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DETERMINATIONOF ACID VOLATILESULFIDE AND SIMULTANEOUSLY EXTRACTEDMETALSIN CORE SEDIMENTS FROM THE KESWICKRESERVOIR, CA

Work Unit: 30070

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SAMPLE HISTORY:

In late January, 1994, sampling of sediment cores in the Keswick basin was conducted by United States Geological Survey (USGS) and California Fish and Game personnel. Upon collection, samples were shipped on ice to the National Fisheries Contaminant Research Laboratory (NFCRC). A total of four samples of core sediment were sent and were received on 1/26/94. These sediments were to be used to prepare elutriates for fish/invertebrate exposure studies. This report presents results for the core samples, which includes the analysis of acid volatile sulfides (AVS) and simultaneously extractable (SEM) metals (aluminum, cadmium, copper, iron, and zinc).

METHODS:

Sediment cores were received in plastic tubes of about 60 cm long and 6 cm I.D. Although we were asked to sample only the upper 18" of each 24" core, this did not seem practical for at least three of the four samples. First of all, it appeared that mixing of the core layers had occurred during shipping for all but sample #10365 (S010594-4 529-J2) because (a) cores were packed horizontally, (b) each contained significant water and an air bubble which promoted mixing, and (c) the grain size was very fine and showed signs of suspension and mixing. Secondly, for three of the samples, the high degree of water and fine particle size would have made it difficult to transfer a specific layer unless the core was first frozen, then cut, and finally thawed and homogenized -- all of which was hard to justify given that the integrity of the layers was uncertain. Sample #10365 was the exception because it did not contain a large water layer and appeared solid enough to allow for convenient transfer of the upper 18" layer. Therefore, for all samples except #10365, essentially the whole core was analyzed. This approach for preparing the sediment cores was approved by Bob Fujimura on 1/27/94.

Each sample (about 1700 mL) was transferred to an acid-cleaned, wide-mouth, two quart Mason jar by carefully removing the core end-caps and allowing the sediment to flow out into the jar. For sample 10365, a plunger fashioned from a wooden rod and a 250-mL polyethylene bottle was used to push the top 18" of the core into the jar. With a layer of polyethylene film placed over the jar, the headspace above sample #10365 was purged for several minutes with oxygen-free nitrogen before the lid was tightened down. Because each of the remaining samples had only a few mL headspace, they were simply covered with polyethylene film and capped tightly. Each sample was then homogenized by vigorous shaking for about 10 min; homogenization was performed both immediately after the transfer from core tubes and just before each was sampled for AVS/SEM analysis (about 24 h after transfer). Samples were stored at 4°C at all times except during sampling and homogenization. After homogenization, sample #10364 through #10366 had a light reddish-brown milkshake appearance; sample 10367 was dark greenish-brown and appeared to consist mostly of sand particles, because most of the solids settled rapidly after shaking.

A 5-g wet aliquant from each sediment sample was processed according to NFCRC SOP C5.156 for determination of AVS and the isolation of the SEM fraction. This method was adapted from the EPA draft method (4/91) written by Allen, Gongmin, Boothman, DiToro, and Mahony, and utilized a silver/sulfide electrode for determining the AVS. Fifty mL of each extract was vacuum filtered through a 0.4 μm polycarbonate membrane. Extracts were analyzed for aluminum, iron, copper, and zinc by inductively coupled argon plasma emission spectroscopy as described in SOP C4.78. Cadmium was determined by graphite furnace atomic absorption spectroscopy employing Zeeman background correction. Percent moisture and loss

on ignition determinations were conducted on a separate aliquant (5 mL) of each sample by overnight drying at 95 - 105°C as described in SOP C5.168, followed by ashing at 500°C as described by SOP C5.197.

Samples were processed through the analytical flow scheme in one block with some or all of the following quality control: procedural blanks, duplicate sample analysis, and pre-extraction spikes. For each element, analysis spikes and a calibration solution were also analyzed. To provide an overview of quality assurance, all quality control results were tabulated to facilitate presentation. The quality control parameters incorporated into this report are in accordance with the NFCRC Director's memorandum of 4/7/88, and also the Fish and Wildlife Service's Region 8 Office of Quality Assurance.

