

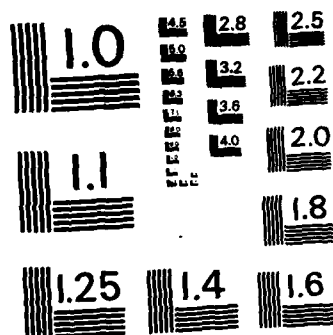
UNCLASSIFIED

DREDGING OPERATIONS TECHNICAL SUPPORT PROGRAM
TRANSFORMATION FIXATION AND... (U) ARMY ENGINEER
WATERWAYS EXPERIMENT STATION VICKSBURG MS J M BRANNON
JAN 84 WES-TR-D-84-1 F/G 13/2

1/3

NS

1
2
3
4
5
6
7
8
9
10



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



US Army Corps
of Engineers

AD A139032



DTIC FILE COPY

**DREDGING OPERATIONS TECHNICAL
SUPPORT PROGRAM**

TECHNICAL REPORT D-84-1

**TRANSFORMATION, FIXATION, AND
MOBILIZATION OF ARSENIC AND ANTIMONY
IN CONTAMINATED SEDIMENTS**

by

James M. Brannon

Environmental Laboratory

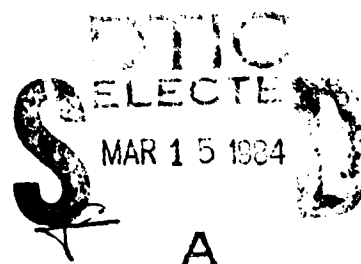
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180



January 1984

Final Report

Approved For Public Release; Distribution Unlimited



Prepared for Office, Chief of Engineers, U. S. Army
Washington, D. C. 20314

84 CC 100

Destroy this report when no longer needed. Do not return
it to the originator.

The findings in this report are not to be construed as an official
Department of the Army position unless so designated
by other authorized documents.

The contents of this report are not to be used for
advertising, publication, or promotional purposes.
Citation of trade names does not constitute an
official endorsement or approval of the use of
such commercial products.

The D-series of reports includes publications of the Environmental
Effects of Dredging Programs:

Dredging Operations Technical Support

Long-Term Effects of Dredging Operations

Interagency Field Verification of Methodologies for
Evaluating Dredged Material Disposal Alternatives
(Field Verification Program)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report D-84-1	2. GOVT ACCESSION NO. A1-A139032	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) TRANSFORMATION, FIXATION, AND MOBILIZATION OF ARSENIC AND ANTIMONY IN CONTAMINATED SEDIMENTS		5. TYPE OF REPORT & PERIOD COVERED Final report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James M. Brannon		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Army Engineer Waterways Experiment Station ~~Environmental Laboratory~~ P. O. Box 631, Vicksburg, Miss. 39180		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Dredging Operations Technical Support Program
11. CONTROLLING OFFICE NAME AND ADDRESS Office, Chief of Engineers, U. S. Army Washington, D. C. 20314		12. REPORT DATE January 1984
		13. NUMBER OF PAGES 205
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22161.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Antimony Arsenic Dredged material Leaching Redox potential		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The potential environmental impacts of arsenic (As) and antimony (Sb) con- taminated sediments were studied with emphasis placed on short- and long-term leaching and sediment conditions that affect mobilization. Under anaerobic conditions, arsenate [As(V)] was reduced to arsenite [As(III)] in a wide range of sediments. In anaerobic Texas City sediment slur- ries, 70% of added As(V) was recovered as water soluble As(III) following three (Continued)		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. ABSTRACT (Continued).

weeks of incubation. Formation of organic As following addition of AS(V) to anaerobic sediments was also demonstrated.

Short-term leaching was conducted with anaerobically incubated unamended and As amended sediments using either distilled or saline water. In both amended and unamended sediment, As(III) was the predominant species released. Releases of As(III) were greatest when sediments were low in iron and high in interstitial water and exchangeable phase As(III). Releases of As(V), As(III), and organic As from sediments were found to be relatively insensitive to the salinity of the mixing water.

Aerobic leaching experiments of six months duration were conducted to determine what As species would be released, the duration of the releases, and the sediment factors affecting releases. Arsenic releases usually persisted throughout the leaching period; releases were higher from amended compared with unamended sediments. Generally, As(III) release predominated initially, followed by As(V) and organic As releases in the first three months. The final three months of leaching were characterized by predominant release of As(V). Conversely, leaching of Black Rock sediments under anaerobic conditions for three months resulted in almost exclusive release of As(III). These results indicate that soluble As releases from sediments are undesirable during the first months of aerobic leaching or at any time during anaerobic conditions because of the high toxicity of As(III). Arsenic releases following six months of leaching were related to sediment iron content and to sediment calcium carbonate (CaCO_3) equivalent concentration.

Short-term releases of Sb from freshwater sediments were enhanced by leaching with saline water. Many sediments amended with Sb also released volatile Sb compounds. In many other ways, Sb behavior in amended and unamended sediment paralleled As behavior, especially short- and long-term releases and sediment properties affecting releases.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

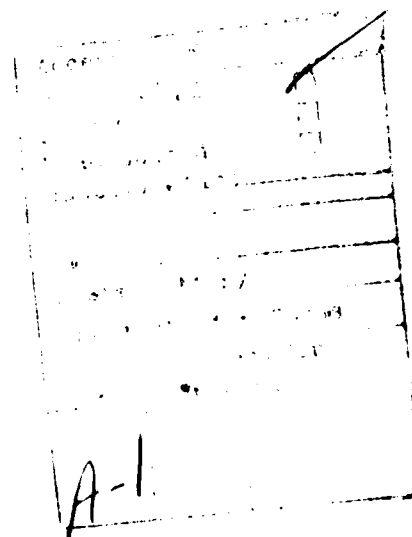
PREFACE

This study was sponsored by the Office, Chief of Engineers (OCE), U. S. Army, under the Dredging Operations Technical Support Program, which is a part of the Office of Environmental Effects of Dredging Programs (EEDP).

The work was conducted during the period January 1979 - June 1983 by the Environmental Laboratory, U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss., under the direction of Dr. J. Harrison, Chief of the Environmental Laboratory (EL), and under the general supervision of Mr. D. L. Robey, Chief of the Ecosystem Research and Simulation Division (ERSD). Program Manager of EEDP was Mr. C. C. Calhoun, Jr., EL.

This study was conducted by Dr. J. M. Brannon, ERSD. Mr. I. Smith, Jr., ERSD, Ms. K. Preston, ERSD, Mr. E. Kost, Analytical Laboratory Group (ALG), and Mr. N. Brown, ALG, assisted with the laboratory experimentation and chemical analyses. This report was written by Dr. Brannon as his dissertation at Louisiana State University, Baton Rouge, La., and was reviewed by Drs. D. Gunnison, R. L. Chen, and R. M. Engler, ERSD.

Commanders and Directors of WES during this study and the preparation and publication of this report were COL Nelson P. Conover, CE, and COL Tilford C. Creel, CE. Technical Director was Mr. F. R. Brown.



