ANALYTICAL TECHNIQUES FOR ARSENIC AND ANTIMONY SPECIATION STUDIES IN INTERSTITIAL WATER OF RIVER SEDIMENTS

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

Guan-Ming Shieh

May 1993

Major Professor: Chien M. Wai, Ph.D.

AUTHORIZATION TO SUBMIT

DISSERTATION

This dissertation of Guan-Ming Shieh, submitted for the degree of Doctor of Philosophy with a major in chemistry and titled "Analytical Techniques for Arsenic and Antimony Speciation Studies in Interstitial Water of River Sediments," has been reviewed in final form, 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 5/26/93
Chien M. Wai

Committee Members Ray von Wandruszka Date 5/27/93
Ray von Wandruszka

Robert L. Kirchmeier Date 5/26/93
Robert L. Kirchmeier

Henry Willmes Date 5/26/93
Henry Willmes

Department Administrator Peter R. Griffiths Date 5/28/93
Peter R. Griffiths

College Dean Kurt O. Olsson Date 6-1-93
Kurt O. Olsson

Final Approval and Acceptance by the College of Graduate Studies

Jean'ne M. Shreeve Date 6/18/93
Jean'ne M. Shreeve

ABSTRACT

Three separation techniques for obtaining interstitial water, i.e., by solvent displacement, modified centrifugation, and gas squeezing, have been investigated. A simple nitrogen gas squeezing technique utilizing an Amicon ultrafiltration cell was found effective to obtain interstitial waters from river sediments. Several analytical techniques for measuring arsenic and antimony species in natural waters were also evaluated. A solvent extraction procedure using ammonium pyrrolidinedithiocarbamate (APDC) as an extractant coupled with neutron activation analysis was chosen for arsenic and antimony speciation studies of interstitial waters in this work.

The distributions of arsenic and antimony species in natural waters and in interstitial waters of the polluted sediments of the Coeur d'Alene River in northern Idaho were investigated. High concentrations of arsenic and high ratios of As(III)/As(V) were observed in the interstitial waters obtained from the sediments of the South Fork of the river. The As and Sb levels in the interstitial waters of the sediments collected from the Coeur d'Alene River were found to be proportional to the levels of these elements in the surface waters, indicating a correlation of pollutants between waters and sediments. The distribution of As species in deep well waters of the Blackfoot Disease endemic area in southwest Taiwan was also studied. High concentrations of As(III) were found in the well waters which may be related to the Blackfoot Disease.

ACKNOWLEDGMENTS

The author wishes to express his sincerest gratitude to Dr. Chien M. Wai for his valuable advice, continuing encouragement and extraordinary patience throughout the academic research and the thesis preparation.

The author would also like to acknowledge many other special people:

- Dr. Ray von Wandruszka for his helpful comments on the manuscript and his instructive counseling.
- Dr. Robert Kirchmeier for his valuable review of the manuscript and suggestions.
- Dr. Henry Willmes for his useful guidance in neutron activation analysis and criticism of manuscripts.

Special thanks are extended to:

- Dr. Jean'ne M. Shreeve for providing an opportunity to study in Idaho which made my stay both educational and enjoyable.
- Dr. Peter Griffiths for his kindly assistance in my curriculum arrangement.
- Professor M. S. Young and his research group at Taiwan National Tsing Hua University for their support in the Blackfoot Disease Study.
- Ms. LeNelle McInturff for her extreme patience in editing the manuscript.
- Dr. Wai's research group for their friendship and cooperation.

Last, but not least, the author is deeply indebted for the support, patience and understanding of my parents, my wife Ling-Li, and my children, Edison, Isaac, and Esther.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

Page

TABLE OF CONTENTS (continued)

Page

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF ABBREVIATIONS

CHEMICALS

APCDT	Ammonium pyrrolidinecarbodithioate (same as APDC)
APDC	Ammonium pyrrolidinedithiocarbamate
DBDTC	Dibenzyldithiocarbamate
DMA	Dimethylarsonic acid
FDDC	Bis(trifluoroethyl)-dithiocarbamate
MIBK	Methyl isobutyl ketone
MMA	Monomethylarsonic acid
MTG	Methylthiogycolate
PCDT	Pyrrolidinecarbodithioate (same as PDC)
PDC	Pyrrolidinedithiocarbamate
TMS	Trimethylsilyl

ANALYTICAL MEANS

AAS	Atomic absorption spectroscopy
ASV	Anodic stripping voltammetry
CD	Conductivity detector
ECD	Electron capture detector
FID	Flame ionization detector
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectroscopy
HG	Hydride generation
HGAAS	Hydride generation atomic absorption spectroscopy
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled argon plasma-atomic emission spectroscopy

CHAPTER ONE

INTRODUCTION

1.1 Arsenic and Antimony Species in Water and Sediments

Arsenic (As) and antimony (Sb) are Group VA elements, also known as pnictides. They occur naturally in soil, mineral water, and sediments with metalloid properties. In water, trivalent and pentavalent arsenic and antimony are predominant species.[1,2] Due to their ubiquitous distribution and toxic properties, arsenic and antimony have become important trace elements in environmental studies. The biological toxicities of arsenic and antimony depend on their chemical form and oxidation state.[4] The total concentrations of As and Sb cannot reliably predict bioavailability, toxicity and distribution in the environment because the mobility, transport, and partitioning of these elements in aquatic systems are a function of the chemical structure. Many biochemical and geochemical processes can drive the speciation reactions and affect the distribution of these elements in sediment/water systems. Thus, trace metal speciation information is more useful than total element concentrations in assessing the environmental impact of a given pollutant. The concentration and transformation of trace elements in water are achieved through sorption/desorption and dissolution/precipitation reactions. Knowledge of chemical speciation of trace elements in sediments is important in the study of pollution potential.[5] Furthermore, sediment interstitial waters are the key phase in the transport of

trace elements from the sediment to the surface water and vice versa. Therefore, it is necessary to investigate the speciation of trace elements in interstitial waters to understand the fate of pollutants in sediments.

Geochemical modeling results indicate that under most environmental conditions As(III) is present as arsenous acid (H_3AsO_3), while As(V) is arsenic acid (H_3AsO_4).[6] Methylstibonic acid [$CH_3SbO(OH)_2$] and antimonates [$Sb(OH)_6^-$] are the major species of Sb(III) and Sb(V). The distribution of the As and Sb species in aqueous systems is controlled by Eh and pH. However, in natural water systems, biotic activities and some metal oxides can affect the distribution of these species. Organic As and Sb compounds, under most environmental conditions, are not major species in natural water. Therefore, trivalent and pentavalent species of arsenic and antimony are the main species of study in this paper.

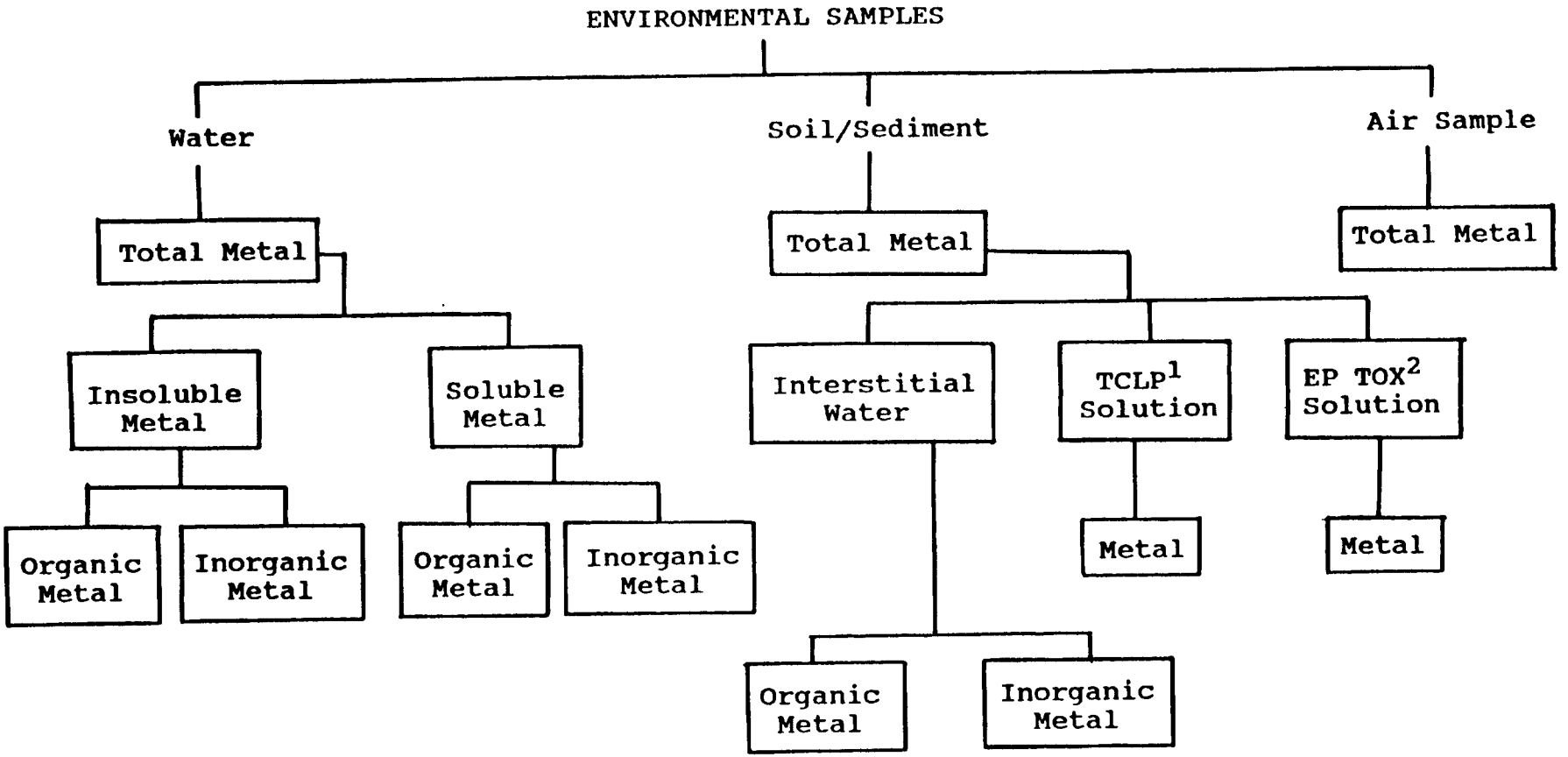
1.2 Analytical Aspects

The development of analytical techniques to reliably measure the concentrations of various chemical forms of arsenic and antimony in natural water is a challenging problem for analytical chemists. In addition, the development of an efficient preliminary extraction method for interstitial water, which must not alter the equilibria between the various chemical species in the sample, is very important. Atomic absorption spectroscopy (AAS), neutron activation analysis (NAA), hydride generation atomic absorption spectroscopy (HGAAS), inductively coupled plasma-mass spectrometry (ICP-MS)

and ion chromatography (IC) were used to study the ability to measure the different species of metal concentrations. In this research both surface water and interstitial water samples were studied for chemical speciation. Since inorganic arsenic and antimony species are predominant in the natural water system, they were the focus of speciation in this study (Figure 1.1). Total insoluble metal and organic metal complexes in water and sediments were also measured.

1.3 Objectives of this Research

There were many acid digestion, extraction, and leaching techniques that have been extensively applied to trace element analysis in sediments and soils. In recent years, the EPA Office of Solid Waste (OSW) has increased efforts to develop more precise extraction methods for testing toxicity leaching processes for metals and organic pollutants. For instance, on March 29, 1990, the EPA promulgated the "Toxicity Characteristic Leaching Procedure" (TCLP)[7] to study the contaminant concentrations in TCLP extracts. This extraction technique gradually will replace the previous "Extraction Procedure Toxicity Test"[8] as the regulatory extraction method for solid waste management. The distribution of trace metals and speciation in interstitial waters of sediments is very important in assessing the potential impact of leaching and



1 Toxic Characteristic Leaching Procedure, EPA, SW-846 method 1311, 1990.

2 Extraction Procedure Toxicity, EPA, SW-846 method 1310, 1990.

Figure 1.1 Analytical Scheme of Environmental Sample for Metal Analysis

toxicity in overlying water. The objectives of this research are summarized as follows:

1. To develop an efficient extraction technique to remove interstitial water from sediments for speciation studies.
2. To evaluate different analytical techniques for arsenic and antimony speciation in interstitial water.
3. To monitor the arsenic and antimony species in interstitial water of sediments along the Coeur d'Alene River and to study the mobilization of these elements in sediments, interstitial water and overlying water.
4. To investigate the environmental impact and toxicity of arsenic in endemic areas of metallic poison.

REFERENCES

1. World Health Organization Geneva Environmental Health Criteria 18:13 (1981).
2. Carson, B.L.; Ellis, H.V., III and McCann, J.L. Toxicology and Biological Monitoring of Metals in Humans, Lewis Publishers Inc., p. 21 (1986).
3. Smith, J.D. The Chemistry of Arsenic, Antimony and Bismuth, Pergamon Press, p. 551 (1973).
4. Arsenic - Medical and Biological Effects of Environmental Pollutants, National Academy of Science (1977).
5. Batley, G.E. Trace Element Speciation: Analytical Methods and Problems, CRC Press (1989).
6. Battelle Pacific Northwest Laboratories Speciation of selenium and Arsenic in Natural Water and Sediments, Vol. 2 (1986).

7. U.S. EPA, SW-846 Test Methods for Evaluating Solid Waste, Method 1311 (1990).

8. U.S. EPA, SW-846, Method 1310 (1986).

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In polluted waters the toxicity of heavy metals depends on their chemical form. Some species may be able to chemically bind with extracellular proteins and other biological molecules, some may adsorb onto cell walls, and others may diffuse through cell membranes. The interactions of metal species with individual cells determine the toxic levels in biological systems. Arsenic and antimony are the two major chemical species of interest in this study because of their toxicity. Arsenic and antimony both belong to the same periodic group and exhibit two main valences, +3 and +5, in natural water. The amount of arsenic in the environment has greatly increased during this century because it is released during coal and oil combustion and from mine wastes. For example, copper ore contains about 0.1% of arsenic, mainly as arsenic sulfide. Antimony also is released from mine wastes of other sulfide ores.

In natural waters, arsenic generally exists in the pentavalent form as $HAsO_4^{2-}$. The trivalent form, H_3AsO_3, is predominant in poorly oxygenated waters. Dimethylarsonic acid (DMA) and monomethylarsonic acid (MMA) are also found in the photic zone of seawater.[3] Trivalent antimony in the form of methylstibonic acid, $CH_3Sb(OH)_4^-$, and pentavalent antimony in the form of antimonates, $Sb(OH)_6^-$, are two major species of

antimony in natural waters. Methyl-antimony compounds also are found in natural water.[4,5]

Toxicity testing has shown that the most toxic form of arsenic is As(III), which is about 50 times more toxic than As(V) and several hundred times more toxic than MMA or DMA.[3] The toxicity of antimony is less well known; however, like arsenic, antimony is regulated as a priority pollutant by the U.S. Environmental Protection Agency (EPA) under the "Resource Conservation Recovery Act" (RCRA).

Interstitial water is the water trapped in the sediment pores or interstitial sites during accumulation of sediment particles. Hence, the terms pore water and interstitial water are used interchangeably. The speciation of interstitial water can help in understanding the chemical interaction between water and the surrounding solid phases of the sediment.[6] Interstitial water also provides the pathway for the diffusion of dissolved species across the sediment and water interface. These interactions are shown in Figure 2.1. In this study some of the most popular of the currently developed techniques for interstitial water removal are reviewed.

In natural waters, arsenic and antimony are widely distributed, yet in trace amounts. According to EPA SW-846 and 600 series analytical methods, the detection limits are 1.0 and 0.2 μg/L for arsenic and antimony, respectively, by graphite furnace atomic absorption spectroscopy. However, the

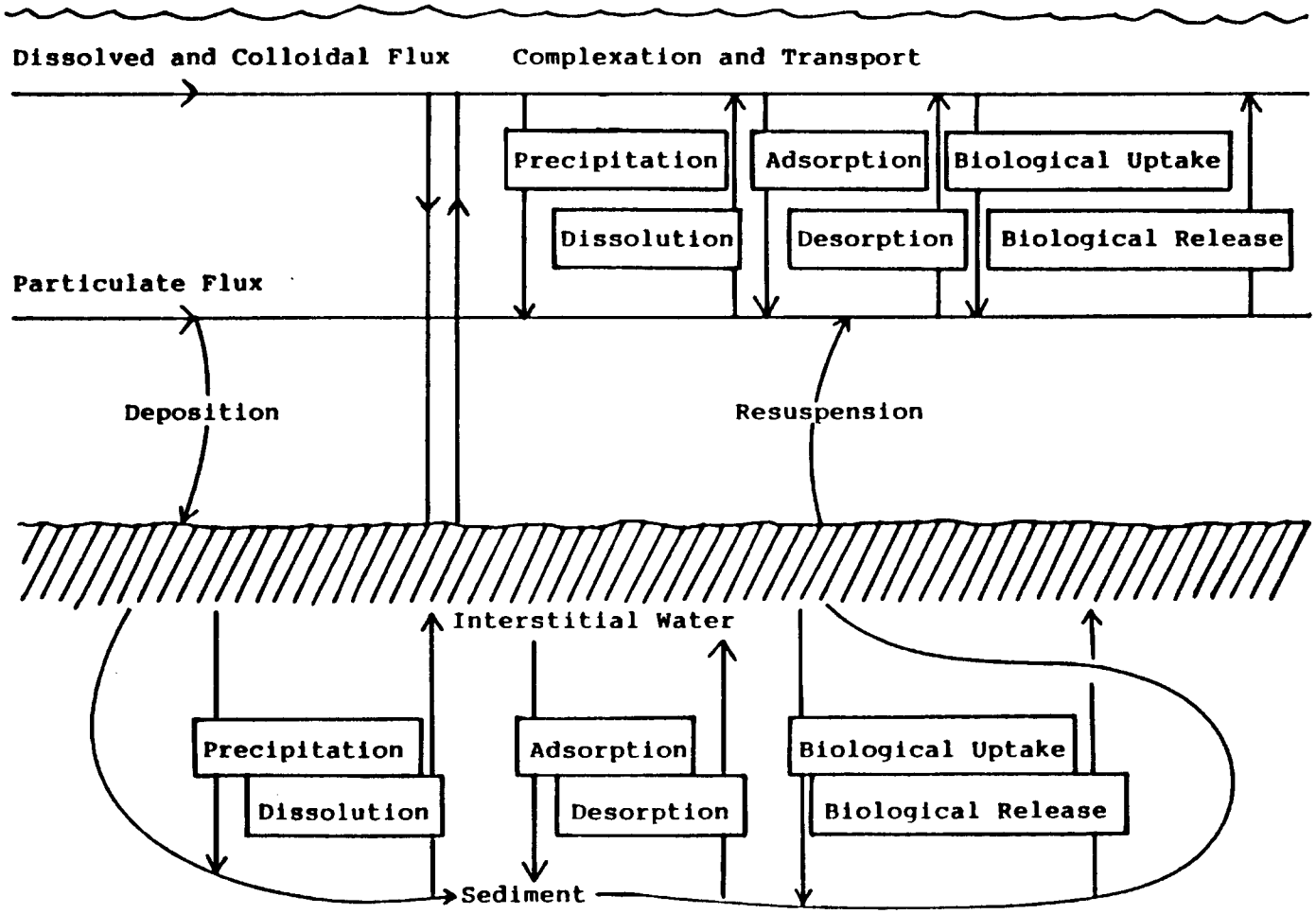


Figure 2.1 Interactions of Trace Metal Speciation in Natural Water Systems

concentrations of total As and Sb in natural waters are found to average 0.1-1.0 and 0.01-1.0 μg/L, respectively.[7,8] A separation and analytical method which is capable of determining nanogram levels of individual species is required. Some separation, preconcentration, and analytical methods including spectroscopic, chromatographic, electrochemical and nuclear techniques are discussed in this chapter.

It is very important in chemical speciation to avoid altering the various chemical species in the sample and thereby changing the equilibria. Therefore, any possible contamination and interconversion of species must be avoided. Sample collection, preservation, and storage during the sample process are the factors that most often prejudice analytical results. A general review of some of the different sample handling processes is presented in this paper.

2.2 Interstitial Water Extractions

Interstitial waters in sediments represent an important phase in the transport of trace elements from the sediment to the surface water and vice versa. It is essential to have an appropriate technique to remove representative interstitial water from sediments for investigation of trace element speciation and transport. The techniques for removing the interstitial water can be classified into squeezing, centrifugation, dilution-extraction (leaching), and dialysis techniques.

2.2.1 Squeezing technique

Squeezing methods include hydraulic squeezing,[9,10] gas-pressure squeezing,[11,12] and mechanical squeezing.[13] The mechanical squeezing techniques for removing interstitial waters are generally designed based on the principle of a low-pressure manual turn-screw piston (Appendix A). The working pressure is about 100 psi. From 100 g of slightly compacted clay, about 20-30 mL of interstitial water can be extracted. This extraction takes about 15 min. Kalil and Goldhaber[14] designed an all-plastic hydraulic squeezer to recover interstitial water. The pressure in the core can reach up to 1000 psi. Squeezing time varies from 10 min to over 1 h, depending upon sediment characteristics and the amount of water desired. Nath et al.[15] modified Manheim's[9] hydraulic squeezer by providing a Teflon inner lining to increase the volume of the sample and to avoid oxidation effects of the sample coming in contact with air. The gas-pressure squeezer is one of the most common methods employed for interstitial water extraction. Hartmann[13] and Reeburgh[11] applied up to 140 psi of gas pressure to drive interstitial water through a rubber membrane in their system (Appendix B). Nitrogen gas is normally used to supply pressure and to avoid oxidation of metal in water.

2.2.2 Centrifugation Technique

Centrifugation, commonly used for interstitial water extraction from soil, now is used increasingly for sediments.[16,17] This method only requires a small amount of

sample; however, only a small volume of interstitial water can be obtained. The conventional centrifugation technique separates water above the sediment for fine-grained compressible sediments; however, it is not efficient to separate water from coarser sediments because there are still many pores which can contain water between the particles. The conventional centrifugation technique was used for water removal in studies of fluid saturation in relation to pore water pressure in geological samples for several decades.[18-20] Improved centrifugation techniques were introduced to obtain better separation of water and sediment. For example, Batley and Giles used trichlorotrifluoroethane for solvent displacement centrifugation to separate water from sediment.[21,22] Some other organic solvents were also applied for water and sediment separation.[23-24]

Continuous-flow centrifugation, however, may leave colloidal in water. By varying the rotation speed and centrifugation time, better separation can be achieved.[25] Also, applying ultracentrifugation or density gradient techniques can avoid colloidal problems in water.[26-28]

2.2.3 Dilution-Extraction Technique

Multiple dilution extraction was carried out by Murthy and Ferrell[22] to compare with conventional pressure squeezing techniques. This method is a leaching process. The procedure is very easy to follow; however, it is hard to achieve equilibration of the metal content in the leachate.[22] More

discussion of this method appears in section 4.2.2 of Chapter Four of this dissertation.

2.2.4 Dialysis Technique

Interstitial water sampling by in situ dialysis was introduced by Hesslein[29] and Mayer.[30] This method possesses the advantages of less labor, less equipment, simplicity, and low cost. Cellulose nitrate, collodion and gelatin are typical materials used to make semipermeable membranes. The diffusion of interstitial water into dialysis bags is due not only to the membrane pore, but also to interaction between solute, solvent and membrane. In classical dialysis, the solvent (diffusate) and the solvent plus solute (retentate) are separated by a membrane. This technique has been applied to seawater samples by Hood.[31,32] Benes et al.[33-36] have applied dialysis to metal speciation in natural water. Benes' group used an acid-washed dialysis bag filled with 100 mL of distilled water immersed in a river to sample interstitial water. In situ dialysis allows maximal replication of interstitial water conditions due to its equilibrium state with the surroundings. However, the membrane used, the parts, and the chemical state of the initial filling water may become potential sources of error.[37] Polycarbonate was found unsuitable for dialyzer material because of iron precipitation problems. Cellulose membranes were found to lead to the underestimation or overestimation of interstitial water solutes. Martens and Klump[38] and Hopner[39] also observed some breakdown of cellulose-based membranes.

2.3 Speciation Techniques

2.3.1 Chromatography

Chromatographic methods are physical methods of separation in which the target components are distributed between two phases. One is a stationary phase bed and the other is a mobile phase which percolates through the stationary bed. The combination of chromatographic separation techniques with a variety of sensitive detectors has been widely applied in speciation studies now. Iverson et al.[40] used chromatographic techniques and GFAAS to study the speciation of arsenic in river water and interstitial water.

Gas chromatography (GC). Gas chromatography (GC) is one of the most frequently employed chromatographic techniques for the separation of arsenic and antimony species. However, only volatile species can be separated in GC. It is necessary in many instances to derivatize the metal species to volatile forms prior to GC separation. The separation of volatile chelates of arsenic and antimony has been an important subject of study.[41,42] Daughtroy et al.[43] chelated As(III) with diethyldithiocarbamate for separation with 5% OV-17 on Anakrom AS and detection by electron capture detector (ECD). Because As and Sb are easily converted to volatile covalent hydrides by reaction with sodium borohydride, hydridization of As and Sb becomes the most popular technique of GC analysis.[44] Arsenic(III), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and Me_3AsO are separated in the form of hydrides through a 6 m x 4.8 mm of 16.5% silicone oil on Chromosorb W

column and detected by ECD, flame ionization detector (FID) and AAS.[45-46] Antimony(III), Sb(V), $MeSb(OH)_2O$ and $Me_2Sb(OH)O$ were hydridized and separated by a 30 cm x 6 mm of 15% OV-3 on Chromosorb W column and detected by AAS.[47] Talmi and Bostick[48] hydridized MMA, DMA and alkylarsine and separated by a 1.8 m x 0.5 mm of 5% Carbowax 20M Chromosorb 101 column for microwave induced plasma analysis. The hydridization reaction is spontaneous and quantitative.

Some other derivatization techniques for changing As and Sb into volatile compounds include complexing with a trimethylsilyl (TMS) complexing agent,[49,50] 2,3-dimercapto-propanol[51] and methylthiogycolate (MTG).[52] However, various parameters such as temperature, solvent, and reaction time may affect the complexation and reduction. Nevertheless, the coupling of GC separation with highly selective and sensitive detection systems can be a powerful analytical method for trace metal speciation.

High-performance liquid chromatography (HPLC): In addition to volatile species, HPLC can separate ions and organometallic compounds. This capacity makes it potentially more suited to metal speciation studies than, for example, GC, in which separations are limited to volatile compounds at elevated temperatures. At high temperature decomposition and species conversion might occur. One other advantage of HPLC separations is that both the stationary and mobile phases can be adjusted to enhance a separation. In addition, HPLC is compatible with a variety of detectors including ultraviolet

(UV), atomic absorption spectroscopy (AAS), inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES) conductivity (CD), fluorimetry, voltammetry and refractive index.

In HPLC separations, reverse-phase columns are most often used for metal ion and organic metal speciation. Arsenic has received far more attention than antimony for speciation study in HPLC separations. Arsenic(III), As(V), MMA, and DMA were separated by a 1′ x 1/8" mic Bondapak-NH_2, Nuclesil-$N(CH_3)$-10, or nucleosil-SO_3H-10 column followed by on-line ICP-AES detection by Morita et al.[53] Because of the large pK_a of the common arsenic species, anion-exchange columns are very useful for arsenic speciation in HPLC systems.[54-56] However, reversed-phase HPLC separation, which utilizes a nonpolar stationary phase and a polar mobile phase is the most versatile and popular method for As and Sb speciation. Teflon or glass-lined stainless steel tubing and fittings are normally used in HPLC systems to avoid sample contamination. Chloride ions are particularly corrosive to stainless steel components. Inert hardware is essential in studies of trace metals in seawater.

Ion exchange chromatography (IEC). This technique utilizes either a cation resin, an anion resin, or a combination of both to separate As or Sb species. A larger sample volume can be loaded onto the column than is possible with HPLC and GC, allowing for potentially lower detection limits with this technique. Grabinski[57] used a AG 50W-X8

cation resin and AG 1-X8 anion resin to separate As(III), As(V), MMA and DMA followed by GFAAS detection. The detection limit was about 10 μg/L for individual species.

2.3.2 Hydride Generation (HG)

The hydride generation technique for the speciation of arsenic and antimony involves selective reduction of hydride-forming species to the corresponding arsine (AsH_3) and stibine (SbH_3). The process is usually generated by reduction with sodium borohydride ($NaBH_4$). The hydride forms of As and Sb then are detected by FAA, GFAA or quartz furnace AA. Only trivalent arsenic and antimony can react with sodium borohydride. Therefore, other species need to be converted into trivalent species in order to generate the hydride forms. The concentrations of other species were obtained by subtraction for the difference.

Andreae[47] applied HG techniques with a quartz cuvette burner to determine Sb(III), Sb(VI), methylstibonic acid and dimethylstibinic acid. Total inorganic antimony was reduced to stibine under low pH in a solution containing iodide and sodium borohydride; Sb(III) was reduced at neutral conditions. The organic Sb was reduced under acid conditions, then collected in a liquid-nitrogen trap and chromatographically separated followed by quartz cuvette AAS detection. A detection limit of 0.3-0.6 ng/mL was obtained. Van Cleuvenbergen et al.[58] have reviewed the use of hydride cold trapping in conjunction with quartz furnace AAS for arsenic speciation. It brings up some problems of matrix inter-

ferences and experimental design. The species of As are separated by controlled heating of the trap, making use of the different boiling points (e.g., arsine, b.p. -55°C; methylarsine, b.p. 2°C; and dimethylarsine, b.p. 35.6°C).

Braman et al.[45,59] separated As(III), As(V) and methylarsenic by controlling the pH of the sample solution because reduction of arsenic is related to the pK_a of the arsenic acid. Yamamoto et al.[60] separated and determined As(III), As(V), Sb(III) and Sb(V) with HG in conjunction with hydrogen-nitrogen flame AA. The detection limit for 100 mL was about 1 ng/L. However, interferences by other elements such as Ag^+, Cu^{2+}, Sn^{2+}, Se^{4+} and Te^{4+} were noted. Han and Wang[61] also determined As(III), As(V), Sb(III), and Sb(V) in river water by hydride-nondispersive atomic fluorescence spectrometry. Both As(V) and Sb(V) were reduced at pH 5.5 with potassium iodide (KI) for total As(V) and Sb(V) determination.

Although hydride generation separates As and Sb species, this technique involves tedious procedures and various interferences occur during the process. Factors such as kinetic control, complexation and pH were shown to affect the reduction of individual As species.[62] Smith[63] investigated the possible interference from 48 elements on arsine generation. Volumes of $NaBH_4$, gas flow rate, collection trap parameters and collection time affecting the hydride generation results were reported by Van Cleuvenbergen et al.[58]

The use of masking agents to reduce specific interference has been recommended by some researchers. Belcher et al.[64] reported that the addition of ethylenediaminetetraacetic acid (EDTA) was effective in reducing interference of arsine generation. An antifoaming reagent was used to overcome the considerable foaming exhibited by some samples such as urine.[65,66]

2.3.3 Precipitation and Adsorption

Various metal hydroxides can be used to precipitate arsenic and antimony species in solution followed by adsorption onto a gel medium. Coprecipitation of As(V) with iron(III) hydroxide has commonly been used as a preconcentration technique for arsenic in water.[67-69] Zirconium(IV) hydroxide has been used to coprecipitate As(III).[70] Nakashima[71] utilized a ferric hydroxide-surfactant-air system at pH 4 to separate Sb(III) and Sb(V) in water. Antimony was converted to stibine and determined by AAS. Sturgeon et al.[72] chelated Sb(III) with APCDT and subsequently adsorped on C18-bonded silica gel. A matrix-free acid solution then eluted through the silica gel to take up As for GFAAS. The detection limit was 0.05 μg/L for 300 mL sample volumes.

Leydon et al.[69] determined As(III) and As(V) in water by dibenzyldithiocarbamate (DBDTC) preconcentration and energy-dispersive x-ray fluorescence spectrometry. The As(III) in the sample solution chelated with DBDTC at pH 2.5 and collected on a membrane filter and was quantified by x-ray

fluorescence spectrometry. Arsenic(V) in the filtrate coprecipitated with hydrated Fe(III) oxide at pH 5.0 and was determined by x-ray fluorescence spectrometry after filtration.

Liu and Yu[73] used sulfhydryl cotton fiber to separate As(III), As(V), Sb(III) and Sb(V) in water. Antimony(III) and As(III) could be absorbed at pH 6.5-7.5 and pH <5, respectively. Antimony(V) and As(V) were reduced to Sb(III) and As(III) after separation. The separate solutions then were determined by HGAAS. The detection limit was 0.01 μg/L in a 200-mL sample. Cotton impregnated with thioglycollic acid ("thiol cotton") was also used by Yu et al.[74] to separate and enrich As(III), As(V), Sb(III) and Sb(V) species. Arsenic(III) was adsorbed on the thiol cotton, and arsenic(V) was determined with GFAA after reduction by the addition of KI and thiourea in 1 M HCl. Terada et al.[75] impregnated thionalide (2-mercapto-N-2-naphthylacetamide) on silica gel (Wakogel C-100, 60-80 mesh) to retain trivalent arsenic and eluted it with 25 mL of 0.01 M sodium borate in 0.01 M NaOH containing 10 mg/L iodine at pH 10. The eluted solution was then measured by AAS.

2.3.4 Electrochemical Technique

Anodic stripping voltammetry (ASV) is one of the most widely applied electrochemical techniques for arsenic speciation because pentavalent arsenic is not electroactive within the potential range of the electrode under general

conditions. Any dissolved oxygen present must be removed prior to the ASV because it causes significant interference.

