Arch Environ Contam Toxicol
DOI 10.1007/s00244-011-9738-z

Selected Trace Elements in the Sacramento River, California: Occurrence and Distribution

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Received: 25 August 2011 / Accepted: 28 November 2011
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Abstract The impact of trace elements from the Iron Mountain Superfund site on the Sacramento River and selected tributaries is examined. The concentration and distribution of many trace elements—including aluminum, arsenic, boron, barium, beryllium, bismuth, cadmium, cerium, cobalt, chromium, cesium, copper, dysprosium, erbium, europium, iron, gadolinium, holmium, potassium, lanthanum, lithium, lutetium, manganese, molybdenum, neodymium, nickel, lead, praseodymium, rubidium, rhenium, antimony, selenium, samarium, strontium, terbium, thallium, thulium, uranium, vanadium, tungsten, yttrium, ytterbium, zinc, and zirconium—were measured using a combination of inductively coupled plasma-mass spectrometry and inductively coupled plasma-atomic emission spectrometry. Samples were collected using ultraclean techniques at selected sites in tributaries and the Sacramento River from below Shasta Dam to Freeport, California, at six separate time periods from mid-1996 to mid-1997. Trace-element concentrations in dissolved (ultrafiltered [0.005-μm pore size]) and colloidal material, isolated at each site from large volume samples, are reported. For example, dissolved Zn ranged from 900 μg/L at Spring Creek (Iron Mountain acid mine drainage into Keswick Reservoir) to 0.65 μg/L at the Freeport site on the Sacramento River. Zn associated with colloidal material ranged from 4.3 μg/L (colloid-equivalent concentration) in Spring Creek to 21.8 μg/L at the Colusa site on the Sacramento River. Virtually all of the trace elements exist in Spring Creek in the dissolved form. On entering Keswick Reservoir, the metals are at least partially converted by precipitation or adsorption to the particulate phase. Despite this observation, few of the elements are removed by settling; instead the majority is transported, associated with colloids, downriver, at least to the Bend Bridge site, which is 67 km from Keswick Dam. Most trace elements are strongly associated with the colloid phase going downriver under both low- and high-flow conditions.

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Knowledge of the spatial and temporal distribution of trace elements in the Sacramento River from Shasta Dam to the delta in San Francisco Bay plays an important role in understanding the impact of mining, agriculture, urban development, and other land-use activities on water quality in north-central California (Gaillardet et al. 2003; Alpers et al. 2000a). Drainage from abandoned or inactive mines, such as those occurring at Iron Mountain, California, can contribute large quantities of toxic trace elements, such as cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn) to the ecosystem of the river, potentially influencing fish populations and causing other environmental concerns (Montoya et al. 1988). Water from the Sacramento River is used extensively for agricultural purposes in north-central California, and irrigation return drainage may contribute significant quantities of agriculturally related trace elements.

Published online: 23 December 2011

The interaction of dissolved trace elements with suspended sediment materials can be an important process in controlling their transport through the hydrologic system (Smith et al. 1992; Davis et al. 1991; Ingri and Widerlund 1994; Alpers et al. 2000b; Antweiler et al. 2000). Fine particle-size sediments (<1 μm in diameter), also referred to as "clay-size colloidal material" (operationally defined as grain size between approximately 0.005 and 1.0 micrometer in diameter), have a high surface area that can strongly influence the sorption or coprecipitation of trace elements (Morel and Gschwend 1987; Kimball et al. 1995). Because suspended particulates in this size range do not physically settle from the aqueous phase (in the absence of aggregation), especially in dynamic hydrologic systems, they can effectively assist in the long-distance transport of trace elements (Lammers 1968; Droppo and Jaskot 1995).

In addition to the common toxic trace metals (e.g., Cd, Cu, Pb, and Zn), other trace constituents that are more difficult to determine, such as rare earths, precious metals, and low crustal-abundance elements, can be used individually or collectively to identify potential sources of contaminants (Aruga et al. 1995; McCleskey et al. 2010) and to provide additional tools to study the transport and fate of toxic materials. The availability of high-sensitivity multielement analytical techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS), provides a method for the quantitative determination of a wide variety of trace elements in water and digested sediment materials at indigenous concentration levels without preconcentration (Taylor and Garbarino 1991; Garbarino and Taylor 1995; Taylor 2001). Elements at greater concentrations, such as calcium (Ca), magnesium (Mg), and sodium (Na), as well as elements difficult to determine by ICP-MS, such as iron (Fe), are readily determined by ICP-atomic emission spectrometric (AES) techniques (Garbarino and Taylor 1979, 1995; Taylor 2001).

For this study, the Sacramento River was sampled at six fixed sites located from below Shasta Dam to the furthest downriver site at Freeport, California (Yolo Bypass during flood conditions). Sites are identified in Table 1, with location and distance from the mouth of the river (assigned by the United States Army Corps of Engineers), and a key to the location of these sites on the map in Fig. 1. The study area is located in north-central California. Several tributaries to the Sacramento River system in the vicinity of Keswick Reservoir were also sampled on a limited basis (Fig. 1 [inset]). The Spring Creek Arm of Keswick Reservoir receives the acidic drainage (pH approximately 4 [Alpers et al. 2000a]) from Spring Creek, which includes significant metal loading from the Iron Mountain site. At the western end of the Spring Creek Arm of Keswick Reservoir, Spring Creek mixes with dilute water from Whiskeytown Lake, which enters the Sacramento River system through the Spring Creek Power Plant, a part of the Central Valley Project completed in 1964, and is maintained by the Bureau of Reclamation. Additional sites were sampled, when possible, to provide information about the sources of metallic contaminants and the effects of variable hydrologic conditions. These additional sites are also included in Table 1 and Fig. 1, and data are presented in Alpers et al. (2000a). Because the focus of this study was the area in the vicinity of Iron Mountain and Keswick Reservoir, additional tributaries, such as Churn, Cottonwood, Mill, Rock, Butte, and Cache Creeks, as well as the Feather and American Rivers, were not sampled.

Samples were collected on six occasions, in July, September, November, and December 1996 and January and May/June 1997. During these periods, hydrologic characteristics varied considerably from relatively low flows during July and September 1996, to the lowest flow conditions in November 1996, to relatively high-flow conditions in December 1996 and severe flood conditions in January 1997. An additional site at the Yolo Bypass (Table 1; Fig. 1) was added for the January 1997 sampling period, during the "New Years" flood. Most of the Sacramento River was being diverted through the Yolo Bypass during this time, and this site represents the lowest point in the drainage basin where Sacramento River water was sampled. During this time, the site at Freeport (Table 1; Fig. 1) contained water almost exclusively originating from the American River (not sampled). A site at Coulsa Basin Drain (Table 1; Fig. 1) was added for the May 1997 sampling period to acquire additional information regarding agricultural irrigation return flows.

