DISTRIBUTION AND MOBILIZATION OF ARSENIC AND ANTIMONY SPECIES IN THE COEUR D'ALENE RIVER SYSTEM

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ABSTRACT

The mining industry along the South Fork of the Coeur d'Alene River in northern Idaho is a major producer of silver, lead, and zinc in the United States. Mining operations in the past have discharged huge amounts of mining wastes into the South Fork of the river causing a serious pollution problem for the Coeur d'Alene River system. Sediments in the South Fork and the Main Stem of the river are contaminated with arsenic(As), antimony(Sb), cadmium(Cd), Lead(Pb), Zinc(Zn), and other metals.

The North Fork water was found relatively uncontaminated and showed very low concentrations of As (<0.26 ng/mL) and Sb (<0.17 ng/mL). Water samples collected from the South Fork showed high levels of As (0.16-1.64 ng/mL) and Sb (1.11-8.25 ng/mL). Relatively lower concentrations of As (0.11-1.48 ng/mL) and Sb (0.23-1.90 ng/mL) were found in the main stem of the river. Arsenic(III) was the predominant form of As in the South Fork and main stem, whereas the North Fork generally had a higher As(V) concentration in water. Antimony(V) was the major Sb species in the three branches of the river.

Leaching of As and Sb from the sediments along the main stem depends on the pH of the water and on the iron and manganese content of the sediments. The amount of As and Sb leached was high in acidic or in basic solutions. The enhanced desorption of As and Sb in basic solutions was probably related to the anionic properties of these elements. An accumulation of As and Sb on the surface sediments was also observed in the delta area where the river enters Lake Coeur d'Alene. The releases of As and Sb from the sediments appear to associate with the free iron oxides and manganese oxides in the sediments. The leaching characteristics of Sb are similar to those of As. However, releases of sediment Sb were generally found linear with respect to time while asymptotic limits on As releases were reached. Significant amounts of Zn, Fe, and Mn were also released during leaching, but Cu, Cd, Pb, and Ni were much less leachable. According to this study, interaction of water with the existing sediments is likely to be a major factor controlling the water quality of the Coeur d'Alene River.

INTRODUCTION

Mining is the main industry along the South Fork of the Coeur d'Alene River in northern Idaho. The area is one of the major silver, lead, and zinc producing areas in the United States. Associated with the mining industry of the area has been the problem of heavy metal pollution. Mining and smelting wastes have been discharged into the South Fork of the river since mining began in this area some 80 years ago. Most of this pollution occurred before the mine tailings ponds were constructed and put into operation in 1968. These settling ponds have greatly reduced the discharge of suspended solids into the river. However, huge amounts of mine tailings had already been deposited. The primary problems of environmental concern in this area today are the operating and abandoned tailings piles scattered throughout the district, the huge quantities of mine wastes accumulated along the streams, and the acid mine drainage from existing mines in the district. The South Fork of the Coeur d'Alene River is a shallow, swiftly flowing stream. The main stem of the Coeur d'Alene River is much deeper and slower moving than the South Fork. The gradient of the South Fork below Wallace is about 5.7 m/km, whereas the main stem has a gradient of about 0.19 m/Km (Norbeck, 1974). Because of the large gradient of the South Fork, most of the mine tailings discharged did not settle until they reached the main stem; only small amounts of sediments are present in the bed of the South Fork. The flow of the main stem of the Coeur d'Alene River is determined primarily by natural discharge from the North Fork with a high flow rate generally found during the spring months at the time of snow melt (Mink et al., 1971). The sediments along the South Fork and main stem of the river are contaminated with metals such as Ag, As, Cd, Cu, Hg, Mn, Pb, Sb, and Zn. The contaminated sediments in the Coeur d'Alene River are being leached to varying degrees by ground water and surface water, and are likely to be a source of pollution in this area for years to come. Arsenic and antimony are among the most interesting elements in environmental studies because of their toxic nature. The toxicity and physiological behavior of these elements are dependent upon their oxidation states. In general, arsenite [As(III)] is considered more toxic than arsenic [As(V)] (NAS, 1977). There is sufficient evidence that inorganic arsenic compounds are skin and lung carcinogens in humans (IARC, 1980; Stokinger, 1981; Tsuchiya, et al.,

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1977). Epidemiologic data appear to indicate that inorganic As(III) compounds represent a greater carcinogenic hazard than As(V) (NAS, 1977). Reduction of arsenate to arsenite inanaerobic sediments would therefore result in an increase in arsenic toxicity. Antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency. The soluble salts of antimony are known to be toxic (Luckey and Venugopal, 1977), and the physiological effects of antimony are also dependent upon its oxidation states (Stokinger, 1981; Elinder and Friberg, 1977; Little, 1976; USEPA, 1980). Antimony trioxide exposure in the workplace has been shown to contribute to human heart diseases, pneumoconiosis and emphysema, and long term exposure of animals to Sb(V) compounds may be fatal (Elinder and Friberg, 1977). Because the toxicities of As and Sb are dependent upon their oxidation states, the quantitation and speciation of these elements become an important part of an environmental monitoring program. As and Sb species can be leached from the contaminated sediments during water-sediment interactions. The mobility and the chemical forms of As and Sb in the contaminated sediments are largely unknown. The distribution of As and Sb species and their potential mobility can be influenced by environmental conditions. If the sediments are removed, transported, and discharged to water or to land, such disturbance will create conditions under which As and Sb may become mobile, resulting in redistribution. Dredging and disposal operations may also lead to a change in the sediment environment, for example, a transition from anaerobic to aerobic conditions. Consequently, transformation and fixation of the As and Sb species may take place. The present work was undertaken to study the effects of the contaminated sediments on water quality with respect to As and Sb species. Field data were collected from a number of selected locations in the Coeur d'Alene River system to study the distribution of As and Sb species in the surface water and their relations to other water quality parameters. Chemical and mineralogical data of the sediments collected are also given to show the current levels of As, Sb and other metals. Laboratory leaching experiments were carried out using the contaminated sediments to study the dissolution of these metal species during water-sediment interactions with respect to pH, metal content, and other water quality parameters under controlled conditions. The results are used to interpret the water quality data and metal transport problems observed in the selected locations of the Coeur d'Alene River system. The factors which control leaching of trace metals from the sediments to the aqueous environment are also discussed. In

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addition, depth profiles of As, Sb and other metals in some sediments were also studied and the accumulation of As and Sb in the sediments was investigated.

Experimental Methodologies

Sampling Stations

Nine sampling stations were selected to study the water quality of the Coeur d'Alene River system. Two more sampling sites from two lakes above the mouth of the Coeur d'Alene River were also investigated at the later part of this study. Figure 1 shows the location of the sampling sites. The first two stations are located along the South Fork of the Coeur d'Alene River. Station 1 is located at Kellogg, and Station 2 is near the Smelterville Flats. Both stations provide information on the quality of water entering the main stem. Station 3 is located on the North Fork to measure the water quality of a relatively unpolluted stream.

Stations 4 through 9 were established along the main stem of the Coeur d'Alene River. Station 4 is the first station below the confluence of the North and South Forks and gives an indication of the effects of dilution and mixing of the North Fork and South Fork waters. Station 5 was established to evaluate the effects of the polluted sediments at the Cataldo Mission Flats. Stations 7 and 8 were chosen to evaluate natural changes along the main stem of the river. Station 9 is above the mouth of the Coeur d'Alene River and can be used to determine the quality of the river water entering Coeur d'Alene Lake.

The three small lakes included in this study are situated in the flood plain along the main stem and are connected to the river by channels. In the spring the lakes may be flooded as the water table rises above the adjacent valley floor. Station 6 (Rose Lake) and Station 10 (Thompson Lake) are located on the north side of the river. During high water in the spring, the river passes through a culvert and seeps across a marsh into Rose Lake. Station 11 (Anderson Lake) is located on the south side of the Coeur d'Alene River and is connected to the river by long winding inlets.

Sampling Procedures

Water samples were collected using one-liter polyethylene bottles. The containers were washed with nitric acid and rinsed with deionized water prior to sample collection. Water samples were

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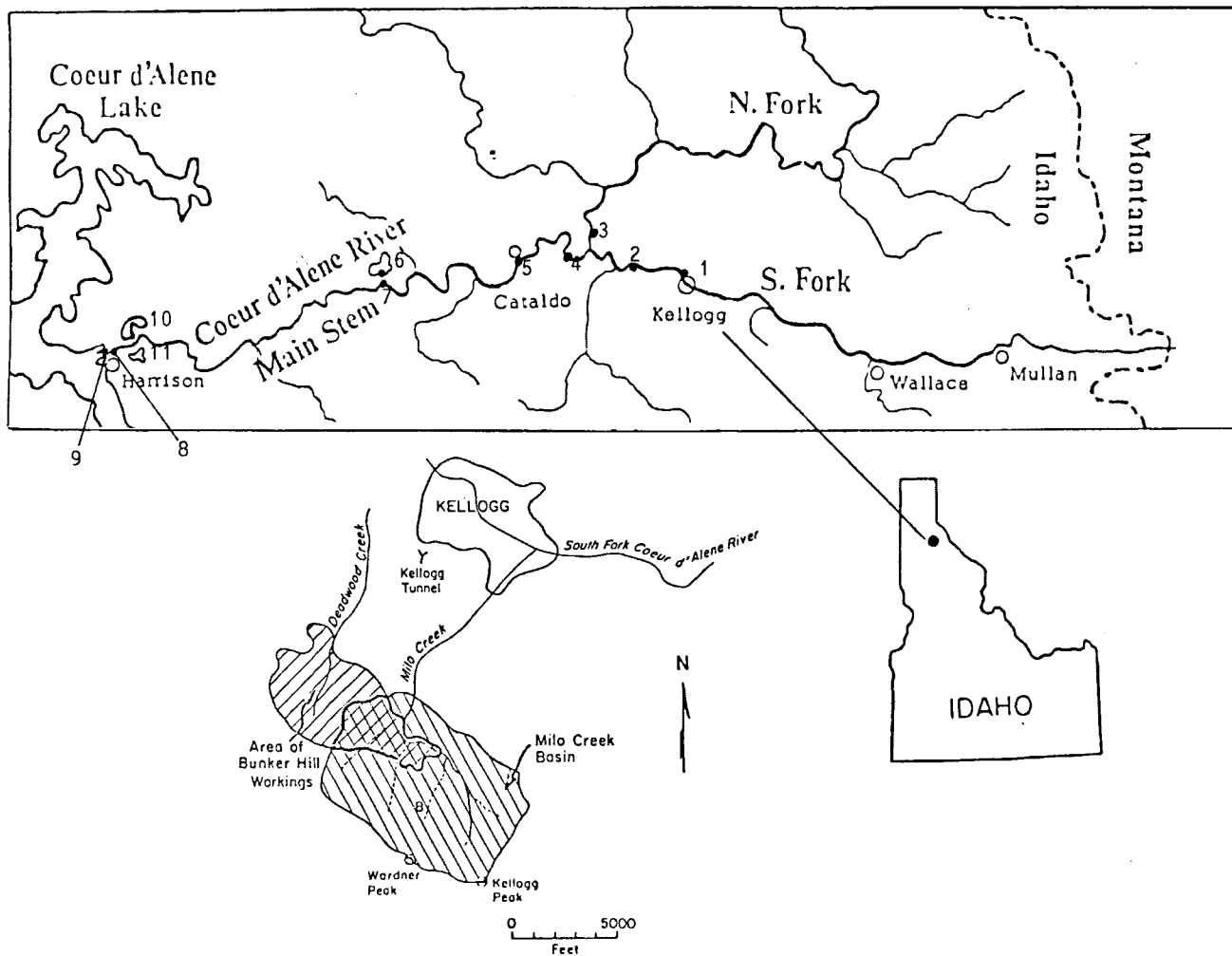
Figure 1. Location of the sampling stations in the Coeur d'Alene River.

obtained from currents of the stream; stagnant areas were avoided. The sample bottles were rinsed thoroughly with stream water at the time of sampling. After collection, water samples were filtered through a 0.45 micron membrane filter. In general, water samples were stored in a refrigerator at about 4°C and were analyzed for As and Sb within a very short time after sampling. Sediment samples were taken at the selected sites using a plastic spade, sealed in plastic bags, and stored at 4°C in a refrigerator until use. Core sediment samples to study the depth profiles of the metals were collected with a coring apparatus.

Analytical Procedures

A. Extraction of Trivalent and Pentavalent Arsenic and Antimony Species from Natural Waters

Ammonium pyrrolidinecarbodithioate (PCDT) is widely used for preconcentration and separation of trace elements from aqueous solutions. The extractibility of metal-PCDT complexes depends on the oxidation state of the elements and the pH of the solution. PCDT forms stable complexes with As(III) and Sb(lll) but not with As(V) and Sb(V). Trivalent As and Sb can be separated from pentavalent As and Sb by extracting the former with PCDT into chloroform in the pH range from 3 to 6 (Mok and Wai, 1987). One advantage of PCDT extraction is that the alkali metals, the alkaline earth metals, the halogens, aluminum, sulfate, and phosphate which do not complex with PCDT can be simultaneously removed during extraction. The PCDT extraction method may serve three general purposes for trace analysis: (1) concentration of trace elements, (2) elimination of matrix interferences, and (3) differentiation of chemical species. Extraction of As(V) and Sb(V) can be achieved by reduction with thiosulfate and potassium iodide at pH 1 followed by PCDT extraction at the same pH value. The As and Sb-PCDT complexes in the organic phase can be back-extracted into a nitric acid solution for neutron activation analysis. The differences in As(III) and Sb(III) concentrations between two aliquots of a water sample with and without reduction give the concentrations of As(V) and Sb(V) in the sample. Detection of 10-2 ug/L of As and Sb can be achieved using this extraction method and neutron activation analysis. The details of this new extraction method for determination of As and Sb species in natural waters are given in our recent publication (Mok and Wai, 1987).

B. Trace Metal Analysis

Neutron activation analysis (NAA) is one of the most sensitive techniques for determining a number of trace elements including As and Sb. This technique has been extensively used for trace analysis of various environmental samples in our laboratory. A TRIGA nuclear reactor located at the Washington State University Nuclear Radiation Center was used for sample irradiation in this study. Samples were normally irradiated with a steady neutron flux of 6×10^{12} n/cm^2 sec for 2 hours, followed by cooling for about one day. The irradiated samples were usually counted for 2000 to 8000 seconds using an ORTEC (Li) detector and a 4096-channel analyzer. The details of the irradiation and counting procedures are given in the literature (Mok and Wai, 1987). The 559.1 keV gamma from 76 As and the 564.1 keV gamma from 122 Sb were used for the identification and quantitation of As and Sb in each sample. Under interference free conditions, NAA is capable of detecting As and Sb at nanogram levels. However, in real samples spectral interference from matrix species can seriously impair the sensitivity of trace element determination by NAA. The concentrations of total As and Sb in most natural water systems are very low, in the range of 10 -9 to 10 -10 g/mL. Without chemical separation and preconcentration, it is difficult to determine As and Sb directly in natural waters by NAA. The PCDT extraction method has greatly improved the sensitivity of As and Sb detection. If we start with a water sample of 100 mL and go through the PCDT extraction procedure, we can detect As and Sb at 10 -11 g/mL level. This level of detection is generally sensitive enough to measure As and Sb species in natural waters. If necessary, the detection limits for As and Sb can be further lowered by using larger sample volumes and longer counting times. Other trace metals including Zn,Cu, Fe, Mn, Cd, Pb, and Ni were determined using direct flame aspiration with an IL-353 atomic absorption spectrophotometer (AAS). The detection limits and sensitivities of seven elements are listed in Table 1.

