CHEMICAL SPECIATION OF ARSENIC AND ANTIMONY IN NATURAL WATER SYSTEMS AND ITS APPLICATIONS TO ENVIRONMENTAL PROBLEMS

A Dissertation
Presented in Partial Fulfillment of the Requirements for the
DEGREE OF DOCTOR OF PHILOSOPHY
with a
Major in Chemistry
in the
COLLEGE OF GRADUATE STUDIES
UNIVERSITY OF IDAHO

by
Wai Man Mok
May 1988

AUTHORIZATION TO SUBMIT

DISSERTATION

This DISSERTATION of WAI MAN MOK, submitted for the degree of DOCTOR OF PHILOSOPHY with a major in chemistry and titled "CHEMICAL SPECIATION OF ARSENIC AND ANTIMONY IN NATURAL WATER SYSTEMS AND ITS APPLICATIONS TO ENVIRONMENTAL PROBLEMS," has been reviewed in final form and approved, as indicated by the signatures and dates given below. Permission is now granted to submit final copies to the College of Graduate Studies for approval.

Major Professor Chien M. Wai Date 5-10-1988
Committee Members Sherry Farwell Date 5-10-1988
Wesley R Harris Date 5-10-88
Henry Willmes Date 5-10-1988
Department Administrator J H Corley Date 5-12-1988
College Dean Galen O. Rowe Date 5/12/88

COLLEGE OF GRADUATE STUDIES FINAL APPROVAL AND ACCEPTANCE:

College of Graduate Studies Dean Jean'ne M. Shreeve Date 6/3/88

ABSTRACT

A method for the speciation of trivalent and pentavalent states of inorganic arsenic (As) and antimony (Sb) in natural waters has been developed. The proposed method first extracts the trivalent As(III) and Sb(III) as pyrrolidinecarbodithioate (PCDT) complexes into chloroform, followed by a nitric acid back-extraction to recover the elements. Arsenic and Sb in the acid solution are determined by neutron activation analysis (NAA). The pentavalent species, As(V) and Sb(V), are reduced to the trivalent state using potassium iodide and sodium thiosulfate and then are extracted with PCDT for NAA. The two-step preconcentration procedure provides a large enrichment factor, eliminates the interfering matrix species, and extends the useful working range of NAA for As and Sb. The extraction method has also been applied to the determination of low levels of As and Sb in biological samples by NAA.

The speciation method has been used to evaluate the distribution of As(III) and As(V) and its relation to other water quality parameters in the groundwater system of a major lead-zinc mine in the Coeur d'Alene Mining District of northern Idaho. It is known that mine wastes containing pyrite (FeS_2) are capable of producing acid waters under oxidizing conditions, and the redox status of groundwater is an important factor in determining the degree of acid water formation and subsequent leaching of metals from mine tailings and ore bodies in this mining area. The results obtained from this study show that the relative concentrations of the arsenic redox pair are correlated with the quality of the mine waters studied and the ratio of As(V)/As(III) has the potential to be a redox indicator for groundwater systems.

The river sediments of the South Fork and the Main Stem of the Coeur d'Alene River are contaminated with As, Sb, and other heavy metals from past mining activities. The distribution of As and Sb species in the river waters has been studied. Trivalent As(III) is the predominant form of arsenic in the South Fork and the Main Stem, whereas the unpolluted North Fork generally has a higher concentration of As(V). The major Sb species in the three branches of the river is Sb(V). Mobilization of sediment As and Sb during sediment-water interactions has been investigated using laboratory leaching experiments. The releases of As and Sb are related to the free iron oxides and free manganese oxides of the sediments.

The effects of the contaminated sediments on the water quality, with respect to As and Sb, of the creeks surrounding the Blackbird area in east-central Idaho have also been investigated. The pentavalent As(V) and Sb(V) are the major species observed in the creek waters. The field observations are consistent with the leaching experiments performed in the laboratory. The contaminated sediments are non-point sources of pollution which should be considered for water quality management planning of the mining areas studied.

WAI MAN MOK

EDUCATION

B.S. Chemistry, Hong Kong Baptist College, Hong Kong, 1980 (with distinction).

Research: Zinc contents in the blood of patients.

M.S. Analytical Chemistry, University of Idaho, Moscow, Idaho, 1983.

Research: Determination of molybdenum in natural water systems and in biological samples.
Determination of uranium in seawater.

Ph.D. Analytical and Environmental Chemistry, University of Idaho, Moscow, Idaho. Took many chemistry courses and did well in research. Expected to graduate in May, 1988, with GPA of 3.95 out of 4.00.

Research: Chemical speciation of antimony and arsenic in natural water systems and its applications to environmental problems.

PUBLICATIONS

1. "Solvent Extraction of Uranyl Dithiocarbamate Complexes for Neutron Activation Analysis," W. M. Mok, H. Willmes, and C. M. Wai, Radiochem. Radioanal. Lett., 1983, 59, 329-335.

2. "Preconcentration with Dithiocarbamate Extraction for Determination of Molybdenum in Seawater by Neutron Activation Analysis," W. M. Mok and C. M. Wai, Anal. Chem., 1984, 56, 27-29.

3. "Solvent Extraction of Molybdenum from Biological Samples and from Coal Fly Ash for Neutron Activation Analysis," W. M. Mok, H. Willmes, and C. M. Wai, Anal. Chem., 1984, 56, 2623-2624.

4. "Arsenic Speciation and Water Pollution Associated with Mining in the Coeur d'Alene Mining District, Idaho," C. M. Wai and W. M. Mok, October 1985. Idaho Water Resources Research Institute, University of Idaho, Moscow, Idaho. Technical Report. 44 pp.

5. "Extraction of Arsenic(III) and Arsenic(V) from Natural Waters for Neutron Activation Analysis," W. M. Mok, N. K. Shah and C. M. Wai, Anal. Chem., 1986, 58, 110-113.
6. "A Chemical Speciation Approach to Evaluate Water Quality Problems in the Blackbird Mining Area, Idaho," C. M. Wai and W. M. Mok, October 1986. Idaho Water Resources Research Institute, University of Idaho, Moscow, Idaho. Technical Report. 48 pp.
7. "Simultaneous Extraction of Trivalent and Pentavalent Antimony and Arsenic Species in Natural Waters for Neutron Activation Analysis," W. M. Mok and C. M. Wai, Anal. Chem., 1987, 59, 233-236.
8. "Distribution and Mobilization of Arsenic and Antimony Species in the Coeur d'Alene River System, Idaho," C. M. Wai and W. M. Mok, October 1987. Idaho Water Resources Research Institute, University of Idaho, Moscow, Idaho. Technical Report, in press.
9. "Determination of Arsenic and Antimony in Biological Materials by Solvent Extraction and Neutron Activation," W. M. Mok and C. M. Wai, Talanta, 1988, 35, 183-186.
10. "Arsenic Speciation and Quality of Groundwater in a Lead-Zinc Mine, Idaho," W. M. Mok, J. A. Riley and C. M. Wai, Water Res., 1988, in press.
11. "Distribution and Mobilization of Arsenic Species in the Creeks around the Blackbird Mining District, Idaho," W. M. Mok and C. M. Wai, Water Res., 1988, in press.
12. "Distribution and Mobilization of Arsenic and Antimony Species in the Coeur d'Alene River, Idaho," W. M. Mok and C. M. Wai, submitted to Environ. Sci. Tech., 1988, for publication.

PROFESSIONAL PRESENTATIONS

1. W. M. Mok, N. K. Shah and C. M. Wai, "Solvent Extraction of As(III) and As(V) from Natural Waters for Neutron Activation Analysis," presented at the 40th Northwest Regional Meeting of the American Chemical Society, June 19-21, 1985. Sun Valley, Idaho.
2. W. M. Mok and C. M. Wai, "Extraction of As(III)-As(V) and Sb(III)-Sb(V) Species from Natural Waters for Neutron Activation Analysis," presented at the 41st Northwest Regional Meeting of the American Chemical Society, June 16-18, 1986. Portland, Oregon.

3. W. M. Mok and C. M. Wai, "Distribution of Trivalent and Pentavalent Arsenic and Antimony Species in the Coeur d'Alene River, Idaho," presented at the 42nd Northwest Regional Meeting of the American Chemical Society, June 17-19, 1987. Western Washington University, Bellingham, Washington.

AFFILIATIONS

American Chemical Society
Sigma Xi
Hong Kong Chemical Society

ACKNOWLEDGMENTS

I express my gratitude to Dr. Chien M. Wai for the direction he gave to my thinking as well as for the continuing stimulus of his teaching.

The author is indebted to many other people, in particular:

- Dr. Sherry O. Farwell for his invaluable criticism of the manuscript.
- Dr. Henry Willmes for his supervision in neutron activation analysis and for reviewing the manuscript.
- Dr. Wesley R. Harris, who gave me extremely useful comments for the manuscript.

I extend my thanks to

- Dr. Jean'ne M. Shreeve for her advice and assistance which made my stay in Idaho both educational and enjoyable.
- Dr. John DeMoura for his helpful counseling.
- Ms. LeNelle McInturff, who helped in editing the manuscript.
- Dr. Wai's research group for their encouragement and friendship.

A deep appreciation is felt for the support of my family.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

A. Arsenic and Antimony in Aquatic Environments

Arsenic (As) and antimony (Sb) are naturally occurring elements ubiquitous in all soils and sediments. Depending on the redox status, these two elements can exist in natural environments in different valence states. The biological toxicities of As and Sb are known to depend on their chemical forms and valence states.[1] In Idaho's mining districts, including the Coeur d'Alene Mining District in northern Idaho and the Blackbird Mining District in central-east Idaho, natural sediments in the surrounding streams are generally contaminated with As, Sb, and other metals. Associated with the mining industry is, therefore, the problem of metal pollution. The primary environmental concerns today are the huge quantities of mine wastes accumulated along the streams, the operating and abandoned tailings piles scattered throughout the districts, and the acid mine drainage from existing mines in the mining districts. It is known that mine wastes containing iron sulfide (pyrite) are capable of producing acid waters under oxidizing conditions.[2,3] The degree of acid water formation and subsequent leaching of metals from mine wastes and ore bodies are to a large extent determined by the redox status of groundwater systems. The contaminated sediments in the streams are also being leached to varying degrees by the surface waters and are likely to be nonpoint sources of pollution in the mining areas. Little information is available in the literature regarding the distribution and mobilization of As and Sb species in the contaminated soils and sediments existing in Idaho's mining areas. The distribution patterns of As and Sb species in natural waters may be related to the potential of acid water formation and quality of surface and ground waters of the mining areas.

Arsenic and Sb have at least five valence states, -3, 0, +1, +3, and +5. Table 1 shows some common As and Sb compounds. The average concentrations of As and Sb in surface seawater are about 1.5 ng/mL[4] and 0.2 ng/mL,[5,6] respectively. Both elements generally exist in natural waters in two oxidation states: the +3 and the +5 states. In surface seawater it appears that the dominant oxidation states are As(V) and Sb(V), but in river waters, the trivalent states may be important. Organic forms of As and Sb are also likely to be present in natural waters. Total As and Sb concentrations in river and lake waters vary considerably, with most values in the range of 0.1-1 ng/mL for As[7] and 0.01-0.1 ng/mL for Sb.[8] The chemical form of As species present in the environment affects its toxicity. Arsenic is a suspected carcinogen.[9] The United States Public Health Service[10] recommends that the arsenic concentration in drinking water should not exceed 10 ng/mL and that water with an arsenic concentration greater than 50 ng/mL should be rejected for human consumption. In Europe, the maximum permissible level of arsenic in drinking water is also listed as 50 ng/mL.[11] Arsenite [As(III)] is generally regarded as about 10 times more toxic to humans than arsenate [As(V)].[12] Sodium methylarsonate and dimethylarsinic acid are roughly 35 times less toxic than arsenite to rats.[13] The distribution and toxicity of Sb are less well-known. Recent studies have shown that Sb exists in the Sb(III) and Sb(V) forms and as methylantimony compounds in natural waters.[14,15] Antimony and its compounds are also listed as priority pollutants by the U.S. Environmental Protection Agency. Andreae et al.[14] suggested that the presence of As and Sb compounds in aerobic natural waters was probably due to similar mechanisms and the exact degree of similarity remains an area for research.

Table 1. Some Common As and Sb Compounds

Valence state	As-compound	Sb-compound
-3	arsine (AsH_3) methylarsine [CH_3AsH_2, $(CH_3)_2AsH$]	stibine (SbH_3) methylstibine [CH_3SbH_2, $(CH_3)_2SbH$]
0	As	Sb
+1	dimethylarsinic acid [$(CH_3)_2AsO(OH)$]	dimethylstibinic acid [$(CH_3)_2SbO(OH)$]
+3	arsenous acid (H_3AsO_3) methylarsonic acid [$CH_3AsO(OH)_2$]	methylstibonic acid [$CH_3SbO(OH)_2$]
+5	arsenic acid (H_3AsO_4)	antimonates $Sb(OH)_6^-$

B. Importance of Trace Element Speciation in Biological and Environmental Studies

Plants are often an integral part of the cycling of trace elements in the environment. Biological analyses, especially plant analyses, are therefore necessary for environmental trace metal studies. The analysis of trace elements in plants can provide important information on environmental contamination. In biological systems, a number of trace elements, including As, Cr, and Se, are essential to life.[16] However, a trace element which is indispensable for normal body functions may be toxic when present at high concentrations. If a toxic element is not biodegradable, once it enters the environment, its potential toxicity is controlled to a large extent by its physico-chemical form.[17] The change in the oxidation state and variation in the chemical form of a trace element can have a profound effect on bioavailability and toxicity. Arsenic provides a useful example. Arsine [AsH_3] is highly toxic. Arsenate is less toxic than arsenite. Arsenate was also reported to be more strongly adsorbed onto soil and sediment components than was arsenite in the acidic to mildly alkaline pH ranges.[18,19] Reduction of arsenate to arsenite in anaerobic sediments would, therefore, result in an increase in As toxicity in an aquatic environment. On the other hand, formation of methylated arsenic compounds from inorganic As would result in decreased toxicity. Thus, in the field of biological and environmental sciences, it is often crucial to know the chemical forms as well as the total amount of an element in a sample. Speciation studies, therefore, have become an important part of environmental research.

C. Objective of this Research

The concentrations of As and Sb in natural waters are often in the range of 0.1 to 1 ng/mL. The concentrations of As and Sb in many biological samples are also low, in the μg/g to ng/g range. Chemical analysis at these concentration levels is a specialized science. The subdivision of these very low total metal concentrations into various fractions of different species is obviously even more difficult, requiring both the skill of the analytical chemist and the sensitivity of the analytical method. The scope of this study is summarized as follows:

A. To develop a method for quantification of trivalent and pentavalent species of inorganic As and Sb in natural waters.

B. To develop a method for the determination of total As and Sb in biological materials.

C. To evaluate the potential of using the As species as an indicator of water quality and as a redox indicator in ground water systems.

D. To study the distribution of inorganic As and Sb species in natural waters.

E. To study the mobilization of As and Sb during water-sediment interactions.

This dissertation contains an introduction, an experimental section, and a literature review followed by a series of papers which have appeared in, been accepted for or submitted for publication in refereed scientific journals. Each chapter is, therefore, written as a separate entity with bibliography.

REFERENCES

1. Arsenic - Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, 1977.

2. Appalachian Regional Commission, "Acid mine drainage in Appalachia", U.S. Govt. Printing Office: Washington, D.C., House Document 91-180, Publication No. 35-4320, 1, p 58; 3, p 17, 1969.

3. Smith, E. E.; Shumate, K. S. "Sulfide to sulfate reaction mechanism," U.S. Govt. Printing Office: Washington, D.C., Document 14010FPSO2/70, 1970.

4. Florence, T. M.; Batley, G. E. CRC Crit. Rev. Anal. Chem. **1980**, 9, 219.

5. Yamamoto, M.; Urata, K,; Murashige, K.; Yamamoto, Y. Spectrochim. Acta, Part B **1981**, 36B, 671.

6. Ammann, K.; Knoechel, A. Z. Anal. Chem. **1981**, 306, 161.

7. Wedepohl, K. H. Handbook of Geochemistry, Springer Verlag: New York, Vol. II/3, Chapter 33, 1978.

8. Wedepohl, K.H. Handbook of Geochemistry, Springer Verlag: New York, Vol. II/4, Chapter 51, 1978.

9. Air and Water Pollution, Subcommittee of the committee on Public Works, U.S. Senate, "Water Pollution," Part 4. U.S. Senate, Ninety-first Congress, Second Session, U.S. Government Printing Office: Washington D.C., 1970.

10. U.S. Department of Health, Educaton and Welfare, Public Health Service, "Drinking Water Standards," Public Health Service Publication, No. 956, U.S. Government Printing Office: Washington D.C., 1962.

11. European Economic Community, Council Directive 75/44 EEC, O.J. No. L194 (July 25, 1975). pp 26-31; Italian Official Gazette No. 141 (May 29, 1976), Law 319.

12. NAS. National Academy of Sciences. "Arsenic-Medical and Biological Effects of Environmental Pollutants," 1977.

13. Peoples, S. A. "Arsenical Pesticides", Amer. Chem. Soc. Symp. Ser. **1975**, 7, 1.

14. Andreae, M. O.; Asmodeh', J. F.; Foster, P.; Von't dack, L. Anal. Chem. **1981**, 53, 1766.

15. Byrd, J. T.; Andreae, M. O. Trans. Amer. Geophy. Union **1982**, 63, 71.

16. Schwarz, K. in "Clinical Chemistry and Chemical Toxicity of Metals," Brown, S. S. (ed.), Elsevier: New York, 1978.

17. Sterritt, R. M.; Lester, J. N. Sci. Total Environ. **1980**, 14, 5.

18. Oscarson, D. W.; Huang, P. M.; Liaw, W. K. J. Environ. Qual. **1980**, 9, 700.

19. Holm. T. R.; Anderson, M. A.; Inverson, D. G.; Stanforth, R. S. in "Chemical Modeling in Aqueous Systems," Jenne, E. A. (ed.), Amer. Chem. Soc. Symp. Ser., 93, American Chemical Society: Washington, D.C., pp 711-736, 1979.

Chapter II

EXPERIMENTAL

A. Analytical Techniques

Neutron activation analysis (NAA) is one of the most sensitive techniques for As and Sb determination. Under interference-free conditions, NAA can easily detect nanogram levels of As and Sb in a sample with good accuracy (Table 2). However, in real samples, spectral interferences from other elements such as Na and Br can greatly limit the selectivity of trace element determination by NAA. Separation and concentration procedures are, therefore, often required for NAA determination of trace elements in natural samples. Solvent extraction with the derivatives of dithiocarbamic acid as chelating agents is a technique widely used for concentration of trace elements. The alkali metals, the alkaline earth metals, and the halogens, which do not complex with dithiocarbamates, can be simultaneously removed during the extraction. Neutron activation analysis, when coupled with the dithiocarbamate extraction procedure, can greatly improve the detection limit and accuracy for the determination of nanogram levels of As and Sb species in real samples. The complexation of dithiocarbamates with trace elements depends on the oxidation states of the elements. The extraction method, therefore, also provides a means of differentiating the As and Sb species in aqueous solutions with different valence states. A dithiocarbamate extraction procedure compatible with NAA was developed and used for the determination of As and Sb species in this study.

Other metal ions in water samples, including Zn, Fe, Mn, Cu, and Cd, were determined by atomic absorption spectrophotometry (Model IL 353) or by inductively coupled plasma-atomic emission spectrometry (ARL Model 35,000 C). Sulfate in river water was determined by ion chromatography (Dionex Model 2000i/SP). Some major and minor elements in river sediments were analyzed by an automated X-ray fluorescence spectrometer (Rigaku Model 3370). Lead and cadmium in sediments were determined by AAS after $HNO_3/HClO_4$ digestion. Mineralogy of sediments was analyzed using a Philips Norelco X-ray diffractometer. The detection limits of different techniques for the elements of interest are presented in Table 2.

Table 2. Detection Limits of AA, ICP-AES, XRF, and NAA for Some Selected Trace Elements

Element	AA(μg/L)[a]	GFAAS[b] (μg/L)	ICP-AES[c] (μg/L)	XRF(%)[d]	NAA(μg)[e]
As	100	0.08	10	---	0.005
Cd	1	0.002	1.5	---	0.005
Cu	2	0.005	1	<1	0.002
Fe	5	0.03	2	<1	---
Mn	3	0.01	1	<1	0.0001
Pb	20	0.007	25	1	---
Sb	60	0.08	40	---	0.007
Zn	0.6	0.003	2	<1	0.1

The detection limits are given under interference-free conditions.

[d] Soil matrix.

Sources: [a-c] Instrumentation Laboratory.

[d] Norrish, K., Chappell, B. W. in <u>Physical Methods in Determinative Mineralogy</u>, (J. Zussman, Ed.), Academic Press: London, 1977.

[e] General Atomic Co., given in sensitivity.

B. Determination of Trivalent and Pentavalent Species of Arsenic and Antimony in Natural Waters by NAA

The details of the analytical procedures for separation and differentiation of trivalent and pentavalent As and Sb species are given in Chapters IV and V.[1,2] A brief description of the analytical method is given in this section.

For the extraction of As(III) and Sb(III), normally a 100-mL sample was placed into a high-density linear polyethylene plastic bottle. A 10-mL citrate buffer was added and the pH was adjusted to a value between 3.5 and 5.5 with HCl or NH_4OH. This was followed by the addition of 4 mL of a 12.5% ethylenediaminetetraacetic acid (EDTA) solution as a masking agent. Chloroform (10 mL) and 2 mL of 5% ammonium pyrrolidinecarbodithioate (APCDT) were then added. The mixture was extracted by shaking vigorously for 10 min on a wrist-action mechanical shaker (Burrell Model 75), and the phases were allowed to separate. After discarding the aqueous phase, the organic phase was washed twice with 10 mL of deionized water. Eight to nine mL of the organic phase was transferred to a 20-mL Beckman polyvial with a fast-turn cap. To back extract As and Sb, 2 mL of 50% HNO_3 was added to the vial, and the mixture was shaken for 10 min. After phase separation, 1.5 mL of the acid solution was pipetted into a 2/5-dram polyethylene vial and heat-sealed for neutron irradiation. A procedure blank made of an equal volume of deionized water was run for each set of experiments.

To determine total inorganic Sb and As, a second aliquot of the water sample was placed in an Erlenmeyer flask and adjusted to a pH about 1.0 with HCl. Reduction of pentavalent As and Sb to their trivalent states was carried out by using 1 mL of a 20-25% sodium thiosulfate solution and 1 mL of a 20% potassium iodide. After a waiting period of 15-30 min, 4 mL of the EDTA solution, 10 mL of chloroform, and 2 mL of the APCDT were added to the plastic bottle, and the complexes were extracted by the procedure described above. The difference in As and Sb concentrations between the two aliquots represents the amount of As(V) and Sb(V) in the water sample.

For water samples with low As and Sb contents, the initial sample size can be increased to 300 mL or 500 mL. The amount of the buffer, the masking agent, and the chelating agent PCDT should also be increased in proportion to the sample size. The volume ratio of the aqueous solution to the organic phase is kept between 10 and 20. After extraction, the volume of the organic phase is reduced to about 10 mL by evaporation at room temperature, and backextraction with nitric acid is carried out according to the procedure described above. No detectable loss of As and Sb was observed during the evaporation process.

Standards were made of solutions containing proper concentrations of As and Sb, heat-sealed in the same kind of polyethylene vials as the samples. All samples and standards were normally irradiated for 2 hours in a 1-MW TRIGA reactor at a steady neutron flux of 6×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$, followed by one day of cooling. Before counting, samples and standards were transferred into new 2/5-dram polyethylene vials using disposable syringes. This sample transfer step is necessary in order to avoid interferences of ^{24}Na and other radioactivities produced in the plastic material of the irradiated vials. Each sample was counted with a large volume coaxial ORTEC Ge(Li) detector with a resolution of about 2.3 keV for the 1332-keV γ from ^{60}Co. Counting times usually varied from 2×10^3 sec to 8×10^3 sec depending on the concentrations of Sb and As in samples. The detector output was fed into an EG&G ORTEC ADCAM (Model 918) multichannel analyzer. The data from the analyzer were processed with an EG&G ORTEC software on an IBM-PC. The 559.1 keV γ from As and the 564.1 keV γ from Sb were used to determine the As and Sb concentrations in samples. Figure 1 shows the γ-ray spectrum in the region of interest for a river water sample obtained by the extraction procedure and NAA.

If the ratio of As/Sb in a sample is large, then a minor peak of ^{76}As which occurs at 562.8 keV (2.7% relative to the 559.1 keV major peak) may cause appreciable interference for the 564.1 keV peak of ^{122}Sb. In general, a correction should be applied to the ^{122}Sb peak using the intensity ratios of As peaks at 559.1 and 562.8 keV. The interference of ^{76}As on ^{122}Sb can be minimized by recounting after allowing the former to decay away. Since the half-life of ^{122}Sb is about 2.5 times longer than that of ^{76}As, we normally recounted samples with high As/Sb ratios 2-4 days after the first count to obtain more reliable ^{122}Sb data.

C. Digestion of Biological Materials and Extraction Procedure

Digestion of biological samples was carried out in a round-bottom flask fitted with a reflux reservoir and a condenser.[3] Usually 1 - 2 g of material were placed into a 50-mL round-bottom flask, and a few glass beads were added. A mixture of HNO_3 and H_2SO_4 (5:4) was added to cover the sample surface, and the sample was soaked overnight. The digestion process started with gentle heating on a heating mantle until foaming ceased. Heat was then increased, and small amounts of the condensed HNO_3 were admitted from the condenser whenever a slight darkening of the digest occurred. This operation was repeated until darkening no longer occurred and the H_2SO_4 boiled with white fumes, after which heating was continued for another 5 min and the apparatus was allowed to cool. The sample solution was diluted with 10 mL of water and boiled for another 5 min. The solution was then transferred into a 100-mL volumetric flask, and the apparatus was rinsed. The rinsing solution was added to the volumetric flask, and the final solution was made up to 100 mL with deionized water.

An appropriate amount (usually 30 mL aliquot) of the digest solution was transferred into a 125-mL polyethylene bottle. The solution was diluted to a volume of about 100 mL and adjusted to pH 1. $Na_2S_2O_3$ (1 mL), 20-25%, and 1 mL of 20% KI were added to the solution to reduce pentavalent As and Sb to trivalent states. The extraction was carried out as described in section II.B.

D. Instrumental Neutron Activation Analysis (INAA) for Sediments

The concentrations of As and Sb in river sediments are generally high enough that direct neutron activation analysis without chemical extraction and separation is feasible.[4] For INAA of river sediments, usually 100 mg of material was irradiated for each sample. Irradiation of larger amounts of samples will result in high levels of radiation from matrix species, making the sample difficult to handle experimentally. Each activated sample was usually counted twice, once 2-3 days and once 5-6 days after the end of irradiation. The irradiation and counting procedures are similar to those described in Section II.B.

REFERENCES

1. Mok, W. M.; Shah, N. K.; Wai, C. M. Anal. Chem. **1986**, 58, 110.
2. Mok, W. M.; Wai, C. M. Anal. Chem. **1987**, 59, 233.
3. Mok, W. M.; Willmes, H.; Wai, C. M. Anal. Chem. **1984**, 56, 2623.
4. Koons, R. D.; Helmke, P. A. Soil Sci. Soc. Am. J. **1978**, 42, 237.

Chapter III

LITERATURE REVIEW

A. Introduction

The chemistry of arsenic (As) and antimony (Sb) in a natural aquatic system is a complex array of homogeneous and heterogeneous chemical, biochemical, and geochemical reactions that together control the dissolved concentrations of As and Sb in the system. Transformation between the different oxidation states and forms of As and Sb may occur as a result of chemical or biochemical reactions.[1] The toxicity of each physico-chemical form of a trace element may be different; therefore, analysis of a water sample for the total concentration of the element alone does not provide sufficient information to predict its toxicity. For example, arsenite is generally regarded as about 10 times more toxic to humans than arsenate.[2] Sodium methylarsonate and dimethylarsinic acid are roughly 35 times less toxic than arsenite to rats.[3] Variations in the chemical form of an element will also affect its degree of adsorption on suspended matter, its rate of transfer to the sediment, and its overall transport in an aquatic system. Arsenate was reported to be more strongly adsorbed on iron and aluminum hydroxides than arsenite.[4] Arsenate and monomethylarsonate were found to be more strongly adsorbed on alluvial soils than dimethylarsinate,[5] and the adsorption could affect the apparent rates of species transformations. To understand the biological or geochemical cycling of As and Sb, it is therefore necessary to study the chemical species of the elements in aqueous systems.[6]

Speciation analysis of an element in a water sample may be defined as the determination of the concentrations of the different physico-chemical forms of the element which together make up its total concentration in the sample. The concentrations of As, Sb, and many other trace elements in natural waters are often very low, in ng/mL to sub-ng/mL levels. Chemical analysis at these concentration levels requires very sensitive analytical methods. Special care must be taken in the collection, filtration, storage, and analysis of the samples because there is a risk of trace element losses or contamination when working with such low levels of analytes.[7] Based on a search of the literature from 1978 to 1988, the methods commonly used for chemical speciation of As and Sb and our current knowledge on the speciation of these two trace elements in natural waters are summarized in this chapter.

B. Sampling, filtration, and storage of water samples

The collection of a natural water sample for trace metal analysis is fraught with dangers of contamination.[8-11] The type of sampling bottle and method of cleaning the containers for chemical analysis must be carefully chosen. High-density linear polyethylene bottles are universally used for collection of water samples. Laxan[12] reported that soaking linear polyethylene bottles in 1.5 M nitric acid for 48 hr at room temperature removed all Cu, Pb, Cd, and Zn leachable by synthetic and natural river water. In our laboratory we soak high-density linear polyethylene bottles in 10% reagent-grade nitric acid for 24-48 hr. After acid washing, the bottle is rinsed thoroughly with deionized water and dried in a class 100 clean hood.

Dissolved metal in a water sample is defined by convention as metal ions which can pass a 0.45 μm membrane filter. The membrane filter should be washed with acid and water before use; otherwise, it can contribute both metals and organic matter to the filtrate.[13] Nuclepore membrane filters (polycarbonate) have the lowest metal content, but they block rapidly. Cellulose acetate membranes are often used for most waters.[11,14]

Despite Andreae's advocacy for freezing as a means for sample preservation,[15] there have been several reports which indicate that the freezing process can induce chemical changes, such as precipitation, which are not reversed on melting.[10] In laboratory experiments at room temperature with As(III) and As(V) in deionized water and ground water samples from pH 2-10.5, Shaikh and co-workers[17,18] found that the oxidation of As(III) was slow and that water samples to be analyzed for arsenic species can be stored for several days to several weeks with minimum preservation. No changes in the concentrations of As and Sb species in natural waters stored at 4 °C for about two weeks were observed in our laboratory. Storage at 4 °C appears to be the safest method for both fresh water and seawater samples.[14,19]

C. Speciation of Arsenic in Natural Waters

1. Separations Based on Hydride Generation Method

Odanaka et al.[20] discussed the determination of inorganic and methylated arsenicals in water and other environmental materials by graphite furnace atomic absorption spectrometry (GFAAS). Sodium hydroxide and nickel nitrate were used in the determination of arsenicals in GFAAS. Arsenite, arsenate, methylarsonic acid and dimethylarsinic acid each gave different sensitivities. Enhancement and depression effects of various coexisting chemical substances were also discussed by these authors. Shaukh and Tallman[21] described arsenic speciation and the determination of nanogram amounts of total arsenic in natural waters by hydride generation and GFAAS. The arsenic species were reduced to their corresponding hydrides, collected in a liquid nitrogen cold trap and then selectively vaporized and swept into the graphite furnace. Chi et al.[22] also determined trace As(III) and As(V) in water by AAS using hydride generation and electrothermal atomization. Water samples at pH 5.8 were treated with $NaBH_4$. As(III) forms a gaseous hydride which is electrothermally atomized for spectrophotometric determina-tion; arsenic(V) is then determined by the difference between total As and As(III). The sensitivity is 0.5 ng/mL of As for 1% absorption. The relative standard deviation is <7% in 15 determinations at ng/mL levels.

The formation of volatile arsenic species during electrothermal atomic absorption spectrometric determination of arsenic was suppressed through the addition of Ni(II) as described by Puttemans and Massart.[23] Many oxidizing agents, including nitric acid, were found to substantially enhance the arsenic signal. The concentrations of these reagents were optimized by simplex optimization. The optimal condition was 2000 μg/mL Ni(II) in 2% nitric acid. The method permits differential determination of inorganic As species in water samples. Howard and Arbab-Zavar[24] determined As(III), As(V), methylarsonic, and dimethylarsinic species in estuarine and river water by trapping their arsines, followed by selective volatilization of the arsines into a quartz atomizer tube of an atomic absorption spectrometer. Ethylenediaminetetraacetic acid was used as a masking agent for interferences.