This report should be cited as follows:

Brannon, J. M. 1984. "Transformation, Fixation, and Mobilization of Arsenic and Antimony in Contaminated Sediments," Technical Report D-84-1, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

TABLE OF CONTENTS

	<u>Page</u>
PREFACE	i
LIST OF TABLES	vi
LIST OF FIGURES	xi
EXECUTIVE SUMMARY	xiv
INTRODUCTION	1
LITERATURE REVIEW	3
Arsenic Speciation and Toxicity	3
Nomenclature of Arsenic Compounds	3
Sources and Concentration of As	4
Physicochemical Transformations	7
Arsenic Adsorption.	20
Arsenic Fixation by Soils and Sediments	23
Arsenic Leaching from Sediment.	29
Arsenic and Phosphorus Cycling.	31
Sources and Concentration of Sb	33
Chemistry of Sb	35
MATERIALS AND METHODS.	38
Sampling Areas.	38

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Field Sampling Procedures	38
Controlled Eh-pH Incubations.	38
Short-Term Leaching	46
Long-Term Leaching.	48
Evolution of Volatile As and Sb Compounds	49
Analytical and Digestion Procedures	49
Quality Control	54
Data Analysis	54
 RESULTS AND DISCUSSION	 55
Experimental and Analytical Variability	55
Transformation and Distribution of Arsenic in Sediments .	59
Short-Term As Releases	77
Leaching Under Controlled Eh-pH Conditions.	87
Long-Term As Releases	96
Fixation and Retention of As by Sediment.	117
Antimony Behavior in Sediments.	132
 SUMMARY AND CONCLUSIONS	 148
Arsenic.	148
Antimony	152
 REFERENCES.	 155

TABLE OF CONTENTS (Continued)

	<u>Page</u>
APPENDIX A	A1
APPENDIX B	B1
APPENDIX C	C1

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Composition of Artificial Seawater	47
2 Mean Coefficients of Variation (%) for Water Soluble Phase Parameters in the Eh-pH, Short-Term Leaching, Long-Term Leaching Studies, and Anaerobic Incubation Studies.	56
3 Mean Coefficients of Variation (%) for Chemical Fractionation Procedures Conducted on Replicate Experiments.	57
4 Analytical Variability, Expressed as a Mean Coefficient of Variation (%) of Ten Randomly Selected Samples	58
5 Some Physical and Chemical Characteristics of the Sediments. .	60
6 Concentrations of As(V), As(III), and Organic As in the Inter- stitial Water of Sediments Incubated Anaerobically for 45 days.	62
7 Concentrations of As(V), As(III), and Organic As in the Exchange- able Phase of Anaerobic Sediments.	63

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
8 Water Soluble Total As (mg/l) in Texas City Sediment Suspensions.	67
9 Adsorption of DSMA From 2.64-l Solution Containing 2.22 mg/l of As and 63.3 g/l of Texas City Sediment Under Differing Eh and pH Conditions	72
10 Concentration (ug/l) of As(V), As(III), Organic As, and Total As in Sediment Distilled Water Leachates	79
11 Arsenic Distribution Coefficients in Short-Term Leachates of Anaerobic Sediments.	81
12 Correlations Between Short-Term Leachate As Distribution Coef- ficients (K) and Sediment Properties	82
13 Concentrations (ug/l) of As(V), As(III), and Organic As in Saline Leachates of Amended Sediments.	84
14 Concentrations (ug/l) of As(V) and As(III) in Saline Leachates of Unamended Sediments	85
15 Effect of Salinity (°/oo) on Short-Term Leachate pH.	86

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
16 Some Physical and Chemical Characteristics of Sediments Leached for One Week Under Specified Eh-pH Conditions	88
17 Concentrations of Water Soluble Phase ($\mu\text{g/l}$) and Exchangeable Phase ($\mu\text{g/g}$) As(III) as a Function of Eh and pH.	93
18 Arsenic Losses ($\mu\text{g/m}^2$) from Unamended Sediments Whose Over- lying Water was Kept Anaerobic (Weeks 1-5) and Aerobic (Weeks 6-8).	95
19 Average Conductivity ($\mu\text{mhos/cm}$) During the Long-Term Leaching Tests.	98
20 Average Leachate pH During the Long-Term Leaching Tests.	100
21 Leaching of As(V), As(III), and Organic As as a Percentage of Total As Leached	114
22 Total Sulfide Concentration and pH of Sediments Following Anaerobic Incubation	119
23 Total As Concentrations in the Interstitial Water, Exchangeable, Easily Reducible, and Moderately Reducible Phases of Sediments Incubated Anaerobically for 45 Days.	120

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
24 Total Net Mass Release ($\mu\text{g/g}$) of As, As(V), As(III), and Organic As from Unamended Sediments During Six Months of Aerobic Leaching	123
25 Total Net Mass Release ($\mu\text{g/g}$) of As, As(V), As(III), and Organic As from As Amended Sediments During Six Months of Aerobic Leaching	124
26 Arsenic Distribution Coefficients (K) Following Six Months of Aerobic Leaching	126
27 Correlations Between the Distribution Coefficient (K) of Various As Species and Sediment Properties Following Six Months Leaching	127
28 Mean Concentrations of As in Ten Sediments Before and After Six Months of Aerobic Leaching	129
29 Mean Concentrations of Selected Chemical Parameters from Ten Sediments Before and After Six Months of Aerobic Leaching. . .	130
30 Total Sb Concentration in the Interstitial Water, Exchangeable, Easily Reducible, and Moderately Reducible Phases of Sediment Incubated Anaerobically for 45 Days.	133

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
31 Antimony Concentration ($\mu\text{g}/\ell$) in Short-Term Leachate and Value of the Distribution Coefficient (K)	136
32 Total Water Soluble Sb Concentrations ($\mu\text{g}/\ell$) from Amended and Unamended Sediments Leached with Water of Varied Initial Salinity	137
33 Cumulative Net Mass Release of Sb ($\mu\text{g}/\text{g}$) from Amended Black Rock Harbor Sediments Leached Under Anaerobic and Anaerobic/Aerobic Conditions	140
34 Antimony Net Mass Release ($\mu\text{g}/\text{g}$), Losses (%), and Distribution Coefficient (K) Following Six Months of Aerobic Leaching . . .	145
35 Mean Concentrations of Fe and Sb Among Ten Sediments Before and After Six Months of Aerobic Leaching	146

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Map showing location of sampling areas	39
2	Redox potential and pH control apparatus for incubating sedi- ment suspensions	41
3	Apparatus for incubating submerged sediments	50
4	Concentration of various As species in the interstitial water of anaerobically incubated sediments (Note scale difference between graphs)	61
5	Influence of oxidation status and pH on water soluble As(V) in Texas City sediment suspensions	68
6	Influence of oxidation status and pH on water soluble As (III) in Texas City sediment suspensions	70
7	Influence of oxidation status and pH on water soluble added organic As in Texas City sediment suspensions.	74
8	Linear regression equations describing disappearance of DSMA	76

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
9 Influence of oxidation status and pH on short-term release of extractable As from Menominee 3 sediment suspensions. . . .	90
10 Influence of oxidation status and pH on short-term release of extractable As from Indiana and Baltimore Harbor sediment suspensions.	91
11 Cumulative As release from unamended sediments under aerobic conditions (Note scale difference between graphs).	101
12 Cumulative As release from amended sediments under aerobic conditions (Note scale difference between graphs).	102
13 Cumulative As (V) release from amended sediments under aerobic conditions (Note scale difference between graphs).	104
14 Cumulative As (V) release from unamended sediments under aerobic conditions (Note scale difference between graphs). . .	105
15 Cumulative As (III) release from amended sediments under aerobic conditions (Note scale difference between graphs). . .	107
16 Cumulative As (III) release from unamended sediments under aerobic conditions (Note scale difference between graphs). . .	108

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
17 Cumulative organic As release from amended sediments under aerobic conditions (Note scale difference between graphs). . .	110
18 Cumulative organic As release from unamended sediments under aerobic conditions	111
19 Cumulative As release from Menominee sediments under aerobic conditions (Note scale difference between graphs).	113
20 Cumulative As release from Black Rock sediments under anaerobic/ aerobic and anaerobic conditions (Note scale difference between graphs).	116
21 Influence of oxidation status and pH on water soluble Sb concentrations in Texas City sediment suspensions.	134
22 Influence of Eh and pH on short-term releases of Sb from sediment suspensions	139
23 Cumulative releases of volatile Sb compounds from Sb amended sediments (Note scale difference between graphs)	142
24 Cumulative Sb releases from sediments under aerobic conditions (Note scale difference between graphs)	143

EXECUTIVE SUMMARY

The potential environmental impacts of arsenic (As) and antimony (Sb) contaminated sediments were studied with emphasis placed on short- and long-term leaching and sediment conditions that affect mobilization.