Arsenic and antimony in the sediments were determined by non-destructive neutron activation techniques. A 0.1 gram sediment was weighed and sealed in a 2/5 dram polyethylene vial. Samples and standards were irradiated together for 2 hours. After cooling for 3-5 days, the samples were counted for 500 - 1800 seconds on the ORTEC Ge(Li) detector. Zinc, Fe, Cu, Mn, Ni and Al in the sediments were determined by X-ray fluorescence (XRF) available in the Geology Department at Washington State University. Fused samples were used when analyzed by XRF. Lead and Cd in the

Table 1. Detection limits and sensitivities of seven elements determined by the IL-353 AAS

	Zn	Mn	Fe	Cu	Cd	Pb	Ni
Detection limit (ug/mL)	0.005	0.01	0.03	0.02	0.005	0.1	0.04
Sensitivity (ug/mL)*	0.02	0.05	0.12	0.1	0.025	0.5	0.15

* For 1% absorbance

sediments were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after an acid digestion procedure using a mixture of concentrated HNO 3 and HClO 4. An ARL Model 35,000 C ICP-AES, located in the College of Agriculture, University of Idaho, was available for this study.

C. Leaching Experiments

Leaching experiments were conducted on six representative sediment samples to study the releases of metals from the sediments. All experiments were conducted at room temperature under atmospheric pressure. In each experiment, a sediment sample of known dry weight was placed in a 1-L polyethylene bottle, and sufficient deionized water was added to each bottle to make a water-to-sediment weight ratio of approximately 15:1. The sediment-water mixture was kept in suspension by continuous stirring with a magnetic stirrer. Samples (250 mL aliquots) were removed from each of the systems at various time intervals and replaced by an equal volume of deionized water and the leaching continued. This volume of water was needed for analytical purposes because of the low As and Sb concentrations in the leaching solution. Replacement of water removed from the system was necessary to maintain a relatively constant water-to-sediment ratio during the leaching process. The leaching solution was filtered through a 0.45 um millipore membrane filter followed by measurement of the pH. Metal contents of the leaching solution were determined by the same procedure as described previously for river water samples.

Water Quality Data

A. Arsenic and Antimony

Arsenic and antimony concentrations in the waters collected from the selected sites along the Coeur d'Alene River are given in Table 2. Table 3 summarizes the mean values and the ranges of As and Sb found in these stations for the entire sampling period of this study. Water samples were collected from December 1986 through June 1987. In December 1986, waters could be sampled only from station 1, 2, and 5 because of snow. The mean pH value of the river water samples is 7.48.

In general, As and Sb concentrations in the river were high in December, January, and June, and became lower during spring run-off. Stations 1 and 2 have shown consistently high readings

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Table 2.   Arsenic and antimony concentrations in the waters from the Coeur d'Alene River
(concentrations in ng/mL)

Dec. 19, 1986

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.58	0.830±0.013	1.079±0.017	0.110±0.010	7.612±0.072
2	7.24	1.357±0.016	1.359±0.011	0.125±0.011	6.758±0.007
5	7.46	0.190±0.007	0.195±0.007	0.053±0.008	0.946±0.019

Jan. 29, 1987

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.92	0.813±0.013	1.151±0.022	0.077±0.006	8.245±0.109
2	7.35	1.370±0.035	1.380±0.026	N.D.	6.745±0.095
3	7.70	0.050±0.006	0.082±0.012	0.027±0.005	0.065±0.010
4	7.27	0.205±0.008	0.254±0.013	0.039±0.007	1.724±0.043
5	7.49	0.165±0.006	0.261±0.017	0.046±0.006	1.381±0.034
6	7.09	0.182±0.013	0.184±0.016	N.D.	0.575±0.025
7	7.34	0.515±0.011	0.523±0.020	0.051±0.006	1.228±0.038
8	7.34	0.470±0.019	0.476±0.019	N.D.	1.161±0.032
9	7.38	0.193±0.012	0.301±0.016	N.D.	0.669±0.024

Feb. 28, 1987

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.43	0.721±0.017	0.872±0.030	0.089±0.008	4.967±0.069
2	7.45	1.140±0.022	1.636±0.037	0.078±0.006	5.415±0.092
3	7.70	0.022±0.009	0.090±0.020	0.017±0.005	0.090±0.010
4	7.48	0.150±0.010	0.260±0.020	0.020±0.006	1.120±0.020
5	7.61	0.110±0.010	0.200±0.020	0.011±0.005	0.820±0.020
6	7.62	0.126±0.008	0.134±0.026	0.024±0.006	0.521±0.036
7	7.66	0.287±0.012	0.310±0.026	0.014±0.007	0.740±0.033
8	7.40	0.330±0.010	0.330±0.030	0.030±0.009	1.050±0.040
9	7.70	0.270±0.012	0.491±0.032	0.027±0.007	0.794±0.041

March 21, 1987

Station	pH	As(III)	As(III)+As)V)	Sb(III)	Sb(III)+Sb(V)
1	7.46	0.225±0.007	0.316±0.033	0.035±0.004	2.024±0.050
2	7.27	0.551±0.012	0.559±0.035	0.026±0.005	2.150±0.052
3	7.48	0.033±0.005	0.252±0.033	0.022±0.005	0.059±0.021
4	7.53	0.119±0.006	0.231±0.030	0.017±0.004	0.517±0.024
5	7.34	0.084±0.011	0.378±0.033	0.023±0.009	0.400±0.036
6	7.50	0.137±0.009	0.293±0.029	0.024±0.006	0.502±0.030
7	7.47	0.099±0.005	0.145±0.029	0.021±0.005	0.346±0.012
8	7.43	0.139±0.012	0.375±0.031	0.041±0.010	0.546±0.032
9	7.47	0.190±0.010	0.237±0.030	0.021±0.005	0.393±0.031

(Table 2 Continued)

April 11, 1987

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.43	0.171±0.006	0.324±0.025	0.017±0.009	1.244±0.038
2	7.49	0.360±0.009	0.368±0.022	0.032±0.010	1.304±0.032
3	7.36	0.044±0.004	0.088±0.017	0.019±0.003	0.106±0.013
4	9.07	0.083±0.008	0.112±0.022	N.D.	0.328±0.023
5	7.35	0.082±0.005	0.155±0.019	N.D.	0.235±0.015
6	7.50	0.161±0.006	0.173±0.008	0.024±0.005	0.513±0.026
7	7.36	0.130±0.005	0.255±0.019	0.042±0.004	0.300±0.024
8	7.33	0.167±0.005	0.461±0.022	0.034±0.004	0.294±0.025
9	7.44	0.355±0.011	0.372±0.032	N.D.	0.445±0.033

May 1, 1987

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.35	0.064±0.004	0.179±0.014	0.025±0.004	1.127±0.024
2	7.33	0.096±0.005	0.166±0.015	0.019±0.003	1.112±0.029
3	7.32	0.026±0.003	0.122±0.015	0.012±0.003	0.074±0.016
4	7.30	0.082±0.004	0.351±0.015	0.016±0.002	0.576±0.019
5	7.37	0.084±0.004	0.147±0.016	0.021±0.004	0.328±0.021
6	7.35	0.184±0.006	0.186±0.014	0.046±0.004	0.528±0.020
7	7.32	0.101±0.005	0.214±0.012	0.011±0.005	0.408±0.020
8	7.33	0.193±0.007	0.286±0.012	0.045±0.005	0.466±0.020
9	7.46	0.723±0.011	0.905±0.017	0.027±0.005	0.921±0.023

June 26, 1987

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	7.54	0.564±0.015	0.766±0.002	0.095±0.007	5.883±0.007
2	7.38	0.841±0.017	0.849±0.023	0.076±0.010	5.110±0.066
3	7.54	0.059±0.006	0.115±0.016	N.D.	0.164±0.029
4	7.56	0.172±0.006	0.275±0.013	0.036±0.006	1.892±0.028
5	7.36	0.167±0.010	0.206±0.016	0.022±0.007	1.302±0.026
6	7.47	0.190±0.007	0.196±0.012	0.032±0.005	0.751±0.018
7	7.47	0.292±0.013	0.300±0.016	0.034±0.007	1.307±0.027
8	7.50	0.220±0.007	0.343±0.014	0.047±0.005	1.270±0.023
9	7.73	0.390±0.012	1.471±0.020	0.037±0.006	1.752±0.026

N.D.: Not detectable

Table 3.   Mean values and ranges of As and Sb in the waters of the Coeur d'Alene River for the sampling period (December, 1986 to June, 1987)

Station	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)
1	0.484 0.064-0.830	0.670 0.179-1.151	0.064 0.017-0.110	4.443 1.127-8.245
2	0.816 0.096-1.370	0.902 0.166-1.636	0.051 0-0.125	4.085 1.112-6.758
3	0.039 0.022-0.059	0.125 0.082-0.252	0.016 0-0.027	0.093 0.059-0.164
4	0.135 0.082-0.205	0.247 0.112 0.351	0.021 0-0.039	1.026 0.328-1.892
5	0.127 0.082-0.190	0.220 0.147-0.378	0.025 0-0.053	0.773 0.235-1.381
6	0.163 0.126-0.190	0.194 0.134-0.293	0.025 0-0.046	0.565 0.502-0.751
7	0.237 0.099-0.515	0.290 0.145-0.523	0.029 0.011-0.051	0.722 0.346-1.307
8	0.253 0.139-0.470	0.379 0.286-0.476	0.033 0-0.047	0.798 0.294-1.270
9	0.354 0.190-0.723	0.630 0.237-1.471	0.019 0-0.037	0.829 0.393-1.752

Concentrations in ng/mL

during the course of this study. Station 1 is adjacent to Bunker Hill Street in Kellogg, and Station 2 is at the east end of the Smelterville Flats. These two stations reflect the high levels of As and Sb in the South Fork of the Coeur d'Alene River. Antimony concentrations of 8.245 ng/mL and 6.758 ng/mL have been noted at Stations 1 and 2, respectively. An arsenic concentration of 1.636 ng/mL has also been observed at Station 2.

Station 3 is at the lower stream of the North Fork before it enters the main stem. The North Fork of the Coeur d'Alene River does not have the industrial development which has occurred along the South Fork. During the period of this study, Station 3 showed very low concentrations of As and Sb; the mean concentrations of arsenic and antimony were 0.125 ng/mL and 0.093 ng/mL, respectively. The values reported here should be close to the geochemical background values of these two elements in the Coeur d'Alene River. Water quality within the Main Stem of the Coeur d'Alene is primarily a result of the mixing of the North Fork and South Fork waters. Station 4 is at Kingston just below the confluence of the North Fork and South Fork. Arsenic and Sb levels at Station 4 are substantially lower than those observed at Stations 1 and 2, reflecting a dilution effect after mixing of the North Fork waters. Station 5, located at the Cataldo Mission Flats, was extensively covered by deposits of old mine tailings in the past. During the sampling period, As and Sb concentrations in the water were found to have mean values of 0.220 ng/mL and 0.773 ng/mL, respectively. Sediments at the Cataldo Mission Flats do not appear to have significant effects on the As and Sb levels of the main stem water. During the sampling period, As ranged between 0.147 and 0.378 ng/mL, while Sb ranged bewtween 0.235 and 1.381 ng/mL at Station 5. Stations 7, 8, and 9 showed a slight increase in concentration of As relative to the concentrations observed at Station 5 upstream. Stations 8 and 9 are near the mouth of the Coeur d'Alene River. Mine wastes have also formed a delta in Lake Coeur d'Alene at the river mouth, which is about 50 km downstream from Kellogg. Substantially higher amounts of As were found in the surface sediments collected from Harrison (209 ug/g) and from the delta area (197 ug/g). Subsequent leaching of As from the sediments may contribute to the higher As levels observed at Stations 8 and 9.

Station 6, which is at Rose Lake, was chosen to evaluate contamination from the community of the river. The As and Sb levels of the water samples from Station 6 were lower than those of Station 7, but higher than the background levels.

Table 3 shows the ranges of As and Sb, respectively, in the waters of the nine stations studied during the sampling period. Comparing the main stem to the South Fork, the former has considerably lower concentrations of As and Sb. Figures 2 and 3 show the mean values of the As and Sb species, respectively, in the river during the sampling period. Trivalent As is the predominant species in the main stem and South Fork, while pentavalent is always the major species observed in the North Fork. Contrary to As, the concentration of pentavalent Sb is always much higher than that of trivalent Sb in all three branches of the river.

Figure 4 shows the distribution of As and Sb in the surface sediments for the stations along the Main Stem of the river. Arsenic in the sediments tends to increase towards the mouth of the river; no definite trend is observed for Sb. Although the As level in the water is lower than that of Sb, a much higher amount of As is found in the surface sediments.

B. Zinc, Manganese, Iron, and Other Trace Metals

The concentrations of Zn, Mn, and Fe in the waters of all nine stations are presented in Tables 4-6. Table 7 shows the mean values and ranges of Zn and Mn for the sampling period. Higher Zn, Mn, and Fe levels were observed in Stations 1 and 2 of the South Fork. During the period of this study, Station 3 at the North Fork showed no detectable concentrations of iron. Zinc and Mn were found only in trace amounts of less than 0.03 ug/mL. The natural background levels of Zn, Mn and Fe in the Coeur d'Alene River are probably close to the values shown in this station.

Zinc and Mn in the Main Stem have overall mean values of 0.50 ug/mL and 0.27 ug/mL, respectively, ranging from 0.18 to 1.07 ug/mL for Zn and 0.05 to 0.79 ug/mL for Mn. The higher values of Zn and Mn observed at Station 4 correspond to its location below the confluence. Dilution of the concentrations of Zn, Mn, and Fe by the North Fork waters is also visualized. Iron concentration in the main stem stations is generally no more than 0.23 ug/mL, with only Station 5 showing a value of 0.31 ug/mL on one occasion in the winter.