The use of ultraclean sampling, sample handling, processing techniques, and high-sensitivity analytical technology (Taylor et al. 1990, 2001) are necessary to produce data that have the maximum interpretability (Shiller and Boyle 1985; Coale and Flegal 1989; Taylor et al. 1990,

Table 1 Sampling sites and map key to locations mentioned in Fig. 1

Sites	Distance[a]	Map key
Sacramento River		
Below Shasta Dam	500	1
Below Keswick Dam	486	5
Above Bend Bridge	415	6
At Colusa	230	7
At Verona	126	8
At Freeport	74	9
Tributaries and bypasses		
Spring Creek near Keswick	488	4
Keswick Reservoir, Spring Creek arm	488	3
Flat Creek near Keswick	489	2
Yolo Bypass	134	11
Colusa Basin Drain	145	10

[a] Distance from the mouth of the river in kilometers

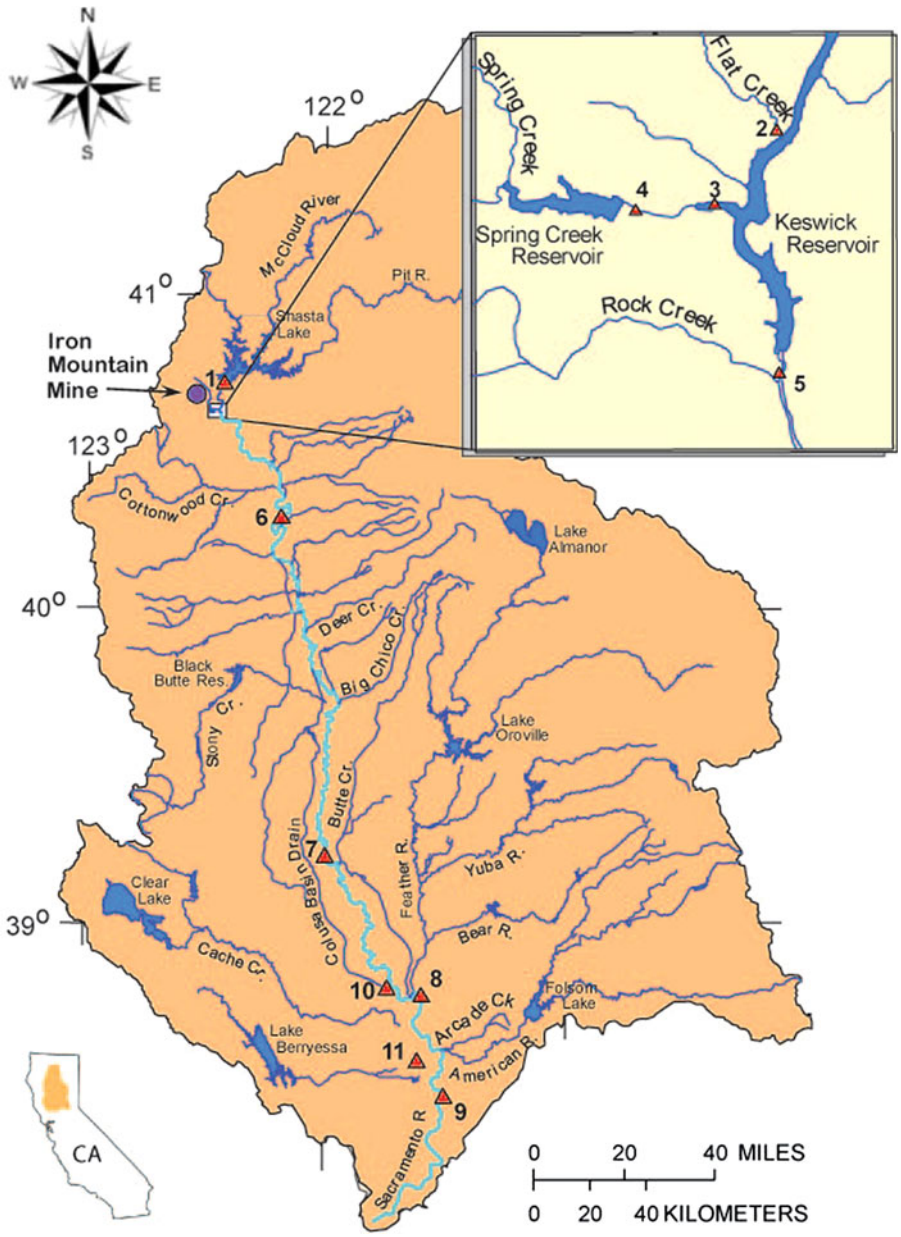

Fig. 1 Map of the Sacramento River Basin with sampling sites as identified in Table 1

1995; Windom et al. 1991; Benoit 1995; Taylor and Shiller 1995). Studies using trace-element data that are not collected with ultraclean handling techniques can result in serious misinterpretation of results. This study employed ultraclean techniques that were developed over many years to produce the most accurate results.

Materials and Methods

Sampling

Sampling was performed by techniques that were suitable for the collection of statistically representative and accurate samples (Leenheer et al. 1989; Kelly and Taylor 1996). Depth- and width-integrated protocols were used for collecting water and suspended sediment with a modified United States Geological Survey D-77 sampler using the equal-discharge-increment method (Webb et al. 1999) followed by compositing in a nonwetting polytetrafluoroethylene (PTFE)-coated stainless-steel churn. At some sites, water was pumped from the river using PTFE tubing with a peristaltic pump. Relative velocities of the river at five or more points along a section across the river were determined during water sample collection for the United States Geological Survey National Water-Quality Assessment Program (Hirsch et al. 1988). These relative velocities were then used to determine volumes to be pumped from each point in the river for compositing. Although this modified method probably did not provide a representative sample of greater

grain-size suspended sediment (silt and sand), which are more abundant near the bottom of the river channel, this method provided a representative sample of the dissolved and clay-sized (colloidal) suspended material (<1 μm in diameter). It is assumed that the colloid material is well-mixed vertically in the river and that this modified equal-width-increment method accounts for adequate width integration (Kelly and Taylor 1996). After compositing, samples were representatively split using a conventional churn splitting technique (Leenheer et al. 1989) into aliquots for field measurements (alkalinity, pH, specific conductance, and suspended sediment concentration), trace and major elements, and anions.

For safety reasons, samples from directly below Keswick Dam and Shasta Dam were collected by pumping with a peristaltic pump on the shore using PTFE tubing from a point location in the river. The river below these dams was considered to be well-mixed due to the narrow channel and turbulent flow. Therefore, it is assumed that a hydrologically representative sample was collected from these two point locations. A short length of silicone tubing essential to the function of the peristaltic pump was dedicated to each field site to prevent potential cross-contamination among samples. The silicone tubing was acid cleaned between sampling events.