RESULTS AND DISCUSSION:

Percent moisture, loss on ignition (LOI), AVS, and SEM results for sediment samples are indicated in Table 1. These results ranged as follows: Percent moisture, 49.9 to 93.8; LOI, 2.7 to 16.5; AVS, <0.09 to 3.86 μM/g; extractable metals in μg/g dry weight: Al, 5000 to 44,600; Cd, 0.95 to 4.80; Cu, 67 to 1,243; Fe, 15,400 to 159,000; and Zn, 149 to 712. SEM/AVS ratios, presented in Table 2, were calculated for those elements measured which are known to form sulfides less soluble than iron or manganese (cadmium, copper, and zinc). The sum (Σ) of the SEM/AVS ratios ranged from 7.47 to 37.1, with most contributions to the ratios coming from copper and zinc (Table 2). Sediments having an SEM/AVS ratio greater than 1 are considered potentially toxic to organisms in the aquatic ecosystem. In general, the AVS concentrations were low (Table 1), suggesting that AVS is not a major factor governing metal solubility in pore waters of these sediments.

Quality control results for the four sample sets are indicated in Tables 3 to 9. Instrument calibration was verified by analyzing calibration solutions prepared from NIST certified stocks during each instrumental run (Table 3). Method precision, measured as relative percent difference (RPD) is presented in Table 4. Agreement was within 30 RPD for all analytes except sulfide. Recoveries of pre-extraction spikes are indicated in Table 5. Pre-extraction blank spike recoveries ranged from 94.5 to 102 percent for all analytes. Recoveries of elements from the pre-extraction sample spike, however, were more variable, ranging from 87.1 to 115 percent for all analytes except sulfide (55.5 percent). Accuracy of pre-extraction spikes in the AVS procedure may be highly variable for reasons that are not currently understood. In the current operationally defined AVS methodology, some sediments may contain components that competitively readsorb extraction metal spikes and thus interfere with quantitative recovery, or some

metals in the samples may react with the added sulfide spike to form other non-acid volatile sulfides, causing an apparent loss of some of the spike. The variable nature of the overall pre-extraction spike recovery results points to the need for additional research to identify variables that affect analyte behavior during the AVS procedure. Poor recovery of spiked metals in the SEM determination has been observed by others as well (Warren Boothman, EPA, personal communication). Analysis spikes, conducted at the instrument as matrix suppression or enhancement checks, ranged from 93 to 101 percent recovery, as presented in Table 6. Mean blank equivalent concentrations were less than the limit of detection for all analytes (Table 7). The method limit of detection and limit of quantitation are presented in Table 8 for each analyte. The 0.09 μg/g dry weight detection limit value was based on a 5 g wet subsample at 75% moisture (1.25 g dry weight). Instrument precision within an analytical run ranged from 0.45 to 3.9 percent relative standard deviation, as presented in Table 9. Overall, the quality control results for this project met quality assurance expectations.

Table 1. Percent water, percent loss on ignition, and concentrations of acid volatile sulfide and simultaneously extracted aluminum, cadmium, copper, iron, and zinc in Keswick Reservoir homogenized core sediment samples. Units expressed as follows: AVS, μmol/g dry weight; SEM, μg/g dry weight.

FWS#	Field ID	% H_2O	% LOI	AVS	Al	Cd	Cu	Fe	Zn
10364	S010593-1 J-32	88.8	10.7	0.52	13700	0.95	489.	94800	300
10365	S010594-4 529-J2	72.4	7.0	1.47	16700	3.25	798.	66200	712
10366	S010593-2 505-J4	93.8	16.5	3.86	44600	4.80	1243.	159000	603
10367	S010594-3 519-J4	49.9	2.7	<0.09	5000	0.97	67.	15400	149

Table 2. Ratio of SEM/AVS for cadmium, copper, and zinc.

DB #	Field Label	Cd	Cu	Zn	Σ[a]
10364	S010593-1 J-32	0.0163	14.8	8.83	23.6
10365	S010594-4 529-J2	0.0197	8.54	7.41	16.0
10366	S010593-2 505-J4	0.0111	5.07	2.39	7.47
10367	S010594-3 519-J4	0.0959	11.7	25.3	37.1

[a]Σ = Σ [Cd,Cu,Zn] μMol/g ÷ AVS μMol/g

Table 3. Performance of NBS 3100 series solutions used for verification of instrument calibration.