Under anaerobic conditions, arsenate [As(V)] was reduced to arsenite [As(III)] in a wide range of sediments. In anaerobic Texas City sediment slurries, 70% of added As(V) was recovered as water soluble As(III) following three weeks of incubation. Formation of organic As following addition of As(V) to anaerobic sediments was also demonstrated.

Short-term leaching was conducted with anaerobically incubated unamended and As-amended sediments using either distilled or saline water. In both amended and unamended sediment, As(III) was the predominant species released. Releases of As(III) were greatest when sediments were low in iron and high in interstitial water and exchangeable phase As(III). Releases of As(V), As(III), and organic As from sediments were found to be relatively insensitive to the salinity of the mixing water.

Aerobic leaching experiments of six months duration were conducted to determine what As species would be released, the duration of the releases, and the sediment factors affecting releases. Arsenic releases usually persisted throughout the leaching period; releases were higher from amended compared with unamended sediments. Generally, As(III) release predominated initially, followed by As(V) and organic As releases in the first three months. The final three months of leaching were characterized by predominant release of As(V). Conversely, leaching of Black Rock sediments under anaerobic conditions for three months resulted in almost

exclusive release of As(III). These results indicate that soluble As releases from sediments are undesirable during the first months of aerobic leaching or at any time during anaerobic conditions because of the high toxicity of As(III). Arsenic releases following six months of leaching were related to sediment iron (Fe) content and to sediment calcium carbonate (CaCO_3) equivalent concentration.

Long-term aerobic leaching caused significant changes in both sedimentary Fe and As phases. Arsenic concentrations in the moderately reducible phase of both amended and unamended sediments showed significant increases following leaching. This increase in As concentration was paralleled by a decrease in easily reducible Fe and an increase in moderately reducible Fe. This change in Fe distribution apparently resulted from formation of more crystalline Fe oxides during the six months of aerobic leaching. Arsenic is therefore not only lost from the system during aerobic leaching, but the As remaining is predominately concentrated in a more immobile sediment phase. This remaining sedimentary As should be highly resistant to further aerobic leaching.

Sediments containing native and added Sb were subjected to similar experimental incubation, extraction procedures, and short- and long-term leaching as in the As experiments. Speciation of Sb was not examined however, so that only total Sb concentrations are available.

Short-term releases of Sb were higher from amended than from unamended sediments. Antimony releases from Sb amended sediments were related to extractable Fe and CaCO_3 equivalent concentrations. Short-term releases of native Sb from freshwater sediments were enhanced by leaching with saline water. This trend would probably not hold true for saline

sediments; Corpus Christi, the only saline sediment tested, did not desorb additional Sb when leached with saline water.

Long-term (six months) releases of Sb were much higher from Sb amended sediments than from sediments containing no added Sb. In most sediments, the majority of Sb release occurred early in the leaching experience. Net mass release of Sb following six months of leaching was directly related to extractable Fe and CaCO_3 equivalent concentration, some of the same factors that affected As release. These results suggest that Sb release from contaminated sediment is more likely to occur during the first few months of aerobic leaching.

Seven out of ten Sb amended sediments released volatile Sb compounds during anaerobic incubation. Two of these sediments released additional Sb under aerobic conditions. This observation indicates that release of volatile Sb compounds from sediments subjected to recent inputs of Sb may be cause for concern.

The main conclusion to be drawn from this portion of the study is that Sb behavior in sediments is very similar to As behavior. Notable exceptions to this general similarity are the pronounced release of volatile Sb compounds from Sb amended sediments and the increased release of Sb from some freshwater sediments leached with saline water. The behavior of As and Sb was otherwise similar during short- and long-term leaching experiments. The properties affecting short- and long-term releases and fixation of these two elements by sediments were also similar.

TRANSFORMATION, FIXATION, AND MOBILIZATION OF ARSENIC
AND ANTIMONY IN CONTAMINATED SEDIMENTS

INTRODUCTION

Arsenic (As) and antimony (Sb) are naturally occurring elements and are found in all soils and sediments. Some natural sediment concentrations have been increased, however, by the use of As and Sb compounds in a wide range of agricultural and industrial applications (Ferguson and Gavis, 1972; Crecelius et al., 1975; Grimanis et al., 1977; Winchester and Nifong, 1970). This contamination complicates evaluation of potential adverse environmental impacts associated with dredging and disposal of As and Sb laden sediments. Little is known concerning As mobility and toxicity in contaminated soils and sediments, and there is an almost complete lack of information on Sb.

Sensitive analytical methods capable of differentiating between the various species of As (As(V), As(III), methylated arsenic compounds) have only recently been developed. Studies conducted prior to these developments are of limited value since the soils and sediments used were only slightly contaminated with As and the various forms of As were not determined. The forms of As in soils and sediments are important since toxicity and environmental behavior are form-dependent. The most toxic form of As to aquatic and mammalian species is arsenite (As(III)). Arsenate (As(V)) is less toxic than As(III) and methylated arsenic compounds are even less toxic (Peoples, 1975). Recent studies indicate that As(V) is more readily adsorbed by soils and sediments than is As(III) in the acidic to mildly alkaline pH range (Holm et al., 1979;

Frost and Griffin, 1977; Gupta and Chen, 1978). Some forms of As may also become more soluble as the pH increases (Johnston, 1978).

Some dredged sediments contain substantial (100 to 300 $\mu\text{g/g}$) amounts of total As. The potential mobility and forms of As in these sediments are largely unknown. However, some sediments containing low amounts of total As (12 $\mu\text{g/g}$) can simultaneously exhibit high concentrations of soluble As (0.15 mg/l) in their interstitial waters (Brannon et al., 1976). Hess and Blanchar (1977) have observed up to 30 mg/l As in soil solutions of anaerobic, As contaminated soils. A high proportion of mobile As may be As(III) since Johnston (1978) has shown that under anaerobic conditions As(V) can be reduced to As(III) in sediments.

While the useful information available on As is limited, even less is known about Sb. To evaluate the potential impact of sediment As and Sb, the environmental conditions which favor mobilization or immobilization of As and Sb must be determined, the factors which control leaching of As and Sb from sediments should be examined, and the environmental conditions and sediment characteristics which control the volatilization of As and Sb compounds should be investigated.