At several of the other locations (see Table 2 in Alpers et al. 2000a), sampling was accomplished by pumping with the same equipment from a boat to collect a depth- and width-integrated sample using a modified equal-width-increment method. The PTFE tubing was supported by a 3-m length of 5 cm-diameter polyvinyl chloride pipe, and the tubing was moved slowly from the surface to a depth of approximately 2.5 m during sampling.

To recover an adequate quantity of colloidal material for chemical analysis, a large volume (approximately 100 L) of whole water was collected for subsequent phase separation. This sample was collected using a peristaltic pump with PTFE tubing directly into HNO_3-cleaned 25-l polyethylene carboys at each of the verticals that were used to create the composite samples.

Sample Processing

To prepare a subsample of the dissolved fraction, a portion of the composited sample was filtered using a Minitan (Millipore) tangential-flow ultrafiltration procedure to separate suspended particulate matter, including colloidal material, from the dissolved phase. A separate set of four (in a stack) 10,000 nominal molecular weight unit pore-size regenerated-cellulose membranes were used at each sampling site to minimize cross-contamination. The ultrafiltrate yielded a dissolved sample consisting of solvated ions and eliminating particulate matter of ≥0.005-μm diameter. Before filtration, the membranes were acid-rinsed with a 1% (v/v) solution of high-purity HNO_3 to remove adsorbed contaminants on the filters followed by thorough rinsing with 18 MΩ deionized water. Tests from previous studies demonstrated that the acid-rinsing process did not deleteriously affect the membrane filters (Leenheer et al. 1989). Duplicate 250-ml samples were collected in acid-washed, high-density polyethylene bottles and preserved by acidification with concentrated high-purity HNO_3. This filtration approach provided a substantially different "dissolved" sample than that traditionally reported in other studies using filters with 0.2- to 0.45-μm pore size, (Goldstein and Jacobsen 1998; Sholkovitz 1995; Shiller and Boyle 1987; Shiller et al. 2001; Shiller 2002; Tricca et al. 1999; Gaillardet et al. 2003; Ingri et al. 2000), resulting in substantially different results and corresponding geochemical interpretations (Benoit 1995). Clearly, when samples are filtered at 0.2 to 0.45 μm, a substantial and variable amount of suspended colloidal material may be included in the dissolved sample (Taylor and Shiller 1995; Shiller and Taylor 1996).

The 100-l sample collected for the recovery of suspended colloids was allowed to gravity-settle at room temperature for 1 h to separate the silt-size fraction material (>5 μm in diameter). After settling, the supernatant phase was filtered with a tangential-flow ultrafilter (Pellicon Model OM-141;

Table 2 Average dissolved measurement detection limits

Element	DL μg/L	Element	DL μg/L
Al	0.05	Mo	0.03
As	0.04	Na[a]	70
Ba	0.01	Nd	0.003
Be	0.02	Ni	0.02
Bi	0.01	Pb	0.006
Ca[a]	20	Pr	0.0005
Cd	0.006	Rb	0.002
Ce	0.001	Re	0.001
Co	0.01	Sb	0.02
Cr	0.2	Se	0.2
Cs	0.06	SiO_2[a]	50
Cu	0.02	Sm	0.003
Dy	0.002	Sr	0.02
Er	0.002	Tb	0.0007
Eu	0.001	Tl	0.005
Fe[a]	0.7	Tm	0.0005
Gd	0.003	U	0.002
Ho	0.0005	V	0.05
K[a]	10	W	0.004
La	0.0005	Y	0.0004
Li	0.1	Yb	0.001
Lu	0.0005	Zn	0.08
Mg[a]	20	Zr	0.01
Mn	0.02		

[a] Determined by ICP-AES

Millipore) using a stack of eight individual 0.005 μm-diameter pore size polyethersulfone-membrane filters (Millipore Corporation 1998). The Pellicon, rather than the Minitan, was chosen for isolating the colloidal-size particulate material because of the greater surface area of the filters (7,440 cm^2 for the Pellicon compared with 240 cm^2 for the Minitan), thus providing a much greater efficiency in processing the 100-l sample. As with the Minitan, separate filter stacks were used at each of the sampling sites to avoid cross-contamination, and all filters were HNO_3-and deionized water-rinsed before filtration.

After the ultrafiltration process was completed, the particulate material was flushed from the surface of each of the membranes by gentle agitation, producing a concentrated slurry of the colloidal particulates, which was collected in a PTFE bag and immediately transferred to a 1-l acid-rinsed PTFE bottle, chilled, and transported to the laboratory for dewatering.

The colloid concentrate was dewatered by spinning successive 50-ml quantities in a polycarbonate centrifuge tube at 12,000 revolutions per minute at 10°C using a Sorval model RC-5B refrigerated centrifuge. Because 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 h to remove the residual moisture.

Laboratory Methods

Instrumentation

Trace element determinations were performed with an inductively coupled plasma-mass spectrometer (ICP-MS) (Elan Model 5000; Perkin Elmer). Aqueous samples were directly introduced into the plasma with a cone-spray pneumatic nebulizer. Multiple internal standards (indium, iridium, and rhodium), selected to cover the entire analytical mass range, were used to normalize the system for drift. Trace elements determined included aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), cerium (Ce), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lithium (Li), lutetium (Lu), manganese (Mn), molybdenum (Mo), neodymium (Nd), nickel (Ni,) lead (Pb), praseodymium (Pr), rubidium (Rb), rhenium (Re), antimony (Sb), selenium (Se), samarium (Sm), strontium (Sr), terbium (Tb), thallium (Tl), thulium (Tm), uranium (U), vanadium (V), tungsten (W), yttrium (Y), ytterbium (Yb), zinc (Zn), and zirconium (Zr). Details of the specific analysis techniques, procedures, and instrumental settings are described elsewhere (Garbarino and Taylor 1995; Taylor 2001; Stroh 1992). Trace concentrations of mercury (Hg) were also determined but are reported elsewhere (Roth et al. 2001). The investigators refer the reader to that article for details of the distribution of inorganic Hg in the Sacramento River water and colloidal sediment material.

Elements present at relatively greater concentration levels, including Ca, Mg, Na, and SiO_2, were determined using ICP-AES techniques using a Jarrell-Ash Atomcomp 975 multichannel emission spectrometer. Fe was also determined by this technique because there is an inability to determine it at low concentration levels by ICP-MS due to unresolved isobaric interferences at its principal isotopes. A description of ICP-AES analysis conditions and procedures are reported by Garbarino and Taylor (1979). Potassium was determined by an ICP-AES technique 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). Detection limits and precisions vary slightly for each analysis run. A summary of average dissolved detection limits for both ICP-MS and ICP-AES (determined at the 95% confidence level) for the study are listed in Table 2.