BID[a]	Ele.	Run Date	Ref. Material	Actual Conc	Meas. Conc 1	Meas. Conc 2	%ERROR 1	%ERROR 2	ISOP[b]	Oper. Init.
02/03/94	Al[c]	02/16/94	NIST 3101	25.	24.58	24.64	-1.7	-1.4	C4.78	RHW
02/03/94	Cd[d]	02/17/94	NIST 3108	2.	2.02	1.962	1.0	-1.9	C5.148	MJW
02/03/94	Cu[c]	02/15/94	NIST 3114	5.	4.782	4.84	-4.4	-3.2	C4.78	RHW
02/03/94	Fe[c]	02/16/94	NIST 3126	25.	25.223	25.048	0.9	0.2	C4.78	RHW
02/03/94	S[e]	02/03/94	NA_2S	20.6	20.2	20.7	-1.9	0.5	C5.156	WGB
02/03/94	Zn[c]	02/15/94	NIST 3168	5.	5.057	4.962	1.1	-0.8	C4.78	RHW

[a]BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b]ISOP = Instrumental standard operating procedure.

[c]units are ppm.

[d]units are ppb.

[e]units are μMol

Table 4. Percent relative standard deviations of element concentrations from duplicate extraction and analysis of samples. Concentrations expressed as μg/g unless otherwise noted.

BID[a]	Ele.	Matrix	Dup1	Dup2	Mean	Diff.[b]	RPD[c]	PSOP[d]	Prep. Init.	ISOP[e]	Oper. Init.
02/03/94	Al	SED EXTR[f]	16661.	12856.	14758.5	3805.	25.8	C5.156	JWA	C4.78	RHW
02/03/94	Cd	SED EXTR	3.25	2.54	2.895	0.71	24.5	C5.156	JWA	C5.148	MJW
02/03/94	Cu	SED EXTR	798.	639.4	718.7	158.6	22.1	C5.156	JWA	C4.78	RHW
02/03/94	Fe	SED EXTR	66174.	53223.	59698.5	12951.	21.7	C5.156	JWA	C4.78	RHW
02/03/94	H_2O[g]	SEDIMENT	72.4	72.3	72.35	0.1	0.14	C5.168	JWA	---	---
02/03/94	LOI[g]	SEDIMENT	7.	6.9	6.95	0.1	1.4	C5.197	JWA	---	---
02/03/94	S[h]	SED EXTR	1.47	0.87	1.17	0.6	51.3	C5.156	WGB	C5.156	WGB
02/03/94	Zn	SED EXTR	712.5	535.4	623.95	177.1	28.4	C5.156	JWA	C4.78	RHW

[a]BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b]Diff = Dup1 - Dup2.

[c]RPD = relative percent difference.

[d]PSOP = standard operating procedure used for chemical preparation of sample.

[e]ISOP = standard operating procedure used for instrumental analysis of sample.

[f]SED EXTR = sediment extract, i.e., analyte extracted from sediment during AVS determination.

[g]units are expressed as percentage (%).

[h]units here are μMol/g.

TABLE 5. Percent recoveries of aluminum, cadmium, copper, iron, sulfide, and zinc in pre-extraction sample spikes.

1 BID[a]	2 Ele.	3 Spike Form	4 Amt.[b] µg	5 Matrix	6 Total µg[c] Meas.	7 Bkgd.[d] µg	8 Spk/Bkgd[e]	9 Spk/Bkgd SD	10 %REC[f]	PSOP	Prep. Init.	ISOP	Oper. Init.
02/03/94	Al	Al+3	10000.	BLK SPK	10066.	11.	909.	4329.	101.	C5.156	JWA	C4.78	RHW
02/03/94	Al	Al+3	10000.	SED EXTR	29932.	20868.	0.48	2.7	90.6	C5.156	JWA	C4.78	RHW
02/03/94	Cd	Cd+2	100.	BLK SPK	94.551	0.036	2777.78	8333.	94.5	C5.156	JWA	C5.148	MJW
02/03/94	Cd	Cd+2	100.	SED EXTR	94.142	4.088	24.4618	141.	90.1	C5.156	JWA	C5.148	MJW
02/03/94	Cu	Cu+2	1000.	BLK SPK	972.5	1.	1000.	8696.	97.2	C5.156	JWA	C4.78	RHW
02/03/94	Cu	Cu+2	1000.	SED EXTR	1887.	1016.	0.98	6.4	87.1	C5.156	JWA	C4.78	RHW
02/03/94	Fe	Fe+3	10000.	BLK SPK	10224.	18.	556.	4717.	102.	C5.156	JWA	C4.78	RHW
02/03/94	Fe	Fe+3	10000.	SED EXTR	95865.	84418.	0.12	0.79	115.	C5.156	JWA	C4.78	RHW
02/03/94	S	Na_2S	660.4	BLK SPK	627.7	0.	30000.	17000.	95.0	C5.156	WGB	C5.156	WGB
02/03/94	S	Na_2S	660.4	SED EXTR	419.3	53.	12.4	34.6	55.5	C5.156	WGB	C5.156	WGB
02/03/94	Zn	Zn+2	1000.	BLK SPK	1010.	1.	1000.	8696.	101.	C5.156	JWA	C4.78	RHW
02/03/94	Zn	Zn+2	1000.	SED EXTR	1883.	881.	1.1	5.7	100.	C5.156	JWA	C4.78	RHW

