
Praseodymium	0.0005	46	17	100	100	87	74	65	52
Rhenium	0.0013	46	83	100	100	93	91	91	87
Rubidium	0.002	46	0	100	100	100	98	98	80
Samarium	0.003	46	74	100	100	96	93	89	85
Selenium	0.2	46	80	100	100	98	98	96	89
Silica[1]	50	46	0	100	100	100	100	98	93
Silver	0.05	46	100	100	100	100	100	100	100
Sodium	70	46	0	100	100	100	96	93	74
Strontium	0.02	46	0	100	100	100	98	98	96
Terbium	0.0007	46	63	100	98	89	78	74	72
Thallium	0.005	46	85	100	100	100	98	98	96
Thulium	0.0005	46	74	100	98	91	89	85	80
Tungsten	0.004	46	2	100	100	93	74	63	37
Uranium	0.002	46	7	100	100	98	96	87	70
Vanadium	0.05	46	4	100	100	100	100	98	93
Ytterbium	0.0014	46	48	100	96	87	74	67	63
Yttrium	0.0004	46	0	100	100	93	85	74	46
Zinc	0.08	46	0	98	98	91	67	59	33
Zirconium	0.01	46	67	100	100	91	83	80	78

[1] Silica was the only substance reported as an oxide.

Table 18. Percentage of duplicate colloid samples whose relative percentage difference of total elemental analysis was below specified values for critical elements

[RPD, relative percentage difference; n, number of duplicate samples. %, percent; <, less than; >, greater than]

RPD	Aluminum	Cadmium	Copper	Iron	Lead	Mercury[1]	Zinc
% < 100%	100	100	100	100	100	100	100
% < 50%	100	100	100	100	100	100	100
% < 25%	100	100	100	100	100	50	100
% < 15%	100	100	100	100	100	50	100
% < 10%	100	100	75	100	75	50	100
% < 5%	25	75	0	75	25	25	75
n > DL	4	4	4	4	4	4	4
Total n	4	4	4	4	4	4	4

[1] Those values of RPD above 25% were less than 10 times the detection limit.

(Appendix 5, table A5-3) indicate that elements such as aluminum, chromium, titanium (Ti), and thallium (Tl) occur mainly in the residual phase, and therefore are interpreted as being not readily bioavailable, despite the fact they are present in colloids in substantial quantities. Other elements, such as cadmium, copper, and zinc, tend to occur primarily in the oxidizable and(or) reducible phases, and are considered likely to be bioavailable, and hence, may possibly be affecting the local aquatic ecology.

Equivalent Colloid Concentrations in Water

To estimate colloid concentrations for use in loading calculations, a technique was devised on the basis of chemical measurements. Although conventional techniques were used to measure suspended sediment concentrations (the results are in Appendix 5, table A5-2), these data are not appropriate for colloidal size material (< 2 μm diameter). Special procedures that require separation of coarser material followed by coagulation and a subsequent gravimetric determination (Guy, 1969) are very complex and generally do not work well for the low concentrations of suspended sediment that were often found during this study. The validity of the procedure that was developed to estimate the colloid concentrations is predicated on several assumptions:

1. A major elemental constituent in the colloidal material, which can serve as an indicator element, can be measured accurately at low concentration in the dissolved phase.
2. The indigenous concentration of this element is relatively low in the dissolved phase.
3. A conventional total recoverable analysis using a partial digestion procedure on a whole-water (unfiltered) sample will dissolve a major fraction of the element from the colloidal suspended material, or preferentially dissolve colloid-size suspended matter, because of the high degree of reactivity and significantly large surface area of colloid material.
4. Colloid-size material is the primary form of suspended matter present at the site, which implies that the silt-size and sand-size material concentrations are small or negligible compared to colloid-size suspended matter, or, if not, a preliminary separation of the coarser suspended matter is performed.

On the basis of these assumptions, the procedure involves the determination of the concentration of an indicator element in the ultrafiltrate of the sample at the site where suspended colloid concentration is to be measured. This ultrafiltrate concentration represents the natural dissolved concentration of the indicator element under the prevailing water chemistry conditions. The concentration of this element also is determined by total recoverable analysis by partial digestion of a representative whole-water (unfiltered) sample taken from the same site at the same time as the ultrafiltrate sample. By subtracting the dissolved concentration from the total recoverable analysis (whole-water digestion) concentration, a concentration of the indicator element attributed to the suspended colloidal material is obtained. By knowing the concentration of the indicator element in the colloidal suspended matter, obtained from independent measurements on a total digestion of the isolated

Table 19. Percentage of replicate colloid samples whose relative standard deviation fell below the specified values for all elements analyzed

[DL, detection limit; µg/L, microgram per liter; RSD, relative standard deviation; n, number of duplicate samples; the values in the table represent the total of those less than the detection limit and those that meet the criteria. %, percent; <, less than]

Element	n	Range (%RSD)						
		% < DL	% < 100%	% < 50%	% < 25%	% < 15%	% < 10%	% < 5%
Aluminum	4	0	100	100	100	100	100	50
Antimony	4	0	100	100	100	75	75	25
Barium	4	0	100	100	100	100	50	25
Beryllium	4	0	100	100	100	100	75	50
Bismuth	4	3	100	100	75	75	75	75
Cadmium	4	0	100	100	100	100	100	75
Calcium	4	0	100	100	100	100	75	75
Cerium	4	0	100	100	75	25	25	0
Cesium	4	0	100	100	75	50	25	0
Chromium	4	0	100	100	100	100	100	75
Cobalt	4	0	100	100	100	100	100	75
Copper	4	0	100	100	100	100	75	25
Dysprosium	4	0	100	100	100	75	75	25
Erbium	4	0	100	100	100	100	75	0
Europium	4	0	100	100	100	50	25	25
Gadolinium	4	0	100	100	100	50	50	25
Holmium	4	0	100	100	100	100	50	0
Iron	4	0	100	100	100	100	100	100
Lanthanum	4	0	100	100	75	25	0	0
Lead	4	0	100	100	100	100	100	50
Lithium	4	0	100	100	100	100	100	100
Lutetium	4	0	100	100	100	75	75	25
Magnesium	4	0	100	100	100	75	50	50
Manganese	4	0	100	100	100	100	100	50
Mercury	4	0	100	100	100	50	50	25
Molybdenum	4	3	100	100	100	100	100	75
Neodymium	4	0	100	100	75	50	25	25
Nickel	4	0	100	100	100	75	75	50
Potassium	4	0	100	100	100	75	50	25
Praseodymium	4	0	100	100	75	75	25	0
Rubidium	4	0	100	50	25	0	0	0
Samarium	4	0	100	100	100	50	0	0
Silica[1]	4	0	100	100	100	100	50	25
Sodium	4	0	100	100	75	75	50	25
Strontium	4	0	100	100	100	100	100	75
Terbium	4	0	100	100	100	75	25	0
Titanium	4	0	100	100	100	100	100	100
Thallium	4	0	100	100	100	100	100	75
Thorium	4	0	100	100	100	75	0	0
Thulium	4	0	100	100	100	75	25	0
Tungsten	4	0	100	100	100	100	25	0
Uranium	4	0	100	100	100	100	100	75
Vanadium	4	0	100	100	100	100	100	100
Yttrium	4	0	100	100	100	50	50	0
Ytterbium	4	0	100	100	100	75	75	25
Zinc	4	0	100	100	100	100	100	75
Zirconium	4	0	100	100	100	100	75	50

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[1] Silica was the only substance reported as an oxide.

Table 20. Percentage of duplicate colloid samples whose relative percentage difference for the sum of sequential elemental analysis was below specified values for critical elements

[RPD, relative percentage difference; values in table represent the total of those less than detection limit and those which meet the criteria; n, number of duplicate samples; DL, detection limit. %, percent]

RPD	Aluminum	Cadmium	Copper	Iron	Lead	Mercury	Zinc
% < 100%	100	100	100	100	100	100	100
% < 50%	100	100	100	100	100	100	100
% < 25%	75	100	100	100	100	100	100
% < 15%	50	75	75	100	100	100	75
% < 10%	50	75	25	50	75	100	75
% < 5%	25	50	0	50	0	75	0
% < 3%	25	25	0	0	0	50	0
% < 1%	25	0	0	0	0	50	0
n > DL	4	4	4	4	4	2	4
Total n	4	4	4	4	4	4	4

colloidal material, the concentration of the colloidal suspended matter can be calculated. This approach was tested and calibrated empirically by creating artificial colloid suspensions from each of the sampling sites where sufficient isolated colloidal material was available (after the other digestions and measurements were completed). These suspensions, which were derived from freeze-dried ultrafilter retentate, were prepared gravimetrically and resuspended in deionized water using ultrasonic agitation and the addition of a surfactant. The artificial colloid suspensions were processed by total recoverable analysis (whole-water digestion) in the same manner as the unfiltered water samples previously described. The recovery of the indicator elements from these total recoverable analyses (whole-water digestions) of the artificial colloid suspensions relative to the known amount of these indicator elements (because a known amount of the isolated colloids were artificially added to deionized water) was computed and used to adjust the sample calculations from the same sites. This calibration approach effectively compensated for any deviations in the chemistry of the colloids or the efficiency of the total recoverable (whole water) extraction process.

Several elements were used to perform the calculations of equivalent colloid concentrations. Aluminum, iron, and several rare earth elements proved to be suitable indicators for these calculations. A correlation diagram is shown in figure 43, which plots colloid concentrations determined using aluminum as the indicator element versus concentrations determined using iron as the indicator element. The linearity of this correlation plot ($R^2 = 0.98$) shows implicitly that concentrations calculated by using either element would yield comparable results. To simplify the presentation of effective colloid concentration data, further discussion of concentrations calculated by this procedure are restricted to results using aluminum as the indicator element.

Total Recoverable Analyses of Whole-Water (Unfiltered) Samples

In addition to dissolved and colloid samples, unfiltered (whole-water) samples were collected, partially digested and analyzed, as described earlier in this report. The results of these analyses are presented in Appendix 4 (table A4-2). As a general rule, total recoverable analysis of whole-water samples usually do not provide as complete and reproducible information as do the sum of dissolved and colloidal samples, mainly because total recoverable analysis is not a complete chemical digestion. For this particular study, however, total recoverable concentrations from whole-water samples tend to agree well with the sum of dissolved and equivalent colloid concentrations (fig. 44) for Cd, Cu, Pb, Mg, Hg, and Zn. The sum of dissolved and equivalent colloid concentrations are referred to as “effective concentration.”

Conventional Membrane and Capsule Filtration

As discussed in an earlier section of this report, in addition to the tangential-flow ultrafiltration samples, two other types of dissolved samples were processed. Filtrate data from a 0.40-μm membrane-filtered (Nuclepore) subsample and a 0.45-μm tortuous-path capsule-filtered (Gelman) subsample were collected to allow a rigorous comparison

Table 21. Percentage of duplicate colloid samples whose relative standard deviation for the sum of sequential elemental analysis was below specified values for all elements analyzed

[Values in the table represent the total of those less than detection limit and those that meet the criteria. DL, detection limit.; n, number of duplicate samples; RSD, relative standard deviation; %, percent; <, less than; >, greater than]

Element	n > DL	Range (%RSD)						
		% < DL	% < 100%	% < 50%	% < 25%	% < 15%	% < 10%	% < 5%
Aluminum	4	4	100	100	100	50	50	25
Antimony	4	4	100	100	100	75	75	0
Barium	4	4	100	100	100	50	50	0
Beryllium	4	4	100	100	100	25	0	0
Bismuth	4	2	100	100	100	100	100	50
Cadmium	4	4	100	100	100	75	75	50
Calcium	4	4	100	100	100	75	75	0
Cerium	4	4	100	100	75	75	75	25
Cesium	4	4	100	100	75	50	25	0
Chromium	4	4	100	100	100	100	100	0
Cobalt	4	4	100	100	100	100	100	0
Copper	4	4	100	100	100	100	50	0
Dysprosium	4	4	100	100	100	100	75	50
Erbium	4	4	100	100	100	50	50	50
Europium	4	4	100	100	100	75	75	50
Gadolinium	4	4	100	100	100	100	75	25
Holmium	4	4	100	100	100	75	50	0
Iron	4	4	100	100	100	100	75	25
Lanthanum	4	4	100	100	75	75	50	25
Lead	4	4	100	100	100	100	100	25
Lithium	4	4	100	100	100	100	25	0
Lutetium	4	4	100	100	100	50	25	0
Magnesium	4	4	100	100	100	75	50	25
Manganese	4	4	100	100	100	100	100	25
Mercury	4	2	100	100	100	100	100	50
Molybdenum	4	2	100	100	100	75	75	50
Neodymium	4	4	100	100	100	75	75	25
Nickel	4	4	100	100	100	75	50	0
Praseodymium	4	4	100	100	75	75	50	0
Rubidium	4	4	100	100	75	50	50	25
Samarium	4	4	100	100	100	75	75	25
Silica[1]	4	4	100	100	100	100	50	0
Strontium	4	4	100	100	100	50	25	0
Terbium	4	4	100	100	100	100	50	0
Thallium	4	4	100	100	100	100	100	0
Thorium	4	4	100	100	100	75	75	0
Thulium	4	4	100	100	100	75	25	0
Titanium	4	4	100	100	100	100	75	25
Tungsten	4	4	100	100	100	100	75	25
Uranium	4	4	100	100	100	75	75	0
Vanadium	4	4	100	100	100	100	50	25
Ytterbium	4	4	100	100	100	75	75	50
Yttrium	4	4	100	100	100	75	75	25
Zinc	4	4	100	100	100	100	75	0
Zirconium	4	4	100	100	75	75	25	0

[1] Silica was the only substance reported as an oxide.

Table 22. Comparison of metal concentrations determined in the study with certified values reported by the National Institute of Standards and Technology for standard reference materials SRM 1566a–Oyster tissue and SRM 50–Albacore tuna

[Mean ± 95 percent CI (confidance interval) for n = 5 (n refers to the number of analyses of the individual SRMs); NIST, National Institute of Standards and Technology; SRM, Standard Reference Material. Units are micrograms per gram dry weight. %, percent; —, not reported]

Metal	NIST SRM 1566a				NIST SRM 50			
	Certified		Observed		Certified		Observed	
	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
Aluminum	202.5	13	136	9	—	—	6.28	1.7
Cadmium	4.15	0.4	4.38	0.17	—	—	0.06	0.03
Copper	66.3	4.3	61.8	3.8	—	—	3.08	0.2
Iron	539	15	518	24	—	—	53	2
Lead	0.371	0.01	0.37	0.07	0.46	—	0.52	0.16
Zinc	830	57	824	26	13.6	1	13.8	0.9

Table 23. Percentage of metal recovered from representative caddisfly samples spiked with a known quantity of metal

[wb, whole body sample; s, spiked sample; c, cytosol sample; p, pellet sample]

Station	Sample Number	Cadmium	Copper	Lead	Zinc
Sacramento River above Churn Creek near Anderson	SRAH1wb/s	100	99	89	101
Sacramento River at Bend Bridge near Red Bluff	SRBH1wb/s	98	90	98	93
	SRBH2wb/s	96	82	90	97
	SRBH1c/s	98	96	97	98
	SRBH2c/s	102	93	94	99
	SRBH1p/s	99	100	97	108
	SRBH2p/s	96	97	96	96
Sacramento River at Tehama	SRTBLK1wb/s	95	93	92	96
	SRTH1wb/s	97	93	87	96
	SRTH2wb/s	99	92	88	99
	SRTH3wb/s	99	94	97	96
	SRTH4wb/s	99	94	88	95
Cottonwood Creek near Cottonwood	SRCCH1wb/s	101	95	87	95
	SRCCH2wb/s	95	85	93	96

between these and ultrafiltrate samples (Appendix 4, table A4-1). Concentration differences for some representative elements (cerium, copper, and iron shown in fig. 45) among the three filter types for three sampling sites in the upper part of the Sacramento River Basin indicate that the commonly used filtration techniques (the capsule and membrane filters) tend to overestimate the amount of dissolved material present, especially at the Sacramento River below Keswick Dam. A more complete discussion of comparisons among the different filtrates is planned as part of subsequent reports.

Table 24. Lead isotopic data for the National Institute of Standards and Technology's standard reference material SRM-981 for filament temperatures of 1,191° to 1,300°C for the VG Sector 54 and VG 54R mass spectrometers

[The "true values" are the commonly accepted corrected values for Todt and other (1993). AMU, atomic mass units; *F*, fractionation factor, in units of percent per AMU; Pb, lead; NIST, National Institute of Standards and Technology; SRM, Standard Reference Material; T, temperature; Uncert., uncertainty. °C, degrees Celsius; %, percent]

Sample	T (°C)	$^{206}Pb/^{204}Pb$	Uncert. (%)	$^{207}Pb/^{206}Pb$	Uncert. (%)	$^{208}Pb/^{206}Pb$	Uncert. (%)	Mean *F* (%/AMU)	Uncert.
True Values		16.9322	0.005	0.914561	0.0044	2.16662	0.006		
Sector 54-Low T									
SRM 981a	1,208	16.884	0.052	0.91325	0.0048	2.1606	0.0042		
SRM 981b	1,191	16.883	0.029	0.91325	0.0045	2.1605	0.0039		
Mean		16.884	0.025	0.91325	0.0032	2.1606	0.0420		
F		0.144	0.013	0.143	0.003	0.140	0.021	0.143	0.003
Sector 54-High T									
SRM 981a	1,299	16.890	0.0264	0.91335	0.0042	2.1613	0.0063		
SRM 981b	1,276	16.888	0.012	0.91335	0.0036	2.1613	0.0054		
Mean		16.888	0.011	0.91335	0.0027	2.1613	0.004		
F		0.130	0.006	0.132	0.003	0.124	0.002	0.128	0.011
54R-Low T									
SRM 981c	1,220	16.885	0.071	0.91343	0.0071	2.1608	0.014		
SRM 981d	1,200	16.889	0.021	0.91347	0.0050	2.1610	0.008		
SRM 981e	1,200	16.887	0.03	0.91331	0.0057	2.1607	0.056		
Mean		16.888	0.016	0.91340	0.022	2.1610	0.007		
F		0.131	0.008	0.127	0.022	0.131	0.004	0.130	0.004
54R-High T									
SRM 981d	1,280	16.894	0.027	0.91352	0.0050	2.1615	0.019		
SRM 981e	1,300	16.897	0.051	0.91355	0.0151	2.1620	0.026		
Mean		16.895	0.023	0.91352	0.0046	2.1617	0.015		
F		0.110	0.012	0.114	0.005	0.114	0.008	0.114	0.004

Table 25. Comparison of lead isotopic data obtained from the VG Sector 54 and VG 54R mass spectrometers for a Shasta Dam colloid sample (collected in December 1996)

[T, temperature; °C, degrees Celsius; Uncert., uncertianty; *F*, fractionation factor; Pb lead. Data are corrected for mass fractionation based on the *F*-values given; uncertainties are absolute values at the 95 percent confidence interval]

Mass Spectrometer	T (°C)	F	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Sector 54	1,360	0.128	18.661 ± 0.015	0.83561 ± 0.00018	2.0426 ± 0.0008
54R	1,285	0.114	18.663 ± 0.014	0.83598 ± 0.00039	2.0432 ± 0.0016