In general, the concentrations of these metals were found to be higher in the low flow of winter and lower in the high flow during spring run-off. An increase of metal concentrations was observed in some stations in June when low flow starts again. Dissolved zinc is high, especially at the South Fork of the Coeur d'Alene River. A high concentration of 4.23 ug/mL zinc was observed in the

Mean Values of As(III) and As(V)

in the CDAR for the Sampling Period
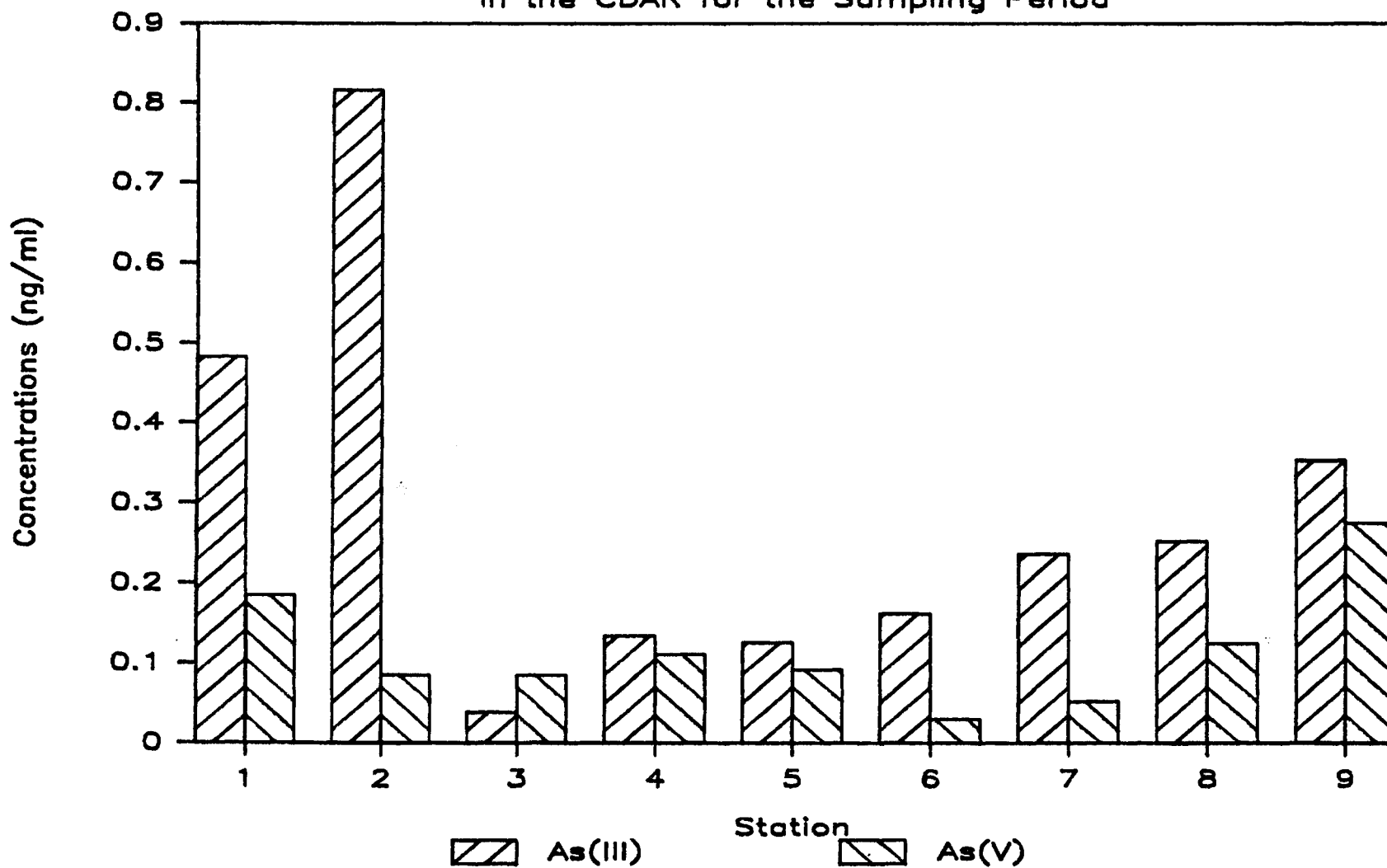
Figure 2. Mean values of As(lll) and As(V) in the Coeur d'Alene River during the sampling period.
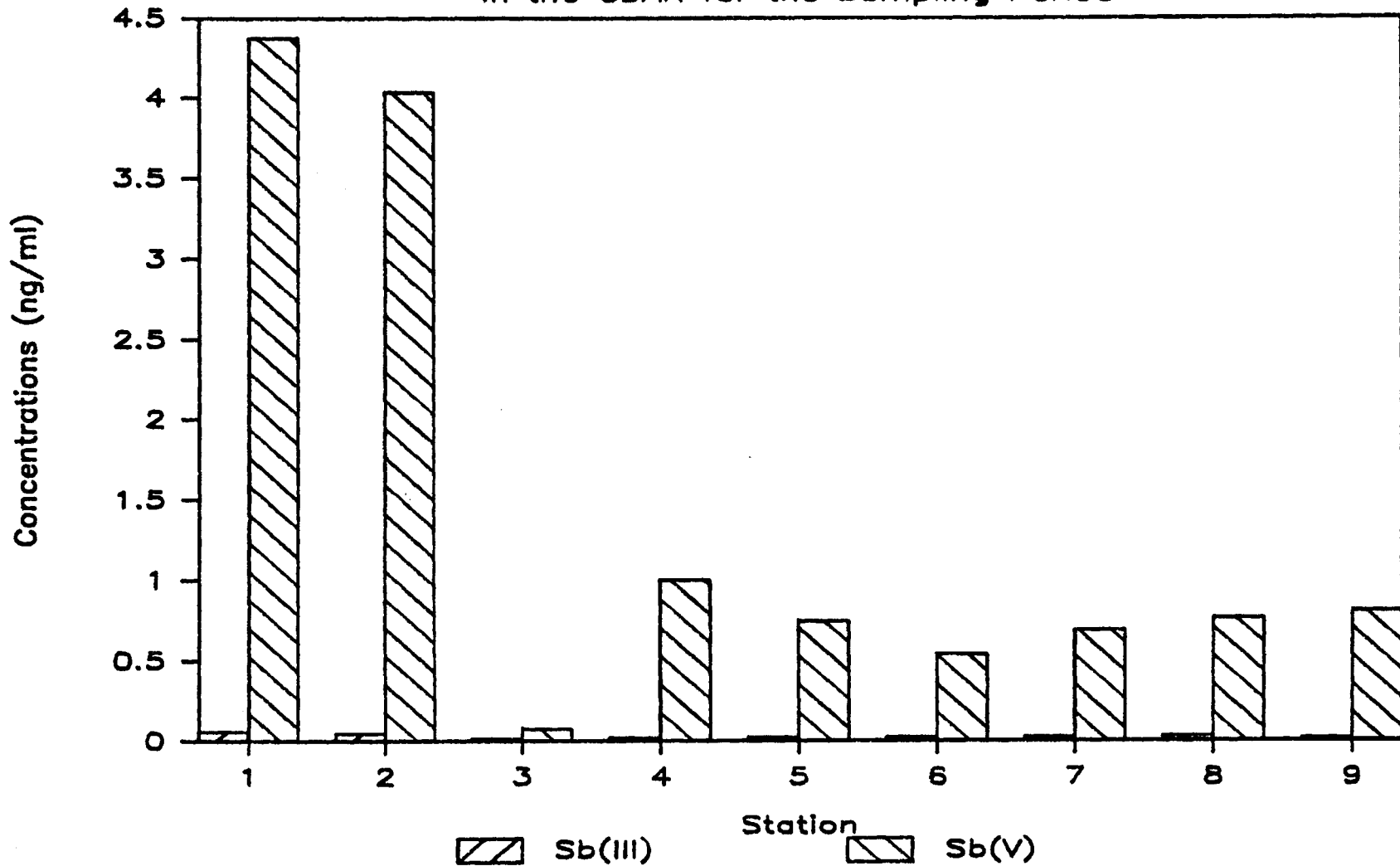
Figure 3. Mean values of Sb(lll) and Sb(V) in the Coeur d'Alene River during the sampling period.

Distribution of surface sediment As,Sb
along the Main Stem
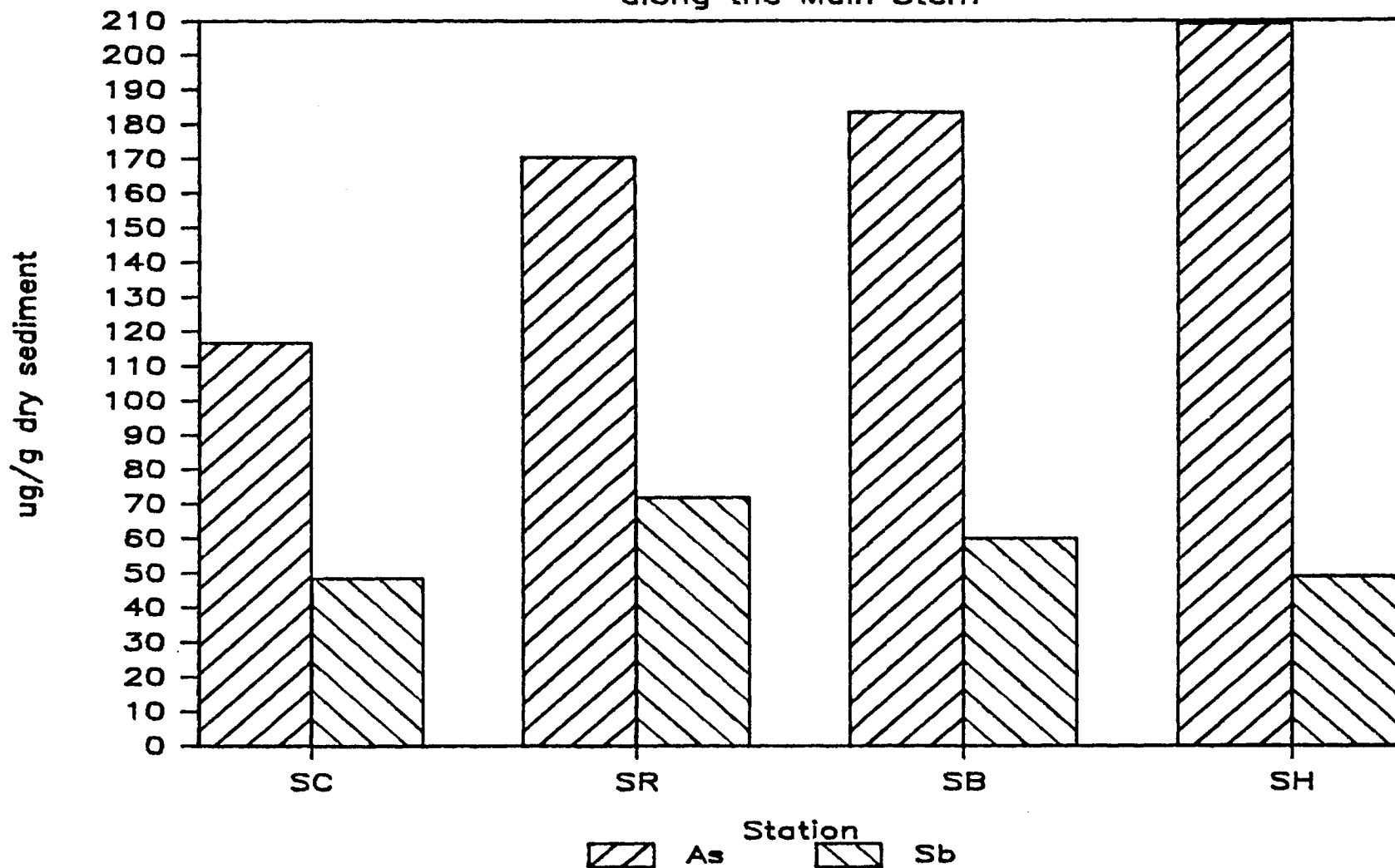
Figure 4. Distribution of As and Sb in the surface sediments along the Main Stem
of the Coeur d'Alene River.
(description of the sampling sites is given in Table 9).

Table 4.   Zinc concentrations in waters from the Coeur d'Alene River

	Station								
	1	2	3	4	5	6	7	8	9
Dec	2.05	4.14	*	*	0.67	*	*	*	*
Jan	2.00	4.23	0.02	0.99	0.75	0.08	1.03	1.07	0.43
Feb	2.04	3.56	0.02	0.93	0.46	0.05	0.73	0.62	0.35
March	1.54	2.52	0.03	0.57	0.28	0.06	0.35	0.36	0.21
April	0.85	1.25	0.02	0.40	0.19	0.04	0.25	0.24	0.18
May	0.67	0.79	0.01	0.42	0.27	0.01	0.32	0.31	0.21
June	1 .20	2.60	0.02	1.17	0.70	0.01	0.44	0.57	0.14

Concentrations in ug/mL
* : Samples could not be collected due to snow

Table 5.   Manganese concentrations in waters from the Coeur d'Alene River

	Station								
	1	2	3	4	5	6	7	8	9
Dec	0.24	1.67	*	*	0.38	*	*	*	*
Jan	0.26	1.84	N.D.	0.47	0.36	0.18	0.79	0.71	0.20
Feb	0.19	1.28	0.01	0.30	0.20	0.24	0.33	0.41	0.17
March	0.12	0.64	0.01	0.14	0.10	0.15	0.11	0.17	0.09

	Station								
	1	2	3	4	5	6	7	8	9
April	0.07	0.36	0.01	0.10	0.05	0.10	0.07	0.09	0.10
May	0.08	0.17	N.D.	0.12	0.08	0.10	0.09	0.11	0.26
June	0.18	0.91	0.02	0.93	0.41	0.08	0.38	0.24	0.20

Concentrations in ug/ml
N.D. : Not detectable
* : Samples could not be collected due to snow

Table 6.   Iron concentrations in waters from the Coeur d'Alene River

	Station								
	1	2	3	4	5	6	7	8	9
Dec	N.D.	0.73	*	*	0.31	*	*	*	*
Jan	0.04	0.12	N.D.	N.D.	0.01	0.28	0.13	0.19	0.15
Feb	0.01	0.26	N.D.	0.10	0.01	0.18	0.23	0.21	0.19
March	N.D.	0.22	N.D.	0.04	0.02	0.11	0.04	0.04	0.08
April	N.D.	0.22	N.D.	0.04	0.02	0.11	0.04	0.04	0.08
May	0.06	0.08	N.D.	0.05	0.06	0.16	0.04	0.06	0.10
June	0.03	N.D.	N.D.	0.19	0.07	0.11	0.15	0.20	0.08

Concentrations in ug/ml
N.D. : Not detectable
* : Samples could not be collected due to snow

Table 7.   Mean values and ranges of zinc, manganese, and iron in the waters of the Coeur d'Alene River for the sampling period

Station	Zn		Mn		Fe	
	Mean	Range	Mean	Range	Mean	Range
1	1.48	0.67-2.05	0.16	0.07-0.26	0.02	0-0.06
2	2.73	0.79-4.23	0.98	0.17-1.84	0.23	0-0.73
3	0.02	0.01-0.03	<0.01	0-0.02	nil	N.D.
4	0.75	0.40-1.17	0.34	0.10-0.47	0.07	0-0.19
5	0.47	0.19-0.75	0.23	0.05-0.38	0.07	0.01-0.31
6	0.04	0.01-0.08	0.14	0.08-0.24	0.15	0.11-0.21
7	0.52	0.25-1.03	0.30	0.07-0.79	0.11	0.04-0.23
8	0.53	0.24-1.07	0.29	0.09-0.71	0.12	0.04-0.21
9	0.25	0.18-0.43	0.17	0.09-0.26	0.11	0.08-0.19

Concentrations in ug/mL
N.D. : Not detectable

South Fork at Station 2. Cadmium had been detected only at Stations 1 and 2 between December and February and was found in concentrations around 0.01 ug/mL with Station 2 showing a value of 0.02 ug/mL on one occasion. The main consequence expected of Cd at such concentrations is its undesirable synergistic effect when combined with zinc. Salmon fry have been reported killed with 0.03 ug/mL Cd plus 0.15 ug/mL zinc (McKee and Wolf, 1963). No Cd was detected in anystation in the sampling period after February. Concentrations of Cu, Pb, and Ni in the river during the study were never above the detection limits of these metals given in Table 1.

C. Arsenic, Antimony and Other Trace Metals in Anderson Lake and in Thompson Lake

Zinc, Cu, Cd, Pb, As, and Sb have been reported to accumulate in the sediments of Anderson Lake and Thompson Lake (Bauer, 1974). Stations 10 and 11 were selected to study the water quality of these lakes and to compare them to the data obtained from the main stem of the river. The results are given in Table 8. Arsenic and Sb were found in higher concentrations compared to the main stem water. Arsenic(III) and Sb(V) are still the predominant species in the lake water; however, Station 10 showed an unexpectedly high value of As(V) in June. The water samples from Thompson Lake also had higher concentrations of iron. The low concentrations of zinc in Stations 6, 10, and 11 suggest that there is no obvious pollution correlation between the lakes and the water of the main stem during the sampling period. The water in the lakes is relatively stagnant and confined. The effects of water-sediment interactions are probably more pronounced in these lakes; however, their water quality is also complicated by stratification and turnover effects. Further studies on the water quality of these lakes and their relationship to the Coeur d'Alene River are desirable.