Tanaka et al.[25] described a method for fractional determination of arsenite, arsenate, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) in natural waters by hydride generation and AAS coupled to a cold-trap concentrator. Arsenic species were reduced with $NaBH_4$ to arsine, methylarsine, and dimethylarsine, respectively, and collected in the cold trap. Separation was brought about by sequential volatilization. Detection limits were 4 parts per trillion (ppt) for arsenite and arsenate, 14 ppt for monomethylarsonic acid, and 26 ppt for dimethylarsinic acid. The relative standard deviations were 4.3% at 5 ng, 5.1% at 5 ng, 4.9% at 20 ng, and 3.7% at 30 ng, respectively. Maher[26] used a zinc-column arsine generator for the determination of methylated arsenic species. Monomethylarsenic (I) and dimethylarsenic (II) were reduced to arsine and subsequently decomposed in a carbon-tube furnace and measured by atomic absorption. The detection limits, based on 3 times the standard deviation of the blank analyses, were 0.006 μg/mL for I and 0.001 μg/mL for II. The relative standard deviations at the 0.05 μg/mL level were 3.2% for I and 2.1% for II.

Yamamoto et al.[27] described a characterization of arsenic in seawater by hydride-generation AAS. A simple digestion procedure with $K_2S_2O_8$ in an alkaline medium is described for the determination of total concentrations of As species in seawater. Combined with the previously proposed method for the differential determination of As(III) and As(V) by hydride generation AAS,[28] the As species in seawater were determined as As(III), As(V), and organoarsenics. Sub-ng/mL concentrations of As in seawater could be detected with a sample volume of 100 mL. Anderson et al.[29] studied the selective reduction of arsenic species in natural waters by continuous hydride generation. The selective reduction method for determination of As species in water is found to be suitable for the analysis of a large number of water samples. The comparison of the data generated from the selective determination of As(III), As(V), monomethylarsonic acid and dimethylarsinic acid using continuous hydride-generation AAS vs. those from a cold-trapping technique showed the selective reduction method required less time for a determination (1 min vs. 10-15 min) but had a higher detection limit (0.2-0.7 vs.

0.1 ng/mL). Yamamoto et al.[30] used flow injection for the generation of arsenic hydrides and other hydrides prior to GFAAS. About 120 samples/hour could be determined by the automated system. When 0.5 mL of a sample was used, the detection limit was 0.2 ng. The method has been used for speciation of As(III) and As(V) in geothermal waters which have a high content of As.

2. Chromatographic Separation

Chromatographic separation and GFAAS were used by Inverson et al.[31] for the speciation of arsenic in river water and pore water. Nickel nitrate was used for matrix modification. Speciation was accomplished by ion-exchange chromatography using AG 50W-X8 cation resin. The detection limit was 2 ng/mL. Grabinski[32] described a separation of As(III), As(V), monomethylarsonate and dimethylarsinate in lake water by ion-exchange chromatography followed by flameless AAS detection. A single column containing both cation (AG 50W-X8)- and anion (AG 1-X8)- exchange resins was used. The overall analytical detection limit was 10 ng/mL for each individual arsenic species. Ficklin[33] separated As(III) and As(V) in ground waters by ion-exchange with a Dowex anion-exchange resin. Arsenic(III) passed through the acetate-form resin, and As(V) was retained. Arsenic(V) was eluted by passage of 0.12 M HCl through the column. The arsenic concentration in the eluent was determined by GFAAS. The detection limit for the concentration of each species was 1 ng/mL. Aggett and Kadwani[34] developed a two-stage anion exchange procedure for the speciation of As in interstitial waters of sediments. Arsenic(III) and dimethylarsinic acid were eluted in succession with a carbonate buffer, and As(V) and monomethylarsonic acid were eluted with a carbon dioxide-sodium chloride solution. Clifford et al.[35] separated As(III) from As(V) by exchange on IRA-458 resin beads in the chloride form. Arsenic(III) passed through the column and was determined by electrothermal atomic absorption spectrophotometry. Arsenic(V) was, in turn, eluted with HCl and determined separately. Tye et al.[36] developed a HPLC-hydride generation AAS method for separation of arsenite, arsenate, monomethylarsonate (MMA) and dimethylarsinate (DMA) in soil waters. Sample preconcentration was achieved with a pellicular anion-exchange column. The arsenic species were then separated on a strong anion-exchange column placed in series with a preconcentration column. Detection limits were 2 ng for arsenite, arsenate and MMA, and 1 ng for DMA. (Bushu et al.[37] proposed a method in which As species obtained through hydride generation were separated by HPLC and detected by ICP-AES. The method was optimized with regard to detection limit, response linearity, and interferences for various arsenic species. The ability to speciate arsenic in drinking water is also demonstrated. Low et al.[38] discussed the interference of chloride in seawater in the speciation of arsenic by ion chromatography. Single peaks may be split into two or more discrete peaks, as a result of the large differences in the ionic strength of the mobile and injection solvents. A simple model is proposed to explain the phenomenon. Cappon[39] described a gas-liquid chromatographic method for speciation of As and a few other selected elements. The discussion includes sample preparation, methodology and column and detector technology with 154 references.

3. Adsorption, Precipitation, and Solvent Extraction Methods

Terada et al.[40] used 2-mercepto-N-2-naphthylacetamide on silica gel for differential preconcentration of ng/mL levels of As(III) and As(V) from aqueous solution. In batch experiments, As(III) was quantitatively retained on the gel from solutions of pH 6.5-8.5, whereas As(V) and organic arsenic compounds were not retained. The chelating capacity of the gel was 5.6 μmol/g As(III) at pH 7.0. The arsenic retained on the column was completely eluted with a solution of 0.01 M sodium borate in 0.01 M NaOH containing 10 mg/L iodine at pH 10. The arsenic was determined by the silver diethyldithiocarbamate method using AAS. Arsenic(V) was determined following reduction to As(III).

A sequential determination of As(III) and As(V) in natural water was utilized by Chakraborti et al.[41] Arsenic(III) was extracted with ammonium-sec-butyl dithiophosphate, back-extracted into water, and measured by GFAAS. Arsenic(V) was subsequently determined after reduction. The detection limit was 0.006 ng/mL. Subramarian et al.[42] determined As(III), As(V), and total As in some polluted waters using an APCDT-MIBK electrothermal atomic absorption spectrometric procedure and a toluene extraction-anodic stripping voltammetric procedure. Results for total As from anodic stripping analysis agreed with results by electrothermal atomization, either directly or using a Ni matrix modifier. The same authors[43] also described an APCDT-MIBK-GFAAS method to determine As(III) selectively in groundwater samples. The method was said to be free from interferences of cations and anions present in the water supplies. The detection limit for As was 0.7 ng/mL. The reliability of the method for the concentration range 5.0-40.0 ng As/mL was 95%±3% and 95%±2% for As(III) and As(V), respectively. Puttemans and Massart[44] extracted As(III) quantitatively from an acidic medium with APCDT and diethyl-dithiophosphoric acid prior to analysis by electrothermal atomic absorption spectrometry. Arsenic(V) can only be extracted after preliminary reduction to the trivalent state using KI or a mixture of $HSO_3^-/S_2O_3^{2-}$. Amankwah and Fasching[45] separated and determined As(III) and As(V) in seawater by solvent extraction and hydride generation AAS. Arsenic(III) and As(V) in sea water are separated by complexing the As(III) with APCDT in the pH range 4.0-4.5 and extracting the complex with $CHCl_3$. Arsenic(III) in the organic phase was stripped into a 1:1 HNO_3-$HClO_4$ mixture and determined by hydride generation AAS. Total As was determined after reduction with KI and the As(V) content is determined by difference. The detection limit for As was 0.031 ng/mL.

Kanako[46] coprecipitated arsenic with ferric hydroxide to determine ng/mL levels in well water. Both As(III) and As(V) are completely coprecipitated at pH 3.5-10.0 with average recoveries in the 98% range.

Yu et al.[47] described a hydride-generation atomic absorption spectrophotometric determination of trace As(III) and As(V) in water by concentration and separation with sulfhydryl cotton fiber. Sulfhydryl cotton fiber showed quantitative adsorption of As(III), but not As(V), in 0.6-8.0 N HCl. Thus, As(III) was separated from As(V) for concentration and determination, whereas As(V) was reduced to As(III) for determination thereafter. For natural waters with added As(III) and As(V) at 2.0-10.0 ng/mL, the recoveries were 92-111% and 85-111%, respectively.

Kawamoto et al.[48] used diethyldithiocarbamate to determine As(III) and As(V) in hot spring water spectrophotometrically after coprecipitation with magnesium ammonium phosphate. Arsenic(III) was determined by subtracting As(V) from total arsenic. Tsuji et al.[49] developed a sequential spectrophotometric determination of inorganic As(III) and As(V) species in groundwaters by coprecipitation with zirconium hydroxide. Silver diethyldithiocarbamate was used for the photometric determination. The recoveries of As(III) and As(V) were quantitative and the relative standard deviation was 5%.

Leyden et al.[50] determined As(III) and As(V) in water by X-ray fluorescence. Arsenic(III) was recovered by precipitation with dibenzyldithiocarbamate and filtration. Arsenic(V) was determined in the filtrate by coprecipitation with hydrated Fe(III) oxide. Arsenic in the precipitate was determined by X-ray spectrometry. The detection limit was in the ng/mL to μg/mL range, and the method will likely not supplant AAS or ICPAES for accuracy and precision.

4. Electrochemical Methods

Henry et al.[51] utilized differential pulse polarography for speciation of As(III), As(V), and total inorganic As. Arsenic(III) was determined directly in 1 M HCl or 1 M H_2SO_4. Total inorganic As was determined after reduction to As(III) with a boiling solution of sodium bisulfite. The difference gave the concentration of As(V). The detection limit for total As using HCl was 7 ng/mL. Buldini et al.[52] determined inorganic and organic As in waters by differential pulse polarography. Arsenic(III) was determined directly in 2 M HCl supporting electrolyte. Total inorganic As was measured after reducing the As(V) with sodium sulfite. Organic As compounds were oxidized prior to analysis. Anion exchange or pre-electrolysis with a mercury cathode was used to eliminate interference from heavy metals. The detection limit was 1 ng/mL. The relative standard deviation was about 1.5% at 50 ng/mL.

Bodewig et al.[53] determined arsenic in natural waters by differential pulse anodic stripping voltammetry. Arsenic(III) was deposited from acid solution onto a rotating gold electrode. Arsenic(V) was determined after reduction to As(III) by gaseous sulfur dioxide. For a deposition time of 4 min, the detection limit was about 0.2 ng/mL. Huang et al.[54]

determined As(III) in sea water using anodic stripping by deposition of As onto the glassy carbon electrode. The total As was determined after the reduction of As(V) by Na_2SO_3. The recoveries for As(III) and As(V) were 106±4% and 101±11%, respectively, with the detection limit of $2x10^{-2}$ ng/mL. Sadana[55] described a method for the determination of As(III) and total inorganic As in the presence of copper by differential pulse cathodic stripping voltammetry at a hanging mercury drop electrode. Drinking water contaminated with Cu(II) was acidified and As was preconcentrated in the mercury drop, followed by cathodic stripping. The detection limit was 1 ng/mL. Cui[56] used a disk Au electrode for the determination of As(III) and As(V) in water by anodic stripping voltammetry. Arsenic(III) was determined first, then the total inorganic As following a reduction of As(V) to As(III) by Na_2SO_3. At pH 3-12, recoveries for As(III) and As(V) at concentrations 10-25 ng/mL and 10-100 ng/mL are 93-105% and 94-106%, respectively. Jaya et al.[57] investigated the anodic stripping voltammetric behavior of As(III) at a Cu-coated glassy-carbon electrode. The effects of copper concentration, acidity, deposition potential and sweep rate on the stripping peak were examined and criteria were given for the choice of experimental conditions. Total inorganic As in the sample was determined after heating with hydrazine hydrochloric acid and hydrobromic acid to reduce As(V) to As(III). The procedure was applicable to the determination of 7.5-750 ng/mL As levels in various types of water samples.

Wals et al.[58] determined As species in surface water and seawater by neutron activation analysis (NAA). Arsenic(III), As(V), and arsenic acid substituted with aromatic ligands were collected by coprecipitation with $Fe(OH)_3$. After irradiation, As was separated and measured. The lower detection limit was 0.01 ng/mL. Orvini et al.[59] described the application of NAA to speciation of As(III), As(V), and a few other trace metals in freshwaters when coupled to specific separation procedures. Gallorini et al.[60] also described the contribution of NAA and radioanalytical techniques to trace element speciation including As in freshwater.

5. Stability Studies

Cheam and Agemian[61] studied the stability of As(III) and As(V) in distilled and natural waters. The stability was determined using hydride generation AAS during 125 days of storage at different pH levels, As concentrations, container materials, and container sizes. Preservation was satisfactory at room temperature if the samples were stored in polyethylene or Pyrex bottles with 0.2% volume sulfuric acid. Crecelius et al.[62] described the analytical methodologies for collection, storage, and analysis of freshwater without significantly altering the speciation of As. Arsenic speciation of water can be achieved using hydride generation AAS. Very rapid freezing by immersion in liquid nitrogen followed by storage at -80 °C is said to be necessary to prevent oxidation of As(III) to As(V) during storage of water samples. At pH 2.3, As(III) was extracted and at pH 11.9, As(V), monomethylarsonic acid and dimethylarsinic acid were extracted. Aggett and Kriegman[63] also studied the preservation of As(III) and As(V) in interstitial water. Arsenic was analyzed by hydride generation AAS. The effect of temperature, pH, and the presence of oxygen on the stability of As(III) in interstitial water was studied. The most effective means of preserving a sample with 1-4 μg/mL of As(III) up to 6 weeks was found to be by acidifying the sample to pH 2 and refrigerating near 0 °C. In the samples studied, deoxygenation appeared to be unnecessary. When these conditions were used, in view of the likely differences in behavior between samples, it would be wise to include the removal of air in the preservation method.

D. Speciation of antimony in natural waters

1. Hydride Generation Methods

Andreae[64] described an atomic absorption spectrometric/hydride generation technique to determine Sb(III), Sb(V), methylstibonic acid and dimethylstibinic acid in natural waters. Total inorganic antimony was reduced to stibine under highly acidic conditions in a solution containing iodide with sodium borohydride; Sb(III) was reduced at near-neutral pH; Sb(V) was then obtained by difference. The organic Sb compounds also were reduced under acid conditions, collected in a liquid-nitrogen-cooled trap, separated chromatographically, and eluted into a quartz cuvette burner or graphite furnace. The absolute detection limit was 30-60 pg of Sb, depending on species and operating conditions. The concentration detection limit was 0.3-0.6 ng/mL for a 100-mL sample. Hitachi, Ltd.[65] determined antimony(III) and Sb(V) in river water and seawater by reducing the sample to SbH_3 and determining the total inorganic Sb. Antimony(III) was determined by selective reduction to SbH_3. The amount of Sb(V) was calculated as the difference between total Sb and Sb(III). Yamamoto et al.[28] described a hydride generation atomic absorption spectrometric method using a hydrogen-nitrogen flame for the differential determination of Sb(III), Sb(V), As(III), and As(V) in seawater based upon selective reduction. Effects of other elements such as Ag^+, Cu^{2+}, Sn^{2+}, Se^{4+} and Te^{4+}, etc. were presented. The method was applied to the determination of these species in sea water and it was found that a sample size of only 100 mL was enough to determine species with a precision of 1.5-2.5%. The same author[66] also reported a differential determination of Sb(III) and Sb(V) by hydride generation AAS with a hydrogen-nitrogen flame. Antimony(III) was determined selectively up to 0.8 μg at pH 8 (borate buffer) in the presence of 100-fold excess Sb(V). The detection limit and the relative standard deviation were 0.4 ng/mL and 1.3%, respectively. Apte and Howard[67] separated Sb(III) from Sb(V) based on the pH dependence of the $NaBH_4$ reduction of Sb. The hydride was cryogenically preconcentrated and was then measured in a quartz tube furnace by AAS. Potentially interfering species were investigated but, at levels expected in natural waters, did not influence the analytical results obtained using the method. Detection limits were about 0.001 ng/mL for Sb(III) and 0.01 ng/mL for total inorganic Sb. Tanaka et al.[68] also determined Sb(III) and Sb(V) in natural waters by hydride generation AAS combined with a liquid nitrogen cold trap. Concentrations of 0.07-0.46 ng/mL Sb(V) were observed in these natural water samples, but Sb(III) was said to be undetected. Yamamoto et al.[30] combined flow injection with hydride generation for the determination of Sb and several other elements by AAS. The possibility of a differential determination according to the oxidation states was exhibited for Sb in geothermal water, and the detection limit for 0.5 mL of sample was 0.04 ng/mL.

Han and Wang[69] determined Sb(III), Sb(V), As(III), and As(V) in river waters by hydride-nondispersive atomic fluorescence spectrometry. Water samples were buffered to pH 5.5 and 5.0 for Sb(III) and As(III) determination, respectively. Total Sb and As were determined after reduction with KI. Antimony(V) and As(V) were determined by a simple subtraction. Recoveries were 90-110%.

2. Adsorption and Solvent Extraction Methods

Sturgeon et al.[70] preconcentarated Sb(III) and Sb(V) from samples of sea water using a combination of chelation with APCDT and subsequent adsorption on C18-bonded silica gel. Eluted analytes were taken up in a matrix-free acid solution suitable for GFAAS. The detection limit was 0.05 ng/mL based on a 300-mL sample volume with a relative standard deviation of 10% at 0.2 ng/mL. The same method was also used by Kramer et al.[71] in the determination of Sb(III) and Sb(V) in seawater.

Nakashima[72] described a flotation method that utilizes a ferric hydroxide-surfactant-air system at pH 4 to separate microgram quantities of inorganic Sb(III) and Sb(V) from water. Antimony was then converted to stibine and determined by AAS with a long absorption cell (60cm x 1.2cm i.d.)

Liu and Yu[73] developed a sulfhydryl cotton fiber concentration separation-hydride atomic absorption method for determination of trace Sb(III) and Sb(V) in water. Antimony(III) in water samples was separated from Sb(V) and concentrated on sulfhydryl cotton fiber by controlling the pH of the water at 6.5-7.5; Sb(V) in water was reduced to Sb(III) following the separation. The detection limit was 0.01 ng/mL in a 200-mL sample.

Subramanian and Meranger[74] studied the solution conditions and other parameters affecting the APCDT-MIBK extraction system for GFAAS determination of Sb(III), Sb(V), As(III), and As(V). The solution conditions for the single or simultaneous extraction of Sb(III) and As(III) were not critical. Arsenic(V) was not extracted over the entire range of pH and acidity studied. Antimony(V) was extracted only in the acidity range 0.3-1.0 M HCl. Simultaneous extraction of total As and total Sb was possible after reduction of As(V) with thiosulfate. Sun et al.[75] described a selective separation and differential determination of Sb(III) and Sb(V) by solvent extraction with N-benzoyl-N-phenylhydroxylamine

(BPHA) and GFAAS using a matrix modification technique. Copper was used as a matrix modifier, and the ashing temperature of Sb in aqueous solution and a BPHA-$CHCl_3$ extract could be raised to 1300 °C and 1100 °C, respectively. The method could detect Sb in various types of water at sub-ng/mL levels.

3. Electrochemical Methods

Metzger et al.[76] developed a stripping voltammetric determination of traces of Sb(III) and Sb(V) in natural waters after selective extraction. Antimony(III) could be distinguished from Sb(V) by coupling extraction with APCDT (I) into MIBK, or with N-benzoyl-N-phenylhydroxylamine (II) into $CHCl_3$, and then determined by anodic stripping voltammetry. After complex formation with (I) in acetate-buffered medium, Sb(III), but not Sb(V), was extracted into MIBK. Antimony(V) was quantified in the aqueous phase after removal of Sb(III) by extraction with (II) into $CHCl_3$ following acidification with HNO_3. The procedures were suitable for Sb speciation studies in relatively unpolluted natural waters. Nagaosa and Sana[77] proposed a procedure for the determination of Sb(III) and Sb(V) in the presence of 5000-fold Cu(II) and 100fold Fe(II) by differential pulse anodic stripping voltammetry following extraction into acetonitrile. Deposition was carried out for 3 min at -0.35V vs. Ag/AgCl electrode. After 30 sec, the stripping curve was recorded at a scan rate of 0.5 mV/s and a pulse amplitude of 10mV. The peak current produced gave a linear calibration curve in the range 0.2-20 ng/mL.

The limit of determination was 0.1 ng/mL at a deposition time of 10 min. The coefficient of variation was 10% for 10 replicate determinations of 1.0 ng/mL Sb(III or V). Gallain and Brihaye[78] also described a routine speciation method for Sb(III), Sb(V), and several other metals in seawater by anodic stripping voltammetry methods.

E. Discussion

Speciation results for As and Sb in natural waters in the past ten years, show that As(III), As(V), methylarsonic acid, dimethylarsinic acid, Sb(III), Sb(V), methylstibinic acid, and dimethylstibonic acid are the As and Sb compounds commonly determined in natural waters. The distribution and speciation of Sb compounds are less widely studied. It was found that basically four methods have been used recently for the investigation of As and Sb speciation in natural waters: selective hydride evolution, chromatography, differential pulse voltammetry, and solvent extraction followed by flame or graphite furnace atomic absorption spectrometry, neutron activation, and perhaps plasma emission spectrometry.

Two early spectrophotometric methods for the speciation of As(III) and As(V) in natural waters, the silver diethyldithiocarbamate method[79-81] and the molybdenum blue method,[82] have been used rarely since the late seventies. Both methods rely on redox-based colorimetry and suffer from rather complex experimental procedures, low sensitivities, and interferences.[83,84] The detection limit for the silver diethyldithiocarbamate method is approximately 10 ng/mL. The molybdenum blue method has a detection limit of 1 ng/mL, but both the accuracy and precision suffer from the low As(III)/As(V) and low As(total)/P ratio normally encountered in the environment. Chemical studies were made by Stauffera[83] to optimize reduced molybdenum blue for As determination in chemically diverse groundwaters. For natural waters with As(V)<30 ng/mL and SiO_2>20 mg/mL, the authors do not recommend the molybdenum blue procedure.

For the past ten years, the hydride generation technique has been used most often for the determination of inorganic and common organic arsenic and antimony species in natural waters. Speciation of these compounds is achieved by the pH-dependent reduction of the species to the corresponding hydrides, separation of the inorganic and organic hydrides by selective volatilization from a cold trap, or by gas chromatographic separation. Graphite furnace atomic absorption spectrometry is most commonly employed for the detection. The disadvantages of the hyride generation method include the requirements that the As or Sb compounds must be reducible to the corresponding hydrides and that the hydrides possess sufficient volatility to allow their transfer to the detector. Uncommon As and Sb compounds may exist which do not fulfill these requirements. Although the determination offers excellent sensitivity and the speciation of As and Sb by selective hydride evolution and AAS has been proposed frequently and has been widely used, interferences are not uncommon, and the accuracy of the method has been questioned.[85,86] Analytical limitations such as molecular rearrangement[87] and incomplete recoveries[88] have been reported. In addition, the accuracy of As speciation data for waters with elevated levels of dissolved ions (such as sediment interstitial water) would require further verification, since sufficient ionic levels will prevent completion of the desired reduction.[89,90] These problems have not been thoroughly investigated.

Ion chromatography and ion-exchange HPLC are readily amenable to the separation of As species because of their large pK_a differences.[91] The ion exchange technique has been used for speciation of As in natural waters. Application of this technique for Sb speciation has not yet been reported. The main advantages of HPLC-AAS or HPLC-ICP are the enhanced selectivity and sensitivity of detection and the minimum requirement for sample pretreatment. Speciation by methods based on hydride generation is attractive for environmental analyses, but it is limited to the determination of those species which can be converted into volatile hydrides. The ion exchange technique possesses the potential advantage that it is impossible to extend or modify the technique to include the analysis of additional environmentally important As species that do not form hydrides readily. It is the best technique for separation of non-volatile As compounds. However, the extension of the ion exchange technique to As speciation in seawater has not yet been reported. The main obstacle to analyzing seawater by this technique is the presence in the sample of a large concentration of sodium chloride[92] which is 10^6-10^7 times more concentrated than the analytes. Although Low et al.[92] eliminated the problem by using Di-n-butylamine phosphate as a surface modifier, the organic modifier will interfere with the detector operation; alternative procedures to overcome this effect of chloride are still under investigation.

The speciation of As and Sb by solvent extraction followed by GFAAS, ICP-AES or NAA has been extensively studied. These methods give high selectivity and sensitivity and also eliminate matrix interferences. Unfortunately, among such extraction systems all attention is focused on the inorganic species only; these methods largely rely on estimating As(V) by arithmetic difference. Appropriate conditions for selective extraction of arsenite, arsenate, methylarsonate and dimethylarsinate using various reagents have been described by Suzuki et al.,[93] but selective extraction of organic As and Sb species from natural waters has not yet been reported and remains an area for research.

Polarographic techniques, especially ASV, are sensitive both to low As and Sb concentrations and to the chemical forms of these elements, so they are attractive for analysis of natural waters. However, the differential pulse techniques do not give the required detection limit for the determination of As and Sb in many natural waters. The detection limit for As and Sb is approximately 0.1-0.2 ng/mL only.

F. Conclusion

Speciation analysis is essential for an understanding of the biological and geochemical cycling of trace elements; simple total element analysis provides little information about these processes. Speciation of trace elements like As and Sb is a very difficult task when the total concentration is at or below the ng/mL level. The above review represents the tip of the iceberg in terms of the methods and their applications in trace element speciation with respect to As and Sb. Each analytical method provides advantages and disadvantages that must be considered with regard to the scope of the study and the available laboratory facilities. The potential for automated analysis such as flow injection has yet to be exploited. It is important to realize that AAS, ICP-AES, ASV, NAA, and XRF have each been used in the elemental determination. Many of the applications of these techniques to the speciation problems have been coupled to preconcentration techniques. The use of chemical methods of concentration, matrix effect minimization, and species isolation provides an essential supplement to the powerful instrumental techniques available. Naturally one tries to avoid these procedures because each step may possibly bring in an analytical error. Yet the hallmark of a good analytical chemist is the ability to recognize and to master the versatility with which each analytical problem has to be approached. It must be emphasized that this review did not reveal that preconcentration or chemical separation is a panacea prior to speciation of As, Sb, or any other trace elements. No method of analysis will be a panacea because the choice will be influenced by the type of water that has to be examined, the element of interest, the number of samples, the required accuracy, precision and sensitivity, the available equipment, and the expert knowledge of the analyst, etc.

REFERENCES

1. Crecelius, E. A. "The Geochemistry of Arsenic and Antimony in Puget Sound and Lake Washington, Washington," Ph.D. dissertation, University of Washington, Seattle, 1974.

2. NAS (National Academy of Sciences) "Arsenic-Medical and Biological Effects of Environmental Pollutants," 1977.

3. Peoples, S. A. "Arsenical Pesticides," Amer. Chem. Soc. Symp. Ser. **1975**, 7, 1.

4. Ferguson, J. F.; Anderson, M. A. "Chemical Forms of Arsenic in Water Supplies and Their Removal," in Chemistry of Water Supply, Treatment, and Distribution, Rubin, A. J., Ed., Ann Arbor Science Publisher, Inc.: Ann Arbor, MI, 1974; pp 137-157.

5. Wauchope, R. D. J. Environ. Qual. **1975**, 4, 355.

6. Whitfield, M.; Turner, D. R. in Chemical Modeling in Aqueous Systems, Jenne, E. A., Ed., American Chemical Society: Washington, D. C., 1979; p 657.

7. Florence, T. M.; Batley, S. E. CRC Crit. Rev. Anal. Chem. **1980**, 9, 219.

8. Patterson, C. C.; Settle, D. M. in Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, LaFluer, F. D., Ed., U.S. Department of Commerce: Washington, D.C., 1976; N.B.S. Spec. Publ. No. 422, Vol. 1, p 321.

9. Batley, G. E.; Gardner, D. Water Res. **1977**, 11, 745.

10. Moody, J. R.; Lindstrom, R. M. Anal. Chem. **1977**, 49, 2264.

11. Tschopel, P.; Kotz, L.; Schulz, W.; Veber, M.; Tolg, G. Z. Anal. Chem. **1980**, 302, 1.

12. Laxen, D. P.; Harrison, R. M. Anal. Chem. **1981**, 53, 337.

13. Cooney, D. O. Anal. Chem. **1980**, 52, 1068.

14. Batley, G. E.; Gardner, D. Estuar. Coast. Mar. Sci. **1978**, 7, 59.

15. Andreae, M. Anal. Chem. **1977**, 49, 820.

16. Adams, D. D.; Darby, D. A.; Young, R. J. in Contaminations and Sediments, Baker, R. A., Ed., Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 2, p 3.

17. Tallman, D. E.; Shaikh, A. U. Anal. Chem. **1980**, 52, 196.

18. Cherry, J. A.; Shaikh, A. U. J. Hydrol. **1979**, 43, 373.

19. Florence, T. M. Water Res. **1979**, 11, 681.

20. Odonaka, Y.; Matano, O.; Goto, S. Bunseki Kagaku **1979**, 28, 517; Chem. Abstr. **1979**, 91, 221843h.

21. Shaikh, A. U.; Tallman, D. E. Anal. Chim. Acta, **1978**, 98, 251.

22. Chi, X.; Xu, J.; Li, X. Fenxi Huaxue **1984**, 12, 278; Chem. Abstr. **1984**, 101, 43274p.

23. Puttemans, F.; Massart, D. L. Mikrochim. Acta **1984**, 1, 261.

24. Howard, A. G.; Arbab-Zavar, M. H. Analyst **1981**, 106, 213.

25. Tanaka, S.; Kaneko, M.; Konno, Y.; Hashimoto, Y. Bunseki Kagaku **1983**, 32, 535; Chem. Abstr. **1983**, 99, 181178b.

26. Maher, W. A. Spectrosc. Lett. **1983**, 16, 865.

27. Yamamoto, M.; Fujishige, K.; Tsubota, H.; Yamamoto, Y. Anal. Sci. **1985**, 1, 47.

28. Yamamoto, M.; Urata, K.; Murashige, K.; Yamamoto, Y. Spectrochim. Acta, Part B. **1981**, 36B, 671.

29. Anderson, R. K.; Thompson, M.; Culbard, E. Analyst **1986**, 111, 1153.

30. Yamamoto, M.; Yasuda, M.; Yamamoto, Y. Anal. Chem. **1985**, 57, 1382.

31. Iverson, D. G.; Anderson, M. A.; Holm, T. R.; Stanforth, R. R. Environ. Sci. Technol. **1979**, 13, 1491.

32. Grabinski, A. A. Anal. Chem. **1981**, 53, 966.

33. Ficklin, W. H. Talanta **1983**, 30, 371.

34. Aggett, J.; Kadwani, R. Analyst **1983**, 108, 1495.

35. Clifford, D.; Caber, L.; Chow, S. Proc. AWWA Water Qual. Technol. Conf., 11th **1984**, 223.

36. Tye, C. T.; Haswell, S. J.; O'Neill, P. O.; Bancroft, K. C. C. Anal. Chim. Acta **1985**, 169, 195.

37. Bushu, D. S.; Krull, I. S.; Demko, P. R.; Smith, S. B., Jr. J. Liq. Chromotogr. **1984**, 7, 861.

38. Low, G. K. C.; Batley, G. E.; Buchanan, S. J. Chromotographia **1986**, 22, 292.

39. Cappon, C. J. LC-GC **1987**, 5, 400.

40. Terada, K.; Matsumoto, K.; Inaba, T. Anal. Chim. Acta **1984**, 158, 207.

41. Chakraborti, D.; De Jonghe, W.; Adams, F. Anal. Chim. Acta **1980**, 120, 121.

42. Subramanian, K. S.; Leung, P. C.; Meranger, J. C. Int. J. Environ. Anal. Chem. **1982**, 11, 121.

43. Subramanian, K. S.; Meranger, J. C.; McCurdy, R. F. At. Spectrosc. **1984**, 5, 192.

44. Puttemans, F.; Massart, D. L. Anal. Chim. Acta **1982**, 141, 225.

45. Amankwah, S. A.; Fasching, J. L. Talanta **1985**, 32, 111.

46. Kanako, E. Bunseki Kagaku **1978**, 27, 250; Chem. Abstr. **1978**, 89, 117426x.

47. Yu, M.; Liu, G. Fenxi Hauxue **1982**, 10, 747; Chem. Abstr. **1983**, 98, 185266f.

48. Kawamoto, H.; Abe, S.; Iijima, N. Bunseki Kagaku **1982**, 31, 341; Chem. Abstr. **1982**, 97, 60683n.

49. Tsuji, H.; Nishimura, K.; Tamari, Y.; Kusaka, Y. Bunseki Kagaku **1984**, 33, 43; Chem. Abstr. **1984**, 100, 126604b.