The objectives of this study are:

- a. Determine the relationship between environmental conditions and arsenic transformations.
- b. Evaluate the environmental conditions which influence the mobilization of As and Sb from sediments over the short and long term.
- c. Identify the processes responsible for fixation of As and Sb in anaerobic sediments.
- d. Determine the effect of anaerobic and aerobic conditions on evolution of volatile As and Sb compounds from sediments.

LITERATURE REVIEW

Arsenic Speciation and Toxicity

The majority of environmental As studies have been conducted using analyses of total As. Arsenic has at least five valence states, -3, 0, +1, +3, and +5. Arsine (AsH_3) and methylarsines [CH_3AsH_2 and $(\text{CH}_3)_2\text{AsH}$] are characteristic of As compounds in the -3 valence state. Arsenic metal is in the 0 valence state, while compounds such as arsenous acid (H_3AsO_3) and methylarsonic acid ($\text{H}_2\text{AsCH}_3\text{O}_3$) are representative of As compounds in the +3 valence state. Arsenic acid (H_3AsO_4) is an As compound in the +5 valence state and dimethylarsinic acid [$(\text{CH}_3)_2\text{AsO}_2\text{H}$] is an As compound in the +1 valence state (Ehrlich, 1981). The form of As in the environment affects its toxicity. Arsenite [As(III)] is generally regarded as about 10 times more toxic to humans than arsenate [As(V)]. By contrast, sodium methylarsonate and dimethylarsinic acid are roughly 35 times less toxic than arsenite to rats (Peoples, 1975). Reduction of arsenate to arsenite in anaerobic sediments would therefore result in an increase in As toxicity. Formation of methylated arsenic compounds from inorganic As results in decreased toxicity.

Nomenclature of Arsenic Compounds

Arsenic compounds with the same structure are often referred to by different names in the literature. Among inorganic As forms, arsenous

acid is also referred to as arsenious acid. In its anion form, this acid is called arsenite. Arsenic acid is also referred to as meta-arsenic acid; its anion form is called arsenate. There is even more diversity of names among organic As compounds. Methylarsonic acid is also called methanearsonic acid or methylarsinic acid. Dimethylarsinic acid is also called dimethylarsonic acid or cacodylic acid.

Sources and Concentration of As

Natural

Arsenic is a naturally occurring element. The average As concentration in the lithosphere is estimated to be 2 ppm (Onishi and Sandell, 1955a). Boyle and Jonasson (1973) reported that the terrestrial abundance of As is on the order of 3 ppm.

Arsenic in rocks is usually associated with sulfur, although other constituents can also bind this element. Shales containing organic matter, sulfides, and iron oxides tend to be high in As (Onishi and Sandell, 1955a). Pyrite, which may contain as much as 6000 ppm As, and other heavy metal sulfides are the principal carriers of As in rocks and in many types of mineral deposits (Boyle and Jonasson, 1973).

At the present time, the contribution of As to the environment from weathering of continental rocks is large compared to the contribution of vulcanism, although vulcanism must have contributed much of the sedimentary As over geological time (Onishi and Sandell, 1955a). Ferguson and Gavis (1972) calculated that 45×10^3 tons yr^{-1} of As is weathered and transported. Such As exists mainly in the dissolved form as soluble arsenates (Boyle and Jonasson 1973). Although arsenite is present in

two minerals, orpiment, As_2S_3 , and arsenolite, As_2O_3 , it is not common in nature (Boyle and Jonasson, 1973), presumably due to oxidation to arsenate.

Arsenic concentrations in seawater have been shown to range from 1.12 to 1.71 $\mu\text{g As/l}$ (Cohda, 1972). Arsenic concentrations in fresh waters may be lower than 1 $\mu\text{g As/l}$ (Nagatsuka and Yagaki, 1976) or as high as 260 $\mu\text{g As/l}$ (Wilson and Hawkins, 1978), depending on the geologic setting. High As concentrations in waters not subject to man-made contamination are often a consequence of As enrichment in the rocks of the area (Bowen, 1966; Wilson and Hawkins, 1978).

Anthropogenic

Man's activities have considerably increased the amounts of As introduced into the environment. In this country man has been responsible for introducing approximately three times more As into the environment than the contribution due to weathering (Ferguson and Gavis, 1972). Arsenic reaches the aquatic environment by way of pesticides (Hendricks, 1945; Ferguson and Gavis, 1972; National Academy of Science (NAS) 1977), fertilizers (Kanamori and Sugawara, 1965; Grimanis et al., 1977), detergents (Angino et al., 1970), combustion of coal (Winchester and Nifong, 1970; Lindberg et al., 1975; Ferguson and Gavis, 1972), smelter operations (Winchester and Nifong, 1970; Ragaini et al., 1977; Crecelius et al., 1975; Ferguson and Gavis, 1972), and sewage (Grimanis et al., 1977). Inputs of As from these sources vary in magnitude, but their impact is generally confined to local areas (NAS, 1977; Walsh and Keeney, 1975; Strohal et al., 1975) of high industrial or agricultural activity. This leads to localization of As contamination.

Since deposits of native arsenic are associated with ores of many heavy metals, mining and smelting operations will increase As concentrations in areas near such activities. Wilson and Hawkins (1978) found that mining operations may increase the As content of stream waters by exposing As-containing rocks to surface waters and by increasing the load of As rich sediments in the stream.

Smelting of metal ores is responsible for large releases of As into the environment. Ragaini et al. (1977) reported that lead smelting operations in the Kellogg Valley of Idaho had resulted in As concentrations ranging from 18-260 $\mu\text{g/g}$ in the soils of the Kellogg Valley. Crecelius et al. (1975) found that the major anthropogenic source of As to Puget Sound is a large copper smelter located near Tacoma. The smelter releases As as: (1) stack dust into the air, 2×10^5 kg/yr of As_2O_3 ; (2) dissolved species in effluents, $2 - 7 \times 10^4$ kg As/yr; and (3) slag particles, 1.5×10^6 kg As/yr. Values are given here only to illustrate the impact that smelter operations can have on localized As concentrations.

Wedepohl (1969) reported that the As content of a large number of coal groups ranged from 3-45 $\mu\text{g/g}$. Ferguson and Gavis (1972) calculated that 2.5 g of As would be released to the atmosphere for every ton of coal consumed. Lindberget al. (1975) reported that As was concentrated in fly ash compared to slag at a coal-fired power plant and was more concentrated in the ash discharged through the stack than in that collected by the precipitator.

Agriculture has been the largest user of refined As, accounting for about 80 percent of the demand (Walsh and Keeney, 1975; NAS, 1977). Most of this As is formulated into pesticides (Ferguson and Gavis,

1972), the use of which has resulted in As concentrations of up to 550 $\mu\text{g/g}$ in treated soils (Walsh and Keeney, 1975). Rock phosphate used to make fertilizer may occasionally contain as much as 2,000 $\mu\text{g/g}$ As (Fleischer, 1973).

Household detergents of high-phosphate type contain from 1-73 ppm As (Angino et al., 1970). Dilution during use, however, reduces the impact of this As in the environment (Sollins, 1970).

Sewage treatment plant outfalls are one way that As enters the environment. Papakostides et al. (1975) reported that discharge from untreated sewage in the upper Saronikos Gulf in Greece has resulted in As concentrations 8-200 times greater than that in surrounding, uncontaminated sediments. Grimanis et al. (1977) reported sediment As concentrations of 1000 $\mu\text{g/g}$ just outside Piraeus Harbor in Greece. The highest concentrations of As was near the outfall of a fertilizer plant. Anderson et al. (1978) has reported the contamination of the Menominee River in Wisconsin by As leaching from a mining slag pile.