Leaching of Sediments

Arsenic, antimony, and other trace metals in the sediments of the Coeur d'Alene River are being leached to varying degrees by ground water and surface water. In addition, mixing of bottom sediments with water will occur as a result of sediment resuspension by propeller wash and by storms. Such mixing will speed up the release of trace metals. To have a better understanding of the chemical behaviors of As and Sb and their mobility during water-sediment interactions, leaching

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Table 8. As, Sb, Zn, Mn, and Fe concentrations in Station 10 (Anderson Lake) and in Station 11 (Thompson Lake)

Station	pH	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)	Zn	Mn	Fe
10 a	7.52	0.592 ± 0.008	0.706 ± 0.027	0.025 ± 0.004	1.260 ± 0.039	0.08	0.04	N.D.
b	7.48	1.064 ± 0.012	1.072 ± 0.021	0.048 ± 0.003	1.344 ± 0.083	0.06	0.04	0.05
c	7.60	0.117 ± 0.006	1.279 ± 0.018	0.052 ± 0.004	2.004 ± 0.027	0.01	0.09	0.06
11 a	7.46	0.671 ± 0.010	0.753 ± 0.027	0.154 ± 0.007	1.007 ± 0.037	0.13	0.48	0.75
b	7.43	0.822 ± 0.010	1.001 ± 0.021	0.052 ± 0.003	1.285 ± 0.028	0.08	0.36	0.89
c	7.59	0.528 ± 0.009	0.534 ± 0.014	0.054 ± 0.004	1.221 ± 0.021	0.06	0.09	0.42

Concentrations of As and Sb in ng/mL
Concentrations of Zn, Mn and Fe in ug/mL
N.D.: Not detectable
a : April, b : May, c : June of 1987

experiments were conducted. The leaching results will then be correlated with the As and Sb species and the water quality data observed in the river.

In the leaching experiments, pH, arsenic, antimony, and other elements including zinc, manganese and iron were monitored. Zinc and manganese were chosen as general water quality indicators because both in SO_4 and $MnSO_4$ are very soluble. Sulfate is a common anion detectable in the water of the Coeur d'Alene River. In the region where sulfate is stable, zinc is mobile and does not form hydrolysis precipitates readily. The monitoring of iron was included because it had been reported that iron was involved in the adsorption of arsenic in surficial sediments (Gupta and Chen, 1978; Pierce and Moore, 1980, 1982). Both hydrous manganese and iron oxides of sediments have strong scavenging effects for metal ions.

A. Sampling

Six sediment samples from the Coeur d'Alene River were selected for leaching. Descriptions of the sampling sites are given in Table 9. The sediments were collected according to the procedures described in the experimental section.

B. Mineralogy and Metal Content of the Sediments

The sediment samples were analyzed by X-ray powder diffraction using a Philips Norelco X-ray diffractometer for identification of minerals. Both the bulk samples and the clay fractions (<5u) were analyzed. X-ray diffraction showed that the samples are mainly composed of quartz, muscovite and siderite with small quantities of Kaolinite. Potassium-feldspar exists in all samples. The clay fraction makes up about 2.0-3.2% of the bulk sample and is composed of essentially the same minerals as those of the bulk samples. The diffraction patterns for the clay fraction are generally less intense than those of the bulk samples, implying a poorer crystallinity.

The concentrations of arsenic, antimony, aluminum, iron, sulfur, and six other trace elements in the sediment samples prior to leaching were analyzed by INAA, XRF, and ICP-AES. The results are presented in Table 10.

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Table 9. Description of the six selected sediment-sampling sites

Station	Site Description
SC	near Cataldo Mission flats, very close to Station 5
SR	at Station 7, near the bridge beyond Rose Lake
SB	near Blue Lake
SH	at Station 8, near Harrison
SM	near the mouth of the Coeur d'Alene River at Coeur d'Alene Lake
SN	on the North Fork before it enters the main stem

Table 10.   Concentrations of arsenic, antimony and nine other elements in the
sediments collected from the Coeur d'Alene River

Sample	ug/g								%		
	As	Sb	Zn	Mn	Cu	Cd	Pb	Ni	Al	Fe	S
SC	117.05	48.72	5703	6081	131	59	4286	16	5.26	8.30	0.59
SR	170.43	72.11	9262	8163	232	77	7874	18	5.08	10.49	1.04
SB	183.50	60.19	5679	11323	182	48	5659	16	4.61	12.41	0.81
SH	209.09	49.20	4409	10021	132	46	5098	12	4.45	11.82	0.63
SM	147.39	48.71	4148	8465	167	41	3912	14	4.82	10.05	0.53
SN	10.68	1.91									

C. Results and Discussion

Sediments were leached with deionized water under aerobic conditions with stirring. The leaching conditions were designed to simulate a situation where the whole mass of the sediment was constantly exposed to the leaching solution. The variations in pH of the water in contact with the sediments during the course of leaching are summarized in Figure 5. Leachates from the sediments showed little change in pH during mixing except that from the North Fork (SN), which had a slightly lower initial pH.

The leaching of As species and other metal ions from the sediments was expressed on a mass release basis. Net mass release for a given chemical constituent is the change in the mass of that constituent in water compared to the mass originally present in the same volume of water. The movement of a chemical constituent from the sediments into water results in a positive net mass release, while a negative value is an indication of the reverse process. The formula for calculating the net release of a chemical constituent during leaching is given as follows:

1st sampling: y released $= V_o \cdot X_1$

2nd sampling: y released $= V_o \cdot X_2 - V_f \cdot X 1$

n^{th} sampling: y released $= V_o \cdot X_n - V_f \cdot (X_{n-1})$

where y $=$ species of interest

X_n $=$ concentration (ng/mL or ug/mL) corresponding

to n^{th} sampling

V_o $=$ volume of water (mL) used in the leaching

process

V_f $=$ volume of water (mL) remaining after sampling

The summation of the net mass release for a specific chemical constituent at a particular sampling period with all preceding net mass releases of that constituent gives the cumulative net mass release (ng/g or ug/g) for the chemical constituent at that specific sampling period. A plot of such data as a function of sampling time gives a cumulative release curve.

1. Releases of Arsenic and Antimony During Leaching

Cumulative releases of arsenic and antimony from sediments are presented in Figure 6 through

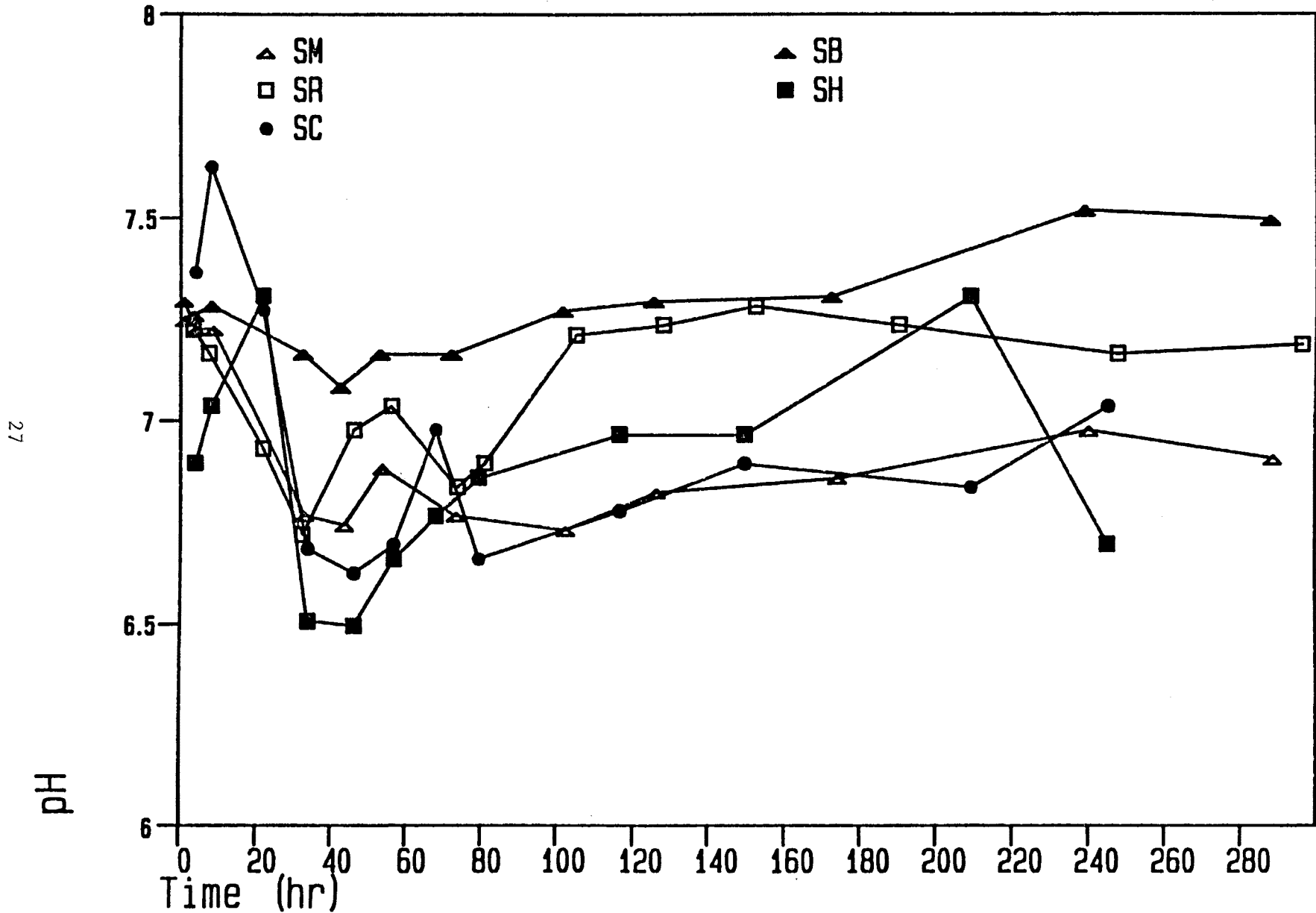# Variation of pH during leaching of sediments

Figure 5. Variation of pH during leaching of the sediments.

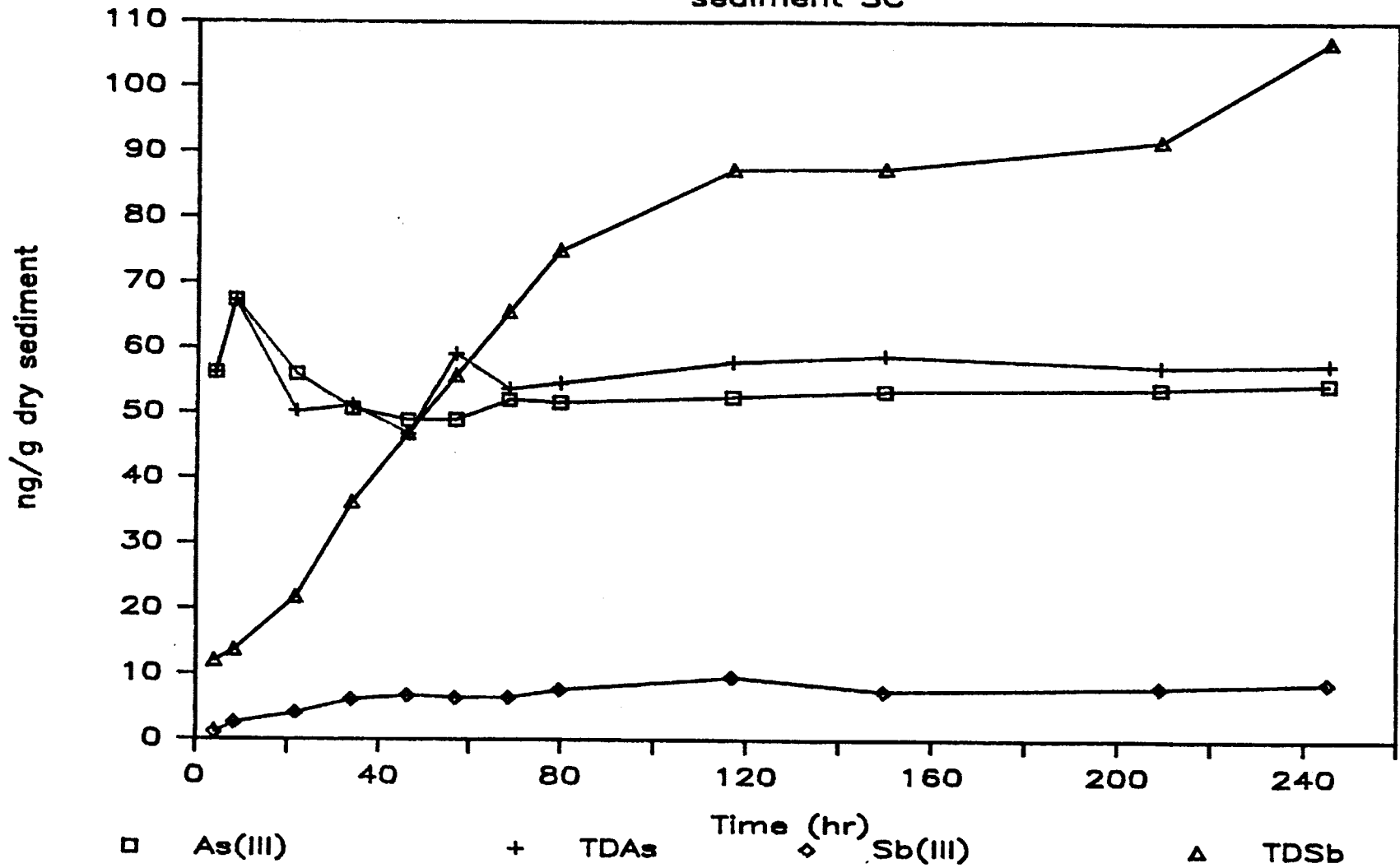# Cumulative Net Mass Releases of As,Sb

sediment SC

Figure 6. Cumulative releases of As and Sb from sediment SC.
           (near Cataldo Mission).
           TDAs=As(111)+As(V), TDSb=Sb(111)+Sb(V)