50. Leyden, D. E.; Goldback, K.; Ellis, A. T. Anal. Chim. Acta **1985**, 171, 369.

51. Henry, F. T.; Kirch, T. O.; Thorpe, T. M. Anal. Chem. **1979**, 51, 215.

52. Buldini, P. L.; Ferri, D.; Zini, Q. Mikrochim. Acta **1980**, 1, 71.

53. Bodewig, F. G.; Valenta, P.; Nuernberg, H. W. Z. Anal. Chem. **1982**, 311, 187.

54. Huang, W. W.; He, C. L.; Li, F. R.; Wang, Q. Z.; Li, J. Shen-tung Hai Yung Hsueh Yuan Hsueh Pao **1980**, 10, 42.

55. Sadana, R. S. Anal. Chem. **1983**, 55, 304.

56. Cui, C. Huanjing Kexue **1985**, 6, 65; Chem. Abstr. **1985**, 103, 42262n.

57. Jaya, S.; Rao, T. P.; Rao, G. P. Talanta **1987**, 34, 574.

58. Wals, T.; Das, H. A.; Van der Sloot, H. A. J. Radioanal. Chem. **1980**, 57, 215.

59. Orvini, E.; Gallorini, M.; Speziali, M. NATO Conf. Ser. [Ser.] **1983**, 1, 6; Chem. Abstr. **1983**, 98, 204070f.

60. Gallorini, M.; Orvini, E.; Sabbioni, E.; Pietra, R. Proc. Int. Conc. Nucl. Methods Environ. Energy Res., 5th, **1984**, 141.

61. Cheam, V.; Agemian, H. Analyst **1980**, 105, 737.

62. Crecelius, E. A.; Bloom, N. S.; Cowan, C. E.; Jenne, E. A. Energy Res. Abstr. **1986**, 11, 39521, E. A. Report 1986, EPRI-EA-4641-Vol. 2; 88 pp. Avail. NTIS.

63. Aggett, A.; Michelle, R. K. Analyst **1987**, 112, 153.

64. Andreae, M. O.; Asmode, J. F.; Foster, P.; Van't dack, L. Anal. Chem. **1981**, 53, 1766.

65. Hitachi, Ltd., Jpn. Kokai Tokyo Koho JP. 27 Apr. 1982, Appl. 80/144,389, 17 Oct. 1980, 2 pp; Chem. Abstr. **1982**, 97, 103628t.

66. Yamamoto, M.; Urata, K.; Yamamoto, Y. Anal. Lett. **1981**, 14, 21; Chem. Abstr. **1981**, 94, 149650k.

67. Apte, S. C.; Howard, A. G. J. Anal. At. Spectrom. **1986**, 1, 221.

68. Tanaka, S.; Nakamura, M.; Yokoi, H.; Yumura, M.; Hashimoto, Y. Bunseki Kagaku **1986**, 35, 116; Chem. Abstr. **1986**, 104, 174208e.

69. Han, H.; Wang, W. Huanjing Huaxue **1985**, 4, 52; Chem. Abstr. **1985**, 103, 42262n.

70. Sturgeon, R. E.; Willie, S. N.; Berman, S. S. Anal. Chem. **1985**, 57, 6.

71. Kramer, C. G.; Yu Guo, H.; Duinker, J. C. Z. Anal. Chem. **1984**, 317, 383.

72. Nakashima, S. Bull. Chem. Soc., Jpn. **1981**, 54, 291.

73. Liu, G.; Yu, M. Fenxi Huaxue **1982**, 10, 680; Chem. Abstr. **1983**, 98, 204074k.

74. Subramanian, K. S.; Meranger, J. C. Anal. Chim. Acta **1981**, 124, 131.

75. Sun, H. K.; Shan, X. Q.; Ni, Z. M. Talanta **1982**, 29, 589.

76. Metzger, M.; Braun, H. Anal. Chim. Acta **1986**, 189, 263.

77. Nagaosa, Y.; Sana, T. Bunseki Kagaku **1984**, 33, 22; Chem. Abstr. **1984**, 100, 167233y.

78. Gillain, G.; Brihaye, C. Oceanol. Acta **1985**, 8, 231.

79. Peoples, S. A.; Lakso, J.; Lais, T. Proc. West. Pharmacol. Soc. **1971**, 14, 178.

80. Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Association: Washington, D. C., 1980; 174 pp.

81. Stratton, G.; Whitehead, H. C. J. Amer. Water Works Association **1962**, 54, 861.

82. Johnson, D. L.; Pilson, E. Q. Anal. Chim. Acta **1972**, 58, 289.

83. Stauffera, R. E. Anal. Chem. **1983**, 55, 1205.

84. Sandhu, S. S.; Nelson, P. Anal. Chem. **1978**, 50, 322.

85. Hinners, T. A. Analyst **1980**, 105, 751.

86. Amankwah, S. A.; Fasching, J. L. Talanta **1985**, 32, 111.

87. Talmi, Y.; Bostik, D. T. Anal. Chem. **1975**, 47, 2145.

88. Carvalho, M. B.; Hercules, D. M. Anal. Chem. **1978**, 50, 2030.

89. Pierce, F. D.; Brown, H. R. Anal. Chem. **1976**, 48, 693.

90. Pierce, F. D.; Brown, H. R. Anal. Chem. **1977**, 49, 1417.

91. Low, G. K.-C.; Hadded, P. R.; Duffield, A. M. J. Chromatogr. **1983**, 261, 345.

92. Jenne, E. A. in "Chemical Modeling in Aqueous Systems," Jenne, E. A., Ed., Amer. Chem. Soc. Symp. Ser. **1979**, 93, 3, American Chemical Society: Washington, D. C.

93. Suzuki, N.; Satoh, K.; Shoji, H.; Imura, H. Anal. Chim. Acta **1986**, 185, 239.

CHAPTER IV

The following manuscript entitled

EXTRACTION OF ARSENIC(III) AND ARSENIC(V) FROM NATURAL WATERS FOR NEUTRON ACTIVATION ANALYSIS

by

W. M. Mok, N. K. Shah and C. M. Wai

has appeared in

Analytical Chemistry, _58_, 110 (1986)

ABSTRACT

Quantification and speciation of arsenic(III) and arsenic(V) in natural waters can be achieved by extracting the former species with pyrrolidinecarbodithioate at pH 1-1.5 into chloroform followed by a nitric acid back extraction for neutron activation analysis (NAA). Besides eliminating interferences from matrix species in natural waters, the two-step extraction procedure also provides a large preconcentration factor for arsenic. Detection of 10^{-2} μg/L of arsenic can be achieved by using this extraction method and NAA. Applications of this method to arsenic speciation studies in natural water systems are discussed.

Because of its toxicity and possible carcinogenicity, arsenic is one of the most widely measured trace metals in many environmental monitoring programs. Arsenic generally occurs in the oxidation states As(III) and As(V) in natural water systems. Information on the distribution of the two oxidation states of arsenic in water is important for some environmental studies. For example, the ratio of the two oxidation states of arsenic may be used as an indicator of redox conditions of natural water systems.[1] Biologically, As(III) is considered more toxic than As(V).[2] The concentrations of total arsenic in most natural water systems are in the range of 10^{-6}-10^{-7} g/L.[3] Analytical methods capable of measuring nanogram levels of As(III) and As(V) are necessary for studying the chemistry of arsenic species in aquatic environments.

Neutron activation is one of the most sensitive techniques for arsenic analysis. Under interference-free conditions, neutron activation analysis (NAA) can easily detect nanogram levels of arsenic in a sample with good accuracy. However, in real samples, spectral interferences from other elements such as Na and Br can greatly limit the sensitivity of arsenic determination by NAA. Radiochemical separations involving anion-exchange and precipitation procedures have been used to isolate ^{76}As ($t_{1/2}$ = 26.4 h) and to eliminate matrix interferences from irradiated water samples for quantification of arsenic.[4] Radiochemical separation applied to water samples after neutron irradiation for arsenic determination has several drawbacks. First, the oxidation states of arsenic in the original samples cannot be distinguished. Second, a large concentration factor cannot be obtained because the amount of sample allowed in each irradiation is limited. Preconcentration and separation of metals from water samples by solvent extraction prior to neutron irradiation have been applied to several systems.[5,6] Extraction before neutron irradiation can avoid the aforementioned drawbacks and also has the advantage of minimizing radiation exposure for the analyst. This paper describes an extraction method for separation and preconcentration of As(III) and As(V) from natural waters prior to NAA. The proposed method, which is simple and sensitive, is suitable for measuring low levels of arsenic species in natural water systems.

EXPERIMENTAL SECTION

Reagents. A stock solution of 1000 μg/mL As(III) was prepared by dissolving 0.1320 g of arsenic trioxide (Allied Chemicals) in 2 mL of 1 M NaOH. After addition of 25 mL of water, the solution was acidified with 4 mL of 1 M HCl and diluted to 100 mL with deionized water. A stock solution of As(V) (1000 μg/mL) was prepared by dissolving 0.4163 g of sodium arsenate (J. T. Baker Co.) with 0.5 mL of concentrated H_2SO_4 and diluting to 100 mL with deionized water. Ammonium pyrrolidinecarbodithioate (APCDT) and sodium diethyldithiocarbamate (NaDDTC) were purchased from the Fisher Scientific

Co. Chloroform used in the extraction was Baker Analyzed reagent. Nitric acid used in the experiments was of Ultrex grade, also from Baker Chemical Co. Deionized water was obtained by treatment of distilled water through an ion-exchange column (Barnstead ultrapure water purification cartridge) and a 0.2-μm filter assembly (Pall Corp., Ultipor DFA). All containers were washed with 2% Liqui-Nox detergent (Alconox, Inc.) solution and then soaked in 10% HNO_3 for at least 24 h. After the containers were soaked, they were rinsed with deionized water and stored in a class-100 clean hood equipped with a vertical laminar flow filter (CCI).

Natural seawater (surface) was collected from the coastal waters near the Seattle area using a 15-L polyethylene bottle and was filtered through a 0.45-μm Millipore membrane filter before use. A river water sample was taken from the Snake River near Lewiston, ID. Groundwater was obtained from a local well near Joel, ID. Mine waters were from the Bunker Hill Mine in the Coeur-d'Alene Mining District, ID. A synthetic seawater was prepared according to the procedure published in the literature.[7]

Extraction Procedures. The extraction solution was prepared by dissolving 5 g of APCDT in 100 mL of deionized water. The solution was always prepared fresh prior to use, filtered to remove the insoluble material, and shaken with chloroform for 1 min to remove bromine and other impurities. A 12% ethylenediaminetetraacetic acid (EDTA) solution was also prepared fresh and was used as a masking agent for the extraction. All water samples analyzed were saturated with chloroform before extraction.

To extract As(III), normally a 100-mL sample was poured into an Erlenmeyer flask equipped with a ground stopper. The water sample was adjusted to pH 1.5 before 2 mL of the extraction solution, 4 mL of the EDTA solution, and 10 mL of chloroform were added. The mixture was shaken vigorously on a mechanical wrist action shaker (Burrell Model 75) for 10 min and then was allowed to sit for 10 min for phase separation. The organic phase was removed from the flask and washed a couple of times with small amounts of deionized water to remove Na and other impurities. Exactly 8 mL of the organic phase was then transferred to a flask and 2 mL of 50% HNO_3 was added to back extract As. The mixture was shaken again for 10 min on the mechanical shaker. After phase separation, 1 mL of the acid solution was transferred into a polyethylene vial for neutron irradiation.

To determine As(V), a second aliquot of the water sample was placed in an Erlenmeyer flask and adjusted to pH 1.0 with HNO_3. Reduction of As(V) to As(III) was achieved by the addition of 1 mL of a 25% sodium thiosulfate solution followed by 1 min of shaking. After a waiting period of 5 min, 2 mL of the extraction solution, 4 mL of the EDTA solution, and 10 mL of chloroform were added to the flask, and the total As(III) was extracted by the procedure described in the previous section. The difference in As concentrations between the two aliquots represents the amount of As(V) in the original water sample. A procedure blank made of 100 mL of deionized water and run through the same extraction procedure was run with each set of experiments. No detectable amount of As was found in any of the blanks.

Sample Irradiation and Counting. The details of sample sealing procedure for neutron irradiation are given elsewhere.[5,6] Standards were made of 1-mL solutions containing proper concentrations of As, heat sealed in the same kind of polyethylene vials as the samples. All samples and standards were normally irradiated for 2 h in a 1-MW TRIGA reactor at a steady neutron flux of 6×10^{12} n/(cm^{2}s), followed by one day of cooling. Before the samples were counted, they and the standards were transferred into new 2/5-dram polyethylene vials using disposable syringes. This sample transfer step is necessary in order to avoid interferences of ^{24}Na and other radioactivities produced in the plastic material of the irradiated vials. Each sample was counted for 2×10^3 s in a large-volume coaxial ORTEC Ge(Li) detector with a resolution of about 2.3 keV at the 1332-keV γ from ^{60}Co. The 559-keV γ from ^{76}As was used to determine the arsenic concentrations in the samples.

RESULTS AND DISCUSSION

One advantage of using dithiocarbamic acid derivatives to extract trace metals from natural waters is that interfering matrix species including the alkali metals, the alkaline-earth metals, and the halogens can be effectively eliminated during extraction. This is particularly useful for NAA because ^{24}Na

($t_{1/2}$ = 15 h) and ^{82}Br ($t_{1/2}$ = 36 h) are generally two of the major interfering isotopes produced from thermal neutron capture of ^{23}Na and ^{81}Br, which are ubiquitous in natural waters. The high neutron capture cross sections of sodium and bromine would result in high-intensity γ peaks that tend to mask small peaks from trace metals in γ spectrometry and limit their determination. In the case of As, the most intensive γ peak of ^{76}As at 559 keV is also close to the 554-keV γ-ray emitted by ^{82}Br. Therefore, elimination of Na and Br is essential in order to detect low levels of As in natural water samples. Recently, metal-dithiocarbamate complexes such as $Bi(DDTC)_3$ and $Pb(DDTC)_2$ have also been used to extract trace metals from natural waters for NAA.[5,8] One reason for using these metal-DDTC complexes is because both Bi and Pb do not produce radioisotopes that would cause interference in γ spectrometry. Selective extraction of metals may be achieved by the use of these metal-dithiocarbamate complexes if the extraction constants of the metals being extracted are greater than that of Bi or Pb. The extraction constant of As(III)-DDTC complex is probably much lower than that of Pb(II), because $Pb(DDTC)_2$ was not able to extract As(III) according to our experiments. The extraction constant of $Bi(DDTC)_3$ is many orders of magnitude greater than $Pb(DDTC)_2$, and hence it is not expected to extract As(III) from aqueous solution.[9,10] Selective extraction of certain metals can also be done by adjusting the pH of solutions as the extraction efficiencies of many metal-dithiocarbamate complexes depend strongly on acidity.

The effects of pH on the extraction of As(III) in deionized water with APDTC are shown in Figure 1. Quantitative extraction of As(III) was observed over a wide range from pH 0.6 to about 6. Above pH 6, the efficiency of extraction of As(III) begins to decrease very rapidly. The extraction curves for Cu(II), Fe(II), Mn(II), and Zn(II) with APCDT from pH 0.7 to 9 are also shown in Figure 1. The extraction efficiencies for Fe, Mn, and Zn are very low (≤10%) at pH <2. Because these metals may be present in polluted waters at high concentrations, extraction at pH <2 would significantly reduce their extraction efficiencies. Another factor that should be considered is the possibility of extracting As(V) in acid solution. According to the literature, As(V) cannot be extracted by APCDT even at low pH. However, in our experiments, a small fraction (2-6%) of As(V) was always found in the organic phase with APCDT extraction at pH ≤1. To avoid the extraction of As(V) and to reduce Fe, Mn, and Zn, a pH value of 1.5 was finally chosen for the extraction of As(III) in our procedure. The pH-dependence curve for As(III) with NaDDTC extraction is similar to the one with APCDT shown in Figure 1. One problem with using NaDDTC at low pH is that it is unstable in acid solution and consequently may result in incomplete extraction of As(III). Indeed, partial extraction of As(III) with NaDDTC was frequently observed at pH <2, especially if shaking was not

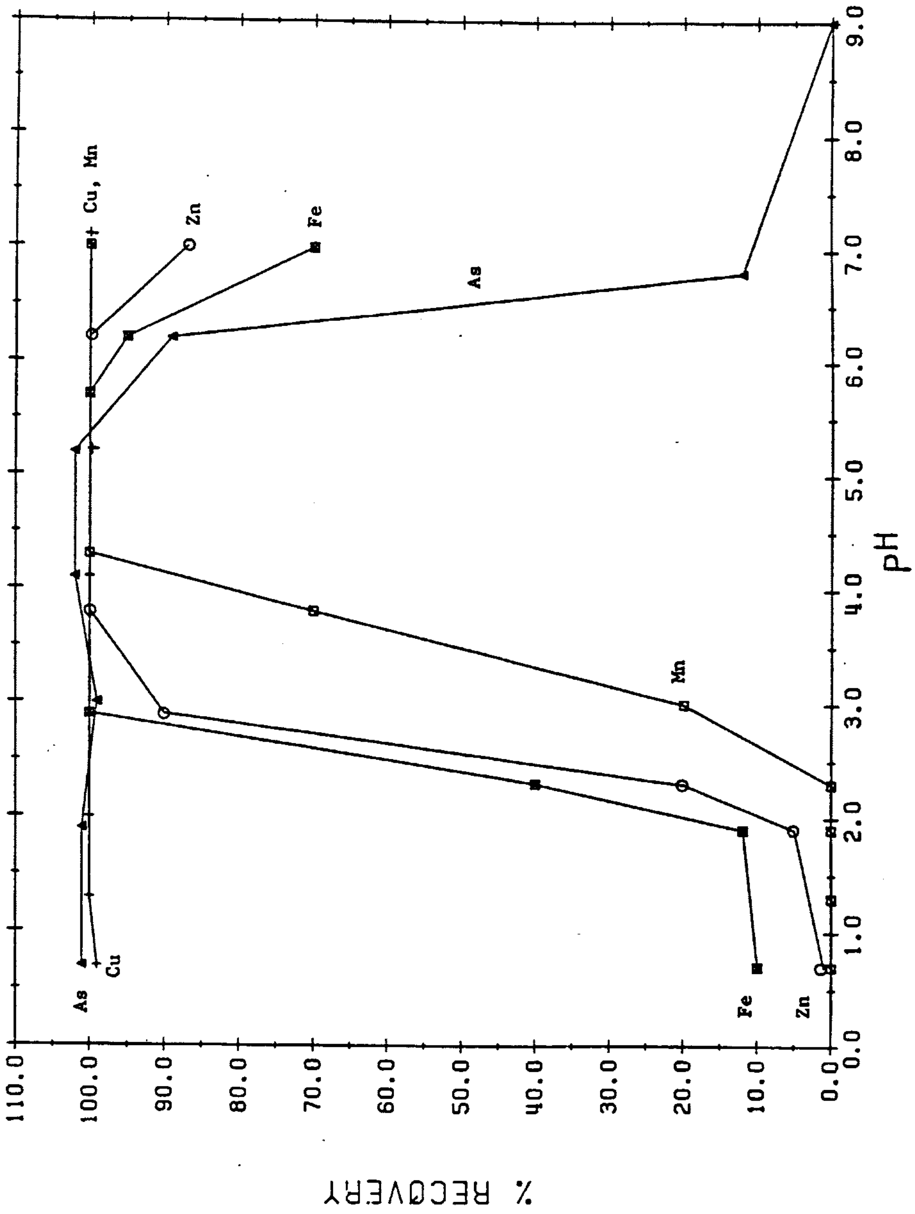

Figure 1. pH dependence of the extraction of As(III) and other metals, Cu(II), Fe(II), Mn(II), and Zn(II), with APCDT from aqueous phase into chloroform. As(V) is not extractable at pH > 1 as discussed in the text.

carried out immediately after the addition of the chelating agent. For this reason, NaDDTC is not recommended as an extracting agent for As(III) in our procedure.

In complex natural water systems, the degree of extraction of As(III) with dithiocarbamate may be significantly reduced due to competition caused by other metal ions present in the system. However, such interferences can be reduced by the use of EDTA as a masking agent.[11] Table 3 shows the results of APCDT extraction carried out with and without the masking agent in a mine water sample spiked with parts-per-billion levels of As. In the absence of EDTA, the percentage of As recovery may not be satisfactory depending upon the water quality. In our experiments, a concentration of about 0.5% EDTA is used to eliminate interferences caused by other concomitant metal ions in complex systems such as natural seawaters and acid mine waters.

Table 3. Effect of EDTA as Masking Agent on Dithiocarbamate Extraction of As from Mine Water[a]

Sample	As(III) added, ng	As(V) added, ng	% Recovery of As(III)	% Recovery of As(V)
Mine water without EDTA	500		81.1 ± 1.9	
Mine water with EDTA	400		102.2 ± 1.6	
Mine water with EDTA		400		107.0 ± 1.9

[a] Sample volume is 50 mL. The results are corrected for the blank As value in sample.

Sodium thiosulfate is an effective reducing agent for As(V). The reduction of As(V) to As(III) with thiosulfate in acid solution is fast; only several minutes are necessary to complete the reduction at pH 1. The efficiency of the reduction process appeared to decrease at higher pH. Addition of potassium iodide to thiosulfate did not seem to enhance the efficiency of reduction. This observation is different from Kamada's report, which indicated that treatment of potassium iodide was essential for the reduction of As(V).[11] Based on our experiments with spiked As(V) samples, a 0.2% sodium thiosulfate solution at pH 1 provides a satisfactory condition for total reduction of As(V) in natural water samples. Our recommended procedure is to shake the solution for 1 min after the addition of thiosulfate followed by a waiting period of 5 min to allow for complete reduction. The difference in As(III) concentrations between two aliquots of a water sample with and without reduction gives the concentration of As(V) in the sample.

The organic-bound As in chloroform can be back extracted into a nitric acid solution for NAA. With a 50% HNO_3 solution, back extraction of As can be achieved within 10 min of shaking. Incomplete extraction of As may result if the acid concentration is less than 30%. The Ultrex grade HNO_3 blank did not show any detectable amount of As under our irradiation and counting conditions. Technical grade HNO_3 should be avoided because it may contain traces of As. After the sample is irradiated, the acid solution containing ^{76}As

can be transferred to a new polyethylene vial using a disposable syringe for γ counting.

The proposed extraction method not only eliminates interferences for NAA but also provides a large preconcentration factor for As. In the APCDT extraction step, the aqueous-to-organic phase ratio is normally kept no more than 20:1. A concentration factor of 20 can be obtained in the first step of the proposed extraction. Another concentration factor of 5 or more can also be obtained in the acid back extraction step. Therefore, a total concentration factor of 100 or more can be achieved from the proposed two-step extraction procedure. The absolute detection limit of As under our experimental conditions and based on 3σ of the background under the 559-keV peak is estimated to be 1 ng. With a preconcentration factor of 100, this method should be able to detect As in natural waters at the 10^{-2} μg/L level. The proposed extraction procedure combined with NAA is likely to be one of the most sensitive methods for determining low levels of As in natural water systems. The extraction method can also be combined with graphite furnace atomic absorption spectrometry (GFAAS) for As determination in natural waters. However, because concentrated HNO_3 is not a preferred matrix for GFAAS, dilution of the acid solution from the back extraction process is necessary in order to reduce matrix interference for As determination. This would result in a smaller preconcentration factor for As. In general, NAA is relatively free from chemical interferences because the γ rays emitted from a nucleus are independent of the chemical environment of the atom. If spectral interference can be eliminated, NAA is likely to be the most reliable technique for trace-element determination in environmental samples.

The proposed method for As extraction and NAA has been applied to the analysis of NBS Standard River Water (SRM 1643a), which is certified to contain 76 ± 7 ng/g of As. Because the certified value does not specify the oxidation state of As, our analysis of this standard reference material followed the procedure for total As determination described in the Experimental Section. With synthetic seawater as the diluent and on the basis of five replicate analyses, the average arsenic content in SRM 1643a determined by this extraction method and NAA was 82.0 ± 2.3 μg/L. The average coefficient of variation for the series of replicates was ± 2.8%. In another case, a mine water sample was spiked with SRM 1643a and the total recovered As was found to correspond to 73 ± 2 μg/L in the reference material. These experimental values agree well with the certified value given by NBS. In addition to SRM 1643a, we have also tested the accuracy of our method by analyzing a seawater reference material (NASS-1) obtained from the Marine Analytical Chemistry Standards Program, National Research Council of Canada. The total As in NASS-1, which has been determined by two different techniques (anodic stripping voltammetry and hydride generation atomic absorption spectrometry), is certified to be 1.65 ± 0.19 μg/L according to the Marine Analytical Chemistry Standards

Program. By use of our extraction method and NAA, the total As in NASS-1 was found to be 1.55 ± 0.05 μg/L based on triplicate analyses of 100-mL aliquots of the seawater reference material. The agreement is again good, indicating that our method for total As determination is reasonably accurate. The accuracy of this extraction method for differentiating As^{3+} and As^{5+} species in water could not be thoroughly evaluated because no standard waters containing known amounts of the two As species were available. However, from our experiments of natural waters spiked with known amounts of As^{3+} and As^{5+}, satisfactory recoveries (>90%) of both arsenic species were observed in most cases as shown in Table 4. The results were corrected for the blank arsenic values.

In the case of natural seawater, a low recovery of spiked arsenic(III) (~72%) was observed. The seawater presumably contained species capable of oxidizing As^{3+} to As^{5+}, since the recovery of total As was found to be satisfactory in this experiment. There have been reports in the literature indicating that when sodium arsenite was added to natural seawater, it could be oxidized to arsenate.[12] This effect was found more pronounced at low As concentrations.[13] The results observed in our experiments with spiked seawater appear to be consistent with these reports.

The results of selective determination of As^{3+} and As^{5+} in various types of natural waters using the proposed extraction method and NAA are presented in Table 5. For

Table 4. Recovery of Spiked As(III) and As(V) from Different Natural Water Systems

Sample	As(III) Added, ng	As(V) Added, ng	% Recovery of As(III)	% Recovery of As(V)	% Recovery of total As
River Water	400		91.8 ± 4.6		
(50 mL)	800	400	104.0 ± 2.1		100.2 ± 2.1
	400	400	107.4 ± 2.5		99.1 ± 2.5
	400	800	103.5 ± 2.5		96.0 ± 2.1
Seawater	400	400	72.4 ± 2.0		88.5 ± 1.8
(100 mL)	800	800	71.4 ± 1.4		98.3 ± 1.4
Mine Water (A)		400		93.2 ± 2.6	
Mine Water (B)	400		86.5 ± 1.6		
Mine Water (C)	400		94.7 ± 1.9		
Mine Water (D)	400		107.2 ± 1.5		

surface waters, either from the river or from the sea, the As^{5+} concentration is appreciably larger than that of As^{3+}. This high As^{5+} content is caused, at least in part, by the high oxidized environment. The average total arsenic for surface seawater is reported to be 2 μg/L.[3] Several competing processes can modify the concentrations of the arsenic species in natural waters, including oxidization of arsenite to arsenate or the reverse reaction, precipitation and adsorption reactions, dissolution of solid material (especially organic matter), diffusion of arsenic from and into the sediments, and the advection due to the compaction flow. The kinetics of the arsenite-arsenate transformation in the ocean or river waters are still not well understood. Both bacterial and marine phytoplankton can reduce arsenate to arsenite, and the reverse reaction is known to be catalyzed by a number of bacteria.[14,15] On the other hand, a high content of arsenic(III) is notable for water samples coming from a deep well indicating a reduced environment for the groundwater. Underground waters collected from a major lead-zinc mine in northern Idaho show varied As(III)/As(V) ratios as shown in Table 5. It is interesting to note that a lower As(III)/As(V) ratio appears to correlate with a higher total arsenic content in the water. This seems to suggest that leaching of arsenic and perhaps other metals may be related to the redox environment of the groundwater system. With the assumption of redox equilibrium, the arsenic ratio may provide a basis for obtaining an indication of redox status for natural waters according to the Nernst equation. Investigations are currently in progress to follow the ratio of As(III)/As(V) as a chemical indicator to evaluate the redox status and quality of groundwaters in a galena-sphalerite mine in Idaho.

Table 5. Selective Determination of As(III) and As(V) in Various Types of Waters

Sample	As(III) found, ng/mL	As(V) found, ng/mL	Total As found, ng/mL
Snake River water	0.7 ± 0.1	3.0 ± 0.1	3.7 ± 0.1
Seawater from Tacoma, WA	<0.04	1.9 ± 0.1	1.9 ± 0.1
Well water from Joel, ID	0.6 ± 0.1	0.5 ± 0.1	1.1 ± 0.1
Mine water (A)[a]	1.9 ± 0.2	12.0 ± 1.3	13.9 ± 1.3
Mine water (B)[a]	2.4 ± 0.1	1.5 ± 0.2	3.8 ± 0.2
Mine water (C)[a]	6.2 ± 0.3	74.2 ± 1.9	80.3 ± 1.9

[a] From the Bunker Hill Mine, Kellogg, ID.

Acknowledgments - This work was supported in part by the Idaho Water Resources Research Institute with funding from the U.S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by DOE.

REFERENCES

1. Cherry, J. A.; Shaikh, A. U.; Tallman, D. E.; Nicholson, R. V. J. Hydrol. (Amsterdam) **1979**, 43, 373.

2. Arsenic-Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, 1977.

3. Wedepohl, K. H. "Handbook of Geochemistry"; Springer Verlag: New York, 1978; Vol. II/3, Chapter 33.

4. Lenvick, K.; Steinnes, E.; Pappas, A. C. Anal. Chim. Acta **1978**, 97, 295.

5. Yu, J. C.; Wai, C. M. Anal. Chem. **1984**, 56, 1689.

6. Mok, W. M.; Wai, C. M. Anal. Chem. **1984**, 56, 2623.

7. Lo, J. M.; Yu, J. C.; Hutchison, F. I.; Wai, C. M. Anal. Chem. **1982**, 54, 2536.

8. Shen, L. H.; Yeh, S. J.; Lo, J. M. Anal. Chem. **1980**, 52, 1882.

9. Wyttenbach, A.; Bajo, S. Anal. Chem. **1975**, 47, 2.

10. Yeh, S. J.; Lo, J. M.; Shen, L. H. Anal. Chem. **1980**, 52, 528.

11. Kamada, T. Talanta **1976**, 23, 835.

12. Johnson, D. L.; Pilson, M. E. Anal. Chim. Acta **1972**, 58, 289.

13. Johnson, D. L.; Pilson, M. E. Environ. Lett. **1975**, 8, 157.

14. Johnson, D. L. Nature (London) **1972**, 240, 44.

15. Osborne, F. H.; Ehrlick, H. L. J. Appl. Bacteriol. **1976**, 41, 295.

CHAPTER V

The following manuscript entitled

SIMULTANEOUS EXTRACTION OF TRIVALENT AND PENTAVALENT ANTIMONY AND ARSENIC SPECIES IN NATURAL WATERS FOR NEUTRON ACTIVATION ANALYSIS

by

W. M. Mok and C. M. Wai

has appeared in

Analytical Chemistry, 59, 233 (1987)

ABSTRACT

Antimony(III) and arsenic(III) in aqueous sample can be simultaneously extracted with ammonium pyrrolidinecarbodithioate (APCDT) into chloroform from pH 3 to 6. Extraction of antimony(V) and arsenic(V) can be achieved by reduction with thiosulfate and potassium iodide at pH 1 followed by APCDT extraction at the same pH value. The Sb- and As- PCDT complexes in the organic phase can be back-extracted into a nitric acid solution for neutron activation analysis (NAA). Detection of 10^{-3} μg/L of antimony and arsenic can be achieved by using this extraction method and NAA. Applications of this method to antimony and arsenic speciation studies in natural water systems are discussed.

Arsenic and antimony are among the most interesting elements in studies of environmental pollution because of their toxic nature. Biologically, As(III) is considered more toxic than As(V).[1,2] Knowledge of the distribution of As(III) and As(V) species in natural water systems is important for environmental monitoring programs. It has also been suggested that the ratio of As(III) to As(V) may be used as a chemical indicator of the redox status of groundwater systems.[3] The distribution and toxicity of Sb(III) and Sb(V) are less well-known. However, antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency. Thus, the toxicity and physiological behavior of As and possibly Sb are dependent on their oxidation states. These elements are found in the environment at very low concentrations. The concentrations of total As and Sb in most natural water systems are in the range of 10^{-9}-10^{-10} and 10^{-9}-10^{-11} g/mL, respectively.[4,5] Analytical methods capable of measuring nanogram levels of As(III), As(V), Sb(III), and Sb(V) are therefore necessary for studying the chemistry of As and Sb species in aquatic environments.

Neutron activation analysis (NAA), when coupled with specific separation procedures, is one of the most sensitive methods for the determination of trace amounts of different species of As, Sb, Se, V, etc.[6,7] We have recently developed a technique for the determination of nanogram levels of As(III) and As(V) in natural waters with dithiocarbamate extraction for NAA.[8] With some modification of the extraction procedure, the technique can be applied to determine As and Sb species simultaneously. The extraction method, which concentrates As and Sb from water and eliminates interfering elements for neutron irradiation, has greatly improved the sensitivity and accuracy for the detection of nanogram levels of As and Sb species in real samples. The details of the extraction procedure are given in the following section. In an attempt to demonstrate applicability to matrices having different chemical compositions, the following standard materials were analyzed: orchard leaves (SRM 1571), coal fly ash (SRM 1633a), and a seawater reference material (NASS-1).