Sample Preparation

The freeze-dried colloidal material was subsampled and decomposed by digestion in a laboratory-grade microwave digestion oven (Model mls 1200 mega; Milestone) using a combination of high-purity nitric (HNO_3), hydrochloric (HCl), and hydrofluoric (HF) acids in a PTFE closed-digestion vessel (Alpers et al. 2000a). After digestion, high-purity boric acid was added to the solutions to complex the excess fluoride that was present from the digestion.

Multielement instrument calibration standards for ICP-AES determinations were matrix-matched with comparable concentrations of reagents used in the digestion procedure. This was performed to simulate the chemical composition of the digest, thus minimizing interelement suppression interference effects. Aliquots resulting from a 10:1 dilution of the digest solutions were used for the high-sensitivity ICP-MS determinations.

Quality Assurance

Extensive effort was employed to perform quality assurance. All samples for dissolved constituents (ultrafilter effluent) were field sampled in duplicate, and all laboratory determinations were performed in triplicate. Because only limited quantities of the freeze-dried colloidal material were available, only single digestions were performed. Solutions of each colloid total digestion were analyzed in triplicate. Field process blanks for each step of sampling and processing, laboratory reagent blanks, and deionized water blanks were analyzed extensively (10% frequency).

Both certified and secondary reference materials were analyzed at a combined frequency of 20% of the samples. Certified reference materials for dissolved constituents from the National Institute of Standards and Technology (NIST) included SRM 1643c and 1643d. In addition, 16 secondary reference materials were used for the elements for which "most probable values" were reported (Peart et al. 1998). For all other elements, including rare earths, standards were prepared by the dilution of concentrates supplied by High Purity Standards, Inc. (Charleston, SC). The reference standard used for the colloid analyses was NIST 2704 Buffalo River Sediment standard reference material. A portion of this standard was digested and analyzed at least once with every batch of six samples digested.

Table 3 lists the results of the analysis of selected metals in standard reference materials used throughout the project. These results are representative of the quality of the data collected for all metals determined. The table lists results for both dissolved analyses using NIST SRM 1643d and sediment analyses using NIST SRM 2704 (Taylor et al. 2000).

Finally, field spike additions were used to establish the percent recovery of selected elements (Alpers et al. 2000a). Typical recoveries at the 90% confidence level for each element ranged from 85 to 115% for Pb (nominal value 50 μg/L) to 90 to 110% for Co (nominal value 5 μg/L). All blanks for filtered samples were measured at or below the respective detection limits for each of the elements determined.

Data Analysis

Concentration data of trace metals for filtered (dissolved) and colloid suspended materials are provided in Alpers et al. (2000a) and Antweiler et al. (2000). A summary of the mean dissolved and mean "equivalent-colloid" concentrations (based on the concentration of the colloids in the sample multiplied by the concentration of the metal in the colloid) for the six sampling periods are listed in Table 4 for each of the mainstem Sacramento River and major tributary sites (Bi and Re were undetected in any of the samples). Data are grouped in approximately downstream order according to the distances of sampling sites from the mouth of the Sacramento River.

Box plots (showing outliers) for both dissolved and equivalent colloidal metal concentrations of the selected elements (Al, Pb, Cd, W, Gd, and Yb) are shown in Fig. 2 for all data collected from the mainstem Sacramento River sites for all sampling periods. For the selected metals, this figure demonstrates that dissolved concentrations generally are observed at lower median concentration values than those for these metals associated with colloidal material. In addition, the concentration distributions for dissolved metals (illustrated by the length of the box plots) are smaller than those observed for the metals associated with the colloidal material. This is expected because of the increased variability in the equivalent colloidal metal concentration, which is due in part to the inclusion of the concentration of the colloidal matter in the calculation of the equivalent metal colloidal concentration

The approach to using downstream spatial distribution diagrams were similar to those described in Taylor et al. (2001) for the selected trace elements, Cu and Pb, and the element Al, as shown in Figs. 3 through 5, respectively. Data are plotted for both dissolved (panel A) and equivalent colloids (panel B) for all six sampling periods (ranging from the lowest flow in November 1996 to the highest flow in January 1997). To show all of the data on the plots, the

Table 3 Summary of representative quality-assurance results for selected metal determinations in National Institute of Standards and Technology Standard Reference Materials 1643d (water) and 2704 (Buffalo River Sediment)

Metal	Conc.	SRM 1643d					Conc.	SRM 2704				
		n	*M*	MAD	Cert	SDs		*n*	*M*	MAD	Cert.	SDs
Ba	μg/L	306	502	18	507	8.9	μg/g	19	400	30	414	12
Ca	mg/L	18	34.7	0.5	35	–	wt.%	19	2.70	0.15	2.60	0.03
Cd	μg/L	622	6.5	0.6	6.47	0.37	μg/g	19	3.7	0.2	3.45	0.2
Cu	μg/L	622	21.3	1.5	20.5	3.8	μg/g	19	96.0	5.9	98.6	5.0
Fe	μg/L	18	106	4	99	8	wt.%	19	4.2	0.2	4.11	0.10
Pb	μg/L	622	18.2	0.7	18.2	0.6	μg/g	19	150	10	161	17
Sr	μg/L	306	296	10	295	3	μg/g	19	120	15	130	–
Tl	μg/L	260	7.3	0.3	7.3	0.3	μg/g	19	1.00	0.03	1.06	0.07
V	μg/L	282	35.3	1.3	35.1	1.4	μg/g	19	89	3	95	4
Zn	μg/L	622	72	3	72.5	0.7	μg/g	19	440	15	438	12

Where *n* number of standard measurements, *Conc* concentration, *M* median determined value, *MAD* median absolute deviation (Rousseeuw 1990), *Cert* certified value, *SDs* SD of certified value, – not available

Table 4 Summary of mean dissolved concentration values (μg/L), mean equivalent colloid concentration values (μg/L), and percentage of element associated with colloidal material for each mainstem Sacramento River and major tributary sampling sites for six sampling periods ranging from July 1996 to May 1997 (listed in downriver order)