Cumulative Net Mass Releases of As,Sb
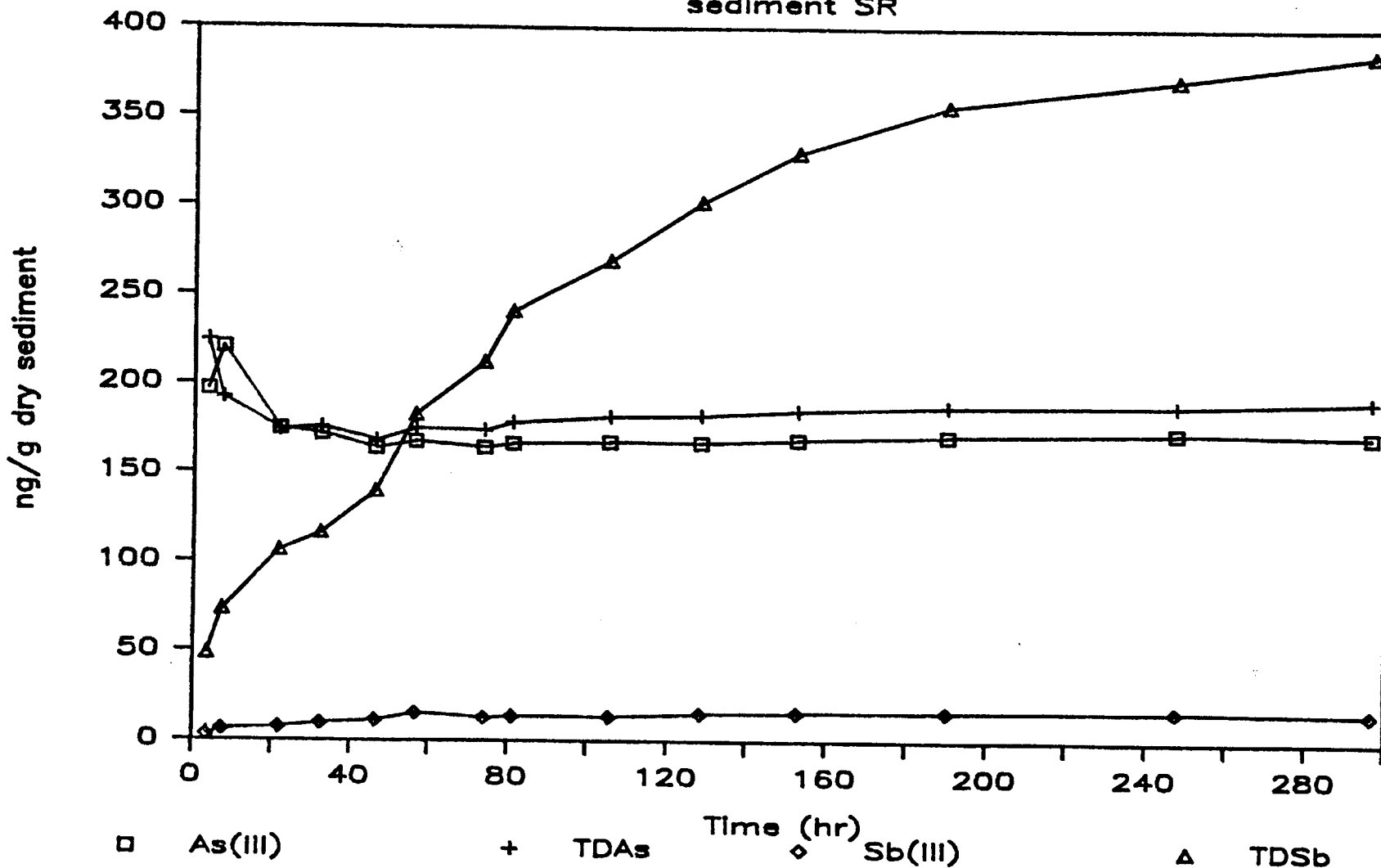
sediment SR

Figure 7. Cumulative releases of As and Sb from sediment SR.
(at station 7, near the bridge beyond Rose Lake).
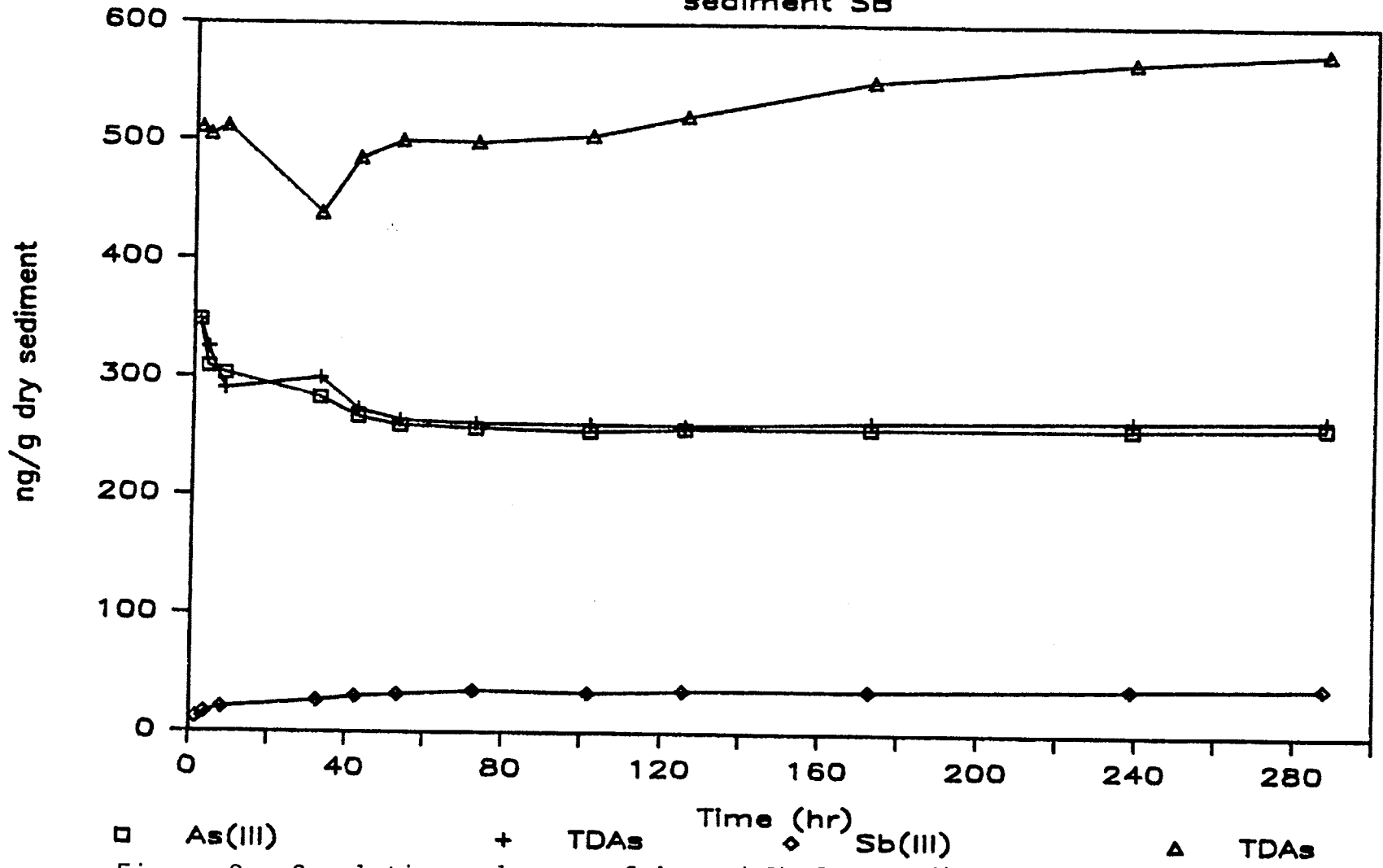TDAs=As(111)+As(V), TDSb=Sb(111)+Sb(V)

Figure 8. Cumulative releases of As and Sb from sediment SB.
(near Blue Lake).
TDAs=As(III)+As(V), TDSb=Sb(III)+Sb(V)

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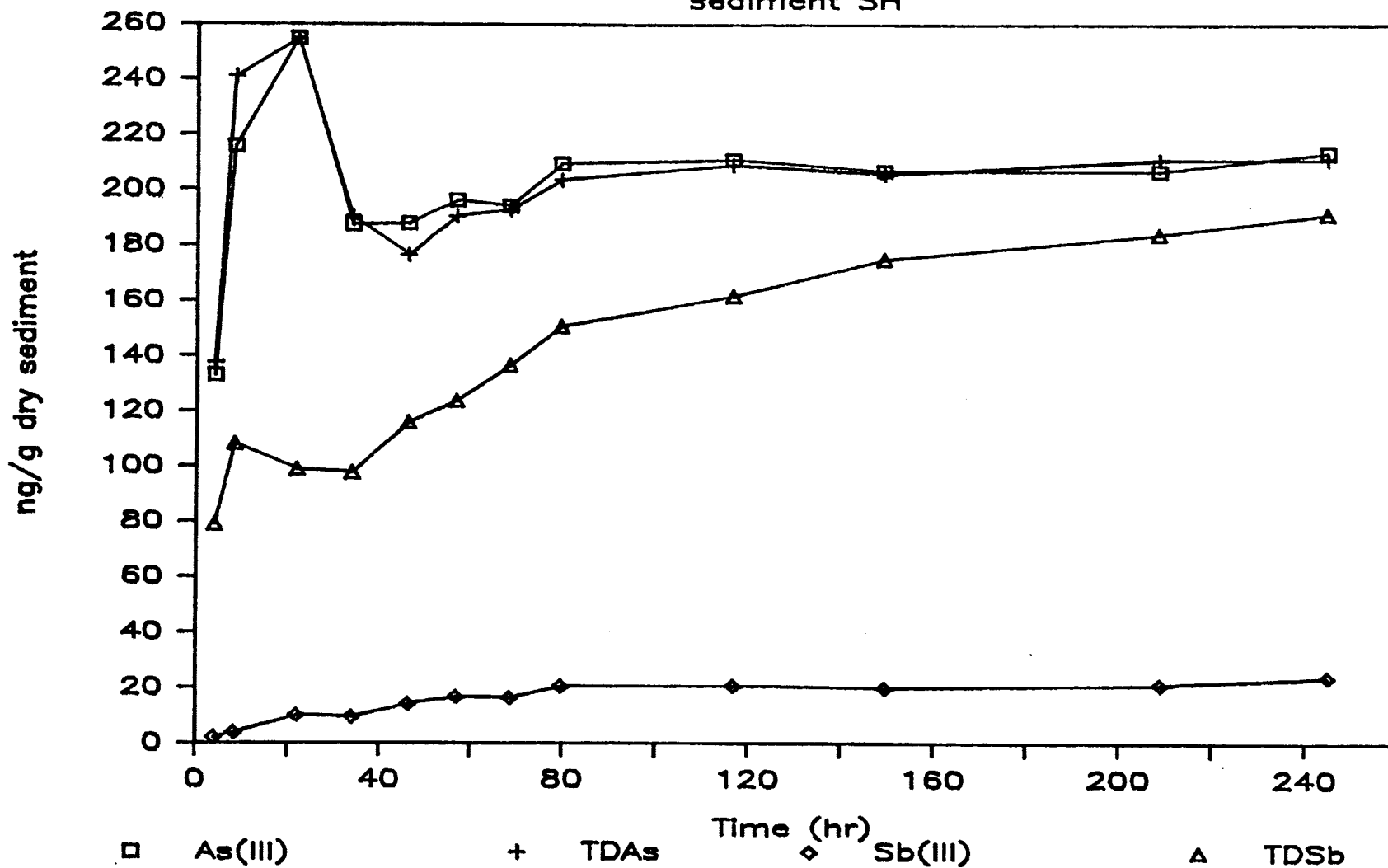# Cumulative Net Mass Releases of As,Sb

sediment SH

Figure 9. Cumulative releases of As and Sb from sediment SH.
(at station 8, near Harrison).
TDAs=As(111)+As(V), TDSb=Sb(111)+Sb(V)

Cumulative Net Mass Releases of As,Sb

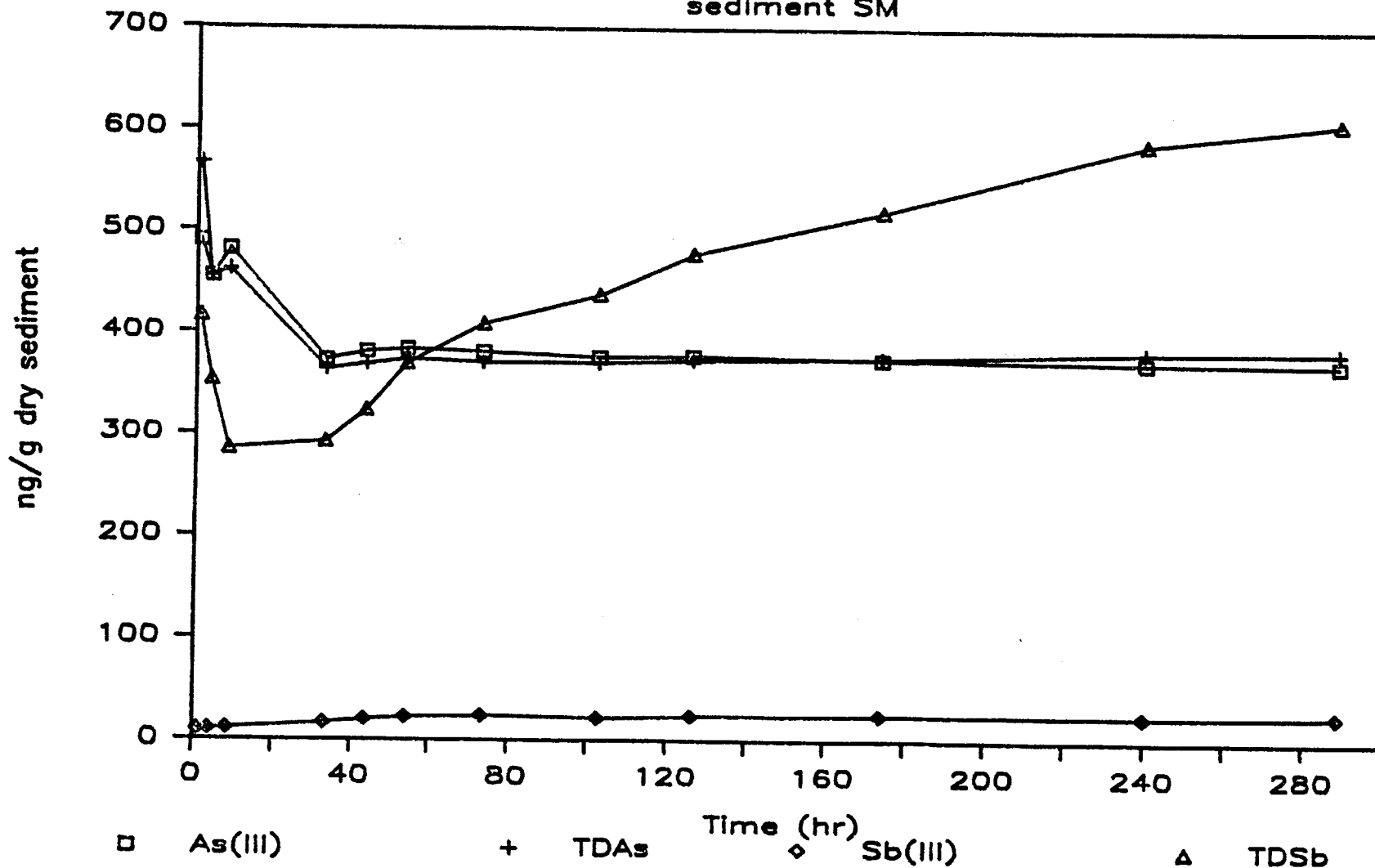### sediment SM

□ As(III)   + TDAs   ◇ Sb(III)   △ TDSb

Figure 10.   Cumulative releases of As and Sb from sediment SM.
(near the mouth of the Coeur d'Alene River).
TDAs=As(III)+As(V), TDSb=Sb(III)+Sb(V)

10. For sediments in the Main Stem the releases of total dissolved inorganic antimony [TDSb = Sb(III)+Sb(V)] were generally linear, whereas the releases of total dissolved inorganic arsenic TDAs = As(III)+As(V)] appeared to approach asymptotic limits. The results showed substantial releases of Sb(V) during leaching. Conversely, leaching under the same conditions resulted in the almost exclusive release of As(III). In a majority of the sediments the release of TDSb always exceeded that of TDAs after a short leaching period, although the total As concentrations in the sediments were generally higher than those of Sb. The net mass releases of As and Sb from the sediments essentially follow the order:

$$Sb(V) > As(III) > As(V) > Sb(III)$$
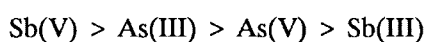
The same trend is observed in the river water of the main stem and the South Fork. Hence, the leaching experiments yielded results showing a significant correlation with the observed river water quality of the main stem and South Fork with respect to arsenic and antimony. Leaching conditions utilized in this study were designed to simulate a "worst" situation where the whole mass of sediment was constantly exposed to water in a confined environment. Particles of the sediments may also be abraded in the course of leaching, making them more susceptible to extraction. However, even under such "worst case" conditions, the release of As from sediments appeared to approach asymptotic limits, indicating that a majority of leachable As would be released within 50-60 hours of mixing. The results also suggest that the dissolution behavior of Sb is slightly different from that of As. The As and Sb concentrations in the river water did not match those in the laboratory leaching experiments simply because of a difference in the leaching time. Water in the river is in an unconfined environment. Leaching of metals from sediments, therefore, depends on the flow of water. The effect is more pronounced at low flow because of longer contact time and smaller water volume in the river. Hence, the As and Sb concentrations in the Coeur d'Alene River are always lower during the high flow rate in the spring months during snow melt, and higher As and Sb concentrations are observed when the flow is low and ground water discharge is the major source.