Metal Concentrations in Streambed Sediments

Samples of streambed sediments were collected during the study according to the protocols described in the previous section of this report. The results of these analyses are presented in Appendix 5 (table A5-1). Figures 46 through 51 are plots for six trace metals (Cd, Cu, Fe, Hg, Pb, and Zn), which compare concentrations in streambed sediment with those in suspended colloidal sediment in relation to downriver distance. As in figures showing concentrations in water versus distance (figs. 36 through 41 and A8-1 through A8-14), the horizontal axis in figures 46–51 has been broken into two sections at different scales to emphasize the upper river sites. Streambed sediments and suspended colloidal sediments near Keswick Reservoir are elevated in certain trace elements (cadmium, copper, lead, and zinc) associated with massive sulfide mineralization, relative to the downriver sites. Other elements, such as iron, have elevated concentrations in suspended colloidal sediment near Keswick Reservoir, but do not have particularly

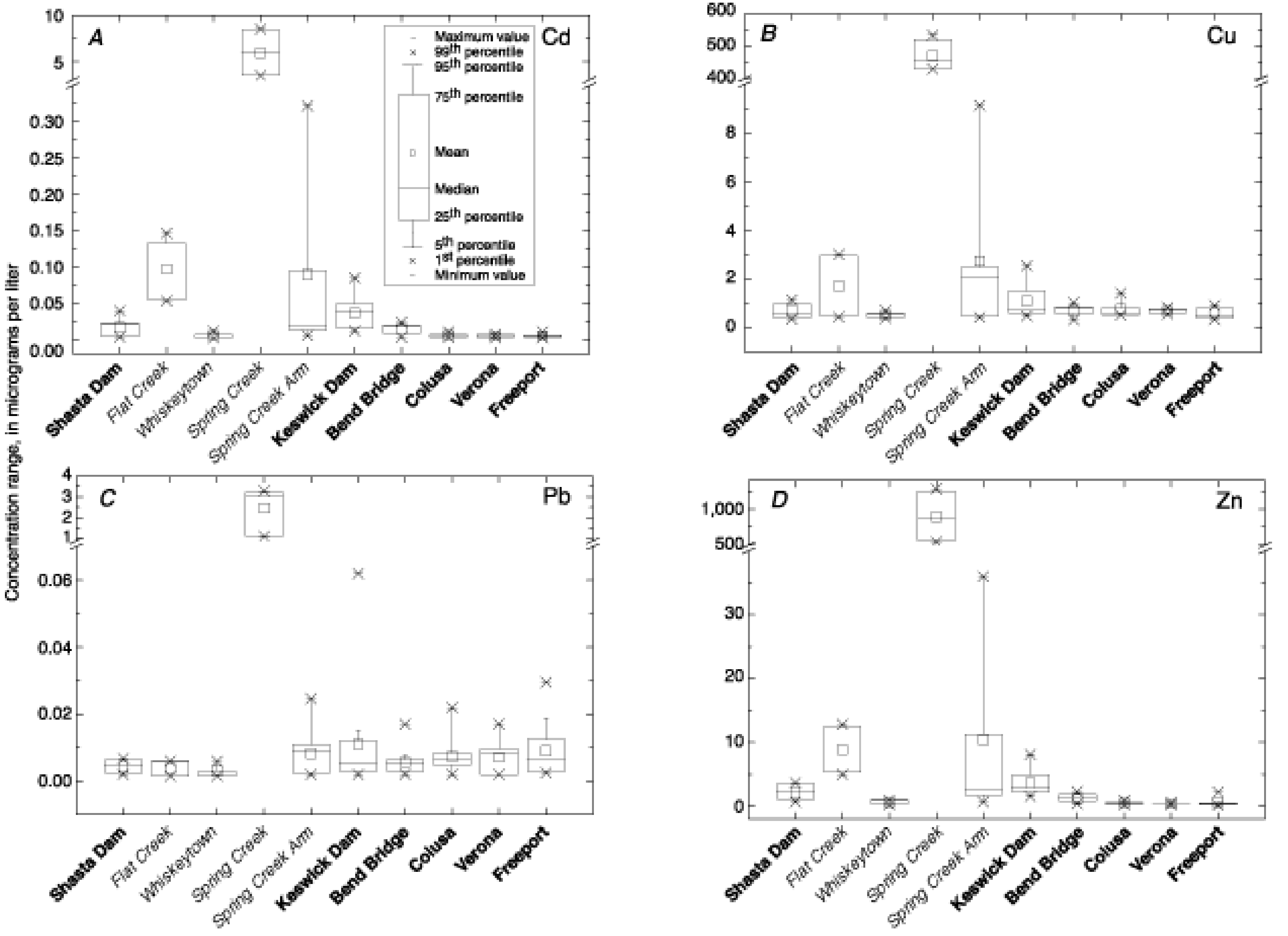

Figure 34. Box plots showing range, mean, and median of dissolved (ultrafiltrate) concentrations in the Sacramento River Basin, California, for *A*. Cadmium, *B*. Copper, *C*. Lead, *D*. Zinc. Site names in bold are mainstem sites and those in italics are tributary sites.

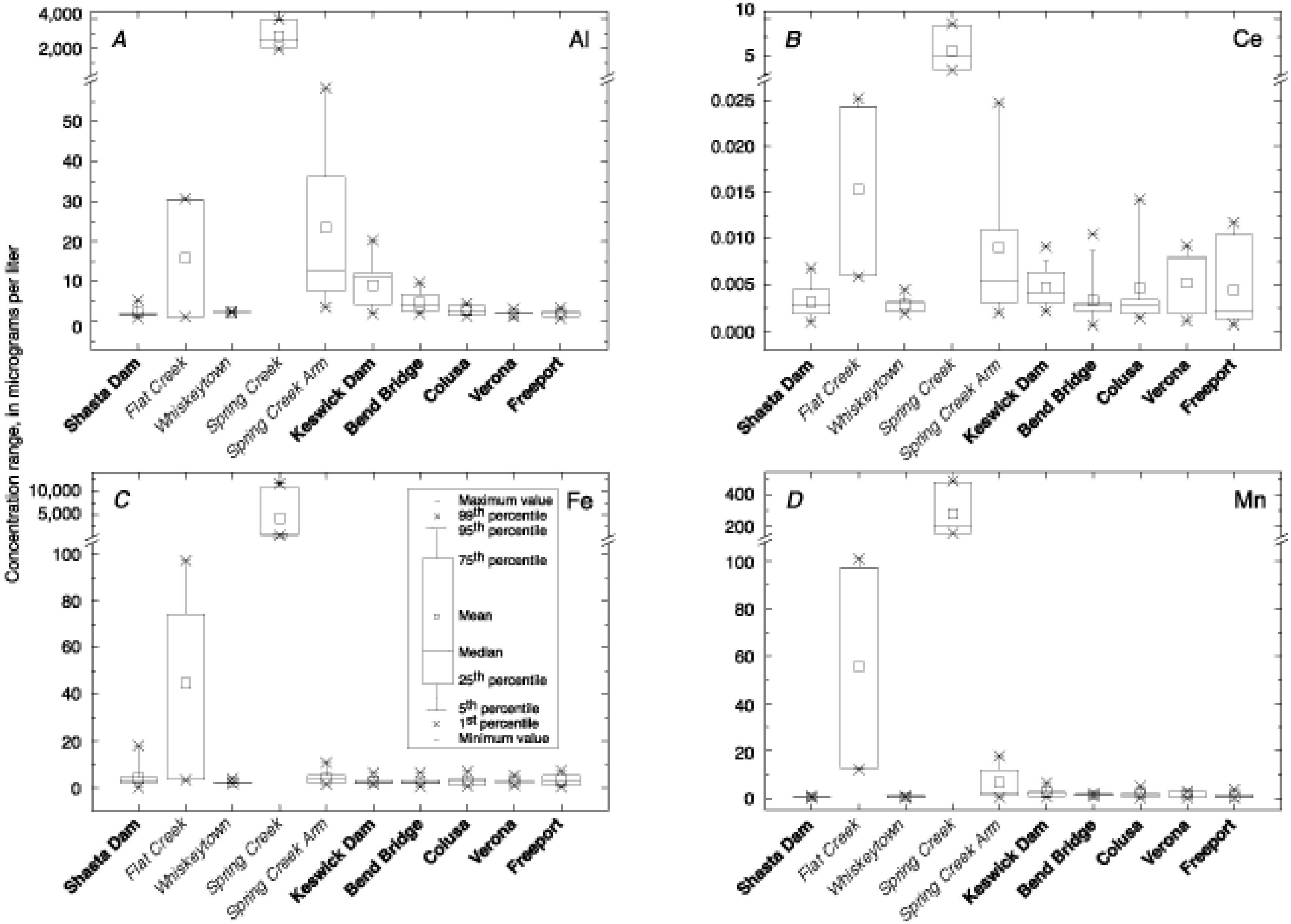

Figure 35. Box plots showing range, mean, and median of dissolved (ultrafiltrate) concentrations in the Sacramento River Basin, California, for *A*. Aluminum, *B*. Cerium, *C*. Iron, *D*. Manganese. Site names in bold are mainstem sites and those in italics are tributary sites.

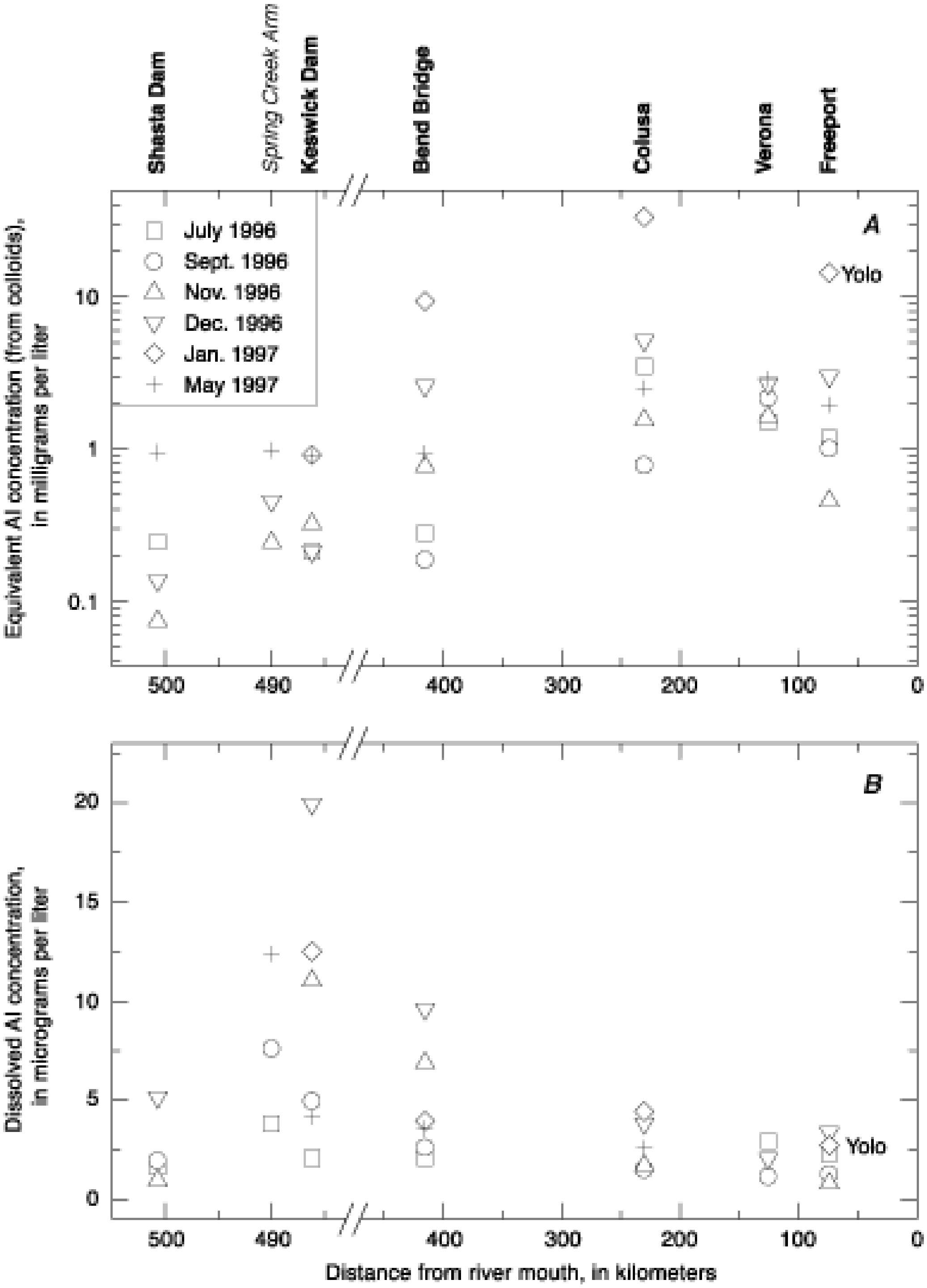

Figure 36. Plots of aluminum (Al) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

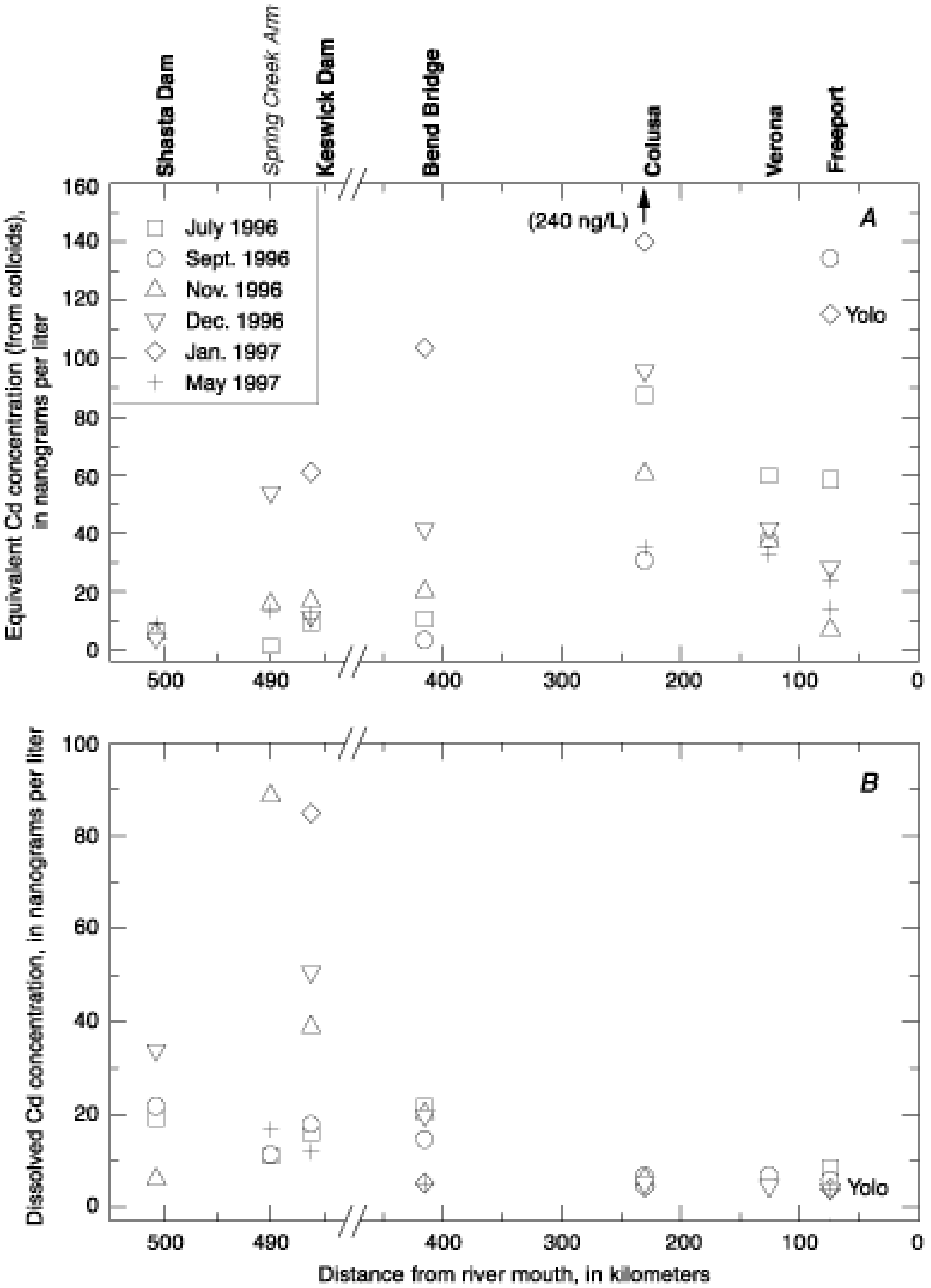

Figure 37. Plots of cadmium (Cd) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

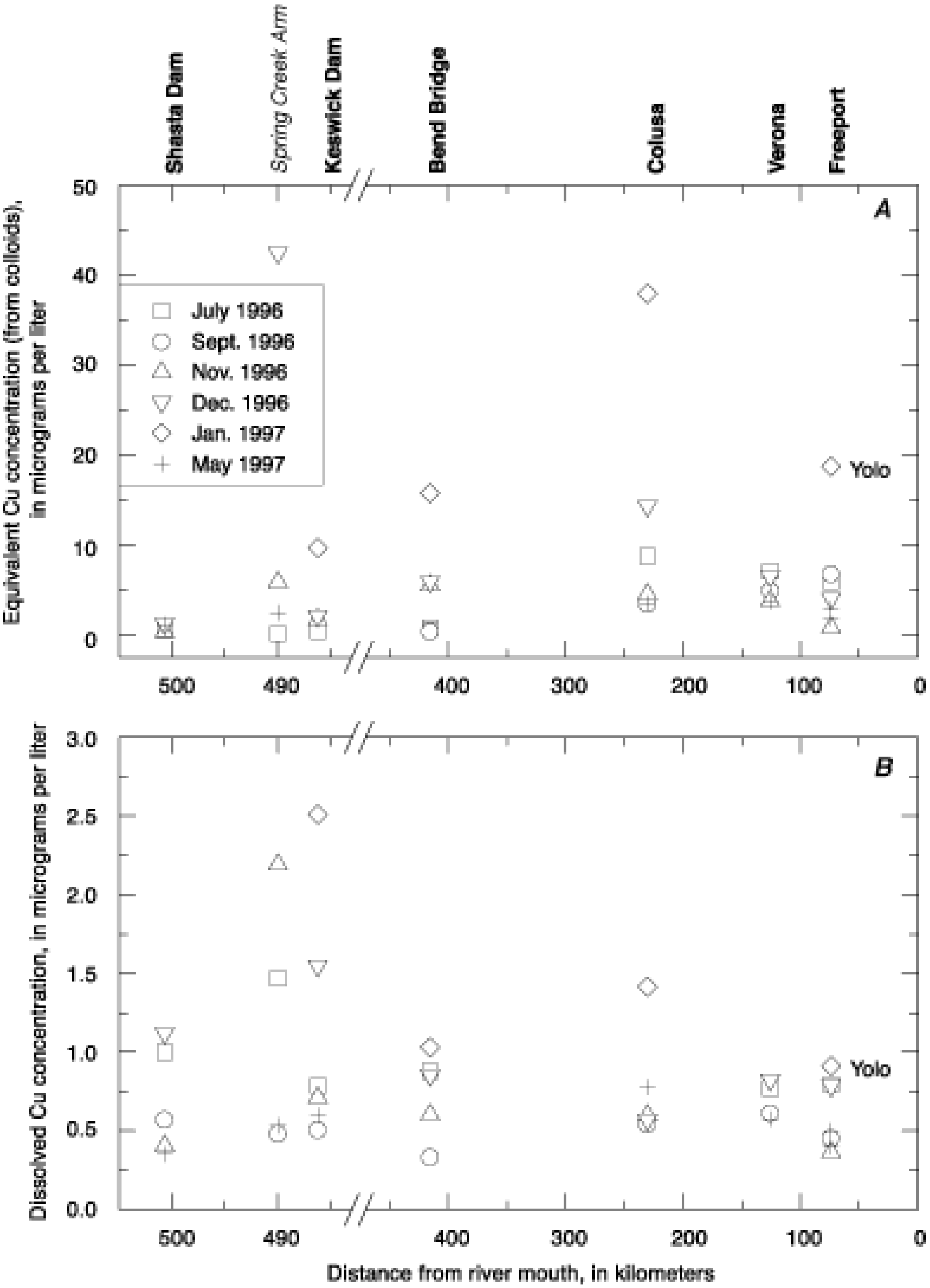

Figure 38. Plots of copper (Cu) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