It is apparent from the preceding review that man's activities can result in contamination of localized areas with As. The impact of this contamination, although localized, can be widespread because of the many possible sources.

Physicochemical Transformations

Arsenate Reduction in Soils and Sediments

It has often been noted that soluble arsenic concentrations are higher under anaerobic conditions than under aerobic conditions. Epps and Sturgis (1939) reported that addition of some arsenic compounds

containing either As(V) or As(III) to flooded soils increased the soluble As content of the soils, presumably due to reduction. Hess and Blanchar (1977) reported that anaerobic incubation of two Missouri orchard soils resulted in As solution concentrations of approximately 30 mg/l, or nearly 40 percent dissolution of the total As in the soil. Clement and Faust (1981) reported that anaerobic conditions in quiescent mud/water reservoirs led to levels of water soluble As, principally as As(III), about 10 times higher than concentrations reached under aerobic conditions. Kanamori (1965) found As concentrations of 10.4, 18.0, and 10.0 $\mu\text{g/l}$ in the anaerobic bottom waters of three lakes compared to 0.70, 0.38, and 1.9 $\mu\text{g/l}$, respectively, in the aerobic surface waters of these same lakes.

It has been suggested that reduction of iron from Fe^{+3} to Fe^{+2} with subsequent dissolution of ferrous arsenate (Kanamori, 1965; Deuel and Swoboda, 1972) can be responsible for the increase in soluble As under anaerobic conditions. It appears, however, that the reasons for increased water soluble As concentrations under anaerobic conditions are more complex than a simple linkage to iron reduction. Johnston (1978) reported large accumulations of arsenite in anaerobic soils and sediments that did not coincide with the dissolution of ferric hydroxides. Theoretical considerations also indicate that As(V) should be reduced to As(III) under anaerobic conditions. Turner (1949) calculated that the reductions of arsenate to arsenite should occur at 77 to 167 mV at a pH of 7.0. Ferguson and Gavis (1972) suggested that arsenate could be used as an electron acceptor in heterotrophic metabolism in the absence of O_2 and NO_3 , such a reaction being energetically favored compared to sulfate reduction. Microbial reduction of As(V) to As(III) should increase As

concentrations in sediment interstitial waters since arsenite should be 4 to 10 times more soluble in some sediments (Albert and Arndt, 1931; Brechley, 1914; Keaton and Kardos, 1940).

Anaerobic reduction of As(V) to As(III) does occur. McBride and Wolfe (1971) demonstrated that arsenate could be reduced to arsenite, then transformed to methylated arsines by methanobacterium under anaerobic conditions. Andreae (1979) reported that up to 20 percent of the total As in anaerobic sediment interstitial water was present as As(III); the remainder being predominately As(V). Myers et al. (1973) observed reduction of arsenate to arsenite in anaerobic activated sludge with conversion of 85 percent of 5 ppm of added arsenate to arsenite occurring in 12 hours. Brunskill et al. (1980) reported that arsenate was reduced to arsenite at the rate of one micromole per liter per day under anaerobic conditions in As contaminated pond water. Takamatsu et al. (1982) reported that As(III) concentrations in flooded paddy soils increased as redox potential decreased to approximately 0 mV.

Arsenate reduction can also apparently occur under aerobic conditions. Heimbrook (1974) has reported isolation of organisms capable of arsenate reduction during aerobic incubations. Johnson (1972) reported arsenate reduction when bacterial populations entered the log growth phase (at about 8 hours) in aerobic Sargasso Sea medium at 20-22°C. Shariatpanahi and Anderson (1981) reported that bacteria (a Pseudomonas sp. and a Corynebacterium sp.) acclimated to growth in arsenate had produced appreciable amounts of arsenite and methylated arsines after exposure to arsenate for 6 hours. Myers et al. (1973) found that aerobic cultures of Pseudomonas fluorescens reduce arsenate to arsenite.

These results indicate that arsenate reduction in differing media can occur in both the presence and absence of oxygen. Highly reducing conditions are not required for arsenate reduction as is the case for sulfate reduction.

Arsenate Reduction by Phytoplankton

In flooded soils and sediments, it appears that arsenate reduction is almost exclusively microbial. Bacterial reduction of arsenate has also been demonstrated to occur in seawater (Johnson, 1972; Johnson and Pilson, 1975). In water, however, phytoplankton also play an important role in determining the species of As in the water. The biogeochemical cycle of As in the surface ocean involves uptake of arsenate by phytoplankton or other biological entities, conversion of arsenate to a number of as yet unidentified organic compounds, and release of arsenite and methylated As species into the seawater (Andreae and Klumpp, 1979; Howard et al., 1982).

The reduction of arsenate by phytoplankton to form arsenite and organo-arsenicals is widely believed to be a detoxifying mechanism (Bottino et al., 1978; Andreae and Klumpp, 1979; Pilson, 1974). Arsenate reduction produces organo-arsenicals which reduce the toxicity of arsenic to algae and other organisms since organo-arsenicals do not appear to affect marine invertebrates (Penrose et al., 1977). Arsenate can act as an inhibitor of phosphate uptake (Planas and Healey, 1978) as well as an uncoupler of mitochondrial oxidative phosphorylation (Blum, 1966; Johnson and Burke, 1978; Planas and Healey, 1978).

Rapid As speciation changes occurring in media surrounding phytoplankton indicate that algal cells are able to reduce, methylate, and

release As to the water column, primarily as arsenite and organo-arsenic compounds (Sanders and Windom, 1980). Andreae and Klumpp (1979) reported that bacteria-free algae grown in seawater with no added As converted arsenate in the original seawater to methylarsonate and dimethylarsinate. Arsenate reduction to arsenite has also been observed in Chlorella, a freshwater green algae (Blasco et al., 1971). Johnson and Burke (1978) found in phytoplankton culture studies that as phosphate is depleted, arsenate reduction occurs at an increasing rate. Approximately 15-20 percent of the total As in productive marine systems is reduced and methylated due to uptake and release by phytoplankton (Sanders, 1979; Sanders and Windom, 1980).

Oxidation of Arsenite

Oxidation of arsenite to arsenate can be both chemically and biologically catalyzed (Johnson and Burke, 1978; Johnson and Pilson, 1975; Turner, 1949). At least 15 strains of heterotrophic bacteria have been isolated which can bring about the oxidation of arsenite to arsenate (Turner, 1949; Turner and Legge, 1954; Osborne and Ehrlich, 1976). Johnson and Pilson (1975) have observed the oxidation of arsenite to arsenate in seawater even under sterile conditions. They found that the arsenite oxidation rate depended on temperature, pH, salinity, and initial arsenite concentration. Increasing the temperature, salinity, or initial arsenite concentration of a solution will increase the arsenite oxidation rate. Differing concentrations of dissolved oxygen do not influence the arsenite oxidation rate (Johnson and Pilson, 1975). In seawater, the natural rate of chemical oxidation of arsenite is about $0.023 \mu\text{moles of arsenite } \ell^{-1} \text{ yr}^{-1}$.

Johnson and Burke (1978), Sanders and Windom (1980), and Scudlark and Johnson (1982) have shown that the actual rate of arsenite oxidation in seawater is much faster than the predicted chemical oxidation. Scudlark and Johnson (1982) reported that abiotic oxidation proceeds at a slow, constant rate. The presence of certain aquatic bacteria, however, rapidly increases arsenite oxidation, resulting in an exponential decrease in As(III) concentrations with time. This indicates that arsenite oxidation in seawater is a combination of chemical and biological oxidation processes.