Sediments from the North Fork are relatively uncontaminated with mining wastes. Arsenic and antimony concentrations in sediment samples from the North Fork of the river are a factor of 10 to 35 lower than those from the main stem (Table 10). The amounts of As and Sb released from the

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North Fork sediments were substantially lower than those from the main stem. The ratios of Sb(V)/Sb(III) in the leachates were much lower relative to the data observed from the leaching of the Main Stem sediments. However, As(V) was found to be the predominant species in the North Fork water, in contrast to the results observed from the leaching experiments which indicated As(III) as the major leachable species. Conversion of As(III) to As(V) under atmospheric pressure is known to be slow without biochemical catalysts (Cherry et al., 1979). The presumption that the biological activity in the North Fork sediment was higher than that in the Main Stem and South Fork provides at least a partial explanation for the observed increase of the As(V) concentration in the water of the North Fork. Without sufficient biological activity, the time required for the oxidation of As(III) to As(V) is probably long relative to the residence time of the water in the South Fork and the Main Stem of the Coeur d'Alene River.

2. Releases of Zinc, Manganese, and Iron During Leaching

The cumulative net mass releases of Zn, Mn, and Fe from the sediments taken from the main stem of the Coeur d'Alene River are shown in Figures 11-15. Although the concentration of Fe in the river water was very low, there were releases of Fe from these sediments. The releases reached a rather constant value in a short time but never exceeded 10-20 ug/g during the leaching period. A very small but detectable amount of Fe was also found in the leachates of sediments SN.

The cumulative curves show that after 10 days of leaching Zn was still being leached from all the samples. Dissolution of Mn from sediments SC, SH, and SR was low but was significantly higher for sediments SM and SB. In general, the dissolution of Zn and Mn from the sediment samples after a short period of leaching showed the following order:

Zn: SC > SH > SR > SM > SB > > SN

Mn: SB > SM > SR = SH = SC > > SN

No Cu and Ni were detected in the leachates. However, very small amounts of Cd and Pb could be leached from some of the Main Stem sediments. The results correlate positively with those observed in the river water except for the releases of Mn from SM and SB.
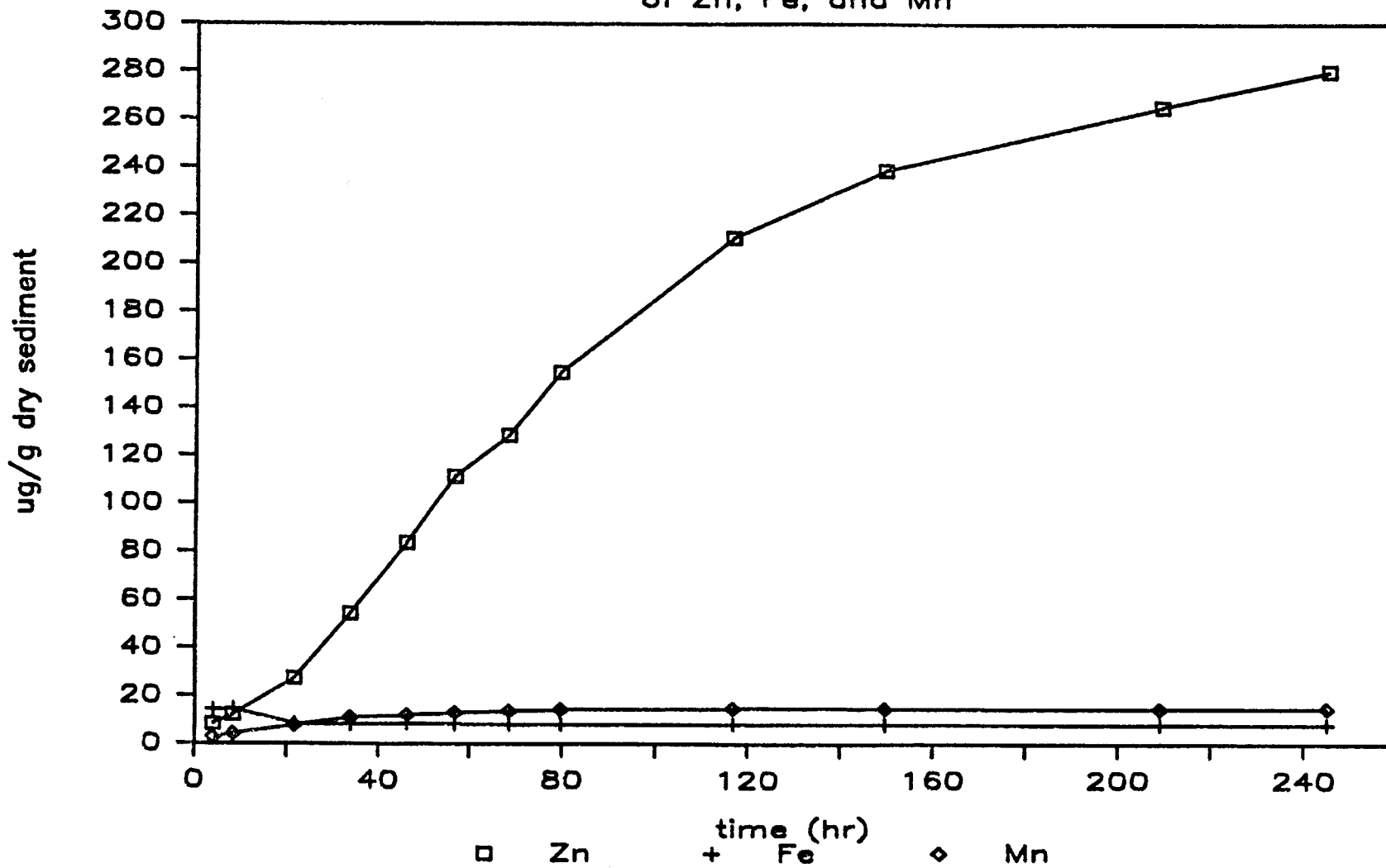
34

Figure 11. Cumulative releases of Zn, Fe, and Mn from sediment SC. (near Cataldo Mission).

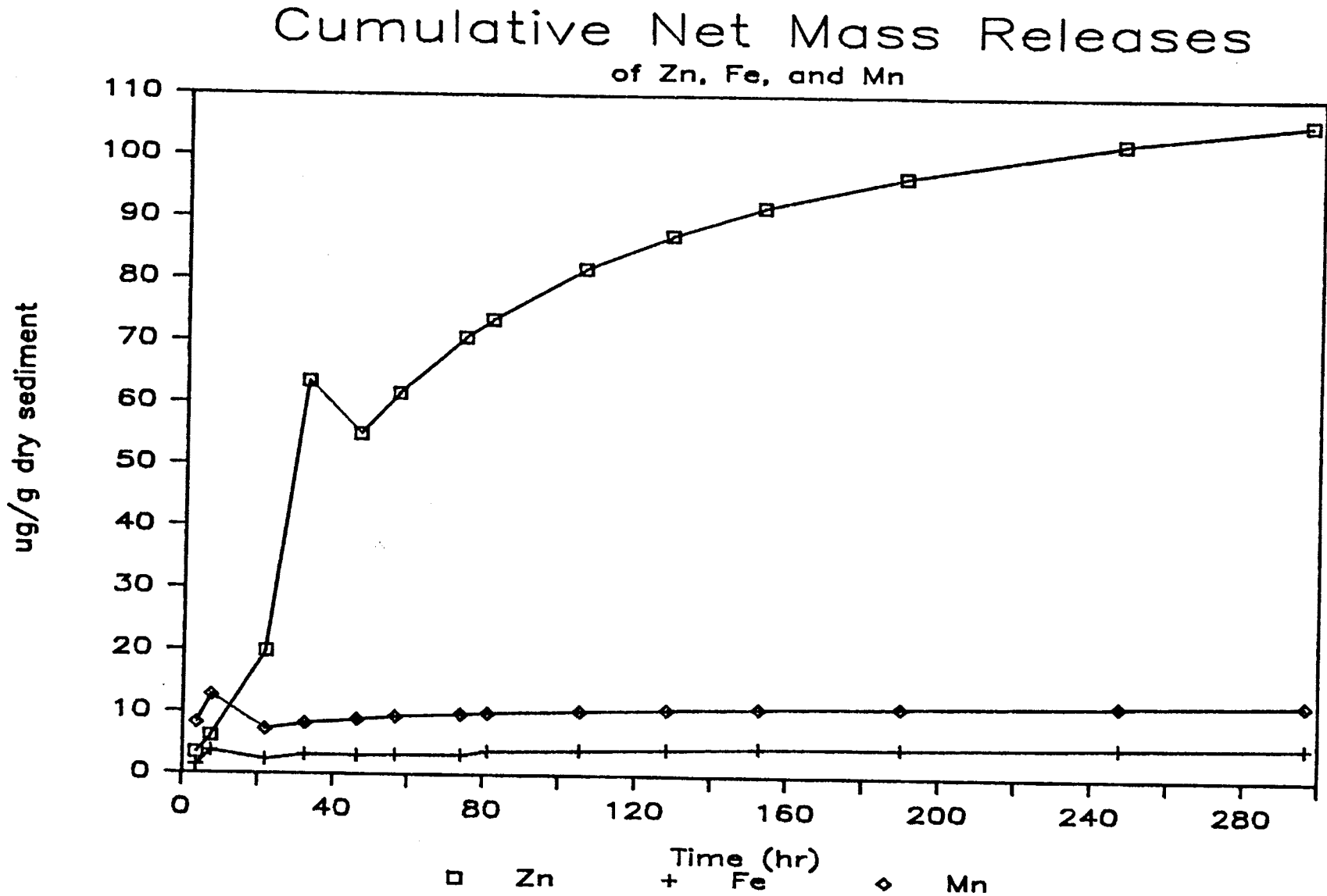# Cumulative Net Mass Releases
of Zn, Fe, and Mn

Figure 12.   Cumulative releases of Zn, Fe, and Mn from sediment SR.
(at station 7, near the bridge beyond Rose Lake).

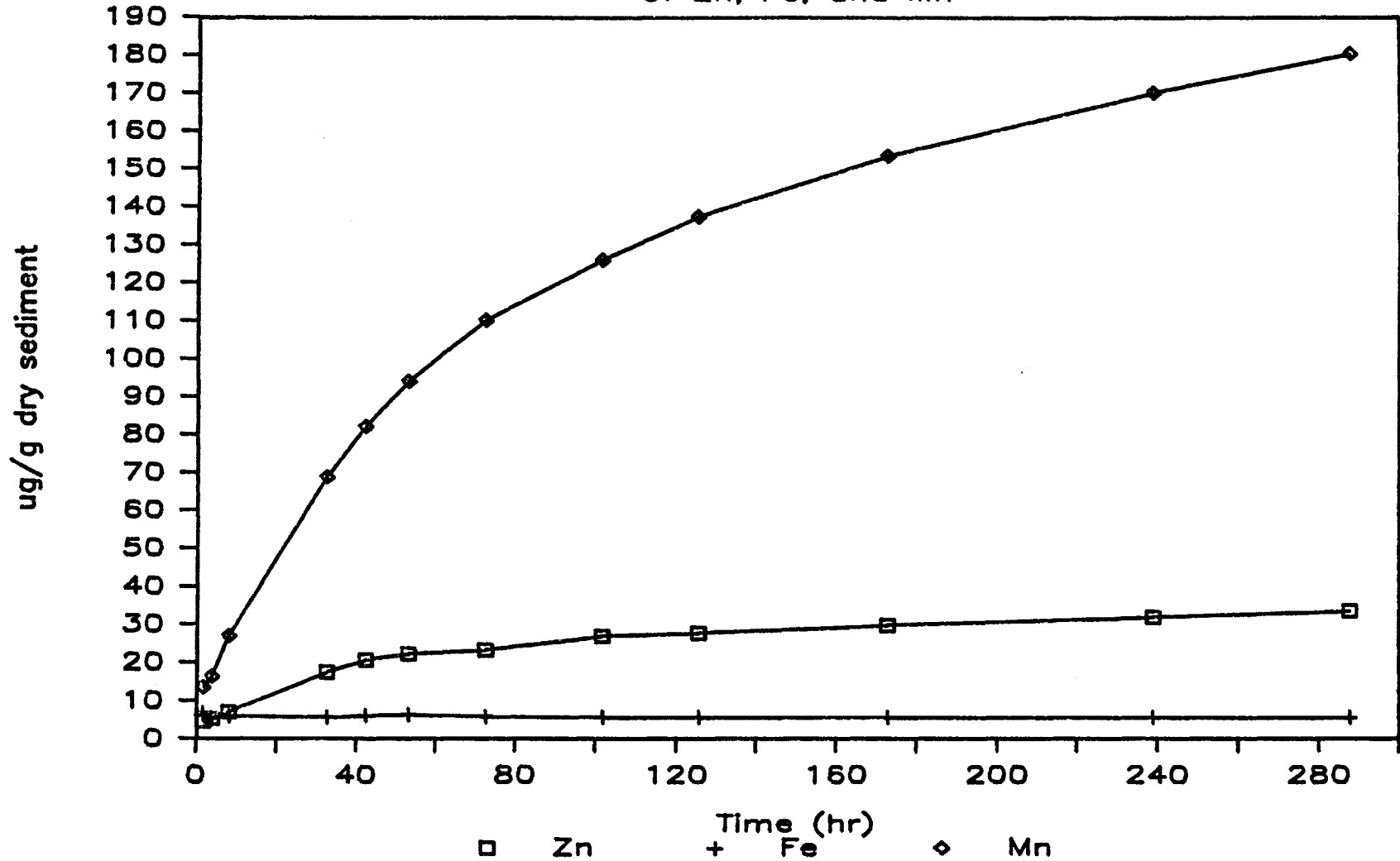Figure 13.   Cumulative releases of Zn, Fe, and Mn from sediment SB. (near Blue Lake).