EXPERIMENTAL SECTION

Reagents. A stock solution of Sb(III) (1000 mg/L) was prepared by dissolution of 0.1972 g of Sb_2O_3 (Baker) in 100 mL of 2.5 M HCl. A stock solution of Sb(V) (1000 mg/L) was prepared by dissolution of 0.2168 g of potassium antimonate in water, making up to 100 mL of 0.1% HNO_3. Stock solutions of As(III) and As(V) were prepared according to the procedures given in our previous paper.[8]

Ammonium pyrrolidinecarbodithioate (APCDT) was obtained from the Fisher Scientific Co. Chloroform used in the extraction was Baker Analyzed reagent. The extraction solution was prepared by dissolving 5 g of APCDT in 100 mL of deionized water. The solution was always prepared fresh prior to use, filtered to remove the insoluble material, and shaken with chloroform for 1 min to remove bromine and other impurities.

Deionized water was obtained by treatment of distilled water through an ion-exchange column (Barnstead Ultrapure Water Purification Cartridge) and a 0.2-μm filter assembly (Pall Corporation Utipor DFA). Ammonium citrate buffer (20%, w/v) was prepared by dissolving 200 g of ammonium citrate, dibasic (ACS grade, Fisher Scientific), in 500 mL of water, adjusting the pH to 7.2 with concentrated ammonia, and making up to 1 L with water. The containers used in this study were cleaned sequentially with a detergent wash, tap water, and distilled water rinse and soaked in 10% HNO_3 for at least 24 h. They were then rinsed with deionized water and stored in a class-100 clean hood equipped with a vertical laminar flow filter (CCI). All other reagents and solutions used were of the highest purity available. Surface seawater was collected off Bainbridge Island in Puget Sound. River waters were collected from the Snake River in Lewiston, ID, and from the Coeur d'Alene River in northern Idaho. The samples were treated as described in our previous paper.[8]

Analytical Procedures. All water samples analyzed were saturated with chloroform before extraction. For the extraction of Sb(III) and As(III), normally a 100-mL sample was placed into a ground-glass-stoppered Erlenmeyer flask. A 10-mL aliquot of citrate buffer was added, and the pH was adjusted to a value between 3.5 and 5.5 with HCl or NH_4OH; the pH range selected for the simultaneous extraction of Sb(III) and As(III) will be explained in the next section. This was followed by the addition of 4 mL of 12.5% ethylenediaminetetraacetic acid (EDTA) solution as a masking agent.[8] Ten milliliters of chloroform and 2 mL of 5% APCDT were then added. The mixture was extracted by shaking vigorously for 10 min on a wrist-action mechanical shaker (Burrell Model 75), and the phases were allowed to separate. After the aqueous phase was discarded, the organic phase was washed twice with 10 mL of deionized water. Exactly 8 mL of the organic phase was transferred to a 20-mL Beckman polyvial with a fast-turn cap. To back-extract Sb and As, 1.5 mL of 50% HNO_3 was added to the vial, and the mixture was shaken for 10 min. After phase separation, 1 mL of the aqueous phase was pipetted into a 2/5-dram polyethylene vial and heat-sealed for neutron irradiation. A procedure blank made of an equal volume of deionized water (100 mL in this case) was run for each set of experiments.

For water samples with low As and Sb contents, the initial sample size can be increased to 300 mL or 500 mL. The amount of the buffer, the masking agent, and the chelating agent PCDT should also be increased in proportion to the sample size. About 20-30 mL of chloroform should be sufficient for effective extraction of the Sb and As complexes. After extraction, the volume of the organic phase can be reduced by evaporation at room temperature. After the volume of chloroform is reduced to less than 10 mL, back-extraction with nitric acid can be carried out according to the procedure described in the previous section. No detectable loss of Sb and As was observed during the evaporation process.

To determine total Sb and As, a second aliquot of the water sample was placed in an Erlenmeyer flask and adjusted to a pH of about 1.0 with HCl. Reduction of Sb(V) to Sb(III) and As(V) to As(III) was carried out by using 1 mL of a 25% sodium thiosulfate solution and 1 mL of a 20% potassium iodide solution. After a waiting period of 15-30 min, 4 mL of the EDTA solution, 10 mL of chloroform, and 2 mL of 5% APCDT were added to the flask, and the complexes were extracted by the same procedure described above. The differences in Sb and As concentrations between the two aliquots represent the amount of Sb(V) and As(V) in the water sample.

NBS orchard leaves reference material was digested with a mixture of HNO_3 and H_2SO_4 in a reflux apparatus while digestion of NBS coal fly ash was carried out by using a mixture of HCl and HNO_3. The digestion procedures are given in the literature.[9]

The details for sample irradiation and counting are given elsewhere.[8] All irradiations were done in a 1-MW Triga reactor at a steady neutron flux of 6×10^{12} n cm^{-2} s^{-1}. Arsenic and Sb were determined as the nuclides ^{76}As ($t_{1/2}$ = 1.10 days, E_γ = 559.1 keV) and ^{122}Sb ($t_{1/2}$ = 2.74 days, E_γ = 564.0 keV) following 2 to 3-h irradiation and a 24-h cooling period. The nuclides were quantified by comparing net photopeak areas with those of standards. Counting times varied from 2×10^3 to 8×10^3 s depending on the concentrations of Sb and As in samples.

RESULTS AND DISCUSSION

Extraction of As(III) and As(V) using APCDT has been described in our previous paper.[8] However, no work has been reported that combines this extraction method for the speciation of Sb with a modern analytical technique such as NAA. Both As and Sb are extremely sensitive to neutron activation. Under interference-free conditions, nanogram levels of As and Sb can be detected by NAA. However, direct measurements of As and Sb in natural waters by NAA are very difficult to carry out because of their low concentrations and matrix interferences. The advantages of using the derivatives of dithiocarbamic acid to extract trace metals from natural waters for NAA have been discussed in the literature.[8] Briefly, the extraction may serve three purposes: (1) concentration and separation of trace metals, (2) elimination of interfering matrix species (such as Na and Br in the case of NAA), and (3) differentiation of metal species.

The effects of pH on the extraction of Sb(III) with APCDT are shown in Figure 2. The experiments were carried out in 100-mL deionized-water samples spiked with 5 ng/mL of Sb(III). Quantitative extraction of Sb(III) was observed in a pH range from 2 M HCl to pH 6. The pentavalent species, Sb(V), was quantitatively extracted from pH 1 to 2 M HCl, but there was virtually no extraction of Sb(V) at pH > 3.0. It can be seen from Figure 2 that simultaneous extraction of Sb(III) and As(III) is possible only in the pH range 3.0-6.0. Since As(V) was practically unextracted over the entire range of pH and

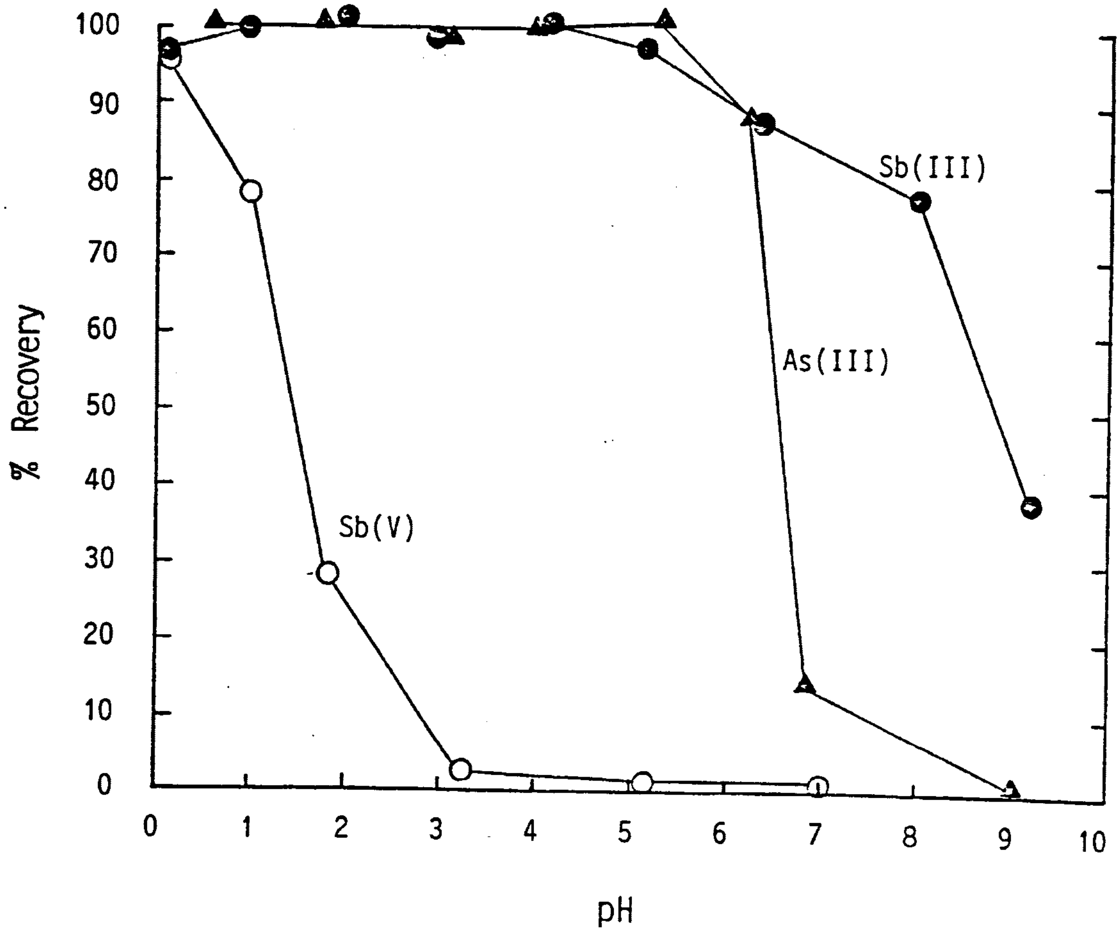

Figure 2. pH dependence of the extraction of Sb(III), Sb(V), and As(III) with APCDT from aqueous phase into chloroform.

acidity studied, a pH range of 3.5-5.5 was chosen as the standard condition for the extraction of As(III) and Sb(III) with the dithiocarbamate. Ammonium citrate was the buffer used to control the pH of the solution during extraction. There is no observable interference caused by the citrate buffer for the extraction of Sb(III) and As(III) using this method.

Sodium thiosulfate is an effective reducing agent for As(V), but it took more than 30 min for complete reduction of Sb(V) to Sb(III) under the same conditions. Radioisotope experiments showed that when a solution contained 0.2% KI and 0.25% $S_2O_3^{2-}$, the reduction was complete in 10 min. Subsequent studies showed that quantitative reduction could not be achieved by KI alone in 25 min. In our experiments, the reduction of Sb(V) and As(V) to their trivalent states was conducted in a 0.25% $Na_2S_2O_3$ and 0.20% KI solution at pH 1 for about 15-30 min. Our recommended procedure is to shake the solution for 5 min with thiosulfate followed by the addition of potassium iodide. This seems to give the best result for the reduction process.

For effective extraction of metal-dithiocarbamate complexes, the aqueous-to-organic-phase ratio should be kept at 20 or less. The shaking time for the extraction of Sb- and As-PCDT by chloroform had also been studied, and 2 min of shaking was found to be sufficient. In general, the required shaking time increases according to the metal concentration in solution, the sample volume used, and the sample matrix. In all our experiments, a shaking time of 10 min is used. Back-extraction with acid allows concentration of As and Sb efficiently into a small volume of aqueous phase, which can then be transferred into a polyethylene vial for neutron irradiation. With a 50% HNO_3 solution, back-extraction of both Sb and As can be achieved with 10 min of shaking. Sb can be stripped completely into a 20% HNO_3 solution, but incomplete extraction of As may result if the acid concentration is less than 30%.

By use of the two-step extraction procedures described in this paper, an overall preconcentration factor of 100 or more can be achieved. The absolute detection limit of Sb and As for 3 h of irradiation and 2×10^3 s counting was estimated to be 1.2 and 1.0 ng, respectively, on the basis of 3σ (standard deviation) of the background under the 564.0-keV peak of Sb and 559.1-keV peak of As. With a preconcentration factor of 10^2, this method should be able to detect Sb and As in natural waters at 10^{-2} μg/L level, or about 10 parts per trillion. If a 500-mL sample and an 8×10^3 s counting time are used, the detection limit of Sb and As can be lowered to 10^{-3} μg/L, or about 1 part per trillion. This detection limit is sensitive enough to measure Sb and As species in most natural water systems.

Recovery of spikes (300 ng added to 100 mL of a seawater reference material (NASS-1) obtained from the Marine Analytical Chemistry Standards Program, National Research Council of Canada) into aqueous samples averaged 98.1 ± 1.7% for Sb, based on three replicate measurements and with blank correction. The total As in NASS-1 was found to be 1.49 ± 0.03 μg/L, which agrees well with the certified value of 1.65 ± 0.19 μg/L. Results for the analysis of NASS-1 are given in Table 6. The accuracy of the method for Sb determination was assessed by comparison of the results with those obtained by using other independent analytical techniques. Agreement with these other values is evident from the data shown in the table.

This method has also been applied to the analysis of an NBS biological standard, orchard leaves (SRM 1571), whose Sb and As contents have been certified to be 2.9 ± 0.3 and 10 ± 2 μg/g, respectively. The standard reference material was digested by using the sulfuric acid/nitric acid mixture described in the literature.[9] On the basis of three replicate analyses, the Sb and As contents in SRM 1571 were determined to be 3.04 ± 0.09 and 8.84 ± 0.11 μg/g, respectively. These experimental values agree well with the reported values. In another case, analysis of Sb and As in digested coal fly ash samples (SRM 1633a) using this extraction method and NAA resulted in 7.54 ± 1.23 μg/g for Sb and 139.0 ± 3.4 μg/g of As in the ash. These experimental values again agree with the values 7 and 145 ± 15 μg/g for Sb and As, respectively, as reported by NBS. All these results indicate that the method for simultaneous determination of total Sb and As is reasonably accurate.

Table 6. Determination of Total As and Sb in Some Reference Materials Using This Extraction Method and NAA

	As		Sb	
Ref Material	This Work	Lit.	This Work	Lit.
Seawater	1.49 ± 0.03 µg/L	1.6 ± 0.19[a] µg/L	0.28 ± 0.02 µg/L	(0.20 ± 0.02)- (0.24 ± 0.02)[d] µg/L
Orchard Leaves (SRM-1571)	8.84 ± 0.11 µg/g	10 ± 2[b] µg/g	3.04 ± 0.09 µg/g	2.9 ± 0.3[b] µg/g
Coal Fly Ash (SRM-1633a)	139 ± 3 µg/g	145 ± 15[b] µg/g	7.5 ± 1.2 µg/g	7 µg/g[c]

[a] Certified value, Marine Analytical Chemistry Standards Program, National Research Council of Canada. [b] Certified value, U. S. National Bureau of Standards. [c] NBS reference value, not certified. [d] From four independent analytical techniques: APCDT-AA (10), electrochemical ASV-HMDE (11), activated charcoal-NAA (12), hydride generation-AA (13).

The accuracy of this extraction method for speciation of Sb(III) and Sb(V) could not be thoroughly evaluated because no standard waters containing known amounts of these two Sb species are available. Deionized water samples spiked with known amounts of Sb(III) and Sb(V) showed satisfactory recoveries of both species as given in Table 7. The results of simultaneous determination of trivalent and pentavalent antimony and arsenic in 100-mL water samples spiked with known amounts of the Sb and As species are presented in Table 8. Satisfactory recoveries of both Sb and As species were also observed. In a previous study, spiked As(III) in a coastal seawater sample was found partially converted to As(V), presumably due to the presence of oxidating species in the natural water system.[8] Other reports also noted that conversion of spiked arsenite to arsenate could take place at low As concentrations.[14,15] For this reason, relatively pure water was used in this study to test the recovery of As and Sb species by the proposed PCDT extraction method.

Table 7. Recovery of Spiked Sb(III) and Sb(V)

amt added, ng		% recovery		
Sb(III)	Sb(V)	Sb(III)	Sb(V)	total Sb
200		101.3 ± 4.2		
400		109.0 ± 2.8		
800		94.6 ± 3.8		
	200		102.0 ± 4.4	
	400		97.0 ± 2.6	
	800		101.6 ± 1.8	
70	400			100.0 ± 7.4
140	800			97.0 ± 3.9

The method presented appears to be suitable for analysis of nanogram to picogram per milliliter levels of Sb and As species in environmental water samples. The determination of Sb and As species in surface seawater and river water samples is shown in Table 9. These values are comparable to those reported in the literature for open ocean water and for river waters.[4,5,16] For surface waters, either from the sea or from the river, Sb(V) and As(V) are known to be the predominant species under the condition of thermodynamic equilibrium. The finding that very low As(III) is present in natural water samples examined agrees well with the statement of Braman and Foreback that arsenate is probably the most common environmental form of inorganic arsenic.[17] However, under a reducing environment, As(III) was found as the major species in ground waters.[8] As shown in Table 9, significant amounts of As(III) are also found in the waters collected from the Coeur d'Alene River in northern Idaho. The river has a serious heavy metal pollution problem caused primarily by the lead, zinc, and silver mining activities in this area.[18,19] The conversion of As(III) to As(V) in water exposed to air is slow in the absence of a catalyst or other oxidizing agent.[3] One possible explanation for the relatively low As(III)/As(V) ratio observed in the Coeur d'Alene River may be due to the lack of biological activities which are probably needed to catalyze the conversion.[20,21]

The ratio of Sb(III)/Sb(V) in most natural water systems was reported to be on the order of 10^{-2}.[22] Competing

Table 8. Recovery of Spiked Sb(III), Sb(V), As(III), and As(V)

ng Added				% Recovery			
Sb(III)	Sb(V)	As(III)	As(V)	Sb(III)	Total Sb	As(III)	Total As
100	100	100	100	89.7 ± 5.9	95.2 ± 3.7	107.8 ± 5.3	108.5 ± 3.2
200	200	200	200	100.2 ± 3.9	98.6 ± 2.8	111.7 ± 3.4	99.0 ± 2.3
300	300	300	300	100.8 ± 3.2	105.4 ± 2.6	104.8 ± 2.8	105.9 ± 2.1

Table 9. Sb and As Concentrations in Seawater and River Waters[a]

Sample Location	Sb(III)	Sb(V)	As(III)	As(V)
Seawater, Bainbridge Island, WA	0.005 ± 0.003	0.24 ± 0.04	0.010 ± 0.005	1.36 ± 0.04
Snake River, Lewiston, ID	0.005 ± 0.003	0.19 ± 0.03	0.02 ± 0.01	1.36 ± 0.36
Coeur d'Alene River, Cataldo, ID	0.044 ± 0.005	1.89 ± 0.07	0.33 ± 0.04	0.34 ± 0.06
Coeur d'Alene River, Kellogg, ID	0.030 ± 0.008	7.03 ± 0.13	0.19 ± 0.04	0.48 ± 0.06

[a] Concentrations expressed in ng/mL.

processes that modify the concentrations of the arsenic species in natural waters, as described in the literature, may also apply to antimony which enters the aquatic environment as a result of the weathering of rocks (which contain an average of 0.16 ppm Sb), from soil runoff, through effluents from mining and manufacturing, and from municipal discharge. Sensitive and reliable methods of measuring antimony species in water are needed for speciation studies. This extraction method provides a large preconcentration factor which is necessary for the determination of low levels of Sb(III) species in water. The proposed analytical method has currently been used to investigate arsenic and antimony species in some groundwater systems in the Coeur d'Alene Mining District in order to obtain a better understanding of the distribution of these species in aquatic environments. The extraction method described in this paper is not limited to NAA. It can be combined with other instrumental techniques such as graphite furnace atomic absorption spectrometry (GFAAS) for arsenic and antimony speciation studies in natural water systems.

Acknowledgments - This work was supported in part by the Idaho Water Resources Research Institute with funding from the U.S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by the Department of Energy.

REFERENCES

1. Arsenic - Medical and Biological Effects of Environmental Pollutants; National Academy of Sciences: Washington, D. C., 1977.

2. Fowler, B. A.; Goyer, R. A.; Mehlman, M. A. Advances in Modern Toxicology; Wiley: New York, 1977; Vol. 2, p. 79.

3. Cherry, J. A.; Shaikh, A. U.; Tallman, D. E.; Nicholson, R. V. J. Hydrol. (Amsterdam) **1979**, 43, 373.

4. Wedepohl, K. H. Handbook of Geochemistry; Springer Verlag: New York, 1978; Vol. II/3, Chapter 33.

5. Wedepohl, K. H. Handbook of Geochemistry; Springer Verlag: New York, 1978; Vol. II/4, Chapter 51.

6. Orvini, E.; Gallorini, M. J. Radioanal. Chem. **1982**, 71, 75.

7. Gohda, S. Bull. Chem. Soc. Jpn. **1975**, 48, 1213.

8. Mok, W. M.; Shah, N. K.; Wai, C. M. Anal. Chem. **1986**, 58, 110.

9. Mok, W. M.; Wai, C. M. Anal. Chem. **1984**, 56, 2623.

10. Sturgeon, R. E.; Willie, S. N.; Berman, S. S. Anal. Chem. **1985**, 57, 6.

11. Whang, C. H. Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1983.

12. Van der Sloot, H. A. Chem. Weekbl. Mag. **1979**, May, 297.

13. Sturgeon, R. E.; Willie, S. N.; Berman, S. S. Anal. Chem. **1985**, 57, 2311.

14. Johnson, D. L.; Pilson, M. E. Anal. Chim. Acta **1972**, 58, 289.

15. Johnson, D. L.; Pilson, M. E. Environ. Lett. **1975**, 8, 157.

16. Martin, J. M.; Whitfield, M.; Wong, C. S.; Boyle, E.; Bruland, K. W.; Burton, J. D.; Goldberg, E. D. Trace Metal in Sea Water; Plenum: New York and London, 1983.

17. Braman, R. S.; Foreback, C. C. Science (Washington, D. C., 1883-) **1973**, 182, 1247.

18. Reece, D. E.; Felkey, J. R.; Wai, C. M. Environ. Geol. (NY) **1978**, 2, 289.

19. Davis, H. T. Environ. Sci. Technol. **1978**, 12, 276.

20. Johnson, D. L. Nature (London) **1972**, 240, 44.

21. Osborne, F. H.; Ehrlick, H. L. J. Appl. Bacteriol. **1976**, 41, 295.

22. Andreae, M. O.; Asmode, J. F.; Foster, P.; Van't dack, L. Anal. Chem. **1981**, 53, 1766.

CHAPTER VI

The following manuscript entitled

DETERMINATION OF ARSENIC AND ANTIMONY IN BIOLOGICAL MATERIALS BY SOLVENT EXTRACTION AND NEUTRON ACTIVATION

by

W. M. Mok and C. M. Wai

has appeared in

Talanta, 35, 183 (1988)

ABSTRACT

Arsenic and antimony in digested biological samples can be extracted with pyrrolidinecarbodithioate at pH 1 into chloroform and stripped with nitric acid for neutron-activation analysis (NAA). The extraction method eliminates interferences from matrix species, including Br and Na, making the accurate determination of low levels of As and Sb in biological materials feasible. The detection limits under the experimental conditions used are 0.005 and 0.006 μg/g for arsenic and antimony, respectively. A comparison of the results obtained for As and Sb in NBS biological standards by this method and by non-destructive instrumental neutron-activation analysis (INAA) is also given.

The determination of trace quantities of arsenic and antimony in the environment is of considerable importance because of toxicological concern.[1-4] Accurate determination of low levels of As and Sb in biological samples can be accomplished only by techniques that are very sensitive and selective. Neutron-activation analysis (NAA) usually meets these requirements. Under interference-free conditions, the sensitivity of NAA for As and Sb is of the order of several nanograms. However, the applicability of non-destructive instrumental neutron-activation analysis (INAA) to biological samples is often limited by spectral interferences from matrix elements, including Na, K, P, and Br. The detection limits of As and Sb by INAA in biological systems may be raised to a level higher than that required for analyzing small samples. In general, INAA can determine As down to about 2 μg/g in most biological materials, assuming a sample weight of 1 g, an irradiation time of 1 hr and a counting time of 10 min.[5] Many biological materials contain less than 2 μg/g As and the concentrations of Sb in these materials are generally even lower. Therefore, in biological materials with low levels of As and Sb, chemical separation, either before or after irradiation, is necessary in order to achieve maximum sensitivity and accuracy for the determination of these two elements by NAA.

Preconcentration of trace metals by solvent extraction prior to neutron irradiation has been applied to natural waters and biological materials in our laboratory.[6-9] Chemical separation before irradiation has the advantages of giving a larger concentration factor for trace elements, allowing sufficient time for laboratory operation, and minimizing exposure of the analysts to radiation. This paper describes such a procedure for the separation of As and Sb from biological materials. The As and Sb concentrations in a number of NBS biological standards have been determined and compared with those from direct INAA. Conditions under which chemical separation for NAA becomes mandatory for accurate determination of these trace elements are discussed.

EXPERIMENTAL

Reagents and Instruments. The concentrated nitric and sulfuric acids used in the sample digestion were Baker Ultrex Reagent grade. Chloroform used in the extraction was EM Science Omnisolv grade. All other chemicals were Baker Analytical grade. Distilled demineralized water was used for making all solutions. All glassware was cleaned by soaking in 10% v/v nitric acid for at least 24 hr, rinsed with demineralized water and dried in a class-100 clean hood equipped with a vertical laminar flow filter (CCI).

Standard As and Sb solutions (1000 mg/L) were prepared by dissolving As_2O_3 and Sb_2O_3, respectively, according to the procedures given earlier.[9] Ammonium pyrrolidinecarbodithioate (APCDT) solution was prepared by dissolving 7.5 g of reagent in 100 mL of demineralized water, filtering, and then extracting with chloroform for purification. Disodium ethylenediaminetetra-acetate (EDTA) solution was prepared by dissolving 12.5 g in 100 mL of demineralized water.

All samples and standards were normally irradiated for 2 hr in a 1-MW TRIGA reactor at a steady neutron flux of 6×10^{12} $n.cm^{-2}.sec^{-1}$ followed by one day of cooling. A large-volume coaxial ORTEC Ge(Li) detector with a resolution of about 2.3 keV at the 1332 keV γ-ray of ^{60}Co was used for activity measurements. The detector output was fed into an EG&G ORTEC ADCAM (model 918) multichannel analyzer. The data from the analyzer were processed by EG&G ORTEC software on an IBM-PC.

Sample Digestion and Extraction Procedure. The biological sample was digested in a round-bottomed flask fitted with a reflux reservoir and condenser as described by Mok *et al.*[8] Usually 1.0-2.0 g of material was placed in a 50-mL round-bottomed flask and a few glass beads were added. A mixture of concentrated nitric and sulfuric acids (5:4 v/v) was added to cover the sample, and the mixture was left overnight. The digestion started with gentle heating on a heating mantle until foaming ceased. The heat was then increased, and small amounts of the condensed nitric acid were admitted from the condenser whenever a slight darkening of the digest occurred. This operation was repeated until no darkening was observed and white fumes were evolved, after which heating was continued for another 5 min and the apparatus then allowed to cool. The sample solution was diluted with 10 mL of water and boiled for another 5 min. The solution was then transferred into a 100-mL standard flask and the apparatus rinsed. The rinsing solution was added to the flask and the solution made up to volume with demineralized water.

A 30-mL aliquot of the digest solution was transferred into a 125-mL polyethylene bottle, diluted to about 100 mL and adjusted to pH 1. One mL of 25% sodium thiosulfate solution and 1 mL of 20% potassium iodide solution were added to reduce quinquevalent As and Sb to their tervalent states. After a waiting period of 15-30 min, 4 mL of EDTA solution, 10 mL of chloroform and 2 mL of APCDT solution were added. The mixture was shaken vigorously for 10 min on a wrist-action mechanical shaker and the phases were allowed to separate. To strip As and Sb, 8 mL of the organic phase were transferred to a 20-mL Beckman polyvial and 2 mL of 50% v/v nitric acid were added. The vial was shaken vigorously for 10 min. After phase separation 1.5 mL of the acid were taken for neutron irradiation. A complete blank was run in the same manner as the samples in each set of experiments. The sample sealing, irradiation and transfer procedures have been described elsewhere.[8,9] Each sample was usually counted for 2000-4000 sec. When the As content in a sample was much higher than that of Sb, the sample was normally recounted after 2-3 days. Appropriate quantities of standards were prepared to cover the expected ranges of As and Sb in the samples. This series of As and Sb standards was analyzed by the procedure above and calibration curves were prepared. The elements were determined by comparing the net photopeak areas with those of the standards.

For INAA, about 100-200 mg of material was irradiated for each sample. Irradiation of more than 200 mg of biological materials per sample often resulted in high levels of radiation from matrix species, making the sample difficult to handle experimentally. Each activated sample was usually counted twice, 2-3 days and 5-6 days after the end of irradiation.

RESULTS AND DISCUSSION

Spectral Interferences. The nuclear data and major interferences for determination of As and Sb by NAA are given in Table 10. The gamma peaks which provide the greatest sensitivity are at 564.1 keV for ^{122}Sb ($t_{1/2}$ = 67.2 hr) and 559.1 keV for ^{76}As ($t_{1/2}$ = 26.4 hr). A major interference for ^{122}Sb and ^{76}As is from the 554.3 keV peak from the decay of ^{82}Br ($t_{1/2}$ = 35.3 hr). The Ge(Li) detector, which has a resolution of about 2.3 keV (FWHM), is capable of resolving these three peaks. However, when the concentration of Br in a sample is high, the greater background and the tailing of the 554.3 keV peak may affect the measurements of ^{76}As and ^{122}Sb. This is illustrated in Fig. 3 which shows the gamma spectra in the region of interest for NBS-SRM-1573 (Tomato Leaves) obtained from INAA and from CNAA by the separation procedure described. The Br concentration in SRM-1573 is 26 μg/g, which is apparently high enough to raise the background, causing a serious problem for Sb and As determination by INAA (Fig. 3b). Another prominent feature of the spectrum is the high background radiation caused primarily by the presence of high

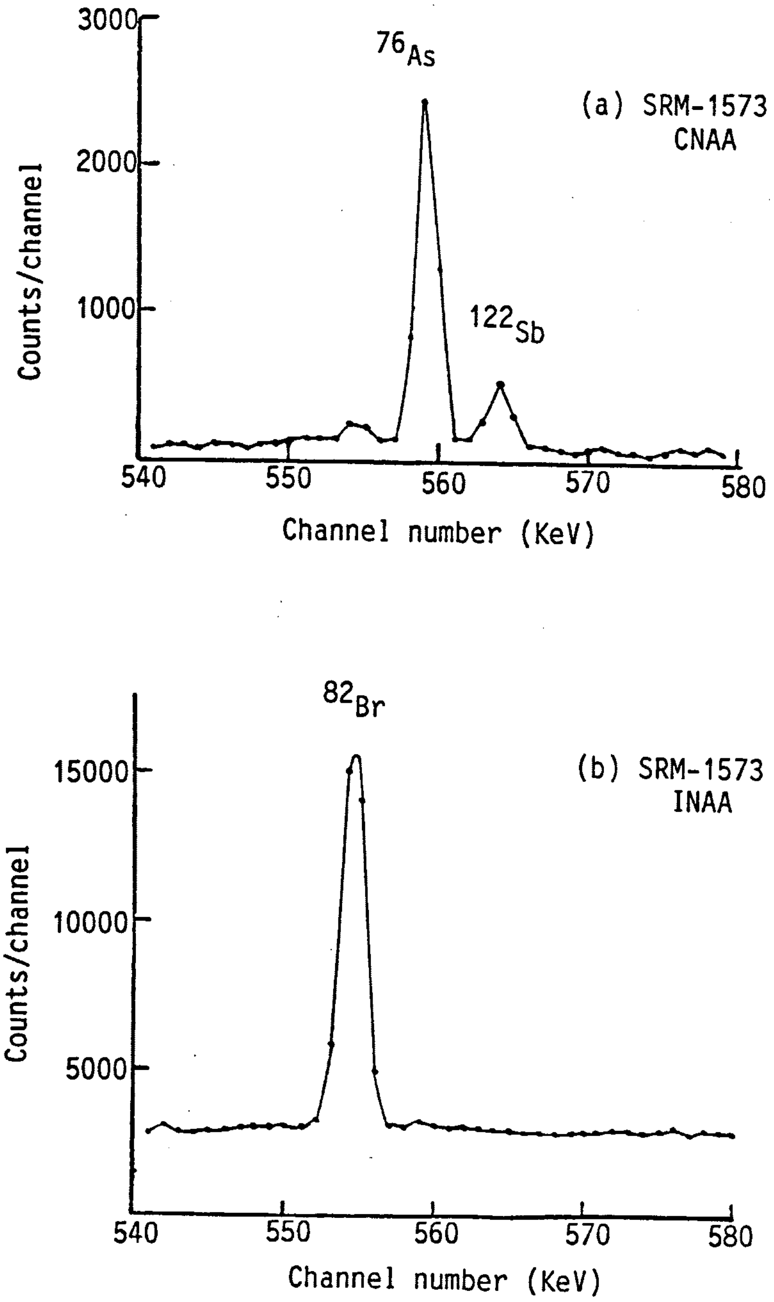

Figure 3. Gamma-spectra of NBS SRM-1573 (Tomato Leaves) in the energy range 540-580 keV. (a) CNAA with PCDT extraction, starting material 2 g. (b) INAA, starting material 0.1 g.

levels of ^{24}Na, ^{42}K, and ^{32}P in the system. This high background radiation would also raise the detection limits of As and Sb significantly. The APCDT extraction procedure effectively removes the alkali metal ions, halides and phosphorus species from the system. As shown in Fig. 3a, the ^{82}Br peak in SRM-1573 after the extraction was barely detectable and the background radiation was significantly reduced. The 559.1 keV peak of ^{76}As and the 564.1 keV peak of ^{122}Sb are well resolved in Fig. 3a, and the detection limits of As and Sb approach those expected under interference-free conditions. With a sample weight of 2 g, under the experimental conditions described in this paper, the detection limits of As and Sb, calculated as the amounts equivalent to 3 times the standard deviation of the background under the appropriate photopeaks, are 0.005 and 0.006 μg/g, respectively. The detection limits can be further lowered by increasing the sample weight, the irradiation time and the counting time.