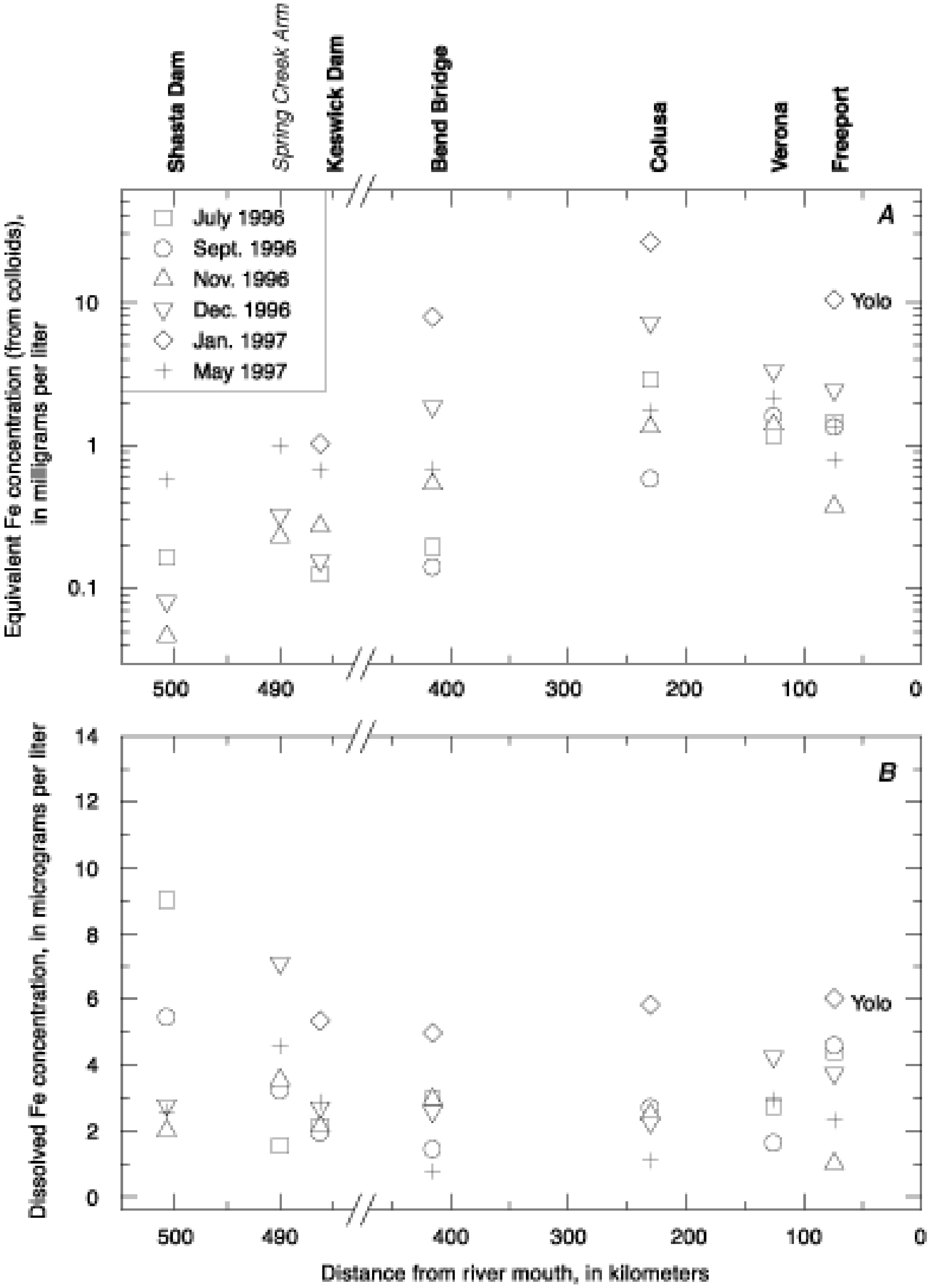

Figure 39. Plots of iron (Fe) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

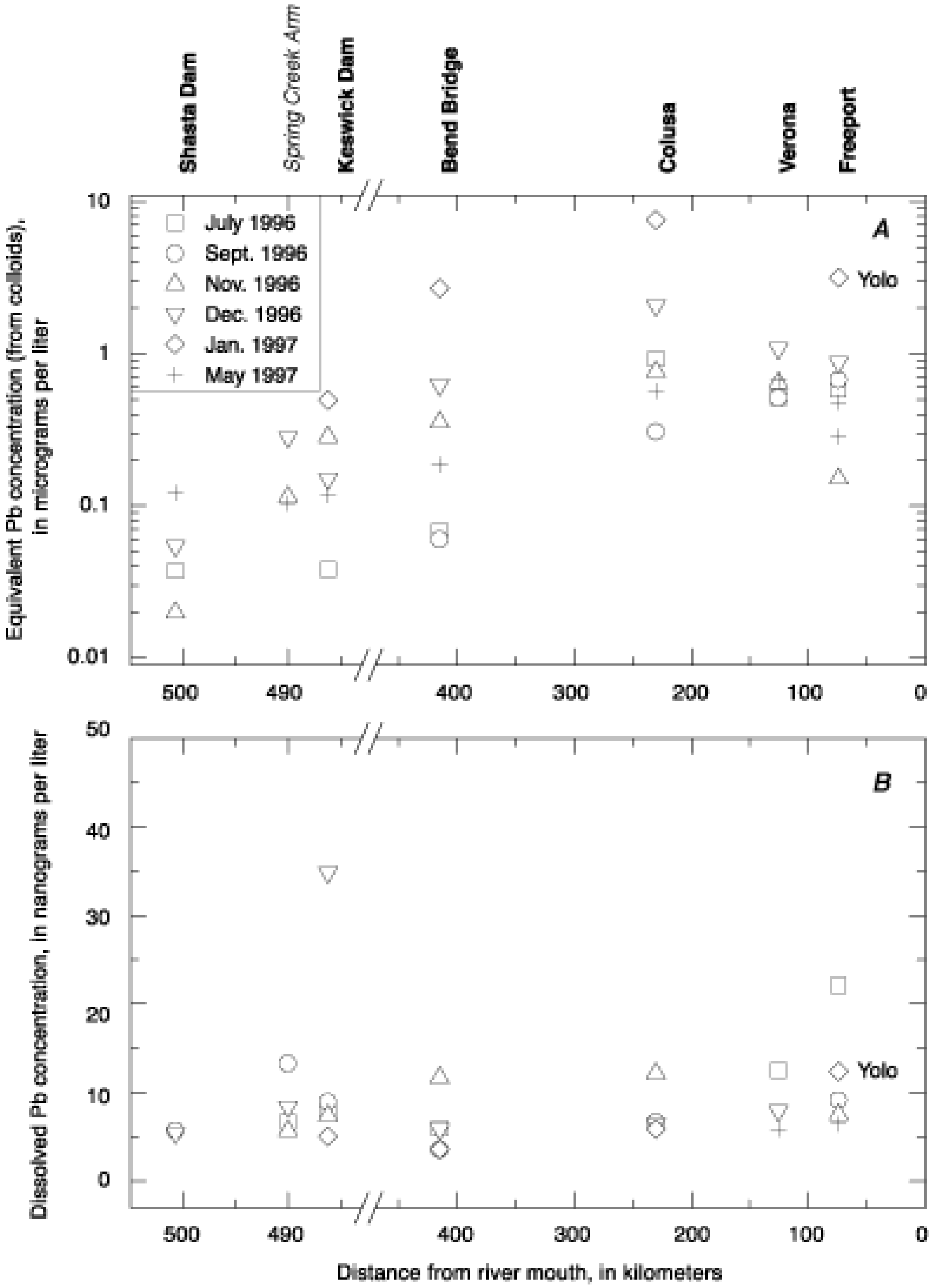

Figure 40. Plots of lead (Pb) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

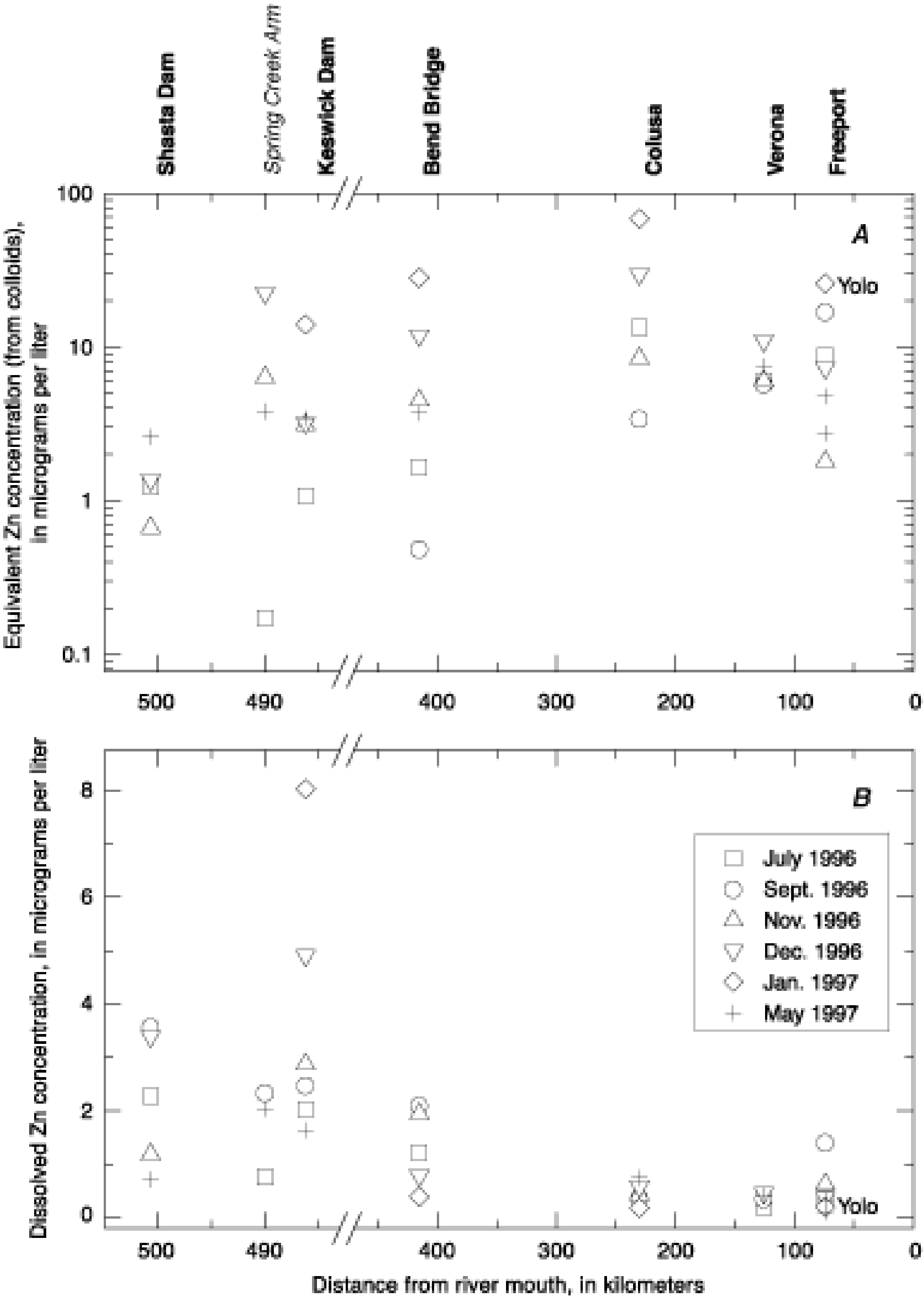

Figure 41. Plots of zinc (Zn) concentration in relation to distance (broken scale) from Sacramento River mouth, California. *A*. Equivalent colloid concentrations *B*. Dissolved (ultrafiltrate) concentrations. Yolo Bypass sample shown instead of Freeport for January 1997. Site names in bold are mainstem sites and those in italics are tributary sites.

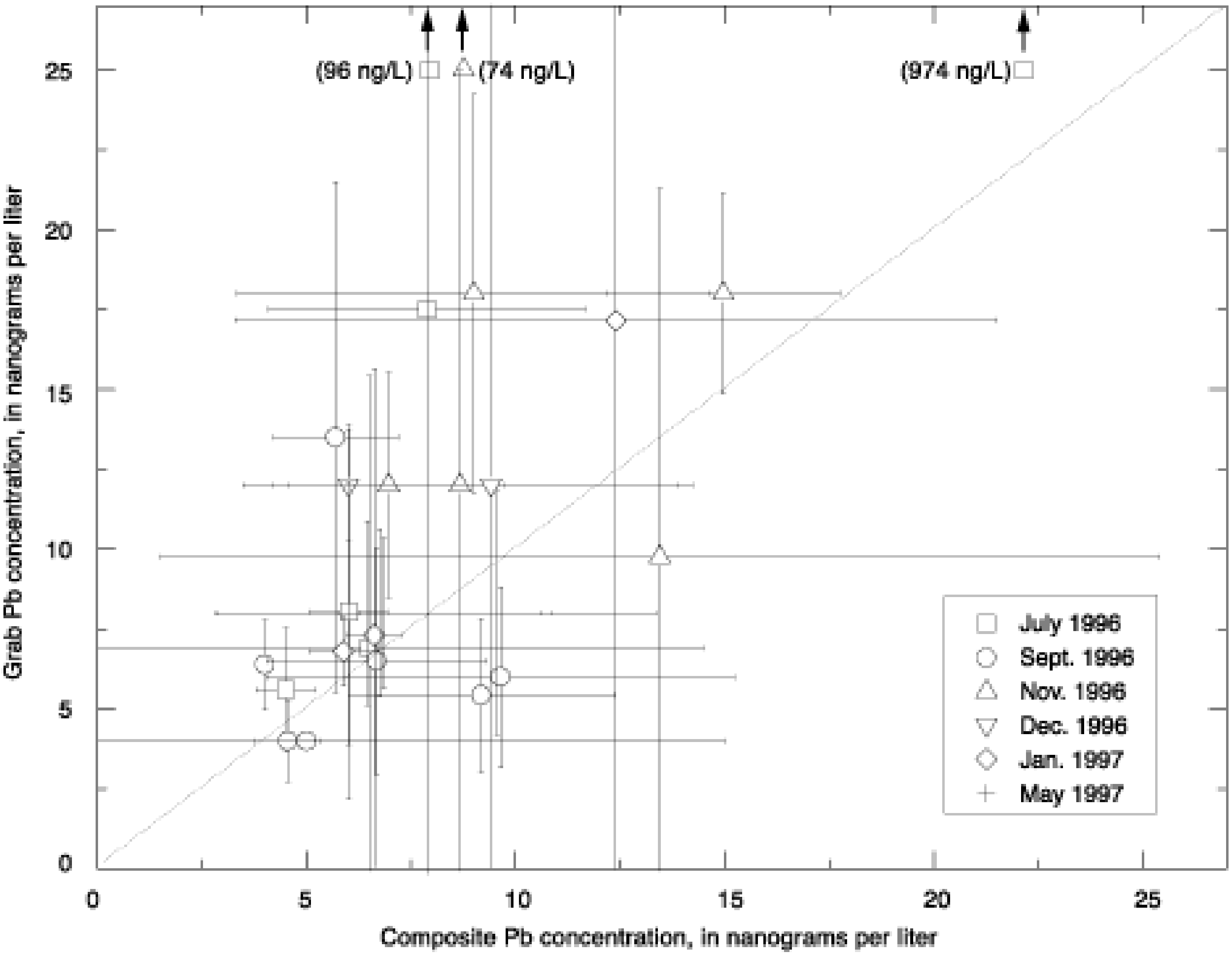

Figure 42. Plot of dissolved (ultrafiltrate) lead (Pb) concentration in composite water samples compared with dissolved (ultrafiltrate) lead concentration in concurrent grab water samples in the Sacramento River Basin, California. Vertical and horizontal lines represent standard deviation based on three to six determinations. Dotted line represents theoretical line of perfect agreement; error bars represent precision based on triplicate (or hextuplicate) analyses. ng/L, nanogram per liter.

elevated concentrations in the streambed sediment at sites downstream of Keswick Reservoir. For many trace elements, higher absolute concentrations are associated with the suspended colloids than with the bed sediments. This effect could possibly be related to the generally smaller grain size and larger surface area of the suspended colloidal sediment, resulting in a greater adsorption of metals.

Metal Concentrations in Caddisfly Larvae

Caddisfly (*H. californica*) larvae samples were collected as described in the previous section of this report. The results of the analyses of these samples are presented in Appendix 7 (tables A7-1 and A7-2) and indicate that *H. californica* in the Sacramento River were exposed to elevated concentrations of bioavailable cadmium, copper, lead, and zinc, with cadmium showing the greatest enrichment. Distribution patterns of cadmium, copper, and lead were consistent with an upstream source at or upstream of Redding. Although all metals were attenuated downstream, the transport of bioavailable metals appears to extend downstream of Tehama (fig. 8). A detailed discussion of the caddisfly data is presented separately (Cain and others, 2000).