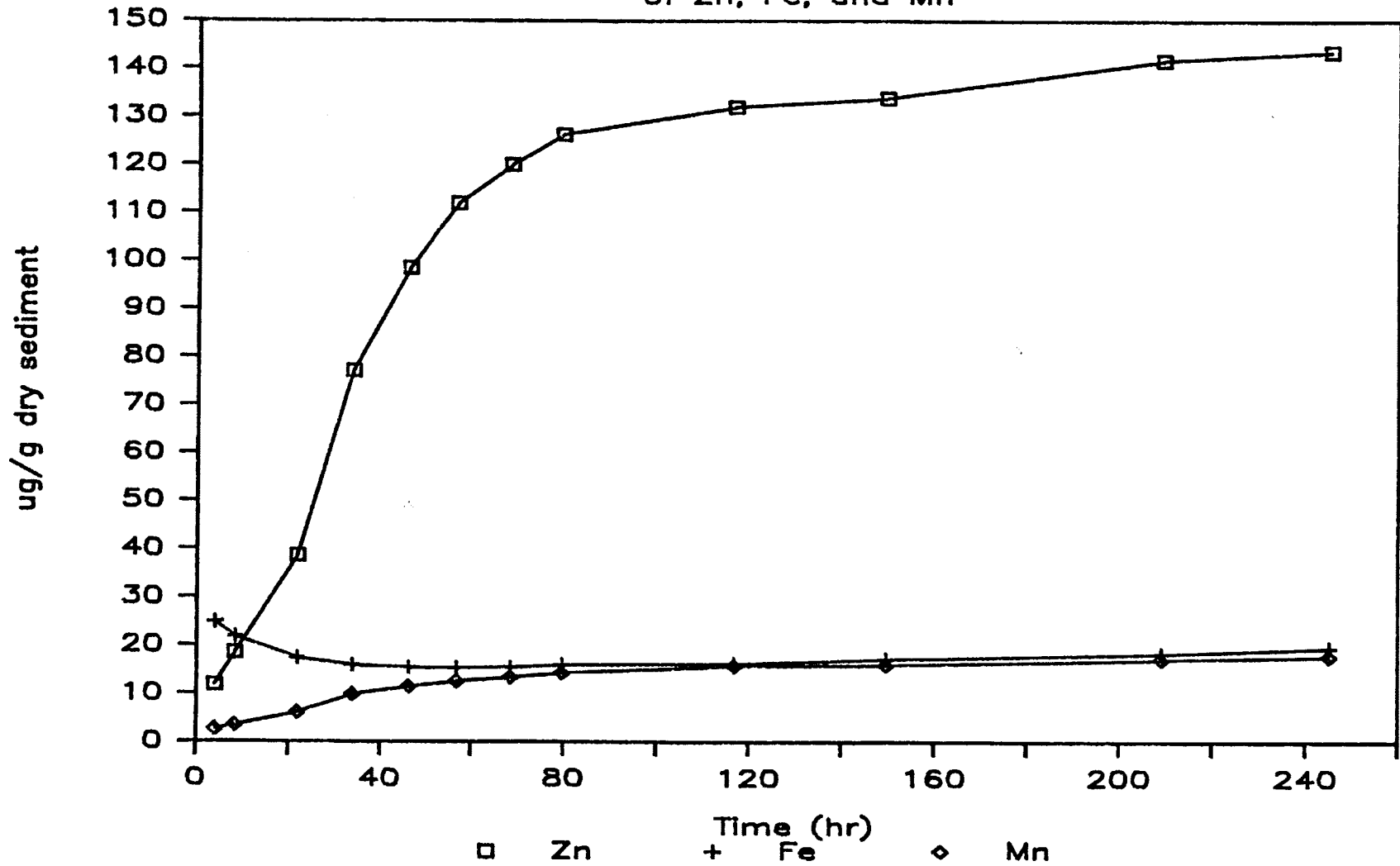# Cumulative Net Mass Releases
of Zn, Fe, and Mn

Figure 14.   Cumulative releases of Zn, Fe, and Mn from sediment SH.
(at station 8, Harrison).

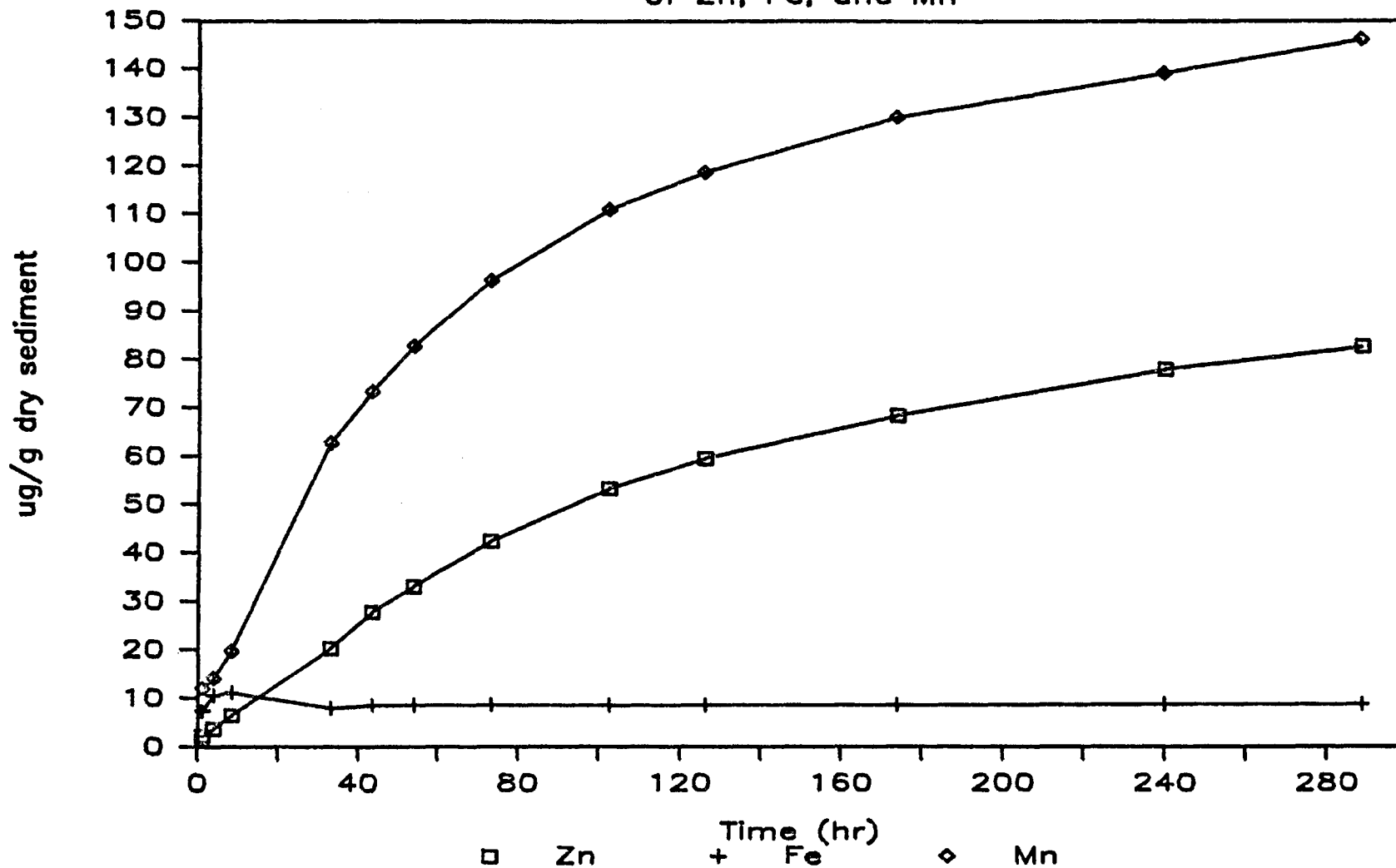# Cumulative Net Mass Releases

of Zn, Fe, and Mn

Figure 15. Cumulative releases of Zn, Fe, and Mn from sediment SM. (near the mouth of the Coeur d'Alene River).

3. Factors Affecting the Releases of Arsenic, Antimony, and Other Trace Metals

Adsorbed metal pollutants may become partly mobilized in the aquatic environment by changes in pH and redox conditions, by increased salinity, or by concentrations of chelators. Some of the factors are discussed in the following sections.

a. Effect of Iron Oxides and Manganese Oxides on Arsenic and Antimony Releases

A chromatographic distribution coefficient (D) is used in this discussion to examine the effects of sediment properties on the partitioning of As and Sb between the sediment and the water. The chromatographic distribution coefficient is defined as the concentration of a species in the solid phase divided by the concentration in the liquid phase,

$$D_{As} = \frac{(TAs)_{sed}}{TDAs}$$

$$D_{Sb} = \frac{(TSb)_{sed}}{TDSb}$$

where D_{As} and D_{Sb} = Chromatographic distribution of coefficients of As and Sb, respectively

TAs_{sed} and TSb_{sed} = total sediment concentrations (ug/g) of As and Sb, respectively

TDAs and TDSb = cumulative net mass releases (ug/g) of total dissolved inorganic As and Sb, respectively, following 10 days of leaching

Values of D for the five sediments studied are given in Table 11. A high D value signifies that more of the total As and Sb in a sediment was retained compared to a sediment with a lower D value. The distribution coefficients for both As and Sb were found to follow the order below:

$$SM < SB < SR < SH < SC$$

In examining the problems of trace metal chemistry in sediments, it is important to be aware of the existence of various metal "pools" to which the trace metals may be adsorbed. The anticipated behavior of these trace metals may therefore be at considerable variance with that actually displayed in the presence of sorptive reservoirs. Both iron oxides and manganese oxides have been reported to

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possess high affinities for many trace metals.

To better define the relationship between arsenic, antimony, iron oxides and manganese oxides in the sediments, a citrate-dithionite extraction method described by Olson and Roscoe (1982) was used to determine the amounts of free iron oxides and manganese oxides in the sediments. The results are summarized in Table 11.

The percentages of free iron oxides from the sediments displayed the same trend as the chromatographic distribution coefficients for As and Sb, though the trend is slightly different in the case of Mn.

% Fe as free iron oxides: SM < SB < SR = SH < SC

% Mn as free manganese oxides: SM < SR = SH < SB < SC

The release of As and Sb from the sediments apparently is not directly related to the total As or Sb content, nor is it dependent directly upon the total Fe or Mn content of the sediments. High D values are associated with larger amounts of free iron oxides, while the free manganese oxides appear to play a relatively minor role. The results suggest that the presence of free iron oxides and manganese oxides is one of the factors affecting the retention of As and Sb.

The adsorption of As by sediment components such as iron and aluminum oxides and hydroxides has been reported (Anderson et al., 1976; Gupta and Chan, 1978; Pierce and Moose, 1980, 1982). Manganese oxides have also been shown to be involved in the adsorption of As (Takamatsu et al., 1985). Arsenic and Sb are expected to have some similarities in geochemical behavior as are other elements from the same group in the periodic table. This study reveals that both the free iron oxides and manganese oxides may be present in sufficient quantities to affect surface properties of the sediments and to result in greater adsorption of As and Sb.

b. Effect of pH on the Mobilization of Arsenic and Antimony

On a regional scale, acid precipitation is probably the most important single factor affecting metal mobility in surface water. In general, it is the trace metals on the surface of the sediments which are most immediately available to release in aqueous environments. To understand the

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Table 11.   Arsenic and antimony distribution coefficients (D) following 10 days
of leaching and the amount of free iron oxides and manganese oxides

Sediment	K_{As}	K_{Sb}	% Fe as free iron oxide	% Mn as free manganese oxide
SC	2032	458	2.73	0.14
SR	902	194	2.41	0.10
SB	692	106	1.71	0.12
SH	990	256	2.27	0.11
SM	384	83	1.46	0.07

release of arsenic and antimony with respect to the acidity, a sediment sample (SR) from the main stem was leached for 40 hrs at controlled pH. Table 12 presents the results.

The desorption of trace metals from the sediments in aqueous solution follows a predictable pattern with decreasing pH. With high levels of Zn, Mn, and Pb in a sediment, a moderately acidic solution under aerobic conditions results in substantial releases of these metals. Even at near neutral pH (pH 6.3), significant amounts of Zn and Mn were still leachable from the sediment. However, the releases of Cu, Cd, and Pb are much smaller (<1 ug/g) at this pH.

Although most of the trace metals displayed enhanced leaching at high pH, As and Sb desorption rose sharply relative to other metals. Leaching of As(V) at pH 8.3 was much higher than pH 4.3 or 6.3. This behavior is expected from As(V) because adsorption of As(V) by soils, clay minerals, and hydrated iron oxides has been shown to peak in the pH range of 3.5 to 5.3 (Frost and Griffin, 1977; Galba, 1972; Pierce and Moore, 1982). Oxidation of As(III) to As(V) with dissolved oxygen is reported to be very slow at neutral pH values but to proceed faster in strongly alkaline or acidic solution and in the presence of certain catalysts (Ferguson and Gavis, 1972; Oscarson et at., 1980; Johnson and Pilson, 1975). The lower concentrations of As(lll) at pH 8.3 is probably due to adsorption processes. The leaching of As(lll) increases in moderately basic solution with the formation of arsenite ions As O_2-.

The mean redox potentials of the solutions during the leachings of the main stem sediments with deionized water were between 0.21-0.27 mV and the mean pH was about 7. The sediments appeared to be slightly aerobic. Arsenic(lll) was the major species found in the leachates. Although the oxidation of the arsenite to arsenate is theoretically possible under aerobic conditions, it actually takes place only at considerably higher potentials than those found in the leachates, and on conditions that there is an appreciable over potential such as a powerful oxidizing agent or catalyst. Therefore, release of As(lll) in the river during water-sediment interactions could still be expected from the contaminated sediments.

The results indicate that higher amounts of Sb will be mobilized into water soluble form under basic leaching conditions. Antimony (V) is the predominant Sb species leached in weakly acidic and in basic solutions, whereas substantial amount of Sb(III) was released in moderately acidic solution. The same result was observed in a sample from the Blackbird Area where the sediment was

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Table 12. Release of metals from the sediments (SR) during leaching as a function of pH

metal	pH=2.7	pH=4.3	pH=6.3	pH=8.3	pH=11.4
As(III)	3075.97	267.32	164.30	7.75	122.06
As(V)	5062.87	20.04	8.65	113.39	1744.74
Sb(III)	194.59	6.10	2.61	4.68	12.68
Sb(V)	8.89	10.60	96.06	1067.60	1605.53
Zn	1519.66	1028.06	39.85	1.51	3.21
Fe	7161.57	5.04	2.72	9.96	27.75
Mn	987.18	351.40	11.13	<0.10	1.24
Cd	13.16	9.58	0.07	<0.05	0.06
Cu	25.43	2.11	0.08	0.29	4.70
Pb	3302.58	474.53	0.73	2.72	16.40
Ni	2.17	0.84	<0.40	<0.40	<0.40

As and Sb concentrations in ng/g of dry sediment
Other metals released are given in ug/g dry sediment

relatively uncontaminated with Sb (Mok and Wai, 1986).

The effects of pH variation not only influence the mobility of As and Sb, but also alter the distribution of the metal species. The observation of an enhanced As and Sb solubility at low and at high pH in our leaching experiments is significant. In mine waters and contaminated sediments disposed of on-land, acidity of surface water can result in an increased leaching of the trivalent As and Sb which are known to be toxic. On the other hand, since lime treatment is a common method to reduce metal contents in acid mine drainage and waste waters related to mine tailings, the discharge of lime treated waste water would increase the pH of river water and consequently might result in a higher As and Sb release from sediment. A near-neutral pH condition will probably favor the long-term stability of mine wastes with respect to As and Sb.

c. Salinity

According to the literature, the decline in metal concentrations in sediments from the vicinity of river mouths towards the open sea can be interpreted in terms of loss of adsorbed metals by solid particles during transit (Olsen et al., 1982). Exchanges between liquid and solid phases can occur at the sediment-water interface and As and Sb may be released from the sediments into the surrounding seawater.

To evaluate the effects of salinity on the releases of As and Sb, the SR sediment was leached with a seawater for a period of 80 hours. The seawater was collected from the Puget Sound, Washington. The concentrations of As(V) and Sb(V) in the original seawater were 1.22+0.02 ng/mL and 0.24+0.04 ng/mL, respectively. Trivalent As and Sb were lower than 0.02 ng/mL in that natural seawater.

Results of this leaching study indicate that the salinity of the water had little impact on the short-term releases of As and Sb from the sediments. Cumulative net mass releases of As and Sb during the leaching period exhibited release patterns similar to that from deionized water leaching. Arsenic(III) and Sb(V) are the major constituents released. Leaching of As is slightly suppressed, but higher amounts of Sb(V) was mobilized into the seawater. Release of Sb(V) was about three times higher compared to that from deionized water leaching of the same type of sediment. The results indicate that disposal of contaminated freshwater sediments in saline environments may result

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in an increased dissolution of Sb.