Cui[76] determined As(III) by ASV with a gold electrode first. The total inorganic arsenic was then determined after reduction of As(V) to As(III) by Na_2SO_3. The recovery rates for As(III) and As(V) at concentrations of 10-25 μg/L and 1.0-100 μg/L were 93-105% and 94-106%, respectively. Metzger and Braun[77] determined Sb(III) and Sb(V) by ASV with selective extraction. Antimony(III) was distinguished from Sb(V) by coupling extraction with ammonium pyrrolidinecarbodithioate (APDC) into methyl isobutyl ketone (MIBK) or n-benzoyl-n-phenylhydroxylamine into $CHCl_3$. Antimony(V) was quantified after Sb(III) was removed with APCDT into MIBK followed by acidification with HNO_3, because Sb(V) becomes labile when the sample is made strongly acidic.[78] Jaya et al.[79] described an ASV method for determining As(III) in water at a copper-coated glassy-carbon electrode. Total inorganic As in the sample was determined after reduction.[80] This method can determine 7.5-750 μg/L of As in various matrices of water samples.

2.3.5 Solvent Extraction

Solvent extraction is one of the most important techniques for preconcentration and separation.[81-85] Solvent extraction also is the postulated process of EPA solid waste preparation and for Cr(VI) determination in waste water. This method is expected to become more important for sample preparation, separation and preconcentration because of increasing concerns over speciation by EPA.[86] Bachmann[87] has

reviewed this technique, referring to many different chelating processes and separation methods. Most of the solvent extraction techniques reported have focused on the separation of inorganic arsenic, antimony and other trace metals; however, a few papers also include the organic species. The solvent extraction techniques preconcentrate and separate metal species by liquid-liquid extraction prior to instrumental analyses, thereby overcoming the difficulties of insufficient sensitivity, interference from matrix elements, or distribution of components in inhomogeneous samples. Solvent extraction in inorganic analysis was also reviewed by Zolotov et al.[88] The review demonstrated that there could hardly be a replacement method for separation and preconcentration of elements as successful as solvent extraction techniques. It was also concluded in the review that further investigation of extraction would appear to be extremely promising for chemical speciation and analysis.

Many different chelating agents have been used to complex trace elements in natural waters.[78,81,89] The selectivity of target species varies as a formation of oxidation states, pH, solvent and masking reagents. Ammonium pyrrolidinecarbo-dithioate (APDC) is one of the most frequently used reagents, along with methyl isobutyl ketone (MIBK) as the extraction solvent. Subramanian and Meranger[90] used APDC-MIBK-GFAAS for As(III)/As(V) and Sb(III)/Sb(V) speciation. However, they could not reliably detect concentrations lower than 1.0 ng/L

even by the most sensitive hydride-evolution-electrothermal atomic absorption spectrometric technique.

Mok and Wai[91] developed a two-step liquid extraction procedure for the simultaneous extraction of trivalent and pentavalent antimony and arsenic species in natural waters for subsequent neutron activation analysis. In this procedure, the extraction conditions were optimized with respect to pH range, buffer, ionic strength, stability and an equilibration time, etc. Some new chelating reagents such as dialkyltin salt[92] and pyrogallol/tetraphenylarsonium chloride[93] were also used for solvent extraction.

2.4 Sample Handling and Pretreatment

In speciation studies, it is very important to use appropriate sampling and preservation processes prior to the analyses to avoid altering the equilibria between the various chemical species in the sample. In addition, any preconcentration, separation, and analytical procedure should be designed to minimize possible contamination, loss of analyte, and interconversion of species.

2.4.1 Sampling

For sediment sampling, grab and core samplers are commonly used in the field. Grab samplers collect large amounts of samples; however, considerable disturbance occurs. Corers sample less volume of sediment, but should be used when a depth profile is of interest. Batley has published a very good review on sediment samplers.[94]

Sampling sediment interstitial water for speciation studies requires extra care, especially with regard to avoiding changes brought about by exposure to oxygen or differences in temperature and pressure. Davison et al.[95] sealed the syringe holes of a corer with polyethylene tape after sampling. The water was then filtered through a sealed filter directly into a polarographic cell for trace metal analysis to avoid oxidation problems with anoxic sediments.

2.4.2 Preservation and Storage

Several reviews of preservation and storage for speciation analysis have been published.[4,95] Batley[94] also has thoroughly reviewed pretreatment and storage procedures for water and sediment. Aggett and Aspell[96] investigated the effects of temperature, pH, and oxygen presence on the stability of As(III) and Sb(III). Acidification of the collected sample is a common preservation technique; however, it was found to increase oxidation rates and cause trivalent As/Sb loss.[46] Crecelius et al.[97] investigated storage methods for As species from environmental samples and concluded that most storage schemes would preserve the total As, MMAA and DMAA concentrations of river water in the μg/L range, but that the original As(III)/As(V) ratio requires extra care for preservation. They also observed that the freezing of water causes the oxidation of As(III) to As(V) except for samples immersed in liquid nitrogen for rapid freezing. Free arsines in natural water samples were found to be stable for a few days if stored in air-tight containers.[46] Arsenic(III) in

sample solutions of seaweed was oxidized to As(V) during storage at room temperature for 4 weeks.[46] Freezing as a preservation method was also reported by several research groups.[98] The natural water samples were frozen below -5°C with dry ice. There was about a 1% loss of As(III) in 2 ppb levels of samples.

2.5 Conclusion

During the last decade, the emphasis on speciation techniques for the analysis of environmental samples has been changed from simple water samples and sediments to include interstitial waters of sediments. Thus, the behavior and fate of an element in the environment can be more reliably predicted because mobility, transport, and partitioning of trace metallic, metalloid, or organic metallic elements in a natural aquatic and terrestrial system are functions of the chemical form of the element. The determination of trace and ultra trace species in natural water requires efficient analytical techniques. The techniques used in sample collection, preparation and storage are also critical in any analyses. It is important to realize that most of the analytical techniques, spectroscopy and chromatography are coupled to preconcentration techniques to lower detection limits. The preconcentration process not only provides higher concentrations of target analytes, but it can also minimize matrix effects. However, additional care needs to be taken to avoid possible contamination during the process. The type of sample, the required accuracy, precision and sensitivity, the

species of interest, and the available equipment need to be considered when choosing extraction and analytical methods.

REFERENCES

1. Elinder, C. and Friberg, L. Toxicology of Metals, Vol. II. National Technical Information Service, PB-268-324, pp. 15-29 (1977).

2. Stokinger, H. Patty's Industrial Hygiene and Toxicology, 3rd ed., Volume 2A, Chapter 29, Wiley-Interscience Publication, pp. 1493-2060 (1981).

3. Morrison, G.M.P.; Batley, G.E. and Florence, T.M. Chemistry in Britain, 793, August (1989).

4. Florence, T.M. and Batley, G.E. CRC Crit. Rev. Anal. Chem. 9:219 (1980).

5. Yamamoto, M. et al. Spectrochim. Acta, Part B 36B:671 (1981).

6. Bourg, A.C.M. and Mouvet, C. Complexation of Trace Metals in Natural Waters, The Hague: Martinus Nihoff, p. 267 (1984).

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

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

9. Manheim, F.T. U.S. Geol. Surv. Prof. Paper 550:256 (1976).

10. Kriukov, P.A. Interstitial Waters of Soils, Rocks and Sediments, Izdatel'stvo Nauka, p. 219, Moscow (1971).

11. Reeburgh, W.S. Limnol. Oceanogr. 12:163-165 (1967).

12. Hartmann, M. Deep Sea Res. 12:225-226 (1965).

13. Siever, R. J. Sed. Petrol. 32:329-331 (1962).

14. Kalil, E.K. and Goldhaber, M. J. Sed. Petrol. 43:553 (1973).

15. Nath, B.N.; Rajaraman, V.S. and Mudholkar, A.V. Indian J. Marine Sci. 17:71-72, March (1988).

16. Aggett, J. and Kriegman, M.R. J. of Water Research 22:407-411 (1988).

17. Lucszynski, N.J. U.S. Geol. Surv. Water Supply Paper 1544-A, 1-8 (1961).

18. Hassler, G.L. and Brunner, E. Trans. Am. Inst. Min. Metall. Eng. 160:114-23 (1945).

19. Marx, J.W. Trans. Am. Inst. Min. Metall. Eng. 192:127-34 (1951).

20. Johnson, A.I.; Prill, R.C. and Morris, D.A. U.S. Geol. Surv. Water Supply Paper 1662-A, 60 (1963).

21. Batley, G.E. and Giles, M.S. Water Res. 13:879 (1979).

22. Murthy, A.S. and Ferrell, R.E., Jr. Clays and Clay Minerals 20:317-321 (1972).

23. Mubarok, A. and Olsen, R.A. Soil Sci. Soc. Am. J. 40:880-882 (1976).

24. Whelan, B.R. and Barrow, N.J. J. Envir. Qual. 9:315-319 (1980).

25. Chakraborti, D.; Adams, F.; Mol, M. V.; Irgolic, K. J. Anal. Chimica Acta 196:23-31 (1987).

27. Carignan, R.; Rapin, F. and Tessier, A. Geochim. Cosmochim. Acta 49:2493 (1985).

27. Steinnes, E. Trace Element Speciation in Surface Waters, Plenum Press: New York, p. 37 (1981).

28. Morrison, G.M.P. in Proc. of 9th Australian Symp. on Analytical Chemistry, Royal Australian Chemical Institute: Sydney, p. 179 (1987).

29. Hesslein, R.H. Limnol. Oceanogr. 21:912-914 (1976).

30. Mayer, L.M. Limnol. Oceanogr. 21:909-912 (1976).

31. Rona, E.; Hood, D.W.; Muse, L. and Buglio, B. Limnol. Oceanogr. 7:201 (1962).

32. Hood, D.W. U.S. Atomic Energy Commission Report TID 23295 (1966).

33. Benes, P. and Steinnes, E. Water Res. 8:947 (1974).

34. Benes, P. and Steinnes, E. Water Res. 9:741 (1975).

35. Benes, P. Water Res. 14:511 (1980).

36. Benes, P. and Majer, V. Trace Chemistry of Aqueous Solutions, Academia: Prague (1980).

37. Bottomley, E.Z. Limnol. Oceanogr. 29:667-670 (1984).

38. Martens, C.S. and Klump, J.V. Geochim. Cosmochim. Acta 44:471-490 (1980).

39. Hopner, T. Environ. Technol. Lett. 2:187-196 (1981).

40. Iverson, D.G.; Anderson, M.A.; Holm, T.R. and Stanforth, R.R. Environ. Sci. Technol. 13:1491 (1979).

41. Uden, P.C. J. Chromatogr. 313:3 (1984).

42. Mortimer, C. H. Limnol. Oceanogr. 16:387-404 (1971).

43. Daughtroy, R.H.; Fitchett, A.W. and Massak, P. Anal. Chim. Acta 79:199 (1975).

44. Andreae, M. O. Limnol. Oceanogr. 24:440-453 (1979).

45. Braman, R.S.; Johnson, D.L.; Foreback, C.C.; Ammons, J.M. and Bricker, J.L. Anal. Chem. 49:621 (1977).

46. Andreae, M.O. Anal. Chem. 49:820 (1977).

47. Andreae, M.O.; Asmode, J.F.; Foster, P. and Van'tdack, L. Anal. Chem. 53:1766 (1981).

48. Talmi, Y. and Bostick, D.T. Anal. Chem. 47:2145 (1975).

49. Butts, W.C. and Rainey, Jr., W.T. Anal. Chem. 43:538 (1971).

50. Henry, F.T. and Thorpe, T.M. J. Chromatogr. 166:577 (1978).

51. Fukui, S.; Hirayama, T.H.; Nohara, M. and Sakagami, Y. Talanta 30:89 (1983).

52. Beckerman, B. Anal. Chim. Acta 135:77 (1982).

53. Morita, M.; Uehiro, T. and Fuwa, K. Anal. Chem. 53:1806 (1981).

54. Woolsen, E.A. and Aharonson, N. J. Assoc. Off. Anal. Chem. 63:523 (1980).

55. Morita, M.; Uehiro, T. and Fuwa, K. Anal. Chem. 52:349 (1980).

56. Ricci, G.R.; Shephard, L.S.; Colovos, G. and Hasler, N.E. Anal. Chem. 53:610 (1981).

57. Grabinski, A.A. Anal. Chem. 53:966 (1981).

58. Cleuvenbergen, V.; Mol, W. E. V.; Adams, F. C. J. Anal. Atom. Spect. 3:169 (1988).

59. Braman, R.S.; Justen, L.L. and Foreback, C.C. Anal. Chem. 44:2195 (1972).

60. Yamamoto, M.; Yasuda, M. and Yamamoto, Y. Anal. Chem. 111:1153 (1985).

61. Han, H. and Wang, W. Chem. Abstr. 103:42262n (1985); Huanjing Huaxue 4:52 (1985).

62. Anderson, R.K.; Thompson, M. and Culbard, E. Analyst 111:1143 (1986).

63. Smith, A.E. Analyst 100:300 (1975).

64. Belcher, R.; Bogdanski, S.L.; Hendon, E. and Townshend, A. Analyst 100:522 (1975).

65. Peterson, M. L. and Carpenter, R. Geochim. Cosmochim. Acta 50:353-369 (1986).

66. Welz, B. and Melcher, M. At. Newsl. 18:121 (1979).

67. Nakashima, S. Analyst 103:1031 (1978).

68. Kaneko, E. Bunseki Kagaku 27:250, 1978; Chem. Abstr. 89:117426x (1978).

69. Leydon, D.E.; Goldback, K. and Ellis, A.T. Anal. Chim. Acta 171:369 (1985).

70. Tsuji, H.K.; Nishimura, Y.; Tamari, Y. and Kusaka, Y. Bunseki Kagaku 33:43 (1984); Chem. Abstr. 100:126604b (1984).

71. Nakashima, S. Bull. Chem. Soc. Jpn. 54:291 (1981).

72. Sturgeon, R.E.; Willie, S.N. and Berman, J.C. Z. Anal. Chem. 317:383 (1984).

73. Liu, G. and Yu, M. Fenxi Huaxue 10:680 (1982); Chem. Abstr. 98:204074k (1983).

74. Yu, M.Q.; Liu, G.Q. and Jin, Q. Talanta 30:265 (1983).

75. Terada, K.; Matsumoto, K. and Inaba, T. Anal. Chim. Acta 158:207 (1984).

76. Cui, C. Huangjing Kexue 6:65 (1985); Chem. Abstr. 103:42262n (1985).

77. Metzger, M. and Braun, H. Anal. Chim. Acta 189:263 (1986).

78. Batley, G.E. and Florence, T.M. J. Electroanal. Chem. 75:763 (1977).

79. Jaya, S.; Rao, T.P. and Rao, G.P. Talanta 34:574 (1987).

80. Sadana, R.S. Anal. Chem. 55:304 (1983).

81. Dean, J.A. and Rains, T.C., eds. Flame Emission and Atomic Absorption Spectrometry, Vol. 3, Dekker: New York (1975).

82. Mizurke, A. Trace Analysis Physical Methods, Morrison, B.H., ed., Wiley: New York (1965).

83. Minczewski, J. Trace Characterization, Meinke and Scribner, eds., p. 365, NBS Monograph 100, U.S. Govt. Printing Office: Washington, D.C. (1967).

84. Stary, J. The Solvent Extraction of Metal Chelates, Pergamon Press: Oxford (1964).

85. Jan, T.K. and Young, D.R. Anal. Chem. 50:1250 (1978).

86. Environmental Protection Agency, SW846 (1990).

87. Bachmann, K. CRC Crit. Rev. Anal. Chem. 12:1 (1981).

88. Zolotov, Y.A.; Kuzimin, N.M.; Petrukhin, O.M. and Spivakov, B.Y. Anal. Chim. Acta 180:137 (1986).

89. Fishman, M.J.; Erdman, D.E. and Steinheimer, T.R. Anal. Chem. 53:182R (1981).

90. Subramanian, K.S. and Meranger, J.C. Anal. Chim. Acta 124:131 (1981).

91. Mok, W.M. and Wai, C.M. Anal. Chem. 59:233 (1987).

92. Shkinev, V.M.; Spivakov, B.Y.; Borobeva, G.A. and Zolotov, Y.A. Anal. Chim. Acta 167:145 (1985).

93. Kratzer, D. and Stary, J. J. Radiochem. Radioanal. Lett. 40:61 (1979).

94. Batley, G.E. Trace Element Speciation: Analytical Methods and Problems, CRC Press, Inc.: Boca Raton, FL, p. 10 (1989).

95. Davison, W.; Woof, C. and Turner, D.R. Nature (London) 295:582 (1982).

96. Aggett, J. and Aspell, A.C. Analyst 101:341 (1976).

97. Crecelius, E.A.; Bloom, N.S.; Cowan, C.E. and Jenne, E.A. Report EPRI-EA-4641, Vol. 2, Battelle Mem. Res. Lab.: Sequim, WA (1986).

98. Hem, J.D. Geochim. Cosmochim. Acta 41:527 (1977).

CHAPTER THREE

ANALYTICAL TECHNIQUES FOR DETERMINING TRIVALENT AND PENTAVALENT ARSENIC AND ANTIMONY SPECIES IN NATURAL WATER

3.1 Introduction

Arsenic and antimony are two of the most interesting trace elements because they can exist in the natural environment in different oxidation states and the toxicity of these elements depends on their chemical forms and oxidation states.[1] The effect of toxicity on aquatic organisms, bioavailability, bioaccumulation, and transport of these trace elements are all dependent upon their species present in the environment. The concentrations of As and Sb in natural water systems normally are in the range of 0.1-1.0 ppb and 0.01-0.10 ppb. The U.S. Public Health Service (USPHS) recommends that the arsenic concentration in drinking water should not exceed 50 ng/mL.[2] There is no USPHS criterion for Sb; however, the U.S. EPA assessment of safe Sb concentration in drinking water is 0.2 ng/mL.[3] Due to the low concentrations of As and Sb present in natural water systems, an analytical method with a sufficiently low detection limit is required. A method capable of determining specific species of As and Sb at ultra-low concentration levels is also required. In this study, different separation and detection techniques were examined. These include ion chromatography (IC), graphite furnace atomic absorption spectroscopy (GFAAS), hydride

generation atomic absorption spectroscopy (HGAAS), inductively coupled plasma-mass spectroscopy (ICP-MS), and ammonium pyrrolidinedithiocarbamate (APDC) solvent extraction with neutron activation analysis (NAA).

3.2 Experimental

3.2.1 Neutron Activation Analysis Coupled with APDC Solvent Extraction

Reagents. All chemicals used were analytical grade unless otherwise stated. Stock solutions (1000 ppm) of the following arsenic and antimony species were prepared. As(III) was prepared by diarsenic trioxide (As_2O_3) obtained from Aldrich. The As_2O_3 was stored in a desiccator and dried at 110°C for 4 hours before use. Diarsenic trioxide (0.3299 g) was dissolved in 5 mL of 1 M NaOH followed by addition of 130 mL of 2 M HCl and then diluted to 250 mL with deionized water. Arsenic(V) 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. Antimony(III) was prepared by diluting 1.647 g of Sb_2O_3 (J. T. Baker) in 1000 mL of 2.5 M HCl solution. Antimony(V) was prepared by dissolving 1.117 g of potassium antimonate in 500 mL of 1% HNO_3 and stirring with a magnetic stirring rod until the reagent was totally dissolved.

An acetate buffer solution at pH 4.5 was prepared by dissolving 0.426 g of sodium acetate (CH_3COONa) in 20 mL of glacial CH_3COOH solution and diluting it to 200 mL with deionized water. Omnisolv grade chloroform (Aldrich Chemical

Co. Inc.) was used in solvent extraction. Ultrapure grade ammonium hydroxide and nitric acid were used to adjust pH. The 12% EDTA, 5% APDC and 20% thiosulfate solutions were all freshly made prior to use.

Instruments. A 1 MW TRIGA nuclear reactor located at Washington State University with a steady flux of 6×10^{12} $n/cm^{-2}s^{-1}$ was used for sample irradiation. A large-volume coaxial ORTEC Ge(Li) detector with a resolution of 2.3 keV at the 1332 keV (from ^{60}Co) and an efficiency of 11% relative to a 7.5 cm x 7.5 cm NaI(Tl) detector was used. An ORTEC ADCAM model 918 multichannel analyzer converts the amplified signals to the number of counts to an IBM-PC-AT equipped with 100/150 MCA software (Figure 3.1) for data processing.

Speciation procedure. Two aliquots of 100-mL water samples are saturated with chloroform before solvent extraction. The pH of one aliquot is acidified to ~1.0 with HNO_3. Thereafter, 1 mL of 25% $Na_2S_2O_3$ and 1 mL of 20% KI solution are added to the sample for 15-30 min to reduce As(V) and Sb(V) to As(III) and Sb(III), respectively.

The reduced aliquot of the sample and the unreduced aliquot then can be taken through the APDC solvent extraction with the following procedure. About 10 mL of acetate buffer are added to each sample, and pH is adjusted to 3.5-5.5 with HNO_3 or NH_4OH. Chloroform (10 mL), 4 mL of 12% EDTA, and 2 mL of 5% APDC solution are added to each aliquot and shaken for 10 min. The mixtures are allowed to stand for 10 min, then

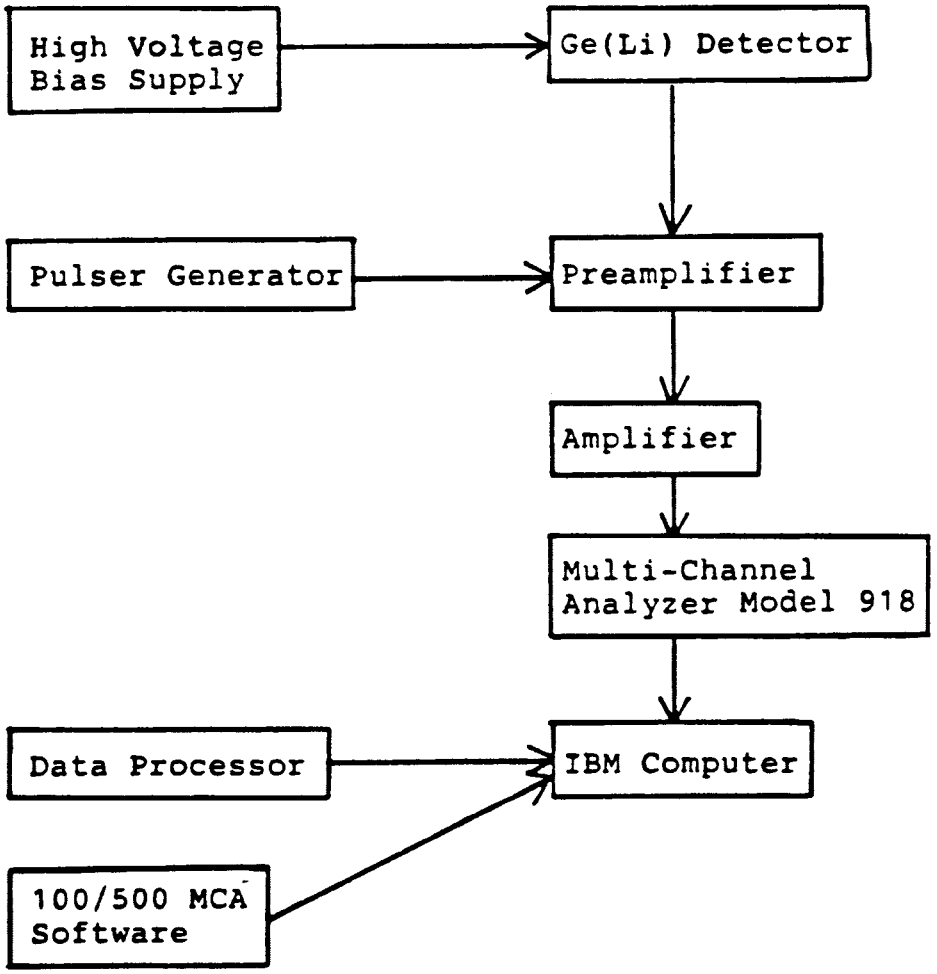


Figure 3.1 Schematic Diagram of Gamma-ray Spectroscopy System

the aqueous phases are discarded. The organic phase (chloroform phase) is washed twice with deionized water. Exactly 8 mL or any precise amount of each organic phase is pipetted out. Exactly 2 mL of 50% HNO_3 is mixed with each organic phase and shaken for 10 min to back extract the As(III) and Sb(III) to the aqueous phase. Each aqueous solution (0.75 mL) is heat-sealed in a 2/5-dram polyethylene vial for neutron irradiation. The samples and As and Sb standards of proper concentrations are irradiated in a 1 MW TRIGA nuclear reactor at a steady thermal neutron flux of $6 \times 10^{12} n/cm^2 s$ for 2 hours, followed by 24 hours of cooling. The irradiated samples are counted on the ORTEC Ge(Li) detector after being transferred to new P.E. vials. The 559.1 keV γ and 564.0 keV γ from ^{76}As and ^{122}Sb, respectively, are used to determine the arsenic and antimony concentrations.

The concentrations of As(III) and Sb(III) are determined from the measurement of the sample without reduction. The concentrations of As(V) and Sb(V) are determined from the difference between the concentrations of the reduced sample and the unreduced sample.

The volume of the interstitial water sample required for analysis can be reduced if only limited amounts of water are obtained. The quantities of reagents then need to be adjusted accordingly. Also, the preconcentration factors can be adjusted according to the detection limit of the analytical instruments and the concentration level of the analyte in the sample.

3.2.2 APDC Solvent Extraction with GFAAS

Reagents and instruments. Reagents for APDC solvent extraction are the same as those in the previous section. Standards of As and Sb are prepared by dilutions of J. T. Baker 1000 ppm standard solutions for atomic absorption spectroscopy. The 1000 ppm mercury(II) back-extraction solution was prepared by dissolving 0.1 g HgO in 5 mL of 2.4% HNO_3 and diluting to 100 mL. An Allied Model IL 655 Controlled Temperature Furnace (CTF) Atomizer is used for atomic absorption analysis.

Procedure. This two-step APDC solvent extraction is similar to the previous section except the back-extraction is carried out by using a Hg(II) solution. The use of a mercury solution has the following advantages: 1. The mercury solution will not interact with the pyrolytical graphite tube in GFAAS as an acid solution will, especially at high temperature. 2. Kinetically, mercury(II) back-extraction is more efficient than acid back-extraction for transferring metals from the organic phase to the aqueous phase.[4] It only takes about 2 min to recover >95% of the metals present into a mercury(II) solution, but it requires about 2 hours for acid back-extraction. In addition, the low atomization temperature and the analytical wavelengths in atomic absorption of mercury are much different from the temperatures found in arsenic and antimony. The presence of a low concentration of Hg(II) in the back-extraction solution does not cause any noticeable interference. The back-extraction with mercury(II) is based

on the theory that the extraction constant of mercury(II) dithiocarbamate is much greater (log K = 41.84) than As(III) (log K = 24.42) or Sb(III) (log K = 26.31).[5,6]

One milliliter of preconcentrated sample was transferred into a 10-mL beaker, and 0.1 mL of a solution containing 0.5% nickel and 10% nitric acid was added. The sample was placed on a hot plate and digested at 75°C for 30 min, allowed to cool, and brought back to exactly 1 mL. The process allowed As to form a stable compound with nickel and permitted pyrolysis in the furnace without loss of analyte.

A 25 μL aliquot of the sample was placed directly into the pyrolytically coated cylindrical graphite furnace cuvette with a 25 μL eppendorf pipet and analyzed according to the EPA's operation conditions for As and Sb.[7,8] If the sample exhibits greater than 0.5 absorbance unit, dilution is recommended for optimum precision. If the background signal is greater than 1 absorbance unit, dilution is also recommended for optimum precision. The temperature and time settings for dry, pyrolysis, and atomization need to be adjusted according to the requirements of different samples to obtain the best results.

3.2.3 Hydride Generation Atomic Absorption Spectroscopy (HGAAS)

Reagents and instruments. Standard solutions for calibration were prepared by dilution of 1000 ppm As(III) and Sb(III) stock solutions. The preparation of the As(III) and Sb(III) stock solutions is described in Section 3.2.1. Sodium

borohydride and octylalcohol were obtained from Aldrich Chemical Co. A 6% (w/v) sodium borohydride ($NaBH_4$) was used for generating arsenic and antimony hydride. This solution was prepared by dissolving 6 g of sodium borohydride in 100 mL of 0.1 N sodium hydroxide solution. The resulting solution was filtered through a Whatman No. 1 filter paper. Argon gas was bubbled through the solution for 5 min every day to remove small bubbles of hydrogen in the solution. This solution was stored in a refrigerator when not in use. One preparation normally lasted for 3 days without noticeable deterioration. A solution used for sample acidification was prepared by mixing 50 mL of 1.5 M HCl with 1 mL of octylalcohol and diluting it to 100 mL with deionized water.

The analyses were performed with a Perkin-Elmer Model 360 atomic absorption spectrophotometer and a MHS-10 hydride generator. For As and Sb analysis, an electrodeless discharge lamp (EDL) and a hollow cathode lamp were used, respectively. The operation was carried out in the analytical laboratory of the Department of Veterinary Science, University of Idaho.

Procedure. The procedures for preconcentration and reduction of the samples were the same as those in section 3.2.1. The nitric acid-octylalcohol mixture (20 mL) was added to 0.5 mL of the sample and analyzed by the HGAAS system. A nitrogen gas was used to strip the hydride from the liquid and carry it into an open-ended air-acetylene quartz cell.

3.2.4 Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)

Apparatus and procedure. A VG Plasma Quad ICP-MS system (VG Instruments Inc., Danvers, MA) was used in the work of arsenic and antimony quantitative analysis. The operation was carried out in the Battelle Pacific Northwest Laboratories, Richland, WA. The detection limits of As and Sb by ICP-MS are 0.4 and 0.02 ng/mL, respectively. Because of the low detection limit of the elements, the natural water samples were directly introduced into the ICP-MS system without the preconcentration process. The isotopes of ^{75}As, ^{121}Sb and ^{123}Sb were used for internal standards. The naturally occurring abundance of ^{75}As, ^{121}Sb and ^{123}Sb is 100%, 57.3% and 42.7%, respectively. The reference blank solution and the matrix for the reference solution used for calibration consisted of 1% (volume) nitric acid (Ultrapure grade). The reference calibration solutions were prepared by dilution of stock solutions with deionized water. A 14 L/min of argon supporting flow rate and 1350 W of RF power were the operating conditions for the argon plasma.

3.2.5 Ion Chromatography

Reagents and instruments. The eluent was prepared by dissolving 0.212 g of Na_2CO_3 and 0.496 g of $NaHCO_3$ in 50 mL methanol and diluting to 1000 mL with deionized water. Sulfuric acid (50 mM) was used as a regenerant. The preparation of As(III), As(V), Sb(III), and Sb(V) standard solutions was detailed in Section 3.2.1. Deionized water used in this work was prepared by passing distilled water through a

Milli-Q ion exchange water purification system (Millipore Corp.). A Dionex Model 4000i with conductivity detector and electrochemical detector was used to determine both the trivalent and pentavalent species of arsenic and antimony. A Dionex OmniPac PAX-500 separator column and a PAX-500 guard column were used in the system. A 50 μL injection loop was used for sample injection. A Dionex AMMS-MPIC anion fiber suppressor was used to convert sodium carbonate to carbonic acid.

Procedures. The eluent flow rate was adjusted to 1.5 mL/min and the regenerant flow rate was 8 mL/min. The guard column and separator column were flushed with eluent for 30 min before running the sample. The samples were loaded to the injection loop and injected onto the columns for separation and detection. The eluent stream first passed through a Dionex electrochemical detector (Pt working electrode, Ag-AgCl reference electrode, +0.5 V applied potential) to determine As(III). A Dionex conductivity detector downstream from the electrochemical detector was then used to measure As(V). A Spectra Physics 4270 Integrator equipped with a second channel module was used to record and calculate peak areas.

3.3 Results and Discussion

The water sample obtained from Paradise Creek in the vicinity of Moscow, Idaho, was tested with the different analytical techniques for comparison. Table 3.1 summarizes the values of As and Sb species obtained by NAA, HGAAS, GFAAS,

Table 3.1 Speciation of Arsenic and Antimony by Different Analytical Techniques in Water of Paradise Creek, Idaho (ppb)

	Method of Speciation				
	With APDC Preconcentration			Without Preconcentration	
Species	NAA	HGAAS	GFAAS	IC	ICP-MS
As(III)	0.1±0.1	0.1±0.1	0.1±0.1	D.L.*	--
Total As	0.4±0.1	0.4±0.1	0.4±0.1	D.L.*	0.4±0.1
Sb(III)	<0.1	<0.1	<0.1	D.L.*	--
Total Sb	0.5±0.1	0.6±0.1	0.5±0.1	D.L.*	0.5±0.1

* Below detection limit

IC and ICP-MS. IC is capable of analyzing As(III), As(V), Sb(III) and Sb(V) directly with connection of conductivity and electrochemical detectors. However, the detection limit of IC for these species is higher than 0.5 ppm, and this limits the application of IC for natural water samples. In addition, the detection of antimony was not stable in the experiments. The reason for this instability is unknown. ICP-MS has the advantage of analyzing low-levels of total As and Sb in water and also offers significantly greater convenience and speed. Although ICP-MS can directly measure As and Sb in natural water without the need of a preconcentration process, it suffers the disadvantage of unavailability of speciation information.

The combination of APDC solvent extraction with NAA, HGAAS or GFAAS provides consistent results for the As and Sb species in the creek water. The standard deviations of As and Sb values obtained by GFAAS were overall higher than those from NAA and HGAAS, probably due to matrix interference of the back-extraction solution.