Lead Isotopes in Colloid Concentrates and Streambed Sediments

Table 26 contains the lead isotope data for both colloid concentrates and streambed sediment samples

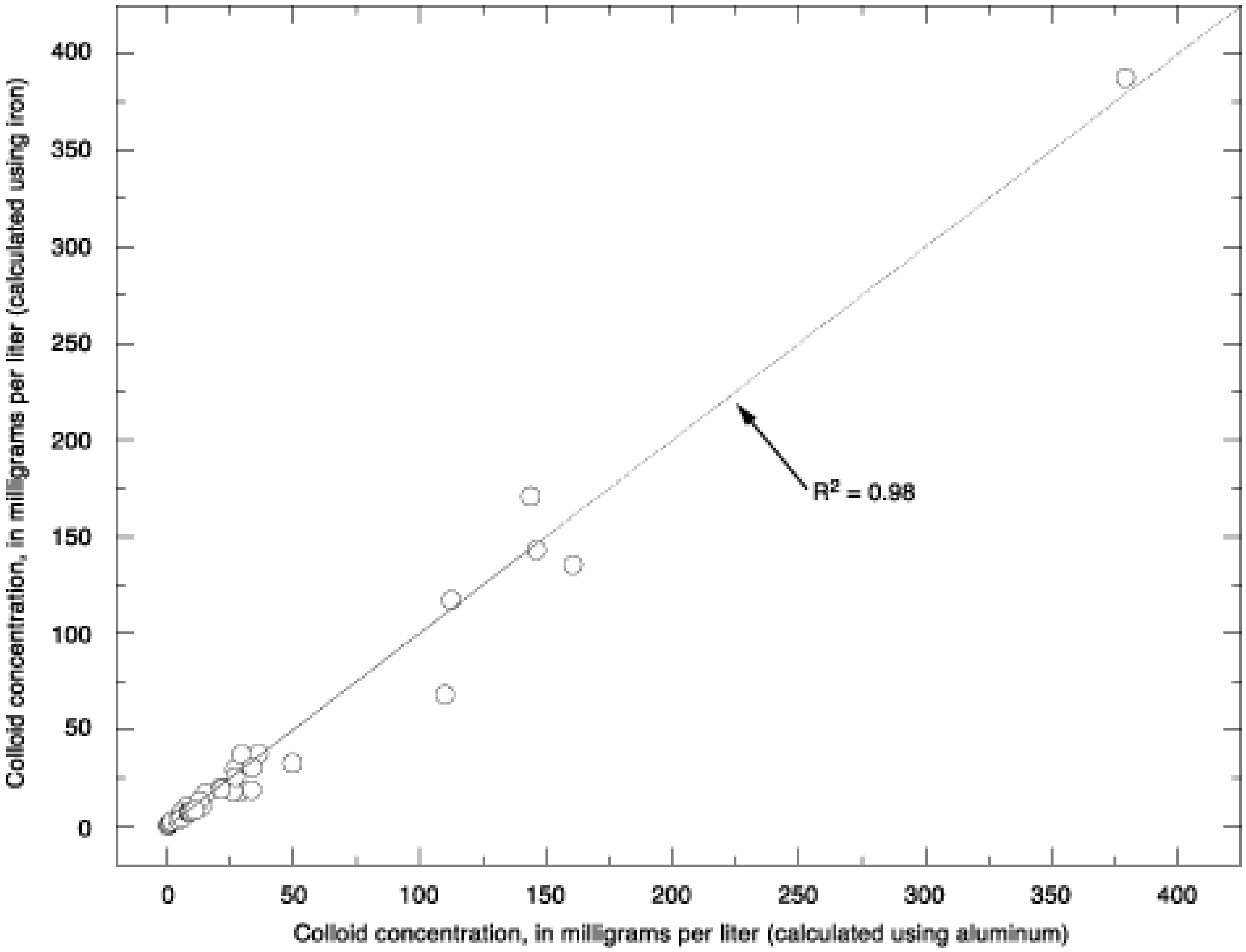

Figure 43. Plot of equivalent colloid concentration in river water computed using aluminum data compared with colloid concentration in river water computed using iron data in the Sacramento River Basin, California. R^2 value is based on linear least-squared regression.

for selected sites in the Sacramento River Basin. Lead isotope data can be used as a tracer to elucidate the possible sources of sediment and are particularly well suited to trace lead from massive sulfide deposits (Church and others, 1993, 1997). Figure 52 is a three-paneled plot of ^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb, and ^{208}Pb/^{206}Pb versus distance from river mouth (broken scale). These plots show the influence of the massive sulfides at Iron Mountain as a source of lead to down-river sites, both in the suspended colloid sediments and in the streambed sediments. At the Bend Bridge site, 71 km downstream of Keswick Dam, the lead isotope signature from the Iron Mountain massive sulfide deposits seems to have been attenuated by more radiogenic lead from other sources such as the granitic rocks of the northern Sierra Nevada.

Figure 53 is another plot of ^{206}Pb/^{204}Pb versus river kilometer (continuous distance scale) that shows consistently higher values of ^{206}Pb/^{204}Pb in suspended colloids collected in January 1997 compared with those collected in December 1996. Values of ^{206}Pb/^{204}Pb in streambed sediments tend to fall between the December 1996 and January 1997 colloid values. These differences could be caused by a shift to more radiogenic (that is, granitic) source rocks from the eastern side of the Sacramento Valley during extreme flooding that took place in January 1997.

The distinctly nonradiogenic lead isotope signature of the massive sulfide deposits at Iron Mountain (Doe and others, 1985) is shown clearly on a plot of ^{206}Pb/^{204}Pb versus ^{208}Pb/^{207}Pb (fig. 54). Lead isotope ratios in the colloid samples collected below Shasta Dam and Keswick Dam plot on a linear trend with the

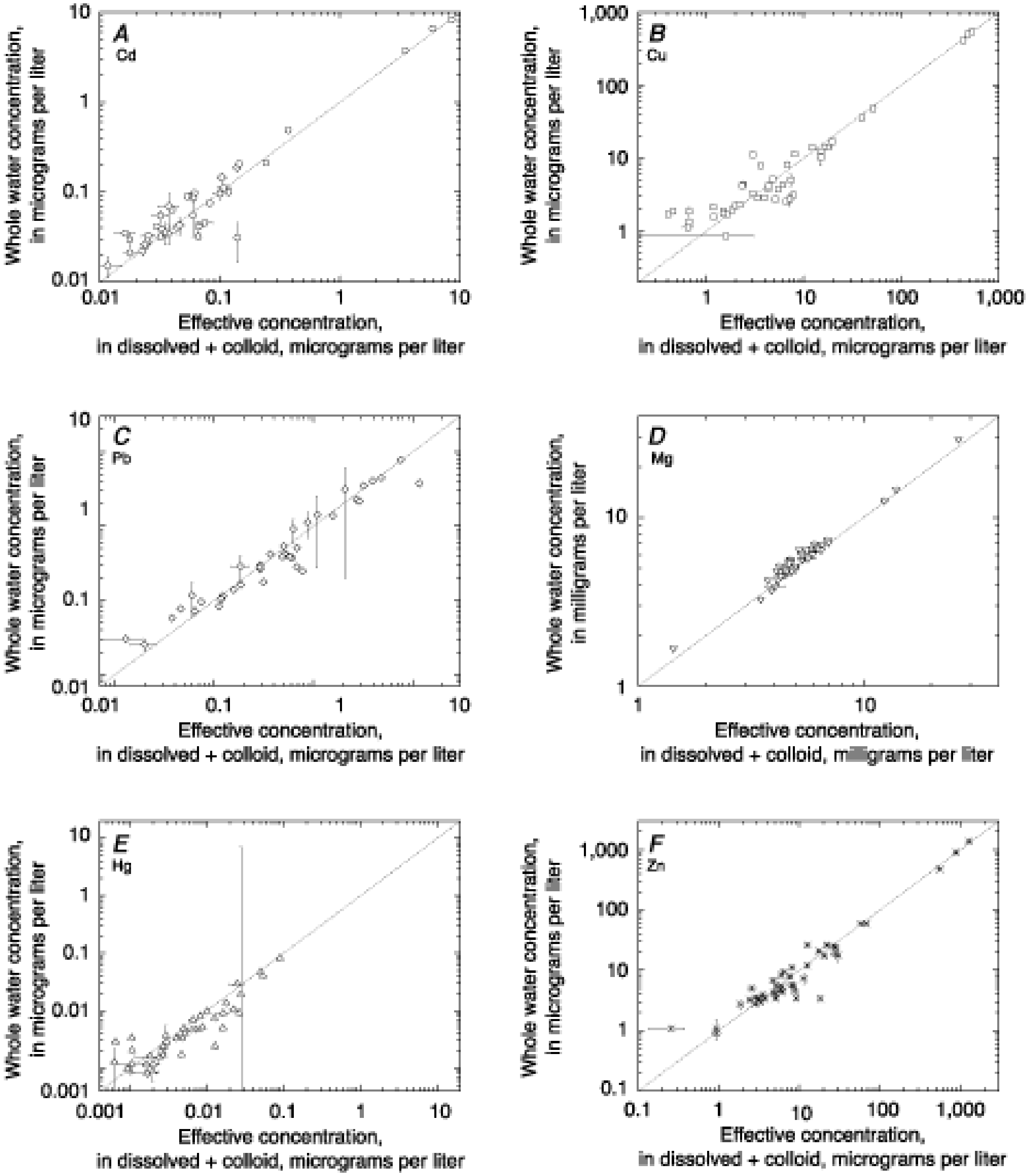

Figure 44. Plots of effective concentration (dissolved plus colloid) compared with total recoverable (whole water) concentration in the Sacramento River Basin, California, for *A*. Cadmium (Cd), *B*. Copper (Cu), *C*. Lead (Pb), *D*. Magnesium (Mg), *E*. Mercury (Hg), *F*. Zinc (Zn). Dotted line represents theoretical line of perfect agreement; error bars represent precision based on triplicate (or hextuplicate) analyses.

data from the Iron Mountain massive sulfide deposit (fig. 54). This linear pattern is consistent with an interpretation that the lead in suspended colloids at Keswick Dam represents a mixture of lead from tributaries to Shasta Lake with lead from Iron Mountain mine and Spring Creek. Mainstem Sacramento River sites downstream from Keswick Dam plot on a different linear trend in figure 54, indicating a different mix of source rocks and(or) other possible contaminant sources such as urban runoff or soils with lead from historic automobile emissions. The suspended colloid sample collected at Tower Bridge during January 1997 represents primarily the American River watershed because of the hydrology of the river during flood conditions and the operation of the Yolo Bypass (as discussed earlier in this report). Therefore, it is not surprising that this point has a much more radiogenic lead signature than other samples from this study, reflecting sources of lead in the Sierra Nevada granitic rocks and other source rocks dominated by continental crust.

The distribution of lead concentrations in streambed sediment and suspended colloids for different sites along the Sacramento River (fig. 55) illustrates the input of lead to the Sacramento River system from Spring Creek. Lead concentrations in both streambed sediment and suspended colloids reach minimum values in the samples collected from the Sacramento River at Colusa. Downstream from Colusa, lead concentrations increase in both sediment and colloids, indicating additional sources of lead either from tributary streams or, more likely, from urban runoff as the more densely populated Sacramento metropolitan area is approached. The ratio ^{206}Pb/^{204}Pb versus lead concentration in sediments and colloids (fig. 56) indicates a fairly strong correlation between elevated lead concentrations and nonradiogenic lead. This trend helps to confirm that the source of lead in the upper part of the watershed is most likely from the massive sulfide deposits hosted in oceanic crust (igneous rocks that originally formed in an oceanic environment, with relatively nonradiogenic lead). Also the colloid sample from the Tower Bridge in January 1997 falls off the aforementioned trend (fig. 56), which is consistent with more radiogenic sources of lead in drainage from the American River watershed.

Anions, Nutrients, Organic Carbon, and Field Parameters

Data for anions, nutrients, organic carbon, and field parameters collected during the study are contained in Appendix 3 (table A3-1). Anions included in this report are chloride, sulfate, and fluoride analyzed in filtered (0.45-µm capsule filter) water samples split from composite samples collected for metal analysis or collected as part of the NAWQA Program. Chloride concentrations ranged from 0.14 mg/L to 5.9 mg/L, with a median value of 2.2 mg/L in the Sacramento River sites. The highest chloride concentration measured was 37 mg/L in a sample from the Colusa Basin Drain, a channel containing mostly agricultural return flows at the time the sample was collected. Sulfate concentrations ranged from 1.7 to 6.0 mg/L in the Sacramento River sites. Higher concentrations were detected in Spring Creek (15–230 mg/L), Flat Creek (9.2–55 mg/L), and the Colusa Basin Drain (92 mg/L). Despite the high sulfate concentrations in these streams, their contribution to the total sulfate load of the Sacramento River is small, and concentrations downstream of these inputs did nor appear significantly elevated with respect to other sites on the Sacramento River. Fluoride concentrations were very near or below the reporting limit of 0.10 mg/L at all sites except for the Colusa Basin Drain (0.4 mg/L).

Nitrogen in the form of nitrite and nitrate ranged from below reporting limits of 0.05 mg/L to a high of 0.25 mg/L in the Sacramento River. The highest ammonia concentration was 0.11 mg/L and the highest combined, unfiltered organic plus ammonia nitrogen concentration was 0.5 mg/L. Thirty-eight of the 41 samples analyzed for organic plus ammonia forms of nitrogen were less than the reporting limit of 0.02 mg/L as nitrogen. Organic carbon concentrations in filtered water samples from all sites ranged from 0.4 to 4.8 mg/L as carbon with a median value of 1.4. The highest value was detected in a sample from the Colusa Basin Drain. Suspended organic carbon concentrations had a median value of 0.30 mg/L and tended to be less than corresponding dissolved organic carbon concentrations.

Water temperatures, specific conductance, and pH values varied in the Sacramento River system both temporally and spatially (table A3-1). Water temperatures changes seasonally from a wintertime low of 8.5°C to a summertime high of 25.5°C. Specific conductance in the Sacramento River ranged from

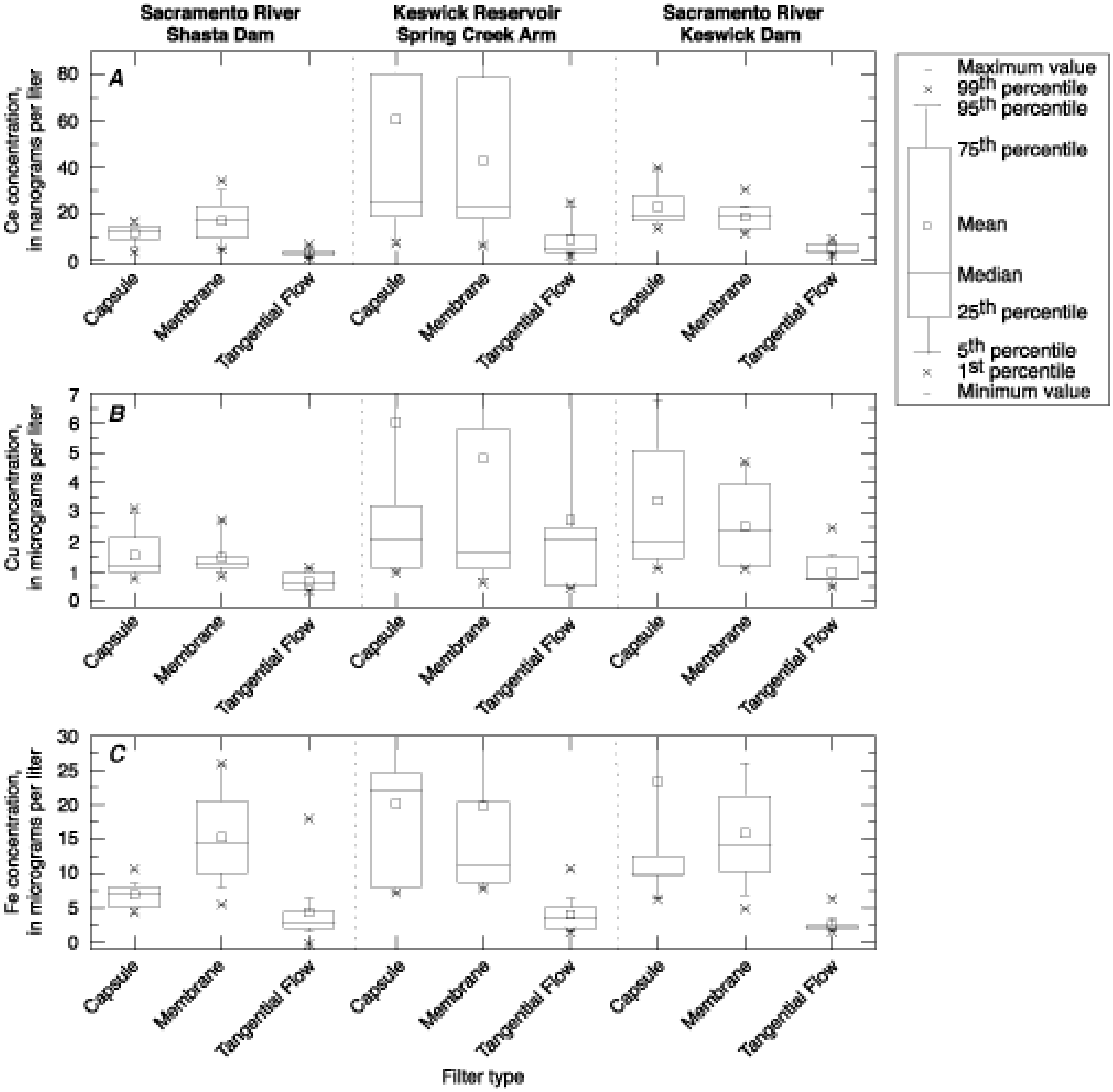

Figure 45. Box plots showing comparison of concentrations from three types of filtered samples at three sites in the upper Sacramento River Basin, California, for *A*. Cerium (Ce), *B*. copper (Cu), *C*. Iron (Fe).

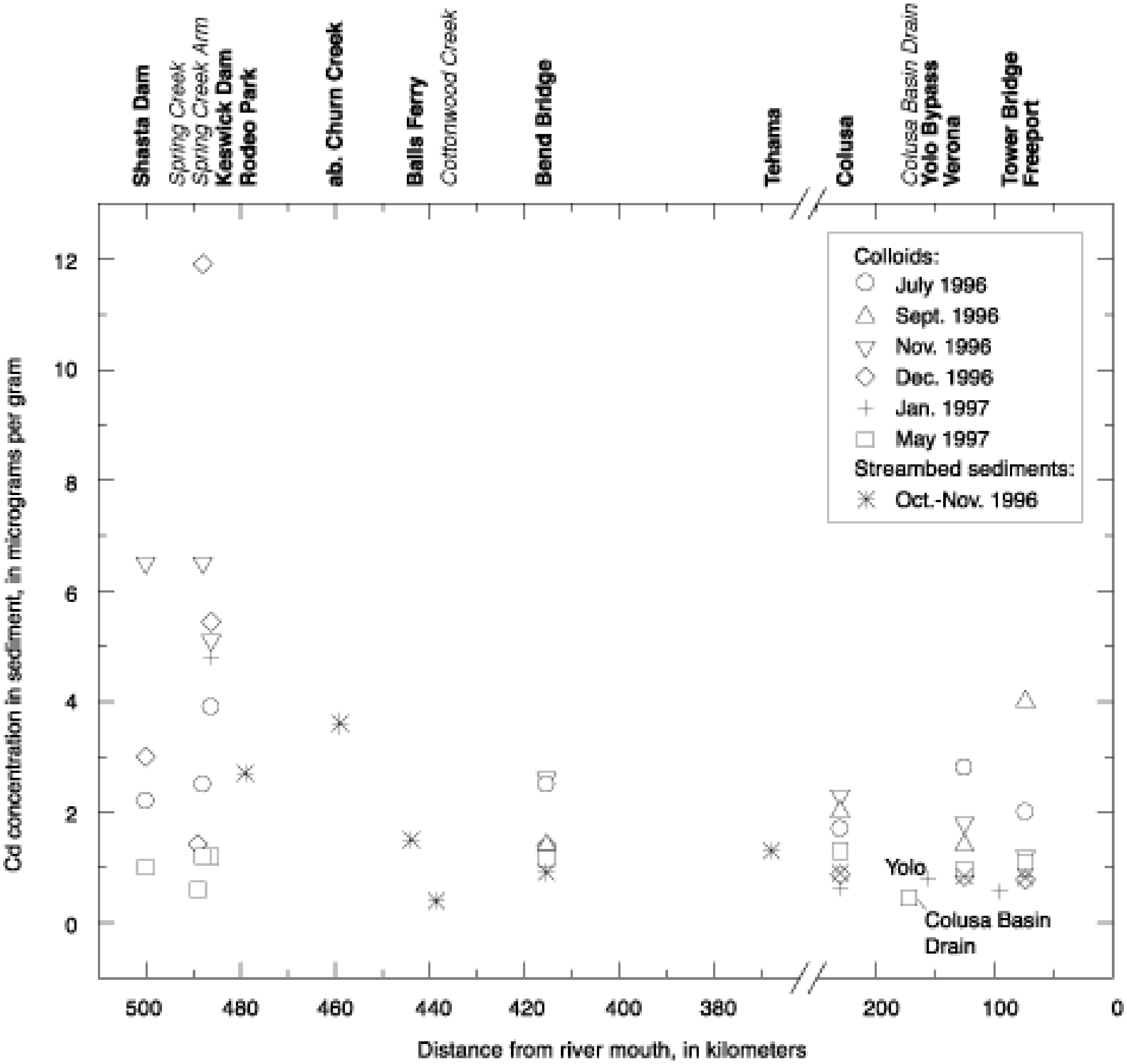

Figure 46. Plot of cadmium (Cd) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

51 to 149 µS/cm, but some tributaries were notably higher. Spring Creek ranged from 129 to 495 µS/cm and the measurement at Colusa Basin Drain on June 6, 1997, was 712 µS/cm. Measurements of pH at mainstem Sacramento River sites ranged from 7.0 to 8.1. The lowest pH measured was 3.7 at the Spring Creek site. Immediately downstream of Spring Creek, in the Spring Creek arm of Keswick Reservoir, the pH ranged from 7.3 to 7.6, which was similar to pH values (7.3 to 7.8) measured in the Sacramento River below Shasta Dam.