[a]BID = Block Initiation Date; a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block".

[b]Spike Amt = the absolute microgram (µg) amount of the spike in the form listed in column 3 which was added to a sample.

[c]Total µg Meas. = the micrograms (µg) of the analyte in the sample spike measured by the instrument (spike + background).

[d]Bkgd µg = Mean background amount in µg; the mean amount in µg from three aliquots of sample taken throµgh the preparation and analysis methodology.

[e]Spk/Bkgd Ratio = the ratio of the spike amount added (column 4) divided by the mean sample background concentration (column 7).

[f]%REC = Total µg Meas. (column 6) - Bkgd. µg (column 7) divided by the Amt µg (column 4) X 100.

TABLE 6. Percent recoveries of aluminum, cadmium, copper, iron, sulfide, and zinc in analysis (post-extraction) spikes analyzed as a matrix suppression or enhancement check.

BID[a]	Ele.	Matrix	Analysis Units	Spk Amt.[b] µg	Vol.	Effec.[c] Conc.	Bkgd.[d] Conc.	Total[e] Conc.	%REC[f]	PSOP	Prep. Init.	ISOP	Oper. Init.
02/03/94	Al	SED EXTR	µg/mL	100.	5	20.0	12.77	32.89	101.	C5.156	JWA	C4.78	RHW
02/03/94	Cd	SED EXTR	ng/mL	0.002	1	2.0	0.666	2.584	95.9	C5.156	JWA	C5.148	MJW
02/03/94	Cu	SED EXTR	µg/mL	25.	5	5.0	1.73	6.381	93.0	C5.156	JWA	C4.78	RHW
02/03/94	Fe	SED EXTR	µg/mL	100.	5	20.0	15.68	35.66	99.9	C5.156	JWA	C4.78	RHW
02/03/94	S	SED EXTR	µM	10.3	1	10.3	1.33	11.5	98.7	C5.156	WGB	C5.156	WGB
02/03/94	Zn	SED EXTR	µg/mL	25.	5	5.0	1.743	6.547	96.1	C5.156	JWA	C4.78	RHW

[a]BID = Block Initiation Date; a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block".

[b]Spike Amt = the absolute microgram (µg) amount of the spike in the form listed in column 5 which was added to a sample.

[c]Effec Conc = The Spike Amt divided by the total solution volume.

[d]Bkgd Conc = the measured concentration of the sample prior to spiking.

[e]Total Conc = the measured concentration of the spiked sample (spike + background).

[f]%REC = percent recovery.

Table 7. Blank equivalent concentrations for procedural blank solutions analyzed as part of a sample group or "block".

BID[a]	Ele	Matrix	Soln. Units	Soln1 Conc.	Soln2 Conc.	Soln3 Conc.	Dil. Vol.	Mean[b] Conc.	Samp.[c] Wgt.	MEAN BEC µg/g	BEC SD µg/g	PSOP	Prep. Init.	ISOP	Oper. Init.
02/03/94	Al	SED EXTR	µg/mL,W[d]	0.122	0.124	0.083	100.	0.10967	5.	2.193333	0.46231	C5.156	JWA	C4.78	RHW
02/03/94	Cd	SED EXTR	ng/mL,D	0.04	0.03	0.059	833.3	0.043	1.25	0.028667	0.00982	C5.156	JWA	C5.148	MJW
02/03/94	Cu	SED EXTR	µg/mL,W	0.011	0.011	0.009	100.	0.01033	5.	0.206667	0.02309	C5.156	JWA	C4.78	RHW
02/03/94	Fe	SED EXTR	µg/mL,W	0.186	0.202	0.16	100.	0.18267	5.	3.653333	0.42395	C5.156	JWA	C4.78	RHW
02/03/94	S	SED EXTR	µMol,D	0.0625	0.	0.	1.	0.02083	1.3	0.016667	0.02887	C5.156	WGB	C5.156	WGB
02/03/94	Zn	SED EXTR	µg/mL,W	0.01	0.012	0.01	100.	0.01067	5.	0.213333	0.02309	C5.156	JWA	C4.78	RHW