Preconcentration prior to instrumental analysis offers a lower detection limit for As and Sb analysis. Furthermore, the APDC solvent extraction method also provides the capability of As and Sb speciation. Neutron Activation Analysis (NAA) is considered to be one of the most sensitive analytical techniques for As and Sb determination. Nanogram levels of As and Sb were detected by this method with good accuracy. NAA coupled with APDC solvent extraction,

therefore, provides a technique for the accurate determination of sub-nanogram levels of As and Sb species in natural water. The analytical results of the determination of As and Sb species in the creek water by NAA and by ICP-MS coupled with APDC solvent extraction are given in Table 3.2. The results show good agreement between NAA and ICP-MS coupled with APDC extraction. In addition, both methods offer the accuracy and convenience of simultaneous determination of As and Sb species. However, at high concentration levels, As measured by ICP-MS may have the advantage of interference of ^{40}Ar-^{35}Cl to the analyte ^{75}As. The ^{121}Sb (57.3%) and ^{123}Sb (42.7%) were two major Sb isotopes measured in ICP-MS. There was no background interference for these two isotopes. The reason for the slightly lower value of total Sb by ICP-MS relative to NAA is not clear.

Table 3.2 Recovery of Spiked Trivalent and Pentavalent Arsenic and Antimony Species by NAA and ICP-MS

Amounts Added		NAA(UI) % Recovery		ICP-MS % Recovery	
As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
100	100	102.2±3.2	103.1±4.2	105.6±2.7	110.5±2.5
200	100	99.4±2.3	101.4±3.5	108.7±3.2	112.4±2.3
100	200	101.3±2.8	104.6±2.8	104.2±2.3	113.9±2.1
Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)
100	200	97.9±2.8	98.5±3.5	89.7±1.2	94.5±1.6
200	100	98.6±3.3	95.9±5.2	87.3±4.6	91.6±2.9
100	200	100.7±1.1	91.8±3.8	88.9±6.5	87.9±6.0

The Paradise Creek water was also spiked with known amounts of As and Sb species for NAA and ICP-MS analysis to

evaluate the efficiency of recovery of the spiked species by APDC extraction. Similar recovery experiments were performed with the deionized water spiked with the same As and Sb standards. Table 3.3 shows good recoveries for both deionized water and the creek water. This indicates that the method for measurement of As and Sb species in natural water by APDC extraction is reliable. For this reason, APDC-NAA was adopted as the appropriate analytical technique for simultaneous determination of As and Sb species in natural water systems in this study.

REFERENCES

1. Penrose, W.R. CRC Crit. Rev. Environ. Control 4:465 (1974).

2. U.S. Public Health Management Guideline, NPS-83, Release No. 1, April (1991).

3. U.S. EPA Environmental Criteria and Assessment Office, U.S. Environmental Protection Agency, Ambient Water Quality Criteria for Antimony, National Technical Information Service: Springfield, VA, PB81-117319 (1982).

4. Lo, J.M.; Yu, J.C.; Hutchison, F.J.; and Wai, C.M. Anal. Chem., 54:2536-2539 (1982).

5. Shieh, G.M. and Wai, C.M., "Stability Constants of Diethyldithiocarbamate Complexes of Antimony, Arsenic and Gallium," unpublished (1993).

6. Wai, C.M., "Preconcentration of Trace Elements by Solvent Extraction," in Preconcentration Techniques for Trace Elements, Z.B. Alfassi and C.M. Wai, eds., CRC Press (1991).

7. Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency: Cincinnati, OH (1979).

8. Methods for Analytes and Properties, SW-846, U.S. Environmental Protection Agency: Cincinnati, OH (1990)

Table 3.3 Recovery of Spiked As(III), As(V), Sb(III) and Sb(V) in the Deionized Water and Paradise Creek Water by APDC-NAA

Samples	Species Added (ng)				% Recovery			
	As(III)	As(V)	Sb(III)	Sb(V)	As(III)	Total As	Sb(III)	Total Sb
Deionized Water (100 mL)	200	200	200	200	104.3	105.7	95.6	101.2
	200	400	200	400	96.5	107.2	86.2	103.5
	400	200	400	200	92.2	108.5	98.5	100.2
	800	200	200	800	94.5	104.2	100.2	108.6
	200	800	800	200	100.2	101.4	100.7	102.6
Paradise Creek Water (100 mL)	200	400	200	400	97.4	104.2	102.3	106.4
	400	200	400	200	97.6	102.5	101.5	98.4
	800	200	800	200	88.4	110.5	100.3	95.4
	200	800	200	800	101.2	100.5	103.5	99.5

CHAPTER FOUR

TECHNIQUES FOR REMOVING INTERSTITIAL WATERS FROM RIVER SEDIMENTS FOR CHEMICAL ANALYSIS

4.1 Introduction

Interstitial waters are aqueous solutions that occupy the pore spaces or voids between particles of soil, sediments, and rocks. They can provide useful information on trace metal equilibria in sediments and reflect the migration pathway, origin of fluids, and impact of trace metals in polluted sediments on water quality.

In marine research, the composition of interstitial waters has been widely investigated because it influences sediment-water interactions, pore water convection, diffusive movement of dissolved ions and the hydrochemical history of marine sediments. In recent years there has been an increased interest in the measurement of heavy metals in interstitial waters of river sediments for environmental studies. Analysis of sediment interstitial waters is useful for water quality control because sediments can bind contaminants by adsorption, biochemical processes, and chemical reactions. All these processes can make concentrations of toxic organic compounds and heavy metals in interstitial waters significantly different from the overlying surface waters. A rapid exchange of dissolved species occurs across the sediment-interstitial water interface. Therefore, the transport between the sediment and surface water is closely related to the

concentration of species within the sediment. Analysis of a sediment core at various depths can give clues to the transport and the accumulation of pollutants as well as chemical conditions affecting such processes in the ecosystem.

In order to study metal species in interstitial waters of river sediments, an appropriate technique for the removal of interstitial water without changing its chemical composition is essential. Various techniques for extracting interstitial waters from sediments have been described in the literature. These techniques are generally based on the principles of squeezing, centrifugation, dilution-extraction (leaching), and dialysis. Each technique has its advantages and disadvantages for specific applications. There have been discussions in the literature concerning modifications of these techniques, mostly to suit the situation of marine sediments and field soils. However, there still is no standard technique for extracting interstitial waters, especially for river sediments.

A general review of the extraction techniques for interstitial waters reported in the literature is given in this chapter. A simple and inexpensive low-pressure direct gas squeezer for the removal of interstitial waters from river sediments is then described. The distributions of arsenic and antimony species as well as other trace metals, including Mn, Zn, Fe and Cu, in the interstitial waters of some river sediments were measured to compare the results obtained by different extraction techniques.

Antimony and arsenic are two of the most interesting trace elements because they can exist in the natural environment in different oxidation states and the toxicity of these elements depends on their chemical forms. For example, the toxicity of arsenite (As^{3+}) is 30-50 times greater than arsenate (As^{5+}) to biological systems.[1,2] Soluble As^{3+} and As^{5+} have been reported to exist in the Coeur d'Alene River in northern Idaho. Information on the distribution of As and Sb species in the interstitial waters of the river sediments is important for understanding the migration of these metal species in the polluted river. Coeur d'Alene River sediments and other unpolluted river sediments were, therefore, collected for this comparison study.

A French agronomist, T. Schloesing,[3] was perhaps the first person in the literature to study interstitial water. He extracted pore fluids from a quantity of soil using a liquid displacement technique and carefully analyzed the effluent in 1866. Since then, studies of soil interstitial water have become a major area of research for soil and plant chemists.[4] In 1895 two British oceanographers, John Murry and R. Irvine, squeezed fluids from a mud sample of the Scottish coast and found a depletion of oxygen, a loss of sulfate, and an increase in bicarbonate alkalinity.[5] This observation indicated that the oxidation of organic carbon (by bacteria) to CO_2 had balanced most of the reduction of sulfate to form sulfide. Murry also suggested that the river-borne and

volcanic supplies of Mn might diffuse into seawater from sediments under syngenetic reduction.[5]

Chlorinity in ocean sediments was studied by a British biologist, R. I. Smith, in the late 1920s.[6] He proposed that higher salinities in the sediments relative to overlying water were due to gravitational convection and downflow of heavier solutions through permeable sediments; however, lower chlorinities could result because of the ground water discharge.

Interstitial water studies drew geochemists' interest in the late 1930s. In the early 1950s more effective sediment squeezers were developed and interstitial water studies encompassed major and minor ions, nutrients, and organic constituents in sediments.

Trace elements in interstitial waters did not attract attention until the mid-1960s when Brooks et al. studied Pacific red clays and found abnormally high concentrations of copper, zinc, lead and other heavy metals.[7] From the 1970s to the present, trace metals in interstitial waters of marine sediments have been extensively studied with most of the work focused on marine diagensis. Little information is available concerning relationships between heavy metals in overlying waters and interstitial waters in river sediments.

4.2 A Review of Instruments and Methods

4.2.1 Sediment Sampling and Storage

Core and grab samplers are commonly used for sampling sediments [Appendix C, D].[8] Grab samplers can collect large

volumes of sediments but often with considerable disturbance. Grab samplers are also incapable of sampling different depths of sediments. In contrast, core samplers are useful for collecting sediments where depth profiling is of interest. The core samplers are usually sealed underwater with polyethylene end caps. In deeper waters, pneumatic or vibrating core samplers which can be operated from a barge are necessary. There are inherent advantages in using a diver for deep water sediment sampling. The diver can clearly determine the most representative sampling point and current velocity. But this approach requires costly equipment and special training. For normal river sediment sampling, which usually occurs in shallow waters, an inexpensive laboratory-designed PVC corer of the desired length with a probe stick of an appropriate diameter fit for the core sampler can be employed.

For speciation studies, in situ extraction of interstitial water would be ideal. If facilities are not available for field sampling, sediments can be put into PVC zip-lock bags right after sampling. The air must be squeezed out, and the zipped up bags can be stored at 4°C for interstitial water extraction later.

4.2.2 Interstitial Water Extraction Techniques

There is no definitive technique for the isolation of "true" interstitial water from sediment, but several preferred methods of removing aqueous phases from sediment for laboratory study have been established. These techniques include leaching, centrifugation, immiscible solvent

displacement, low-pressure mechanical squeezing, hydraulic squeezing, direct gas squeezing, and dialysis.

For brittle soils or consolidated rocks, leaching may be the most appropriate recourse to assess the composition of the interstitial water. Usually the leaching involves a two-step procedure. First, an exact weight of a sample is dried at 105°C for 48 hours after which the weight is measured again to determine the moisture content. Subsequently, the sediment is mixed with water and the mixture is shaken on a wrist-action shaker for 6 hours. After phase separation, the supernatant solution is removed for analysis. The elemental composition of the interstitial water can be assessed from the analytical data and the moisture content of the sediment. However, the metal concentrations in leachates are influenced by temperature, length of leaching, type of sediment, and precipitation of solid phases.[9] Murthy and Ferrell[10] found that Ca and Mg values are almost constant for different dilution factors. This is because the ions, such as Ca^{2+}, Mg^{2+}, Sr^{2+} and CO_3^{2-}, tend to dissolve from mineral matter in the sediment. Also, it is difficult to reach equilibration of the leaching solution at low dilutions. At high dilutions, it is even harder to achieve linearity by extrapolation from successive dilutions. Murthy and Ferrell's leaching results sometimes showed more than 100% deviations.[10]

The immiscible solvent displacement method involves the use of a dense inert organic solvent of low solubility (e.g., trichlorotrifluoroethane), which is centrifuged with a

sediment sample to expel its aqueous phase. The greater density of the organic fluid floats the aqueous phase to the top of the centrifuge tube [Appendix E]. The ideal solvent should be less dense than the sediment and considerably more viscous than the interstitial water to assure a distinct fluid phase boundary of sediment-solvent-water phase. In addition, the solvent should be non-reactive with salts and insoluble in water. Trichloro-trifluoroethane was used by Batley and Giles,[11] chloroform was used by Mubarak and Olsen,[12] and trichloroethylene and 1,1,1-trichloroethane were used by Whelan and Barrow[13] for interstitial water studies.

Centrifuge extraction is commonly used for the removal of soil moisture and is now increasingly used for sediment interstitial waters. Edmunds and Bath[14] have described the physical basis of this technique and investigated the recovery of interstitial waters from consolidated geological materials. For fine-grained compressible sediments, the water will be separated onto the top of the sediments. For coarser sediments, most of the water will still be present between the voids of uncompressible particles, and only a small fraction of the water will be collected on the top of the sediments. In this case, a modified centrifugation device, which separates the sediments out in a compartment on the top, can be used to extract more interstitial waters. The centrifugation technique has several disadvantages: (1) only a small sample can be used for each centrifuge tube, (2) the

apparatus is difficult to clean, and (3) the volume of water collected is small.

The pressure squeezing technique generally includes low- and high-pressure mechanical squeezing, low- and high-pressure gas squeezing, and hydraulic squeezing. This technique is carried out by applying pressure by gas, hydraulic press or hand (screw) directly or indirectly to squeeze out interstitial waters from unconsolidated or consolidated samples. Descriptions of this technique are given by Kriukov[15] and by Manheim.[9]

The dialysis technique is well suited for in situ separation of interstitial waters (Appendix F). The dialysis probe essentially consists of one or more dialysis bags (samplers) filled with particle-free distilled water. The dialysis probe is then inserted into the river sediment. It is left there long enough for the water in the bag and the ambient water to reach equilibrium. The time required to reach equilibrium varies from a couple of hours to four weeks.[8,16] The dialysis bags are then retrieved and cut open to get the interstitial waters.

4.3 Analysis of Interstitial Waters in River Sediments

The extraction of interstitial waters from marine sediments generally involves squeezing the sediment at high pressures, followed by filtration and chemical analysis.[9] A leaching technique was also used for the marine interstitial water removal,[17] but this method is not suitable for accurate analysis of water composition other than for estimation of

salinity.[18] Centrifugation is commonly used for removing interstitial waters in soils.[14] Recently, an in situ dialysis technique for interstitial water extraction from lake and river sediments was introduced by Hesslein[19] and Mayer,[20] and it has become increasingly popular.[21,22] However, dialysis is subject to several potential sources of error. For instance, polycarbonate was found to be unsuitable for dialyzer construction because of iron precipitation problems. Also, the initial presence of dissolved O_2 in the compartments can significantly affect sample composition. Incomplete equilibration, membrane breakdown, contamination or the possible development of an electrical potential across the membrane may interfere with the free diffusion of ions.

Modifications on the above techniques have been developed. The suitability of these techniques for trace metal speciation studies in interstitial waters of river sediments is still unknown.

The concentrations of trace metals including Mn, Fe, Cu and Zn in the interstitial waters of river sediments extracted by low-pressure direct gas squeezing, modified centrifugation and solvent displacement followed by 0.45 μm membrane filtration were measured. Speciation of As and Sb in interstitial waters obtained by the three extracting techniques was also investigated.

4.3.1 Interstitial Water Removing Techniques

Sediments were sampled from the St. Joe River (loam), Harrison-Anderson Lake (silty loam), and Smelterville (loam)

in Idaho. Test results of particle size distribution are presented in Table 4.1.

Table 4.1 Particle Size Distribution and Moisture Content of Sediment Samples*

Sediment	Particle Size Distribution % Sand	% Clay	% Silt	Texture (USDA 1950)	% H_2O
St. Joe	62.5	3.3	34.2	loam	38.20
Harrison-Anderson	56.8	19.2	24.0	silty loam	40.25
Smelterville	39.0	11.0	50.0	loam	50.20

* The tests were performed in the Soil Science Department, University of Idaho.

Modified centrifugation technique. This modified centrifugation technique was proposed by Elkhatib et al.[23] to remove interstitial water from soil. The centrifugation assembly is shown in Fig. 4.1.

About 25 g of sediment sample were placed in 38-mL high-speed polypropylene tubes with Whatman #42 ashless filter paper of the appropriate diameter on the hole-drilled bottom of the tube. Each polypropylene centrifuge tube was inserted into a 50-mL high-speed stainless steel tube with a hard PVC support having eight drilled holes. Eight of these centrifuge tubes were placed in an IEC CENTRA-8 Centrifuge. The tubes were centrifuged at 5000 rpm for 60 min. After centrifugation the interstitial waters of the sediments were collected on the bottom of the stainless steel centrifuge tubes, followed by 0.45 μm membrane filtration (Millipore). The membrane filter was washed with acid and water before use to prevent contamination of organic matter and metals.[24] Cellulose

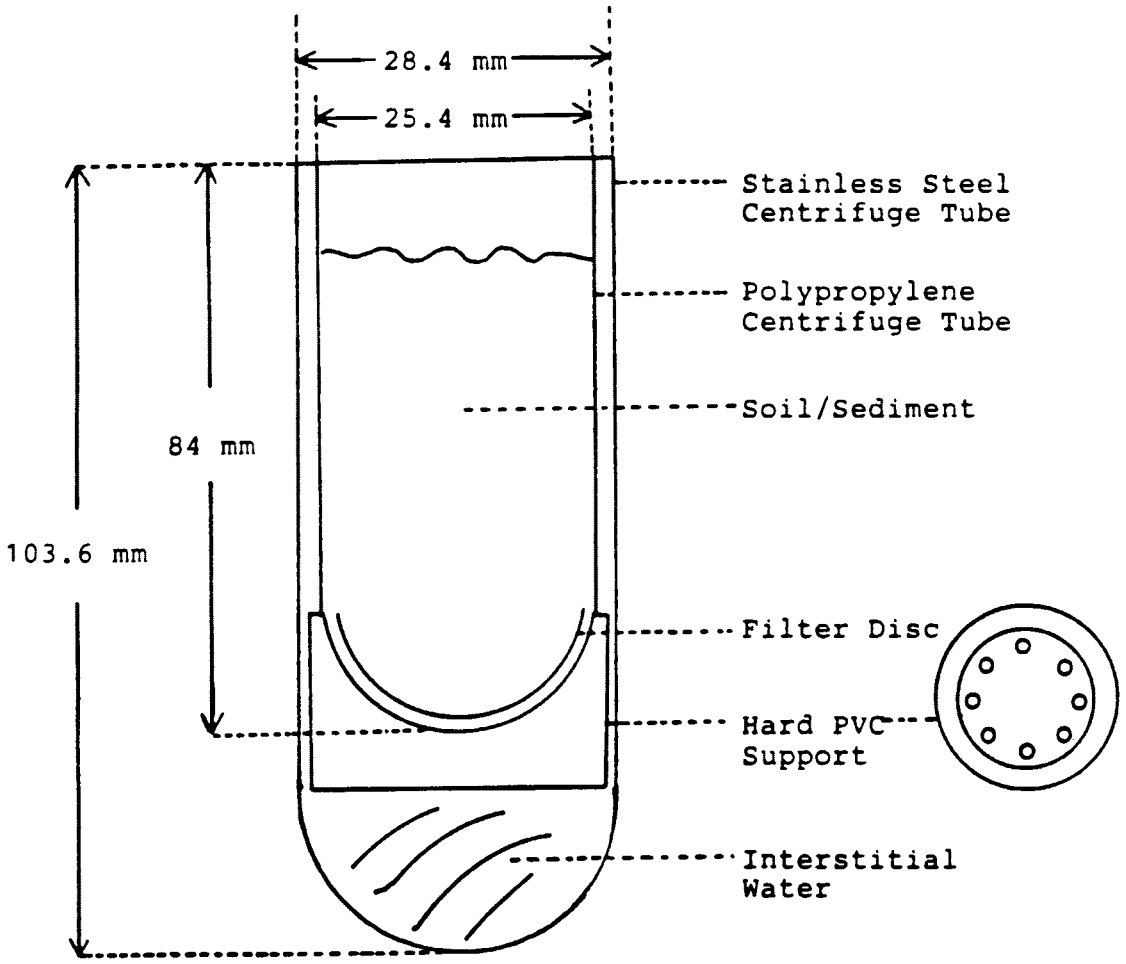


Figure 4.1 Centrifugal Assembly for Interstitial Water Extraction

acetate membranes were usually used for filtration. Although Nuclepore membrane filters (polycarbonate) have a lower metal content, they block easily.

The interstitial waters obtained were stored in polyethylene bottles for chemical analysis. For speciation studies, the waters were usually analyzed immediately after filtration.

Solvent displacement technique. The solvent displacement technique combines the principle of immiscible displacement with conventional centrifugation. It was proposed by Mubarak.[25]

About 20 g of sediment sample were placed in a 50-mL centrifuge tube; carbon tetrachloride (20 mL) was then added to the tube. The tube was tightly stoppered and shaken for 1 min. The tube was then placed in an IEC CENTRA-8 centrifuge at 5000 rpm for 90 min. Since the density of CCl_4 was much higher than water, the interstitial water in the sediment was displaced by the organic solvent. The water was immiscible with CCl_4 and rose to the upper layer where it could be removed for chemical analysis.

Low-pressure gas squeezing technique. A low-pressure direct gas squeezing technique using an Amicon Ultrafiltration Cell (Model 402) was developed in this study. The setup is shown in Fig. 4.2. Major parts of the apparatus include: (i) a top cap with a pressure relief valve, (ii) a transparent sleeve, (iii) a base with a porous membrane support disk, and (iv) a stainless steel toggle latch assembly.

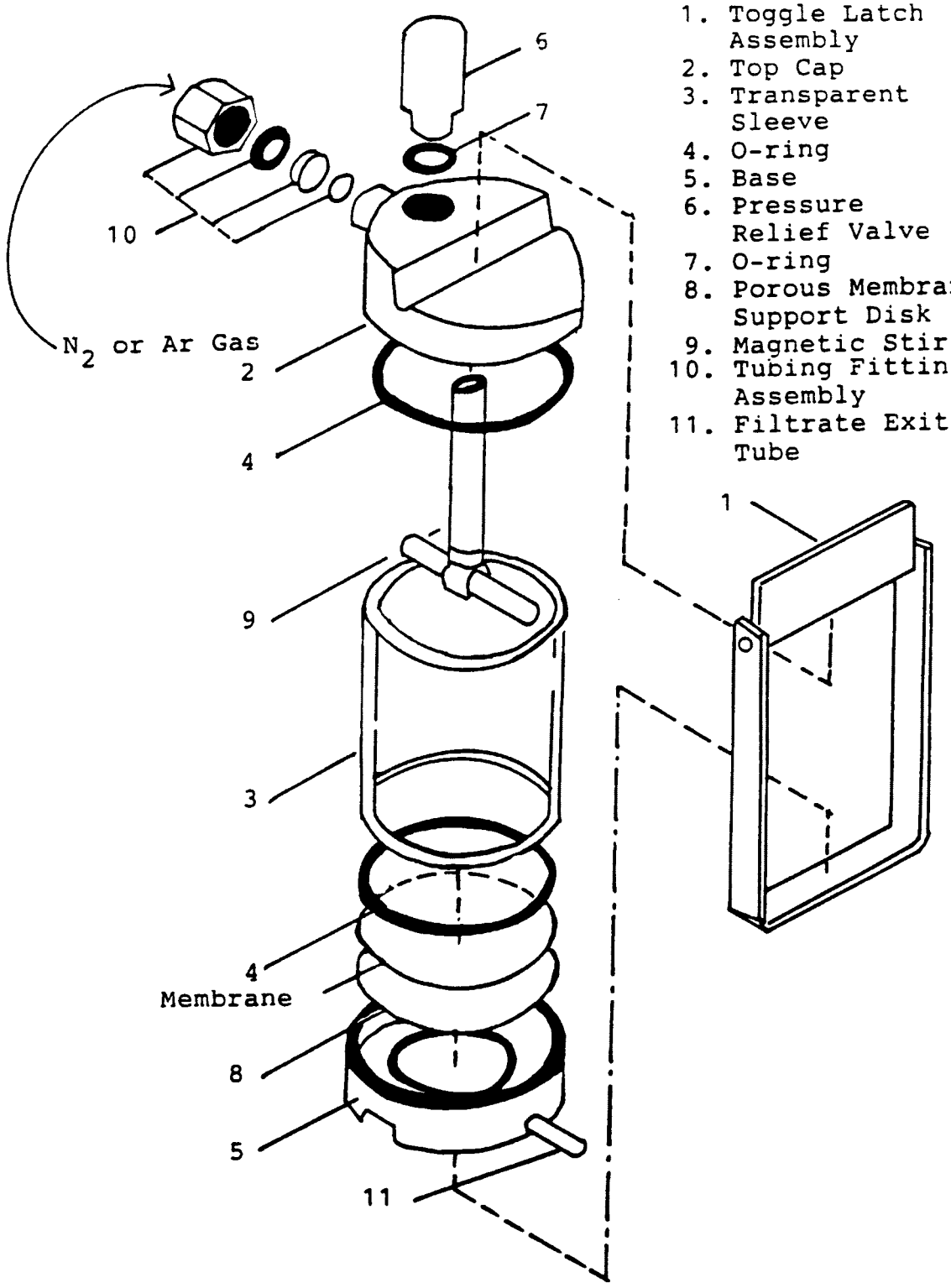


Figure 4.2 A Low-Pressure Direct Gas Pressure Squeezer

About 500 g of sediment sample were contained in the transparent sleeve on the base set on an O-ring in contact with the porous membrane support disk. Another O-ring was attached to the top cap recess. The cap was placed on the sleeve so that the inlet pressure fitting was situated at 180° opposite to the filtrate exit tube located at the base. The toggle latch was then applied to the assembly. The pressure relief valve on the cap was closed. Nitrogen gas was applied directly to the system at different pressures to squeeze out interstitial water. The volume of water collected at different pressures was measured. The time required to squeeze certain amounts of water was also recorded. The interstitial water was filtered through a 0.45 μm membrane for analysis.

4.3.2 Trace Metal Analysis

Reagents and instruments. All standard solutions of Mn, Zn, Fe and Cu for atomic absorption spectrometry (AAS) were prepared from J. T. Baker 1000 ppm standard solutions. Distilled demineralized water was used for making all solutions. All containers were cleaned with Liquinox detergent, rinsed with distilled water, and soaked in 10% v/v nitric acid for at least 20 hours. After rinsing with demineralized water, they were dried in a class-100 hood equipped with a vertical laminar flow HEPA filter. The concentrations of Mn, Zn, Fe and Cu were determined by atomic absorption spectrometry (Varian Model 1100/1200).

4.3.3 As and Sb Speciation

Reagents and instruments. Standard As and Sb solutions used for neutron activation analysis (NAA) were prepared by diluting J. T. Baker 1000 ppm standard solutions. Chloroform used in the solvent extraction was EM Science Omnisolv grade. Baker Ultrex Reagent grade nitric acid was used for back extraction. Ammonium pyrrolidinedithiocarbamate (APDC) was purchased from the Fisher Scientific Co. The 5% APDC solution was prepared by dissolving 5 g of reagent in 100 mL of deionized water, filtering to remove insoluble materials, and shaking with chloroform for 1 min to remove bromine and other impurities. This solution was always made fresh prior to use to prevent decomposition. Disodium ethylenediaminetetra-acetate (EDTA) solution was prepared by dissolving 12 g of reagent in 100 mL of demineralized water (warmed to 10°C and stirred to dissolve). The EDTA solution was also made fresh for each experiment.

Deionized water was obtained by treating distilled water with a Barnstead Ultrapure water purification cartridge and Pall Corporation Utipor DFA 0.2 μm filter assembly. An acetate buffer solution was prepared by dissolving 0.106 g of sodium acetate anhydrous salt in 5 mL acetic acid, then diluting it to 50 mL. The pH value then should be about 4.5. Sodium thiosulfate solution (25% w/v) and 20% potassium iodide solution (w/v) were each made from EM Science Co. GR grade reagents. Ultrapure grade ammonium hydroxide was used to adjust pH.

Analytical procedures. All interstitial waters were saturated with chloroform before solvent extraction. The interstitial waters were analyzed within 24 hours after separation from sediments; otherwise they were acidified with nitric acid to pH 2 and stored in a 4°C refrigerator for analysis later. For As(III) and Sb(III) extraction, 100 mL of water sample were put into a 250-mL high-density PE bottle. A 10-mL aliquot of acetic buffer was added, and the pH was adjusted to a value between 3.5 and 5.5 with nitric acid or ammonium hydroxide. Freshly prepared EDTA (4 mL), 10 mL of chloroform, and 2 mL of freshly made APDC solution were added to the bottle. The bottle was capped and double sealed with parafilm. It was shaken vigorously for 10 min by a Burrell Model 75 wrist-action mechanical shaker. The solution was then transferred to a clear, narrow test tube. After a waiting period of about 10 min to allow phase separation, most of the aqueous solution was discarded. The organic phase was washed twice with 10 mL of deionized water. The organic solution (8 mL or any precisely known volume) was transferred to a 20-mL Beckman high-density PE bottle. Exactly 2 mL of nitric acid were added to the bottle, and the mixture was capped and double sealed with parafilm to assure no leaking while shaking. The mixture was shaken for 10 min and transferred to a test tube. After phase separation the aqueous phase was removed for analysis.

The aqueous solution (0.75 mL) was transferred into a 2/5-dram polyethylene vial and heat-sealed. The vial was

irradiated in a 1 MW TRIGA nuclear reactor with a steady flux of 6 x 10^{12} $ncm^{-2}s^{-1}$ for 2 hours, followed by a cooling period of 15 hours. The irradiated samples were transferred into new 2/5-dram polyethylene vials with a volume adjustable eppendorf pipet to avoid interferences of ^{24}Na, ^{82}Br, and any other radioactivities produced from the polyethylene vials during irradiation. This step was very helpful in eliminating the interference of ^{82}Br (554.3 KeV γ energy) to the ^{76}As peak (559.1 keV). The irradiated sample was counted with an ORTEC Ge(Li) detector, and the signals were recorded on an EG&G ORTEC ADCAM Model 918 multichannel buffer. The data were processed with an IBM-PC-XT equipped with 100/150 MCA software. The nuclides and gamma energies used for identification were ^{76}As at 559.1 keV and ^{122}Sb at 564.0 keV.

To determine As(V) and Sb(V), the pH value of another 100-mL aliquot of water was adjusted to 1.0 with HNO_3, and 1 mL of 25% $Na_2S_2O_3$ solution and 1 mL of 20% KI solution were added. The mixture was set aside for 15-30 min to allow reduction of As(V) and Sb(V) to be completed. After reduction the solution was extracted with APDC following the same procedure described previously for As(III) and Sb(III). The results represent the total As and Sb concentrations. The concentrations of As(V) and Sb(V) are the difference between the two aliquots.

4.3.4 Results and Discussion

Table 4.2 shows the results of water recovery observed from the three interstitial water extracting techniques.

Table 4.2 Comparison of Water Recovery from Sediments by Different Extraction Techniques

Sediments	Extraction Technique	Sample Weight (g)	Water Volume Extracted (mL)	(mL/100 g)	Time (min)	% Water Recovery*
Harrison-Anderson Lake	Low-Pressure D. Gas Squeezing	250	53.7	21.5	20	53.4
	Modified Centrifugation	130	17.5	13.4	60	33.4
	Solvent Displacement	200	19.2	9.6	90	25.1
St. Joe River	Low-Pressure D. Gas Squeezing	350	38.5	11.0	20	28.7
	Modified Centrifugation	120	14.2	11.8	60	31.0
	Solvent Displacement	250	23.5	9.4	90	24.6
Smelterville	Low-Pressure D. Gas Squeezing	200	32.0	16.0	20	31.8
	Modified Centrifugation	140	18.2	13.0	60	25.8
	Solvent Displacement	220	20.5	9.3	90	18.6

* Weight of water obtained per 100 g of sediment divided by total moisture weight content in 100 g of sediment (based on weight loss of sediment).

Water recovery was calculated from the weight of water obtained divided by the total weight of the moisture content in the sediment. The water volume and recovery rate vary by the three different extraction techniques. For example, using 250 g of Harrison-Anderson Lake sediment, 53.7 mL of interstitial water can be obtained in 20 minutes by the low-pressure direct gas squeezing techniques. The modified centrifugation technique results in the recovery of only 17.5 mL of interstitial water from 130 g of sediment in 60 minutes. The solvent displacement technique can extract 18.2 mL of interstitial water from 200 g of sediment in 90 minutes. Converting the mass of the sediment to 100 g, 19.4 mL of water were extracted from 100 g of Harrison-Anderson Lake sediment, but only 13.4 g/100 mL and 9.1 g/100 mL were extracted using the modified centrifugation and solvent displacement techniques, respectively. The low pressure direct gas squeezing method required only 20 min to obtain the interstitial water shown in Table 4.2. The modified centrifugation and solvent displacement methods required 60 min and 90 min, respectively. Obviously, low-pressure direct gas squeezing provides a more efficient way of removing interstitial water.

Since sediments may vary widely in particle size, porosity and chemical composition, the efficiency of extraction of interstitial water may be different from one sample to another. For example, the average percentage of recovery of the interstitial water from Harrison-Anderson Lake

is more than that from the St. Joe River. This is probably due to the higher water content and different particle size distribution of the Harrison-Anderson Lake sediments (Table 4.1). It may also be related to more complicated factors such as pore size, pore shape, and particle composition, etc.

For modified centrifugation and solvent displacement, only small amounts of sediment can be placed in each centrifuge tube. In addition, water was dissolved in the organic phase and there was water loss during the separation of organic and aqueous phases. These factors can further reduce the volume of water extracted by solvent displacement.