Particulate Size Distribution

Suspended Colloids

As discussed in a previous section of this report, all of the colloidal samples were subjected to a

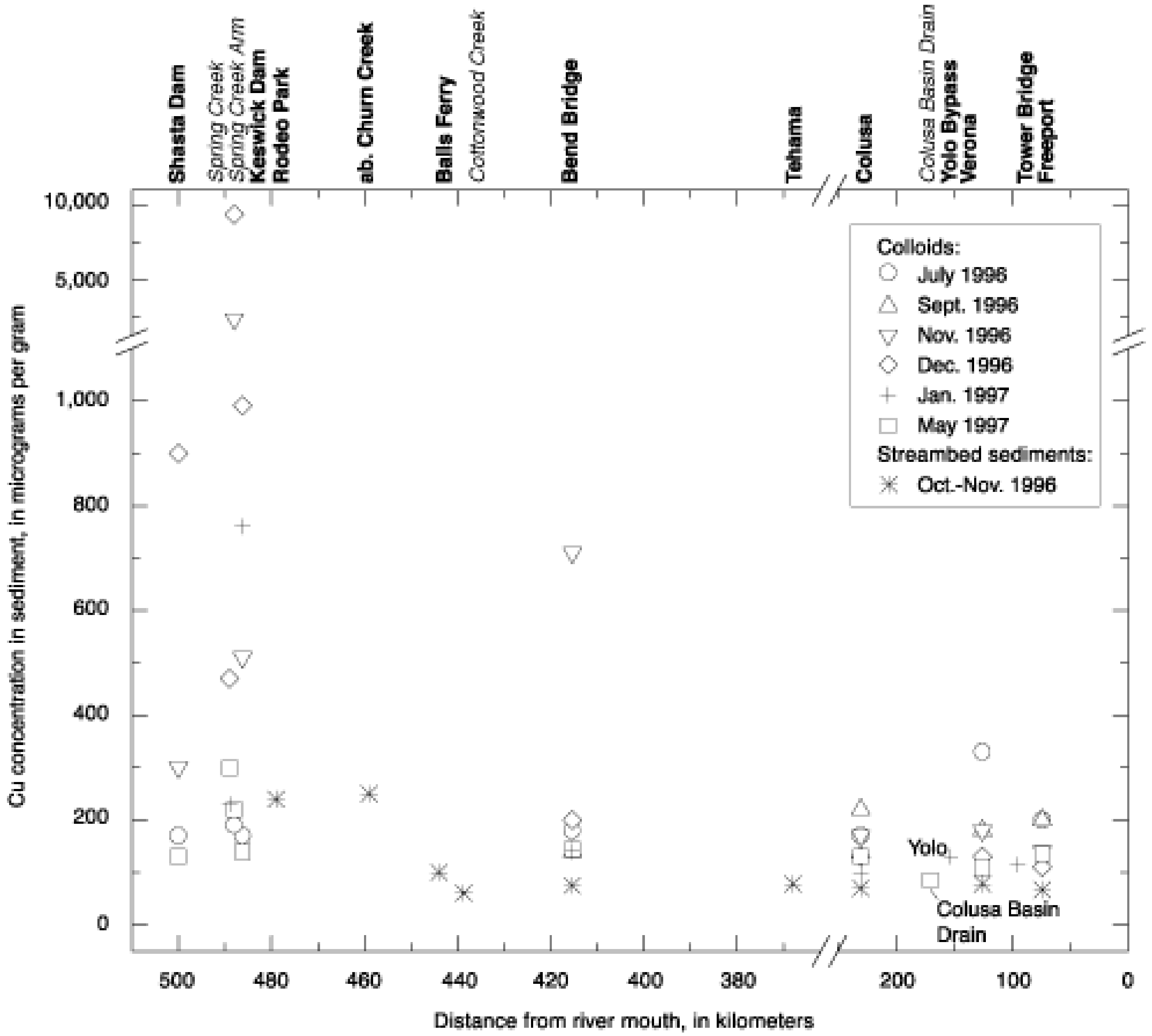

Figure 47. Plot of copper (Cu) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

particulate size distribution analysis. The results of these analyses are presented in Appendix 6 (table A6-1). Figure 57 shows a selected sample of those data, the particle size distribution for colloids collected during September 1996. The particulate size distribution from below Shasta Dam, Keswick Reservoir in Spring Creek arm and below Keswick Dam seem to be unimodal, whereas the three most downstream sampling sites (Colusa, Verona, and Freeport) show definite traces of bimodal distributions. Similar patterns were obtained for sampling periods other than September 1996 as well.

Streambed Sediments

The particulate size distributions for eight streambed sediment samples from the mainstem Sacramento River and for one sample from a tributary

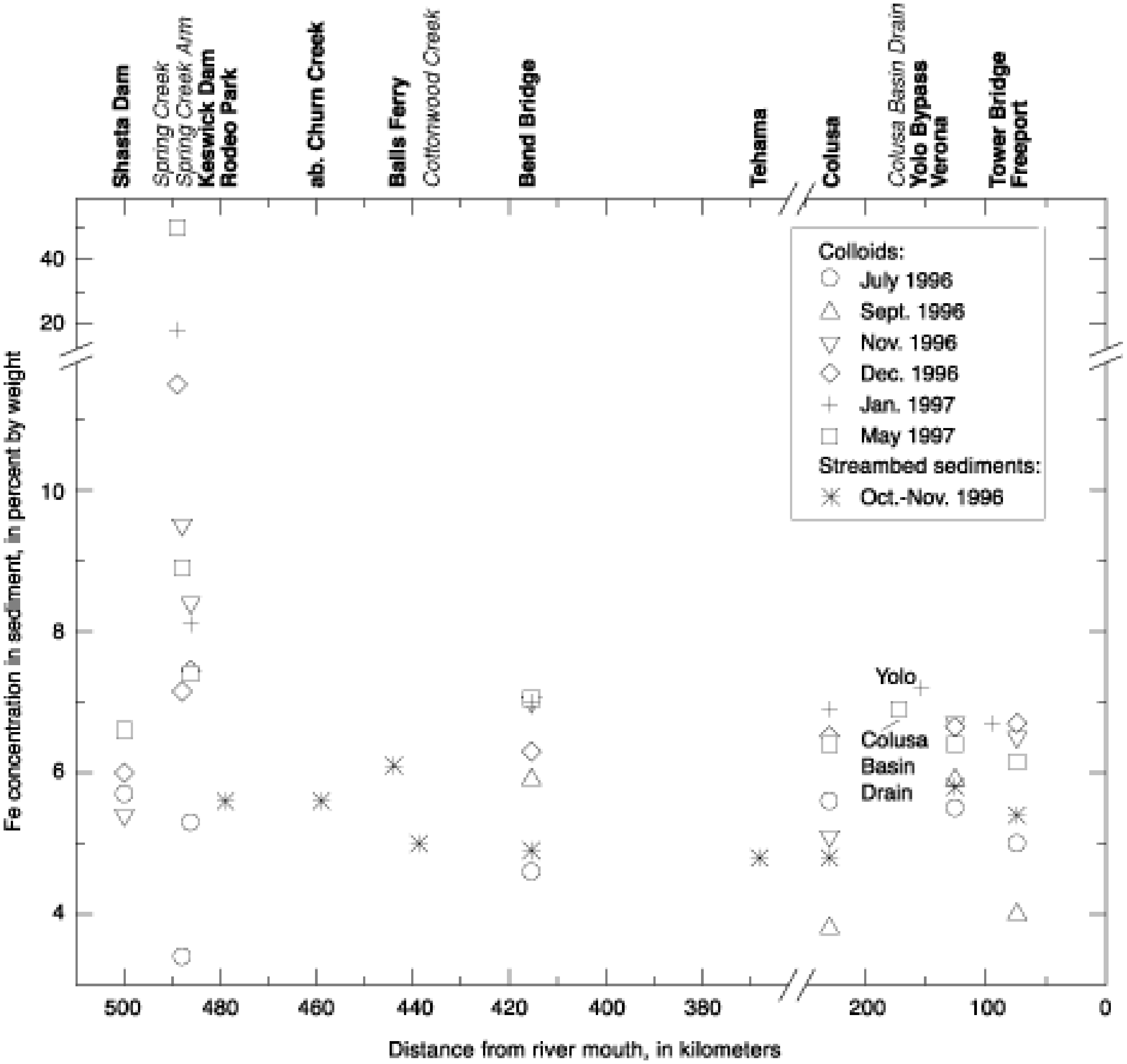

Figure 48. Plot of iron (Fe) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

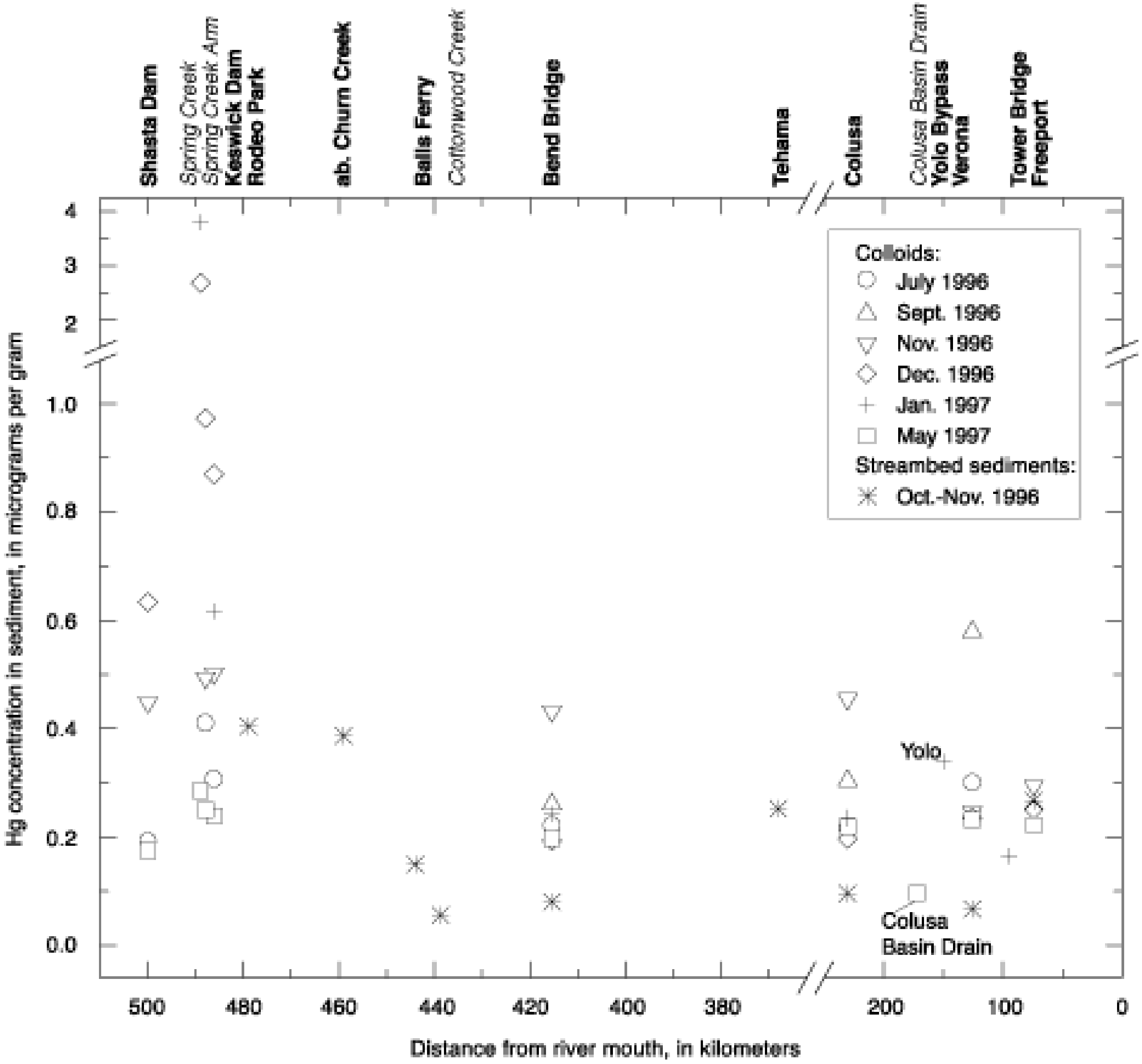

Figure 49. Plot of mercury (Hg) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

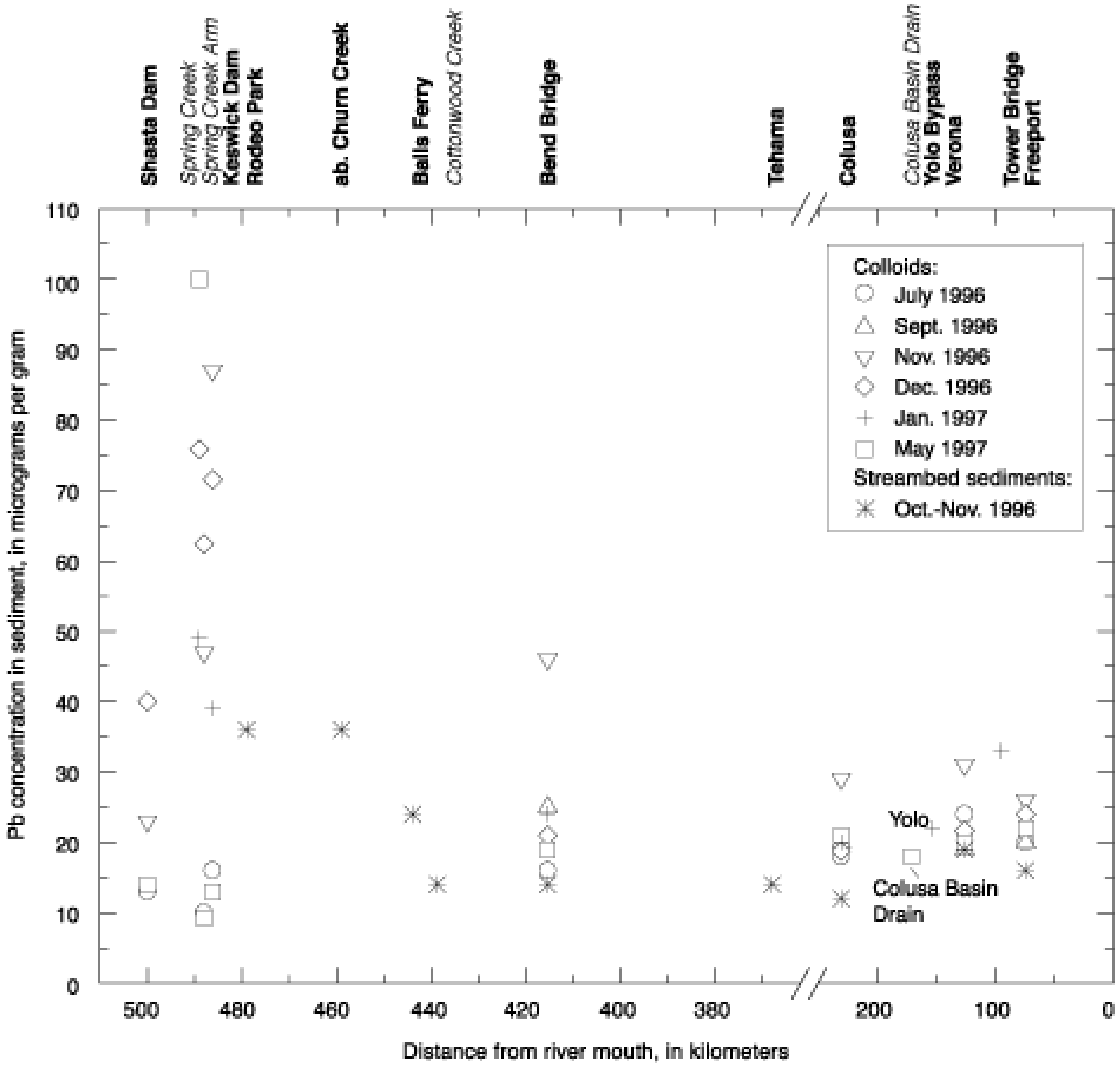

Figure 50. Plot of lead (Pb) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

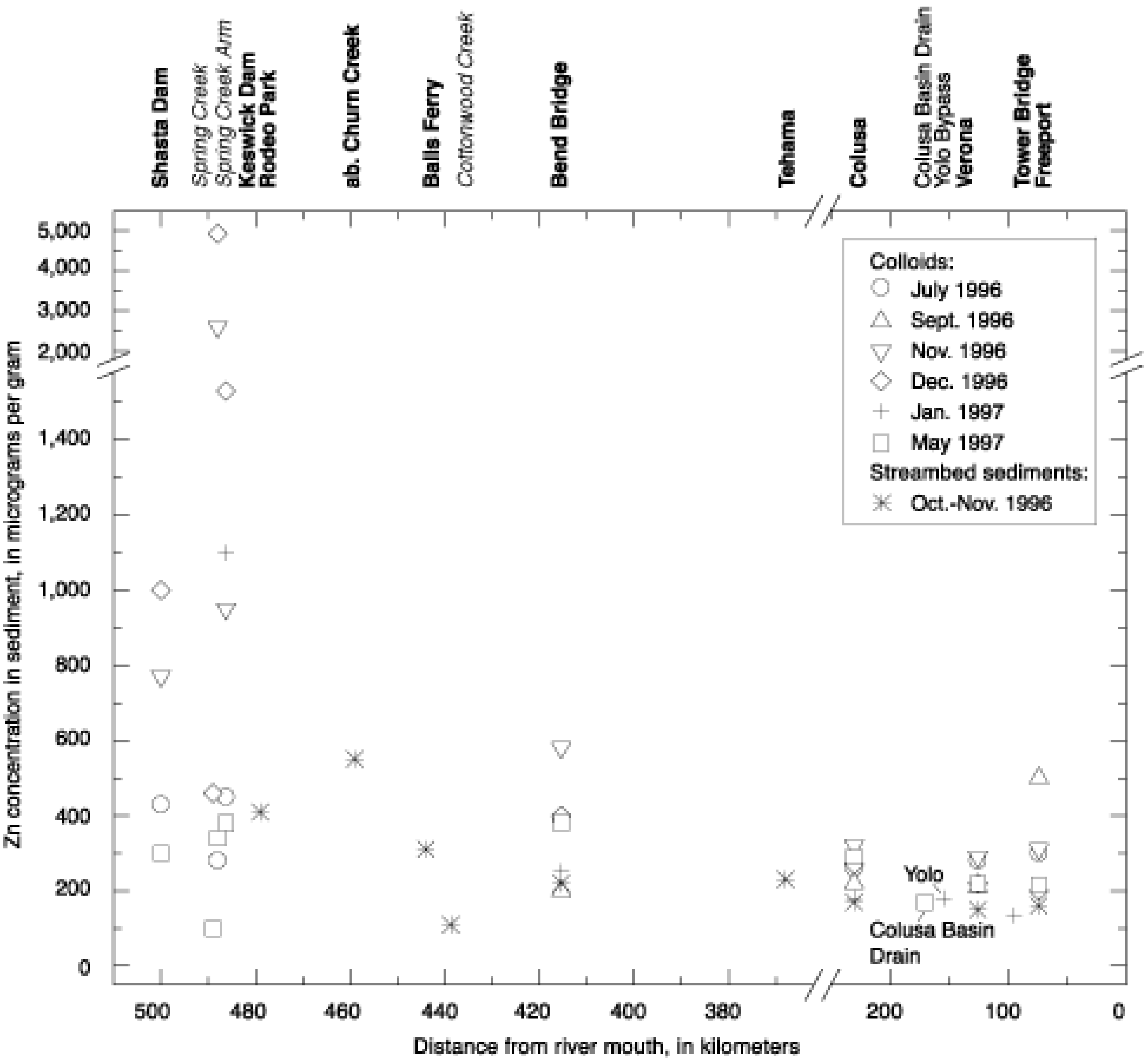

Figure 51. Plot of zinc (Zn) concentrations in suspended colloids and streambed sediment in relation to distance (broken scale) from Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