In sediments, arsenite oxidation appears to be primarily chemically catalyzed. Oscarson et al. (1980) reported that sediments from five lakes in Canada oxidize As(III) to As(V). The oxidation was found to be an abiotic process with microorganisms playing a relatively minor role. Oscarson et al. (1981a) reported that removal of Mn from the sediments greatly decreased the oxidation of As(III). They also found that synthetic Mn(IV) oxide was a very effective oxidant for As(III), indicating that Mn in the sediment was probably the primary electron acceptor in the oxidation of As(III). Conversion of As(III) to As(V) by naturally occurring carbonate and silicate minerals common in sediments was not noted by Oscarson et al. (1981a). Oscarson et al. (1981b) found that Fe(III) oxide does not convert As(III) to As(V) within 72 hours. Sedimentary Mn(IV) oxides may therefore serve to decrease the concentration of As(III) in sediment interstitial waters or in natural waters rich in particulate matter containing Mn(IV) oxides.

Arsenic Methylation in Sediments

Methylated arsenic oxyacids can be produced in water by both bacteria and phytoplankton (McBride and Wolfe, 1971; Andreae, 1979; Johnston, 1978; Braman, 1975). It is unclear at present, however, whether methylated As oxyacids are formed directly from arsenite in sediments or as oxidation products of methylated arsines. Oscarson et al. (1981b) have postulated that since methylation of inorganic arsenicals is essentially a reduction reaction, the abiotic oxidation of As(III) to As(V) by sediments would tend to counteract the methylation process. Wood (1974) and Ridley et al. (1977) felt that methylated As oxyacids could be formed during oxidation of methylated arsines which can be produced under both aerobic and anaerobic conditions (Cox and Alexander 1973; McBride and Wolfe, 1971). Wood (1974) postulated that the interstitial waters of anoxic sediments serve as sources of biomethylated arsines which are oxidized to methylated oxyacids following diffusion into aerobic environments. This may, however, not be the means by which methylated As oxyacids are formed. Andreae (1979) reported that no methylated As compounds were found in the interstitial waters of oxic and anoxic sediments, although arsenite was present. Johnston (1978) has reported accumulation of methylated As oxyacids during anaerobic sediment incubations, indicating that methylated As oxyacids can be formed from arsenite without methylated arsine precursors. Takamatsu et al. (1982) found that as redox potential fell in a flooded soil, arsenate was reduced to arsenite and the concentration of dimethylarsinic acid increased and that of methylarsonic acid decreased. Braman (1975) has also reported that when arsenite and nutrient media were

added to pond water samples under aerobic conditions, methylarsonic acid appeared first, followed by methylated arsines.

As can be seen in the preceding paragraph, there is reason to believe that methylated As oxyacids can form in sediments by direct methylation of arsenite or by oxidation of methylated arsines. Both mechanisms may be operative in sediments but results pinpointing the predominant pathway in sediment are lacking.

Demethylation Reactions

Degradation of methylated As oxacids has been extensively studied, especially in aerobic soils. Arsenate has been shown to be the degradation product of methanearsonic acid (Von Endt et al., 1968) and of dimethylarsinic acid (Schuth et al., 1974). Tracer studies using ^{14}C labeled methylated arsenic oxyacids have shown that after 30 days of aerobic incubation, 1.7 percent to 16 percent of the methanearsonic acid added to a soil will have degraded to form $^{14}\text{CO}_2$ and arsenate (Dickens and Hiltbold, 1967; Von Endt et al., 1968). Degradation of from 5 to 41 percent of added dimethylarsinic acid has been reported in aerobic soils (Schuth et al., 1974; Woolson, 1976). Holm et al. (1980) have reported that methylarsinic and dimethylarsinic acids are subject to demethylation in anaerobic sediments. These demethylation reactions are apparently carried out by microorganisms, as no changes were noted in sterilized control sediments. There was apparently no interconversion of methylarsinic acid to dimethylarsinic acid or the reverse reaction in spiked samples (Holm et al., 1980). Shariatpanahi et al. (1981) found that four species of bacteria, Nocardia, Flavobacterium, Achromobacter, and Pseudomonas, demethylated monosodium methanearsonate under aerobic

conditions to produce arsenate methylarsines. Enterobacter and Aeromonas produced only methylarsines and Alcalgens produced only arsenate.

Evolution of labeled CO_2 from aerobic soils treated with methylated As oxyacids is closely related to the amounts of soil organic matter initially present (Dickens and Hiltbold, 1967). Oxidation of methylated As oxyacids is thought to occur coincidentally with metabolism of soil organic matter with little specific response to the arsenicals on the part of the microbial population (Dickens and Hiltbold 1967; Hiltbold, 1975).

Hiltbold (1975) felt that a first-order function appeared to be the most realistic representation of methylarsonic acid metabolism in soils. He cited the observations of Woolson et al. (1973) and Von Endt et al. (1968) of equal percentage losses among widely differing rates of application as support for the first-order function. Holm et al. (1980) presented a model describing the interaction of adsorption and biological demethylation of methylated As species. The model was tested against the results of As demethylation experiments in sediments assuming first-order kinetics and Langmuir adsorption, and agreement between theory and experiment was found. Shariatpanahi et al. (1981) reported that microbial biotransformation of monosodium methanearsonate was biphasic and followed a first-order composite exponential equation. Rate of disappearance constants reported by Shariatpanahi et al. (1981) appeared to be largely independent of bacterial species, presumably due to similar biotransformation enzymes. It therefore appears that first-order kinetics are a viable tool for representing demethylation of methylated As compounds in soils and sediments.

Other Organic Arsenicals

Organic arsenicals other than methylarsinic and dimethylarsinic acids exist in the environment, most commonly as metabolites in aquatic organisms. Wrench et al. (1979) reported that arsenoanalogues of substances such as phosphorylethanolamine and phosphorylcholine were possibly present in shrimp and phytoplankton. Woolson et al. (1976) reported that several unidentified As compounds were separated from extracts of algae, daphnids, Gambusia, and crayfish treated with ^{74}As . Edmonds and Francesconi (1981) have isolated arsenobetaine from school whiting (Sillago bassensis) caught off Western Australia.

Organic arsenicals other than methylarsinic and dimethylarsinic acid have also been found in sediments and flooded soils. Johnston (1978) reported detection of an unidentified organic arsenical in the interstitial water of Barataria Bay sediments. Takamatsu et al. (1982) identified an arsenic compound with the formula $\text{C}_5\text{H}_7\text{AsO}_3\text{H}_2$ in a flooded soil. The arsenic compound contained aliphatic hydrocarbon groups whose carbon chains were longer than that of methyl groups. These results demonstrate that a wide variety of organic arsenicals occur in the environment, especially in aquatic organisms. In sediments, the diversity of organic arsenicals appears to be much more limited.

Generation of Volatile As Compounds

Production of volatile As compounds in soils and sediments is of interest due to the toxicity of arsine and alkyl arsines (NAS, 1977). Decreased As concentrations in a flooded soil have been attributed to production of volatile As compounds (Reed and Sturgis, 1936). Volatile arsenic compounds have also been detected when a stream of air was

passed through water overlying flooded soils (Epps and Sturgis, 1939). Woolson and Isensee (1981) reported that when high concentrations of sodium arsenite or methylated arsenic compounds are added to soils, total losses of As from the soil average 14 to 15 percent of that applied each year, regardless of the source.