Table 10. Nuclear Data for Neutron Activation of As and Sb, and Major Spectral Interferences

Nuclide	Abundance of parent %	Cross section, *Barns*	Half-life of daughter	Major gamma peak, *keV*
^{76}As	100	4.5	26.4 hr	559.1
^{122}Sb	57.3	6	67.2 hr	564.1
^{24}Na	100	0.53	15.0 hr	1368.5
^{42}K	6.8	1.2	12.4 hr	1524.6
^{82}Br	49.5	3	35.3 hr	554.3
^{32}P	100	0.18	14.28 d	bremsstrahlung

Generally speaking, As concentrations in biological materials are several times higher than those for Sb. If the ratio of As/Sb in a sample is large, then a minor peak of ^{76}As at 562.8 keV (2.7% relative to the 559.1 keV major peak) may cause appreciable interference with the 564.1 keV peak of ^{122}Sb. In general, a correction should be applied to the ^{122}Sb peak by using the intensity ratios of the As peaks at 559.1 and 562.8 keV. The interference of ^{76}As with ^{122}Sb can be minimized by recounting after allowing the former to decay. Since the half-life of ^{122}Sb is about 2.5 times that of ^{76}As, we normally recounted samples with high As/Sb ratios 3-4 days after the first counting, to obtain more reliable ^{122}Sb data.

INAA vs. CNAA for As and Sb Determination in Biological Samples. The concentrations of As and Sb in four NBS standard biological reference materials, determined by INAA and by CNAA with the proposed separation method, are given in Table 11. The bromine contents of these standard reference materials vary from 9 μg/g in SRM-1575 (Pine Needles) to 26 μg/g in SRM-1573 (Tomato Leaves). In samples with high As and Sb contents, such as SRM-1571, or with low bromine content as in SRM-1575, the As and Sb values obtained by INAA are in good agreement with the values given by NBS. In samples with high bromine and low As and Sb contents, as in SRM-1573, INAA failed to provide meaningful As and Sb values. In order to determine low levels of As and Sb in biological materials by NAA, chemical separation appears necessary. The As and Sb values in the four standard reference materials determined by

Table 11. Determination of As and Sb in some NBS standard reference materials by INAA and by the proposed CNAA

Reference material	As, μg/g			Sb, μg/g		
	CNAA	INAA	NBS value	CNAA	INAA	NBS value
Orchard Leaves 1571	8.84 ± 0.11	10.8 ± 0.2	10 ± 2	3.04 ± 0.10	2.83 ± 0.04	(2.9)[*]
Pine Needles 1575	0.24 ± 0.01	0.22 ± 0.01	0.21 ± 0.04	0.19 ± 0.01	0.20 ± 0.01	(0.2)
Citrus Leaves 1572	2.89 ± 0.03	3.07 ± 0.02	3.1 ± 0.3	0.068 ± 0.003	N.D.	(0.04)
Tomato Leaves 1573	0.25 ± 0.01	N.D.	0.27 ± 0.05	0.047 ± 0.003	N.D.	no values given

[*] Values in parentheses are not certified, but are given for reference by NBS.
All values are based on triplicate analyses.
N.D., not detected.

the APCDT separation and NAA are in good agreement with the values given by NBS (Table 11). Antimony is generally more difficult to determine than arsenic because of its low concentrations in biological systems. In the case of SRM-1572 (Citrus Leaves), the As/Sb ratio approaches 44 and Sb can be determined accurately only by CNAA. It should be pointed out that the NBS Sb values quoted are not certified values, but values for reference only. The Sb concentration in SRM-1573 (Tomato Leaves) has not been reported before in the literature.

This CNAA method has been applied to the analysis of sagebrush samples collected from Idaho Falls (Table 12). The As and Sb levels in these samples are low, comparable to those found in SRM-1573 (Tomato Leaves). Without pre-irradiation separation, As and Sb in sagebrush are hardly detectable by INAA. With the APCDT extraction method, well resolved ^{76}As and ^{122}Sb peaks with low background radiation were observed for these samples. The concentrations of Sb in the sagebrush samples were determined by CNAA to be in the range 41-49 ng/g.

Table 12. As and Sb in Three Sagebrush Samples, Determined by the Proposed CNAA Method*

Sample	As, μg/g	Sb, μg/g
1	0.156 ± 0.003	0.041 ± 0.003
2	0.188 ± 0.003	0.049 ± 0.002
3	0.160 ± 0.002	0.041 ± 0.002

* All values are based on triplicate analyses.
Samples were collected from Idaho Falls, Idaho, in Nov. 1986.

CONCLUSION

The APCDT extraction procedure eliminates matrix interferences and concentrates As and Sb from plant digests for NAA. The detection limits for As and Sb in biological materials are estimated to be 0.005 and 0.006 μg/g, respectively. The proposed CNAA technique proves to be a sensitive and reliable method for the accurate determination of low levels of As and Sb in biological samples, as demonstrated by the results obtained from NBS standards.

Acknowledgments. This work was supported in part by a grant from the Westinghouse Idaho Nuclear Company, Inc. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by the Department of Energy.

REFERENCES

1. Harrington, J. M.; Middaugh, J. P.; Morse, D. L.; Houseworth, J. Am. J. Epidemiol. **1978**, 108, 377.
2. Hernbery, S. in Origins of Human Cancer, H. H. Hiatt (ed.), Vol. 4, pp. 147-157. Cold Spring Harbour Laboratories, New York, 1977.
3. Rail, C. D.; Hadley, W. M. J. Environ. Health **1976**, 39, 173.
4. Luckey, T. D.; Venugopal, B. Metal Toxicity in Mammals, Vol. 1, p. 139. Plenum Press: New York, 1977.
5. Brooks, R. R.; Ryan, D. E.; Zhang, H. Anal. Chim. Acta **1981**, 131, 1.
6. Mok, W. M.; Wai, C. M. Anal. Chem. **1984**, 56, 27.
7. Yu, J. C.; Wai, C. M. ibid. **1984**, 56, 1689.
8. Mok, W. M.; Willmes, H.; Wai, C. M. ibid. **1984**, 56, 2623.
9. Mok, W. M.; Wai, C. M. ibid. **1987**, 59, 233.

CHAPTER VII

The following manuscript entitled

ARSENIC SPECIATION AND QUALITY OF GROUNDWATER IN A LEAD-ZINC MINE, IDAHO

by

W. M. Mok, J. A. Riley, and C. M. Wai

has been accepted for publication in

Water Research

ABSTRACT

The variations of As(V)/As(III) ratio, with respect to metal contents and pH in groundwater of a major lead-zinc mine in the Coeur d'Alene Mining District, Idaho were studied. A wide range of arsenic concentrations and As(V)/As(III) ratios were observed in the groundwaters collected from this mine. Samples with high As(V)/As(III) ratios were generally acidic ($pH<3$) and contained elevated metal levels. Seasonal variations of the arsenic species ratio were found to correlate positively with metal contents in water and were attributed to changing in redox environments and leaching of metals by groundwaters. Arsenic is less soluble in mine waters with $pH>3$, and its chemical behavior appears to be controlled by iron hydroxide precipitate. In comparison with Eh measurement by a platinum electrode, the As(V)/As(III) ratio seems to be a more sensitive indicator for evaluating redox status of a groundwater system. Arsenic species in surface waters collected from the Coeur d'Alene River were also measured for comparison.

INTRODUCTION

Arsenic in natural waters occurs in the oxidation states As(III) and As(V). The ratio of the two oxidation states may be used as an indicator of redox status of a groundwater system.[1] Redox potential is an important factor affecting the chemistry of mine wastes and related water quality problems. For example, serious heavy metal pollution of groundwater and surface water has been reported to be associated with the mine wastes of the Coeur d'Alene Mining District in northern Idaho.[2,3] Mine wastes in this area generally contain sulfide minerals including pyrite (FeS_2) and arsenopyrite (FeAsS) which are often present with galena (PbS), sphalerite (ZnS), and tetrahedrite ($(Cu,Fe,Zn,Ag)_{12}Sb_4S_3$) in the ore bodies. It is known that mine wastes containing pyrite are capable of producing acid water under oxidizing conditions.[4] Subsequent leaching of the wastes by acid water generally results in poor quality water.

We have recently studied the distribution of arsenic species in the groundwater of a major lead-zinc mine in the Coeur d'Alene Mining District. Variations of As(V)/As(III) ratio with respect to metal contents and pH in groundwaters from several locations of the mine were monitored over a period of several months. Some data regarding the distribution of arsenic species in surface water of the Coeur d'Alene River are also given. The potential of using the arsenic redox pair as an indicator of water pollution problems associated with mine wastes in groundwater flow systems is discussed.

EXPERIMENTAL

1. Study Area. Water samples were collected underground at the Bunker Hill Mine near Kellogg, Idaho, and from the Coeur d'Alene River. The mine is about one mile deep with more than 150 miles of underground workings in a highly faulted block of massive quartzites, argillites and argillaceous quartzites. The mine currently is not in production, but is being maintained in operational condition. The monitoring sites chosen for this study were in the "upper country" of the mine on the 5 and 9 levels. The portal to the 5 level is the Reed Tunnel, and the portal to the 9 level is the Kellogg Tunnel (Figure 4). These two levels are the only workings in the upper country which allow routine access. Figure 5 presents a schematic diagram of the underground flow and site relationships in the upper country of the mine. The "upper country" consists of the workings from 9 level to the surface in the eastern part of the mine, which underlies Milo Creek. This part of the mine is very important with respect to water quality because a major proportion of the metal load discharging through the Kellogg Tunnel originates in this part of the mine. Water samples were collected from May 1 to July 30 of 1985.

Surface water samples were also collected from the Coeur d'Alene River in order to evaluate the As concentration and the distribution of As species in the river. The source of

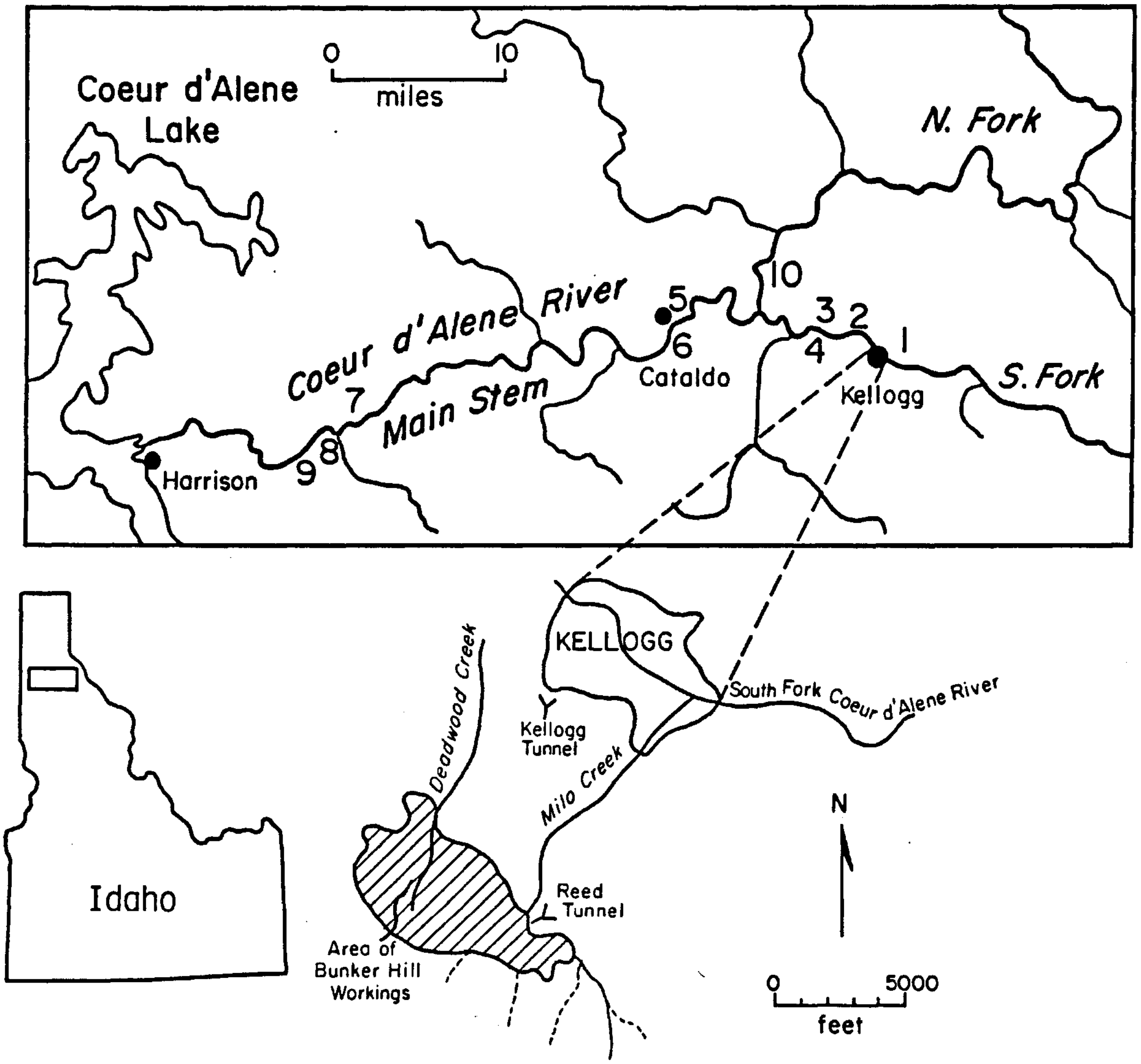

Figure 4. Location of Bunker Hill Mine and sample collecting sites along the Coeur d'Alene River.

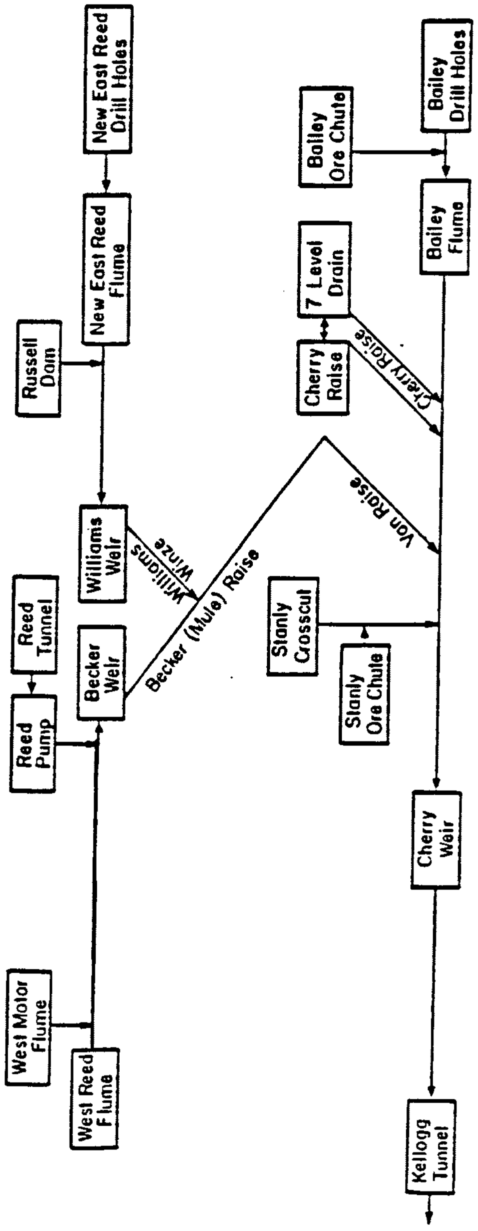

Figure 5. Schematic diagram of the underground flow and site relationships in the upper country of the Bunker Hill Mine.

the As in the river is from the mine tailings which had been deposited during mining operations from 1886 until approximately 1965. The mine water no longer carries any heavy metals into the river. Ten sampling sites were chosen: four along the South Fork, one on the North Fork, and five along the Main Stem after the confluence of the North and South Forks (Figure 4). The South Fork is heavily impacted by the historical tailings disposal practices. The North Fork is virtually free from any negative impacts from mining. The Main Stem is impacted only to a limited degree because the majority of flow originates in the North Fork.

2. Sample Collection And Analysis. Water samples were collected from the mine and from the river using 1 L polyethylene bottles. After collection, water samples were filtered through 0.45 μm membranes, acidified to pH 2 with HCl, and stored in a refrigerator at about 4 °C until analyzed. At pH between 2 and 10.5, the As(V)/As(III) ratio in water samples remains relatively constant for up to three weeks without appreciable loss of As from solution.[1] All our samples were analyzed for total dissolved inorganic arsenic and As(III) within a few days after sampling. The analytical procedures for determining As(V) and As(III) in water are given in the literature.[5] Basically, the method involves extraction of As(III) with ammonium pyrrolidinecarbodithioate (APCDT) at pH around 1-1.5 into chloroform followed by a nitric acid back-extraction to recover the metal for neutron activation analysis. Extraction of As(V) is achieved by

reduction with thiosulfate at pH 1 to As(III) followed by APCDT extraction described above. The difference in two aliquots with and without reduction gives the concentration of As(V). This extraction method not only concentrates arsenic species but also eliminates common interfering ions such as the alkali metals, alkaline earth metals, halogens, and phosphate. The extraction may be interferred by those metal ions which react with PCDT. These interferences can be substantially reduced by the use of ethylenediaminetetraacetic acid (disodium salt)[6] and by the two-step extraction method we proposed.[5] The applicability of this method to very complex matrices having different chemical compositions has been demonstrated in our recent publication.[7] Using this extraction method and neutron activation analysis, the detection limit of arsenic in water is about 0.01 ppb for a 100 mL sample. Other metal ions including Cd, Cu, Fe, Mn, and Zn were determined by atomic absorption spectrometry (AAS) or by inductively coupled plasma - atomic emission spectrometry (ICP-AES).

RESULTS AND DISCUSSION

Variations of As(V)/As(III) ratio, total arsenic, cadmium, copper, iron, manganese, and zinc in groundwaters collected from eight locations on 5 and 9 levels of Bunker Hill Mine during the sampling period are summarized in Table 13. The hydrology of the Bunker Hill Mine is complex and remains only partially understood. Based on the information available from a recent study,[8] the sources of water at some

Table 13. Summary of arsenic and other metals in the groundwaters on 5 level and on 9 level of the Bunker Hill Mine.

		ppb			ppm				
Sampling Locations	pH	As(III)+ As(V)	As(III)	As(V)/ As(III)	Zn	Fe	Mn	Cd	Cu
1. CW*	2.7-2.8	143.9-1336.1	15.9-42.3	8.1-30.6	352.9-660.3	284.6-678.9	73.9-95.3	0.82-1.48	0.86-1.88
2. BW**	2.9-3.0	106.7-463.7	15.5-35.3	6.0-12.1	294.5-646.8	364.7-811.0	53.0-77.7	0.48-1.56	0.17-0.69
3. KT*	2.7-2.9	2.7-47.7	1.0-3.8	1.7-11.6	102.6-151.8	47.1-102.0	42.5-73.8	0.18-0.37	0.25-0.47
4. NERF**	5.8-6.4	1.9-3.3	1.2-2.6	0.3-0.6	<0.1	0.6-1.0	0.4-0.7	<0.01	<0.02
5. RTF**	5.4-5.8	0.1-0.5	0.1-0.2	<0.1	1.3-2.1	<0.1	0.2-0.6	<0.01	<0.02
6. RPB**	5.3-5.7	0.1-0.2	0.1-0.2	0.1-0.5	1.2-1.9	<0.2	0.2-0.5	<0.01	<0.02
7. BOC*	3.6-3.9	3.3-8.5	1.8-6.1	0.1-1.7	0.2-0.6	7.1-8.2	0.9-1.1	<0.02	<0.02
8. WW**	3.5-3.8	1.5-6.5	0.5-6.3	<0.5	25.6-66.1	7.0-16.4	7.0-14.2	0.02-0.20	<0.03

*: at 9 level; **: at 5 level; CW: Cherry Weir; BW: Becker Weir; KT: Kellogg Tunnel; NERF: New East Reed Flume; RTF: Reed Tunnel Flume; RPB: Reed Pump Back; BOC: Bailey Ore Chute; WW: Williams Weir

sampling locations are known. For example, sample location Cherry Weir (CW) represents the total gravity drainage of the eastern portion of the mine above 9 level, including poor quality waters from abandoned workings near the surface. Sample location Kellogg Tunnel (KT) represents the total mine discharge. The discharge is treated and released to the South Fork of the Coeur d'Alene River after meeting EPA standards. Descriptions of other locations are given in the text with the discussion of water quality data.

Data given in Table 13 reveal some interesting aspects regarding the distribution of arsenic species in groundwater of the Bunker Hill Mine and its relations to water quality in general. First, the As(V)/As(III) ratios in the water samples showed a wide range from a low value of 0.1 to a high value of about 30. Second, water samples with high As(V)/As(III) ratios were acidic ($pH<3$) and had higher metal contents. Third, examination of the data showed that the As(V)/As(III) ratio in mine water samples varied significantly with time at certain locations.

Figure 6 shows the variations of As(V)/As(III) ratio, iron, zinc and total arsenic in water samples collected from Cherry Weir from May 1 to July 30, 1985. Similar trends were also observed in Becker Weir (BW) and Kellogg Tunnel (KT). In the late spring, the ratio of As(V)/As(III) in Cherry Weir water was as high as 30.6 and the concentrations of Fe, Zn, and total As reached at their maximum values of about 678.9 ppm, 660.3 ppm, and 1336.1 ppb, respectively. In the late

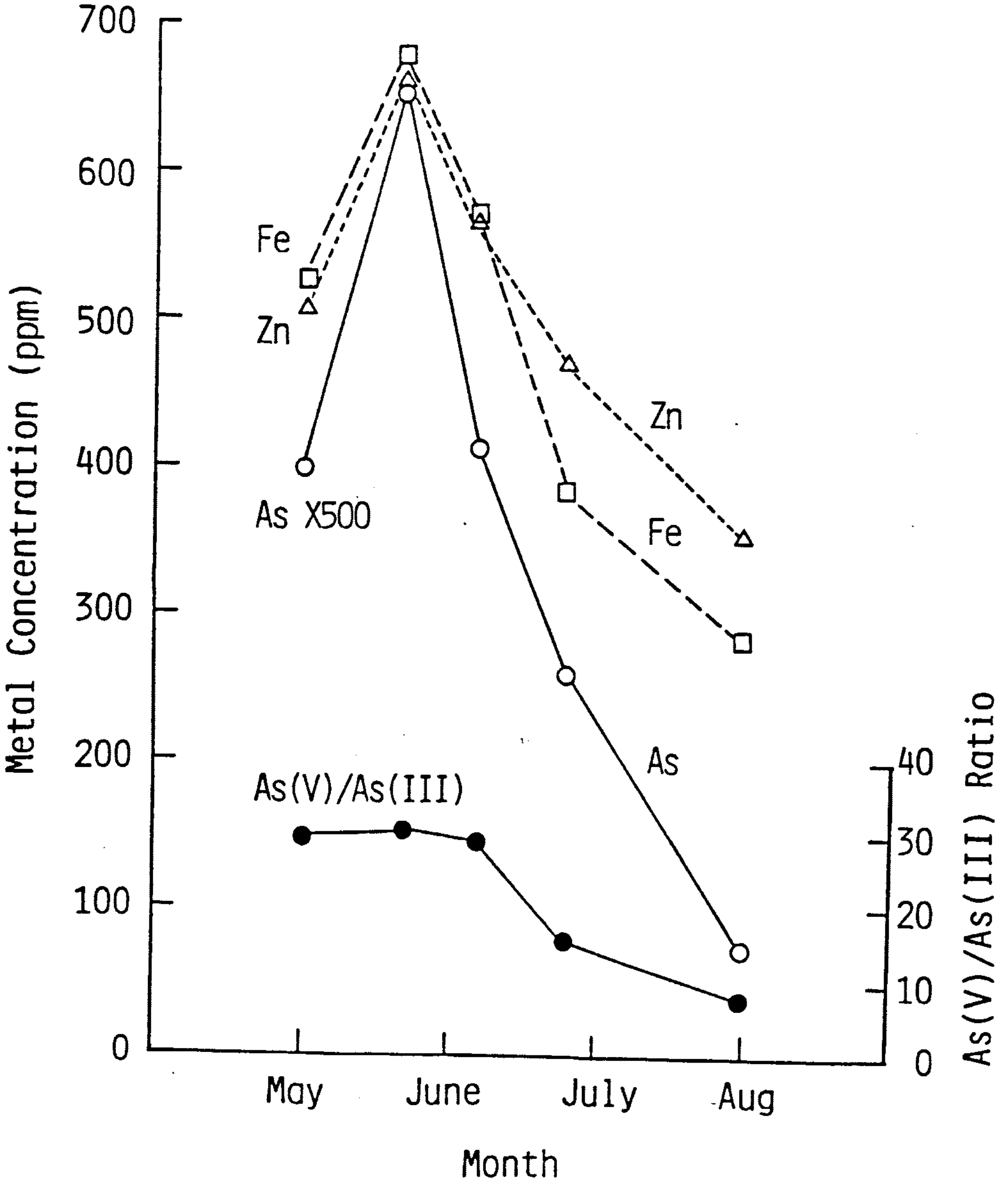

Figure 6. The variations of As(V)/As(III) ratio and the concentrations of total arsenic, zinc, and iron of the water collected from May 1 to July 30 of 1985 in Cherry Weir.

summer, the ratio of As(V)/As(III) dropped to about 8.1, and the lower As(V)/As(III) ratio is associated with significantly lower levels of Fe, Zn, and total As at 284.6 ppm, 352.9 ppm, and 143.9 ppb, respectively. The variations in As, Zn, and Fe levels are consistent with the discharge pattern measured by Riley,[8] reflecting a flushing mechanism operating at the Cherry Weir site. The high ratio of As(V)/As(III) found in Cherry Weir water during the spring runoff was presumably caused by leaching of acid reaction products from oxidized ores and mine wastes in certain locations of the upper part of the mine. The overall process for the oxidation of arsenopyrite may be written as:

$$4FeAsS + 13O_2 + 6H_2O = 4FeSO_4 + 4H_3AsO_4 \qquad (1)$$

Under highly acidic conditions, arsenic in this form is quite mobile. Poor quality water from a pyrite-rich ore body in the upper part of the mine is known to be related to the Cherry Weir system. Formation of acid water in the Bunker Hill Mine was discussed previously by Wai et al.[2] Oxidation of pyrite is known to be a major mechanism of acid water formation in this mine. Ferrous sulfate produced in Reaction (1) is not likely to be a major source of dissolved iron in the mine water. The fate of ferrous ions and the subsequent precipitation of ferric hydroxide are discussed in the literature.[4,2]

During spring runoff, the CW is flushed. The rather stagnant pool of water is mixed with the bad quality water from the pyrite-rich ore body, resulting in increased As, Fe, and Zn concentrations and higher As(V)/As(III) ratio. In the late summer, the mine becomes less aerobic after being flushed with "fresh" water over a period of time. This results in a lower As(V)/As(III) ratio and reduced metal concentrations in the groundwater. The dissolved O_2 of surface water in the Coeur d'Alene River also showed a seasonal variation. Data from EPA Storet System reveals that the dissolved O_2 in the surface water is higher in winter and in spring. On the average, the dissolved O_2 in winter (Nov.-Feb.) is 2.5 ppm higher than in summer (June-Aug.), while the dissolved O_2 in late spring (Apr.-May) is 1.1 ppm higher than in summer. The average dissolved O_2 throughout a year is about 10.8 ppm.

Two other locations, Kellogg Tunnel (KT) and Becker Weir (BW), also showed low pH values (<3) with high As(V)/As(III) ratios and higher metal content. Water from BW was a mixture of groundwaters from fractures, ore chutes, stopes, and rock bolt holes. The As(V)/As(III) ratios in BW and KT waters varied from 12.1 to 6.0 and from 11.6 to 1.7, respectively, during the course of this study. Variation of As(V)/As(III) ratio in the water of these locations was also found to correlate positively with metal contents including those of Cd, Cu, Fe, Mn, Zn, and total As in water. Also, the pH of water from these locations did not change during the sampling period.

Good quality waters with low metal contents and pH>5 appeared to have low As(V)/As(III) ratios, generally. This is illustrated by data given in Table 13 for locations New East

Reed Flume (NERF), Reed Tunnel Flume (RTF), and Reed Tunnel Pump Back (RPB). Groundwaters from these locations were produced by fractures, rock bolts, drill holes, and ore chutes. Water quality data from these locations support our assumption that under reducing environment indicated by the arsenic redox pair ratio, oxidation of iron sulfide minerals and leaching of metal ions are limited. One interesting case is the water from Bailey Ore Chute (BOC), which had a pH around 4 but with low metal content. Water from this location is produced from faults, fractures, and drill holes of the mine. This area is also drained with most of the water coming from a very good water quality tributary on the 7 level, thus resulting in a dilution of metal content. The low As(V)/As(III) ratio in the water from BOC suggests a rather reducing environment.

Water samples from Williams Weir (WW) are weakly acidic with higher levels of Zn (25-66ppm) and Fe (5-16ppm). However, the arsenic content is not consistently high and the As(V)/As(III) ratios are less than 0.5. This location receives water from drill holes, rock bolts, fractures, ore chute, stopes, and faults. An analysis of the "yellow-body" ($Fe(OH)_3$) that precipitated along the flow path of a tributary to the WW site had 44 ppm As. Arsenic(V) may become immobile because of coprecipitation on hydrous iron oxides that form under a weakly acidic condition (pH>3). Utimately As(V) may form the mineral scorodite ($FeAsO_4 \cdot 2H_2O$).[9] Both As(III) and As(V) may also be adsorbed onto the hydrous iron oxide. It is speculated that the adsorption of the As species onto the iron oxides and the coprecipitation of As(V) into the hydrous iron oxides are factors affecting the distribution of the As species in WW.

The concentrations of arsenic in the mine-water samples vary considerably from location to location. The total arsenic concentration probably depends on the amount of arsenic-containing minerals in contact with the groundwater flow system. Most of the arsenic is likely controlled by sorption on and transport of iron-bearing materials, and the As(V)/As(III) ratio is determined by redox sources of the environment and by conditions of the groundwater.

A platinum electrode generally is used for measurement of Eh of natural water systems.[10] Measurements of Eh of water at CW with a standard platinum electrode during the sampling period showed values fluctuating from 445 to 510 millivolts with no obvious trend. According to the Eh-pH diagram of the As-H_2O system, the predominant arsenic species in natural waters in the pH range are $H_2AsO_4^-$ and H_3AsO_3.[1]

$$H_3AsO_3 + H_2O = H_2AsO_4^- + 3\ H^+ + 2\ e^- \qquad (2)$$

The Eh obtained from thermodynamic calculations based on Nernst's equation involving these arsenic species and the measured pH at CW shows a high value of 454 millivolts at As(V)/As(III) ratio of 30.6 and a low value of 428 millivolts at As(V)/As(III) ratio of 8.1. The As(V)/As(III) ratio shows a much wider range and is more consistent than the measured Eh value with regard to the water quality parameters observed in this groundwater system. The platinum electrode is convenient and easy to handle. Thus, there is still considerable interest among geologists in the use of Eh measured by a platinum electrode as a parameter for mapping variations in the level of oxidative degradation in the field. However, the Eh as measured by a platinum electrode is subjected to certain essential objections. Whitfield[11] in a review of the capability of the electrode technique for measurement of Eh, indicates that its usefulness is restricted to a region that is bounded by the Pt-oxides and Pt-sulfide stability field. Other difficulties such as chemical reactions at the liquid junction of the reference electrode, low exchange current densities, and the predominance of mixed potentials in hydrochemically complex environments give rise to instability and poor reproducibility of the Eh measurements. With the analytical method we developed for As detection, it is possible to obtain detectable concentrations for the As(III) and As(V) in an aquatic environment. Using our analytical method, the ratios of the arsenic species in water can be measured with relative standard deviations less than 10%.

Variation of As concentration in an aquatic system and the As(V)/As(III) ratios could be suitable indicators for water quality evaluation. However, the As(V)/As(III) ratio also depends on other factors beyond the pE-pH relationship. The ratio assumes that the dissolved As are in simple ionic forms as shown in the pE-pH diagram without consideration in terms of complexation. The use of this ratio assumes that the system is in equilibrium. The interaction of As with substances like ferric oxides and the slow arsenic oxidation kinetics may therefore pose a risk that an observed As(V)/As(III) ratio may reflect a transitory condition in a particular groundwater zone rather than the actual environmental redox conditions. Thus the observed range of As(V)/As(III) may also reflect factors other than the redox potential which controls this ratio.