Table 26. Lead isotopic data for suspended colloids and streambed sediments from the Sacramento River and some of its tributaries

[Data are corrected for mass fractionation during mass spectrometry of 0.11% ± 0.03% to 0.14% ± 0.02% per atomic mass unit based on analyses of NIST's standard reference material SRM-981. Uncertainties are absolute values at the 95% confidence interval; NIST, National Institute of Standards and Technology; Pb, lead; mm/dd/yy, month/day/year; %, percent]

Location	Date (mm/dd/yy)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Suspended Colloid Samples						
Sacramento River Sites						
Sacramento River below Shasta Dam	12/12/96	18.661 ± .015	15.593 ± .014	38.117 ± .040	0.83561 ± .00018	2.0426 ± .0008
Sacramento River below Keswick Dam	12/11/96	18.185 ± .017	15.506 ± .016	37.697 ± .045	0.85269 ± .00019	2.0731 ± .0009
Sacramento River below Keswick Dam	1/02/97	18.344 ± .014	15.521 ± .014	37.791 ± .039	0.84609 ± .00018	2.0602 ± .0008
Sacramento River above Bend Bridge	12/12/96	18.785 ± .014	15.602 ± .013	38.452 ± .039	0.83053 ± .00017	2.0469 ± .0008
Sacramento River above Bend Bridge	1/03/97	18.866 ± .009	15.620 ± .010	38.554 ± .032	0.82799 ± .00017	2.0436 ± .0008
Sacramento River at Colusa	12/16/97	18.792 ± .011	15.605 ± .012	38.474 ± .035	0.83040 ± .00017	2.0473 ± .0008
Sacramento River at Colusa	1/04/97	18.905 ± .008	15.629 ± .010	38.631 ± .032	0.82668 ± .00017	2.0434 ± .0008
Sacramento River at Verona	12/18/96	18.808 ± .012	15.619 ± .012	38.536 ± .036	0.83043 ± .00017	2.0489 ± .0008
Sacramento River at Freeport	12/17/97	18.844 ± .011	15.639 ± .011	38.629 ± .034	0.82993 ± .00017	2.0499 ± .0008
Sacramento River at Tower Bridge	1/06/97	19.115 ± .011	15.699 ± .011	39.223 ± .035	0.82130 ± .00017	2.0520 ± .0008
Tributary Sites						
Spring Creek below Debris Dam near Keswick	12/11/96	18.103 ± .010	15.493 ± .011	37.620 ± .034	0.85586 ± .00018	2.0782 ± .0008
Spring Creek below Iron Mountain Road	1/02/97	18.079 ± .009	15.508 ± .010	37.649 ± .032	0.85782 ± .00017	2.0825 ± .0009
Keswick Reservoir, Spring Creek arm, near Keswick	12/11/96	18.153 ± .008	15.511 ± .010	37.697 ± .031	0.85532 ± .00018	2.0788 ± .0009
Distributary Site						
Yolo Bypass at I-80 near West Sacramento	01/07/97	18.896 ± .010	15.625 ± .011	38.620 ± .034	0.82688 ± .00017	2.0438 ± .0008
Streambed Sediment Samples						
Sacramento River Sites						
Sacramento River at Rodeo Park	10/23/96	18.234 ± .013	15.542 ± .015	37.835 ± .048	0.85236 ± .00030	2.0750 ± .0013
Sacramento River above Churn Creek	10/22/96	18.354 ± .016	15.515 ± .017	37.964 ± .047	0.84532 ± .00048	2.0685 ± .0014
Sacramento River at Balls Ferry	10/22/96	18.704 ± .008	15.600 ± .010	38.389 ± .032	0.83404 ± .00017	2.0524 ± .0008
Sacramento River above Bend Bridge	10/22/96	18.819 ± .012	15.601 ± .012	38.482 ± .038	0.82901 ± .00021	2.0449 ± .0010
Sacramento River at Tehama	10/23/96	18.823 ± .019	15.591 ± .021	38.442 ± .059	0.82829 ± .00050	2.0423 ± .0016
Sacramento River at Colusa	11/14/96	18.871 ± .013	15.601 ± .014	38.520 ± .041	0.82672 ± .00030	2.0413 ± .0011
Sacramento River at Verona	11/13/96	18.874 ± .010	15.625 ± .011	38.590 ± .034	0.82788 ± .00019	2.0446 ± .0009
Sacramento River at Freeport	11/15/96	18.877 ± .008	15.632 ± .010	38.597 ± .032	0.82812 ± .00017	2.0447 ± .0008
Tributary Site						
Cottonwood Creek near Cottonwood	10/23/96	18.921 ± .010	15.638 ± .012	38.646 ± .035	0.82646 ± .00033	2.0425 ± .0010

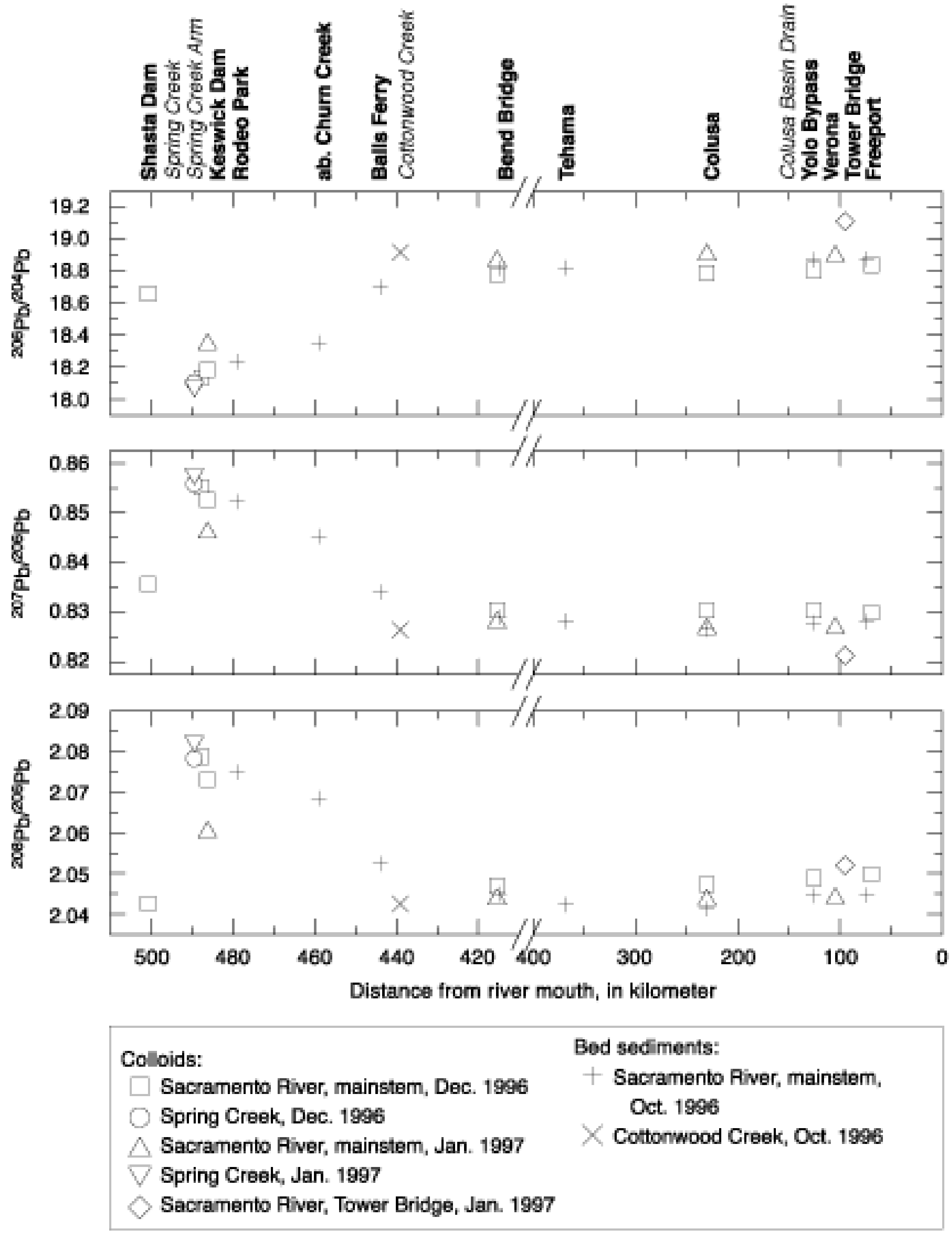

Figure 52. Plots of lead (Pb) isotope ratios in relation to distance (broken scale) from the Sacramento River mouth, California, for streambed sediments and suspended colloids. *A*. $^{206}Pb/^{204}Pb$, *B*. $^{207}Pb/^{206}Pb$, *C*. $^{208}Pb/^{206}Pb$. Site names in bold are mainstem sites and those in italics are tributary sites.

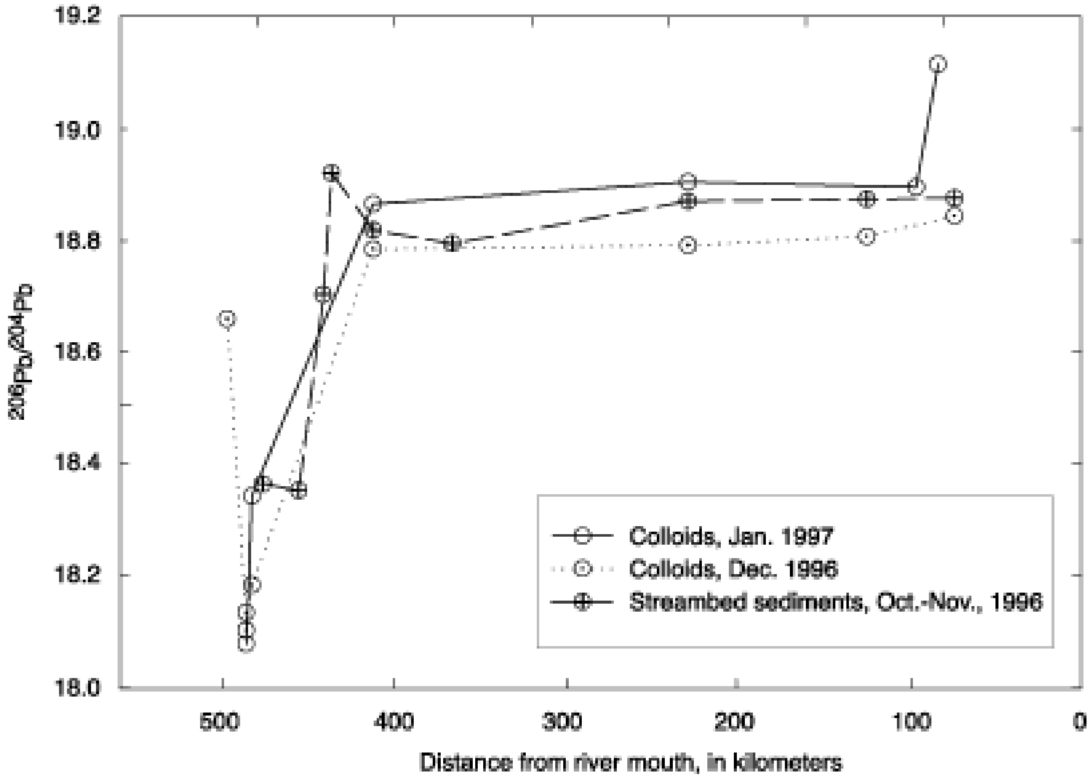

Figure 53. Plot of ^{206}Pb/^{204}Pb in relation to distance (continuous scale) from the Sacramento River mouth, California, for streambed sediments and suspended colloids.

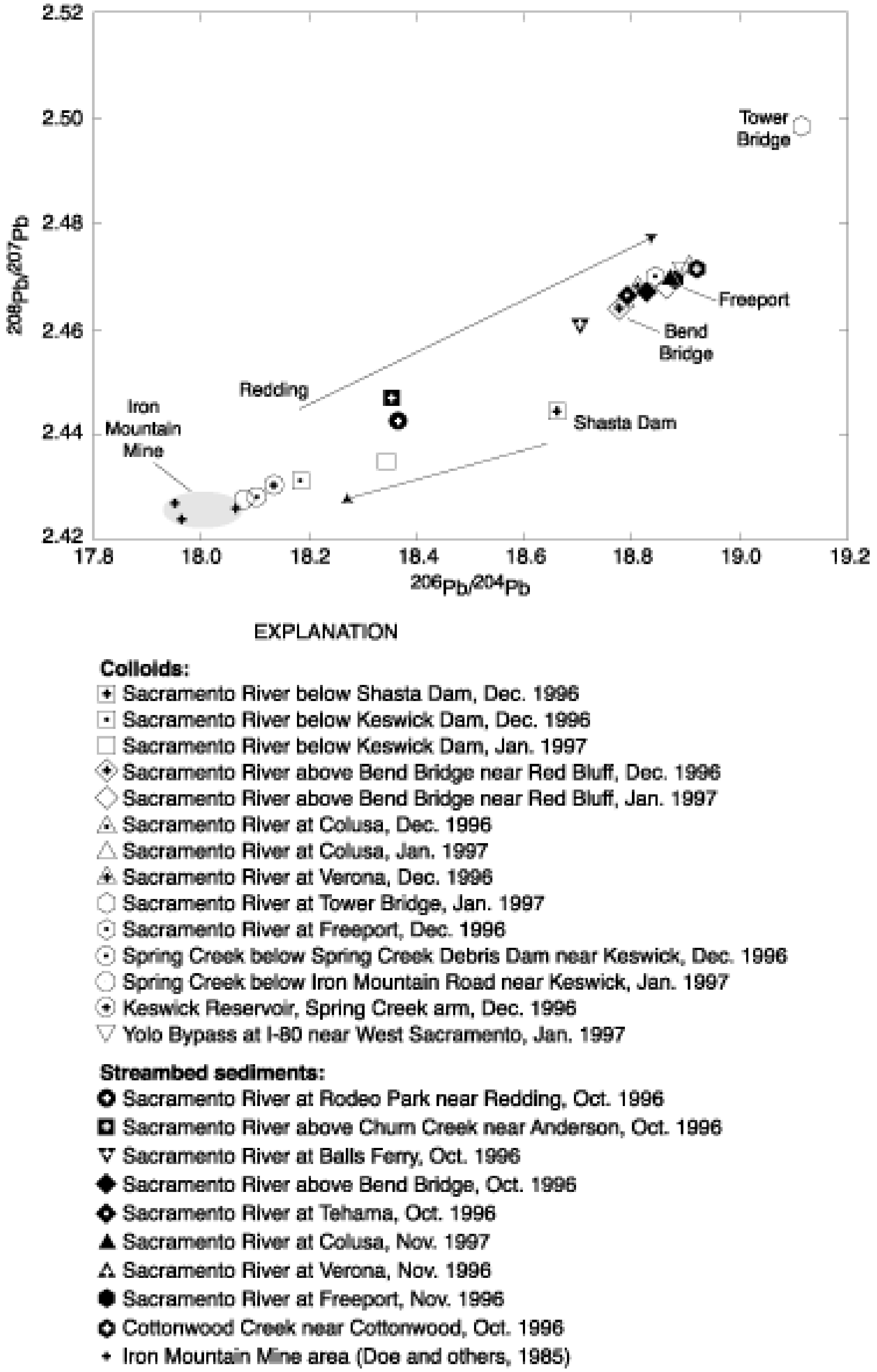

Figure 54. Plot of $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{207}Pb$ for streambed sediments and suspended colloids in the Sacramento River Basin, California.

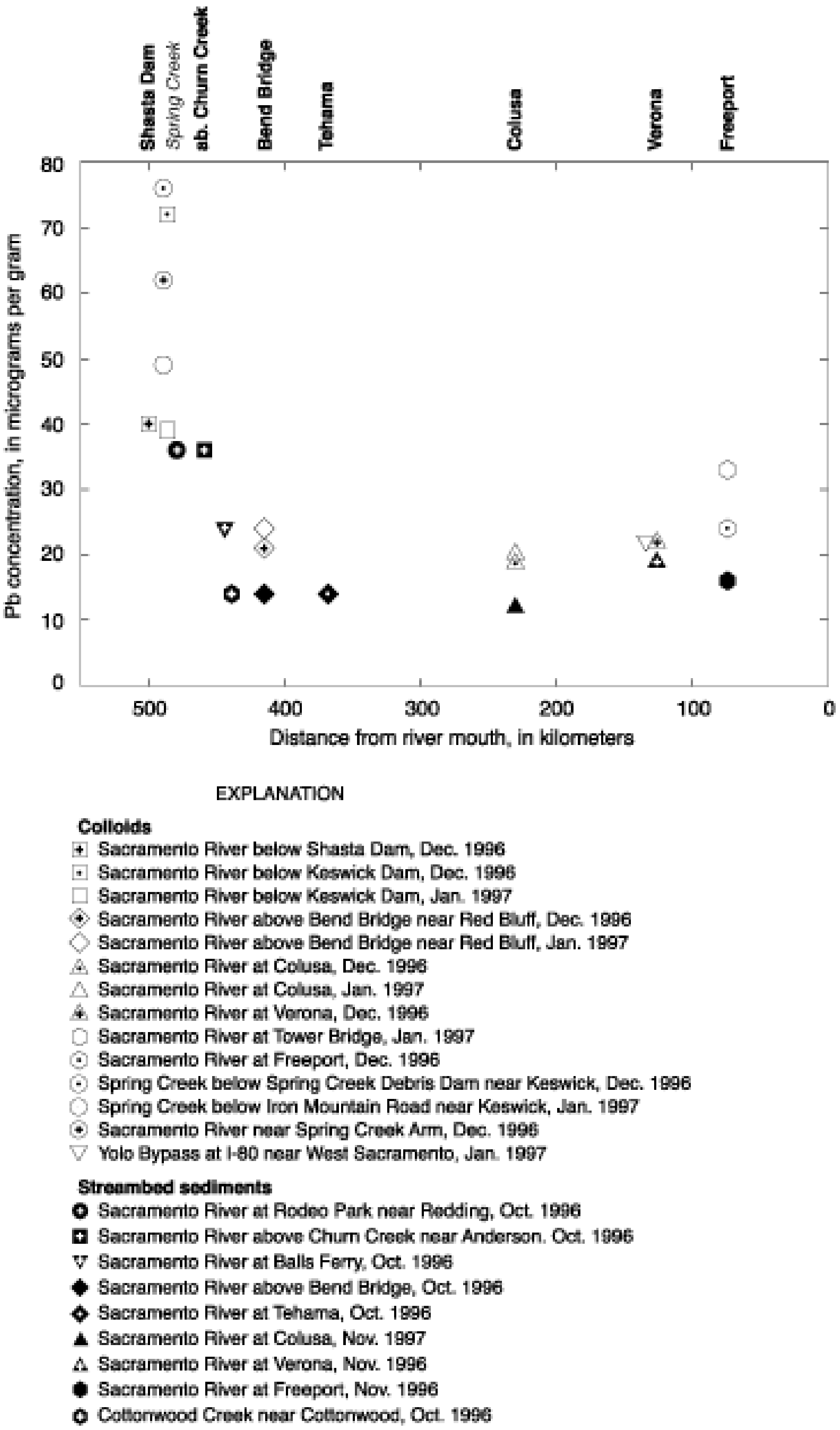

Figure 55. Plot of lead (Pb) concentration in streambed sediments and suspended colloids versus distance (continuous scale) from the Sacramento River mouth, California. Site names in bold are mainstem sites and those in italics are tributary sites.