Sites	Al	As	Ba	Be	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Gd	Ho	La	Li	Lu	Mn
Mainstem																				
Below Shasta dam																				
Dissolved	2.27	0.97	12.2	<0.04	0.023	0.003	<0.01	0.28	<0.06	0.69	0.004	<0.003	<0.001	4.8	0.005	<0.0007	0.0045	1.9	<0.0006	0.50
Colloid	352	<2	1.62	0.0040	0.0062	0.059	0.063	0.46	0.017	0.775	0.012	0.0077	0.0026	216	0.016	0.0023	0.024	0.14	0.0012	6.46
% Colloid	99		12		21	95		62		53	75			98	76		84	7		93
Below Keswick Dam																				
Dissolved	9.49	0.84	11.0	<0.04	0.042	0.005	0.04	0.28	<0.06	1.30	0.004	0.003	<0.002	3.2	0.005	0.0009	0.0047	1.7	0.0007	2.8
Colloid	462	<1	3.01	0.0070	0.02	0.12	0.15	0.97	0.02	2.58	0.028	0.018	0.0051	397	0.036	0.0054	0.045	0.15	0.0026	6.78
% Colloid	98		21		32	96	79	78		66	88	86		99	88	86	91	8	79	71
Bend bridge																				
Dissolved	4.78	0.70	12.8	<0.04	0.017	0.004	<0.01	0.27	<0.06	0.71	<0.003	<0.004	<0.002	2.8	0.004	0.0008	0.0033	1.5	<0.0004	1.5
Colloid	2350	<2	19.2	0.054	0.032	1.01	0.78	6.44	0.19	4.94	0.12	0.077	0.028	1890	0.17	0.022	0.42	1.38	0.012	31.2
% Colloid	100		60		65	100		96		87				100	98	96	99.	48		95.
Colusa																				
Dissolved	2.80	1.1	16.0	<0.04	<0.008	0.005	<0.01	0.26	<0.06	0.78	0.005	<0.003	<0.002	2.9	0.006	<0.002	0.0039	1.9	0.0005	2.0
Colloid	7810	<20	60.3	0.170	0.091	2.73	2.61	18.4	0.69	12.1	0.35	0.25	0.079	6650	0.45	0.070	1.14	5.49	0.039	121
% Colloid	100		79			100		99		94	99			100	99		100	74	99	99
Verona																				
Dissolved	1.95	1.06	17.5	<0.04	<0.008	0.005	<0.01	0.23	<0.003	0.69	<0.003	<0.003	<0.002	2.9	0.004	<0.0007	0.0034	1.4	0.0004	1.6
Colloid	2170	<2	14.2	0.043	0.042	0.752	0.78	5.68	0.11	5.17	0.090	0.061	0.022	1930	0.13	0.017	0.33	1.41	0.0093	48.1
% Colloid	100		45			100		96		88				100	98		99	50	96	97
Freeport																				
Dissolved	2.78	0.75	14.5	<0.04	<0.008	0.007	0.016	0.22	<0.003	0.68	<0.004	<0.003	<0.002	3.5	0.005	<0.0007	0.0052	1.0	0.0007	2.2
Colloid	3940	<7	35.9	0.10	0.056	2.74	1.10	7.09	0.25	6.29	0.17	0.096	0.044	2840	0.25	0.030	1.13	1.78	0.014	59.0
% Colloid	100		71			100	99			90				100	98		100	64	95	96

Sites	Mo	Nd	Ni	Pb	Pr	Rb	Sb	Se	Sm	Sr	Tb	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Mainstem																				
Below Shasta Dam																				
Dissolved	0.28	0.008	0.63	0.006	0.0014	2.1	0.033	0.18	<0.006	47	<0.0007	<0.008	<0.0006	0.090	3.2	0.044	0.017	0.0023	2.2	0.013
Colloid	<0.03	0.039	0.576	0.058	0.008	0.006	<0.04	0.011	0.435	0.278	0.0023	0.0011	0.0009	0.0076	0.60	0.0073	0.052	0.0077	1.47	1.05
% Colloid		83	48	91	85	0.3		5.8		0.6				7.9	16	14	75	77	40	99
Below Keswick Dam																				
Dissolved	0.28	0.009	0.85	0.015	0.0015	1.8	0.039	0.11	0.004	42	<0.0007	<0.008	<0.0006	0.074	2.5	0.043	0.024	0.0021	4.1	0.011
Colloid	<0.05	0.075	1.60	0.187	0.015	0.016	0.026	0.024	0.619	0.339	0.0053	0.0024	0.0022	0.012	1.30	0.011	0.121	0.017	4.31	1.48
% Colloid		89	65	93	91	1	40	18	99	0.8				14	34	20	83	89	51	99
Bend Bridge																				
Dissolved	0.25	0.006	1.0	0.007	0.001	1.5	0.041	0.3	<0.004	48	<0.0008	<0.008	<0.0006	0.061	2.3	0.034	0.014	0.0020	1.2	0.012
Colloid	<0.3	0.475	5.89	0.664	0.110	0.050	0.150	0.129	1.54	2.53	0.021	0.014	0.0095	0.074	5.90	0.053	0.566	0.076	8.39	7.04
% Colloid		99	85	99	99	3.2	79	30		5				55	72	61	98	97	87	100

Table 4 continued

Sites	Mo	Nd	Ni	Pb	Pr	Rb	Sb	Se	Sm	Sr	Tb	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Colusa																				
Dissolved	0.32	0.011	1.0	0.009	0.0016	1.3	0.072	0.16	<0.005	68	<0.0008	<0.008	<0.0006	0.086	2.6	0.040	0.016	0.0024	0.46	0.017
Colloid	<1	1.39	15.4	2.04	0.315	0.169	0.426	0.375	7.69	10.3	0.069	0.051	0.030	0.240	22.0	0.194	1.54	0.244	21.8	26.6
% Colloid		99	94	100	99	12	86	70		13				74	89	83	99	99	98	100
Verona																				
Dissolved	0.34	0.007	0.47	0.012	0.0009	1.0	0.060	0.10	<0.004	68	<0.0008	<0.008	<0.0006	0.13	2.7	0.033	0.013	0.0015	0.36	0.013
Colloid	<0.04	0.396	4.96	0.685	0.088	0.042	0.130	0.101	2.77	3.84	0.017	0.010	0.0071	0.072	5.74	0.069	0.403	0.055	7.21	5.92
% Colloid		98	91	98	99	4	68	50		5.3				36	68	68	97	97	95	100
Freeport																				
Dissolved	0.23	0.016	0.46	0.009	0.0020	1.0	0.047	0.14	<0.006	56	<0.0008	<0.008	<0.0006	0.092	2.0	0.026	0.013	0.0023	0.65	0.020
Colloid	<0.4	1.01	5.99	1.24	0.251	0.071	0.211	0.232	2.11	6.78	0.032	0.022	0.012	0.186	7.84	0.171	0.742	0.091	9.98	8.38
% Colloid		98	93	99	100	6.6	82	62		11				67	80	87	98	98	94	100