Of the various aquatic environments, it appears that the natural groundwaters may be the most suitable systems for applying As species as a sensor of redox levels because groundwater generally moves slowly along its flow paths and hence allows the As redox pair to adjust to the electron activity of the solution. The As window is well above the windows of redox pairs like SO_4^{2-}-HS^- and HCO_3^--CH_4 and is far below the window for dissolved oxygen. In much of this domain As species may have the potential to serve as a more sensitive redox indicator relative to platinum electrode measurements.

In the absence of biological activities or oxidizing agents, the conversion of As(III) to As(V) under atmospheric pressure is slow.[1] The slow kinetics has advantages and disadvantages in the use of arsenic species as a redox indicator in groundwater flow systems. If equilibrium is maintained locally, the measured As species ratio may truly indicate the redox status of the local environment. On the other hand, if the flow is relatively fast compared to the conversion of arsenic species, the ratio of the arsenic redox pair may be used as a tracer to study the groundwater flow patterns. The later characteristic appears to show a greater contribution in the groundwater systems studied in this work. The use of the As species pair as a redox indicator will undoubtedly have its limitations. Its application to the lead-zinc mine is a first step in our research to evaluate its potential as a redox and a water quality indicator.

The South Fork of the Coeur d'Alene River is the ultimate discharge area for the mine-water after it passes through the water treatment plant. The South Fork and North Fork are within steep, narrow valleys. They come together to form the Main Stem. The South Fork is a shallow, swiftly flowing stream whereas the Main Stem is much deeper and slower moving. The average gradients of the South Fork and the Main Stem Coeur d'Alene River have been estimated to be about 5.7 m/km and 0.19 m/km, respectively.[3] The distance from the confluence to the river's mouth is about 50 km. The sediments in South Fork are contaminated with mine wastes and tailings. The Main Stem is also contaminated by sediments from South Fork. The contaminated sediments and mine tailings along the river have been shown to cause degradation of water quality. However, the North Fork is relatively uncontaminated by mine wastes as indicated by the low lead, zinc, and iron contents in its sediments.[3]

The distributions of arsenic species in surface waters from the Coeur d'Alene River also were investigated because the chemical mechanisms controlling the leaching of metals from river sediments by the surface water may be similar to those occurring in the mine (Table 14). One significant observation of the surface waters from the South Fork and the Main Stem Coeur d'Alene River is the low As(V)/As(III) ratio. Zinc level is higher than that of iron. In well-oxygenated waters, arsenic should be present in the pentavalent state. But the arsenic(V) may adsorb onto the hydrous iron oxides present in the contaminated sediments and mine tailings. Arsenic in the trivalent state is not common under surficial conditions. The trivalent arsenic in the river waters probably exists as H_3AsO_3 which is the stable form of As(III) below pH 8.[1] Arsenic(III) in this form is mobile. Inasmuch as the mineral constituents of sediments are cation exchangers, arsenic is not immobilized by contact with these minerals.[9] Thus the low As(V)/As(III) ratios observed presumably are caused by the immobilization of As(V) through coprecipitation and sorption onto the iron hydroxide.

The dissolved oxygen in surface water of the three branches of the Coeur d'Alene River was reported to be about the same.[12] High dissolved oxygen values around 11.5 ppm were found in the months from November to March and low values around 8 ppm were found from June to August. The difference between the dissolved oxygen in surface water of the South Fork and the North Fork was generally within 0.2 ppm. These results are consistent with those retrieved from the EPA's Storet System for the past 20 years. Based on the available data, the amount of dissolved oxygen in the surface water of

Table 14. Arsenic, Zn, Fe, and Mn in surface waters at different locations along the Coeur d'Alene River.

Sample Location	pH	ppb		As(V)/As(III)	ppm		
		As(III)+As(V)	As(III)		Zn	Fe	Mn
1	7.3	2.68±0.06	2.42±0.06	0.10	1.52	<0.01	0.17
2	7.3	2.87±0.06	2.22±0.05	0.29	1.65	0.01	0.19
3	7.2	2.01±0.06	1.59±0.05	0.26	2.20	<0.01	0.72
4	7.2	1.79±0.05	1.57±0.05	0.14	2.32	<0.01	0.74
5	7.3	0.46±0.03	0.30±0.03	0.53	0.85	<0.01	0.16
6	7.3	0.44±0.03	0.27±0.03	0.63	0.85	<0.01	0.16
7	7.1	0.78±0.04	0.69±0.04	0.13	0.50	0.05	0.41
8	7.2	1.50±0.05	1.16±0.04	0.29	0.01	<0.01	0.04
9	7.3	0.71±0.04	0.41±0.03	0.73	0.04	1.14	0.50
10	7.1	0.17±0.04	<0.03	>5.66	<0.01	0.01	<0.01

Sample locations are indicated in Figure 4.

the Coeur d'Alene River appears to depend on temperature. The drastic difference in As(V)/As(III) ratio observed between the South Fork and the North Fork is apparently not caused primarily by the dissolved oxygen in water.

According to this study, the biologically more toxic As(III) species is the predominant As form in the South Fork and the Main Stem of the river. It was just the opposite in water samples collected from the North Fork although the total As content in North Fork water was much lower (Table 14). Savage and Rabe[13] have shown that the macrobenthic diversity of riffle areas in the South Fork was much less than that in adjacent North Fork water. Conversion of As(III) to As(V) under atmospheric pressure is known to be slow without biochemical catalysts.[1] Therefore the low As(V)/As(III) ratio observed may also reflect a lack of biochemical activities in the South Fork and Main Stem Coeur d'Alene River. Without sufficient biological activities, the time required for the oxidation of As(III) is probably long relative to the residence time of water in South Fork and Main Stem Coeur d'Alene River.

Acknowledgements - This work was supported in part by the Idaho Water Resources Research Institute with funding from the U.S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by the Department of Energy. The authors are grateful to the Bunker Hill Company for supporting this study. However, the views and

conclusions presented in this paper may not reflect the veiws and conclusions of the supporting entities.

REFERENCES

1. Cherry, J. A.; Sahikh, A. U.; Tallman, D. E.; Nichlson, R. V. J. Hydrol. **1979**, 43, 373.

2. Wai, C. M.; Reece, D. E.; Trexler, B. D.; Ralston, D. R.; Williams, R. E. Environ. Geol. **1980**, 3, 159.

3. Reece, D. E.; Felkey, J. R.; Wai, C. M. Environ. Geol. **1978**, 2, 289.

4. Smith, E. E. and Shumate, K. S. Sulfide to Sulfate Reaction Mechanism, U.S. Govt. Printing Office, Washington, D.C., Document 14010FPS02/70, 1970.

5. Mok, W. M.; Shah, N. K.; Wai, C. M. Anal. Chem. **1986**, 58, 110.

6. Kamada, T. Talanta **1976**, 23, 835.

7. Mok, W. M.; Wai, C. M. Anal. Chem. **1987**, 59, 233.

8. Riley, J. A. "Acid Water Implications for Mine Abandonment, Coeur d'Alene Mining District, Idaho," University of Idaho, Moscow, Idaho. M.S. Thesis, 1985.

9. Wilson, F. H.; Hawkins, D. B. Environ. Geol. **1978**, 2, 195.

10. Langmuir, D. "Eh-pH Determinations" in Methods of Sedimentary Petrology, Carver, R. E., Ed., Wiley-Interscience: New York, NY, 1970; p. 597.

11. Whitfield, M. Limnol. Oceanogr. **1974**, 19, 857.

12. Mink, L. H.; Williams, R. E.; and Wallace, A. T. Effects of industrial and domestic effluents on the water quality of the Coeur d'Alene River Basin. Idaho Bureau of Mines and Geology, Pamphlet 149, 1971.

13. Savage, N. L. and Rabe, F. W. Northwest Sci. **1973**, 47, 159.

CHAPTER VIII

The following manuscript entitled

DISTRIBUTION AND MOBILIZATION OF ARSENIC SPECIES IN THE CREEKS AROUND THE BLACKBIRD MINING DISTRICT, IDAHO

by

W. M. Mok and C. M. Wai

has been submitted for publication in

Water Research

ABSTRACT

The sediments in the creeks around the Blackbird Mining Area are heavily contaminated with As from the local mining operations. Laboratory experiments indicate that the major As species leached from the sediments under atmospheric pressure is As(V). Release of As was found to be pH dependent and was related to the total iron and free iron oxides in the sediments. Leaching under nitrogen atmosphere resulted in an increased release of As and is likely associated with the reduction of ferric-arsenate compounds to the more soluble ferrous-arsenate forms. It seems that both adsorption of As on iron-rich oxides on the surface of the sediments and incorporation of As into the sediments by coprecipitation with hydrous iron oxides are factors controlling mobilization of sediment As.

The field observations are consistent with results observed from laboratory experiments. Leaching of contaminated sediments appears to be a mechanism responsible for the transport of As and other trace metals in the creeks. The contaminated sediments are a nonpoint source of pollution that should be considered in water quality management planning for the Blackbird Mining Area.

INTRODUCTION

The Blackbird Mine, located at the edge of the Frank Church Primitive Area in east-central Idaho, is one of the largest potential sources of cobalt in the United States.[1] Two streams drain the Blackbird mining area: Blackbird Creek to the south and Bucktail Creek to the north of the mine. These streams both flow into Panther Creek, a major tributary of the Salmon River (Figure 7). Mining operations from the late 40's to the late 60's left many waste piles and dumps in this area. The impact of these past mining activities on the surrounding streams is rather severe. For example, no salmon spawning beds have been observed in the streams around the Blackbird Mine since 1962; their disappearance was attributed to toxic discharge from the mining area.[2] Severe water quality problems were also reported in the late 70's.[3,4]

Production at this mine in the late 60's had been halted because of increasing competition from foreign imports. The cobalt shortage in the late 70's resulted in a reopening of the mine in 1980. However, because of a depressed metal market in the past few years, the Blackbird Mine was closed again in 1984. The major cobalt mineral found in the Blackbird area is a cobalt-arsenic sulfide called cobaltite. Chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) are often present with cobaltite in the ore. Mine wastes and tailings containing iron sulfides are capable of producing acid waters under oxidized conditions.[5,6]

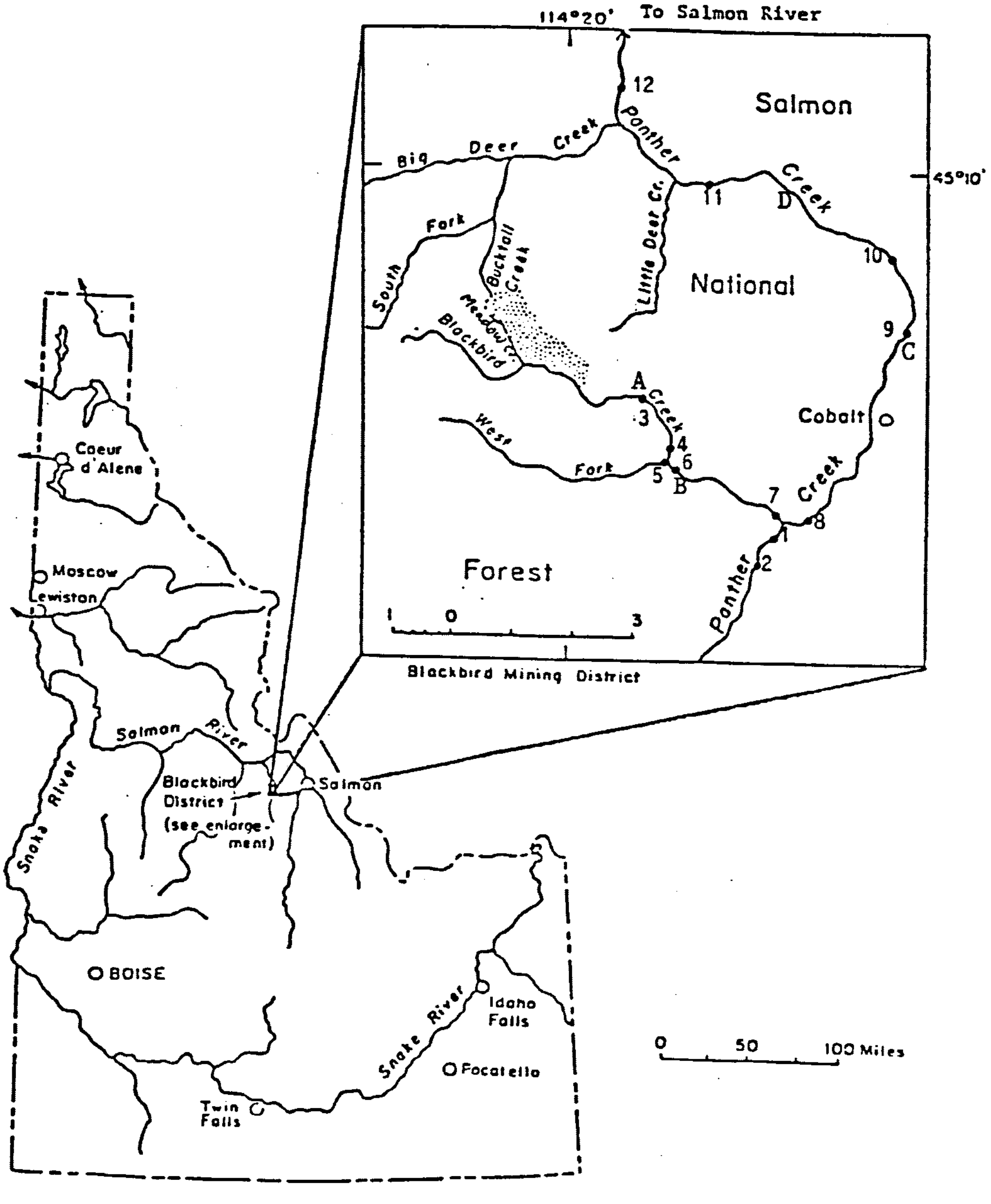

Figure 7. Sample collecting sites on Blackbird Creek and on Panther Creek. (Stations 1-12: water sample collecting sites; Stations A-E: sediment sample collecting sites; E is on Panther Creek, before it enters the Salmon River)

The sediments in the creeks around the Blackbird Mining district are being leached to varying degrees by the creek waters. Knowledge of the distribution of the As(III) and As(V) species in natural water systems is important for environmental consideration of geochemical and biological cycling of the element. Biologically, As(III) is considered more toxic than As(V).[7] The mobility of As in the contaminated sediments around the Blackbird Area was previously undocumented; thus, this research was designed to study the leaching of inorganic As(III) and As(V) in creek waters from representative sediments collected from the Blackbird area. Current levels of trace metals including cobalt, copper, and manganese in the creek waters and their releases observed in leaching experiments are also reported. Factors which control the mobility of As from the sediments to the aqueous environment are discussed. Since Sb is chemically similar to As, a comparison of the distribution and mobilization of these two elements in the Blackbird Area is also given.

EXPERIMENTAL

Sample Collection

Five sediment samples, two from Blackbird Creek and three from Panther Creek, were selected for the leaching experiments of this study. Locations of the sampling sites are shown in Figure 7 by letters, except for site E which is in Panther Creek before it enters the Salmon River. Sediments were taken from the creeks with plastic shovels. After collection, samples were sealed in plastic bags and stored at 4 °C until used. Leaching experiments were usually conducted within a week after collection.

Surface water samples were collected from the creeks using one-liter high-density linear polyethylene bottles. All containers used were washed with nitric acid and rinsed with deionized water. The locations of the 12 sampling stations are shown by numbers in Figure 7. Samples were collected on August 31, 1985, and on May 26, 1986. After collection, water samples were filtered using a 0.45 μm membrane filter. Arsenic analyses were done within 4-5 days after sampling. Filtered samples were also preserved by acidification to pH 2 with HNO_3 and analyzed for Co, Cu, and Mn.

Sample Analysis

Quantification and speciation of As(III) and As(V) in the creek waters and leaching solutions were done by extraction with pyrrolidinedithiocarbamate (PCDT) into chloroform followed by a nitric acid back-extraction for neutron activation analysis (NAA). Samples were irradiated in a 1 MW TRIGA reactor with a steady neutron flux of $6X10^{12}$ n/cm^2 sec. A large-volume coaxial ORTEC Ge(Li) detector was used for gamma activity measurements. The detector output was fed into an EG&G ORTEC ADCAM (Model 918) multichannel analyzer, and the data were processed by EG&G ORTEC software on an IBM-PC. The details of the extraction method and NAA procedures are given in the literature.[8]

The other metals, including Co, Cu, Mn, and Fe, were analyzed using an IL-353 atomic absorption spectrometer (AAS) or an ARL Model 35,000C Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Determination of metals in the sediments was carried out using HNO_3/HCl digestion, similar to that described by Abernathy et al.,[9] followed by NAA, AAS or ICP-AES.

Leaching Experiments

Leaching experiments were carried out in the laboratory under atmospheric pressure and room temperature. Each experiment began with 60 g of sediments mixed with 800 mL of deionized water. 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 sediments was constantly exposed to the solution. The sediment-water mixtures were kept in suspension by continuous stirring with a magnetic stirrer throughout the whole period of leaching. The leaching experiments involved the measurement of pH and the analysis of leaching solutions for As(III), As(V), Co, Cu, and Mn at various time intervals for 10 days.

Field Observation and Laboratory Studies

Since relationships between the ratio of As(V)/As(III), pH, and other water quality parameters can be defined in laboratory controlled leaching experiments, the water quality data observed from the field may be correlated with laboratory results. This field observation combined with laboratory studies may provide useful information for understanding the factors which control the leaching and transport of As and other metals during sediment-water interactions and for investigating water pollution problems associated with the contaminated sediments in the aquatic system under investigation.

RESULTS AND DISCUSSION

Table 15 summarizes the metal content of the sediments. The sediments from Blackbird Creek in general had higher concentrations of As, Co, Cu, Mn, and Fe than the sediments from Panther Creek. All these sediments showed high levels of arsenic (42-2550 μg/g).

Table 15. Concentrations of As, Co, Cu, Mn and Fe in the sediments collected from Blackbird Creek and from Panther Creek.

Sample	As (μg/g)	Co (μg/g)	Cu (μg/g)	Mn (μg/g)	Fe (%)
A	1120.6	311.9	2330.2	183.3	10.7
B	2550.4	471.0	2595.4	167.2	12.9
C	42.1	94.1	118.5	233.3	1.9
D	132.5	156.7	294.8	1548.0	3.2
E	135.4	543.9	1029.6	583.0	0.8

Releases of As, Co, Cu, and Mn during Leaching

The pH values of the leachates from Blackbird Creek sediments A and B were slightly below 5. The low leachate pH values suggest a stronger acid production capability for these sediments. Contaminated sediments which are capable of producing acid generally contain oxidized forms of iron and pyrite.[10] Sediments from Panther Creek (C-E) maintained a pH value of approximately 6.8 to 7.4 during leaching. Figure 8 shows the variation of pH values of solutions during leaching of sediments B (from Blackbird Creek) and C (from Panther Creek).

The cumulative net mass releases of As(III) and As(V) from the sediments from locations B and C are shown in Figure 9. Sediments from the other locations showed similar trends. As shown in Figure 9, the sediments generally exhibited a higher initial release of As(V) followed by a rather asymptotic pattern during the leaching period. Cumulative As(III) releases from the sediments were much lower than the releases of As(V). In the case of sediment A, As(III) was not detected during the course of leaching. The variations in As(V)/As(III) ratios during the course of leaching were generally small, and As(V) was the major species released. Another important observation is that, although Blackbird Creek sediments had much higher As contents than those of Panther Creek, the release of As from Blackbird Creek sediments during leaching was very low.

Contrary to the leaching behavior of As, the releases of Co, Cu, and Mn from the Blackbird Creek sediments were higher than those from Panther Creek sediments. The weakly acidic solutions produced during the leaching of Blackbird Creek sediments apparently increased the release of these trace metals from the sediments. The unusual behavior of As during

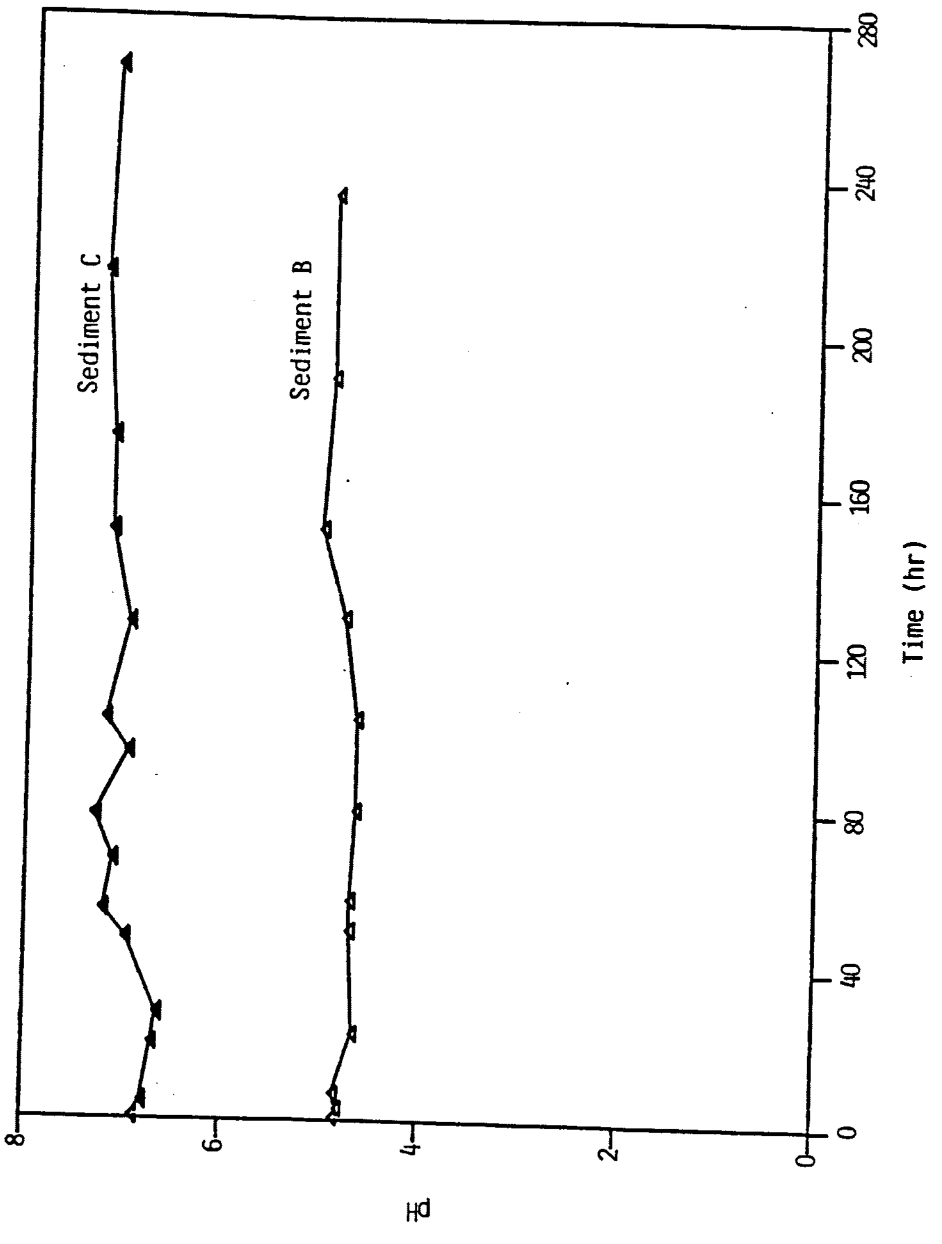

Figure 8. Variation of pH during leaching of the sediments.

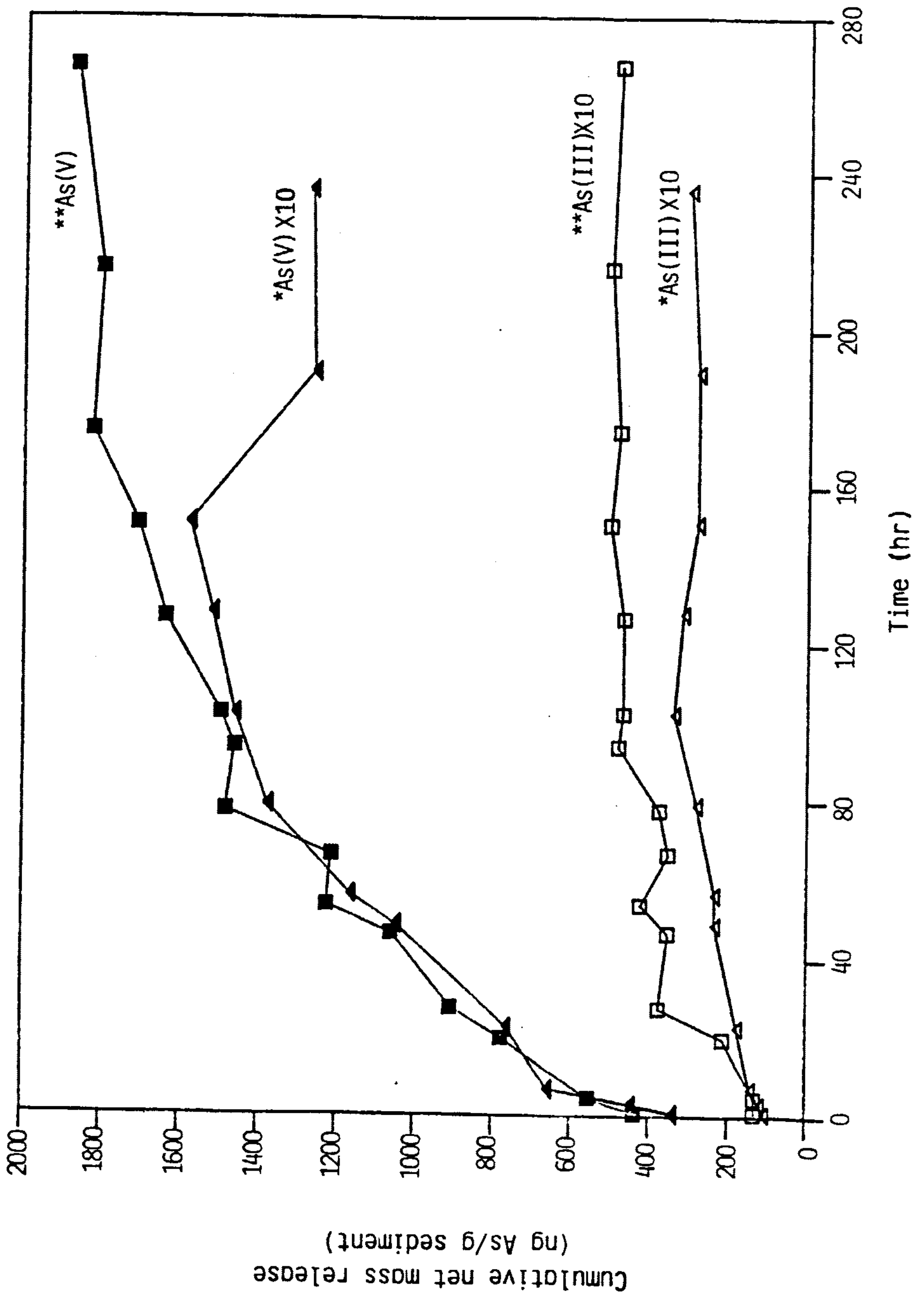

Figure 9. Cumulative release of As(III) and As(V) from sediment B (*) and from sediment C (**). Scales for *As(III), *As(V), and **As(III) were expanded 10 times.

leaching is related to the high iron content of the sediments of Blackbird Creek; effects of iron on As release will be discussed later. Table 16 shows the concentrations of As(III), As(V), and the other trace metals in the leachates of the sediments after ten days of leaching. Leaching of the sediments resulted in ng/mL levels of arsenic and μg/mL levels of the other trace metals in the leaching solutions.

Table 16. Concentrations of As(III), As(V), Co, Cu, and Mn in the leaching solution (10 days of leaching).

	ng/mL		μg/mL		
Sediment	As(III)	As(V)	Co	Cu	Mn
A	<0.01	3.99	3.34	2.52	0.22
B	2.24	9.24	12.48	2.65	0.81
C	3.09	114.86	<0.10	0.02	<0.10
D	1.70	28.33	0.31	0.05	0.04
E	0.31	7.06	0.11	0.01	<0.01

Leaching under Nitrogen Atmosphere

An experiment was performed under nitrogen atmosphere to evaluate the effect of an oxygen-free environment on the leaching of arsenic. Sediment C was randomly chosen for this experiment. The system was stirred continuously with a magnetic stirrer in a sealed flask, and nitrogen was flushed through the system to maintain an oxygen-free environment.