Accumulation of Arsenic and Antimony in Sediments

Arsenic and Sb may be released to the environment in significant quantities through leaching of exposed wastes. Arsenic commonly accumulates in the uppermost layers of lake sediments. For example, high concentrations of As have been found in Lake Washington (Crecelius, 1975) and in Loch Lomond (Farmer and Cross, 1979) with reported values of 210 and 473 ug/g, respectively, in the uppermost sediments compared to concentrations of 12 and 18 ug/g deep down.

Sediment cores were taken from the Coeur d'Alene River to study the vertical distributions of As and Sb. The locations of the sediment cores are given below:

Sediment Core	Location
C1	Station 2 on the South Fork
C2	Station 3 on the North Fork
C3	Station 7 on the main stem
C4	From the delta area in Lake Coeur d'Alene at the mouth of the Coeur d'Alene River

Figures 16 and 17 show the vertical distributions of As and Sb in the upper layers of the sediments. The concentration profiles of Sb in the sediments appear to parallel those of As. Antimony concentrations were lower than As with the exception of the C1 sediment from the South Fork. The lowest As and Sb concentrations in the sediments were found at Station 3 on the North Fork. Concentrations of As and Sb in the North Fork sediment core averaged 9.41 ug/g and 1.87 ug/g, respectively. These values were probably close to the background concentrations in that area. No apparent vertical variations in the concentrations of As and Sb were observed in the North Fork sediment (C2).

Sediment cores from the South Fork (C1) and the main stem (C3) showed much higher As and Sb concentrations. However, there were no systemic variations in the vertical distributions of As and Sb. The water currents in the river could erode and redeposit surface sediments. The results

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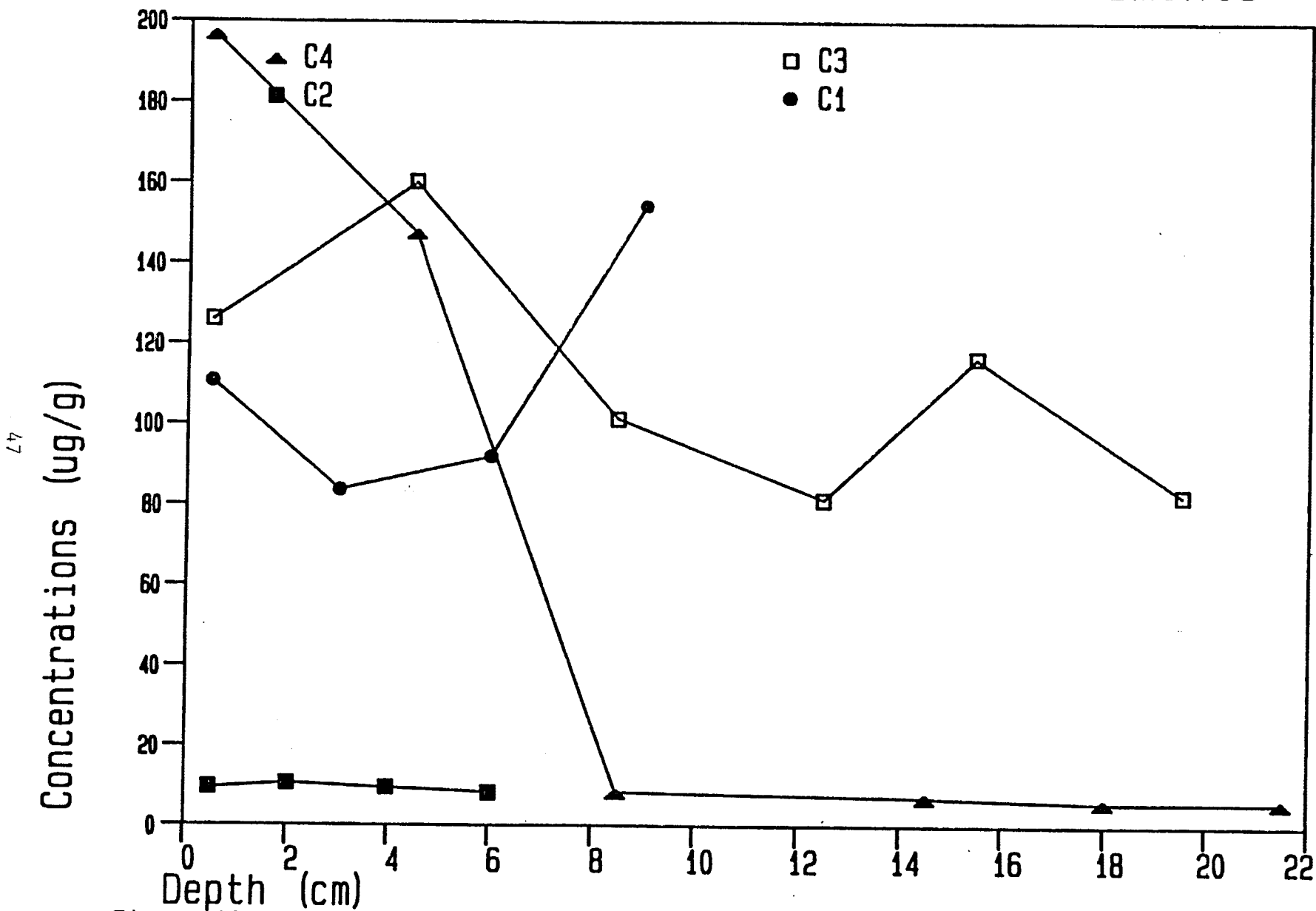
Vertical Distribution of As in Sediments

Figure 16.   Concentration profiles of As in the sediment cores.
(Description of the sampling sites is given in the text).

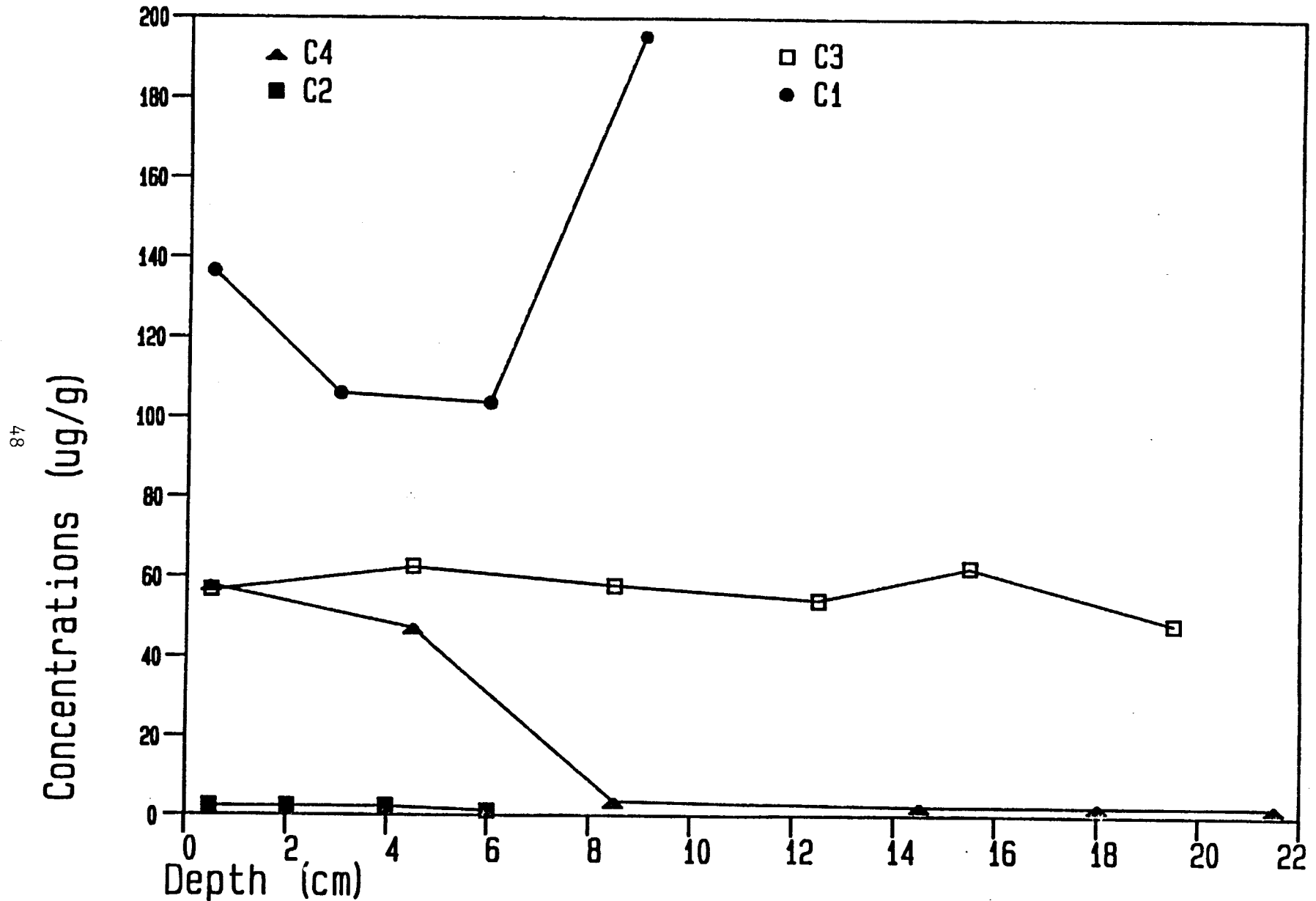# Vertical Distribution of Sb in Sediments

Figure 17. Concentration profiles of Sb in the sediment cores.
(Description of the sampling sites is given in the text).

also suggest that the sedimental accumulation of As and Sb probably extends to greater depths than that shown in Figures 16 and 17.

The sediment core from C4, which is located in Lake Coeur d'Alene at the mouth of the Coeur d'Alene River, displayed a distinct profile for the vertical distributions of As and Sb. The sediment core showed high As and Sb concentrations at the surface (197 ug/g As and 58 ug/g Sb), decreasing with depth to concentrations of a few ug/g. In addition, the delta area sediment also showed a strong correlation between the vertical distributions of As and Sb and those of Fe and Mn (Table 13).

The fixation of As in lake sediments has usually been attributed to adsorption onto hydrous Fe oxide (Neal et.al., 1979; Farmer and Cross, 1979). Correlations between As and Mn have also been reported (Crecelius, 1975; Takamatsu et al., 1985). Our results indicate that not only As but also Sb was associated with Fe and Mn; these associations were related to the iron-and manganese-oxides which control the surface properties of the sediments.

SUMMARY

An analytical method for the speciation of trivalent and pentavalent arsenic and antimony species in natural waters at concentrations as low as 0.01 ng/mL has been developed and applied to studies of the distribution of trivalent and pentavalent arsenic and antimony species in the Coeur d'Alene River in northern Idaho conducted between December 1986 and June 1987. The North Fork water was found relatively uncontaminated and showed very low concentrations of As (<0.26 ng/mL), Sb (<0.17 ng/mL), and other trace metals. Samples from the stations on the South Fork had higher levels of As (0.16-1.64 ng/mL), Sb (1.11-8.25 ng/mL), Zn (0.67-4.23 ug/mL), and Mn (0.07-1.84 ug/mL). The mean value of Fe in the South Fork was lower than 0.30 ug/mL. Arsenic and Sb in the main stem ranged from 0.11 to 1.48 ng/mL and from 0.23 to 1.90 ng/mL, respectively. Zinc concentration in the main stem was also lower than that in the South Fork water. Cadmium was detected only at the stations on the South Fork between December and February in concentrations around 0.01-0.02 ug/mL.

| Table 13. | | Vertical distributions of As, Sb, Fe, and Mn in the sediments from the delta area of Lake Coeur d'Alene (0-22 cm) | | |

	ug/g		%	
Depth(cm)	As	Sb	Fe	Mn
0.5	196.96±2.88	58.06±0.43	11.19	0.97
4.5	146.63±2.56	47.13±0.41	9.20	0.71
8.5	7.84±0.48	2.99±0.12	2.44	0.06
14.5	7.37±0.32	1.96±0.09	2.45	0.02
18.0	6.21±0.33	1.82±0.10	2.34	0.02
21.5	5.63±0.36	2.20±0.11	2.22	0.02

As and Sb were determined by INAA based on quadruplicate analyses.
Fe and Mn were determined by XRF.

Arsenic(III) was the predominant form of As in the South Fork and main stem, whereas the North Fork generally had a higher As(V) concentration. Antimony(V) was the major Sb species in all three branches of the river. In the South Fork and main stem, Sb concentration were also higher than As concentrations in those waters.

The leaching of sediments using deionized water under aerobic conditions resulted in almost exclusive release of Sb(V). However, As(III) was the major form of As released. Releases of sediment Sb were generally linear while asymptotic limits on As releases were reached. Significant amounts of zinc, Fe, and Mn were also released during leaching, but Cu, Cd, Pb, and Ni were much less leachable.

The field data are generally correlated with the results observed from the laboratory leaching experiments. The leaching of As and Sb from sediments depends on the pH of the solution. Higher amounts of As and Sb were leached with both acidic and basic solutions. The behavior of antimony in the sediments is generally similar to that of As. Notable exceptions to this similarity are the pronounced release of Sb(III) at low pH and the increased release of Sb from fresh-water sediments leached with saline water. The releases of both As and Sb from the sediments during leaching are associated with the iron oxides and manganese oxides present in the sediments. A chromatographic distribution coefficient (D) was used to evaluate the leaching of As and Sb from the sediments. The D values for Sb following ten days of leaching are lower than those of As, suggesting that Sb is less strongly retained by the iron oxides and manganese oxides in the sediments. This also explains the fact that although the sediments from the main stem had higher concentrations of As than Sb, the reverse is true in the main stem river water and in the solutions of the leaching experiments. The accumulation of As(III) in the sediments which were slightly aerobic and the lack of biological activity may also explain the low As(V)/As(III) ratios found in the South Fork and the Main Stem water samples. According to this study, interaction of water with the existing sediments is likely to be a major factor controlling the distribution of As and Sb species and the water quality of the Coeur d'Alene River.

Contamination of surface layers of sediments with As and Sb can be clearly inferred by comparing the As and Sb contents of three sediment cores (C1, C3, and C4) with a core (C2) taken from the North Fork which is relatively unpolluted. The As and Sb concentrations in the surface

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layers of the sediments C1, C3, and C4 were 9-18 times and 18-60 times, respectively, higher than those in the C2 sediments. High As and Sb concentrations in the sediment core from the delta area of Lake Coeur d'Alene are attributed to the input of contaminated sediments from the river. The few centimeters at the surface of the delta area sediments were brown, while those below were dark grey. Iron and manganese are enriched in the surface sediments of the core and show a strong correlation with As and Sb. Our experimental results showed that the presence of free iron oxides and free manganese oxides was a factor affecting the retention of As and Sb. These oxides in the surficial layers of the sediments were probably in sufficient quantities to result in greater adsorption of As and Sb.

The North Fork is relatively undeveloped, as reflected by its good water quality. The South Fork is receiving industrial discharges and as a result the concentrations of dissolved metals are high. The quality of water in the main stem of the Coeur d'Alene River is affected by discharges from the South Fork and by the leaching process in the river. Even if there were no mixing with water from the South Fork, zinc and other trace metals might still be present in the water because of the leaching of the polluted sediments. Water quality management planning for the Coeur d'Alene River should, therefore, consider the non-point sources of contamination including leaching of the river sediments. The existence of As, Sb, and other heavy metals in the sediments of the Coeur d'Alene River is primarily the result of the uncontrolled discharge of mine wastes into the river during past mining operations. The current data obtained from this area with respect to As and Sb will certainly be valuable in environmental planning and consideration for other similar mining areas.

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