According to Mubarak and Olsen's[12] studies on the solvent displacement technique, it took 2 hours of centrifuging a clay soil sample at about 7800 rpm to remove 50-52% of the water. Their studies also indicated that the difference in the amount of interstitial waters extracted in 2 hours and in 3 hours is small. Ninety minutes of centrifugation time were chosen in this study because only a comparatively insignificant amount (<35%) of water was obtained between the 90-minute and 2-hour time periods. Generally speaking, there is more interstitial water extracted in less time using low-pressure direct gas squeezing compared to the other two techniques. Figure 4.3 indicates that a comparatively small percentage of water can be removed after a period of 10 minutes extraction by the low-pressure direct gas squeezing technique. For instance, in the first 10 min 19 mL of interstitial water was extracted, but for the next 10 min only 2.5 mL of water was extracted, for a

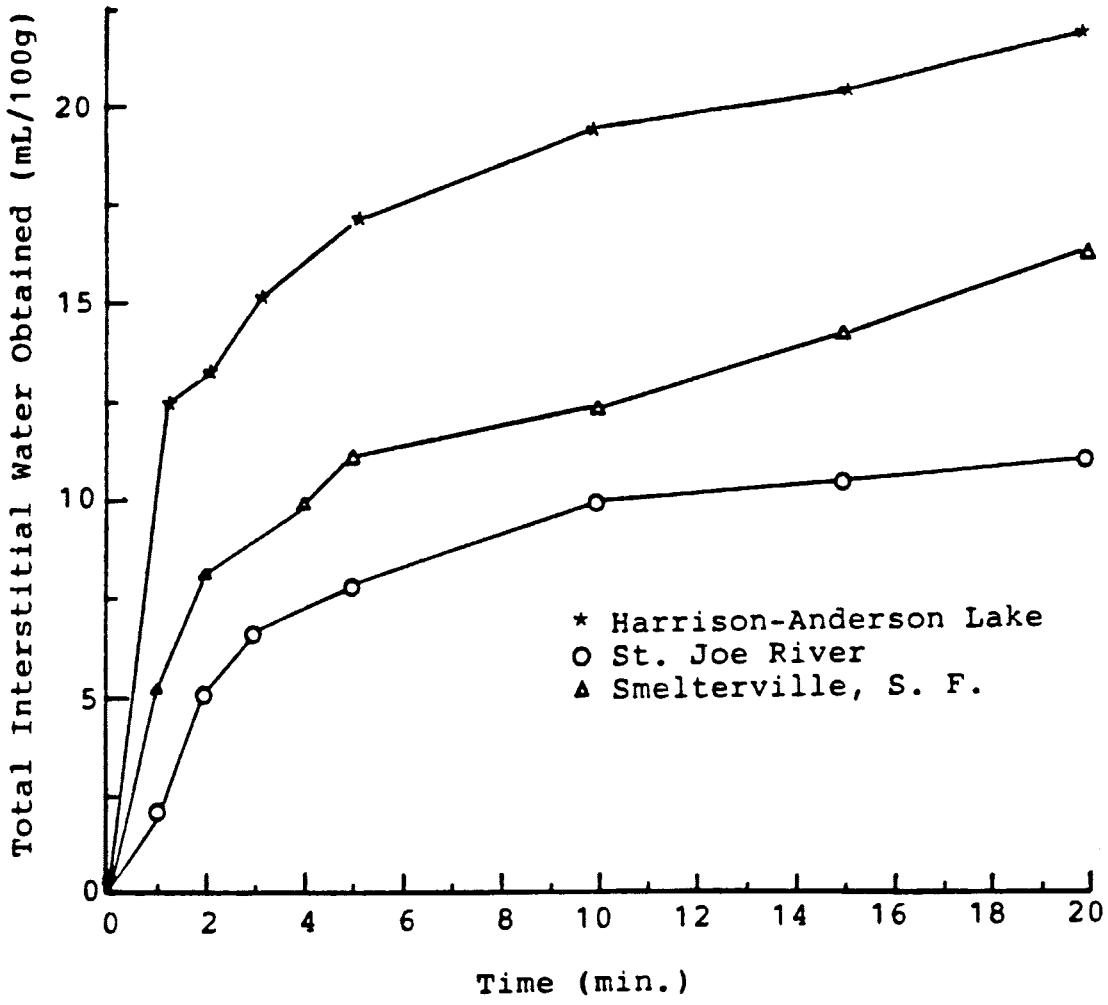


Figure 4.3 Volume of Interstitial Waters Removed from Sediments as a Function of Time by Low-Pressure Direct Gas Squeezing Technique (up to 30 psi)

total of 21.5 mL in the Harrison-Anderson Lake sediment. The extractions of water for the St. Joe River and Smelterville, South Fork Coeur d'Alene River were similar. However, significantly more water was removed from the sediments in the Smelterville, South Fork of Coeur d'Alene River and Harrison-Anderson Lake than from the St. Joe River. Again, it may be due to lower water content in the St. Joe River sediment.

Figure 4.4 indicates the percentage of water recovery at different applied pressures in the low-pressure direct gas squeezing technique. The recovery is in the range of 28.7% to 53.7% for the different sediments. According to conventional soil moisture classification,[26] gravitational, capillary and hygroscopic waters contained in soil are characterized by the bound energy of moisture and soil solids (Appendix G). The hygroscopic water is the water bound tightly by the soil solids at tension values greater than 31 bars. This is not the water desired as an interstitial water. The gravitational water would be dripping out before the extraction. The water extracted in the pressure range shown in Figure 4.3 is most likely the capillary water.

When applying high pressure, the percentage of water removed from the St. Joe River sediment was smaller compared to the other sediments (Figure 4.4). This indicates that interstitial waters contained in larger particles, as in the case of the St. Joe River sediments, are easier to remove at low pressures. However, for the sediments with fine particles, high pressure would remove more water. In

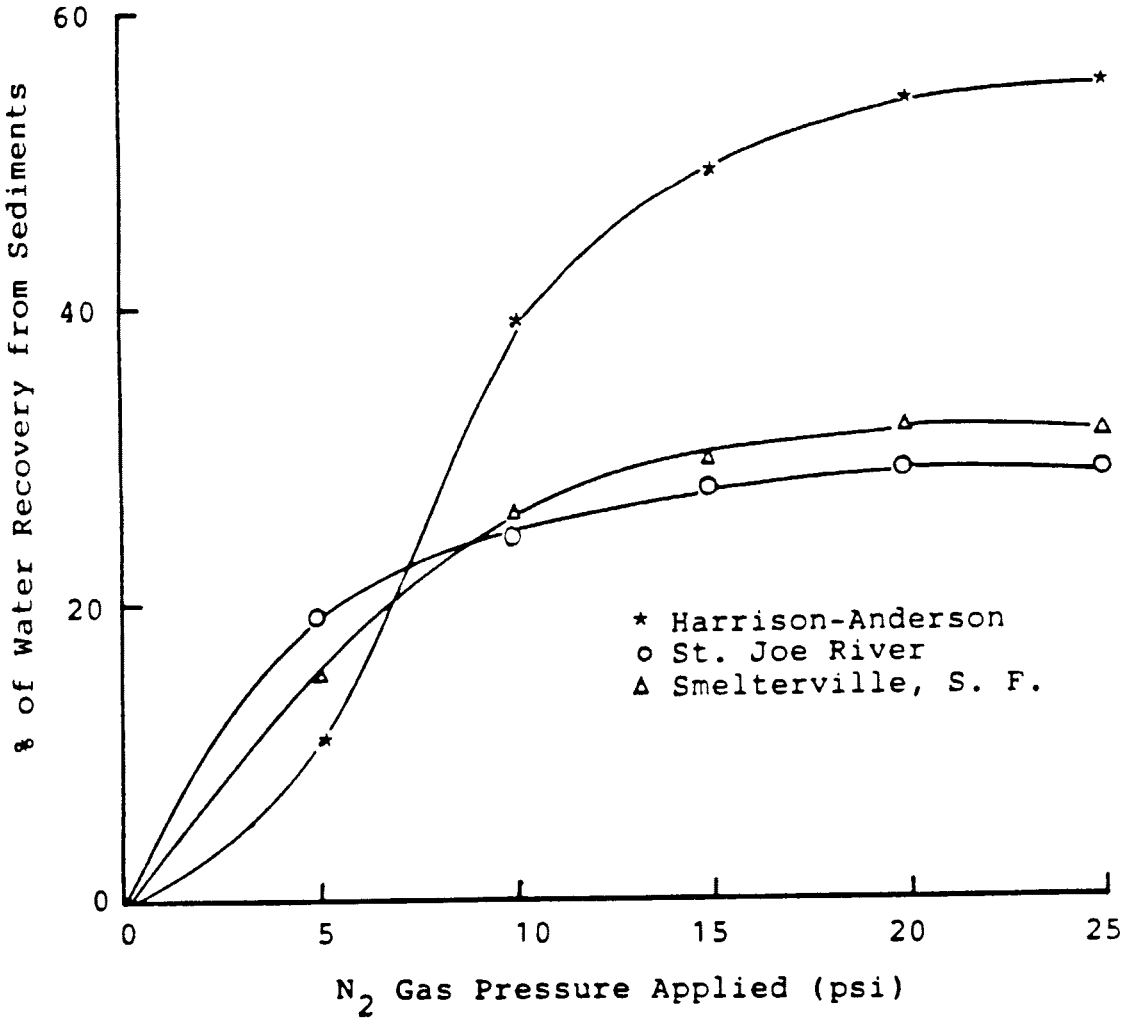


Figure 4.4 Percentage Recoveries of Total Water Content from Sediments vs. Applied Pressure by Low-Pressure Direct Gas Squeezing Technique

addition, a smaller percentage of water was recovered from the St. Joe River. Overall, most of the interstitial water can be removed at 20 psi by the low-pressure direct gas squeezing technique.

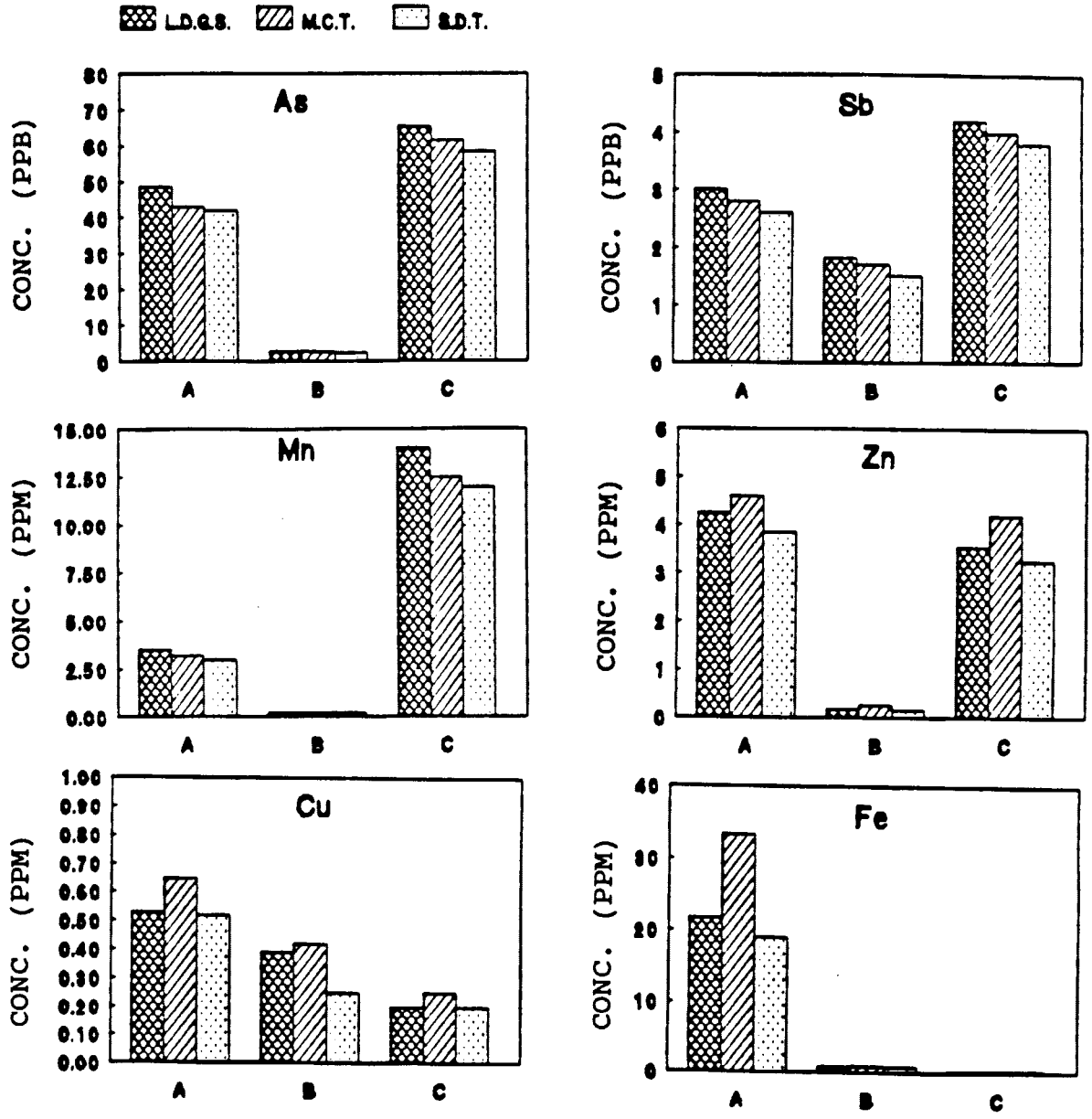
Table 4.3 summarizes the metal contents and species of arsenic and antimony found in the interstitial waters by three different techniques. In general, the data appear to show a consistent trend for different methods. For example, the zinc concentrations in Harrison-Anderson interstitial water were 4.60 ppm, 4.40 ppm, and 3.85 ppm extracted by the three different techniques. The average value is 4.28±0.28, with the largest deviation from the mean value being 7.4%. The concentrations of Cu in the interstitial water were 0.65 ppm, 0.56 ppm, and 0.52 ppm for the three different techniques. The average is 0.58±0.08 ppm, and the largest deviation from the mean value is 13%. The measured concentrations of metals from the water extracted by the solvent displacement technique were overall lowest among the three extraction techniques. Of the three methods, the low pressure squeezing technique showed the highest content of metals overall.

Figure 4.5 presents a clear picture for the comparison of metal concentrations among the three extraction techniques. Overall, the metal contents in the interstitial waters obtained by low-pressure direct gas squeezing were a little higher than the other two techniques. Taking arsenic as an example, the concentrations were 48.5 ppb, 43.0 ppb, and 43.8 ppb in Harrison-Anderson Lake sediments extracted by low-

Table 4.3 Concentrations of As(III), As(V), Sb(III) and Sb(V), and Other Trace Metals in Interstitial Waters of Sediments by Different Extraction Techniques

Sediment	Extraction Technique*	Concentration (ppm) Mn	Zn	Cu	Fe	Arsenic in ppb (III)	(V)	Total	Antimony in ppb (III)	(V)	Total
Harrison-Anderson Lake	LDGS	3.52 ±0.2	4.24 ±0.10	0.53 ±0.08	21.7 ±0.1	28.5 ±1.2	20.0 ±0.1	48.5 ±1.5	1.5 ±0.1	1.4 ±0.1	2.9 ±0.2
	MCT	3.20 ±0.3	4.60 ±0.13	0.65 ±0.09	33.3 ±0.1	27.3 ±1.0	15.7 ±0.1	43.0 ±1.3	2.7 ±0.1	0.1 ±0.1	2.8 ±0.2
	SDT	3.08 ±0.3	3.85 ±0.08	0.52 ±0.07	19.5 ±0.1	24.9 ±1.0	18.9 ±0.1	43.8 ±1.4	1.4 ±0.1	1.2 ±0.1	2.6 ±0.2
St. Joe River	LDGS	<0.1	0.17 ±0.08	0.39 ±0.10	0.85 ±0.1	1.2 ±0.2	1.6 ±0.2	2.8 ±0.4	0.2 ±0.1	1.6 ±0.1	1.8 ±0.1
	MCT	<0.1	0.25 ±0.10	0.42 ±0.11	0.95 ±0.1	1.3 ±0.2	1.4 ±0.2	2.8 ±0.4	0.3 ±0.1	1.4 ±0.1	1.7 ±0.1
	SDT	<0.1	0.15 ±0.09	0.25 ±0.08	0.80 ±0.1	1.2 ±0.3	1.3 ±0.3	2.6 ±0.3	0.1 ±0.1	1.4 ±0.1	1.5 ±0.1
Smelterville South Fork	LDGS	14.0 ±0.2	3.54 ±0.03	<0.05	<0.1	39.5 ±1.4	25.8 ±1.2	65.3 ±1.6	2.2 ±0.3	2.0 ±0.1	4.2 ±0.3
	MCT	12.5 ±0.3	4.20 ±0.05	<0.05	<0.1	40.5 ±1.4	21.0 ±1.1	61.5 ±1.8	2.1 ±0.3	2.0 ±0.1	4.0 ±0.3
	SDT	12.0 ±0.2	3.25 ±0.04	<0.05	<0.1	31.5 ±1.3	27.0 ±1.0	58.5 ±1.8	0.6 ±0.2	3.3 ±0.1	3.8 ±0.3

* LDGS = Low-pressure Direct Gas Squeezing
MCT = Modified Centrifugation Technique
SDT = Solvent Displacement Technique



A. Harrison-Anderson Lake
B. St. Joe River
C. Smelterville, South Fork

Figure 4.5 Concentration of Metals in Interstitial Waters of Sediments by Different Extraction Techniques

pressure gas squeezing, modified centrifugation, and solvent displacement, respectively. Similarly, the concentrations were 2.8 ppb, 2.8 ppb, and 2.6 ppb in the interstitial water of St. Joe River sediments and 65.3 ppb, 61.5 ppb, and 58.5 ppb in the Smelterville, South Fork sediments. This may be related to the concentration variation in different squeezing pressures by low-pressure direct gas squeezing.

In Figure 4.6 and Table 4.4 it is shown that the concentration of total arsenic in the interstitial water was found to increase from 32.5 ppb to 62.8 ppb as the squeezing pressure was increased from 5 psi to 20 psi for the Harrison-Anderson Lake sediments. Similarly, the trend was also observed in the St. Joe River and Smelterville sediments. Since the amounts of water removed by low-pressure direct gas squeezing were a little larger than by the other two techniques, we can attribute this higher concentration phenomenon to the small amounts but high arsenic concentration water extracted at high squeezing pressure.

The concentration of antimony was 4.2 ppb in the interstitial water of the Smelterville sediment obtained by the low-pressure gas squeezing technique. However, the concentrations were 4.0 ppb and 3.8 ppb by the modified centrifugation and solvent displacement techniques, respectively. This also corresponds to the lower concentration of antimony extracted at a higher squeezing pressure as shown in Figure 4.6 and Table 4.4. The concentrations of Sb in the interstitial water of Smelterville

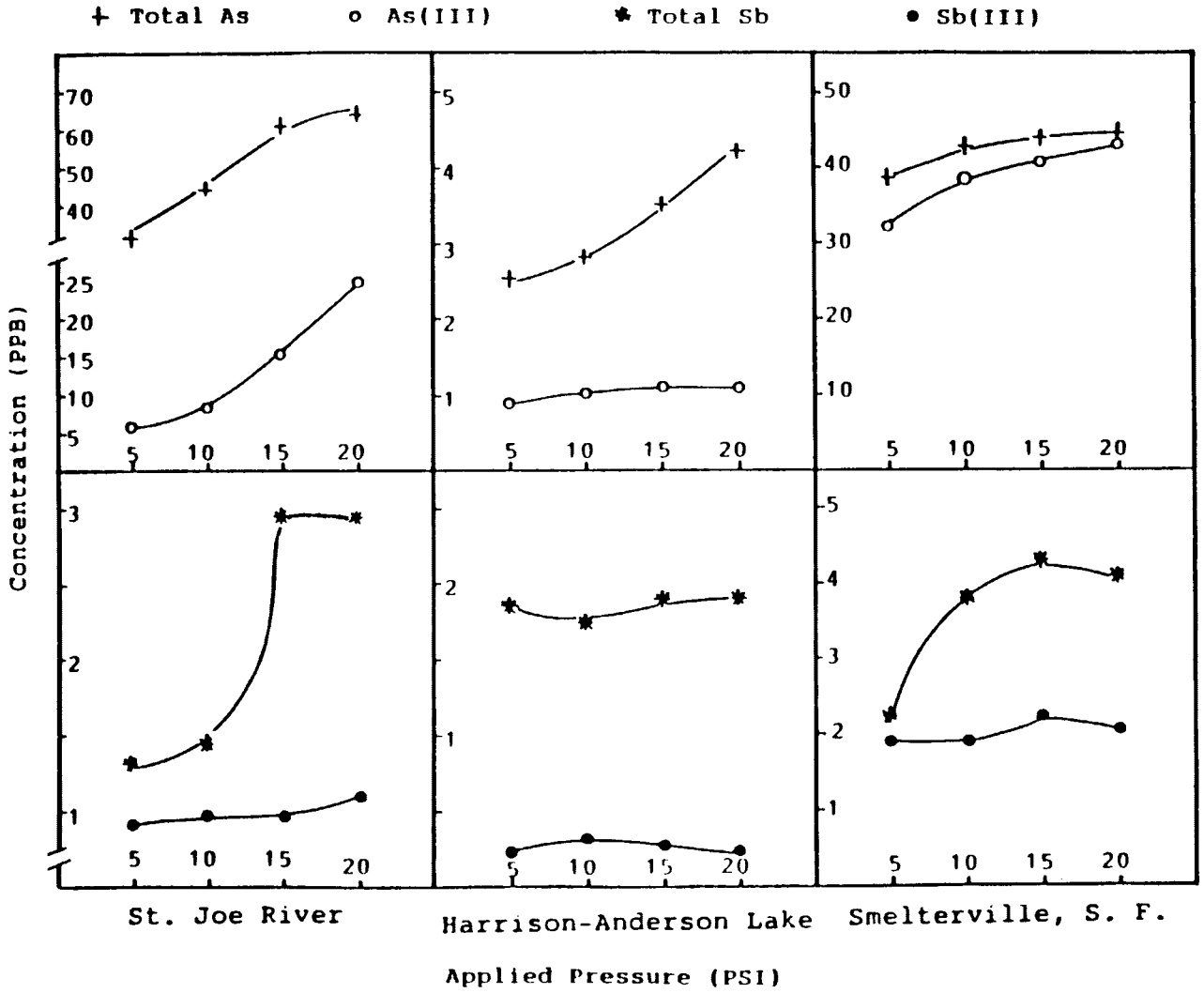


Figure 4.6 Concentrations of As and Sb Species in Interstitial Waters of Sediments at Different Applied Pressures of Low-Pressure Direct Gas Squeezing

Table 4.4 Concentrations of Trace Metals, As(III), As(V), Sb(III) and Sb(V) in Interstitial Waters of Sediments at Different Applied Pressures in Low-pressure Direct Gas Squeezing Technique

Sediment	Applied Pressure	Concentration (ppm) Mn	Zn	Cu	Fe	Arsenic in ppb (III)	(V)	Total	Antimony in ppb (III)	(V)	Total
Harrison-Anderson Lake	5 psi	3.6 ±0.2	3.91 ±0.10	0.30 ±0.10	14.7 ±0.3	5.8 ±0.2	26.7 ±0.8	32.5 ±0.9	0.9 ±0.1	0.5 ±0.1	1.3 ±0.2
	10 psi	3.9 ±0.2	4.22 ±0.11	0.48 ±0.12	18.5 ±0.3	7.9 ±0.2	37.9 ±0.9	45.8 ±1.0	0.9 ±0.1	0.5 ±0.1	1.4 ±0.2
	15 psi	4.2 ±0.3	4.53 ±0.10	0.62 ±0.15	22.6 ±0.4	15.4 ±0.6	45.4 ±1.1	60.8 ±1.2	0.9 ±0.1	2.0 ±0.1	2.9 ±0.2
	20 psi	4.5 ±0.3	3.22 ±0.09	0.60 ±0.15	25.2 ±0.4	24.3 ±0.8	38.5 ±1.0	62.8 ±1.1	1.2 ±0.1	1.6 ±0.1	2.8 ±0.2
St. Joe River	5 psi	0.5	0.65 ±0.03	0.62 ±0.14	5.5 ±0.2	0.9 ±0.1	1.6 ±0.1	2.6 ±0.3	0.2 ±0.1	1.6 ±0.1	1.9 ±0.2
	10 psi	0.1	0.52 ±0.04	0.58 ±0.13	4.2 ±0.2	1.0 ±0.1	1.8 ±0.1	2.8 ±0.3	0.3 ±0.1	1.4 ±0.1	1.8 ±0.2
	15 psi	0.1	0.12 ±0.02	0.50 ±0.12	2.0 ±0.2	1.2 ±0.1	2.2 ±0.2	3.5 ±0.2	0.3 ±0.1	1.6 ±0.1	1.9 ±0.2
	20 psi	<0.1	0.10 ±0.02	<0.05	<0.1	1.3 ±0.1	2.9 ±0.2	4.2 ±0.3	0.2 ±0.1	1.7 ±0.1	1.9 ±0.2
Smelterville South Fork	5 psi	11.4	3.39 ±0.09	<0.05	<0.1	32.5 ±0.8	6.2 ±0.2	38.7 ±1.0	2.0 ±0.2	0.3 ±0.1	2.2 ±0.2
	10 psi	12.5	3.02 ±0.10	<0.05	<0.1	38.4 ±0.9	4.4	42.8 ±1.1	2.0 ±0.2	2.0 ±0.1	3.9 ±0.3
	15 psi	13.2	2.40 ±0.08	<0.05	<0.1	41.2 ±1.0	2.3	43.5 ±1.1	2.1 ±0.1	2.2 ±0.1	4.3 ±0.4
	20 psi	13.2	2.12 ±0.07	<0.05	<0.1	40.2 ±1.0	3.1	43.4 ±1.0	2.0 ±0.2	2.1 ±0.1	4.1 ±0.4

sediments dropped from 4.3 ppb to 4.1 ppb as the squeezing pressure was increased from 15 psi to 20 psi.

The lower concentrations of zinc, copper and iron in the water extracted by low-pressure direct gas squeezing compared to the modified centrifugation extraction techniques shown in Figure 4.5 can also be attributed to the decreasing trend of zinc, copper and iron concentration along with the increasing pressure applied, shown in Figure 4.7. Obviously, the modified centrifugation technique did not extract efficiently at the high-pressure portions of interstitial waters which contain lower concentrations of the metals zinc, copper and iron. The low concentrations may be due to the deposition of metal sulfide minerals. Overall, the concentration discrepancies of metals between low-pressure gas squeezing and the other two techniques follow this trend. However, the analytical deviation or possible adulteration from solvent to the water in extraction may shift the result slightly making the interpretation harder.

Generally speaking, the results obtained using the three different interstitial water extraction techniques were consistent. Conventional gas or mechanical squeezing techniques which apply pressure to a piston or diaphragm were not mentioned because they were operated at very high pressures, considered beyond the "safe" pressure of ordinary laboratory operations. In addition, contamination may occur due to the metal or stainless steel material used in the construction of the high pressure squeezer. The commercially

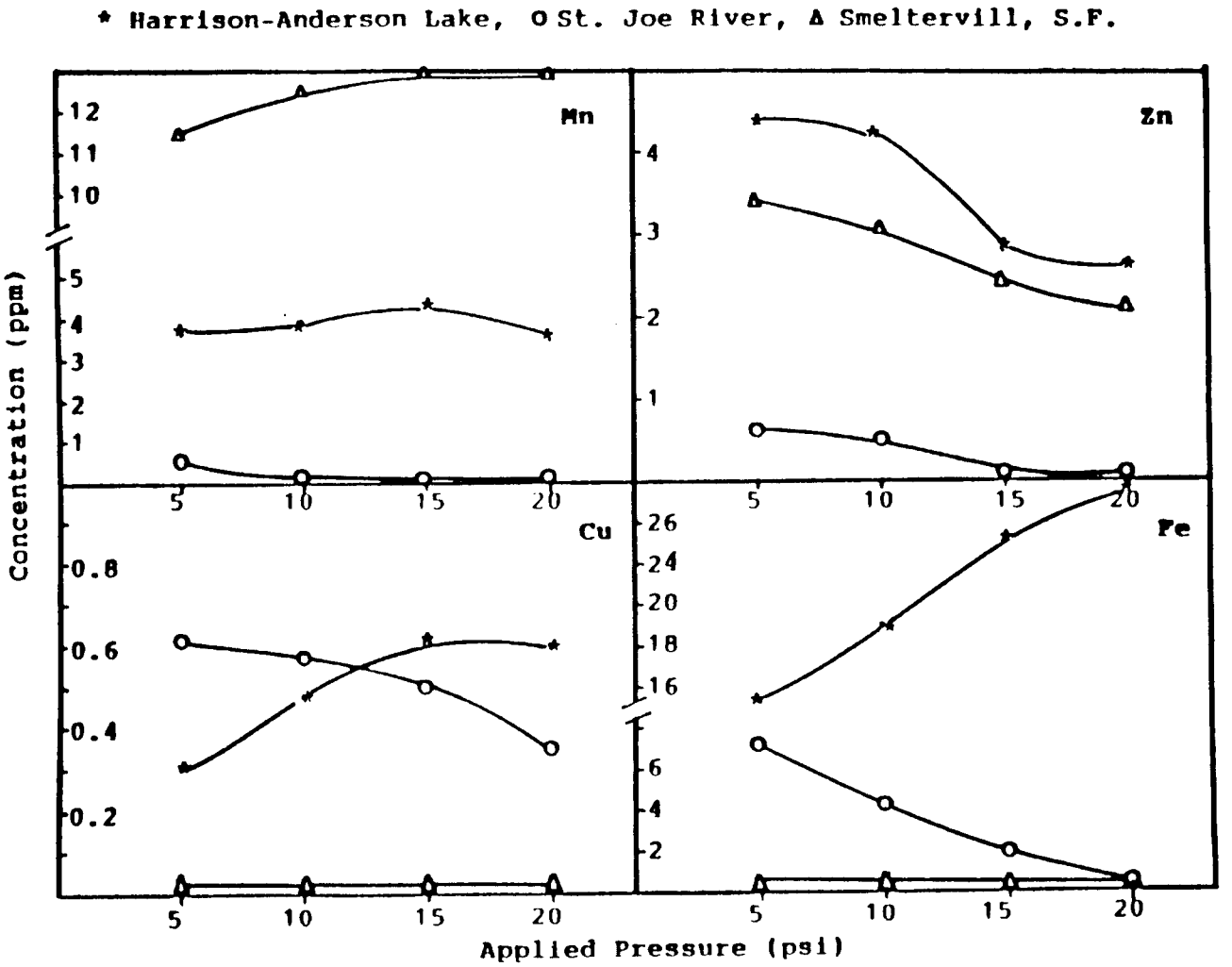


Figure 4.7 Concentrations of Trace Metals in Interstitial Waters of Sediments at Different Applied Pressures of Low-Pressure Direct Gas Squeezing

available low-pressure direct gas squeezer described in this chapter has no metal alloy in contact with sediment samples, thus eliminating possible metal contamination.

Table 4.5 gives a comparison of the three extraction techniques discussed in this chapter in terms of speed, volume of sediment required, chemicals involved, and cost. For unconsolidated river sediments with high moisture content, the low-pressure direct gas squeezing technique appears to provide an efficient and convenient extraction method to remove interstitial water. In addition, the low-pressure direct gas squeezing technique has an advantage in studying the speciation of metals in interstitial waters at different pressures.

Table 4.5 Comparison of Different Interstitial Water Extraction Techniques

	Extraction Technique		
	S.D.T.[1]	M.C.T.[2]	L.D.G.S.[3]
Time	Slow	Slow	Fast
Volume of Sediment	Small	Small	Large
Chemical	Toxic	None	None
Cost	Expensive	Less	Less

1 Solvent Displacement Technique
2 Modified Centrifugation Technique
3 Low-pressure Direct Gas Squeezing Technique

REFERENCES

1. Arsenic - Medical and Biological Effects of Environmental Pollutants, National Academy of Science: Washington, D.C. (1977).

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

3. Schloesing, M.T. Compt. Rend. 63:1007-1012 (1866).

4. Mehlich, A. and Drake, M. Am. Chem. Soc. Monograph 126:286-327 (1958).

5. Murry, J. and Irvine, R. Trans. Roy. Soc. Edinburgh 37:481-507 (1893).

6. Smith, R.I. J. Marine Biol. Assoc. 34:33-46 (1955).

7. Brooks, R.R.; Presley, B.T. and Kaplan, I.R. Geochim. Cosmochim. Acta 32:397-414 (1968).

8. Handbook for Sampling and Sample Preservation of Water and Water Wastewater, EPA-600/4-82,029 (1982).

9. Manheim, F.T. Clays and Clay Minerals 22:337-343 (1974).

10. Murthy, A.S.P. and Ferrell, R.E., Jr. Clays and Clay Minerals 20:317-321 (1972).

11. Batley, G.E. and Giles, M.S. Water Res. 13:879 (1979).

12. Mubarak, A. and Olsen, R.A. Soil Sci. Soc. Am. J. 40:880-882 (1976).

13. Whelan, B.R. and Barrow, N.J. J. Environ. Qual. 9:315-319 (1980).

14. Edmunds, W.M. and Bath, A.H. Envir. Sci. Technol. 10:467-472 (1976).

15. Kriukov, N.J. Izdatel'stvo Nauka, Moscow, 219 (1971).

16. Glaubig, R.A. and Goldberg, S. Soil Sci. Soc. Am. J. 52:536-537 (1988).

17. Devine, S.B.; Ferrell, R.E., Jr. and Billings, G.K. Chem. Geol. 12:219-228 (1973).

18. Scholl, D. Sedimentology U.S. Navy Electronics Laboratory: San Diego, CA, 2:156-163 (1963).

19. Hesslein, R. Lamont-Doherty Geological Observatory of Columbia University, Limnol. Oceanogr. 29:912-914 (1976).

20. Mayer, L. Limnol. Oceanogr. 29:909-911 (1976).

21. Carignan, R. National Water Research Institute, Limnol. Oceanogr. 29(3):667-670 (1984).

22. Bottomley, E.Z. Limnol. Oceanogr. 29(3):671-673 (1984).

23. Elkhatib, E.A.; Hern, J.L. and Staley, T.E. Soil Sci. Soc. Am. J. 51:578-583 (1987).

24. Cooney, D.O. Anal. Chem. 52:1608 (1980).

25. Mubarak, A. Soil Sci. Soc. Am. J. 40:329-331 (1976).

26. Brady, N. The Nature and Properties of Soils, 9th Edition, MacMillan Co., p. 100 (1984).

CHAPTER FIVE

ARSENIC AND ANTIMONY SPECIATION OF INTERSTITIAL WATERS IN COEUR D'ALENE RIVER SEDIMENTS, IDAHO

5.1 Introduction

The Coeur d'Alene River is located in Shoshone and Kootenai counties of northern Idaho. The river is divided into three sections: the North Fork, the South Fork and the Main Stem. Since 1890, mining of lead, silver and zinc has been the major product along the South Fork of the Coeur d'Alene River. In addition, considerable amounts of cadmium, copper, antimony, and gold were produced in the Coeur d'Alene Mining District. On a national basis in mineral production, the South Fork Mining District was ranked first in silver and antimony, second in lead, third in zinc, and ninth in gold for many years.[1]

The raw sewage of the mining communities of this area was discharged into the South Fork of the river and has caused a complex pollution problem. Although legislation of water quality control has reduced the present discharge of tailings, there had been large amounts of mine tailings deposited in the river sediments already. The subsequent leaching of sediments led to surface water pollution. The leaching processes of sediments may be closely related to the status of interstitial water. In this study, the content of some trace metals in the interstitial waters in the Coeur d'Alene River sediments was measured along with different depths and locations. Arsenic

and antimony speciation also were investigated. In addition, different leaching processes and a digestion of the sediment were carried out. Finally, X-ray fluorescence was used to check the sediment composition.