Sites	Al	As	Ba	Be	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Gd	Ho	La	Li	Lu	Mn
Tributaries																				
Spring Creek																				
Dissolved	2830	1.41	17	0.077	6.0	5.7	7.9	0.37	0.094	470	2.2	1.20	0.28	4300	3.1	0.40	2.4	4.6	0.12	280
Colloid	1670	1	7.40	0.08	0.02	0.06	0.25	1.18	0.07	10.6	0.027	0.023	0.003	15400	0.031	0.006	0.020	0.31	0.004	2.1
% Colloid	37	41	30.	51	0.33	1	3	76	43	2	1	2	1	78	1	1	1	6	3	1
Keswick Resevoir (SCA)																				
Dissolved	23	0.20	5.6	<0.02	0.09	0.01	0.18	0.36	<0.002	2.7	0.004	0.003	<0.001	4.00	0.01	0.001	0.0051	0.69	<0.0005	6.8
Colloid	425	<0.1	1.33	0.01	0.02	0.22	0.23	2.69	0.015	12.7	0.085	0.053	0.014	393	0.12	0.017	0.085	0.12	0.006	5.6
% Colloid	37		30		0.3	1	3	76		2	1	2		78	1	1	0.8	6		0.7
Flat Creek																				
Dissolved	16	0.27	5.3	<0.02	0.10	0.015	0.25	<0.05	<0.02	1.7	0.013	0.009	0.002	4.5	0.017	0.0028	0.007	0.23	0.002	56
Colloid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
% Colloid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Yolo Bypass																				
Dissolved	2.7	0.78	13	<0.01	<0.005	0.011	0.021	0.12	<0.002	0.91	0.004	0.003	0.001	6.0	0.006	0.0010	0.008	0.78	<0.0004	1.7
Colloid	14400	<7	121	0.32	0.12	5.62	4.03	30.2	1.40	18.7	0.63	0.42	0.14	10400	0.79	0.12	2.30	8.50	0.063	144
% Colloid	100		90			100	100	100		95	99	99	99	100	99	99	100	92		99
Colusa Basin Drain																				
Dissolved	0.89	2.8	91	<.02	<0.005	0.007	0.036	<0.2	<0.02	1.3	0.008	0.01	<0.001	3.2	0.007	0.0022	0.008	8.7	0.002	0.20
Colloid	13000	<8	103	0.29	0.071	5.30	3.86	28.9	1.01	13.7	0.55	0.34	0.13	11100	0.72	0.10	2.25	11.6	0.048	241
% Colloid	100		53			100	99			91	99	97		100	99	98	100	57	96	100

Sites	Mo	Nd	Ni	Pb	Pr	Rb	Sb	Se	Sm	Sr	Tb	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Tributaries																				
Spring Creek																				
Dissolved	<0.05	5.2	2.7	2.5	1.0	1.7	<0.1	0.99	2.0	26	0.40	0.21	0.13	0.15	<0.04	0.013	11	0.85	900	0.035

Table 4 continued

Sites	Mo	Nd	Ni	Pb	Pr	Rb	Sb	Se	Sm	Sr	Tb	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Colloid	0.63	0.05	2.04	3.25	0.030	0.34	0.24	0.28	0.016	0.43	0.005	0.015	0.003	0.02	0.7	0.029	0.17	0.029	4.36	<20
% Colloid		1	43	57	3	17		22	0.8	1.6	1.2	6.7	2.3	12		69	1.5	3.3	0.5	
Keswick Reservoir (SCA)																				
Dissolved	0.09	0.010	2.8	0.011	0.002	0.27	0.03	<0.2	<0.003	18	<0.0008	<0.004	<0.0003	0.021	0.36	0.022	0.027	<0.001	10	<0.008
Colloid	<0.02	0.20	6.11	0.13	0.036	0.066	0.009	<0.03	0.073	0.20	0.017	0.0008	0.006	0.015	0.65	0.024	0.39	0.039	8.17	<1
% Colloid		95	69	92	95	20	23			1.1				42	64	52	94		45	
Flat Creek																				
Dissolved	0.15	0.020	0.41	<0.01	0.0033	0.18	0.04	<0.1	0.013	17	0.002	<0.004	0.001	<0.002	0.21	<0.004	0.083	0.010	8.9	<0.004
Colloid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
% Colloid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Yolo Bypass																				
Dissolved	0.24	0.014	0.88	0.012	0.0024	0.48	0.075	0.13	0.005	53	0.001	<0.004	0.0004	0.060	1.7	0.024	0.026	0.003	0.20	0.017
Colloid	<0.4	2.59	24.5	3.17	0.59	6.34	0.29	0.76	0.68	14.4	0.12	0.082	0.053	0.42	36.0	0.35	2.74	0.42	25.9	38.9
% Colloid		99	97	100	100	93	79	85	99	21	99		99	88	95	94	99	99	99	100
Colusa Basin Drain																				
Dissolved	2.6	0.012	1.1	0.010	0.002	0.48	0.26	0.32	<0.003	440	0.001	<.004	0.002	1.3	9.1	0.038	0.066	0.01	0.30	0.013
Colloid	<0.5	2.41	27.3	2.89	0.58	6.91	0.19	0.69	0.63	19.3	0.11	0.071	0.041	0.29	30.5	0.29	2.41	0.34	27.3	28.9
% Colloid		100	96	100	100	94	42	68		4.2	99		95	18	77	88	97	97	99	100

Values represent actual calculated detection limits for specific analysis runs; *SCA* Spring Creek Arm of Keswick Reservoir. Detection limits determined at the 95% confidence level ($n = 15$)

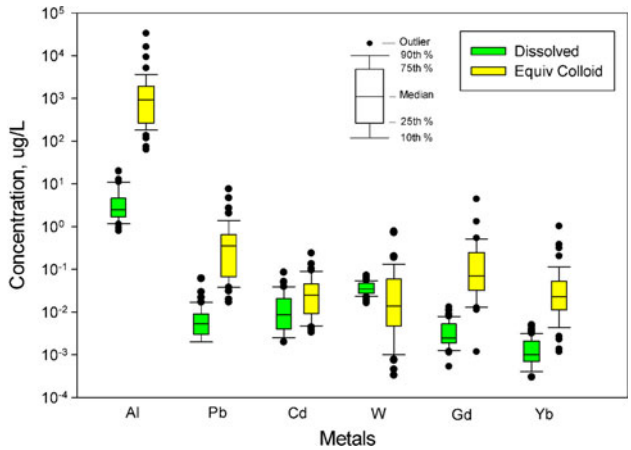

Fig. 2 Concentrations of Al, Pb, Cd, W, Gd, and Yb in both dissolved (green) and colloidal material (yellow) in Sacramento River for all sampling sites and all sampling periods

ordinate axis has a broken scale to facilitate viewing. Error bars represent the precision of replicate analytical measurements. Lines are used to connect data points for visual interpretation only and should not be used to imply interpolative significance.

Figure 3a shows the downstream concentration profiles for Cu. This figure also shows data points for Spring Creek in both November and December 1996, which are substantially greater dissolved concentrations (approximately 530 and 420 µg/L, respectively) than the values measured in the Sacramento River sampled below Keswick Reservoir (approximately 1 to 3 µg/L). Equivalent colloid concentrations are shown in Fig. 3b.