The releases of other trace metals during leaching under nitrogen atmosphere did not show significant differences from those obtained under aerobic conditions. However, the leaching under oxygen-free conditions resulted in higher concentrations of arsenic in the leachates (Figure 10). A

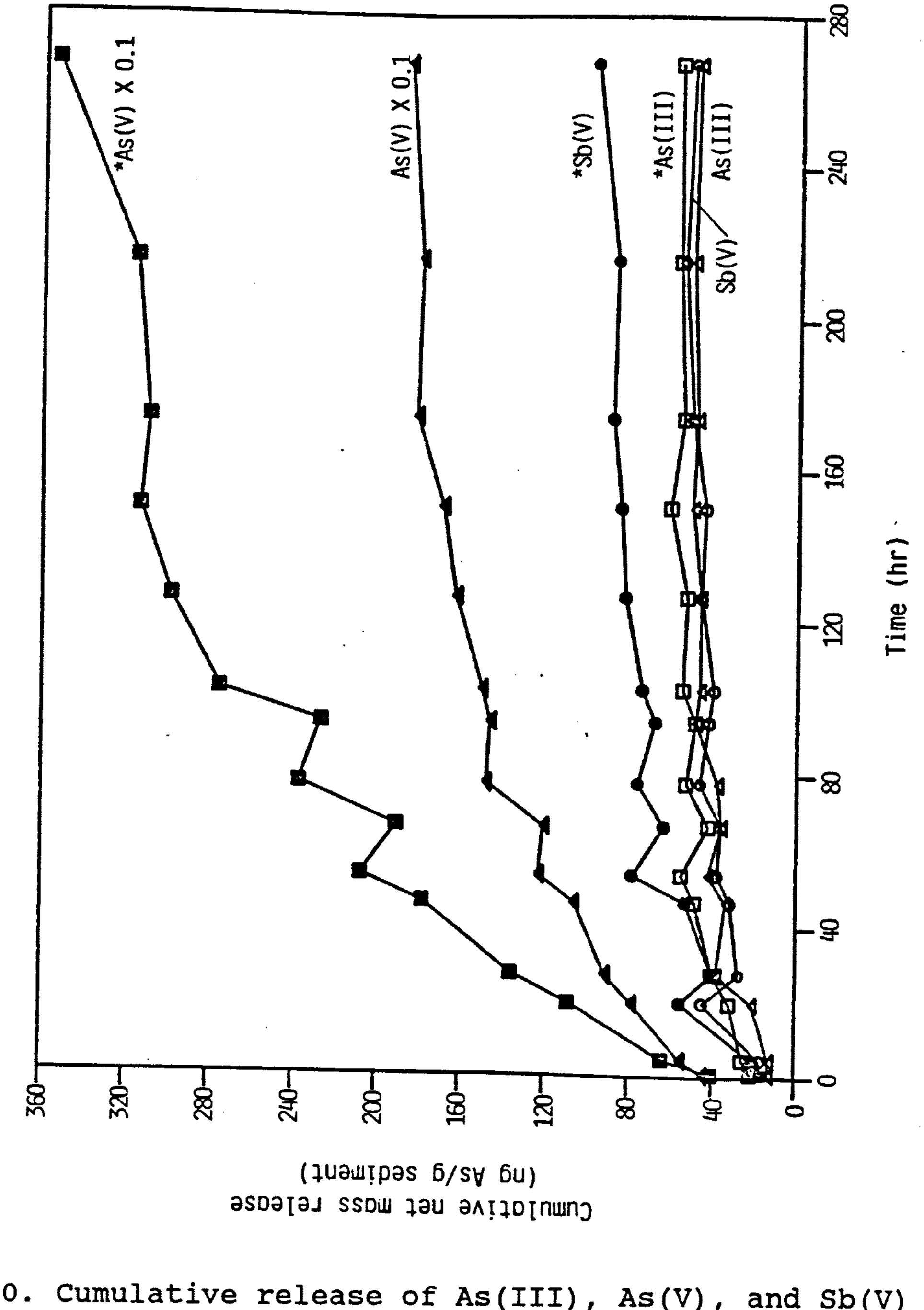

Figure 10. Cumulative release of As(III), As(V), and Sb(V) from sediment C under aerobic conditions and under oxygen-free environment (*). Scales for As(V) and *As(V) were reduced 10 times.

higher As(V)/As(III) ratio was also observed, and the As(V)/As(III) ratio tended to increase slowly during the course of leaching, reflecting the continuous release of more As(V). There was also an increased release of Sb which is discussed later. Furthermore, the leaching also resulted in higher concentrations of dissolved iron (Figure 11), indicating a relationship between sediment As and Fe. Our observation is consistent with the release of arsenic from the leaching of contaminated soils reported by Deuel and Swoboda.[11] The leaching of soils in an oxygen-free environment was reported by these authors to result in higher soluble As(V). The increase in soluble As(V) was attributed to ferric arsenate and other ferric ions being reduced to the relatively more soluble ferrous form.[11]

Effect of Sediment Iron on As Release

The chromatographic distribution coefficient (D) was used to examine the effect of sediment Fe on the partition of As between sediments and leachates. To obtain the D values, total As concentrations (μg/g) in sediments were divided by the cumulative net mass release (μg/g) of As following 10 days of leaching. The D values were obtained in our experiments following a procedure described in the literature.[12] Values of D for the five sediments (A-E) are summarized in Table 17. A high D value signifies that more of the total sediment As was retained as compared to a sediment with a low D value. Although the concentrations of As in sediments from Blackbird Creek were found to be much greater than those in sediments

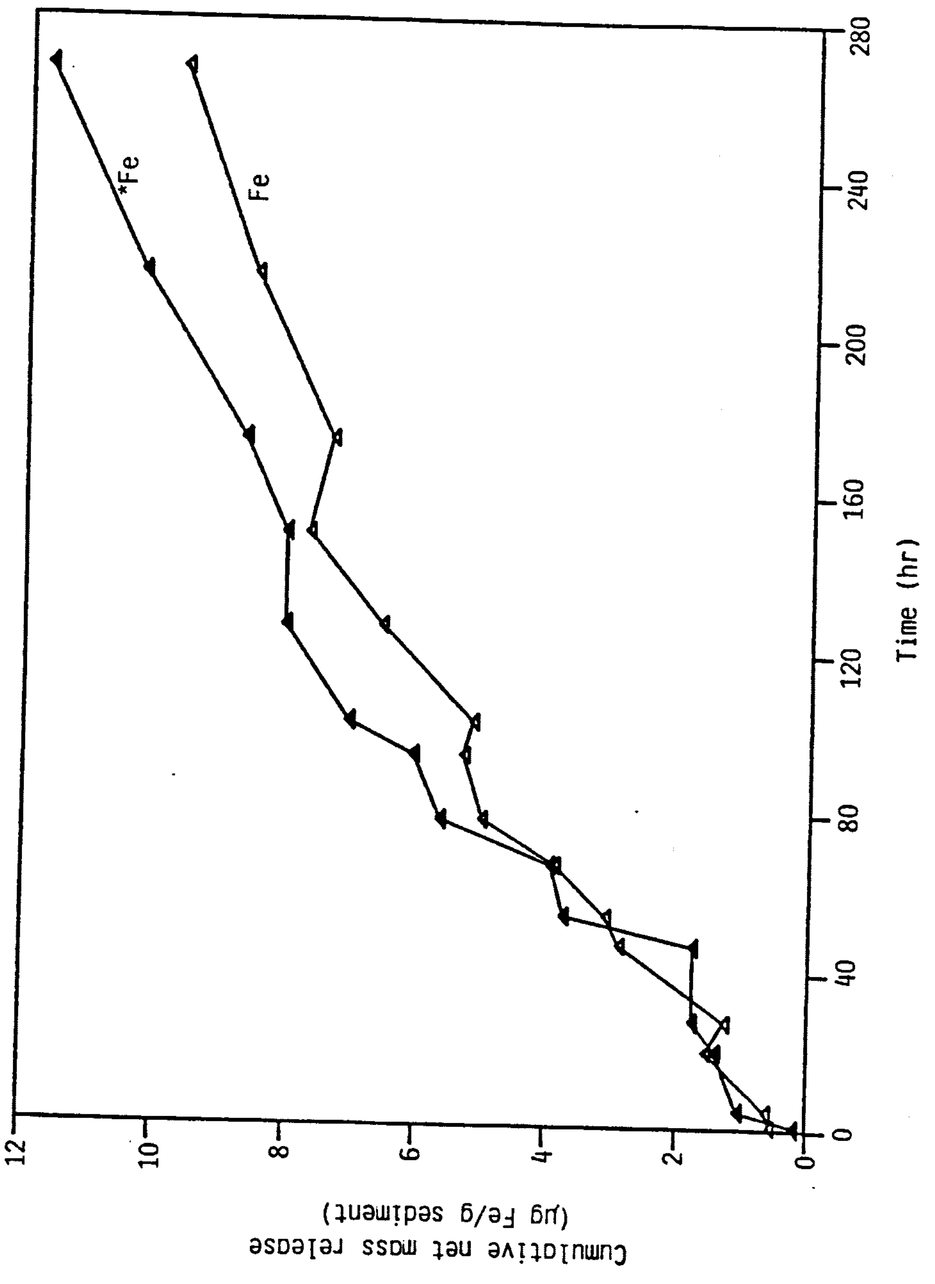

Figure 11. Cumulative release of Fe from sediment C under aerobic conditions and under oxygen-free environment (*).

from Panther Creek, a much lower release of As (as shown by the high D values) from the former was observed, indicating that more of the As in the Blackbird Creek sediments was retained. The Fe content of Blackbird Creek sediments was found to be at least four times higher than that of Panther Creek sediments. A citrate-dithionite extraction method[13] was employed to determine the amount of free iron oxides in the sediments. The D values for As(III) and As(V) correlated strongly with sediment Fe content and free iron oxides (correlation coefficients > 0.92), indicating that both sediment Fe content and free iron oxides were important factors affecting the retention of As in the sediments. The results agree well with the literature reports that oxides of iron strongly adsorb As compounds.[14-16] Under weakly acidic to basic conditions, As(V) can be coprecipitated on hydrous iron oxides with the formation of the mineral scorodite ($FeAsO_4 \cdot 2H_2O$) which is very insoluble.[17,18] It is speculated that both adsorption of As on the iron rich oxides existing on the surfaces of the Blackbird Creek sediments and the incorporation of As into the sediments by coprecipitation at the time of formation of hydrous iron oxides[19] are factors responsible for the observation that Panther Creek sediments yield more As upon leaching although As contents of Blackbird Creek sediments are higher.

Table 17. Distribution coefficients (D) of the arsenic species following about 10 days of aerobic leaching under atmospheric pressure.

Sediment	As(III)	As(V)
A	N.D.	17483
B	82645	20040
C	833	24
D	4808	288
E	16000	709

N.D.: As(III) was not detectable during the course of leaching.

Effect of pH on Leaching of As from the Sediments

The effect of pH on the leaching of As and the other trace metals was also studied (Table 18). The sediment sample used in this experiment was taken from Station 11. Concentrations of As and the other trace metals were measured after 30 hours of sediment-water contact time at controlled pH and under atmospheric pressure with continuous stirring.

Table 18. Amounts of As, Co, Cu, and Mn leached at different pH values (30 h of leaching).

Metal	pH=3.8	pH=6.3	pH=9.1	pH=11.5
As(III)	7.32×10^{-2}	2.63×10^{-3}	2.80×10^{-2}	2.96×10^{-2}
As(V)	0.12	0.19	3.61	15.85
Co	22.53	1.18	<0.1	<0.1
Cu	13.23	0.14	0.43	6.20
Mn	28.86	0.36	0.05	N.D.

Sediment sample was taken from Station 11. Amounts released are given in μg/g sediment. N.D.: not detected

The release of trace metals follows a predictable pattern of increasing release at low pH. Accordingly, acid precipitation is a cause of great environmental concern on a regional scale. The release of As from the sediments was found to be low at pH values close to neutral. Maximum adsorption of arsenite and arsenate by hydrated iron oxides has been reported to occur at pH 7.0 and pH 3.5 to 5.3, respectively.[15,16] The release of As rose again in basic solutions. This behavior is somewhat distinct for As, because the anionic forms of arsenic are more mobile in basic solutions.[20] The observation of an enhanced arsenic release from contaminated sediments in basic solutions suggests a cause for environmental concern when alkaline solutions are discharged into a creek with sediments contaminated with mine wastes. Lime treatment is a common method to reduce metal content in acid mine drainages and waste waters related to mine tailings. Discharge of lime-treated waste water would increase the pH of creek water and subsequently might result in a higher As release from the contaminated sediments.

Arsenic and the Other Trace Metals in the Creek Waters

The creek water was essentially neutral. Arsenic and other trace metal concentrations measured in the creek waters are presented in Table 19.

Table 19. Concentrations of As, Co, Cu, and Mn in the creek waters.

Station		ng/mL		µg/mL		
		As(III)	As(V)	Co	Cu	Mn
1	a	0.34±0.03	0.78±0.05	<0.1	<0.01	<0.01
	b	0.41±0.04	0.37±0.06	<0.1	0.01	0.01
2	a	0.30±0.07	0.70±0.11	<0.1	<0.01	<0.01
	b	<0.02	0.80±0.07	<0.1	0.01	<0.01
3	a	<0.03	1.00±0.40	2.07	1.76	0.38
	b	0.18±0.04	0.93±0.08	0.78	0.79	0.10
4	a	0.81±0.07	<0.05	0.67	1.36	0.28
	b	0.17±0.04	0.38±0.09	0.74	0.60	0.09
5	a	0.40±0.05	<0.05	0.38	<0.01	0.15
	b	0.23±0.04	0.99±0.07	0.10	<0.01	0.02
6	a	0.27±0.04	0.43±0.06	1.34	0.43	0.27
	b	0.32±0.05	0.16±0.09	0.67	0.37	0.09
7	a	0.91±0.09	2.03±0.14	0.90	0.07	0.17
	b	0.53±0.04	1.48±0.10	0.33	0.16	0.04
8	a	0.76±0.07	0.74±0.01	0.04	0.02	0.01
	b	<0.03	1.68±0.07	0.05	0.03	<0.01
9	a	0.90±0.10	5.30±0.10	0.07	0.02	0.01
	b	0.11±0.07	1.51±0.09	0.03	0.16	<0.01
10	a	<0.05	5.32±0.09	0.03	0.01	<0.01
	b	0.14±0.03	2.04±0.08	0.04	0.02	<0.01
11	a	0.40±0.10	3.70±0.02	0.03	0.01	<0.01
	b	<0.03	1.68±0.06	0.01	0.02	<0.01
12	a	2.11±0.08	2.30±0.14	0.02	0.04	<0.01
	b	0.07±0.04	1.80±0.08	0.03	0.06	<0.01

a: August, 1985; b: May, 1986

The concentrations of Co, Cu, and Mn in creek waters measured at the locations on Panther Creek above the confluence of Blackbird Creek (Stations 1 and 2, pH values of water: 7.0-8.0) were very low, about 0.01 µg/mL or less.

Total As was also low, with an average of 0.93±0.16 ng/mL. This value is comparable to the value of 1.38±0.37 ng/mL found in the Snake River near Lewiston, Idaho,[8] but it is higher than the As levels found in other unpolluted natural waters. For example, As in the North Fork of the Coeur d'Alene River in northern Idaho was found to be 0.13 ng/mL,[21] and As in the river water collected from around Yakushima Island in Japan was reported to be 0.21 ng/mL.[22] Elevated levels of Co, Cu, and Mn, in the range from 0.01 to 2.0 μg/mL, were observed in Blackbird Creek (Stations 3-7, pH values of water: 6.6-7.4). Arsenic levels in Blackbird Creek waters were not significantly different from those observed at Stations 1 and 2.

Although As content of the sediments of Panther Creek below the confluence of Blackbird Creek was much lower than that of Blackbird Creek, As concentrations in Panther Creek waters (Stations 8-12, pH values of water: 7.3-7.9) were found to be higher, while the concentrations of other trace metals were comparatively lower than those in Blackbird Creek. These field observations were consistent with the results observed from our laboratory leaching experiments. The high Fe content and free iron oxides in sediments from Blackbird Creek are definitely factors which inhibit the release of As.

Arsenic and the other trace metals in the creek waters are most likely controlled by the leaching of sediments. Water in the creek is in an unconfined environment. Leaching of metals from sediments, therefore, also depends on the flow of water. The effect should be more pronounced at low flow because of longer water-sediment contact time and smaller water volume in the creek. Lower concentrations of As and the other trace metals in the creek waters were usually observed in May during the high flow from spring run-off compared to those observed in August.

Antimony in Creek Waters

A preliminary study of antimony was also carried out because antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency, and the soluble salts of antimony are known to be toxic.[23] Antimony and As are expected to have some similarities in geochemical behavior as are other elements from the same group in the periodic table. Antimony in aqueous solutions was determined by a modification of the PCDT extraction method reported by Mok et al.[8] Details of this extraction method for simultaneous determination of As and Sb species in natural waters are given in a recent publication.[21]

The concentrations of Sb in the leaching solutions were at least three orders of magnitude lower than those of As. Of the sediments studied, only sediments C and D showed detectable amounts of Sb, primarily Sb(V), during leaching. Antimony(III) was not detected. Cumulative net mass releases of Sb(V) from sediment C are also shown in Figure 10. Leaching under nitrogen atmosphere also resulted in an elevated release of Sb(V) (Figure 10). Antimony concentrations in the water samples collected in May 1986 were also analyzed. Total inorganic Sb in the water samples from Blackbird Creek and from Panther Creek was generally less than 0.05 ng/mL, except for sites #7, #10, and #11 where the total Sb concentrations were found to be 0.25±0.08 ng/mL, 0.16±0.03 ng/mL, and 0.23±0.04 ng/mL, respectively. The Sb species detected in water from these sites was virtually all Sb(V). The Sb level in the Snake River near Lewiston, Idaho, was found to be around 0.2 ng/mL, with Sb(V) as the predominant species.[8] Based on these preliminary data, it appears that Sb is unlikely to be a metal of environmental concern in the drainages of the Blackbird area.

Conclusions

1. Sediments from Blackbird Creek and from Panther Creek are heavily contaminated with As. Total As concentrations in the creek waters are high relative to some unpolluted rivers, and As(V) is always the major species found in the creek waters.

2. The mobility of arsenic in creek waters is closely tied to the iron content and free iron oxides of the creek sediments. Free iron oxides probably act as a sink and inhibit the release of As. The sharp increase in release of As in basic solutions may have consequences for the application of lime or limestone in the minimization of acid water problems.

3. In sediments where Sb was released during leaching, only Sb(V) could be detected. Apparently, Sb(V) is also the dominant species in the creek water. The leaching

characteristics of Sb(V) appear to be similar to those of As except the amount of Sb leached from the sediments is much lower compared with As.

4. Leaching of the contaminated sediments is a mechanism responsible for the transport of As and other trace metals in the creeks. Water quality planning for the Blackbird area should, therefore, consider such nonpoint sources of contamination.

Acknowledgments. This work was supported in part by the Idaho Water Resources Research Institute with funding from the U.S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the reactor sharing program supported by the Department of Energy. The views and conclusions presented in this paper may not reflect the views and conclusions of the supporting entities.

References

1. Mineral and Water Resources in Idaho, United States Geological Survey, 1975, Special Report No. 1, p. 66.

2. Corley, D. R. "Biological sampling of Panther Creek above and below the introduction of mining wastes," Idaho Fish and Game Dept.: Boise, ID, 1967, 10 p.

3. Platts, W. S.; Martin, S. B.; Primbs, E. R. J. Water Quality in an Idaho Stream Degraded by Acid Mine Waters USDA For. Ser. Gen. Tech. Rep. INT-67, Intermt. For. Range Exp. Stn.: Ogden, UT, 1979, 19 p.

4. Baldwin, J. A. "Analysis of water resource problems related to mining in the Blackbird Mining District," University of Idaho, Moscow, Idaho. M.S. Thesis, 1977, 232 p.

5. Appalachian Regional Commission, Acid mine drainage in Appalachia, U.S. Govt. Printing Office: Washington, D.C., House Document 91-180, Publication No. 35-4320, V. 1, p. 58; V. 3, p. 17, 1969.

6. Smith, E. E.; Shumate, K. S. Sulfide to Sulfate Reaction Mechanism, U.S. Govt. Printing Office: Washington, D.C., 1970, Document 14010FPSO2/70.

7. NAS. Medical and biological effects of environmental pollutants - Arsenic National Academy of Sciences: Washington, D.C., 1977, p. 117.

8. Mok, W. M.; Shah, N. K.; Wai, C. M. Anal. Chem. **1986**, 58, 110.

9. Abernathy, A. R.; Larson, G. L.; Mathews, R. C., Jr. Water Res. **1984**, 18, 351.

10. Wai, C. M.; Reece, D. E.; Trexler, B. D.; Ralston, D. R.; Williams, R. E. Environ. Geol. **1980**, 3, 159.

11. Deuel, L. E.; Swoboda, A. R. Soil Sci. Soc. Amer. Proc. **1972**, 36, 276.

12. Brannon, J. M.; Patrick, W. H., Jr. Environ. Sci. Technol. **1987**, 21, 450.

13. Olson, R. V.; Roscoe, E. Jr., Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties Page, A. L., Ed., Agronomy Monograph No. 9 (2nd Edition) 1982.

14. Gupta, S. K.; Chan, K. Y. J. Wat. Poll. Cont. Fed. **1978**, 50, 493.

15. Pierce, M. L.; Moore, C. B. Env. Sci. Tech. **1980**, 14, 214.

16. Pierce, M. L.; Moore, C. B. Water Res. **1982**, 16, 1247.

17. Wilson, F. H.; Hawkins, D. B. Environ. Geol. **1978**, 2, 195.

18. Aggett, J.; Roberts, L. S. Environ. Sci. Technol. **1986**, 20, 183.

19. Mok, W. M.; Riley, J. A.; Wai, C. M. Water Res. **1988**, in press.

20. Theis, T. L.; Wirth, J. L. Environ. Sci. Technol. **1977**, 11, 1096.

21. Mok, W. M.; Wai, C. M. Anal. Chem. **1987**, 59, 233.

22. Tanizaki, Y.; Nagatsuka, S. Bull. Chem. Soc. Jpn. **1983**, 56, 619.

23. Luckey, T. D.; Venugopal, B. Metal Toxicity in Mammals Plenum Press: New York, V. 1, 1977, p. 139.

CHAPTER IX

The following manuscript entitled

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

by

W. M. Mok and C. M. Wai

has been submitted for publication in

Environmental Science and Technology

ABSTRACT

Sediments from the Main Stem and the South Fork of the Coeur d'Alene River are contaminated with As, Sb, and other heavy metals from the local mining operations. Water samples from the South Fork and Main Stem showed high levels of As (0.11-1.64 ng/mL) and Sb (0.23-8.25 ng/mL) relative to those from the North Fork (0.26 ng/mL As and 0.17 ng/mL Sb). Arsenic(III) was found to be the predominant form in the waters of the South Fork and Main Stem of the Coeur d'Alene River, whereas the North Fork generally had higher As(V) concentrations. The major inorganic Sb species was Sb(V) in all three branches of the river. Laboratory experiments indicate that As and Sb can be leached from the sediments, and the results are correlated with the water quality in the field. Leaching of As and Sb species from the contaminated Main Stem sediments depends on the pH values of the water as well as on the free Fe-oxides and Mn-oxides present in the sediments. Arsenic is found to be more strongly retained in the sediments than Sb is. Interactions of water with the contaminated sediments are likely to be non-point sources of pollution that control the distribution and mobilization of As and Sb species in that aquatic environment.

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.[1] Mining and smelting wastes have been discharged into the South Fork of the river since mining began in this area some 80 years ago. The installation of settling ponds for mill wastes in 1968 has greatly reduced the present discharge of mining wastes into the river from the active mining operations. However, huge amounts of mine tailings have already been deposited in the river and spread to the valley due to flooding and the changing of river channels. These contaminated sediments are being leached to varying degrees by surface water and groundwater and are likely to be non-point sources of pollution in this area for years to come.

Antimony and arsenic are present in the mine wastes in significant amounts. The distribution and mobility of these two elements in the contaminated sediments of the Coeur d'Alene River system are not known. Antimony and As are interesting for environmental studies because their toxicity and physiological behavior depend on their oxidation states. Biologically, As(III) is considered more toxic than As(V).[2] The relative toxicity of Sb(III) and Sb(V) is less known; however, soluble salts of Sb have been shown to be toxic.[3] Knowledge of the chemical factors controlling the distribution and mobilization of the As and Sb species in natural water systems is important for environmental control and monitoring of these toxic metals as well as for an understanding of their geochemical and biological cyclings.

The Coeur d'Alene River system can be divided into three components: the North Fork which supports a rather healthy aquatic community, the South Fork which has received mining wastes for over 80 years, and the Main Stem which has been affected by the conditions of the South Fork. The South Fork of the Coeur d'Alene River is a shallow, swiftly flowing stream; the Main Stem of the river is much deeper and slower moving than the South Fork. The gradient of the South Fork is about 5.7 m/km, while the gradient of the main stem is only about 0.19 m/km.[4] Because of the large gradient of the South Fork, most of the mine tailings discharged to the South Fork did not settle out until they reached the Main Stem.

The present work was undertaken to study the distribution and speciation of inorganic As and Sb species in the Coeur d'Alene River and to investigate the effects of the contaminated sediments on water quality. Factors affecting the mobility of As and Sb at the sediment-water interface are discussed. Besides As and Sb, current levels of Zn, Mn, Fe, and sulfate in the river are also reported.

EXPERIMENTAL SECTION

Sampling

Nine sampling stations were selected to study the distribution of As and Sb in the Coeur d'Alene River system (Figure 12). Samples were collected from December 1986 through June 1987 for this study. Water samples were collected using 1-L high-density linear polyethylene bottles. The containers were washed with nitric acid and rinsed with deionized water prior to sample collection. Water samples were filtered through 0.45 μm membranes and stored in a refrigerator at about 4 °C prior to chemical analysis, which usually took place within several days after collection. Filtered samples were also preserved by acidification to pH 2 with HNO_3 for Zn, Mn, and Fe analysis.

Sediment samples were taken at seven selected locations (Table 20). The sediment samples were sealed in plastic bags and stored at 4 °C in a refrigerator until used. A sediment core (22 cm in length) was also taken from the delta area at the mouth of the Coeur d'Alene River using a core sampling apparatus. Six core increments were analyzed to study the vertical distribution of As and Sb in the sediment column.

Analysis of Water Samples

A pyrrolidinecarbodithioate (PCDT) extraction procedure was used for the simultaneous determination of trivalent and pentavalent inorganic species of arsenic and antimony in natural waters. The details of the extraction procedure are given in the literature.[5] The extraction procedure not

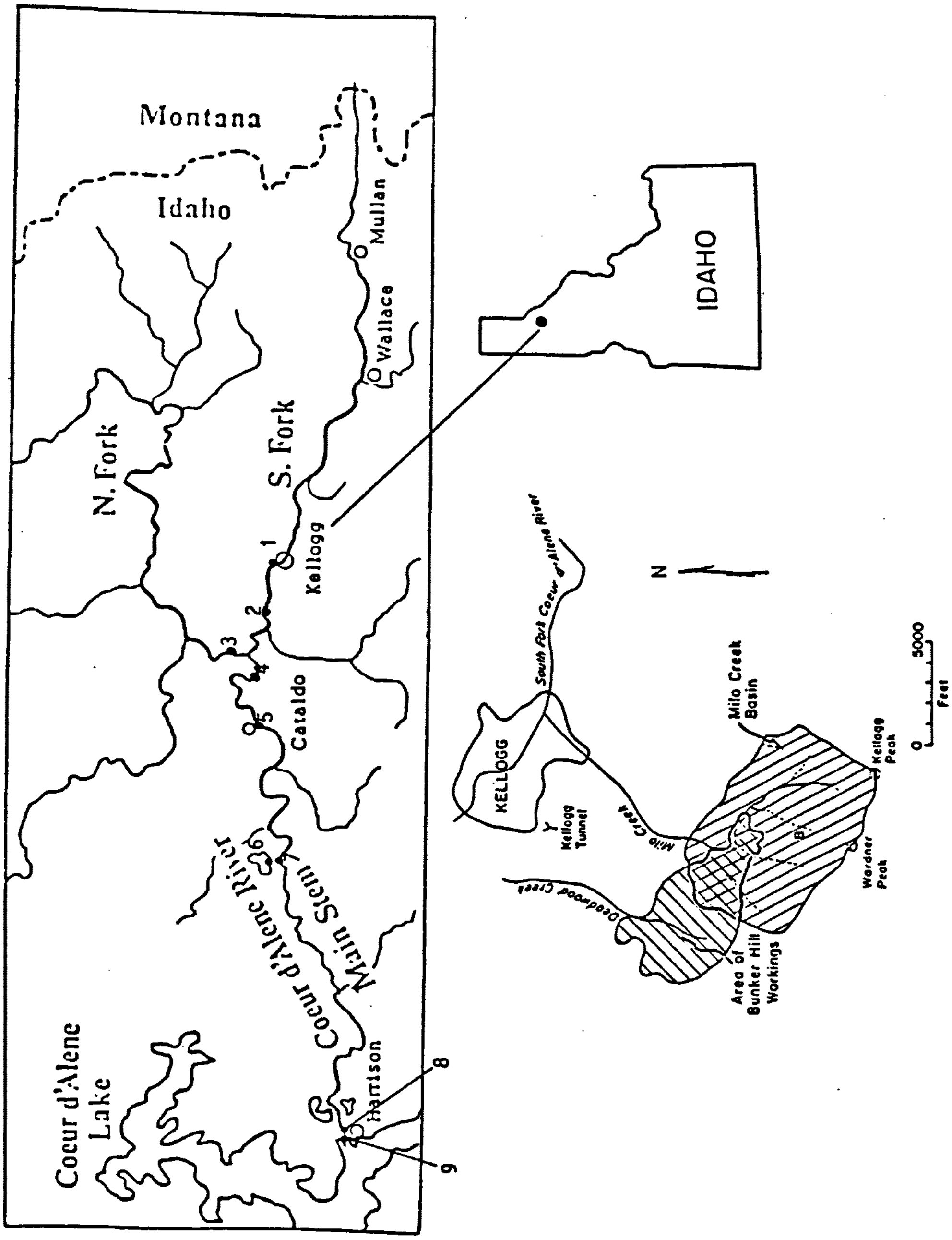

Figure 12. Location of the sampling stations in the Coeur d'Alene River.

Table 20. Description of the seven selected sediment-sampling sites.

Station	Site Description
SC-Main Stem	Near Cataldo Mission flats, very close to Station 5
SR-Main Stem	At Station 7, near the bridge beyond Rose Lake
SB-Main Stem	Near Blue Lake
SH-Main Stem	At Station 8, near Harrison
SM-Main Stem	Near the mouth of the Coeur d'Alene River
SN-North Fork	At Station 3 before the North Fork enters the Main Stem
SS-South Fork	At Station 2 of Smelterville Flats

only concentrates As and Sb species but also eliminates common interfering ions, such as the alkali metals, alkaline earth metals, halogens and phosphate. The applicability of this method to water samples with complex matrices and different chemical compositions has been reported.[5]

Samples and standards were irradiated in a TRIGA nuclear reactor and counted using an ORTEC Ge(Li) detector. The detector output was fed into an EG&G ORTEC ADCAM (Model 918) multichannel analyzer. Data from the analyzer were processed by EG&G ORTEC software on an IBM-PC. The details of the sample preparation, irradiation, and counting for NAA are given elsewhere.[5] A detection limit of 10^{-3} ng/mL As and Sb can be achieved using this extraction method and neutron activation analysis. Concentrations of Zn, Mn, and Fe were determined using an IL-353 Atomic Absorption Spectrophotometer or an ARL Model 35,000C Inductively Coupled Plasma-Atomic Emission Spectrometer. Sulfate was analyzed by a Dionex Model 2000-I ion chromatograph.

Leaching experiments were carried out to study the release of As, Sb, Zn, Mn, and Fe from the sediments. All experiments were conducted at room temperature under atmospheric pressure. In each system, a sample, usually 60 g of sediment, was placed in a 1-L high-density linear polyethylene bottle and 800 mL of distilled deionized water were added. The sediment-water mixture was kept in suspension by continuous stirring with a magnetic stirrer. The leaching experiments involved the measurement of pH and the analysis of leachates for As, Sb, Zn, Mn, and Fe.

Arsenic and Sb in the sediments were determined by a non-destructive neutron activation technique. Samples for neutron activation analysis were first air dried and ground to less than 200 mesh. Approximately 0.1 gram of the dry sample was sealed in a 2/5-dram polyethylene vial. Samples and standards were irradiated together for 2 hours in the TRIGA reactor. After cooling for a few days, the samples were counted for 500-4000 seconds on the ORTEC Ge(Li) detector. Manganese, Zn and Fe in the sediments were determined by a Rigaku 3370 automated X-Ray fluorescence spectrometer.

RESULTS AND DISCUSSION

Water Quality Data

Table 21 summarizes the mean values and the ranges of As and Sb in the waters collected from the selected sites along the Coeur d'Alene River. The mean pH value of the river water samples is 7.5.

Table 21. Mean values and ranges of As and Sb in the waters of the Coeur d'Alene River for the sampling period.

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 0.082-0.190	0.247 0.112-0.351	0.021 0-0.039	1.026 0.328-1.893
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

Stations 1 and 2, located in the South Fork of the river, have shown consistently high metal readings during the course of this study. Antimony concentrations as high as 8.3 and 6.8 ng/mL have been noted at Stations 1 and 2, respectively. Arsenic concentrations of 1.2 and 1.6 ng/mL have also been observed at Stations 1 and 2, respectively. Station 3 is at the lower end of the North Fork before it enters the Main Stem. During the period of this study, Station 3 never showed As and Sb concentrations above 0.25 and 0.16 ng/mL, respectively. Water quality within the Main Stem of the Coeur d'Alene River is affected by the mixing of the North Fork and South Fork waters. Station 4 is located just below the confluence of the North Fork and South Fork. The substantially lower As and Sb concentrations at Station 4, compared with those observed at Stations 1 and 2, reflect a dilution effect after mixing with the North Fork waters. Average As and Sb concentrations in Stations 5, 7, 8, and 9 along the Main Stem ranged from 0.11 to 1.47 ng/mL and from 0.24 to 1.89 ng/mL, respectively. The main stem waters generally have considerably lower concentrations of As and Sb compared to the South Fork waters.

Figures 13 and 14 show the mean values of the trivalent and pentavalent As and Sb species in the river during the sampling period. Arsenic(III) is the predominant species in the Main Stem and South Fork, while a slightly higher concentration of As(V) is always observed in the North Fork. Contrary to As, the concentration of Sb(V) is always much higher than that of Sb(III) in all three branches of the river.

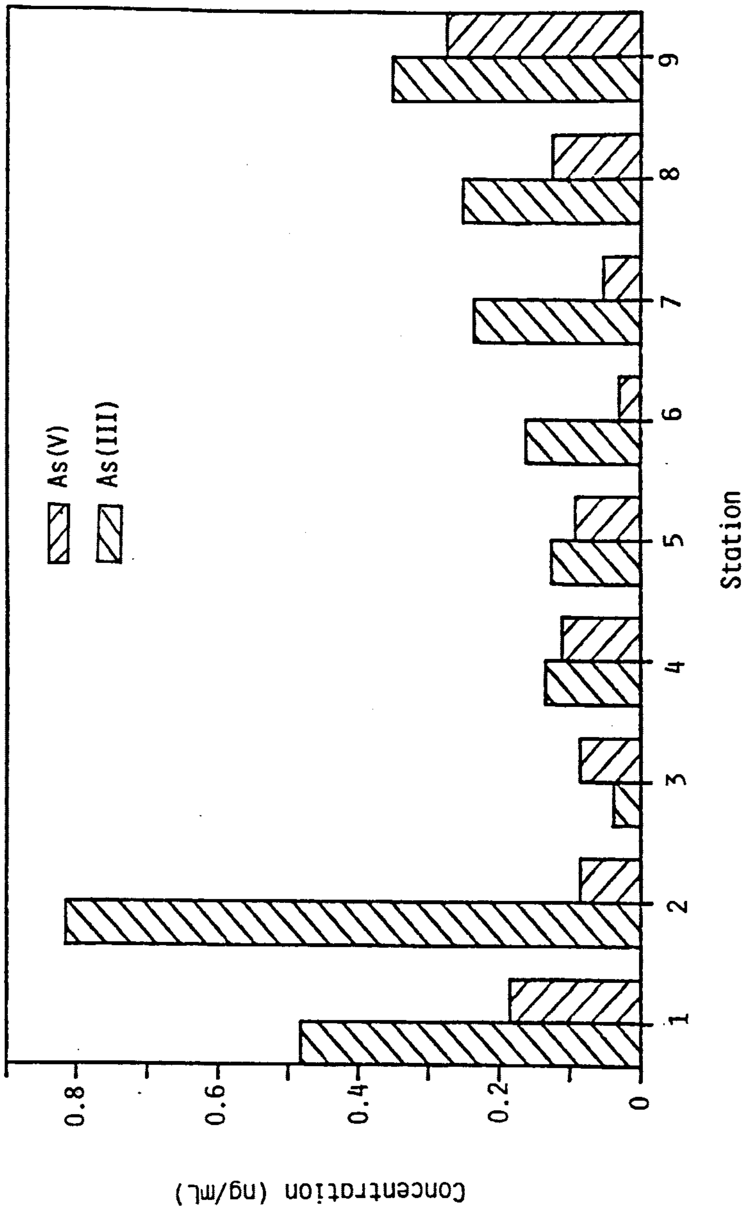

Figure 13. Mean values of As(III) and As(V) in the Coeur d'Alene River during the sampling period.