The vertical distribution of dissolved Zn, Mn, Cu, and Fe in sediment profiles was studied. Dissolved arsenic and antimony species distributed in the sediment profiles and surface water were also compared to interpret the model of dissolution, migration and precipitation. In addition, the correlations of leaching results and interstitial water data obtained from the sediments were also investigated.

5.2 Experimental

5.2.1 Sample Collection

The sampling area (Figure 5.1) included one station at the St. Joe River, two stations close to the inlet of Lake Coeur d'Alene, two stations at the Main Stem, one at Rose Lake, one at the North Fork, and two at the South Fork. Sediments were collected by corers of 1.2 m in length and 4 cm of I.D. Shallow water sediments near the river bank were sampled. The collected sediments were immediately divided into sections by depth and put into PVC zip-lock bags. After squeezing out air, the bags were stored in a cooler which contained dry ice. The surface water samples were collected in 1-liter high-density linear polyethylene bottles which had been triple rinsed with river water. The bottles had been cleaned with nitric acid and rinsed with deionized water prior

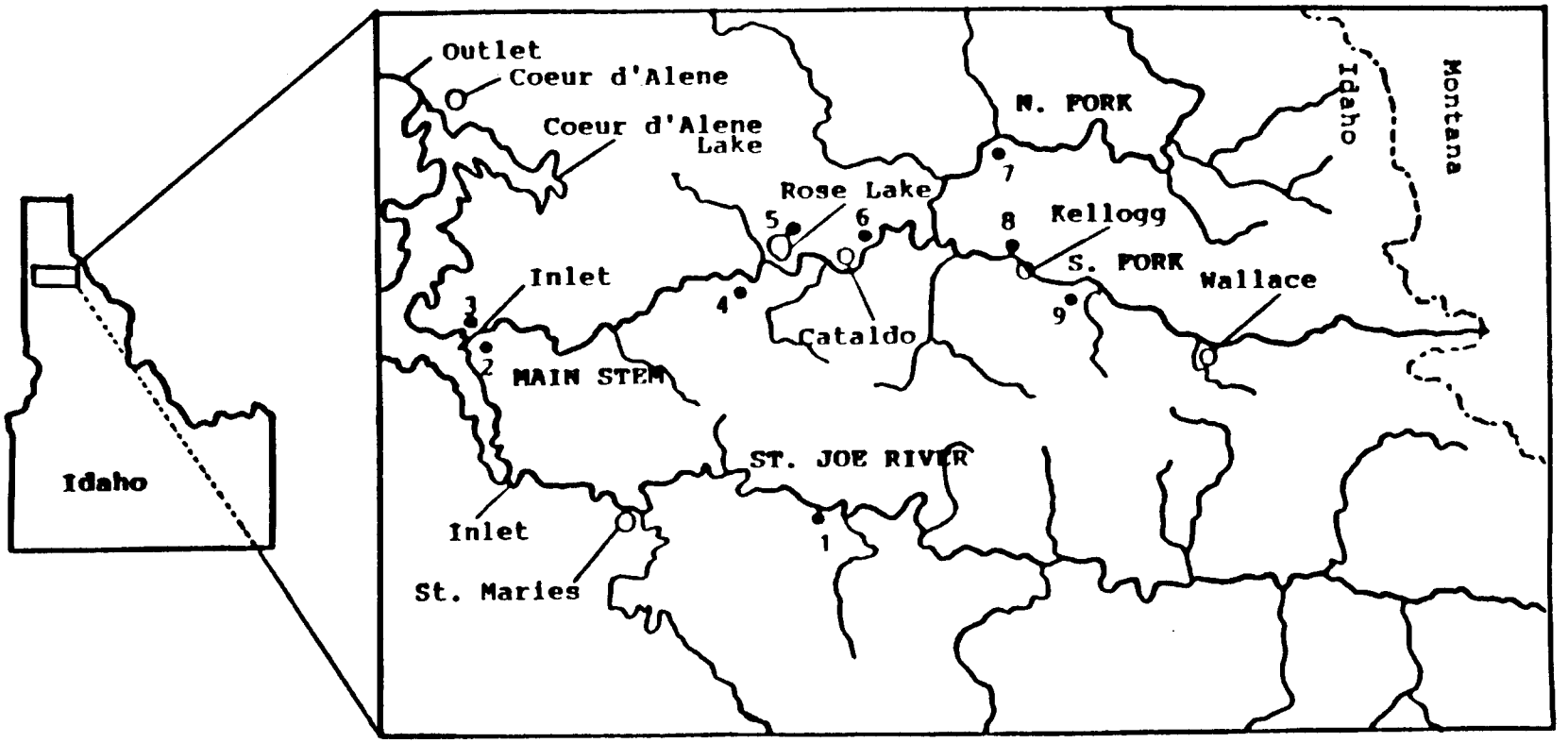


Figure 5.1 Sample Collecting Sites Along the Coeur d'Alene River

to sampling. The filled bottles were then stored in the cooler for transport back to the laboratory.

5.2.2 Collection and Analysis of Interstitial Water

The extraction of interstitial water was performed with an Amicon Ultrafiltration Cell Model 402, a commercially available direct gas squeezer, at applied pressures up to 60 psi. The details of the method were characterized in the previous chapter (Section 4.3.1). The interstitial water obtained was filtered through a 0.45 μm Millipore filter and collected in acid-cleaned high-density P.E. bottles. A portion of the samples was acidified to pH 2 with HCl, then kept at 4°C until the time of analysis. The other portion of each of the samples was separated into two aliquots. One aliquot was acidified to about pH 1.0. Reduction of As(V) to As(III) and Sb(V) to Sb(III) was processed by adding 1 mL per 100 mL of water sample of 25% sodium thiosulfate solution and 20% potassium iodide solution. About 15-30 min were required to complete the reduction. Then, the two aliquots were preconcentrated with two-step APDC solvent extraction for NAA of As(III), As(V), Sb(III), and Sb(V) according to the procedures described in Section 3.2.1. Because limited amounts of interstitial waters were available for chemical analysis, the initial sample size in some cases was reduced to 50 mL, or as low as 20 mL. The amounts of the reducing agent, the buffer, the masking agent, and the chelating agent were also decreased proportionately according to the sample size. In order to obtain a high preconcentration factor, the volume

of the organic solvent and the back-extraction acid solution can be decreased. However, the aqueous-to-organic phase ratio should not exceed 20 for effective extraction of the metal-dithiocarbamate complexes. In addition, an extraordinarily small size of the solvent or the acid solution may cause larger deviation of the result and inconvenience in extraction. Since the metal content in the interstitial water of sediments is normally higher than that in surface water, an average preconcentration factor of 10 to 20 should be enough.

The extracted samples were irradiated in a 1-MW TRIGA reactor at a steady neutron flux of 6×10^{12} $ncm^{-2}s^{-1}$ for 2 hours followed by a 24-hour cooling period. The photopeak areas of arsenic ($E\gamma$ = 559.1 keV) and antimony ($E\gamma$ = 564.0 keV) were quantified and compared with those of standards to determine the concentration of the water samples. The difference of the concentration between the aliquot of reduction and the aliquot of non-reduction represents the concentration of As(V) and Sb(V). The other acidified portion of the samples was used to determine the metal content of Mn, Zn, Cu, and Fe by atomic absorption spectrometry.

5.2.3 Leaching Experiments

The sediment collected from the Smelterville Flats of the South Fork Coeur d'Alene River was used for the leaching experiments. The leaching experiments were carried out in the laboratory under atmospheric pressure and room temperature. For the first set of leaching experiments, 240 g of two aliquots of the sediments were placed in two round-bottomed

flasks. Water (800 mL) was then added to each flask. There are two open holes on the top of the container cap. A stirring rod of a mechanical stirrer was inserted into the flasks and suspended in the water above the sediment through one hole of each flask (water-phase stirring). The other hole of each flask was used to introduce air in one and nitrogen gas in the other. After a period of 10 days leaching, the surface water and the interstitial water were analyzed to measure the content of As(III), As(V), Sb(III), Sb(V) and selected metals with the analytical technique as previously described.

For the second set of leaching experiments, 60 g of two aliquots of the sediments were each mixed with 600 mL of deionized water. The sediment-water mixtures were kept in suspension by constantly stirring with a magnetic stirrer (two-phase mixing). One was leached under aerobic conditions by introducing air, the other under anaerobic conditions by introducing nitrogen gas. After a period of 10 days leaching, the mixtures were set till phase separation; then the surface water and interstitial water were analyzed.

5.2.4 Acid Extraction and X-ray Fluorescence Analysis of the Sediments

About 10 g of a wet sediment sample were placed in a 500-mL beaker, then 40 mL of 4 N HCl were added. The sample was heated on a hot plate at 90°C for 30 min. The volume was then adjusted to 100 mL when the sample cooled down. The water then was analyzed by the methods described previously

for determining the content of the metals and species of As and Sb. The major and trace element composition of the sediment was determined by a Rigaku 3370 Automated Sequential X-ray Spectrometer. The operating conditions for each element are listed in Appendix H.

5.3 Results and Discussion

5.3.1 Trace Metals in Interstitial Water

The purpose of this study was to investigate the relationship of metal contents between the overlying (surface) water and the interstitial water in the sediments of the Coeur d'Alene River. Table 5.1 summarizes the metal contents of surface waters collected from the eight sampling stations along the Coeur d'Alene River and a station in the St. Joe River. The metal concentrations in the South Fork of the Coeur d'Alene River (in Smelterville and in Kellogg) were on average about 5-45 times higher than those in the St. Joe River. Arsenic concentrations in the South Fork waters were 2.9±0.3 and 2.1±0.3 ppb in Smelterville and in Kellogg, respectively. The total arsenic concentrations in South Fork waters were about 4-6 times higher than that of the St. Joe River. However, comparing the concentrations of As(III), those in Smelterville and in Kellogg would be 18 and 21 times higher than that in the St. Joe River. Since As(III) is biologically more toxic than As(V), the water quality of the South Fork is obviously undesirable with respect to arsenic. The concentrations of antimony were 4.6±0.4 and 4.3±0.3 ppb, respectively, in the waters collected from Smelterville

Table 5.1 Concentrations of As, Sb, Mn, Zn, Cu and Fe in the Surface Waters at Different Locations along the Coeur d'Alene River

Sample Locations	ppb				ppm			
	As(III)	As(III) +As(V)	Sb(III)	Sb(III) +Sb(V)	Zn	Mn	Cu	Fe
1. St. Joe River	0.1 ±0.1	0.5 ±0.1	<0.1	<0.1	0.04 ±0.02	<0.1	<0.05	<0.1
2. Harrison-Anderson Lake	1.1 ±0.1	1.9 ±0.2	<0.1	0.2 ±0.1	0.02 ±0.01	<0.1	<0.05	<0.1
3. Harrison-Delta	0.3 ±0.1	0.8 ±0.1	<0.1	0.1 ±0.1	<0.01	<0.1	<0.05	<0.1
4. Main Stem Rose Lake	0.2 ±0.1	0.4 ±0.1	<0.1	<0.1	0.42 ±0.03	<0.1	<0.05	<0.1
5. Rose Lake	0.1 ±0.1	0.5 ±0.1	<0.1	<0.1	0.30 ±0.03	<0.1	<0.05	<0.1
6. Main Stem Cataldo	1.5 ±0.2	2.0 ±0.3	<0.1	1.0 ±0.1	0.07 ±0.01	<0.1	<0.05	<0.1
7. North Fork Linfor	<0.1	0.2 ±0.1	<0.1	<0.1	0.01 ±0.01	<0.1	<0.05	<0.1
8. South Fork Smelterville	2.7 ±0.4	2.9 ±0.3	<0.1	4.6 ±0.4	1.79 ±0.05	0.3 ±0.1	<0.05	<0.1
9. South Fork Kellogg	2.6 ±0.3	2.1 ±0.3	<0.1	4.3 ±0.3	1.45 ±0.05	0.3 ±0.1	<0.05	<0.1

and from Kellogg. They were also much more concentrated than that in the St. Joe River. The As and Sb concentrations in the North Fork were both lower than that in the St. Joe River.

Water of the North Fork is running from the mountains of northern Idaho. Rain and winter snow are the major sources of the springs in the mountains. The North Fork joins the South Fork near Kingston and becomes the Main Stem of the Coeur d'Alene River. The As and Sb concentrations in the Main Stem at Cataldo were 2.0±0.3 and 1.0±0.1 ppb, respectively, which indicated a dilution effect of the water from the South Fork when added to that from the North Fork. The average concentrations of As and Sb in the Main Stem were lower than those in the South Fork. Rose Lake and Harrison-Anderson Lake are the lateral lakes of the Coeur d'Alene River. The metal concentrations of these two lateral lakes were similar to those in the Main Stem. However, in Harrison-Anderson Lake the concentrations of the metals were comparatively higher than those in Rose Lake. The concentrations of Zn and Mn in the South Fork at the Smelterville Flats and near Kellogg were also higher than those in the North Fork, Main Stem, or St. Joe River. The contents of Fe and Cu in the surface water of the samples were all below the detection limits of AAS, 0.1 ppm and 0.05 ppm, respectively.

Studies of metal compositions of interstitial waters are important for understanding the correlations of the sediment conditions and overlying water quality. At each water sampling station, we also collected sediment samples with

corers. No sediment around the sampling station of the North Fork was collected because the materials from the top down to 12 cm depth were gravel and very coarse sand. Large particle size gravel and coarse sand retain little interstitial water and probably have insignificant effects on overlying water quality. Table 5.2 shows the concentrations of As(III), total As, Sb(III), total Sb, Zn, Mn, Cu, and Fe in the interstitial waters from the sediments of the Coeur d'Alene River measured by FAAS and by APDC extraction-NAA. The metal concentrations of interstitial waters given in Table 5.2 are 5-21 times higher than those of overlying waters shown in Table 5.1. For instance, the total arsenic in interstitial waters of Smelterville and Kellogg was 62.5±2.0 and 52.6±1.8 ppb, respectively, which was about 20-25 times more concentrated than that in the overlying waters. However, the concentration ratios (R) of zinc between interstitial water and overlying water in the South Fork Smelterville and Kellogg were only about a factor of 2. This is probably due to the zinc released into the South Fork from other mine waste related sources. However, the ratio (R) of zinc in Harrison-Anderson was over 170. This was also true for the R values of iron. The manganese in the South Fork showed much higher concentration in interstitial waters. Rapin et al.[3] have reported the distributions of major chemical forms of some metals in the extracted solution of sediment and their relations to the interaction with interstitial water. They indicated that trace metal concentrations in interstitial

Table 5.2 Concentrations of As, Sb, Mn, Zn, Cu and Fe in the Interstitial Waters of Coeur d'Alene River Sediments

Sample Locations	ppb				ppm			
	As(III)	As(III) +As(V)	Sb(III)	Sb(III) +Sb(V)	Zn	Mn	Cu	Fe
1. St. Joe River	1.1±0.2	2.8±0.4	0.1±0.1	1.2±0.2	0.18±0.01	<0.1	<0.05	0.8 ±0.1
2. Harrison-Anderson Lake	22.3±1.0	42.5±1.6	1.6±0.2	2.7±0.3	3.52±0.04	2.9	<0.05	18.5 ±0.4
3. Harrison-Delta	2.0±0.2	4.1±0.3	0.1±0.1	2.0±0.2	0.92±0.02	<0.1	<0.05	<0.1
4. Main Stem Rose Lake	2.6±0.2	3.5±0.3	0.2±0.1	1.9±0.2	1.20±0.02	0.2	<0.05	<0.1
5. Rose Lake	1.6±0.1	3.0±0.2	0.1±0.1	1.6±0.2	0.20±0.01	<0.1	<0.05	<0.1
6. Main Stem Cataldo	6.8±0.5	8.4±0.6	1.5±0.2	3.0±0.3	1.05±0.02	0.8	<0.05	<0.1
7. North Fork Linfor	--	--	--	--	--	--	--	--
8. South Fork Smelterville	40.6±1.5	62.5±2.0	1.9±0.2	4.0±0.4	4.15±0.04	12.9	<0.05	7.6 ±0.2
9. South Fork Kellogg	28.4±1.2	52.6±1.8	1.8±0.2	3.6±0.3	3.68±0.04	8.7	<0.05	6.9 ±0.3

water were affected by the form of iron. In addition, iron oxides and manganese oxides have been reported as important factors in the control of trace metals in interstitial water.[4-6]

Comparatively high concentrations of metal in the interstitial water of the Harrison-Anderson Lake sediment may be due to the unique geographic location. The lake is located on the inlet of Coeur d'Alene Lake. During the regular time, water from upstream brought with it abundant metal ingredients which were infused into the lake through a narrow channel. During the dry season when the water flowed back into Coeur d'Alene Lake and the water level in Harrison-Anderson Lake ran low, the sediments along the shore were exposed. Metals deposited in the sediment and the water gradually dried out until the high water season brought down more metals. However, specific mechanisms for trapping so much iron are not clear.

Table 5.3 illustrates that acid extraction digested most of the soluble and insoluble metals out from sediments. However, for leaching processes two-phase mixing released more metals than water-phase stirring (Section 5.2.3) because of the vigorous contact between the leaching solution and sediments. Comparing the aerobic and anaerobic conditions for leaching, more Zn was present in leaching solutions under aerobic conditions. The concentrations of Zn in aerobic leaching were 10.6±0.5 and 48.0±1.0 μg/g for water-phase

Table 5.3 Comparison of Concentrations of As, Sb, Zn, Mn, Cu, and Fe in Solutions of Different Leaching Conditions and Acid Extraction

Metal	Conditions and Methods: Aerobic (Air) Water-Phase Stirring	Aerobic (Air) Two-Phase Mixing	Anaerobic (N_2) Water-Phase Stirring	Anaerobic (N_2) Two-Phase Mixing	Acid Extraction
Zn	10.6±0.5	48.0±1.0	7.4±0.4	30.6±0.8	3590±50
Mn	1.8±0.1	11.6±0.4	5.8±0.3	7.6±0.2	1550±25
Cu	<0.05	<0.05	<0.05	<0.05	1410±22
Fe	2.4±0.1	3.6±0.6	3.1±0.2	4.2±0.2	16600±300
As(III)	$(2.7\pm0.2)\times10^{-3}$	$(14.6\pm0.8)\times10^{-3}$	$(3.5\pm0.2)\times10^{-3}$	$(14.9\pm0.7)\times10^{-3}$	94.6±2.5
As(V)	$(0.6\pm0.1)\times10^{-3}$	$(0.2\pm0.1)\times10^{-3}$	$(0.7\pm0.1)\times10^{-3}$	$(0.3\pm0.1)\times10^{-3}$	4.2±0.4
Sb(III)	$(2.5\pm0.2)\times10^{-3}$	$(4.0\pm0.3)\times10^{-3}$	$(1.1\pm0.1)\times10^{-3}$	$(8.9\pm0.8)\times10^{-3}$	379±5.0
Sb(V)	$(12.5\pm0.2)\times10^{-3}$	$(97.2\pm2.0)\times10^{-3}$	$(18.6\pm0.3)\times10^{-3}$	$(140\pm2.0)\times10^{-3}$	51.3±1.0

Sediment of Smelterville, South Fork, was tested for leaching. Amounts released are expressed in μg/g sediment.

stirring and two-phase mixing, respectively. The concentrations of Zn in anaerobic conditions were 7.4±0.4 and 30.6±0.8 μg/g, respectively. Zinc apparently tended to leach out more from sediment into water in oxidizing conditions. However, it was the opposite for iron. This probably is due to the formation of iron hydroxide precipitates in aerobic environments.[7-10] Manganese also tended to dissolve in oxidizing environments. No comparison for copper was made because of the low concentration of Cu in the sample. The concentration of As(III) was a little higher under aerobic conditions than under anaerobic. This may be due to the release of As from As_2S_3. Also, in anaerobic conditions the As(V)/As(III) ratio increased slightly. This reflects the continuous release of more As(V) in oxygen-free conditions. The high As(V) in oxygen-free leaching was probably due to ferric arsonate being reduced to its relatively more soluble ferrous form.[10]

Table 5.4 shows the concentrations of metals in the interstitial waters extracted from the Smelterville sediments after the leaching processes. The As and Sb concentrations in the original interstitial water of the South Fork (Smelterville) sediment were much higher than in the interstitial water obtained after leaching. For example, the concentration of total arsenic in the interstitial water of the sediment after leaching under atmosphere was 1.0±0.2 ppb (Table 5.4, column A), which is about 60 times lower than the

Table 5.4 Comparison of Concentrations of As, Sb, Zn, Mn, Cu, and Fe in the Interstitial Waters of the Smelterville Sediments after Leaching in Different Conditions

	Interstitial Waters*			
	(Air)		(N_2)	
Metal	A	B	C	D
Zn	3.65±0.04	4.45±0.05	3.85±0.04	2.82±0.04
Mn	3.4±0.2	6.6±0.3	7.5±0.3	14.5±0.3
Cu	<0.05	<0.05	<0.05	<0.05
Fe	3.5±0.2	4.2±0.3	4.5±0.3	3.5±0.2
As(III)	$(0.5\pm0.1)\times10^{-3}$	$(1.1\pm0.2)\times10^{-3}$	$(0.6\pm0.1)\times10^{-3}$	$(1.3\pm0.1)\times10^{-3}$
As(V)	$(0.5\pm0.1)\times10^{-3}$	$(1.1\pm0.1)\times10^{-3}$	$(0.4\pm0.1)\times10^{-3}$	$(1.3\pm0.1)\times10^{-3}$
Sb(III)	$(0.2\pm0.1)\times10^{-3}$	$(0.5\pm0.1)\times10^{-3}$	$(0.3\pm0.1)\times10^{-3}$	$(0.5\pm0.1)\times10^{-3}$
Sb(V)	$(1.9\pm0.2)\times10^{-3}$	$(3.7\pm0.4)\times10^{-3}$	$(1.0\pm0.1)\times10^{-3}$	$(3.8\pm0.5)\times10^{-3}$

* Interstitial water was obtained from the sediment after the leaching process in Table 5.3. The concentration is in ppm level.

A: Sediment after aerobic water-phase stirring
B: Sediment after aerobic two-phase mixing
C: Sediment after anaerobic water-phase stirring
D: Sediment after anaerobic two-phase mixing

total arsenic found in the original interstitial water (62.5±2.0 ppb). The concentration of total antimony in the interstitial water after the same leaching was lowered by about a factor of 2 relative to the original interstitial water. The concentrations of other metals such as Zn, Mn, and Fe show the same trend of decrease in the interstitial water after leaching, but to a lesser degree. The results obviously indicate that the metal ions were removed from the interstitial water during the leaching process.

5.3.2 Depth Profile of As and Sb Speciation in the Interstitial Waters of Sediments

The interstitial waters in the sediments from the St. Joe River, the Harrison-Anderson Lake and the Smelterville South Fork were analyzed to show the concentration distribution of the metals in depth profile. The reason we selected these three stations was that the St. Joe River is a wild and scenic river (classified by the National Forest Service). Water from the St. Joe River should provide a background value of trace metals and species. According to the results of a previous study (Section 5.3.1), we selected the Smelterville South Fork because of its higher pollution level. The Harrison-Anderson Lake sample was chosen because its pollution level lies between those of the St. Joe River and Smelterville, giving us three levels of water qualities to compare. Figure 5.2 shows the vertical distribution of As(III), total As, Sb(III), total Sb, Fe, Cu, Mn and Zn in the interstitial water from sediment

cores of the St. Joe River. Point zero stands for the sample of overlying water.

Generally speaking, the chart shown in Figure 5.2 shows an increasing trend of metal content in the interstitial waters starting from the top of the sediment. The metal contents in the surface water, 0 cm, are lower than those in the interstitial water. The metal concentrations in the interstitial waters between 2-6 cm show an increasing trend for total As, As(III), total Sb, and Sb(III). This indicates that the As and Sb in the surface sediment are mobilized by diffusion upward to the surface and are finally washed away by the surface water. It has been shown that surfaces of freshly precipitated ferric hydroxide and manganese oxides are also highly active sites for immobilizing dissolved As and Sb by adsorption and coprecipitation.[11]

Therefore, the immobilization and diffusion processes should reduce the concentrations of As and Sb in the top 4 cm of the sediments. The concentrations of Cu, Fe, Mn, and Zn in the interstitial water also increase with depth, reaching a maximum around 2 cm, then start to decrease. This may be related to the precipitation of metal sulfides in the more reduced environment of the deeper sediment. The dissolved As, Sb, Fe, Cu, Zn, and Mn in the interstitial waters show a decreasing trend between 6-12 cm in the depth profile. This probably suggests the formation of insoluble metal sulfide along the reducing condition in the deeper sediment.

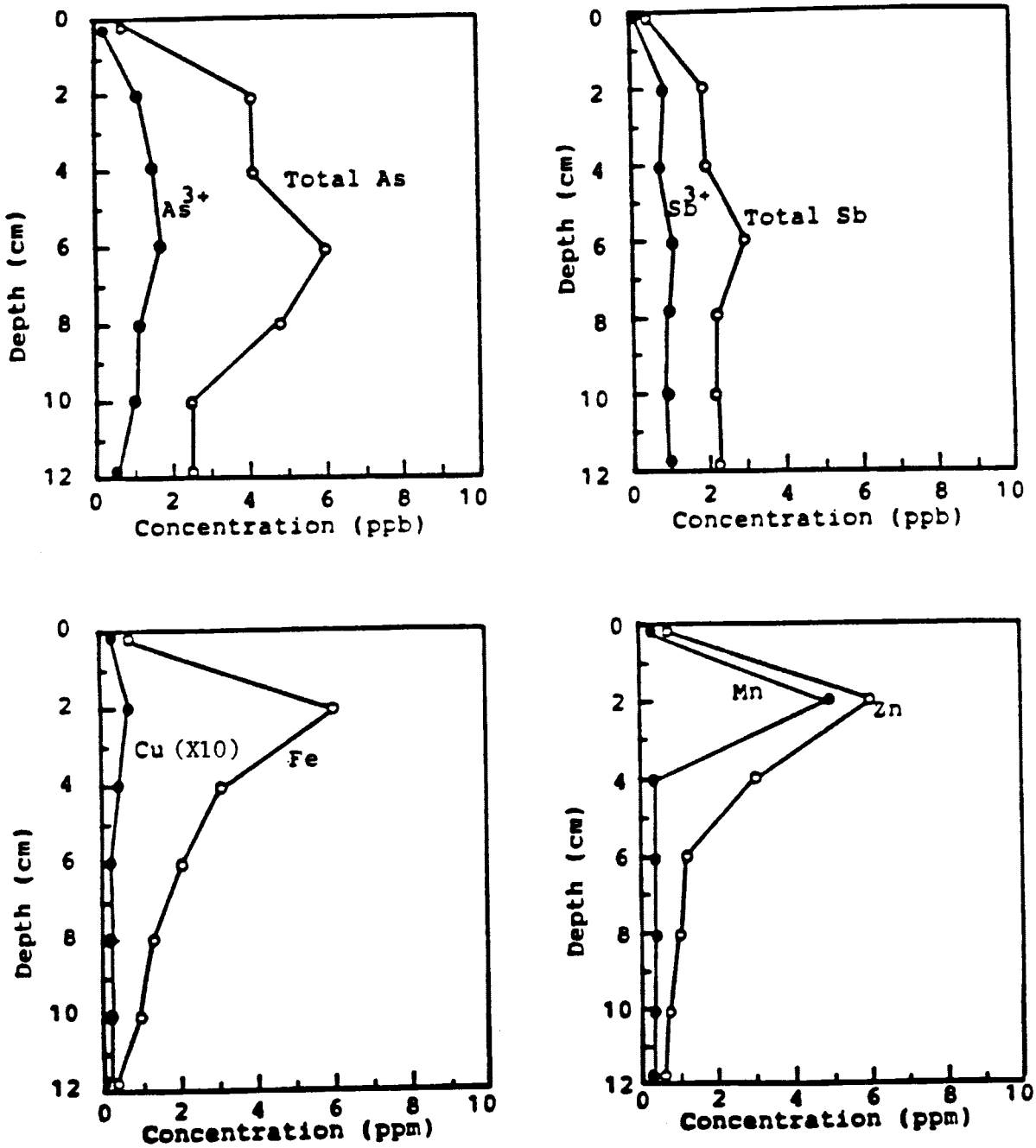


Figure 5.2 Trace Metal Concentration Profiles in the Interstitial Water of St. Joe River Sediment

Figure 5.3 shows the trend of metals in the depth profile of interstitial water in the sediment of Harrison-Anderson Lake. The metal distribution pattern is similar to that of the St. Joe River, but the concentration levels are higher compared with those of the St. Joe River. The ratio of As(III)/As(V) also increases. The depletion of As(V) in the interstitial waters of upper layer sediments is in agreement with a previous study by Crecelius[12] which reported coprecipitation of arsenate with iron hydroxide and manganese oxides. The details of As adsorption onto hydrous Fe and their incorporation into sediments are given in the literature.[15,16] According to the study of Aggett and O'Brien,[17] the soluble species of As and Fe, which originate from buried sediment, could diffuse upward and release into the lake water. In addition, the biological activity in the sediments would assist the release of metals into lake water. The high concentrations of metals on the top 2-4 cm in the interstitial water of Harrison-Anderson Lake is due to the upward movement of the interstitial water during the annual six-month period of low precipitation. The upward movement of interstitial water is significant when there is no water running over the sediments and evaporation of the surface water continues. Figure 5.3 appears to show this effect.