[a]BID = Block Initiation Date; a date assigned to each member of a group of samples that will identify the samples as a member of the group or "block".

[b]Mean Conc. = the mean solution concentration of the procedural blanks for a block, n=3.

[c]Samp. Wgt. = weight used for BEC calculation (g).

[d]results expressed as either wet (W) or dry (D) weight.

TABLE 8. Limit of detection (LOD) and limit of quantitation values for the sample groups. Units are μg/g dry weight except S (AVS) which is μmol/g dry wt.

BID[a]	Ele	Matrix	W/D/L[b]	Sample[c] SD	Blank[d] SD	LOD[e]	LOQ[f]	PSOP	Prep. Init.	ISOP	Oper. Init.
02/03/94	Al	SED EXTR	D	13.22132	1.7320508	40.	132.	C5.156	JWA	C4.78	RHW
02/03/94	Cd	SED EXTR	D	0.032747	0.009609	0.10	0.33	C5.156	JWA	C5.148	MJW
02/03/94	Cu	SED EXTR	D	1.305118	0.1154701	3.9	12.9	C5.156	JWA	C4.78	RHW
02/03/94	Fe	SED EXTR	D	19.28756	1.5275252	58.	191.	C5.156	JWA	C4.78	RHW
02/03/94	S	SED EXTR	D	0.009815	0.0288675	0.09	0.3	C5.156	WGB	C5.156	WGB
02/03/94	Zn	SED EXTR	D	2.579406	0.1154701	7.7	25.4	C5.156	JWA	C4.78	RHW

[a]BID = Block Initiation Date; a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block".

[b]W/D/L = wet, dry, or liquid; D = values expressed as dry weight.

[c]Sample SD = the standard deviation of low level sample concentrations.

[d]Blank SD = the standard deviation of procedural blank concentrations.

[e]LOD = limit of detection calculated as:

$$3\ [SD_b^2 + SD_s^2]1/2$$

where SD_b = standard deviation of the blank and SD_s = standard deviation of a low level sample.

[f]LOQ = limit of quantitation calculated as 3.3 x LOD. Values between the LOD and LOQ have poorer accuracy and thus poorer reliability.

Table 9. Instrumental precision and sensitivity within analytical "runs".

BID[a]	Ele	Run Date	Std.[b] Conc.	VOL[c] (μL)	Initial Abs/Read	Mean[d] Read	# of checks	SD[e]	%RSD[f]	Char.[g] Mass	ISOP	Oper. Init.
02/03/94	Al	02/16/94	5.	---[i]	2932.	3068.	3	119.6	3.9	---[i]	C4.78	RHW
02/03/94	Cd[h]	02/17/94	2.	10.	0.077	0.077	3	0.00115	1.5	1.14	C5.148	MJW
02/03/94	Cu	02/15/94	1.	---[i]	4624.	4603.	3	20.6	0.45	---[i]	C4.78	RHW
02/03/94	Fe	02/16/94	5.	---[i]	7958.	8319.	3	317.2	3.8	---[i]	C4.78	RHW
02/03/94	S	02/03/94	20.6	---[i]	---	20.53	6	0.2805	1.4	---[i]	C5.156	WGB
02/03/94	Zn	02/15/94	1.	---[i]	3664.	3752.	3	93.4	2.5	---[i]	C4.78	RHW

[a]BID = Block Initiation Date; a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block".

[b]Std. Conc. = units in ppm unless otherwise noted.

[c]VOL (μL) = microliters of standard injected into graphite furnace.

[d]Mean Read = units are absorbance, concentration, or intensity depending upon instrumentation used.

[e]SD = standard deviation.

[f]%RSD = percent relative standard deviation.

[g]Char. Mass = picograms of the analyte that will give 1% absorption.

[h]concentrations here are ppb due to graphite furnace analysis.

[i]non-furnace technique used.