The downstream concentration profile for dissolved Pb (Fig. 4a) shows a substantial increase in concentration at the site below Keswick Dam compared with the further-upstream site, i.e., below Shasta Dam, for the December

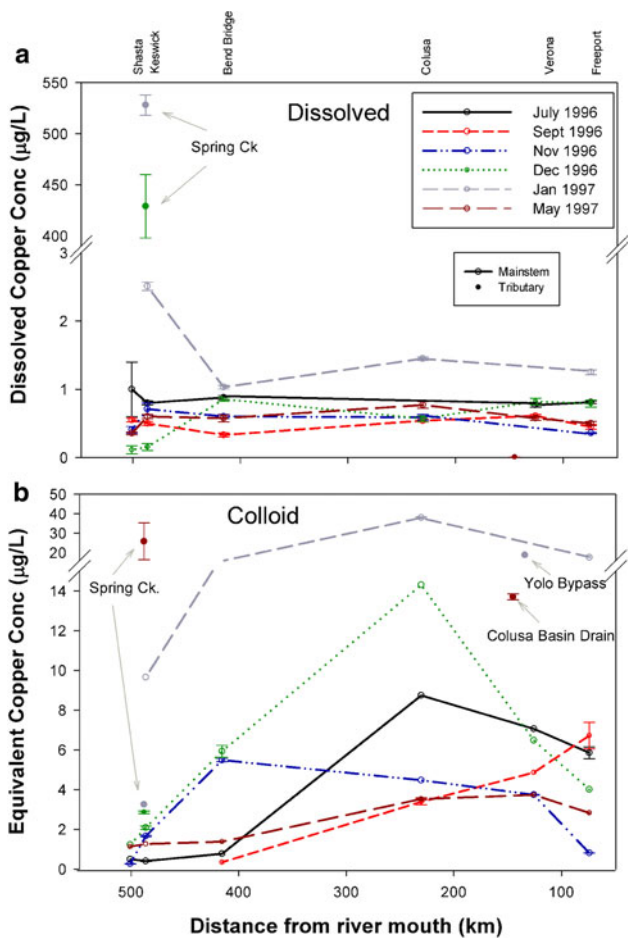

Fig. 3 Downstream distribution plots for Cu in the Sacramento River mainstem and selected tributaries for all six sampling periods. **a** Dissolved concentrations (µg/L). **b** Equivalent colloid concentrations (µg/L). *Error bars* represent the precision of replicate analytical measurements. *Lines* used to connect data points are for visual interpretation only and should not be used to imply interpolative significance

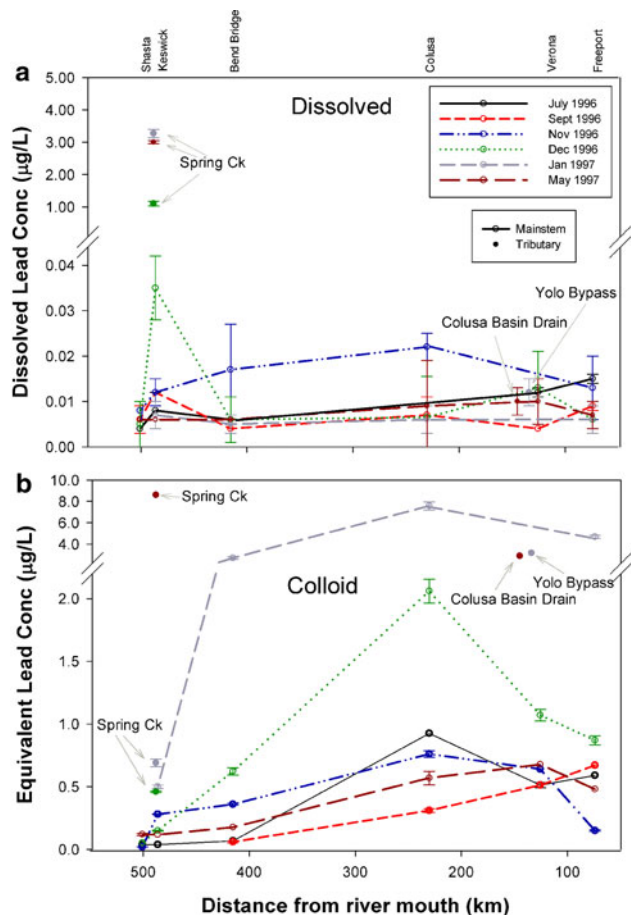

Fig. 4 Downstream distribution plots for Pb in the Sacramento River mainstem and selected tributaries for all six sampling periods. **a** Dissolved concentrations (µg/L). **b** Equivalent colloid concentrations (µg/L). *Error bars* represent the precision of replicate analytical measurements. *Lines* used to connect data points are for visual interpretation only and should not be used to imply interpolative significance

1996 sampling. This can possibly be explained by the increased concentration of Pb in Spring Creek from mine drainage (note Fig. 4 data point, which enters Keswick Reservoir upstream from the dam). This is similar to the Al profile (Fig. 5a) and the increased concentration of dissolved Al in Spring Creek for the same sampling period. Other trace elements, including Ce, Cu, Fe, and Mn, show similar behavior.

Most of the trace elements, including the rare earth elements (REEs), are predominately observed in the dissolved phase in the upper part of the Sacramento River (Spring Creek and Keswick Reservoir). The colloid phase transports greater amounts per liter of river water downstream of Keswick Dam than the dissolved phase for many of the elements analyzed. Proceeding downriver, the proportion of trace elements associated with the colloidal material increases from 90% to 99.8% depending on the sampling period.

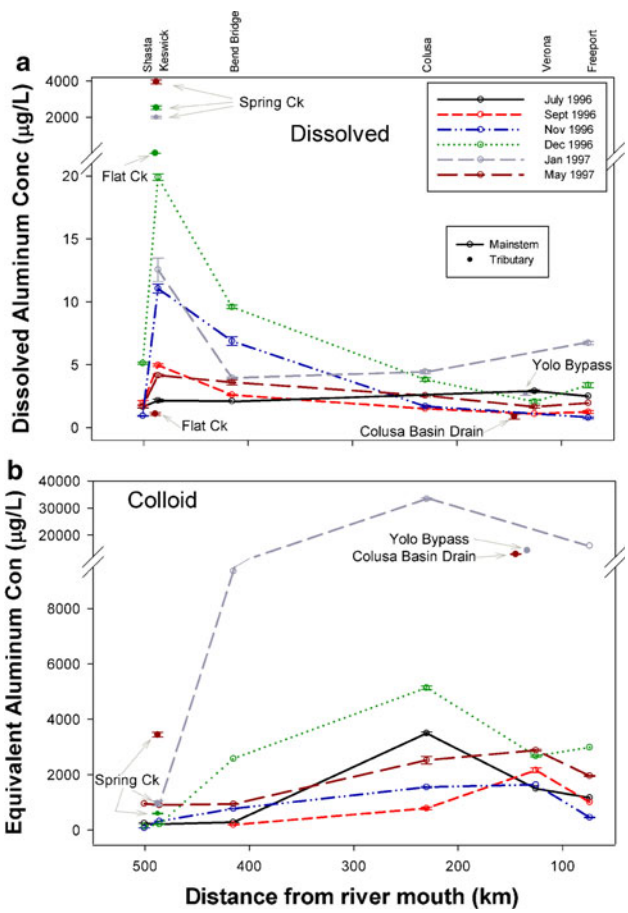

Fig. 5 Downstream distribution plots for Al in the Sacramento River mainstem and selected tributaries for all six sampling periods. **a** Dissolved concentrations (µg/L). **b** Equivalent colloid concentrations (µg/L). *Error bars* represent the precision of replicate analytical measurements. *Lines* used to connect data points are for visual interpretation only and should not be used to imply interpolative significance