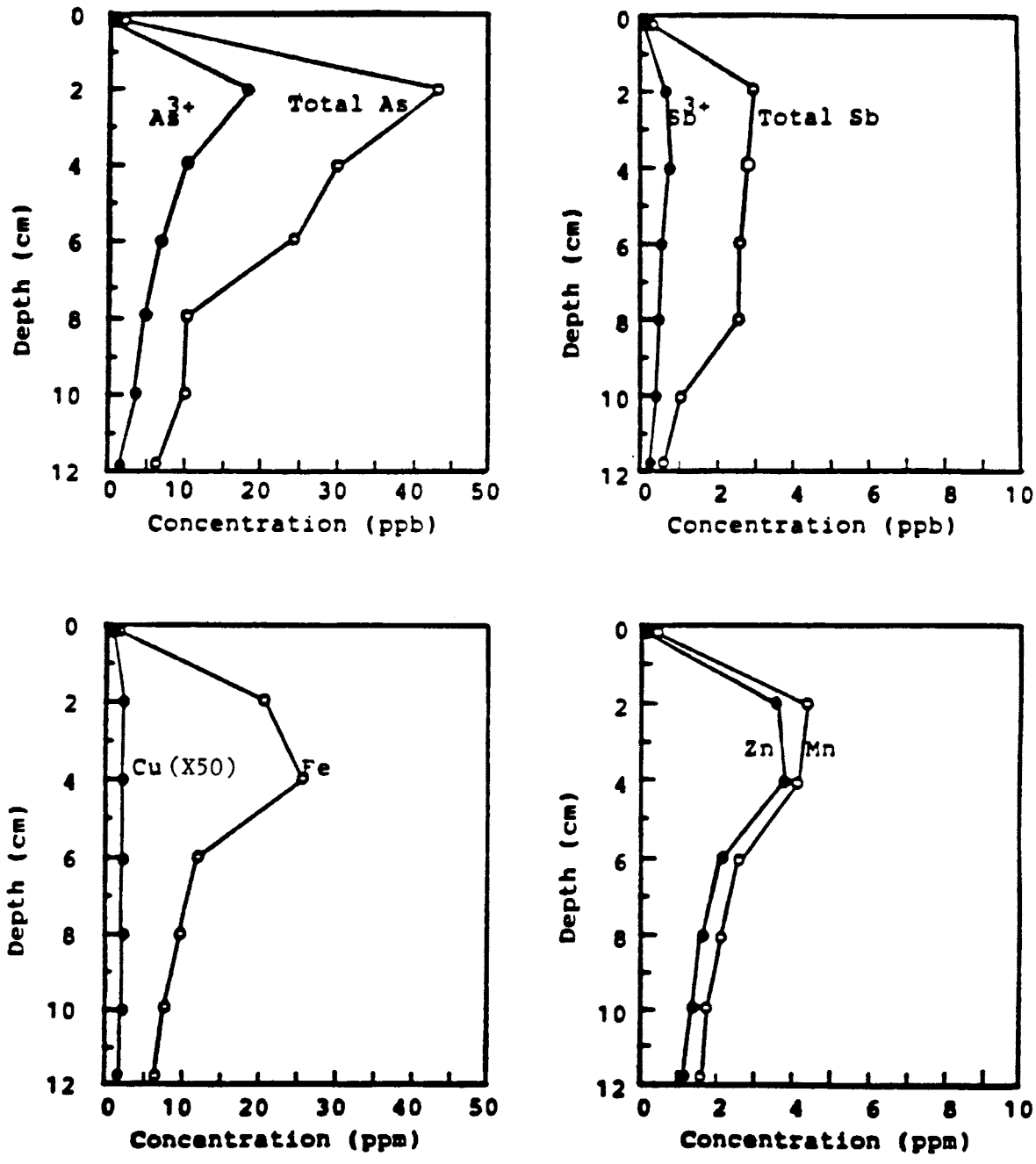


Figure 5.3 Trace Metal Concentration Profiles in the Interstitial Water of Harrison-Anderson Lake

In Figure 5.4, the concentration profiles of metals in the interstitial water of Smelterville sediments generally increase with the depth of the sediment, reach a maximum at 6 cm, then decrease with added depth. The distribution pattern is similar to that of As and Sb in the St. Joe River. The low concentrations of As and Sb in the sediment at 0-4 cm in depth indicate the high diffusion rate of metals by overlying water. The increasing trend of As, Sb, Fe, and Mn in the 0-6 cm depth of the sediment profile is probably due to the coprecipitation of As and Sb with insoluble iron hydroxide and manganese oxide in the more oxidizing zone of the sediment. After 6 cm in depth, the formation of insoluble metal sulfides decreases the concentrations of soluble metals in the reducing sediment. However, the concentration of Zn possessed an increasing trend along the depth of the sediment. This probably reflects the increased ZnS in the deeper reducing zone of the sediment. This probably is due to the high content of zinc ore, sphalerite (ZnS), in the sediments in the Smelterville area. The element composition shown in Table 5.5 indicates the high content of Zn in the sediments of the South Fork, Smelterville, which is related to ZnS. The high content of ZnS in the deeper sediment at the same time leached more soluble Zn to interstitial water around the sediment particles. This could bring up the concentration of Zn in the interstitial water in the deeper profile of the sediment.

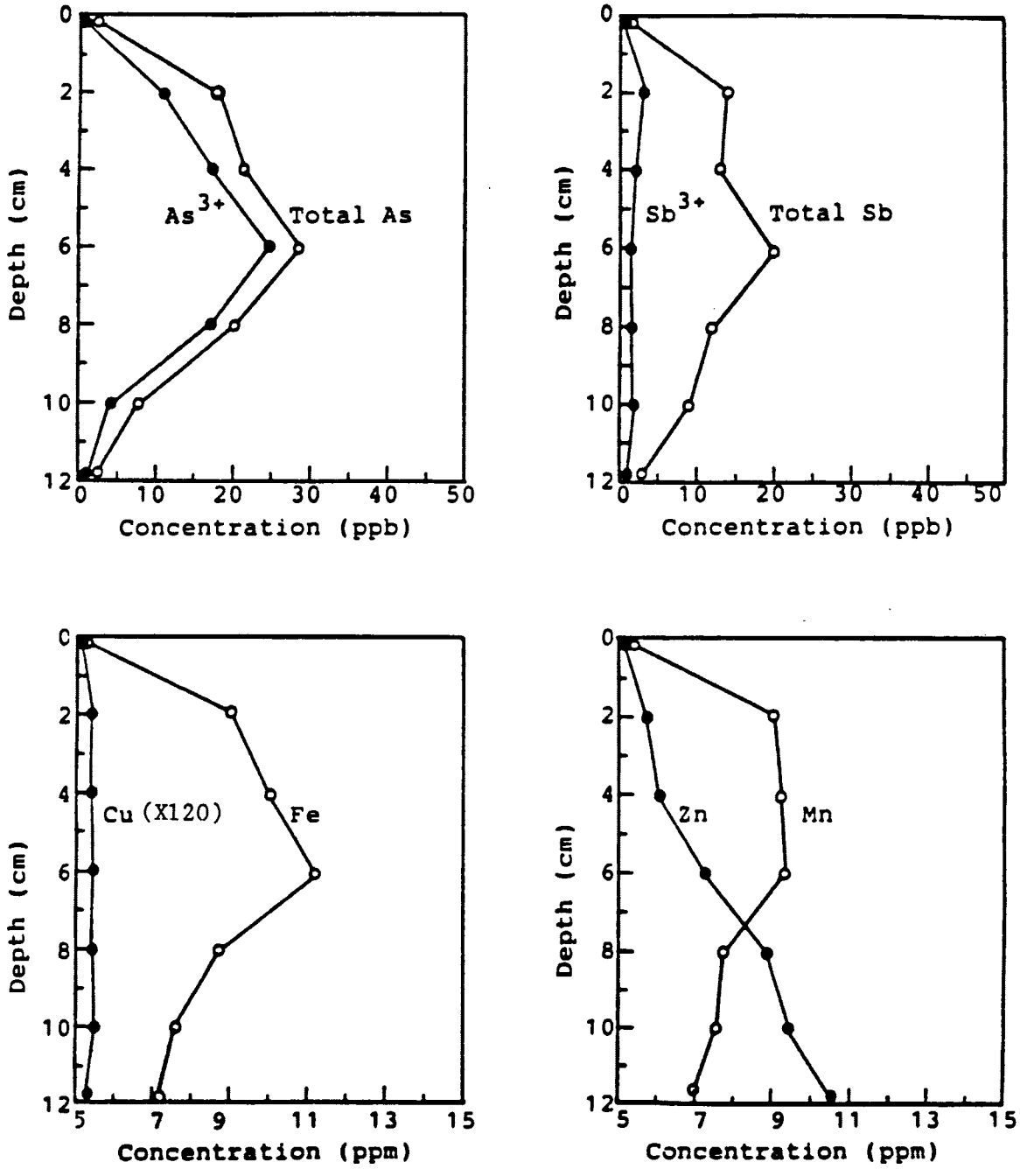


Figure 5.4 Trace Metal Concentration Profiles in the Interstitial Water of South Fork, Smelterville

Table 5.5 Concentration of Elements in the Sediments of St. Joe River and South Fork Coeur d'Alene River (Smelterville) by XRF

	St. Joe River	Harrison-Anderson Lake	South Fork Smelterville
Normalized Results (weight %)			
SiO_5	77.78	69.76	73.78
Al_2O_3	11.53	9.74	11.89
TiO_2	0.659	0.482	0.617
FeO	3.37	13.76	7.50
MnO	0.047	1.114	0.346
CaO	0.97	0.68	0.85
MgO	1.42	1.10	0.82
K_2O	2.11	2.24	2.55
Na_2O	2.00	0.95	1.27
P_2O_5	0.114	0.276	0.373
Trace Elements (ppm)			
Ni	21	11	21
Cr	32	24	35
Sc	14	10	13
V	51	38	41
Ba	490	678	767
Rb	90	91	110
Sr	82	57	105
Zr	243	267	276
Y	36	41	38
Nb	14.0	12.8	14.6
Ga	12	12	13
Cu	18	122	234
Zn	59	4120	4662
Pb	19	5075	4230
La	40	35	35
Ce	83	210	202
Th	11	0	0

In general, Figure 5.4 shows much higher metal contents in the interstitial water of the Smelterville sediment. This must be related to the high level of metals in the sediment. The dissolved metals would gradually release to the surface water and increase the concentrations of metals in the river.

For arsenic species, the most significant change is that high concentrations of As(III) relative to As(V) were found in the interstitial waters of the Smelterville sediment. The ratio of As(III)/As(V) was as high as 6 at 6 cm depth, and the average of all interstitial waters from different depths was 1.8. In comparison, the ratios of As(III)/As(V) in Harrison-Anderson Lake and the St. Joe River interstitial waters were on the average 1.1 and 0.6, respectively. In well-oxygenated waters, arsenic should be present in the pentavalent state. The low level of As(III) found in the St. Joe River indicates the river is in a natural state. Under reduced environments, As(V) may absorb onto the hydrous iron oxides present in the contaminated sediments and mine tailings. Lack of biological activities can also reduce the conversion of As(III) to As(V) in water. The high ratios of As(III)/As(V) found in the interstitial waters of the Smelterville sediment indicate a high level of pollution in the South Fork of the Coeur d'Alene River. Antimony is apparently not a sensitive redox indicator of natural water. As shown in Figure 5.4, Sb(V) still exists as the predominant antimony species in the interstitial water. This also corresponds to the Sb(V) as the major species of total Sb content in the Coeur d'Alene River water.

The particle structure of sediments also affects the deposition and resuspension of metals between overlying water and interstitial water. The particle size studies of the sediments in the St. Joe River, Harrison-Anderson Lake and Smelterville South Fork are shown in Table 5.6. The texture classifications were determined by using the USDA method (Appendix I). Overall the structures are very similar in different depths. However, down to the 8-12 cm depth sediments in Smelterville South Fork contain more sand. The rate of release and deposition of metals will be faster there compared with the sediments between 0 and 8 cm in depth.

Table 5.6 Particle Size Distribution and Moisture Content in the Depth Profile of Coeur d'Alene River Sediment

Sediment	Depth (cm)	% Sand	% Clay	% Silt	Texture USDA 1950	% H_2O
St. Joe River	0-2	66.4	4.5	29.1	S. Loam	36.8
	2-4	63.2	4.4	32.4	S. Loam	33.1
	4-6	62.5	3.3	34.2	S. Loam	36.6
	6-8	64.5	3.6	31.9	S. Loam	49.7
	8-10	64.1	3.1	32.8	S. Loam	38.4
	10-12	66.9	3.9	29.2	S. Loam	40.6
Harrison-Anderson Lake	0-2	55.4	18.6	26.0	S. Loam	42.50
	2-4	57.6	19.2	24.0	S. Loam	40.25
	4-6	57.9	15.4	26.7	S. Loam	35.40
	6-8	56.3	13.2	30.5	S. Loam	36.20
	8-10	63.9	14.6	21.5	S. Loam	37.40
	10-12	72.8	12.0	15.2	S. Loam	30.20
Smelterville South Fork	0-2	53.0	11.0	36.0	Loam	62.9
	2-4	39.0	11.0	50.0	S. Loam/Loam	55.5
	4-6	59.0	9.0	32.0	S. Loam	49.1
	6-8	69.0	7.0	24.0	S. Loam	40.9
	8-10	83.0	5.0	12.0	L. Sand	28.7
	10-12	80.0	5.0	15.0	L. Sand	27.0

REFERENCES

1. Eisenbarth, F. and Wrigley, J. A Plan to Rehabilitate the South Fork Coeur d'Alene River, Idaho Water Resource Board (1978).

2. Mok, W.M. and Wai, C.M. Anal. Chem. 59:233 (1987).

3. Rapin, F.; Nembrini, G.P.; Förstner, U. and Garcia, J.I. Environ. Tech. Lett. 4:387-396 (1983).

4. Förstner, U. and Wittmann, G. Metal Pollution in the Aquatic Environment, 2nd Ed., Springer-Verlag: Berlin, 486 (1981).

5. Jenne, E.A. Adv. Chem. Ser. 73:337-387 (1968).

6. Aggett, J. and Roberts, L.S. Envir. Sci. Technol. 20:183-186 (1986).

7. Moore, J.N.; Ficklin, W.H. and Johns, C. Envir. Sci. Technol. 22:432-437 (1988).

8. Berner, R. "Biogeochemistry of Organic Matter at the Sediment-Water Interface" Comm. Natl. Recherche Scient. (France) Reports Paris (1980).

9. Berner, R. Am. J. Sci. 275:88-96 (1975).

10. Deuel, L.E. and Swoboda, A.R. Soil Sci. Soc. Amer. Proc. 36:276 (1972).

11. Hem, J. Geochim. Cosmochim. Acta 41:527-538 (1977).

12. Crecelius, E.A. Limnol. Oceanogr. 20:441 (1975).

13. Takamatsu, T.; Kawashima, M. and Koyama, M. Water Res. 19:1029 (1985).

14. Farmer, J.G. and Cross, J.D. Radiochim. Radioanal. Lett. 39:429 (1979).

15. Aggett, J. and Lybley, S. Envir. Sci. Technol. 20:183 (1986).

16. Wilson, F.H. and Hawkins, D.B. Environ. Geol 2:195 (1978).

17. Aggett, J. and O'Brien, A. Envir. Sci. Technol. 19(3):231 (1985).

CHAPTER SIX

ARSENIC AND ANTIMONY SPECIATION OF GROUNDWATER AND SEDIMENT INTERSTITIAL WATERS IN THE BLACKFOOT DISEASE AREA OF SOUTHERN TAIWAN

6.1 Introduction

6.1.1 Historical Aspects

Blackfoot Disease is a unique chronic disease which was discovered on the southwest coast of Taiwan. Only a few cases were found before 1930. Since then, an increasing number of cases of Blackfoot Disease have been reported. The number of patients reached a peak during the period from 1956 to 1960 and attracted the public's attention.[1] The symptoms of Blackfoot Disease start with spotted discoloration on the skin of the extremities, especially the feet.[2] The spots change from white to brown and eventually to black, hence, the name Blackfoot Disease. Several years after the initial symptoms appear, the spotted skin gradually thickens and looks like rubber. The skin then cracks and ulcerates. The affected extremities need to be amputated or the patient may die.

After a preliminary survey and investigation, the high concentration of arsenic in the drinking water of the endemic area indicated a relationship to the incidence of this disease. In addition, the symptoms of Blackfoot Disease are similar to those of chronic arsenicism, a disease caused by arsenic poisoning.[3] This drew more attention to the

investigation of arsenic pollution in the drinking water of the Blackfoot Disease area in Taiwan.

The endemic area of Blackfoot Disease is on the southwest coast of Taiwan. Artesian wells were the main source of drinking water in that area. Because of the salty taste and a shortage of shallow well water, deep wells were drilled to depths of more than 200 feet after 1930 to obtain water of low salt content. In the following years the number of patients suffering from Blackfoot Disease increased until the early 1960s when the government there began providing clean tap water to some villages in that area. Although purified tap water from the Che-Wein Chi reservoir, a reservoir located about a hundred miles north of the endemic area, became the only source of drinking water after 1970, thousands of cases of Blackfoot Disease have been found thereafter.[3] In the late eighties, some cases of Blackfoot Disease still occurred. However, they are considered chronic effects or independent cases.

According to several reports from Taiwan, arsenic is considered as a target toxicant related to Blackfoot Disease.[5] The concentrations of total arsenic in some deep artesian well water were found as high as 1 mg/L (ppm), which is 20 times greater than the U.S. Public Health's permissible level (0.05 mg/L) of total arsenic in drinking water.[4] The As concentrations in some of the drinking waters of Fallon, Nevada, and Bakersfield, California, are around 0.1 and 0.5 ppm, respectively; however, no adverse effects have been

observed in those areas.[5] The As concentration in the drinking water of Antofagasta, Chile, is 0.8 ppm; the people there suffer from melanosis, hyperkeratosis, pneumonia and myocardial ischemia. The concentration of total arsenic can not explain this phenomenon; therefore, speciation of As was investigated in this paper.

6.1.2 Objectives of this Study

Arsenic occurs extensively in the environment in different chemical species exhibiting different toxicities and biological activities. Arsine (AsH_3) is a highly toxic species, yet it is scarcely found in natural waters. Arsenite (As^{3+}) and arsenate (As^{5+}) are two major species existing in natural water systems; the former is about 30-50 times more toxic to biological systems than the latter.[6,7] In addition, arsenate is absorbed more strongly by soil and sediment than arsenite in acidic or mild alkaline conditions.[8,9] Reduction of arsenate to arsenite in anaerobic sediments can cause an increase of arsenic toxicity in an aquatic system. In contrast, the oxidation of arsenite or methylation of arsenic from inorganic forms can reduce the toxicity. The toxicity of the various arsenic compounds in decreasing order is as follows: arsines > arsenite (inorganic) > arsenoxide (trivalent with two bonds joined to oxygen) > arsenate (inorganic) > pentavalent arsenicals (such as arsonic acids) > arsonium compounds (four organic groups with a positive charge on arsenic) > metallic arsenic.

In this study the distribution of As^{3+}, As^{5+} and total As in the well waters of the Blackfoot Disease area was investigated. Because the incidence of Blackfoot Disease is related to deep-well water, the analyzed samples include deep-well and shallow-well water for comparison. Although the artesian well waters are no longer used for drinking, they are now used to supply fish culturing ponds, a huge newly developed business in that area. The grown fish are sold in domestic fish markets. Therefore, the fish pond water and the interstitial water of the sediments were also analyzed. Antimony species, Sb^{3+} and Sb^{5+}, were also analyzed. Total As and Sb concentrations were measured in order to evaluate As and Sb species other than the inorganic trivalent and pentavalent species. In addition, As and Sb contents in filtered 0.45 μm membranes were analyzed to determine insoluble and colloidal As and Sb entrapped on the membrane.

6.2 Experimental

6.2.1 Sample Collection

Three deep-well water samples, one shallow-well water, one fish pond water, and one interstitial water sample of the fish pond sediment were obtained from the Blackfoot Disease endemic area in southwest Taiwan. The sampling sites included Paotai and Peiman, two townships which were greatly affected by Blackfoot Disease, located on the southern part of Taiwan between Chai-Y and Tainan cities (Figure 6.1).

Samples were collected in October 1989 and January 1990, respectively. The well waters were pumped out from under-

ground and allowed to run for 5 min before sampling. The waters were then collected with high density PE bottles. The water samples were filtered and extracted with APDC at the sampling site immediately after collection to minimize possible interconversion of the As and Sb species. This on-site filtration of samples was highly recommended especially for the sample matrix containing high concentrations of hydrous iron(III) oxides which may cause coprecipitation or adsorption of As and Sb. Three cores of a fish pond sediment were obtained using a bamboo corer. The collected sediment layers were surface to 50 cm in depth and were put into PVC zip-lock bags right after sampling and stored at 4°C.

6.2.2 Sample Treatment

Water Sample for NAA. The water samples were filtrated through a 0.45 μm vacuum filtration system. After collecting 1 L of water sample, this filtering membrane was saved for later NAA analysis to measure insoluble and colloidal As and Sb entrapped on the membrane. The filtrated samples were saturated with chloroform before extraction. One aliquot of water (100 mL) was acidified to pH ~1.0 with HNO_3. Thereafter, 1 mL of 25% Na_2SO_3 and 1 mL of 20% KI were added to the sample to complete the reduction of As(V) and Sb(V). The reduced aliquot and another aliquot of 100 mL unreduced sample were then taken through the APDC solvent extraction process as described in Figure 6.2.

Membrane for NAA. The used membranes, after filtering through 1000 mL of water sample, were irradiated in a 1 MW

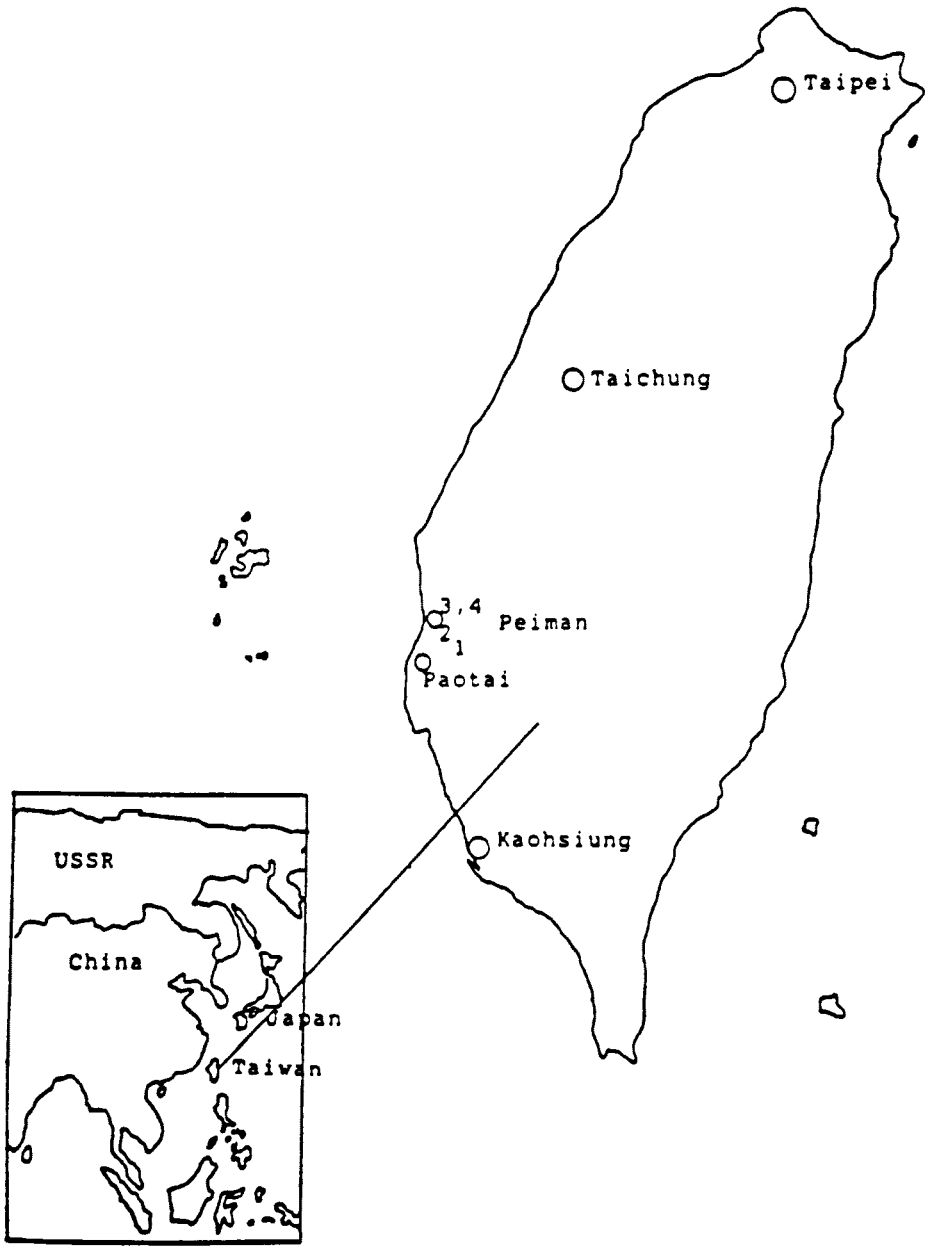


Figure 6.1 Sampling Locations of Well Water and Sediments in Blackfoot Disease Endemic Area

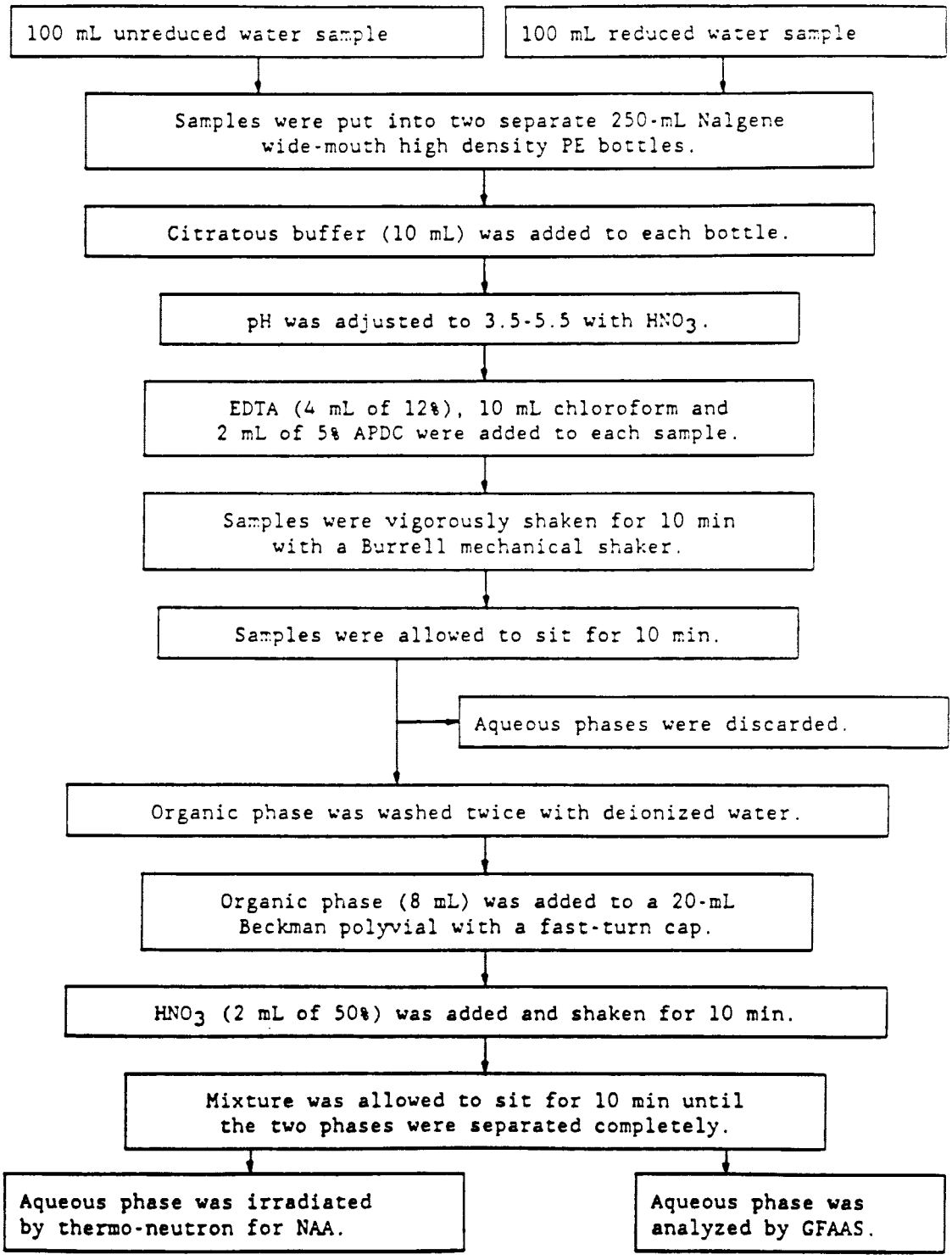


Figure 6.2 **Flow Chart of Arsenic and Antimony Speciation for Aqueous Samples**

Triga nuclear reactor with a steady flux of 6.0×10^{12} n $cm^{-2}s^{-1}$ for 2 hours, followed by a 24-hour cooling period. The membranes spiked with a known amount of As and Sb standard solutions were also irradiated under the same conditions. The concentrations of insoluble As and Sb were obtained by comparing the activities of As and Sb of the sample with that of the spiked membrane.

Water Samples for GFAAS and HGAAS. The well water samples were digested with EPA SW-846 Method 7060 followed by graphite furnace atomic absorption spectrometry to determine total As and Sb.[10] The total concentration of the As and Sb in the water consists of inorganic species, total insoluble species, and other organic species in the sample.

According to the EPA method 3020, an aliquot of a 100-mL water sample was transferred to a 250-mL Griffin beaker. Hydrogen peroxide (2 mL of 30%) and 1 mL of concentrated HNO_3 were added to the beaker. The beaker was covered with a ribbed watch glass and heated for 1 hour at 95 °C until the volume was about 50 mL. The sample was allowed to cool down and the volume was brought back to 100 mL with 0.2% nickel nitrate solution. This sample then was ready for GFAAS and HGAAS.

Acid Digestion of Sediment. According to the EPA method 3050, a representative sediment sample (1.0 to 2.0 grams) was accurately weighed to the nearest 0.0001 gram and added to a 250-mL conical Phillips beaker. Nitric acid (10 mL of 1:1) was added to the beaker, mixed thoroughly and covered with a

watch glass. The sample then was refluxed on a hot plate at 95 °C for 15 min without boiling. After the sample was cooled to room temperature, 5 mL of concentrated HNO_3 were added. The watch glass was replaced and the sample refluxed for 30 min to decompose the organic matrix. The watch glass was washed with deionized water. When the sample was cooled down, the beaker was recovered with a ribbed watch glass and the solution allowed to evaporate to 5 mL without boiling. Thereafter, 2 mL of deionized water and 3 mL of 30% H_2O_2 were added to the beaker, which was then returned to the hot plate with the watch glass on the top. The sample was warmed to start the peroxide reaction. In this step care must be taken to prevent losses due to excessively vigorous effervescence. When the sample was cooled down, 1-mL aliquots of 30% H_2O_2 were continously added with warming until the effervescence subsided. At this step the color and general sample appearance remained unchanged with the addition of H_2O_2. However, the total amount of 30% H_2O_2 added to the solution should not exceed 10 mL. The sample was heated until the volume had been reduced to approximately 5 mL. After cooling to room temperature, the sample was filtrated through a Whatman No. 42 filter paper and diluted to 100 mL with deionized water.

Interstitial Water. About 400 g of sediment obtained from the fish pond were put into an Amicon model 402 ultrafiltration cell. The system is described in section 4.3.1. An appropriate size of Whatman No. 42 ashless filter

paper was placed on the porous membrane support disk of the cell. The pressure of argon applied to the cell was 0.25, 0.50 and 2.00 kg/cm^2 sequentially to obtain interstitial waters. The interstitial water obtained was then filtrated through a 0.45 μm membrane for solvent extraction. The initial amount of the interstitial water for solvent extraction was 20 mL due to the limited amounts of water obtained from each squeezing. However, since only 1 mL of 50% HNO_3 was used to back-extract the metals, the preconcentration factor was still sufficiently high for NAA.

6.2.3 Analysis

Neutron Activation Analysis. The solvent extracted samples and standard solutions of As and Sb in a 50% HNO_3 matrix were heat-sealed in 1/8 ounce-polyethylene vials for irradiating under the conditions described in section 6.2.2. Accordingly, the 0.45 μm filter membranes with insoluble metals entrapped on them were irradiated for analysis. The standard solutions of As and Sb were spiked in blank membranes for irradiation to match the matrix with the membrane sample.

Two solution samples in 1/8-ounce P.E. vials were sealed in one 2-dram P.E. vial to avoid leaking and contamination when pressure built up inside the vials. Each membrane was directly sealed in a 2-dram P.E. vial due to its size and shape. Since the membranes did not cause an increase in vapor pressure as for the liquid samples, a single vial was sufficient for neutron irradiation. Eight large polyethylene vials were mounted on one turret holder and loaded to the

reactor core for neutron irradiation. Each layer in the holder contained a standard to ensure the same geometric position for irradiation when the sample revolved in the irradiation tube in the reactor core.

The irradiated samples were transferred to new vials to avoid the interference of ^{24}Na and any other matrix in the irradiated P.E. vials. The vials were thoroughly rinsed with 1 mL of 1 M HNO_3 and transferred into the new vials with the sample.

The samples then were placed on the detector head of a high resolution ORTEC Ge(Li) detector for gamma counting. The average counting time for each sample was about 2400 seconds; however, this varied from sample to sample. If the signal was too weak or the background was too high, then a longer counting time was required to achieve better resolution of the signal and accuracy. The counting of samples and standards was recorded and analyzed with preprogrammed Lotus software. The factors of decay and period of counting were all considered and programmed in the software to obtain the data. The energies of gamma rays at 559.1 Kev and 564.0 Kev were used for quantification of As and Sb, respectively.

Graphite Furnace Atomic Absorption Spectroscopy. The digested samples of well water and sediment were analyzed with a Perkin-Elmer Model 5100 atomic absorption spectrometer equipped with an HGA-600 graphite furnace, As-60 autosampler and 5100 PC software. The Perkin-Elmer arsenic electrodischargeless lamp and Sb hollow cathode lamp were used

as source lamps. Pyrolytically coated graphite tubes with L'vov platforms were used to contain samples.

The blank solution with the same acid matrix as the samples was used to zero absorption. The standard solutions of As and Sb were prepared by diluting 1000 ppm stock solutions of As and Sb. Deionized water and HNO_3 were prepared by a sub-boiling process which was performed in Institute of Nuclear Science, National Tsing Hua University, Tsing-chu, Taiwan.

The operational parameters of GFAAS are given in Table 6.1. Low pyrolysis temperatures were used at step 2 because the artesian well samples did not contain complicated organic matrices. This low heating also prevented loss due to premature atomization. The slow heating rate during pyrolysis avoided splashing and loss of sample in the graphite tube due to abrupt increases in temperature. The absorption signals were taken at step 4 during atomization. The characteristic mass, the number of picograms required to give 0.0044 absorbance (A-S), was 15.2 and 25.0 pg/0.0044 A-S for As and Sb, respectively. The values were close to those in the standard conditions recommended by the instrument manufacturer, which were 15.0 and 22.0 pg/0.0044 A-S.