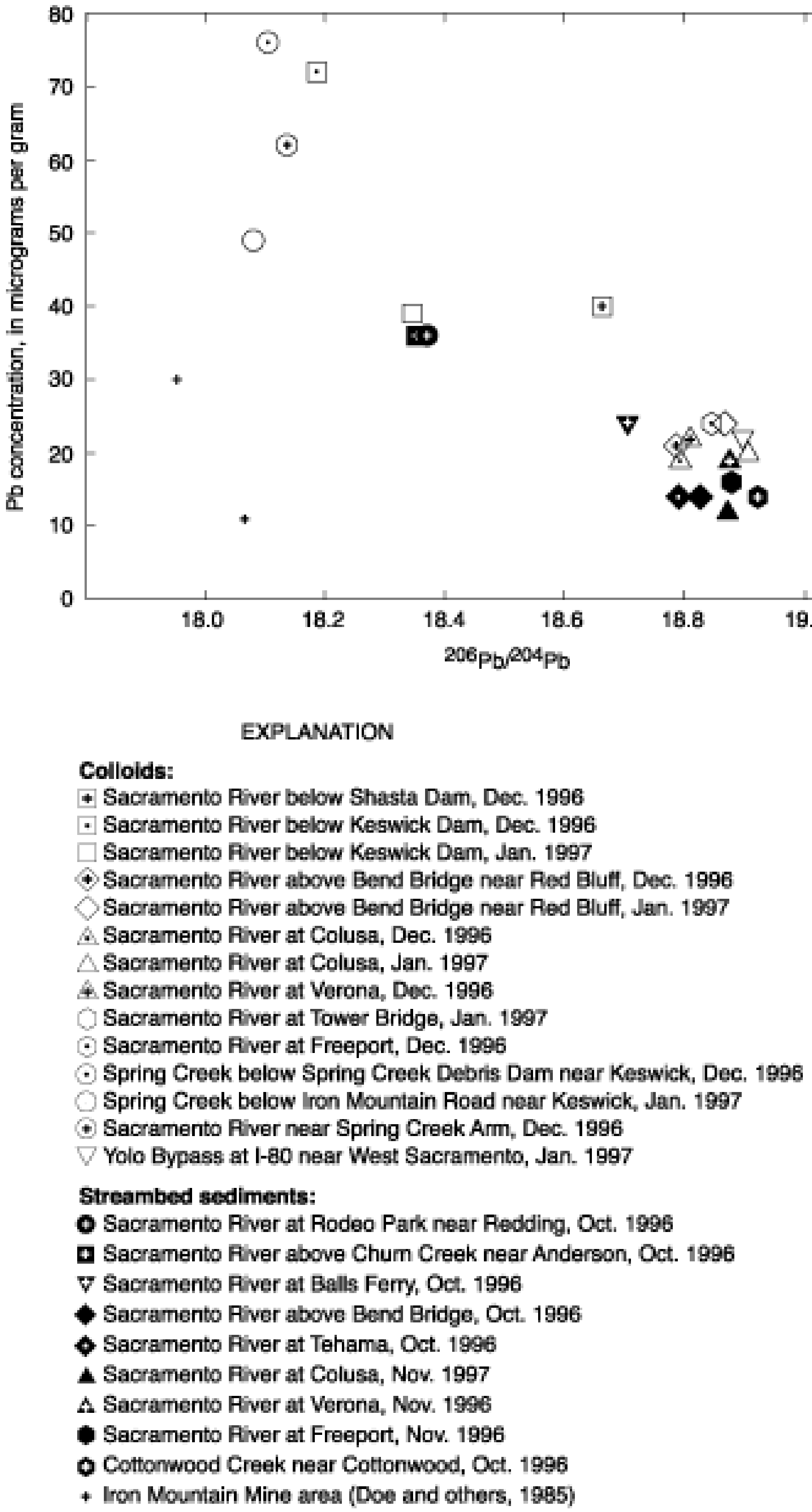

Figure 56. Plot of ^{206}Pb/^{204}Pb versus lead concentration for streambed sediments and suspended colloids in the Sacramento River Basin, California. Pb, lead.

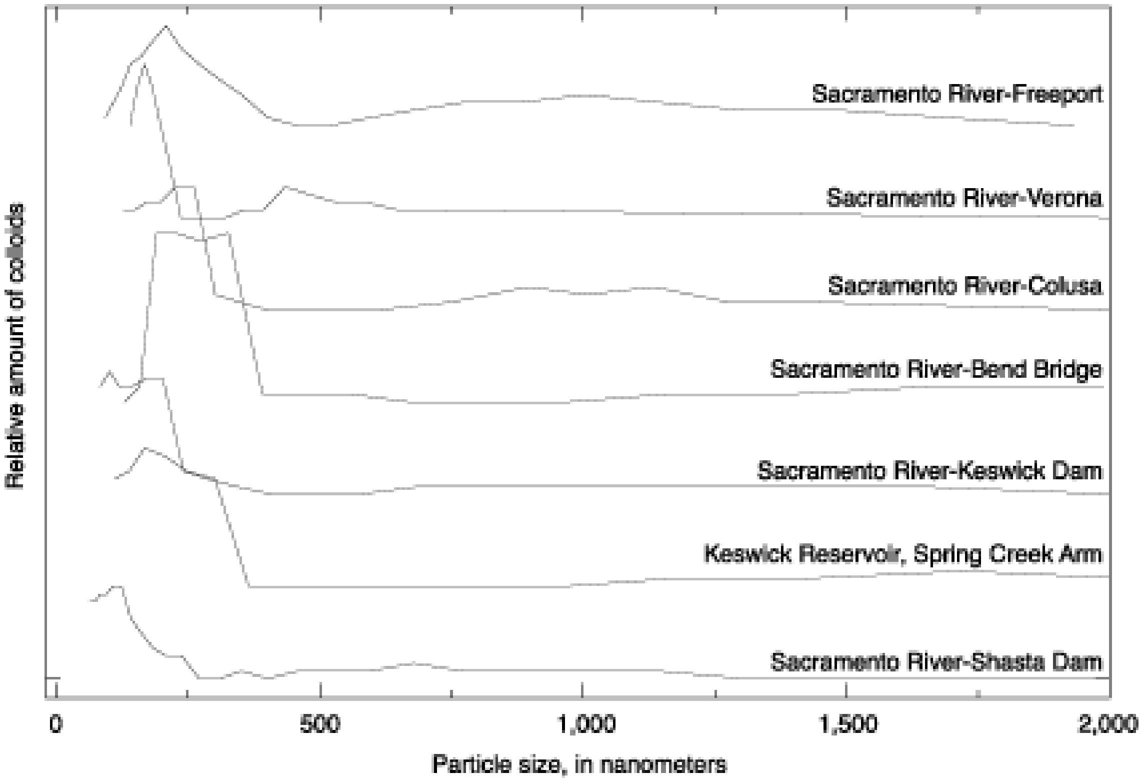

Figure 57. Plot of particulate size distributions for colloid samples collected during September 1996 along the Sacramento River, California.

(Cottonwood Creek) are also given in Appendix 6 (table A6-2). These distributions were determined using whole sediment samples, whereas the fraction of the sediment that was analyzed chemically was the part that passed through a 62-µm screen, as described earlier. The proportion of the whole sediment that passed through the 62-µm screen ranged from 3 to 44 percent, by weight, with a median value of 11 percent, by weight. The sand-sized fraction (62 µm to 2.0 mm) comprises more than 50 percent, by weight, of eight of the nine samples analyzed; the only exception was the sample from Bend Bridge, which had 63 percent, by weight, larger than 2.0 mm (table A6-2).

Summary and Conclusions

Charles N. Alpers, Howard E. Taylor, *and*
Joseph L. Domagalski

Results from this study represent some of the first available data of high quality for dissolved and colloidal concentrations of trace elements in the reach of the Sacramento River from Shasta Dam to Freeport. The primary purposes of this report are to document the methods and quality assurance and quality control procedures used in this study and to provide the resulting data in accessible format.

This study used a multidisciplinary approach to improving the understanding of metal distribution, fate, and transport in the Sacramento River. Samples of water, streambed sediment and(or) caddisfly larvae were collected on one or more occasions during the period between June 1996 and July 1997 at 11 sites along the reach of the Sacramento River between Shasta Dam and Freeport; at 7 different tributary sites; and at 1 distributary site, the Yolo Bypass. Water samples were collected and processed using ultraclean techniques necessary for accurate and precise determination of trace and ultratrace constituents. Tangential-flow ultrafiltration (0.005-µm equivalent pore size) was used to determine “dissolved” concentrations that were compared with results from conventional filtration (0.45- and 0.40-µm pore size). The ultrafiltrates give a better approximation to truly dissolved metal concentrations and allow the extent of colloidal transport to be assessed.

During six sampling periods between July 1996 and June 1997, colloid concentrates were prepared using the retentate from tangential-flow ultrafiltration of large (approximately 100 L) water samples from six mainstem Sacramento River sites (below Shasta Dam, below Keswick Dam, at Bend Bridge, at Colusa, at Verona, and at Freeport), and the Yolo Bypass at Interstate 80 during high flow. The colloid concentrates were analyzed for total metals and some were also subjected to sequential extractions to determine forms of metals in operationally defined fractions: reducible (including hydrous iron and manganese oxides), oxidizable (including organic material and sulfides), and residual (surviving both of the previous extractions).

It was generally found that the sum of dissolved and colloidal concentrations using ultrafiltrates and retentate (colloid concentrate) samples was a more reliable way to estimate total water-column loadings rather than conventional whole-water analyses.

Some other key results of this study are as follows:

1. A. significant proportion of the trace metals transported in the Sacramento River between Shasta Dam and Freeport occurs in colloidal form (operationally defined as grain size between about 0.005- and 1.0-μm diameter). Colloids represent the dominant form of aluminum, iron, lead, and mercury in the water column and are an important factor in the distribution of other trace metals. The proportion of loading that is colloidal as opposed to "dissolved" (less than about 0.005-μm diameter) generally decreases in the order copper greater than zinc and cadmium.
2. The influence of metal-laden acidic drainage from the Iron Mountain mine site (by way of Spring Creek and the Spring Creek arm of Keswick Reservoir) can be seen in data from water samples from the site below Keswick Dam, where historically, the Basin Plan water-quality standards for copper have been exceeded. (The Basin Plan standard for copper in this area is 5.6 μg/L, which is based on a hardness of 40 mg/L and filtration using a 0.45-μm filter.) Some water-quality standard exceedances occurred in January 1997, despite ongoing operation of the lime neutralization plant at Iron Mountain, which reportedly removes about 80 percent of cooper loads and about 90 percent of zinc and cadmium loads from Spring Creek. In mid-December 1996, conventionally filtered copper concentrations were 4.6 to 5.1 μg/L and zinc ranged from 6 to 9 μg/L. During flood conditions in early January 1997, conventionally filtered copper concentrations were 4 to 9 μg/L and zinc ranged from 9 to 16 μg/L. Ultrafiltrates (0.005-μm equivalent pore size) of water samples from below Keswick Dam in December 1996 and January 1997 had copper concentrations about 40 to 70 percent lower than the conventional (0.40- and 0.45-μm) filtrates and zinc concentrations were 10 to 50 percent lower, indicating significant colloidal transport of copper and to a lesser extent, zinc.
3. Lead isotope data in colloid concentrates and streambed sediments provide a useful fingerprint or natural tracer for lead contamination from Iron Mountain mine drainage by way of Spring Creek and Keswick Reservoir. In streambed sediment and suspended colloid samples taken during 1996 and 1997, lead contamination from Iron Mountain is a relatively significant component of the total lead found at Sacramento River sampling sites at Rodeo Park (in Redding) and above Churn Creek (near Anderson), is a much lesser component at Balls Ferry, and is a relatively minor component of the lead in colloids and streambed sediment at Bend Bridge (near Red Bluff) and at sites further downstream.
4. Bioaccumulation of metals in caddisfly larvae was assessed at five sites in the Sacramento River between Redding and Tehama and at one reference site (Cottonwood Creek, near Redding). Samples were taken in October 1996. Cadmium concentrations in caddisfly larvae from Sacramento River sites were enriched 5 to 36 times than those from the reference site. Cadmium concentrations of the whole body ranged from 0.7 to 2.2 μg/g, dry weight. Of this total, approximately 60 percent (0.4 to 1.3 μg cadmium per gram, dry weight) was associated with the cell cytosol, an

intracellular fraction that is indicative of metal bioavailability. Concentrations in the Sacramento River are comparable with other areas severely impacted by mining, such as the Clark Fork River downstream of Butte, Montana (Cain and others, 2000). Concentrations of copper and zinc also showed some enrichment in caddisfly whole bodies and cytosol fractions, which were enriched 1.4 to 3.0 times. The caddisfly data indicate that bioavailable forms of cadmium persist in the Sacramento River downstream of Tehama.

5. The geochemical forms of metals in colloid concentrates from the Sacramento River were evaluated using sequential extraction techniques. During May and June 1997, cadmium was dominantly associated with the reducible (iron–manganese oxide) fraction at all mainstem sampling sites, whereas copper and zinc were more or less evenly distributed between reducible and residual (refractory) fractions at all sites, with a small amount present in the oxidizable (organic plus sulfide) fraction. These results are consistent with the caddisfly bioaccumulation data that indicate that cadmium is relatively more bioavailable than copper or zinc in the river reach between Redding and Tehama.
6. The concentrations of total inorganic mercury in the Sacramento River increased during storm water runoff and were above the EPA water-quality criterion for aquatic life (12 ng/L) during high flows in December 1996 and January 1997, from the Bend Bridge site located near Red Bluff, downstream to Freeport. Dissolved inorganic mercury concentrations (based on 0.005-μm equivalent pore-size ultrafiltration) were found to be very low and relatively constant under a variety of flow conditions, but dissolved plus colloidal concentrations were found to increase with increasing discharge and suspended sediment transport. The concentrations of colloidal mercury were found to be similar to those measured in whole-water samples. Therefore, much of the mercury transported in the Sacramento River is in the colloidal size fraction. Sequential extraction of mercury from the colloid fraction, using specific chemical reagents, showed that most of the mercury is in operationally defined oxidizable and residual fractions with only a minor component in the reducible fraction. The implications for the bioavailability of mercury from these colloidal forms of mercury are currently unknown and represent a logical extension of this research.

REFERENCES CITED

Allen, Terance, 1990, Particle Size Measurement (4th ed.): London, U.K., Chapman & Hall, 806 p.

Alpers, C.N., Antweiler, R.C., Taylor, H.E., Dileanis, P.D., and Domagalski, J.L., 2000, Metals transport in the Sacramento River, 1996–1997. Volume 2: Interpretation of metal loads: U.S. Geological Survey Water-Resources Investigations Report 00-4002, 106 p.

Anderson, S.W., Rockwell, G.L., Friebel, M.F., and Webster, M.D., 1997, Water Resources Data, California; Water Year 1996. Volume 4. Northern Central Valley Basins and the Great Basin from Honey Lake Basin to Oregon State Line: U.S. Geological Survey Water-Data Report CA-97-4, 469 p.

Antweiler, R.C, and Taylor, H.E., 1999, A pseudo-flow injection system for the analysis of major and trace metals by axial ICP–AES *in* Rocky Mountain Conference on Analytical Chemistry, Final Program and Abstracts, Denver, Colorado, July 25–Aug. 1, 1998: Society for Applied Spectroscopy, abs. no. 4.

Bailey, E.H., ed., 1966, Geology of northern California field trip guides: California Division of Mines and Geology, Bulletin 190-E.

Ball, J.W., and Nordstrom, D.K., 1991, User's Manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox. elements in natural waters: U.S. Geological Survey Open-File Report 91-183, 189 p.

Barrie, C.T., and Hannington, M.D., eds., 1999, Volcanogenic massive sulfide (VMS) deposits and subaqueous hydrothermal systems: Reviews in Economic Geology, v. 8, 672 p.

Bradley, W.W., 1918, Quicksilver resources of California, *with a section on* Metallurgy and ore-dressing: California Division of Mines and Geology Bulletin 78, 389 p.

Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of dissolved organic carbon by UV-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.

Butler, J.N., 1982, Carbon dioxide equilibria and their applications: Reading, Mass., Addison-Wesley Publishing Company, 259 p.

Cain, D.J., Carter, James, Fend, S., Luoma, S.N., Alpers, C.N., and Taylor, H.E., 2000, Metal exposure to a benthic macroinvertebrate, *Hydropsyche californica,* related to mine drainage in the Sacramento River: Canadian Journal of Fisheries and Aquatic Sciences, v. 57, p. 380–390.

California Department of Water Resources, 1993, California water plan update: California Department of Water Resources Bulletin 160-93, draft, v. 2, 347 p.

———1998a, Discharge data on Shasta Dam, accessed May 19, 1998 at http://cdec.water.ca.gov/selectQuery.html (site code SHA).

———1998b, Discharge data on Keswick Dam, accessed March 4, 1998 at http://cdec.water.ca.gov/selectQuery.html (site code KES).

———1998c, California water plan update: California Department of Water Resources Bulletin 160-98, v. 1, variously paged.

Cameron, A.E., Smith, D.H., and Walker, R.L., 1969, Mass spectrometric analysis of nanogram quantities of lead: Analytical Chemistry, v. 41, p. 525–526.

Capel, P.D., Nacionales, F.C., and Larson, S.J., 1995, Precision of a splitting device for water samples: U.S. Geological Survey Open-File Report 95-293, 6 p.

Chao, T.T., and Zhou, L., 1983, Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments: Soil Sciences Society of America Journal, v. 47, p. 225–232.

Church, S.E., Holmes, C.W., Briggs, P.H., Vaughn, R.B, Cathcart, J.D., and Marot, Margaret, 1993, Geochemical and lead-isotope data from stream and lake sediments, and cores from the upper Arkansas River drainage: Effects of mining at Leadville Colorado on heavy-metal concentrations in the Arkansas River. U.S. Geological Survey Open-File Report 93-534, 61 p.