Theoretical considerations imply that generation of arsine is unlikely in soils, sediments, or other biological systems since arsine is stable only at redox potentials below the stability limit of water (Bohn, 1976). This is supported by experimental evidence that arsine is not present in the atmosphere (Johnson and Braman, 1975), anaerobic bottom waters (Andreae, 1979), anaerobic activated sewage sludge (Myers et al., 1973), or anaerobic soils (Deuel and Swoboda, 1972). Clement and Faust (1981) found that anaerobic incubation of reservoir sediment led to accumulation of As(III), but further reduction to the various arsines was not found. Johnson and Braman (1975) found that all of the inorganic As fraction was present as particulate matter. Myers et al. (1973) was unable to detect the presence of arsine even though 60 percent of the arsenite was lost from an anaerobic activated sludge within 24 hours. Cheng and Focht (1979) found, however, that addition of arsenate, arsenite, monomethylarsonate, and dimethylarsinate to three flooded soils resulted in arsine production in all three soils from all substrates. Cheng and Focht (1979) also reported that resting cell suspension of Pseudomonas and Alcaligenes produced arsine as the sole product when incubated anaerobically in the presence of arsenate and arsenite. Bacterial transformation of arsenite to arsines and methylated arsines has also been shown by other workers (McBride and Edwards, 1977; Ridley et al., 1977) to occur in sediments. It is evident that

arsine can be produced in some sediments and bacterial cultures under anaerobic conditions despite the predicted unfavorable thermodynamics of the process.

Large amounts of arsenic (up to 60 percent) can be lost from both aerobic and anaerobic systems as volatile methylated arsines (Challenger, 1945; McBride and Wolfe, 1971; Woolson and Kearney, 1973; Braman, 1975). Johnson and Braman (1975) showed that, on average, approximately 20 percent of the total As in air samples exists as alkyl arsines. Alkyl arsines are unlikely to be produced in the water column. Sanders and Windom (1980) reported that no volatile As species were released from phytoplankton cultures even though a large amount of arsenate was reduced by the algal cultures. Production of alkyl arsines by soils and sediments has been well documented (Cheng and Focht, 1979; Woolson and Kearney, 1973; McBride and Edwards, 1977; Akins and Lewis, 1976).

Larger amounts of alkyl arsines will apparently be generated under anaerobic compared to aerobic conditions. Akins and Lewis (1976) reported that the greatest loss of ^{74}As activity (introduced as disodium methanearsonate (DSMA) - ^{74}As) occurred in a soil that contained 11 percent organic matter and was maintained under reduced conditions. All treatments amended with organic matter showed a marked increase in ^{74}As evolution over the corresponding treatment which had received no organic matter (Akins and Lewis 1976). Cell extracts and whole cells of Methanobacterium strain M.O.H. reduce and methylate arsenate to dimethylarsine under anaerobic conditions (McBride and Wolfe, 1971). McBride and Edwards (1977) reported that whole cells of methanogenic bacteria in varied anaerobic environments (rumen fluid, sewage sludge) produced unidentified, volatile As compounds thought to be alkylarsines.

Woolson and Kearney (1973) found that more arsenic was lost from dimethylarsinate-treated soils under flooded than under nonflooded conditions.

Appreciable amounts of alkyl arsines may also be lost from soils and sediments under aerobic conditions. Woolson and Kearney (1973), although finding that more As was lost from dimethylarsinate-treated soils under anaerobic conditions, also reported appreciable As losses under aerobic conditions. Under aerobic conditions about 35 percent of the cacodylic acid was converted to a volatile organoarsenical and lost from the system while 41 percent was metabolized to $^{14}\text{CO}_2$ and arsenate within 24 weeks after application (Woolson and Kearney, 1973).

The arsenic compounds from which alkyl arsines are produced appear to be cause for some disagreement. Cox (1974) reported that treatment of soils with dimethylarsinic acid resulted in generation of dimethylarsine and trimethylarsine. Similar results were obtained with sodium arsenite, methylarsonic acid and phenylarsonic acid (Cox, 1974). Cheng and Focht (1979) reported, however, that methylarsine and dimethylarsine were only produced in flooded soils following treatment with methylarsonate and dimethylarsinate, respectively. They found no evidence for the methylation of any arsenical in soil or culture and concluded that reduction to arsine, not methylation to trimethylarsine, was the primary mechanism for loss of gaseous arsenicals from soil (Cheng and Focht, 1979). Cox and Alexander (1973), however, reported isolation from soil and sewage of three different fungi capable of producing trimethylarsine when growing in the presence of methylarsonic acid. Cox (1975) investigated the ability of the fungi to produce trimethylarsine under varying pH and arsenic compound additions. He concluded that the

reduction process appears to require that arsenic acids be present in the undissociated form before reduction will proceed.

These results indicate that the potential exists for evolution of methylated arsines from both aerobic and anaerobic environments; however, some disagreement exists on the As substrate required, and the release of methylated arsines from anaerobic sediments remains in doubt. Wong et al. (1977) has shown that addition of arsenate or arsenite to sediment-water mixtures containing nutrient broth, glucose, and yeast extract results in release of methylated arsines. However, oxidation status of the mixture could not be determined from the available data. Andreae (1979) reported that B. C. McBride (in a personal communication) had found significant yields of methylated arsines from all anaerobic systems except marine sediments. Methylated arsines produced in such sediments may be irreversibly bound soon after formation (Andreae, 1979).

Arsenic Adsorption

Arsenite

The dissociation status of the various As compounds will determine if the compounds are present as neutral molecules or as anions subject to adsorption. This is well illustrated by considering the case of arsenious acid $[\text{As}(\text{OH})_3]$. Successive pK_a values for arsenious acid have been reported as 9.23, 12.13, and 13.40 (NAS, 1977). The first dissociation constant indicates that arsenious acid is a very weak acid. Therefore, the fraction of the total As(III) present in solution as H_2AsO_3^- will be small in acidic or weakly basic solutions but will

increase as the pH approaches 9.23 (Frost and Griffin, 1977). The existence of the As^{+3} cation in aqueous solution does not have any experimental support (NAS, 1977). This change in status from an uncharged molecule to an anion as the pH becomes more basic is reflected in the adsorption behavior of arsenite in the environment even though existence of an ionic species is not a prerequisite for adsorption.

Everest and Popiel (1957) reported that the maximum adsorption of arsenite by an anion exchange resin was at pH 9.2. Gupta and Chen (1978) found that variations in arsenite adsorption on activated alumina and bauxite over the pH range of 4 to 9 were slight. Frost and Griffin (1977) showed an increase in adsorption of As^{+3} by clay minerals as pH increases in the range from 3 to 9. Pierce and Moore (1980, 1982) reported that arsenite adsorption by amorphous iron hydroxides went through a maximum at approximately pH 7. As(V) is also more strongly adsorbed onto soil and sediment components than is As(III) in the acidic to mildly alkaline pH range (Oscarson et al., 1980; Holm et al., 1979).