6.3 Results and Discussion

The analytical results of four artesian well waters that were sampled in October 1989 are shown in Table 6.2. The concentrations of total arsenic in three deep-well waters were high compared with that in shallow-well water, and about 10

Table 6.1 Operational Parameters of GFAAS for Arsenic and Antimony Analysis

Parameter		Arsenic					Antimony			
HGA Graphite Furnace	Step	Temp (°C)	Ramp (s)	Hold (s)	Gas Flow (mL/min)	Step	Temp (°C)	Ramp (s)	Hold (s)	Gas Flow (mL/min)
	1	120	1	35	300	1	120	1	50	300
	2	600	5	10	300	2	600	5	5	300
	3	20	1	15	300	3	20	1	15	300
	4	2100	0	5	0	4	2000	0	5	0
	5	2600	1	5	300	5	2600	1	5	300
Wavelength (nm)		193.7					217.6			
Carrier Gas		Argon					Argon			
Lamp Current (MA)		20					20			
Slit (nm)		0.7					0.7			
Model		Peak Area					Peak Area			
Atomizer		L'vov Platform					L'vov Platform			

Table 6.2 Concentration of Soluble As(III), As(V), Sb(III) and Sb(V) in Groundwater in the Blackfoot Disease Area, Taiwan Sampled in October 1989 (in ppm)

Sample Location	Species			
	As(III)	As(III) +As(V)	Sb(III)	Sb(III) +Sb(V)
Well #1	0.32±0.03	0.48±0.03	(3.5±0.2) $\times 10^{-4}$	(12.0±0.4) $\times 10^{-4}$
Well #2	0.40±0.04	0.47±0.03	(4.7±0.2) $\times 10^{-4}$	(12.0±0.4) $\times 10^{-4}$
Well #3	0.33±0.02	0.49±0.03	(3.2±0.2) $\times 10^{-4}$	(10.0±0.3) $\times 10^{-4}$
Well #4 (shallow well)	(7.0±0.4) $\times 10^{-3}$	(25.0±1.0) $\times 10^{-3}$	(0.8±0.1) $\times 10^{-4}$	(5.0±0.2) $\times 10^{-4}$

times the maximum limit of the U.S. Public Health Service (50 ppb). The antimony level, however, was in the normal range of drinking water. The concentration of As in the shallow well water was about 7 ppb. This may explain why few cases of Blackfoot Disease were found before deep wells became prevalent. The high level of arsenic in deep-well drinking water was assumed to be associated with the prevalence of Blackfoot Disease in the endemic area in Taiwan. However, it should be pointed out that the As concentrations in some other places such as Fallon, Nevada, and Bakersfield, California, were also found in the range of 0.1-0.7 ppm.[5] But, there were no adverse effects discovered there.

Although arsenic is virtually a synonym for poison to the general public, recognition of variations of arsenic species

may lead to a more realistic appreciation of the impact on natural and biological systems. Table 6.2 also shows high percentages of As^{3+} in total As content. The As^{3+} percentages are 67%, 85%, and 67% of the total As found in well waters #1, #2 and #3, respectively. The high level of As^{3+} in the well water may be linked to Blackfoot Disease because the toxicity of As^{3+} is about 30-50 times greater than As^{5+} to biological systems.[6,7] In comparison, only about 3% of As^{3+} was found in total dissolved arsenic in the shallow well water.

The analytical results of total As in water sampled in January 1990 for Wells #1, #2, #3, and #4 are 0.54±0.04, 0.54±0.03, 0.56±0.04 and $(25.0\pm1.0)\times10^{-3}$ ppm, respectively (Table 6.3). The concentrations of total Sb in Wells #1, #2, #3, and #4 are 1.4, 1.5, 1.2 and 0.7 ppb, respectively. The concentrations of total As and Sb found in January 1990 were slightly higher than those sampled in October 1989. This is probably due to the dilution effect of high rain precipitation in August and September. The As^{3+} percentages remain at 72%, 83% and 60% of total As in the waters collected in January 1990 for Wells #1, #2 and #3, respectively.

The concentrations of Sb^{3+} and total Sb in January 1990 waters are close to those obtained in October 1989. They both show very trace amounts compared with the concentrations of As. Also, the predominant species of Sb is Sb(V).

The concentrations of As^{3+} and total As in fish pond water are 2.2×10^{-3} and 2.2×10^{-2} ppm, respectively. They are apparently much lower than those found in the deep well

Table 6.3 Concentration of Soluble As(III), As(V), Sb(III), and Sb(V) in the Groundwater, Fish Pond Water and Interstitial Water in the Blackfoot Disease Area, Taiwan Sampled in January 1990 (in ppm)

Sample Location	Species				pH
	As(III)	As(III)+As(V)	Sb(III)	Sb(III)+Sb(V)	
Well #1	0.39±0.02	0.54±0.04	(4.3±0.2) $\times10^{-4}$	(14.2±0.3) $\times10^{-4}$	8.4
Well #2	0.45±0.03	0.54±0.03	(5.0±0.2) $\times10^{-4}$	(15.3±0.3) $\times10^{-4}$	7.8
Well #3	0.34±0.02	0.56±0.04	(3.8±0.1) $\times10^{-4}$	(12.4±0.2) $\times10^{-4}$	8.4
Well #4 (shallow)	8.3×10^{-3}	(25.0±1.0) $\times10^{-3}$	(1.1±0.1) $\times10^{-4}$	(6.8±0.2) $\times10^{-4}$	7.3
Fish Pond	(2.2±0.1) $\times10^{-3}$	(22.0±1.0) $\times10^{-3}$	(0.4±0.1) $\times10^{-4}$	(1.2±0.1) $\times10^{-4}$	6.9
I.S.W.* (0.25 kg/cm^2)	(17.6±0.8) $\times10^{-3}$	(56.3±1.5) $\times10^{-3}$	(0.9±0.1) $\times10^{-4}$	(5.6±0.1) $\times10^{-4}$	-
I.S.W.* (0.50 kg/cm^2)	(14.3±0.6) $\times10^{-3}$	(76.5±1.8) $\times10^{-3}$	(0.9±0.1) $\times10^{-4}$	(7.8±0.2) $\times10^{-4}$	-
I.S.W.* (2.00 kg/cm^2)	(10.2±0.4) $\times10^{-3}$	(84.7±2.0) $\times10^{-3}$	(1.0±0.1) $\times10^{-4}$	(9.2±0.2) $\times10^{-4}$	-

* I.S.W. indicates the interstitial water obtained from sediments of the fish pond.

waters. The dilution of rain precipitation and the mixing of the shallow well water with the deep well water in the fish pond application may be two major factors which reduced the metal concentrations. In addition, uptaking across the epithelia of aquatic organisms may also lead to lower levels of As. The predominant species of As in the fish pond water is As(V). The total concentration of As in the fish pond water (22 ppb) is lower than the U.S. Public Health Service's permissible level of As in drinking water. The interstitial

water was separated from the fish pond sediment by the low-pressure gas squeezing technique described in Chapter Four, section 4.3.1. The total concentrations of As(III), As(III)+As(V), Sb(III), and Sb(III)+Sb(V) in interstitial waters obtained from different pressures are given in Table 6.3. The As and Sb concentrations in the interstitial water are all higher than the fish pond water. The total concentrations of As and Sb in the interstitial water increase with squeezing pressure. However, the As(III) concentrations in the interstitial water decrease as the applied gas pressure increases.

The total As and Sb contents in the sediment samples of the fish pond are given in Table 6.4. The Sb concentrations in the sediments are about 4-5 times lower than that of arsenic, but the total Sb in the surface water is 19 times lower than that of As. According to the analytical results in Table 6.5 the sum of arsenic species other than As(III) and As(V) is minor. They are 3.6%, 6.3%, and 6.3% in Wells #1, #2, and #3, respectively. The insoluble As content averages about 5% of the total As found in these samples.

Table 6.4 Total As and Sb in Fish Pond Sediment Samples

Sample	As (μg/g)	Sb (μg/g)
1	0.52±0.02	0.12±0.01
2	0.45±0.02	0.10±0.01
3	0.48±0.02	0.08±0.01
Average	0.48±0.02	0.10±0.01

Table 6.5 Concentrations of Total, Insoluble and Other Species of As and Sb in Well Water in the Blackfoot Disease Area (in ppm)

Sample Location	As			Sb		
	Total As	Insoluble As	Others	Total Sb	Insoluble Sb	Others
Well #1	0.574 ±0.004	0.021 ±0.001	0.013 ±0.001	(15.0±0.2) $\times 10^{-4}$	(0.5±0.1) $\times 10^{-4}$	(0.5±0.1) $\times 10^{-4}$
Well #2	0.587 ±0.004	0.037 ±0.002	0.010 ±0.001	(15.0±0.3) $\times 10^{-4}$	(0.6±0.1) $\times 10^{-4}$	--
Well #3	0.657 ±0.005	0.042 ±0.002	0.053 ±0.004	(13.0±0.3) $\times 10^{-4}$	(0.6±0.1) $\times 10^{-4}$	(0.5±0.1) $\times 10^{-4}$
Well #4 (Shallow)	(27.0±0.4) $\times 10^{-3}$	<0.1 $\times 10^{-3}$	(3.7±0.1) $\times 10^{-3}$	(7.7±0.2) $\times 10^{-4}$	<0.1 $\times 10^{-4}$	(0.9±0.1) $\times 10^{-4}$
Fish Pond	(5.2±0.2) $\times 10^{-3}$	<0.1 $\times 10^{-3}$	(3.0±0.1) $\times 10^{-3}$	(1.2±0.1) $\times 10^{-4}$	<0.1 $\times 10^{-4}$	(0.8±0.1) $\times 10^{-4}$

Summary. A case study of the speciation of As and Sb indicates high concentrations of As(III) in the deep well waters of the Blackfoot Disease area in Taiwan. However, further investigations are required to understand the relationship between arsenic species and Blackfoot Disease.

REFERENCES

1. Jaag, O. Advances in Water Pollution Research, Vol. 1, Pergamon Press (1964).

2. Yen, S. National Cancer Institute Monograph 10, U.S. Government Printing Office: Washington, D.C., pp. 81-107 (1963).

3. Tseng, W.-P. Environmental Health Perspective, 19:109-119 (1977).

4. U.S. Public Health Management Guideline, NPS-83, Release No. 1, April (1991).

5. Lu, F.J. and Liu, T.M. Research Report of Blackfoot Disease, Taiwan University Medical School, 23:23 (1985).

6. Arsenic-Medical and Biological Effect of Environmental Pollutants, National Academy of Sciences: Washington, D.C. (1977).

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

8. Cherry, J.A. and Shaikh, A.U. J. Hydrol. 43:377 (1979).

9. Florence, T.M. Water Res. 11:681 (1979).

10. U.S. EPA SW-846, Vol 1A, Method 3020, September (1986).

CHAPTER SEVEN

The following manuscript entitled

Simultaneous Determination of Arsenic and Antimony Species in Environmental Samples by Supercritical Fluid Chromatography

by

K.E. Laintz, G.M. Shieh, and C.M. Wai

has appeared in

Journal of Chromatographic Science, 30, 120-123 (1992).

CHAPTER SEVEN

SIMULTANEOUS DETERMINATION OF ARSENIC AND ANTIMONY SPECIES IN ENVIRONMENTAL SAMPLES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

Abstract

Simultaneous separation and quantitation of arsenic(III) and antimony(III) can be achieved by extraction with lithium bis(trifluoroethyl)dithiocarbamate followed by supercritical fluid chromatographic analysis (SFC). Arsenic(V) and antimony(V) are extracted after reduction with potassium iodide and sodium thiosulfate. Detection limits of 7 pg As and 11 pg Sb are achieved using this extraction method and SFC. Application to natural water and biological sample analysis is discussed.

7.1 Introduction

Arsenic and antimony are two elements of considerable environmental concern because of their toxic nature. Speciation of these elements is important since their toxicity and physiological behavior are largely dependent upon oxidation state. Inorganic arsenic usually occurs in natural waters in two oxidation states, arsenite and arsenate, with the former being more toxic to biological systems.[1] The ratio of As^{3+} to As^{5+} has also been suggested as an indicator of the redox status of ground water systems.[2] The distribution and toxicity of the inorganic antimony species Sb^{3+} and Sb^{5+} are less known, but the U.S. Environmental Protection Agency considers antimony as a priority pollutant. Obviously,

accurate determination of As and Sb species in natural samples is important for environmental monitoring programs.

Neutron activation analysis (NAA) coupled with solvent extraction using pyrrolidinecarbodithioate (PCDT) has been used to determine inorganic As and Sb species in natural waters.[3] Speciation of As and Sb can also be achieved using a less rigorous extraction method followed by subsequent chromatographic analysis. For example, bis(trifluoroethyl)-dithiocarbamate (FDDC) has been used to extract a number of metal ions from aqueous solution followed by gas chromatographic analysis.[4] However, these metal chelates exhibit some degree of thermal and chemical lability, and this can cause problems in gas chromatographic analyses. Since supercritical fluid chromatography (SFC) is generally more suited for the analysis of thermally labile compounds,[5] it appears to be the chromatographic method of choice for metal chelate analysis. In recent studies, fluorinated dithiocarbamates such as FDDC were shown to be an effective chelation agent for use in SFC analysis of metals using CO_2 as a mobile phase.[6] The improved chromatographic behavior was attributed to the higher stabilities of the fluorinated metal chelates and their enhanced solubilities in supercritical CO_2 relative to the non-fluorinated ones. In this paper, speciation of As and Sb are reported for natural water and biological samples using FDDC chelation and subsequent SFC analysis.

7.2 Experimental

SFC Instrumentation. The chromatographic analyses used for this study were performed on a Lee Scientific model 602 supercritical fluid chromatograph (Dionex). The fluid pump was cooled using a Neslab RTE-110 constant temperature bath. This system was equipped with a FID detector, and injection was accomplished with a timed-split rotary injection valve. A 5 m 100 μm ID by 195 μm OD SB-Methyl-100 Superbond capillary column (Lee Scientific) was used with CO_2 as the mobile phase (SFC grade, Matheson). All chromatograms were recorded and processed using an HP 3390A integrator. Temperature and pressure conditions for the analyses were computer controlled and are reported in the subsequent Results and Discussion section.

Reagents and Materials. Stock solutions for As^{3+}, As^{5+}, Sb^{3+}, and Sb^{5+} used in this study were prepared according to the procedure outlined in the literature.[3,7] Ammonium pyrrolidinecarbodithioate (APCDT) was obtained from the Fisher Scientific Co. Lithium bis(trifluoroethyl)dithiocarbamate was synthesized according to the procedure outlined in the literature,[8] which gives a substantially higher yield than the comparable synthesis yielding the sodium salt of the ligand.[9] The starting material for the synthesis, bis(trifluoroethyl)-amine, was purchased from PCR Research Chemicals. Other chemicals used in the synthesis, including n-butyl lithium (2.5 M in hexane) and carbon disulfide, were obtained from Aldrich Chemical Co. Other chemicals such as chloroform,

dichloromethane, nitric acid, hydrochloric acid, etc. were purchased from EM Science. Ammonium citrate buffer was prepared as outlined in the literature.[3] Concentrated nitric acid, concentrated sulfuric acid, and 30% hydrogen peroxide (Baker Ultrapure Reagents) were used for digestion of biological samples.

Deionized water was prepared by passing distilled water through a Barnstead Ultrapure Water Purification Cartridge and a 0.2 μm filter assembly (Pall Corp. Ultipor DFA). All glassware, plastic vials, and containers used in this study were washed with a 2% Liquinox solution and soaked for 24 hours in a 10% nitric acid bath. After removal from the acid bath, they were rinsed several times with deionized water and stored in a clean hood equipped with a vertical laminar flow filter.

Sedimentary interstitial water samples were obtained by low pressure direct gas squeezing of 500 g sediment samples with nitrogen at a pressure of 30 psig in an Amicron Ultrafiltration Cell model 402. The shallow water sediments from the Coeur d'Alene River used in this particular study were collected at points located near Harrison Lake and Smelterville, near Kellogg, Idaho. Sediments were also collected from the St. Joe River, which is considered a natural, scenic river in northern Idaho. These sediment samples were obtained using 1.2 m by 4 cm ID sample corers at sampling points near the river bank, and sampling was carried out to a depth of 12 cm. The sediments were then placed in

PVC zip-lock bags, and after having all the air pressed out, submersed in dry ice and stored in a cooler. Sufficient sediment samples were then gas-squeezed to obtain between 100 and 300 mL interstitial water samples. The interstitial water was then filtered through a 0.45 μm Millipore membrane filter and stored in a refrigerator in polyethylene bottles at 4°C prior to analysis.

Sample Irradiation and Counting. NAA was used in the study as an intralaboratory comparison technique for the analysis of the interstitial water samples. The details for sample irradiation and counting are given in the literature.[7] All standards and samples were irradiated in a 1 MW-TRIGA reactor at a steady neutron flux of 6×10^{12} n $cm^{-2}s^{-1}$ followed by a 12-hr cooling period. Each sample was counted using a large volume coaxial ORTEC Ge(Li) detector with a resolution of 2.3 keV at the 1332 keV γ from ^{60}Co. The 559 keV γ from ^{76}As and the 564 keV γ from ^{122}Sb were used to determine sample concentrations. These nuclides were quantified by comparing the net photopeak areas with those of standards of the appropriate concentrations.

Analytical Procedures. The $As(FDDC)_3$ and $Sb(FDDC)_3$ complexes were prepared by adding excess amounts of a 5% Li(FDDC) solution to As^{3+} or Sb^{3+} solutions at pH 3. The resulting precipitates were extracted with dichloromethane by shaking for approximately 10 minutes in a glass stoppered Erlenmeyer flask. The organic phase was then separated and washed with deionized water. The complexes were

recrystallized from a 1:1 (v/v) chloroform/ethanol solution. These complexes were then used for calibration purposes.

For the extraction experiments, all water samples analyzed were saturated with dichloromethane prior to extraction. Typically, a 100 mL sample was placed in a round glass stoppered Erlenmeyer flask. A 10 mL aliquot of citrate buffer was added. After adjusting the pH to between 3.5 and 5.5 with either HCl or NH_4OH, 2 mL of 5% Li(FDDC) solution was added along with 10 mL of dichloromethane. The mixture was shaken for 10 minutes on a Burell model 75 mechanical wrist-action shaker. After phase separation, the organic phase was washed with deionized water and subsequently allowed to evaporate to dryness. Exactly 100 μL of dichloromethane was used to reconstitute to extracted metal chelates for SFC analysis. In cases of low As and Sb concentrations, the initial water sample size was increased to 200 or 300 mL. The amount of added extraction solutions was increased proportionately. To determine total As and Sb, a second aliquot of the water sample was placed in an Erlenmeyer flask. This was then acidified to pH 1 with HNO_3. Reduction of As^{5+} to As^{3+} and Sb^{5+} to Sb^{3+} was accomplished by the addition of 1 mL each of a 25% sodium thiosulfate solution and a 20% potassium iodide solution. After 30 minutes, 2 mL of the 5% Li(FDDC) solution was added, and the sample extracted as indicated previously. The differences between total As and Sb concentrations and the concentrations of As^{3+} and Sb^{3+} in the first aliquot represent concentrations of As^{5+} and Sb^{5+}.

The extraction method using APCDT for the determination of As and Sb species for NAA for comparative purposes is similar to that used for FDDC extraction and SFC analysis. The details of the NAA procedure are given elsewhere.[3]

Urine samples were digested with HNO_3 and H_2O_2 following the procedure outlined in the literature.[10] NBS orchard leaves and pine needles reference materials were digested with a mixture of concentrated HNO_3 and H_2SO_4 in a reflux apparatus according to the procedure outlined in the literature.[11]

7.3 Results and Discussion

It was previously shown that As and Sb FDDC complexes could be separated by SFC from a mixture containing Zn, Ni, Co, Fe, Hg, As, Sb, and Bi with excellent resolution using a 5 m SB-Methyl-100 100 μm ID column.[6] The separation was carried out with an initial CO_2 pressure of 100 atm followed by a 4.0 atm/min pressure ramp after a 6.50 min hold time and an oven temperature of 100°C. Using these conditions, calibration and quantitation were based upon peak areas. In the generation of calibration curves, it was found that the lowest concentration that was reproducibly detectable was 1 ppm of metal-FDDC complex for both As and Sb. The timed-split injection was calibrated so that the total amount of sample injected would be known. A detection limit of 1 ppm based upon an 80 nL injection subsequently corresponds to a detection limit of 7 pg for As^{3+} and 11 pg for Sb^{3+} based on an injection volume of 80 nL.

Recovery of spiked As and Sb species using FDDC extraction and SFC analysis was studied using a tap water sample spiked with concentrations expected to bracket those concentrations present in natural water samples. The results of this study are summarized in Table 7.1, and a chromatogram of the metal chelates extracted in the spiked tap water sample is shown in Figure 7.1. The spiked samples range from 0.1 μg to 15 μg added to 100 mL of tap water of both As and Sb trivalent and pentavalent species, which corresponds to a concentration range of 1 ppb to 150 ppb. A second aliquot of sample was reduced using sodium thiosulfate and potassium iodide for the determination of total As and Sb. Pentavalent concentrations were then subsequently determined by subtraction. From the results summarized in Table 7.1, it can be seen that this technique produces satisfactory recovery results for the purpose of arsenic and antimony speciation studies.

Since As and Sb concentrations in biological samples are also of interest, recovery of As and Sb from a urine sample was also studied. Prior to FDDC extraction and SFC analysis, the urine samples were digested with HNO_3 and H_2O_2. Only total inorganic As and Sb can be determined in these samples as a result of oxidation during digestion. The results of the recovery study are also summarized in Table 7.1. The concentrations of As and Sb varied from 0.1 mg to 1.0 mg spiked into 100 mg of urine which corresponds to a range of 1.0 μg/g to 10 μg/g. The spiked concentrations were also

Table 7.1. Recovery of Spiked As(III), As(V), Sb(III), and Sb(V) in Water and Urine Samples

Water Sample:			
Amount Added (μg)*		% Recovery	
As(III)	As(V)	As(III)	As(total)
0.1	0.1	91.3 ± 5.9	94.6 ± 6.1
0.5	0.5	89.8 ± 6.5	96.2 ± 6.3
5.0	5.0	84.4 ± 8.4	92.8 ± 6.8
10.0	10.0	93.4 ± 6.6	95.6 ± 6.2
15.0	15.0	97.0 ± 6.8	101.0 ± 6.1
Sb(III)	Sb(V)	Sb(III)	Sb(total)
0.1	0.1	97.6 ± 6.3	98.6 ± 6.4
0.5	0.5	100.1 ± 6.5	98.5 ± 6.4
5.0	5.0	98.0 ± 6.1	99.7 ± 6.7
10.0	10.0	96.3 ± 7.2	94.5 ± 7.1
15.0	15.0	93.4 ± 6.1	100.9 ± 7.5
Urine Sample:			
Amount Added (mg)*		% Recovery	
As(III)	Sb(III)	As(total)	Sb(total)
0.1	0.1	90.9 ± 6.6	92.1 ± 6.7
0.5	0.5	97.8 ± 7.1	98.6 ± 7.2
1.0	1.0	98.0 ± 7.5	93.4 ± 7.3

* Amount added to 100 mL water sample

chosen to bracket expected concentrations in biological samples. The recovery of As and Sb from the urine samples also shows satisfactory results.

The sediments of the Coeur d'Alene River are contaminated with toxic metals including As and Sb due to the mining of lead, zinc, and silver in the past decades. The distribution of metal species in the interstitial waters of the river sediments is important to the understanding of the migration

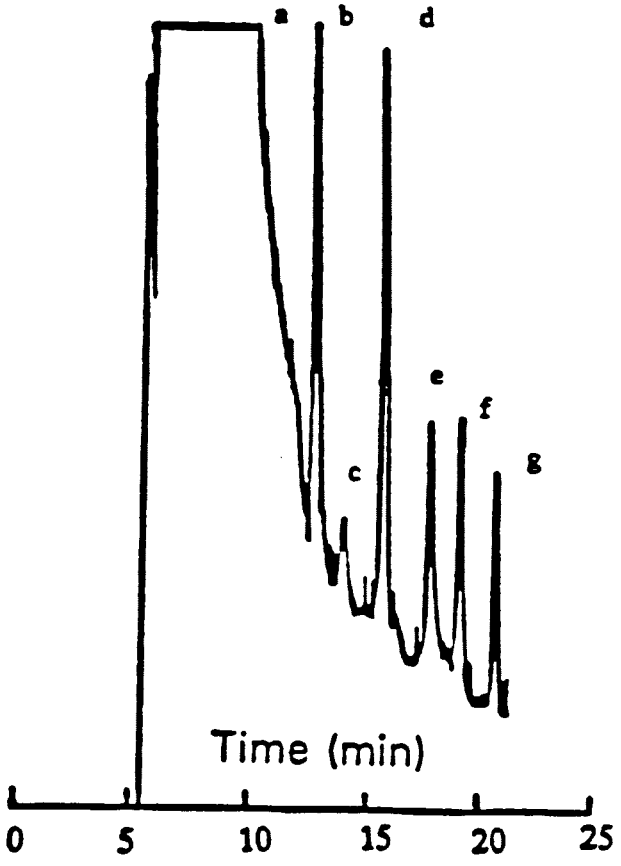


Figure 7.1 Chromatogram of As^{3+} and Sb^{3+} Spiked Tap Water Sample Produced Using Lee Scientific 5 m x 100 μm ID SB-Methyl-100 Capillary Column with FID. SFC conditions: 80 nL injection, 100°C oven temperature, hold time 6.50 min at 100 atm, pressure ramp of 5.0 atm/min to 250 atm. Peak a: CH_2Cl_2, b: Li(FDDC), c: solvent impurity, d: $Zn(FDDC)_2$, e: $Fe(FDDC)_3$, f: $As(FDDC)_3$, g: $Sb(FDDC)_3$.

and environmental fate of As and Sb in river waters. For this reason, the described method for inorganic As and Sb speciation in water samples was used for the analysis of these elements in several interstitial water samples from sediments of the Coeur d'Alene River. The interstitial waters were obtained from the sediments using direct pressure gas squeezing. It was found that sufficient quantities of interstitial water could be obtained in about 30 min under 30 psig of nitrogen. A chromatogram of the extracted metal-FDDC complexes from interstitial water obtained at Smelterville, Idaho, is shown in Figure 7.2. The peaks for $As(FDDC)_3$ and $Sb(FDDC)_3$ are clearly separated from the FDDC complexes of Zn, Cu, Fe, and Mn, which are also present in the sample.

The results of the FDDC-SFC analysis of the three interstitial water samples are summarized in Table 7.2. Since solvent extraction with APCDT followed by NAA was used as a collaborative method to evaluate the accuracy of the described method, these results are also presented in Table 7.2 for comparison. The interstitial water sample from Harrison Lake was found to contain 25.8±1.8 and 18.2±3.5 ppb of As^{3+} and As^{5+}, respectively, while Sb^{3+} and Sb^{5+} concentrations were determined to be 1.7±0.1 and 1.5±0.2 ppb, respectively. The As^{3+} and As^{5+} concentrations of the interstitial water of the St. Joe River sample site were determined to be 1.2±0.1 and 1.7±0.1 ppb, respectively, and Sb^{3+} and Sb^{5+} concentrations were determined to be 0.3±0.1 and 1.5±0.2 ppb, respectively. Finally, the interstitial water sample from the Smelterville

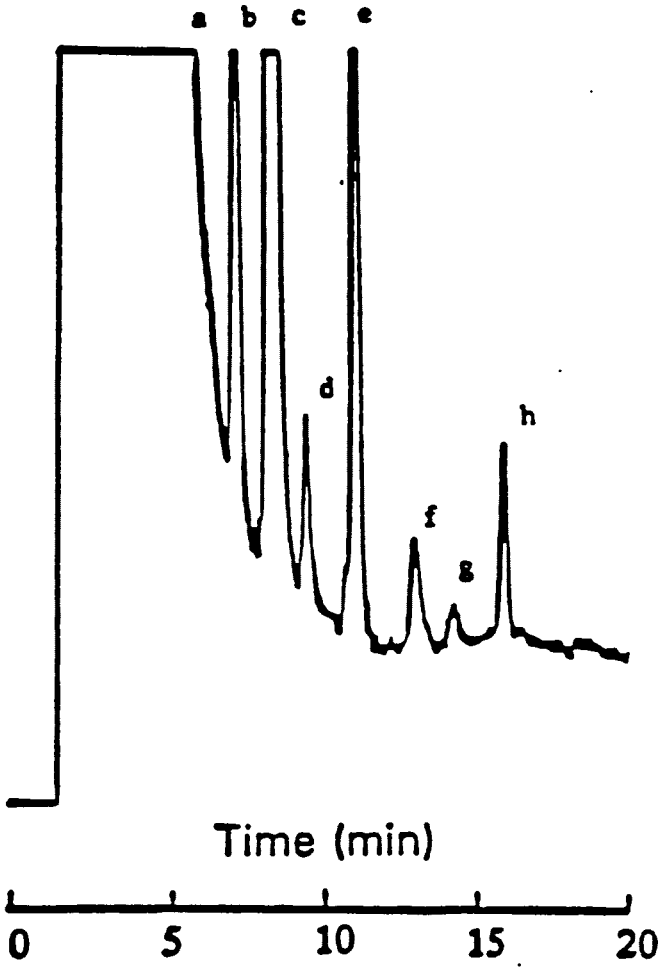


Figure 7.2 Chromatogram of Interstitial Water Sample Taken from Smelterville, Idaho, Sampling Site. Chromatogram produced using Lee Scientific 5 m x 100 μm ID SB-Methyl-100 capillary column with FID. SFC conditions: 80 nL injection, 100°C oven temperature, hold time 6.50 min at 100 atm, pressure ramp of 4.0 atm/min to 250 atm. Peak a: CH_2Cl_2, b: Li(FDDC), c: $Zn(FDDC)_2$, d: $Cu(FDDC)_2$, e: $Fe(FDDC)_3$, f: $As(FDDC)_3$, g: $Sb(FDDC)_3$, h: $Mn(FDDC)_2$.

sediments was found to contain 38.7±2.7 and 23.7±4.0 ppb of As^{3+} and As^{5+}, respectively, while Sb^{3+} and Sb^{5+} concentrations were determined to be 1.7±0.1 and 2.1±0.2 ppb, respectively. These results agree with those obtained by NAA as shown in Table 7.2.

Table 7.2. Concentration of As(III), As(V), Sb(III), and Sb(V) in Interstitial Water of Sediments from the Coeur d'Alene River, Idaho

Sample Site	Concentrations (ng/mL)			
	As(III)	As(V)[a]	Sb(III)	Sb(V)[a]
		SFC		
Harrison Lake	25.8±1.8	18.2±3.5	1.7±0.1	1.5±0.2
St. Joe River	1.2±0.1	1.7±0.1	0.3±0.1	1.5±0.2
Smelterville	38.7±2.7	23.7±4.0	1.7±0.1	2.1±0.2
		NAA		
Harrison Lake	25.1±2.1	18.7±2.1	1.5±0.1	1.3±0.1
St. Joe River	1.2±0.1	1.6±0.1	0.2±0.1	1.4±0.2
Smelterville	39.5±1.0	24.4±2.2	2.0±0.1	2.0±0.1

[a] As(V) and Sb(V) were determined by subtraction from total amounts present in the reduction sample.

Extraction of As and Sb with FDDC followed by SFC analysis was also applied to NBS biological standard materials. The standard reference materials orchard leaves (SRM 1571), whose As and Sb contents have been certified to be 10±2 and 2.9±0.3 μg/g, respectively, and pine needles (SRM 1575), whose As concentration has been certified at 0.21±0.04 μg/g, were used. For the pine needles sample, the Sb concentration is given as 0.2 μg/g by NBS for reference, but it is not the certified value. These standard reference materials were digested as previously described. The results

of the FDDC-SFC analyses of the NBS reference materials are summarized in Table 7.3. On the basis of triplicate analyses, As and Sb concentrations in NBS orchard leaves were found to be 9.1±0.6 and 3.3±0.4 μg/g, respectively, and As and Sb concentrations in NBS pine needles were determined to be 0.19±0.01 and 0.19±0.01 μg/g, respectively. These results agree well with the reported values, indicating that FDDC extraction followed by SFC analysis is also a viable method for simultaneous determination of total As and Sb in biological samples.

Table 7.3. Determination of Total As and Sb in Biological Reference Materials Using FDDC Chelation and SFC

Reference Material	As (μg/g)	
	This Work	NBS Value
Orchard Leaves SRM 1571	9.1±0.6	10±2
Pine Needles SRM 1575	0.19±0.01	0.21±0.04
	Sb (μg/g)	
	This Work	NBS Value
Orchard Leaves SRM 1571	3.3±0.4	2.9±0.3
Pine Needles SRM 1575	0.19±0.01	(0.2)[a]

[a] Value given for reference by U.S. National Bureau of Standards, not certified.

7.4 Conclusions

The extraction of trace quantities of As(III) and Sb(III) from aqueous solutions using FDDC followed by SFC separation and quantitation provides a unique method of speciation of these elements in environmental samples. The extraction technique eliminates organic matrix interferences and preconcentrates the metal species by conversion to chelates

suitable for SFC analysis. As^{5+} and Sb^{5+} are extracted after reduction with sodium thiosulfate and potassium iodide. This method has been applied to As and Sb speciation of interstitial waters obtained from contaminated river sediments and for total As and Sb determinations in biological samples. Furthermore, this method has shown a novel application of supercritical fluid chromatography for metal chelate analysis.

Acknowledgments

This material is based upon work supported by the Idaho EPSCoR Program of the National Science Foundation under Grant No. RII-8902065. Neutron irradiations were done at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by the Department of Energy.

REFERENCES

1. Cullen, W. and Reimer, K. Chem. Rev. 89:713-764 (1989).
2. Mok, W. and Wai, C. Water Res. 22(6):769-774 (1988).
3. Mok, W. and Wai, C. Anal. Chem. 59:233-236 (1987).
4. Neeb, R. Pure Appl. Chem. 54:847-852 (1982).
5. White, C. and Houck, R. HRC&CC 8:293-296 (1985).
6. Laintz, K.; Yu, J. and Wai, C. Anal. Chem., in press.
7. Mok, W.; Shah, N. and Wai, C. Anal. Chem. 58:110-113 (1986).
8. Sucre, L. and Jennings, W. Anal. Lett. 13(A6):497-501 (1980).
9. Tavlardis, A. and Neeb, R. Fresenius Z. Anal. Chem. 292:135-140 (1978).
10. Aggarwal, S.; Kinter, M.; Wills, M.; Savory, J. and Herold, D. Anal. Chem. 62:111-115 (1990).
11. Mok, W.; Willmes, H. and Wai, C. Anal. Chem. 56:2623-2624 (1984).