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.

Doe, B.R., Delevaux, M.H., and Albers, J.P., 1985, The plumbotectonics of the West Shasta mining district, eastern Klamath Mountains, California: Economic Geology, v. 80, p. 2136–2148.

Domagalski, J.L., 1998, Occurrence and transport of total mercury and methyl mercury in the Sacramento River Basin, California: Journal of Geochemical Exploration, v. 64, no. 1, p. 277–291.

Domagalski, J.L., Knifong, D.L, MacCoy, D.E., Dileanis, P.D., Dawson, B.J., and Majewski, M.S., 1998, Water quality assessment of the Sacramento River Basin, California: Environmental setting and study design: U.S. Geological Survey Water-Resources Investigations Report 97-4254, 31 p.

Edwards, T.K. and Glysson, G.D., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods of determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A-1, 545 p.

Friedman, L.C., and Erdmann, D.E., 1982, Quality assurance practices for the chemical and biological analyses of water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A6, 181 p.

Garbarino, J.R., Taylor, H.E., 1979, An inductive-coupled plasma atomic-emission spectrometric method for routine water quality testing: Applied Spectroscopy, v. 33, no. 3, p. 220–225.

———1995, Inductively-coupled plasma-mass spectrometric method for the determination of dissolved trace elements in natural water: U.S. Geological Survey Open-File Report 94-358, 88 p.

Guy, HY.P, 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 6, chap. C1, 58 p.

Hayes, H.C., 1993, Metal associations in suspended sediments and bed sediments from the Mississippi River: Golden, Colo., Colorado School of Mines, M.S. thesis, 131 p.

Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for a national water-quality assessment program: U.S. Geological Survey Circular 1021, 42 p.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.R., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Hunerlach, M.P., Rytuba, J.J., and Alpers, C.N., 1999, Mercury contamination from hydraulic placer-gold mining in the Dutch Flat mining District, California, *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: U.S. Geological Survey Water-Resources Investigations Report 99-4018-B, 179–189 p.

Hunrichs, R.A., Pratt, D.A., and Meyer, R.W., 1998, Magnitude and frequency of the floods of January 1997 in northern and central California, Preliminary determinations: U.S. Geological Survey Open-File Report 98-626, 120 p

Kelly, Todd, and Taylor, H.E., 1996, Concentrations and loads of selected trace elements and other constituents in the Rio Grande in the vicinity of Albuquerque, New Mexico, 1994: U.S. Geological Survey Open-File Report 96-126, 45 p.

Kimball, B.A., Callender, 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, no. 3, p. 285–306.

Kinkel, A.R., Jr., Hall, W.E., and Albers, J.P., 1956, Geology and base-metal deposits of West Shasta copper-zinc district, Shasta County, California: U.S. Geological Survey Professional Paper 285, 156 p., 21 pls.

Kuehner, E.C., Alvarez, R., Paulsen, P.J., and Murphy, T.J., 1972, Production and analysis of special high-purity acids purified by sub-boiling distillation: Science of the Total Environment, v. 105, p. 191–209.

Leenheer, J.A., Meade, R.H., Taylor, H.E., and Pereira, W.E., 1989, Sampling, fractionation, and dewatering of suspended sediment from the Mississippi River for geochemical and trace-contaminant analysis, *in* Mallard, G.E., and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the technical meeting, Phoenix, Arizona, September 26–30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 501–511.

Ludwig, K.R., 1979, Calculation of uncertainties of U-Pb isotope data: Earth and Planetary Science Letters, v. 46, p. 212–220.

MacCoy, D.E., and Domagalski, J.L., 1999, Trace elements and organic compounds in streambed sediment and aquatic biota from the Sacramento River Basin, California, October and November, 1995: U.S. Geological Survey Water-Resources Investigations Report 99-4151, 37 p.

Meade, R.H., ed., 1996, Contaminants in the Mississippi River, 1987–92: U.S. Geological Survey Circular 1133, 140 p.

Millipore Corporation, 1993, Selecting a membrane for concentration, desalting, and buffer exchange of macromolecules (ultrafiltration): Bedford, Mass., Millipore Corporation.

Morton, J.L., Zierenberg, R.A., and Reiss, C.A., eds., 1994, Geologic, hydrothermal, and biologic studies at the Escanaba Trough, Gorda Ridge, offshore northern California: U.S. Geological Survey Bulletin 2022, 359 p.

National Oceanic and Atmospheric Administration, 1996, Climatological Data. California (Annual Summary): National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 100, no. 13.

———1997a, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 1.

———1997b, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 2.

———1997c, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 3.

———1997d, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 4.

———1997e, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 5.

———1997f, Climatological data. California Monthly Reports: National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, v. 101, no. 6.

Nordstrom, D.K., Alpers, C.N., Coston, J.A., Taylor, H.E., McCleskey, R.B., Ball, J.W., Ogle, S., Cotsifas, J.S., and Davis, J.A., 1999, Geochemistry, toxicity, and sorption properties of contaminated sediments and pore waters from two reservoirs receiving mine drainage, *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: U.S. Geological Survey Water-Resources Investigations Report 99-4018-A, 289–296 p.

Nordstrom, D.K., Jenne, E.A., and Averett, R. C., 1977, Heavy metal discharges into Shasta Lake and Keswick Reservoir on the Upper Sacramento River, California: A reconnaissance during low flow: U.S. Geological Survey Open-File Report, 76-49, 25 p.

Nordstrom, D.K., and Southam, G., 1997, Geomicrobiology of sulfide mineral oxidation: Reviews in Mineralogy, v. 35, p. 361–390.

Norris, R.M., and Webb, R.W., 1990, Geology of California (2nd ed.): New York, John Wiley, 541 pages.

Patton, C.J., and Truitt, E.P., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of total phosphorous by a Kjeldahl digestion method and an automated colorimetric finish that includes dialysis: U.S. Geological Survey Open-File Report 92-146, 39 p.

Peart, D.B., Antweiler, R.C., Taylor, H.E., Roth, D.A., and Brinton, T.I., 1998, A reevaluation and extension of the scope of elements in the U.S. Geological Survey standard reference water samples: Analyst, v. 3, p. 455.

Pritt, J.W., and Raese, J.W., eds., 1995, Quality assurance/ quality control manual: National Water Quality Laboratory: U.S. Geological Survey Open-File Report 95-443, 35 p.

Rantz, S.E. and others, 1982a, Measurement and computation of streamflow: Volume 1. Measurement of stage and discharge: U.S. Geological Survey, Water-Supply Paper 2175, p. 1–284.

———1982b, Measurement and computation of streamflow: v.. 2. Computation of discharge: U.S. Geological Survey, Water-Supply Paper 2175, p. 285–631.

Rice, C.A., Tuttle, M.L., and Reynolds, R.L., 1993, The analysis of forms of sulfur in ancient sediments and sedimentary rocks: Comments and cautions: Chemical Geology, v. 107, p 83–95.

Roth, D.A., 1994, Ultratrace analysis of mercury and its distribution in some natural waters of the United States: Fort Collins, Colo., Colorado State University, Ph.D. dissertation, 309 p.

Rousseeuw, P.J., 1990, Robust estimation and identifying outliers, *in* Handbook of Statistical Methods for Engineers and Scientists, H.M. Wadsworth, ed.: New York, McGraw Hill, p. 16.1–16.24.

Schoenherr A.A., 1992, A natural history of California: Berkeley, Calif., University of California Press, California National History Guides series, no. 56, 772 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Shelton, L.R., and Capel, P.D., 1994, Guideline for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-458, 20 p.

Slotton, D.G., Ayers, S.M., Reuter, J.E., and Goldman, C.R., 1997a, Gold mining impacts on food chain mercury in northwestern Sierra Nevada streams: Davis, Calif., University of California Water Resources Center, 46 p.

———1997b, Cache Creek Watershed preliminary mercury assessment, using benthic macro-invertebrates. Final report for the Regional Water Quality Control Board–Central Valley Region, and the National Science Foundation, 36 p.

Stookey, L.L., 1970, FerroZine-a new spectrophotometric reagent for iron: Analytical Chemistry, v. 42, p. 779–781.

Stanley, D.L., Shampine, W.J., and Schroder, L.J., 1992, Summary of the U.S. Geological Survey National Field Water Quality Assurance Program from 1979 through 1989: U.S. Geological Survey Open-File Report 92-163, 14 p.

Stumm, W., and Morgan, J.J., 1981, Aquatic chemistry: New York, John Wiley & Sons, 780 p.

Syvitski, J.P.M., 1991, Principles, methods, and application of particle size analysis: Cambridge, U.K., Cambridge University Press, 368 p.

Taylor, H.E., and Garbarino, J.R., 1991, The measurement of trace metals in water resources: Monitoring samples of inductively coupled plasma-mass spectrometry: Spectrochimica Acta Reviews, v. 14, nos. 1–2, p. 33–43.

Taylor, H.E., Garbarino, J.R.,and Brinton, T.I., 1990, The occurrence and distribution of trace metals in the Mississippi River and its tributaries: The Science of the Total Environment, p. 369–384.

Taylor, H.E., and Shiller, A.M., 1995, Mississippi River methods comparison study: Implications for water-quality monitoring of dissolved trace elements: Environmental Science and Technology, v. 29, p. 1313–1317.

Taylor, H.E., Shiller, A.M., Garbarino, J.R., and Brinton, T.I., 1995, Intercomparison experiments on dissolved trace-metal data from the Mississippi River and some of its tributaries, 1989–90: U.S. Geological Survey Open-File Report 93-628, 28 p.

Todt, W., Cliff, R.A., Hanser, A., and Hofmann, A.W., 1993, Re-calibration of NBS lead standards using a ^{202}Pb + ^{205}Pb spike, *in* 7th Conference of the European Union of Geosciences Structure and evolution of the European lithosphere and upper mantle : Physics of the Earth and Planetary Interiors, v. 79, no. 1–2, p. 396.

Unruh, D.M., 1982, The U-Th-Pb age of equilibrated L chondrites and a solution to the excess radiogenic Pb problem in chondrites: Earth and Planetary Science Letters 58, p. 75-94

U.S. Army Corps of Engineers, 1991, Sacramento River, sloughs, and tributaries, California 1991 aerial atlas: Collinsville to Shasta Dam: Sacramento, Calif., U.S. Army Corps of Engineers, 43 p.

U.S. Environmental Protection Agency, 1992, Environmental Endangerment Assessment, Iron Mountain Mine, Redding, California: CH2M Hill (Redding, California), report prepared for the U.S. Environmental Protection Agency.

U.S. Geological Survey, 1998, Hydrographs from the Automatic Data Processing Center, accessed February 23, 1998 at http://water.wr.usgs.gov.

Ward, J.R., and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

Waychunas, G.A., Rea, B.A., Fuller, C.C., and Davis, J.A., 1993, Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate: Geochimica et Cosmochimica Acta, v. 57, p. 2251–2269.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

Glossary

Accuracy The measure of the degree of conformance of values generated by a specific analytical method with the true or expected value of that measurement. In this study, accuracy is evaluated by measurement of standard reference materials, spike recoveries, and blanks, and is quantified by the value of REC (Percentage Recovery).

Anion Negatively charged aqueous ion. Examples of common anions in natural waters are chloride (Cl^-) and sulfate (SO_4^{2-}).

Bias Systematic error in laboratory measurements.

Capsule filter A sealed, disposable filtration device through which raw water is pumped to remove particulates. In this study, the term refers to a tortuous-path filter (manufactured by Gelman), with nominal pore diameter of 0.45 micrometers, that is used routinely by the USGS's NAWQA Program.

Cation Positively charged aqueous ion. Examples of common cations in natural waters are sodium (Na^+) and calcium (Ca^{2+}).

Certified value Concentration of a substance in a standard reference material that is certified as correct by an official agency or organization, such as the National Institute of Standards and Technology.

Colloids Fine particles suspended in water. In this study, the lower size limit of colloid particles is operationally defined by passage through a tangential-flow ultrafilter with pore size of 10,000 nominal molecular weight limit (NMWL), or daltons, approximately equivalent to 0.005 micrometers. The upper limit of grain size for colloids in this study is operationally defined by settling for one hour (approximately 1 micrometer).

Colloid concentrate Sample of suspended colloids derived from raw water using ultrafiltration methods. In this study, typically 100 liters of raw water were processed to generate a concentrate of about 0.5 liters in volume that contained a mass of colloidal solids in the range of 0.02 to 2 grams. The concentrate was freeze-dried and then analyzed in a manner similar to that of streambed sediment samples.

Completeness Percentage of analyses meeting the data quality objectives for accuracy and precision in the Quality Assurance Project Plan (see Appendix 1).

Critical elements The elements of most interest to stakeholders in the Sacramento River watershed; operationally defined to include cadmium, copper, lead, mercury, and zinc. Iron and aluminum are included in some discussions of critical elements because of the importance of these major elements to trace element transport.

Detection limit The minimum concentration of a substance that can be measured and reported with 95 percent confidence that the analyte concentration is greater than zero.

Dissolved concentration The concentration of a substance that is present in water, exclusive of suspended particles. For this study, the ultrafiltrate is assumed to be the best approximation to truly dissolved concentrations.

Duplicate sample A split sample of any matrix (water, sediment, or tissue) taken for quality assurance purposes to assess the variability of either field conditions or laboratory methods.

Effective concentration A calculated quantity that represents the sum of the equivalent colloid concentration in water and the dissolved concentration, based on ultrafiltrates for this study.

Equipment blank A water sample taken for quality assurance purposes. The sample consists of deionized water that is put in contact with an individual piece of water-sample processing equipment. The blank is designed to detect contamination problems associated with specific pieces of equipment.

Equivalent colloid concentration in water A calculated quantity that represents the concentration in water of a constituent based only on the colloid-sized particles. The quantity is calculated in this study using chemical data from the colloid concentrates and whole-water (unfiltered) concentrations of aluminum, with the assumption that essentially all aluminum in the whole-water samples is in colloidal form and that the dissolved aluminum concentrations are negligible.

Field blank A water sample taken for quality assurance purposes that consists of deionized water processed in a similar manner to unknown water samples. The blank is designed to detect contamination problems, such as airborne dust, associated with specific field sites.

Laboratory blank A water sample taken for quality assurance purposes that consists of deionized water put through the analysis procedure in a manner identical to unknown samples. The blank is designed to determine detection limits and baseline shifts for analytical methods.

Major elements Elements that are in greatest abundance in a water or solid sample includes major cations and major anions. Major cations in water generally include calcium, magnesium, manganese, potassium, silicon (Si), and sodium.

Membrane filter A wafer-thin, disposable filtration device that is placed inside a holder for each use. In this study, the term refers to a polycarbonate membrane (manufactured by Nuclepore) with uniform holes of 0.40 micrometers in diameter.

MPV Most probable value. Concentration of substance in a noncertified standard reference material that is provided on the basis of analysis by numerous laboratories, usually as the median value. (Compare with certified value.)

Oxidizable Fraction of sequential extraction that is liberated by digestion of a sediment or colloid sample with an oxidizing solution. In this study, a persulfate solution is used to extract metals associated with organic and sulfide components.

Precision The degree of similarity among independent measurements of the same quantity. For this study, precision is quantified by the values of Relative Percentage Difference (RPD) and Relative Standard Deviation (RSD).

REC Percentage Recovery. Quantity computed for the evaluation of accuracy of laboratory analytical data using standard reference materials or recovery of known concentrations of analytes in spiked samples.

For standard reference materials:

$$REC_{SRM} = \frac{\text{measured value}}{\text{certified or most probable value}} \times 100$$

For spike recoveries:

$$REC_{SPIKE} = \frac{\text{measured value}}{\text{expected value}} \times 100$$

where the expected value is the original measured concentration in the sample plus the known concentration of the spike.

RPD Relative Percentage Difference. Quantity computed for the evaluation of precision (or variability) of laboratory analytical data using randomly submitted split samples.

$$RPD = \frac{\text{difference between reported values}}{\text{average reported value}} \times 100$$

RSD Relative Standard Deviation. A quantity computed for the evaluation of precision (or variability) of data. Relative standard deviation is the standard deviation of a series of measurements divided by the average of those measurements times 100:

$$RSD = \frac{\text{standard deviation}}{\text{average reported value}} \times 100$$

Rare earth elements The chemical elements between atomic numbers 57 and 71, inclusive. These elements are lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The chemical characteristics of these elements are generally very similar.

Redox Oxidation-reduction. Certain elements can exist at more than one valence state, such as iron(II) and iron(III); the redox state refers to the relative abundance or chemical activity of the various valences of such elements.

Reducible Fraction of sequential extraction that is liberated by digestion of a sediment or colloid sample with a reducing solution. In this study, a hydroxylamine hydrochloride solution is used to extract metals associated with iron and manganese oxide components.

Replicate sample A split sample of any matrix (water, sediment, or tissue) taken for quality assurance purposes to assess the variability of either field conditions or laboratory methods; similar to a duplicate sample, but not limited to two splits.

Residual Fraction of sequential extraction that is remaining after step-wise digestion of a sediment or colloid sample with both reducing and oxidizing solutions. In this study, a complete digestion using hydrofluoric acid, nitric acid, and hydrochloric acid was used dissolve the residual fraction.

Retentate During the tangential-flow ultrafiltration process, the stream retaining the colloidal material, that does not pass through the filters.

Sequential extraction A process that is designed to determine the concentrations of metals associated with different chemical forms in a solid sample of streambed sediment or colloid concentrate. The sequence of extractions used in this study was: (1) reducible (hydroxylamine hydrochloride), (2) oxidizable (persulfate), and (3) residual (complete digestion using hydrofluoric acid, nitric acid, and hydrochloric acid).

SRM Standard Reference Material. Standard used to evaluate accuracy and precision of laboratory measurements in various matrices including water, solids, and biological tissues. SRMs used in this study are distributed by the National Institute of Standards and Technology (NIST) and by the U.S. Geological Survey (USGS). NIST provides certified values for certain constituents in its SRMs and often provides noncertified, “for informational purposes” values for other constituents. The USGS provides “most probable value” concentrations for constituents in its noncertified Standard Reference Water Samples.

Tangential-flow ultrafiltration A filtration process that results in separation of extremely fine particles from water by passing the water repeatedly along the surfaces of a stack of filter membranes; only a small proportion of the water passes through the filters on a given pass; the water is recirculated until the desired volume of ultrafiltrate is attained, or the desired concentration of colloids; in this study, filters with a nominal pore size of 10,000 NMWL or daltons (equivalent to approximately 0.005 micrometers) were used with Minitan and Pellicon units (manufactured by Millipore Corp.).

Total digestion For streambed sediments and colloid concentrates, a chemical procedure that results in complete dissolution of the samples so that the chemical composition can be determined; in this study, complete digestion was achieved using hydrofluoric acid, nitric acid, and hydrochloric acid.

Total recoverable analysis For unfiltered water samples, a procedure that results in partial extraction of metals from suspended solids; in this study, nitric acid was added in the field to prevent precipitation of iron oxides, then hydrochloric acid was added in the laboratory.

Trace elements Elements that are generally present in very low concentrations in water or solid samples.

Ultrafiltrate The water that passes through a tangential-flow ultrafilter; operationally the best approximation to truly dissolved component of water; in this study, an ultrafilter pore size of 10,000 NMWL (equivalent to approximately 0.005 micrometers) were used.

Ultrafiltration see Tangential-flow ultrafiltration.

Whole-water sample An unfiltered (raw) water sample.