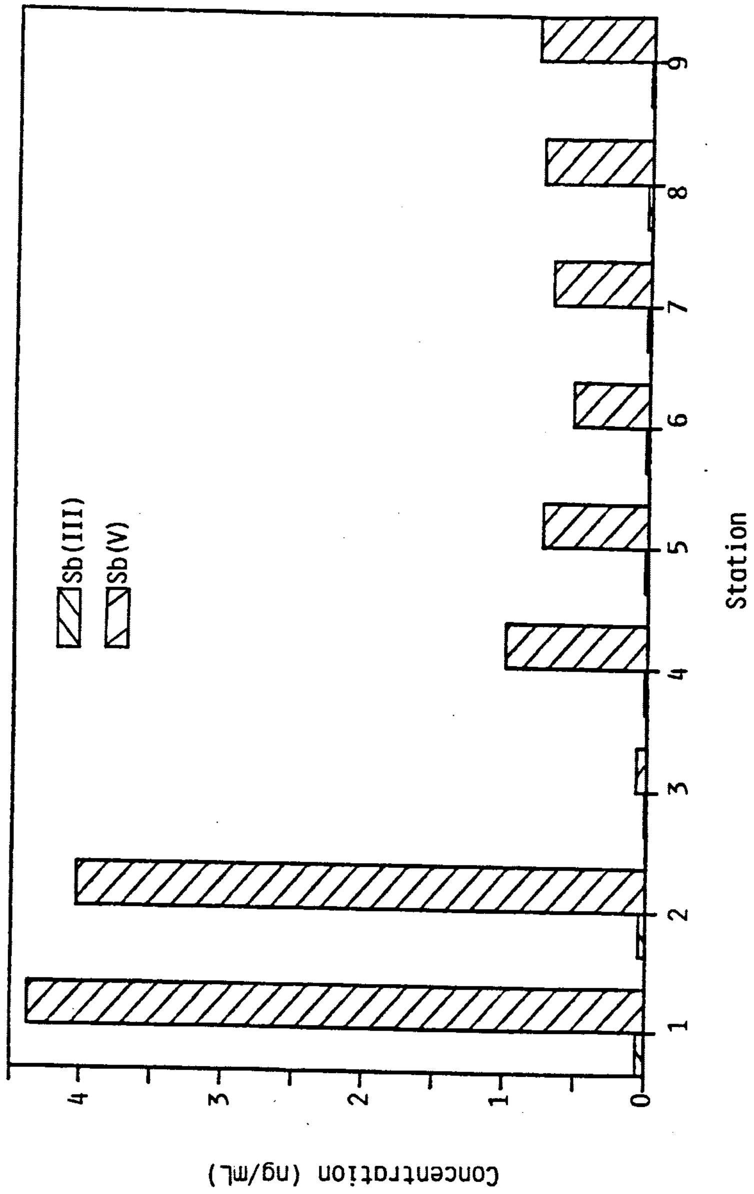

Figure 14. Mean values of Sb(III) and Sb(V) in the Coeur d'Alene River during the sampling period.

The St. Joe River, which lies south of the Coeur d'Alene River, is classified as a wild and scenic river by the National Forest Service. Water of the St. Joe River should provide some information about the background values of As and Sb in the natural environment. The As and Sb levels in the North Fork were also compared to those in the river water of the Yokushima Island in Japan, which was reported to have scarcely any pollution.[6] In addition, water samples from the delta area in Coeur d'Alene Lake at the mouth of the Coeur d'Alene River and from the southern part of Coeur d'Alene Lake, which is considered to be much less polluted, were also analyzed. The results are listed in Table 22. The As and Sb concentrations in the southern part of Lake Coeur d'Alene, about 0.36 and 0.48 ng/mL, respectively, were lower than those in the delta area (0.44 and 1.66 μg/L for As and Sb, respectively). The total As concentration in the North Fork (0.12 μg/L) was comparable to the values from the St. Joe River and from the river of Yokushima Island. The total Sb level of the former, however, was higher than the levels of the other two rivers.

Table 22. As and Sb levels in North Fork of Coeur d'Alene River, in Lake Coeur d'Alene, in St. Joe River, and in the river water around the Yokushima Island of Japan.

Station	Date	As(III)+As(V) (ng/mL)	Sb(III)+Sb(V) (ng/mL)
North Fork	6-26-87	0.115±0.016	0.164±0.029
Southern Lake Coeur d'Alene	8-15-87	0.357±0.005	0.480±0.011
Delta Area	8-15-87	0.440±0.005	1.656±0.020
St. Joe River	8-15-87	0.276±0.004	0.044±0.005
River in Japan*		0.210±0.020	0.013±0.002

*Reference 10

Figure 15 shows the concentrations of As and Sb in the surface sediments for the stations along the Main Stem of the river. Arsenic concentration in the sediments appears to increase towards the mouth of the river (117 μg/g at Cataldo - 209 μg/g at Harrison). Although As concentration in the surface sediments was much higher than that of Sb (As/Sb ratio varies from 2-4), the As level in the water was relatively low (As/Sb ratio varies from 0.2-0.8).

Table 23 summarizes the mean values and ranges of Zn, Fe, Mn, and sulfate in the Coeur d'Alene River waters during the sampling period. Zinc, Mn, and sulfate were also used as water quality indicators because both $ZnSO_4$ and $MnSO_4$ are very soluble. High Zn, Mn and Fe levels were observed at Station 2 of the South Fork. Zinc and Mn in the North Fork (Station 3) were found only in trace amounts (<0.03 μg/mL). Zinc and Mn

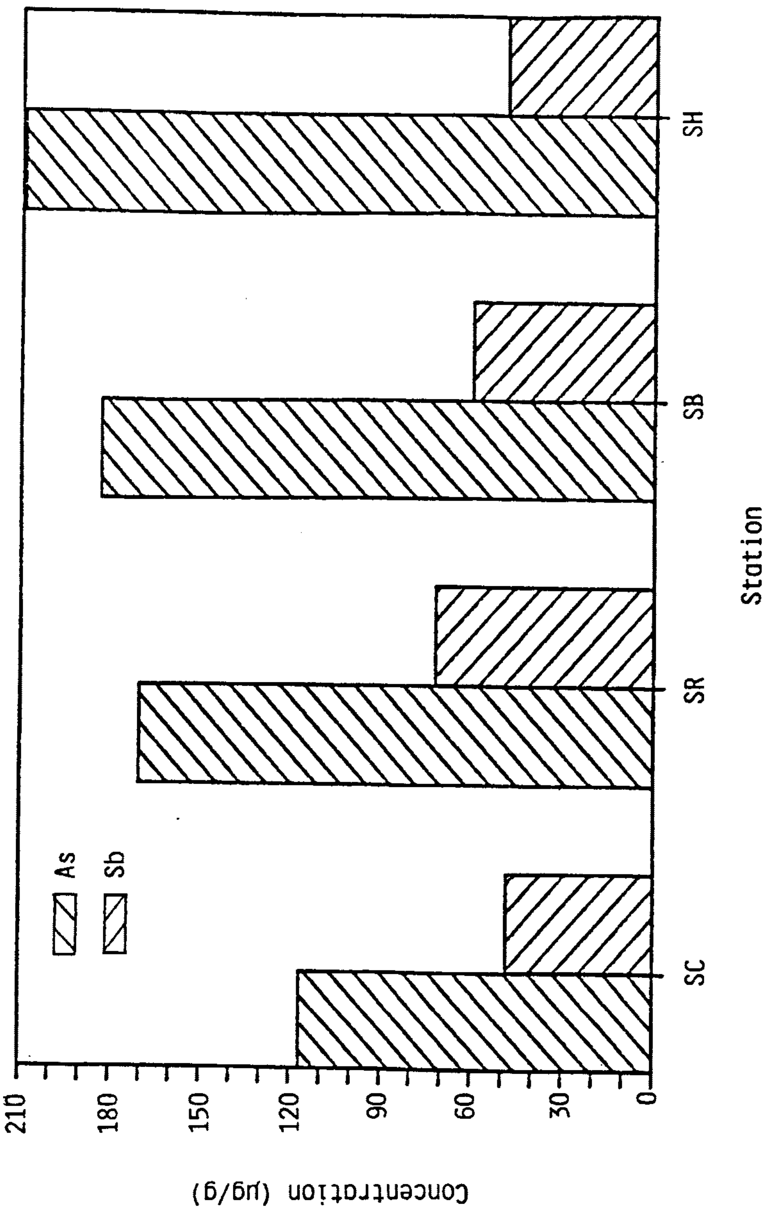

Figure 15. Concentrations of As and Sb in the surface sediments along the Main Stem of the Coeur d'Alene River.

Table 23. Mean values and ranges of Zn, Mn, Fe, and sulfate in the waters of the Coeur d'Alene River for the sampling period.

	Zn		Mn		Fe		SO_4^{2-}	
Station	Mean	Range	Mean	Range	Mean	Range	Mean	Range
1	1.48	0.67-2.05	0.16	0.07-0.26	0.02	0-0.06	23.11	6.41-40.23
2	2.73	0.79-4.23	0.98	0.17-1.84	0.23	0-0.73	54.27	7.57-120.38
3	0.02	0.01-0.03	<0.01	0-0.02	N.D.	nil	2.69	2.13-3.34
4	0.75	0.40-1.17	0.34	0.10-0.47	0.07	0-0.19	17.00	5.31-35.18
5	0.47	0.19-0.75	0.23	0.05-0.38	0.07	0.01-0.31	12.64	4.37-24.73
6	0.04	0.01-0.08	0.14	0.08-0.24	0.15	0.11-0.21	7.95	6.66-9.00
7	0.52	0.25-1.03	0.30	0.07-0.79	0.11	0.04-0.23	13.03	4.20-26.60
8	0.53	0.24-1.07	0.29	0.09-0.71	0.12	0.04-0.21	13.30	4.43-26.75
9	0.25	0.18-0.43	0.17	0.09-0.26	0.11	0.08-0.19	7.86	4.08-12.75

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

in the Main Stem have overall mean values of 0.50 μg/mL and 0.27 μg/ml, respectively, ranging from 0.18 to 1.07 μg/mL for Zn and 0.05 to 0.79 μg/mL for Mn. Sulfate concentrations in the river were high with mean values varying from 2.69 μg/mL at Station 3 of the North Fork to 54.27 μg/mL at Station 2 of the South Fork.

In general, the concentrations of As, Sb, SO_4^{2-} and the other trace metals studied were found to be higher in the low flow of winter and lower in the high flow during the spring months at the time of snow melt. An increase of metal and sulfate concentrations was also observed in some stations in June when the water level falls down. Figure 16 shows the seasonal variations in the concentrations of the ions studied at Station 2 during the sampling period. Similar trends were observed at other stations.

Station 6 was established in Rose Lake at a point close to the river. During high water in the spring, the river sometimes passes through a culvert and seeps into Rose Lake. This station was arbitrarily chosen to evaluate contamination from the community of the river. Arsenic(III) and Sb(V) were still the predominant species observed in the lake water samples. The low concentrations of Zn, Mn, and sulfate in the lake water suggested that there was no obvious correlation between Rose Lake and the main stem during the sampling period.

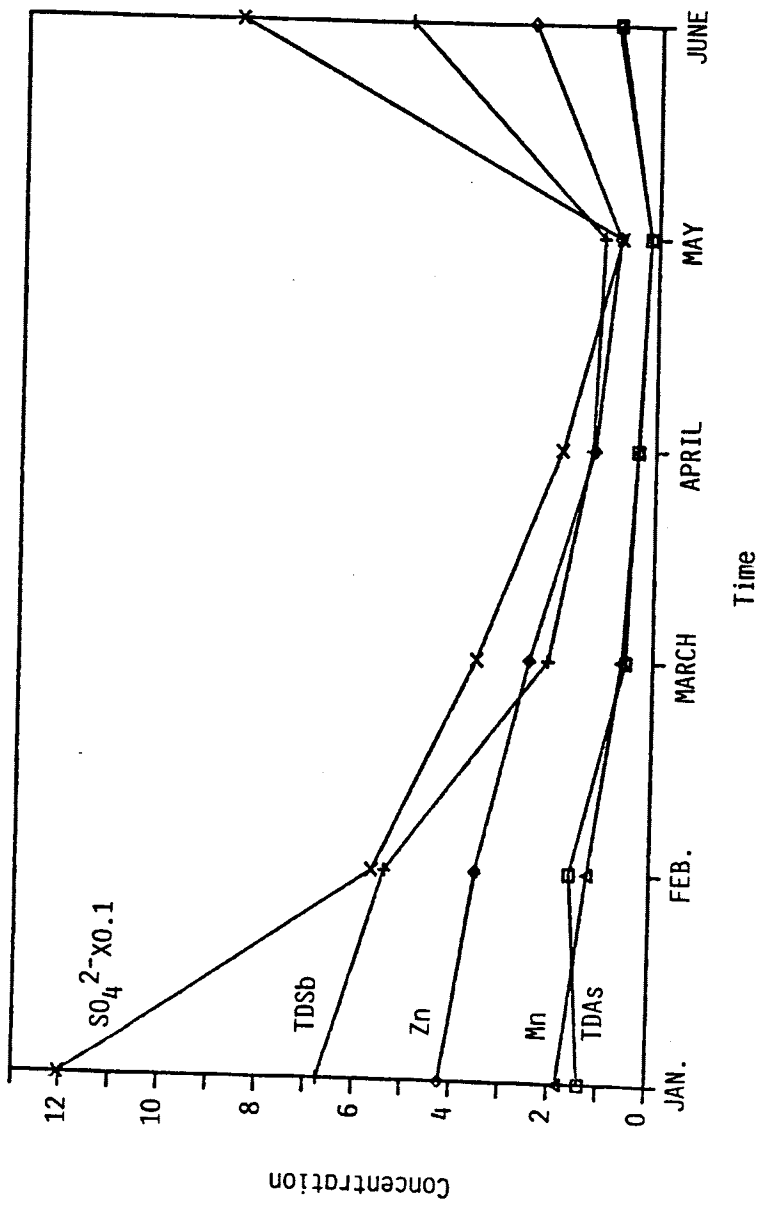

Figure 16. Variation in the concentrations of TDAs, TDSb, Zn, Mn, and SO_4^{2-} at Station 2 as a function of time during the sampling period. TDAs = As(III) + As(V), TDSb = Sb(III) + Sb(V).

Leaching of As, Sb and Other Metals from the Sediments

X-ray diffraction showed that the sediment samples were mainly composed of quartz, muscovite, and siderite with small quantities of Kaolinite. Potassium-feldspar existed in all samples. The clay fraction made up about 2.0-3.2% of the bulk sample and was composed of essentially the same minerals as found in the bulk samples. The diffraction patterns for the clay fraction were generally less intense than those of the bulk samples, implying a poorer crystallinity.

The As, Sb, Zn, Fe, and Mn contents of the sediments studied are presented in Table 24. The North Fork sediments (SN) showed much lower metal contents than those from the Main Stem Coeur d'Alene River.

Table 24. Concentrations of As, Sb, Zn, Mn, and Fe in the sediments collected from the Coeur d'Alene River.

	µg/g				%
Sample	As	Sb	Zn	Mn	Fe
SC	117.05	48.72	5703	6081	8.30
SR	170.43	72.11	9262	8163	10.49
SB	183.50	60.19	5679	11323	12.41
SH	209.09	49.20	4409	10021	11.82
SM	147.39	48.71	4148	8465	10.05
SN	10.68	1.91	142	186	2.57
SS	111.00	136.81	9430	17285	21.24

As and Sb were determined by INAA based on quadruplicate analyses.
Zn, Mn, and Fe were determined by XRF.
Description of sampling sites is given in Table 20.

Six sediment samples, five from the Main Stem and one from the North Fork, were leached with deionized water under aerobic conditions with stirring. The description of sampling sites is given in Table 20. Leachates from the sediments in all the leaching experiments showed very little variation in pH during the course of leaching. The mean pH in the leachates was 6.9. Cumulative releases of As and Sb from the Main Stem sediments (SR) are shown in Figure 17. Trends observed in other sediments from the Main Stem were similar to those of sediment SR. Antimony(V) was the predominant Sb species released during leaching. Conversely, leaching under the same conditions resulted in the almost exclusive release of As(III). The releases of total arsenic [TDAs=As(III)+As(V)] appeared to approach asymptotic limits. Although the As content in the sediments was higher than that of Sb, the release of TDSb always exceeded that of TDAs after a short leaching period. The same trend was observed in the concentrations of As and Sb in the South Fork and Main Stem waters. The leaching experiments yielded results correlating with the observed river water quality with respect to arsenic and antimony.

Leaching of metals from sediments in a river should also depend upon the flow of water. The effect was more pronounced at low flow because of longer sediment-water contact time and smaller water volume in the river. The As and Sb concentrations in the Coeur d'Alene River were always lower during the high flow rate in the spring runoff. Higher As and Sb

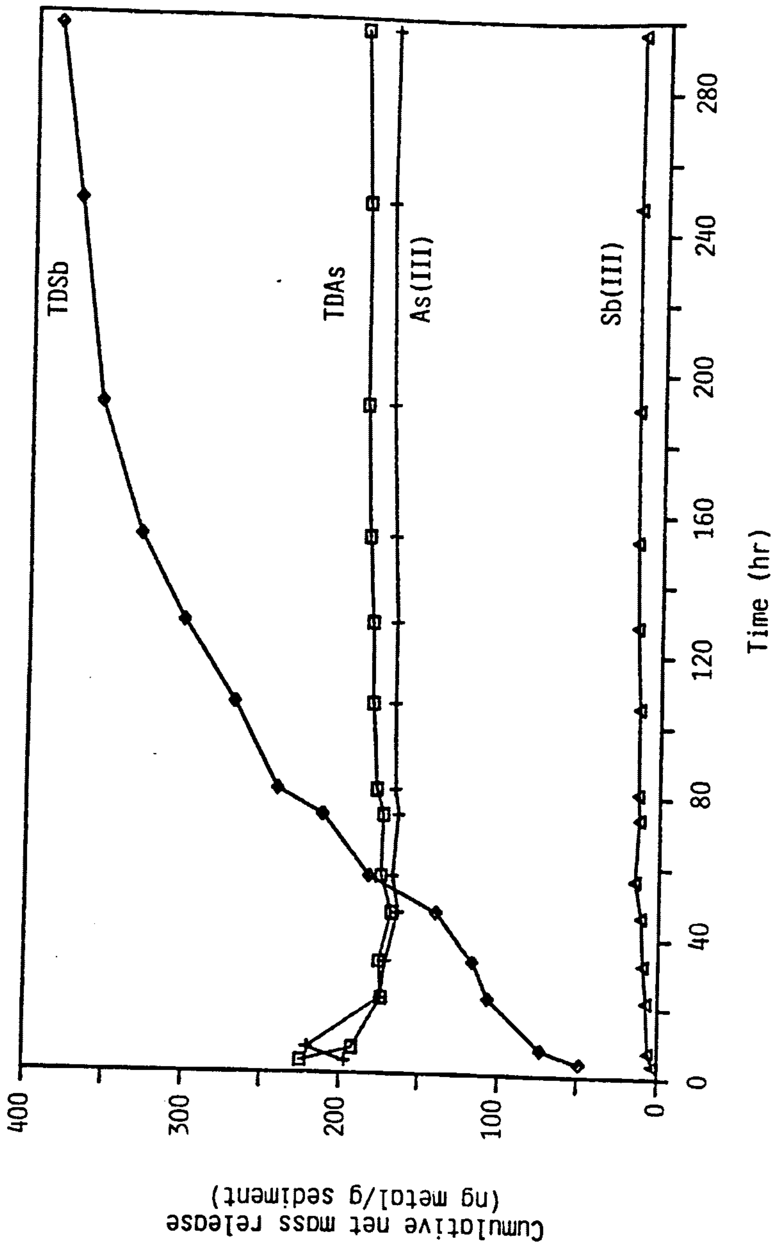

Figure 17. Cumulative releases of As and Sb from sediment SR. TDAs = As(III) + As(V), TDSb = Sb(III) + Sb(V).

concentrations were observed in the river water when the flow was low and groundwater discharge was the major source.

Sediments from the North Fork were relatively uncontaminated with mining wastes. Arsenic and antimony concentrations in the sediment samples from the North Fork of the river were one-tenth to one-thirty-fifth of those from the Main Stem. Leaching experiments also indicated that As(III) and Sb(V) were the major leachable species from the North Fork sediments. The amounts of As and Sb released during leaching were substantially lower than those from the Main Stem, in agreement with the water quality data observed in the river. However, arsenic(V) concentration was found to be slightly higher than that of As(III) in the North Fork water samples, in contrast to the results observed from the leaching experiments. Several competing processes could modify the concentrations of the arsenic species in natural waters, including oxidization of arsenite to arsenate or the reverse reaction, precipitation and adsorption reaction, etc. The kinetics of the arsenite-arsenate transformation in river waters are still not well understood.

The cumulative net mass releases of Zn, Mn, and Fe from sediment SR are illustrated in Figure 18. The other sediment samples behaved similarly to SR in the leaching process. The amounts of Fe leached were lower than those of Zn and Mn. The releases of these metals from the Main Stem sediments were also substantially higher than those from the North Fork

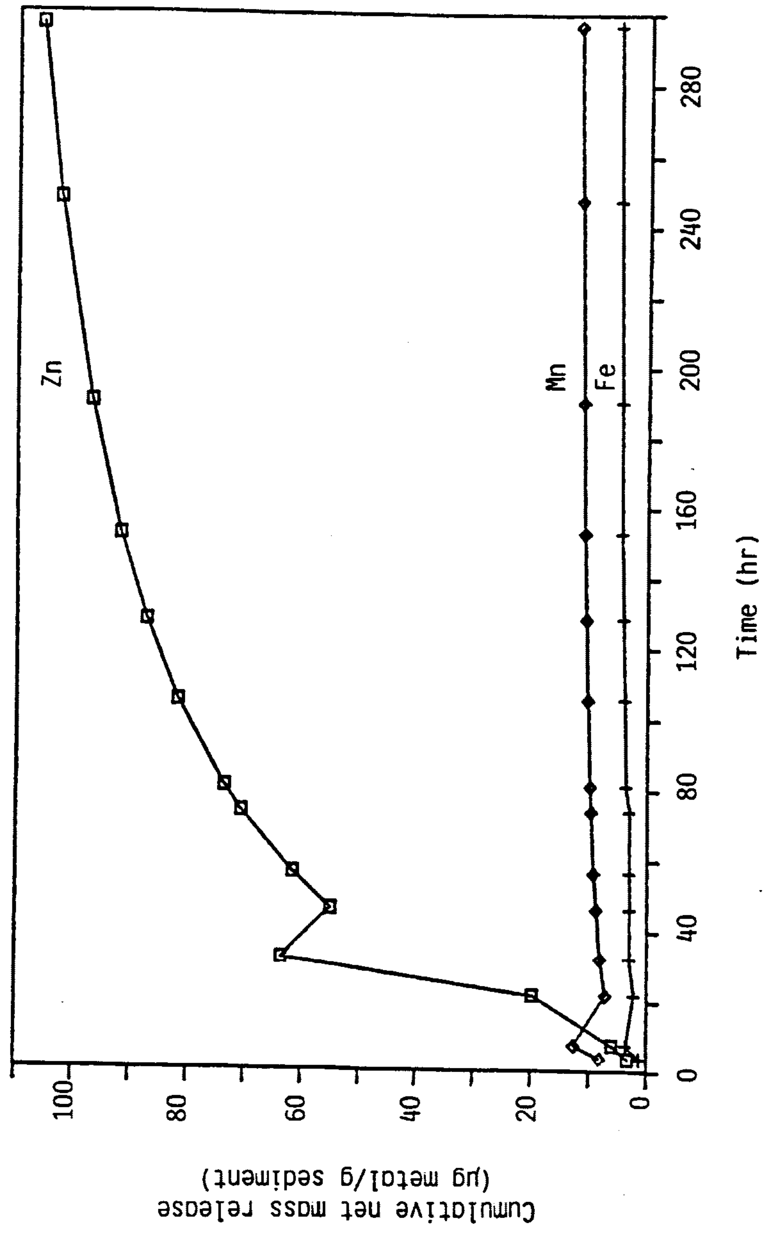

Figure 18. Cumulative releases of Zn, Mn, and Fe from sediment SR.

(sediment SN). The results are consistent with those observed in the river waters.

Depth Profiles of Arsenic and Antimony in Sediments

Table 25 shows the vertical distribution of As, Sb, Fe, and Mn in a sediment core from the delta area of Lake Coeur d'Alene at the mouth of the Coeur d'Alene River. The surface sediments (0 - 7 cm) were brown, while those below were dark grey. The sediment core showed high As and Sb concentrations at the surface (197 μg/g As and 58 μg/g Sb), decreasing with depth to concentrations of a few μg/g. The concentration profiles of As and Sb paralleled those of Fe and Mn, and the sediments showed a very strong correlation between the vertical distributions of As and Sb and those of Fe and Mn, with correlation coefficients of 0.99. The fixation of As in

Table 25. Vertical distribution of As, Sb, Fe, and Mn in the sediments from the delta area of Lake Coeur d'Alene (0-22 cm).

	μg/g		%	
Depth(cm)	As	Sb	Fe	Mn
0.5	196.96	58.06	11.19	0.97
4.5	146.63	47.13	9.20	0.71
8.5	7.84	2.99	2.44	0.06
14.5	7.37	1.96	2.35	0.02
18.0	6.21	1.82	2.34	0.02
21.5	5.65	2.20	2.22	0.02

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

sediments has been attributed to adsorption onto hydrous Fe oxide.[7-9] Arsenic may also become incorporated into sediments by coprecipitation at the time of formation of the hydrous oxides.[10-12] Associations between sediment As and Mn have also been reported.[7,13] Our results indicate that both As and Sb were associated with Fe and Mn. The abnormally high As and Sb concentrations in the surface sediments resulted from the input of these trace metals from the Coeur d'Alene River and were likely influenced by the physicalchemical properties of the sedimentary column. It was reported that after burial of surface sediments, Fe, Mn, As, and Sb compounds redissolve under reducing conditions at depth and migrated upwards to the top layers where substantial amounts of As and Sb had become immobilized along with Fe and Mn in the oxidizing zone.[7,8,13]

Effects of Free Iron Oxides and Manganese Oxides upon the Release of Arsenic and Antimony during Water-Sediment Interactions

Both iron oxides and manganese oxides possess high affinities for many trace metals. To examine the effects of sediment iron oxides and manganese oxides upon the partitioning of As and Sb between the river sediments and the water, the chromatographic distribution coefficient (D) was used and a citrate-dithionite extraction method[14,16] was employed to determine the amounts of free iron oxides and manganese oxides in the Main Stem sediments used in the leaching experiments. To obtain such D values, total As concentrations ($\mu g/g$) in sediments were divided by the cumulative net mass release of total As (µg/g) following 10 days of leaching. The same was true for Sb. The D values were obtained in our experiments following a procedure described in the literature.[17] Values of D for the sediments and their corresponding free iron oxides and manganese oxides are summarized in Table 26. A high D value signifies that a trace element in the sediment was retained more strongly than another one with a low D value.

Table 26. Arsenic and antimony distribution coefficients (D) following 10 days of leaching and the amounts of free iron oxides and manganese oxides.

Sediment	D_{As}	D_{Sb}	% Fe as Free Iron Oxides	% Mn as Free Manganese Oxides
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

Description of sampling sites is given in Table 20.

The linear correlation coefficients between the distribution coefficients for As and free iron oxides and manganese oxides were 0.87 and 0.83, respectively. The corresponding correlation coefficients for Sb and free iron oxides and manganese oxides were 0.90 and 0.75, respectively. The results suggest that the existence of free iron oxides and manganese oxides in the sediments is a significant factor affecting the release of As and Sb during water-sediment interactions. The higher D values for As relative to Sb (Table 26) also suggest that the former is more strongly retained than the latter. Under weakly acidic to basic conditions, As(V) can be coprecipitated on hydrous iron oxides with the formation of the mineral scorodite ($FeAsO_4 \cdot 2H_2O$), which is very insoluble.[10-12] It is speculated that both stronger adsorption of As on the existing oxide surfaces and the incorporation of As into the sediments by coprecipitation at the time of formation of hydrous oxides are factors responsible for the observation that, although As concentration was higher than Sb concentration in the sediments, the reverse was observed in the Main Stem and the South Fork river water.

Effect of pH on Mobilization of Arsenic and Antimony

On a regional scale, acid precipitation is probably an important factor affecting metal mobility in surface water. To study the release of arsenic and antimony with respect to acidity, sediment sample (SR) from the Main Stem was leached for 40 hours at controlled pH. Table 27 presents the results. The releases of total As and Sb from the sediments in aqueous solution followed a predictable pattern of increasing release with decreasing pH. The release of As and Sb also rose sharply at high pH. This behavior is distinct of As and Sb because they both possess an anion chemistry in aqueous solution.

Table 27. Release of As, Sb, Zn, Mn, and Fe from 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

As and Sb concentrations in ng/g of sediment.
Other metals released are given in µg/g sediment.

The results indicate that pH variation not only influences the mobility of As and Sb, but also alters the distribution of the metal species. The observation of an enhanced As and Sb solubility both at low and at high pH in our leaching experiments is significant. Since lime treatment is a common method used to deal with acid mine drainage and waste waters related to mine tailings, the discharge of lime-treated waste water with high pH might result in a higher As and Sb release from the sediment in contact. A near neutral pH condition would favor the long-term stability of mine wastes with respect to As and Sb.

CONCLUSION

Arsenic(III) was the predominant form of inorganic As in the South Fork and Main Stem of the Coeur d'Alene River, whereas the North Fork generally had higher As(V) concentrations. The major inorganic Sb species was Sb(V) in all three branches of the river. The Main Stem sediments were highly contaminated with As and Sb. In general, the water quality observed in the field was correlated with the results observed from the laboratory leaching experiments. Interaction of water with the contaminated sediments was likely to be a major factor controlling the distribution of As and Sb species in that aquatic environment. Release of As and Sb was related to the free iron oxides and manganese oxides present in the sediments. Mobilization of As and Sb was more likely to occur in sediments low in iron oxides and manganese oxides. Arsenic was more strongly retained in the sediments than Sb, as reflected by the observation that, although the concentrations of As in the Main Stem sediments were higher than those of Sb, the reverse was true in the Main Stem river water and in the solutions of the leaching experiments. pH fluctuation in water also affected the release of As and Sb from sediments. Acid precipitation is an important factor affecting As and Sb mobility in surface water. On the other hand, the sharply increasing release of As and Sb at high pH might also influence the application of a lime treatment method to reduce metal content in acid mine drainage and waste waters related to mine tailings.

The extent to which As and Sb are leached into the river water is also dependent on the flow of the river. The effect is more pronounced at low flow. It is possible that even if there is zero discharge of mine wastes into the river in the future, the water quality of the river may remain affected by the leaching of the polluted sediments, and the concentrations of As and Sb in the Main Stem may still be higher than the geochemical background values. Water quality management planning for the Coeur d'Alene River should, therefore, also consider the non-point sources of contamination, including leaching of the river sediments.

The pollution problem existing 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 to environmental planning and consideration for the Coeur d'Alene Mining District and other similar mining areas.

Acknowledgements. This work was supported in part by the Idaho Water Resources Research Institute with funding from the U.S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the reactor sharing program supported by the Department of Energy. However, the views and conclusions presented in this paper may not reflect the views and conclusions of the supporting entities.

REFERENCES

1. Davis, H. T. Environ. Sci. Technol. **1978**, 12, 276.

2. Arsenic - Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, 1977.

3. Luckey, T. D.; Venugopal, B. Metal Toxicity in Mammals, Vol. 1, Plenum Press: New York, 1977; p. 139.

4. Norbeck, P. M. M.S. Thesis, University of Idaho, Moscow, ID, 1974.

5. Mok, W. M.; Wai, C. M. Anal. Chem. **1987**, 59, 233.

6. Tanizaki, Y; Negatsuka, S. Bull. Chem. Soc. Jpn. **1983**, 56, 619.

7. Crecelius, E. A. Limnol. Oceanogr. **1975**, 20, 441.

8. Farmer, J. G.; Cross, J. D. Radiochem. Radioanal. Lett. **1979**, 39, 429.

9. Neal, C; Elderfield, H.; Chester, R. Mar. Chem. **1979**, 7, 207.

10. Mok, W. M.; Riley, J. A.; Wai, C. M. Water Res. **1988**, in press.

11. Aggett, J; Lybley, S. Environ. Sci. Technol. **1986**, 20, 183.

12. Wilson, F. H.; Hawkins, D. B. Environ. Geol. **1978**, 2, 195.

13. Takamatsu, T; Kawashima, M.; Koyama, M. Water Res. **1985**, 19, 1029.

14. Jackson, M. L. "Soil Chemical Analysis - Advanced Course," 2nd ed., published by the author, University of Wisconsin, Madison, WI, 1969.

15. Anderson, B. J.; Jenne, E. A. Soil Sci. **1970**, 109, 163.

16. Olson, R. V.; Roscoe, E. in Methods of Soil Analysis, 2nd ed.; Agronomy Monograph No. 9; Page, A. L., Ed., Madison, WI, 1982.

17. Brannon, J. M.; Patrick, Jr., W. H. Environ. Sci. Technol. **1987**, 21, 450.