CHAPTER EIGHT

CONCLUSION

In recent years, the determination of trace elements for the evaluation of their environmental impact has changed from a simple determination of total concentration towards species content and from single environmental samples toward a more sophisticated fractionation of relevant samples. These changes in focus result from a recognition of toxicity, geochemical cycles, biochemical and ecotoxicological significance of the fate and species of pollutants. The speciation of ultra trace elements in sediment/water systems has received increasing attention recently as there is considerable interest not only in the biochemical and geochemical cycles of rivers but also in the horizontal, vertical and seasonal variations. However, there still remains insufficient information in the area as a result of difficulties arising from inappropriate analytical techniques, unsatisfactory sampling and storage procedures, and inadequate pretreatment processes. Thus, several preconcentration and speciation methods have been studied and used for the environmental samples in this paper. They were found successful in those applications. For speciation measurement in some cases surface waters, interstitial waters and sediments were analyzed to help us to understand the interactions between sediments and overlying waters. The migration of trace As and Sb between the interface of sediment and overlying water is tightly related to the species.

In the study of the Coeur d'Alene River the leaching process from mine wastes in the river is the primary source of the pollution. The interstitial water indicates the bridge of the leaching process between sediment and water. In addition, the ratio between different species, especially As(III)/As(V), provides the redox status of water and sediment systems. The possible mechanisms for migration of trace As and Sb between sediment-overlying water include chemical transformation, bio-oxidation, sorption, dissolution, precipitation, complexation and diffusion. This study shows that environmental toxicity and impact can be reasonably well predicted if the speciation models of a metal in water, interstitial water and sediment are known.

In view of this study, several conclusions can be made.

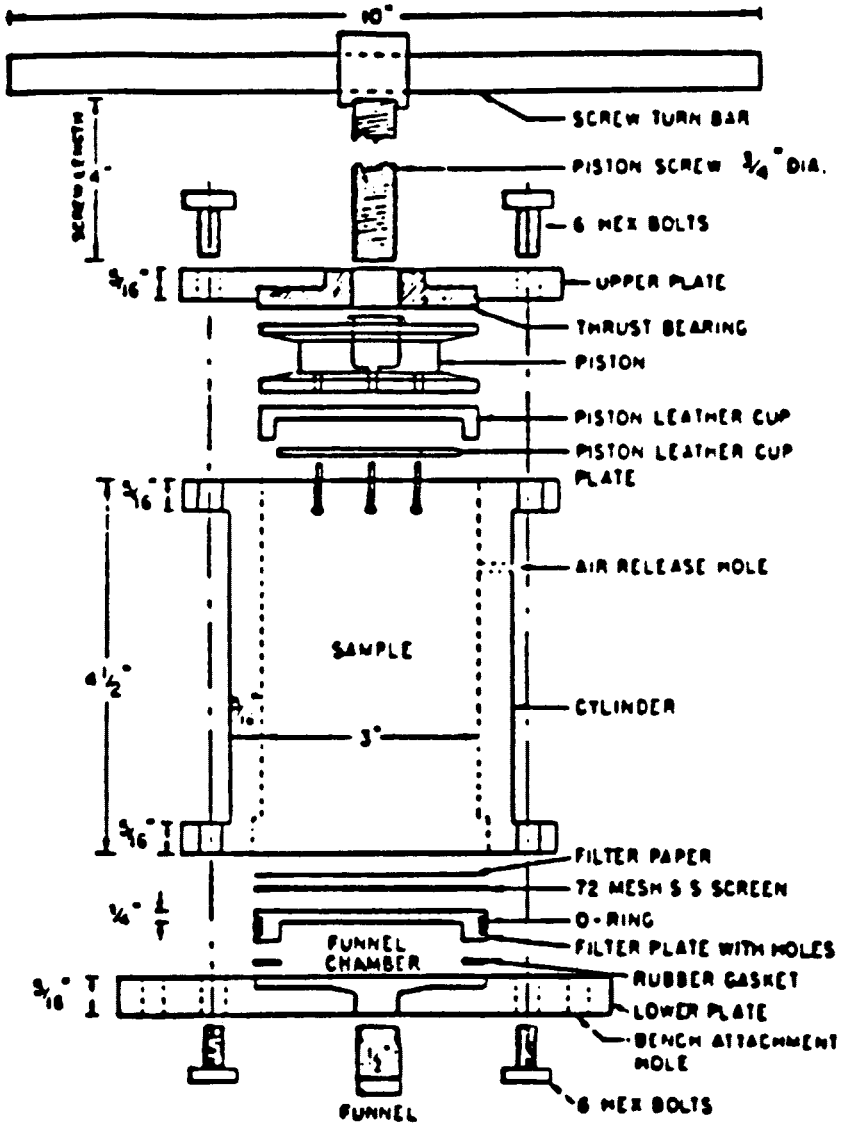
1. Gas-pressure squeezing utilizing an Amicon ultra-filtration cell provides an appropriate technique for removing interstitial water from sediments.
2. Solvent extraction with APDC is an effective preconcentration process prior to instrumental analysis for arsenic and antimony speciation studies in natural waters.
3. The high concentration of arsenic and low ratio of As(V)/As(III) in the interstitial waters of the sediments of the Coeur d'Alene River reflect the pollution of the river.
4. The dissolved As(III) and the total As in the interstitial water generally increase with the depth of

the sediment, reach a maximum around 6 cm, then decrease with the depth. This is probably caused by a series of complex reactions including the surface leaching, the diffusion of the metal ions, and the precipitation of iron in the reduction zone of the sediment.

5. High concentrations of As(III) are found in the deep well waters of the Blackfoot Disease area in Taiwan, which may be related to the cause of the disease.
6. Interstitial water provides a pathway for the diffusion of dissolved metal species across the sediment-water interface. It is probably an important mechanism for postdepositional remobilization of trace elements in the sediments.
7. Bis(trifluoroethyl)dithiocarbamate is an effective chelating agent for supercritical fluid chromatographic analysis of As(III) and Sb(III).

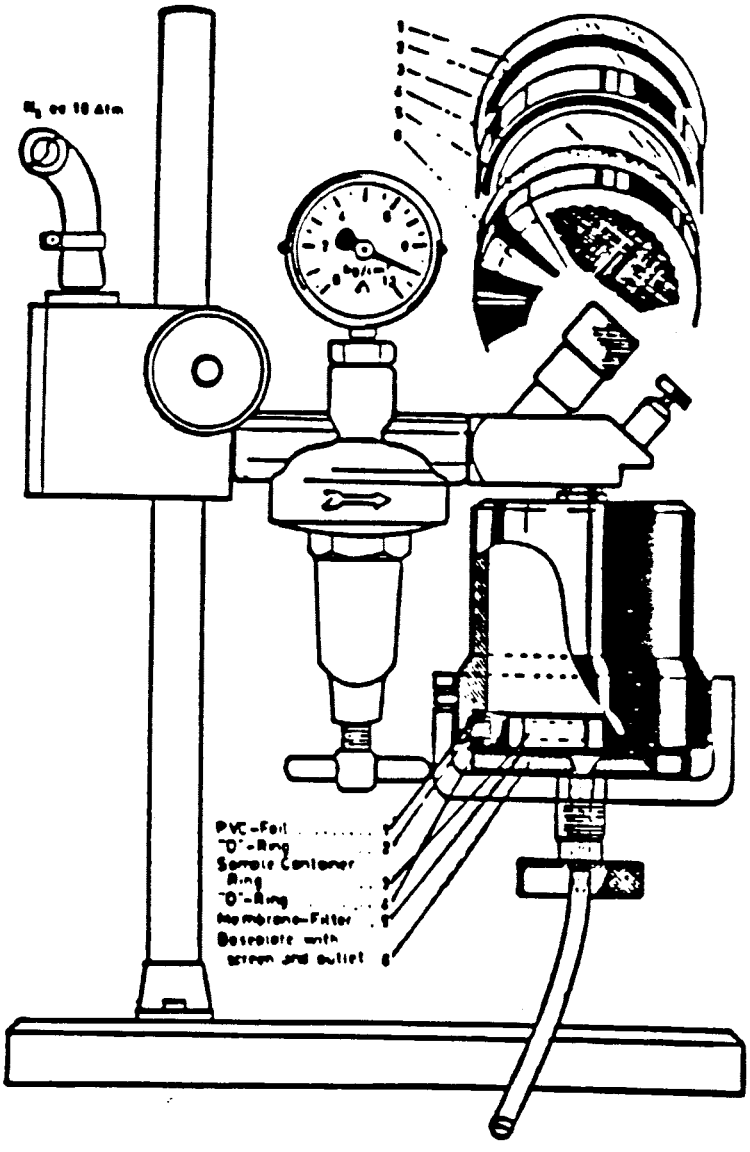
So far, there are few reports of the interstitial water behavior of arsenic and antimony species. More research on the chemical reactivity and transformation of arsenic and antimony in interstitial water can be developed in the future to acquire better understanding in this area.

APPENDIX A: DIAGRAM OF MANUAL TURN-SCREW SQUEEZER*



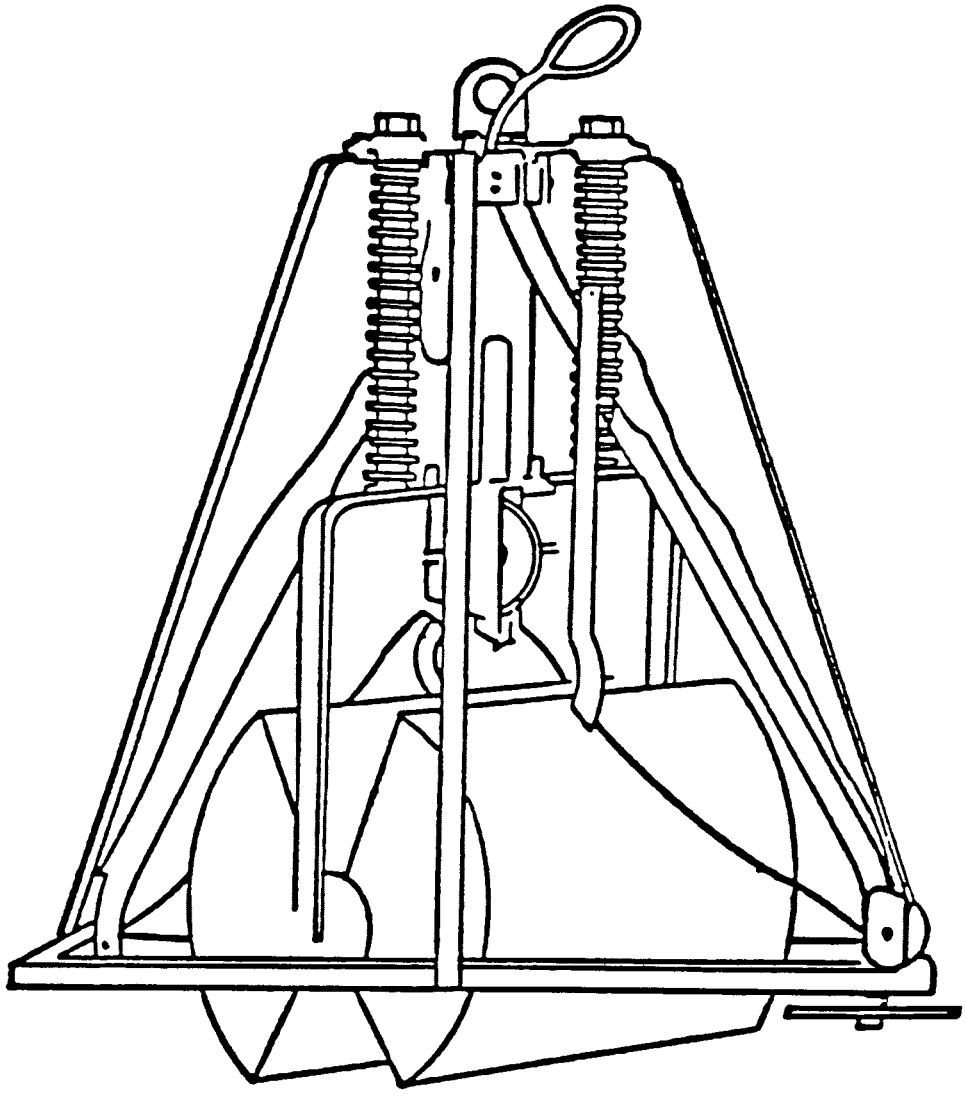
* Reproduced from Raymond Siever J. of Sedimentary Petrology 32:331 (1962)

APPENDIX B: GAS PRESSURE SQUEEZER*



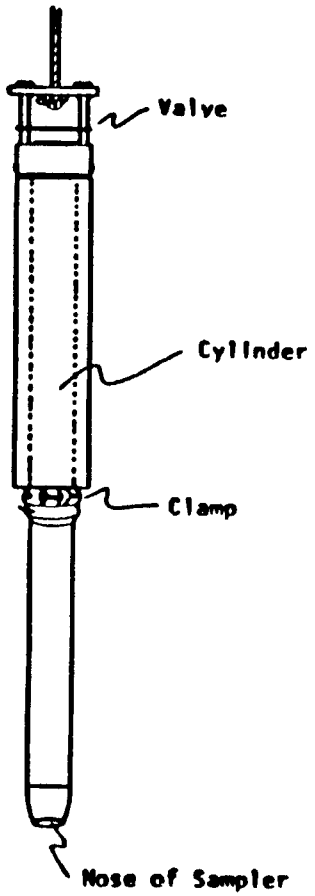
* Reproduced from Martin Hartmann Deep-sea Research 12:225 (1965)

APPENDIX C: SMITH-MCINTYRE (ABERDEEN) GRAB*

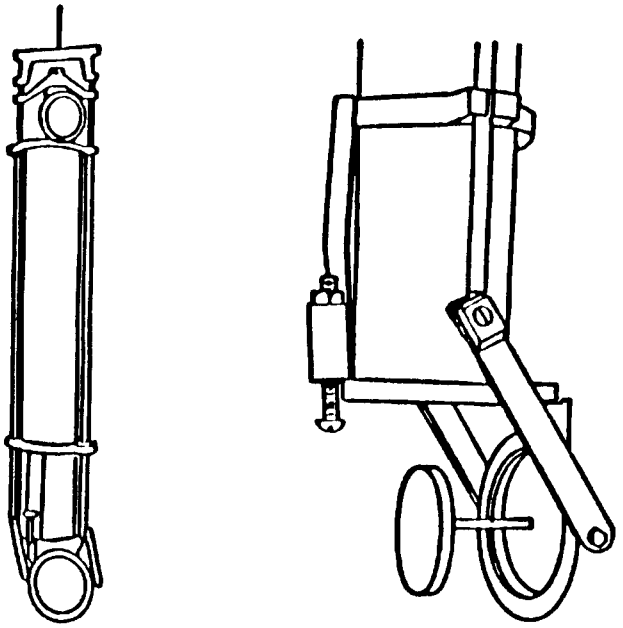


* Reproduced from Handbook for Sampling and Sample Preservation of Water and Wastewater EPA-600/4-82-029, 212 (1982)

APPENDIX D: CORE SAMPLERS*



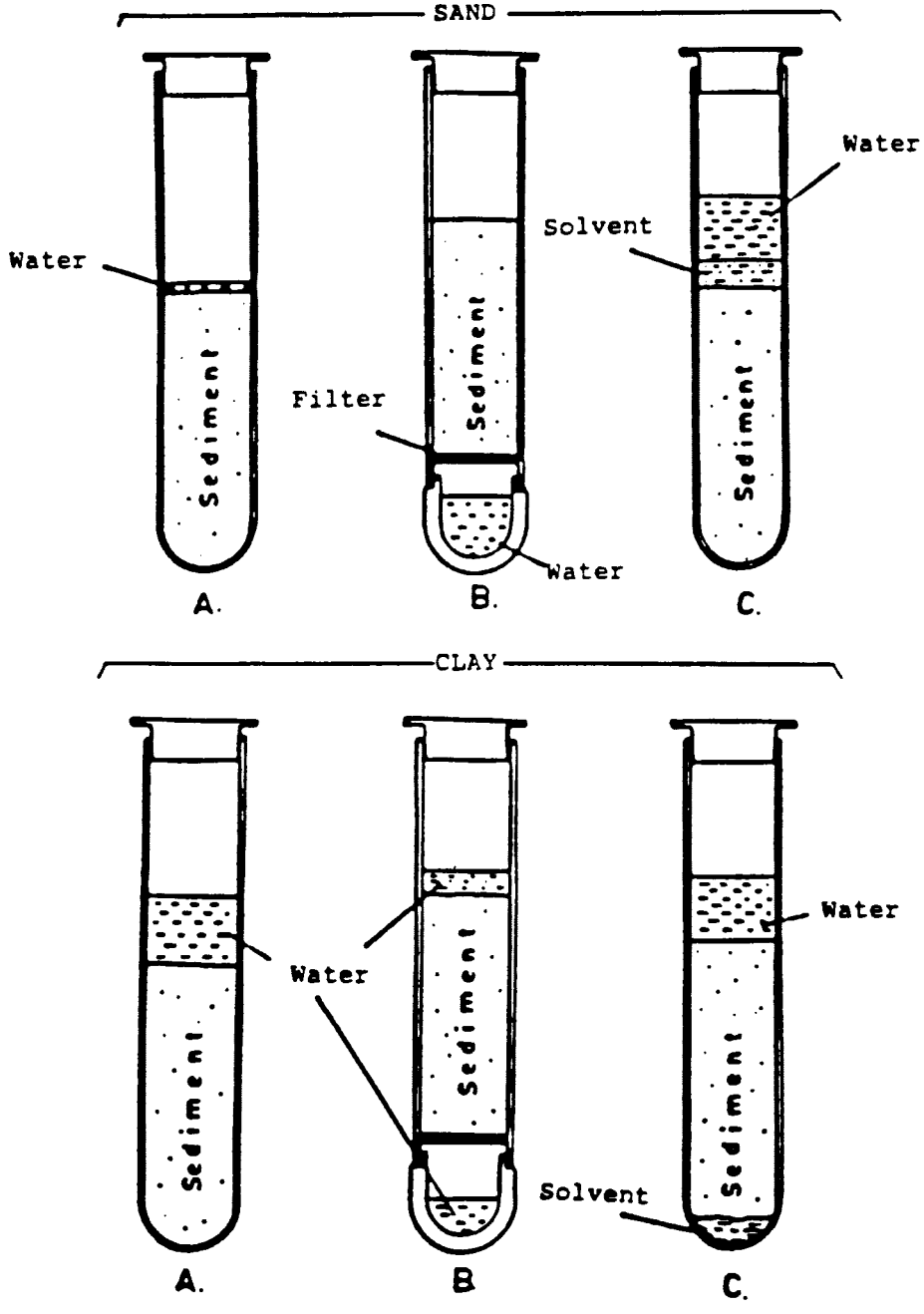
Side View-Vertical Core Sampler



Elgmork's Core Sampler

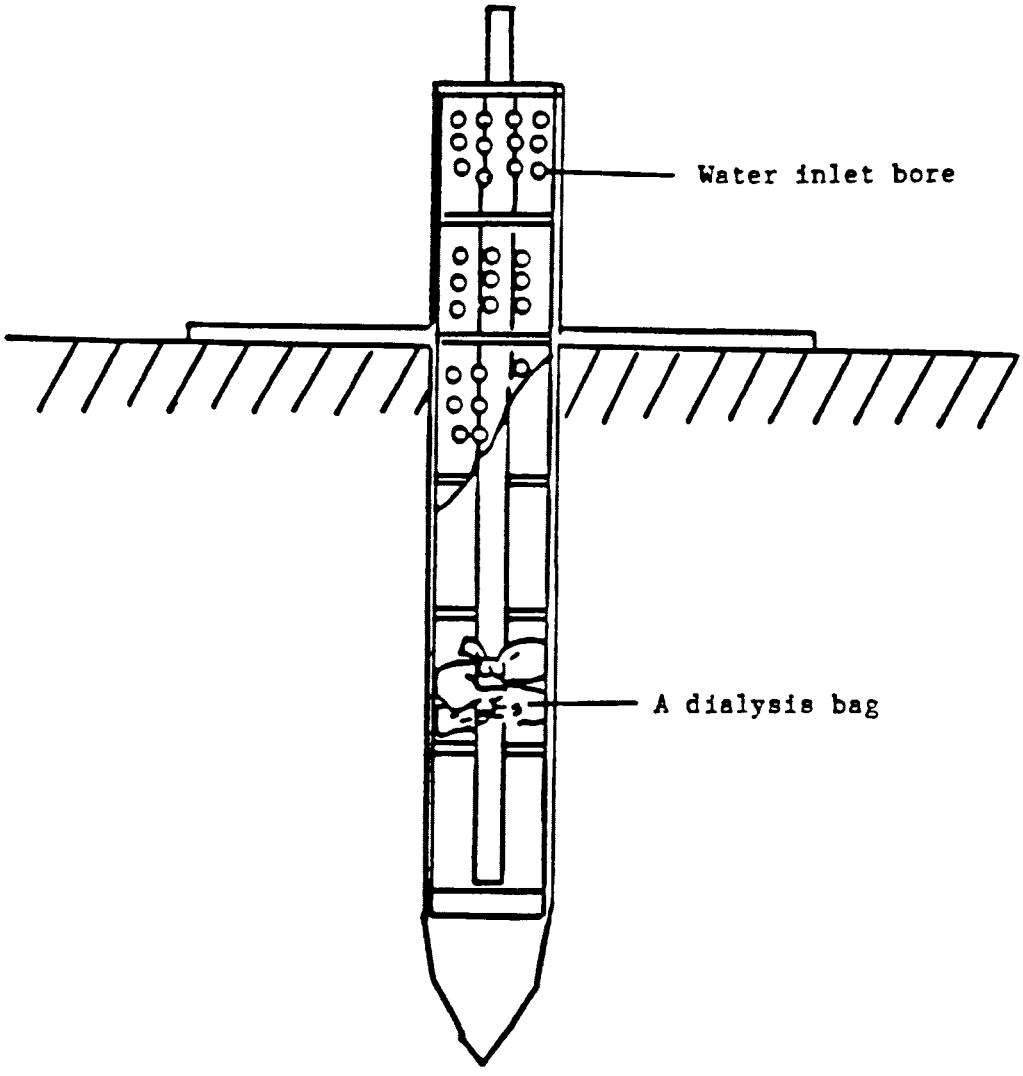
* Reproduced from Handbook for Sampling and Sample Preservation of Water and Wastewater EPA-600/4-82-029, 213 (1982)

APPENDIX E: CENTRIFUGATION METHODS FOR THE SEPARATION OF INTERSTITIAL WATERS FROM SEDIMENTS

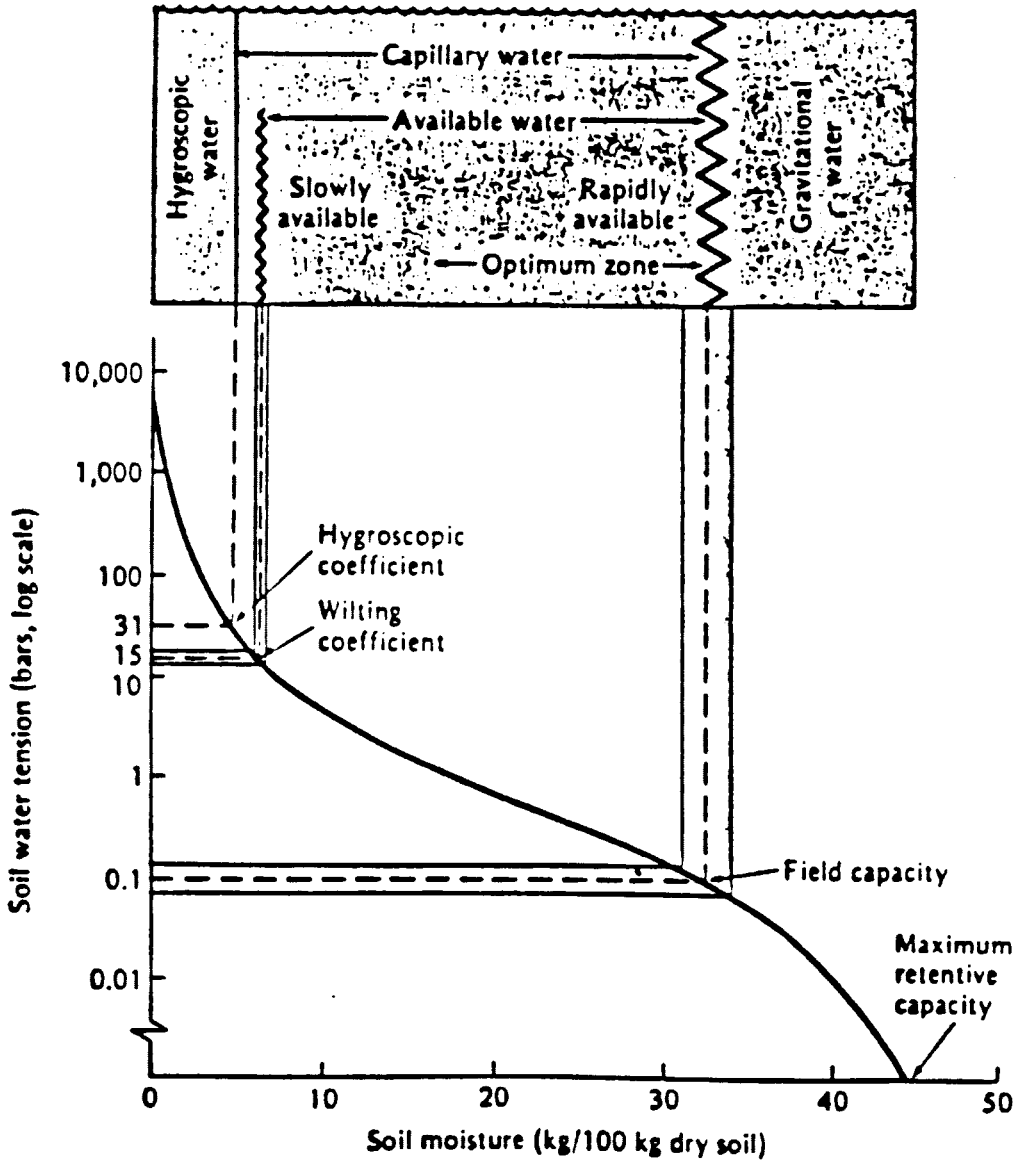


A: Direct centrifugation
B: Basal-cup collection
C: Solvent displacement

APPENDIX F: SCHEMATIZED INTERSTITIAL WATER SAMPLER WITH ONE DIALYSIS BAG IN PLACE



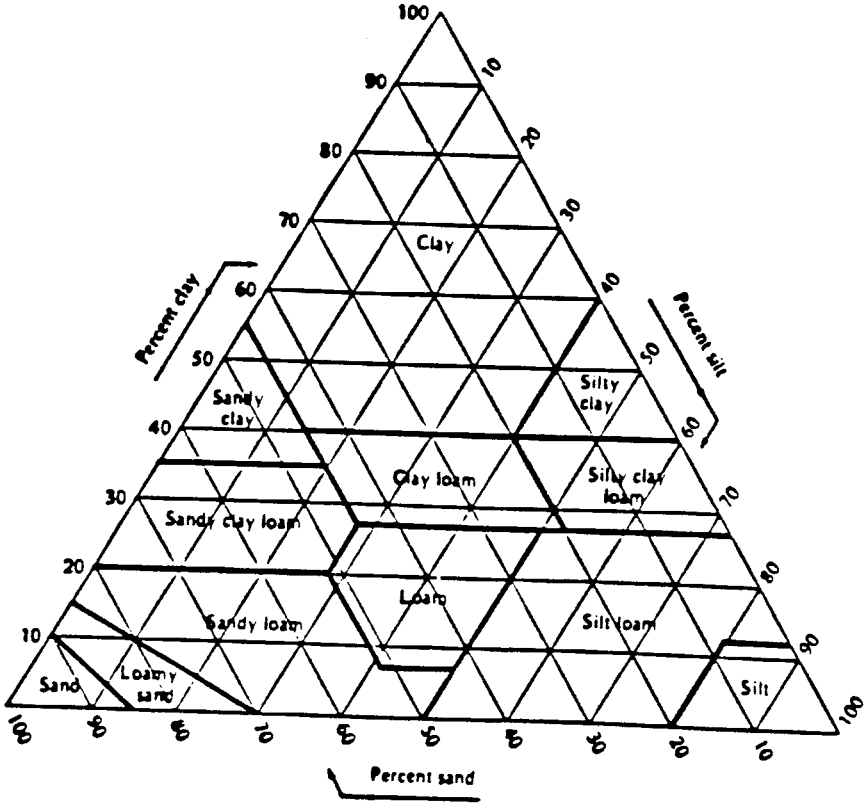
APPENDIX G: TENSION-MOISTURE CURVE OF A LOAM SOIL



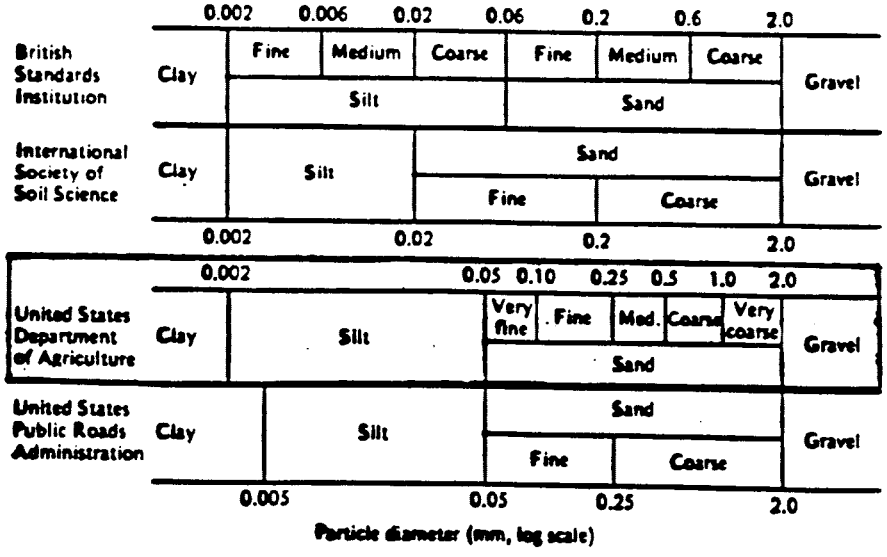
APPENDIX H: XRF SPECTROMETER OPERATING CONDITIONS; RHODIUM (Rh) TARGET, 50 Kv/50MA, FULL VACUUM, AND 25 MM MASK

Element		Slit	Crystal	Counter	Pk2θ	Count (secs.)	Background 2θ	Count (secs.)	Background 2θ	Count (secs.)	Corrected For
Si	Kα	C	PET	FPC	109.040	40	-	-	-	-	
Al	Kα	C	PET	FPC	144.730	40	-	-	146.260	20	
Ti	Kα	F	LiF200	FPC	86.205	40	85.000	20	-	-	
Fe	Kα	F	LiF200	FPC	57.515	40	-	-	-	-	
Mn	Kα	F	LiF200	FPC	63.000	40	-	-	63.800	20	
Ca	Kα	F	LiF200	FPC	113.160	40	-	-	-	-	
Mg	Kα	F	RX35	FPC	19.760	40	18.000	10	22.000	10	
K	Kα	C	LiF200	FPC	136.710	40	-	-	138.300	20	
Na	Kα	C	RX35	FPC	24.060	40	-	-	25.700	20	
P	Kα	C	GE	FPC	140.870	40	143.000	20	-	-	
Ni	Kα	F	LiF200	FPC	48.650	160	47.770	80	49.570	80	
Cr	Kα	F	LiF200	FPC	69.390	160	68.400	40	70.790	40	V,La
Sc	Kα	C	LiF200	FPC	97.790	160	97.080	160	-	-	Ca
V	Kα	F	LiF200	Sc	76.880	160	76.240	160	-	-	Ti
Ba	Lα	F	LiF200	FPC	87.240	160	-	-	88.060	80	Ti,Sc
Rb	Kα	F	LiF220	Sc	37.930	80	36.880	40	38.720	40	
Sr	Kα	F	LiF220	Sc	35.785	80	35.260	40	36.880	40	
Zr	Kα	F	LiF220	Sc	32.030	80	31.615	40	33.030	40	Sr,Th
Y	Kα	F	LiF220	Sc	33.825	80	33.030	40	35.260	40	Rb,Th
Nb	Kα	F	LiF220	Sc	30.370	80	29.870	40	31.615	40	Y
Ga	Kα	F	LiF220	Sc	56.130	80	55.500	40	56.880	40	
Cu	Kα	F	LiF200	FPC	45.005	80	-	-	46.720	80	
Zn	Kα	F	LiF220	Sc	60.520	80	60.000	80	61.100	40	
Pb	Lβ	F	LiF200	Sc	28.240	160	27.610	80	28.680	80	
La	Lα	F	LiF200	FPC	82.970	160	82.300	80	84.000	80	
Ce	Lβ	F	LiF200	FPC	71.660	160	70.790	80	72.700	80	
Th	Lα	F	LiF220	Sc	29.215	160	38.720	80	40.000	80	

APPENDIX I: CLASSIFICATION OF SOIL PARTICLES AND MAJOR SOIL TEXTURAL CLASSES



A. Major soil textural classes



B. Classification of soil particle size by four different systems