A substantial proportion of the trace metals transported in the Sacramento River between Shasta Dam and Freeport occur in colloidal form. Colloids represent the dominant form of Al, Fe, and Pb in the downriver water column and are an important factor in the distribution of other trace metals (Alpers et al. 2000a). Figure 5a shows the downstream distribution of Al, and Fig. 5b shows the distribution of equivalent Al concentrations for colloids. Diagrams for other trace metals associated with the colloidal material show similar distributions to that observed for Al. Greater distribution variability in concentration between trace metals would be expected for suspended material than is observed. This observation can probably be explained due to the non-settling nature of colloidal material, thereby making the distributions more similar to dissolved concentrations.

The equivalent trace element concentrations originating from the suspended colloids are relatively low in the upper reach of the river, gradually increasing to a maximum somewhere in the river reach near the Colusa site, and followed by a decrease to some nominal concentration level similar to that observed in the upper reach of the river. This observation suggests that there is possibly a source of input of colloids in the sediment between the Bend Bridge and Colusa sites, which is enriched in trace elements. This input is probably from one or more of the several tributaries entering the Sacramento River in this reach and probably has a greater relative impact under low-flow conditions.

In addition, Fig. 6 shows a distribution plot of the ratio of the Zn concentration in the dissolved phase to the concentration of Zn in the isolated colloidal material plotted *versus* the downstream distance on the Sacramento River, Spring Creek, and the Spring Creek Arm of Keswick

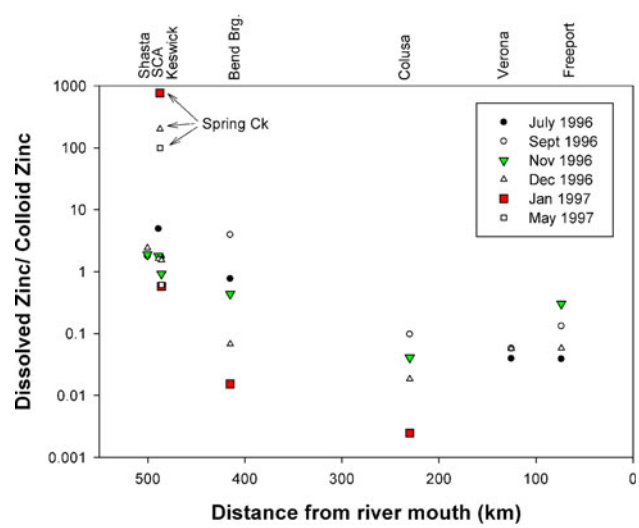

Fig. 6 Plot of the ratio of dissolved Zn to the colloidal Zn *versus* Sacramento River sampling sites (including Spring Creek and Spring Creek arm of Keswick Reservoir) for six sampling periods. SCA = Spring Creek Arm of Keswick Reservoir

Reservoir. Zn is a representative element that shows the same behavior as Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl, Zr, and all of the REEs. This figure shows that in Spring Creek, the majority of Zn is present in the dissolved phase (>99.9%). In the Spring Creek Arm of the Keswick Reservoir and to sites downstream in the Sacramento River, the proportion of Zn in the dissolved phase *versus* the amount present in the colloidal phase rapidly decreases until reaching the Colusa site, where approximately 5% of the Zn, depending on the sampling period, is dissolved with the remainder in the colloidal form. From Colusa to sites further downstream, this proportion remains virtually constant, suggesting that equilibrium is reached. The other metals previously mentioned have somewhat different absolute proportions, but the observed trends are similar.

It can also observed in Fig. 6 that during the sampling period of highest discharge (January 1997) the highest proportion of metals are observed associated with the colloid material (often >99.9%), suggesting that the "dissolved-to-colloid ratio" is dependent on the total amount of suspended sediment present. It is also apparent that most, if not all, of the trace metal load from Spring Creek (predominately in the dissolved phase) is actually transported the entire distance downriver regardless of whether it is in the dissolved or colloid phase. Regardless of phase, large concentrations of metal are being delivered to San Francisco Bay, which potentially becomes available to the Bay biota.

Conclusion

The results of this study indicate that during low-flow conditions, a marginal increase in dissolved trace element concentrations in the Sacramento River occurs in the Keswick Reservoir area, probably resulting from contributions from Iron Mountain by way of Spring Creek. Below the Keswick Reservoir, the concentrations rapidly decrease downriver and stabilize at relatively low concentration levels. Under high-flow conditions (January 1997), substantially greater concentrations of dissolved trace metals are introduced into Keswick Reservoir, as reflected in the composition of water released from Keswick Dam in January 1997 (Cu = 2.5, Cd = 0.085, and Zn = 8 μg/L).

Most of the trace elements are observed in Spring Creek in the dissolved form. On entering the Spring Creek Arm of Keswick Reservoir, the metals are at least partially converted by precipitation or adsorption to the particulate phase. Despite this observation, few of the elements are removed by settling; instead, the majority are transported downriver associated with the suspended colloids. Most trace elements are strongly associated (>80%) with the colloid phase transported downriver to the Colusa site and beyond under both low- and high-flow conditions.

The equivalent trace element concentrations associated with colloidal material consistently increased between the Bend Bridge and Colusa sites. For example, in November 1996, Cu increased in equivalent-colloid concentration from approximately 0.1 to 5 μg/L, whereas Cd increased from 0.005 to 0.06 μg/L and Zn from 1 to 8 μg/L. At high flow in January 1997, the trace element colloid-equivalent concentrations for Cu ranged from <10 to 38 μg/L; for Cd from <0.06 to 38 μg/L; and for Zn from <14 to 68 μg/L.

The REEs are observed at generally low concentrations, some at or near their measured detection limits. The dissolved rare earth concentrations in Spring Creek are approximately 900 times greater than those observed in the Sacramento River sites.

Acknowledgments The authors acknowledge the contributions of Joseph Domalgalski, Michael Hunerlach, Dale Peart, and Terry Plowman. We also thank Susan Riggins and James Crock for their review of an earlier version of this manuscript. The use of trade names is for identification purposes only and does not imply endorsement by the United States Geological Survey.

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