Arsenate

Arsenic acid (H_3AsO_4) is a fairly strong acid with pKa values reported as 3.6, 7.3, and 12.5 (Pierce and Moore, 1982). Arsenate therefore exists as a negatively charged species in all pH's of environmental interest. This charge status is reflected by the adsorption behavior of arsenate. Frost and Griffin (1977) reported that arsenate adsorption by kaolinite and montmorillonite was highest at pH 5, roughly corresponding to the highest percentage of arsenate in the H_2AsO_4^- form. The shape of the arsenate adsorption-pH curves suggested to Frost and Griffin (1977) that the amount of arsenate adsorption is dependent upon

the concentration of H_2AsO_4^- ions in solution. Gupta and Chen (1978) reported that adsorption of arsenate by activated alumina or bauxite was relatively constant in the pH range of 3 to 7, then decreased above pH 7. Galba (1972a) reported that arsenate adsorption by five soils peaked in the pH range 3.5 to 5.3, then steadily decreased as pH increased. Anderson et al. (1976) found that arsenate adsorption by amorphous aluminum hydroxide is independent of pH at low pH, but began to decrease in the pH range of 5 to 7 as pH increased. Arsenate adsorption by the aluminum hydroxide was dependent on pH_{IEP} (pH of the isoelectric point) and T_{IEP} (adsorption at the isoelectric point (Anderson et al. 1976)). Pierce and Moore (1982) reported that at concentrations normally found in natural waters, a pH of 4.0 was optimum for arsenate adsorption by amorphous iron hydroxides. In general, arsenate adsorption by sediments and soils will be highest in acidic media.

Methylated Arsenic Acids

Methylarsonic acid is dibasic with pKa values of 3.61 and 8.24 at 18°C (Ferguson and Gavis, 1972). At pH 5.93 essentially all of the methylarsonic acid exists as the univalent anion. Dimethylarsinic acid is monobasic with a pKa value of 6.19 at 25°C (Ferguson and Gavis, 1972). The proportions of univalent anion form increases from near 0 at pH 4 to essentially 100 percent at pH 8.5. It can be seen from these data that the methylated arsenic acids will exist as anions at the pH's (5-8) normally encountered in the environment, suggesting that they will be strongly adsorbed. This appears to be the case, because the magnitude of adsorption on 16 soils was found to increase in the order dimethylarsinic acid < arsenate $\approx$ methylarsonic acid in the pH range of

4.8 to 7.6 (Ferguson and Gavis, 1972). Anderson et al. (1978) has also reported that methylarsonic acid is adsorbed more strongly than dimethylarsinic acid.

Arsenic Fixation by Soils and Sediments

The strong adsorption of all ionic As species by iron and aluminum oxides and hydroxides (Ferguson and Anderson, 1974; Wiklander and Alvelid, 1951; Gupta and Chen, 1978; Pierce and Moore, 1980, 1982) indicates that As may be associated with these components in soils and sediments. This has indeed been shown to be the case. In aerobic soil systems, iron and aluminum hydroxides have been demonstrated to be the major sink for added As (Johnson and Hiltbold, 1969; Woolson et al., 1971; Jacobs et al., 1970; Fordham and Norrish, 1974). Similar findings have been reported for As in relatively noncontaminated anaerobic sediments (Creclius et al., 1975; Brannon et al., 1976).

Hydrous iron and aluminum oxides adsorb As because As anions are strongly attracted by the positively charged Fe and Al compounds (Boyle and Jonasson, 1973; Shnyukov, 1963). Because manganese oxides generally have a negative charge at the pH's (5-8) normally encountered in the aquatic environment (Healy et al., 1966; Oscarson et al., 1980; Parks, 1967), arsenic is not associated with manganese oxides unless they are ferriferous (Boyle and Jonasson 1973). Livesey and Huang (1981) have shown that As retention by four soils from Saskatchewan, Canada, at As concentrations of up to 2.15 ppm does not proceed through the precipitation of sparingly soluble arsenate compounds, but through adsorption mechanisms. There is strong evidence that As(III) and As(V) are

adsorbed as such with no change of oxidation state (Oscarson et al. 1981b).

Selective extraction techniques corrected for As readsorption have suggested that most As was adsorbed by amorphous Fe and Al components in a number of soils (Jacobs et al., 1970). Fordham and Norrish (1974) showed that goethite was the component principally responsible for arsenate uptake by a Kent sand. The native phosphorus retained by the soil was associated with the same goethite particles responsible for arsenate retention. Jacobs et al. (1970) reported that the amount of As adsorbed by soils was in the same order as the amount of Fe_2O_3 and Al_2O_3 extracted by citrate-dithionite-bicarbonate. Ferguson and Anderson (1974) have suggested that occlusion of As by iron (Fe) and aluminum (Al) hydroxides may be a likely mechanism of As removal from solution. The ability of soils to fix arsenate is proportional to the soils' Fe content (Woolson et al. 1971; Hurd-Karrer, 1939; Misra and Tiwari, 1963a, b; Vandecaveye, 1943).

In sediments, Fe has also been implicated in As fixation. Crecelius et al. (1975) found that 66 percent of the total As in Puget Sound sediments was oxalate extractable. Oxalate extraction removes only amorphous Fe and Al oxides (Jacobs et al., 1970), and has been shown to quantitatively remove all As added to soils (Jacobs et al., 1970). Brannon et al. (1976) reported that citrate-dithionite extractable As (As associated with Fe oxides) accounted for from 59 to 97 percent of the total As in sediments from Mobile Bay, Ala.; Bridgeport, Conn.; and Ashtabula, Ohio. Neal et al. (1979) reported that authigenic As in North Atlantic deep-sea sediments is associated with authigenic

Fe, suggesting that As is scavenged from seawater by a sedimentary Fe phase.

Aluminum oxides are less effective than Fe in fixing arsenate (Vandecaveye 1943; Woolson et al. 1971), but Al nevertheless forms relatively insoluble arsenates which can also fix As (Woolson et al., 1971). Wiklander and Fredriksson (1946) showed that Al oxide binds As, but not to the same degree as Fe oxide. Iron compounds have also been reported to fix greater amounts of As than Al compounds. Akins and Lewis (1976) reported that the Fe-As fraction predominated in a large number of surface soils with a history of inorganic As application. The Fe-As fraction accounted for an average of nearly 44 percent of the soil As, followed in abundance by Al-As (27 percent), Ca-As (16 percent), water soluble As (6 percent), and nonextractable As (7 percent).

Woolson et al. (1971) reported that most of the soil As was found as Fe-As (0.1 $\underline{N}$ NaOH extractable) although Al and Ca-As (0.5 $\underline{N}$ NH_4F and 0.5 $\underline{N}$ H_2SO_4 extractable As, respectively) may predominate if the amount of "reactive" Al or Ca is high and "reactive" Fe is low. Woolson et al. (1971, 1973) extracted As from a large number of soils with 0.5 $\underline{N}$ NH_4F followed by 1 $\underline{N}$ NaOH and concluded that As was associated with Al and Fe in the soil. Livesey and Huang (1981) have reported that arsenate adsorption maxima were linearly related to amounts of ammonium oxalate-extractable Al, and to a lesser extent to clay and ammonium oxalate-extractable Fe.

Texture is often related to As fixation (Woolson et al., 1971; Small and McCants, 1962) because both reactive Fe and Al usually vary directly with the clay content of soils (Woolson et al., 1971). Wauchope (1975) found that adsorption of arsenate, methylarsonate, and

cacodylic acid were strongly correlated with clay and iron oxide contents of soils.

It appears that As is not associated with organic matter to any appreciable degree. Brannon et al. (1976) did not detect As in the organic fraction of sediments from Mobile Bay, Ala., Bridgeport, Conn., or Ashtabula, Ohio. Crecelius et al. (1975) found that less than 10 percent of the As in sediments from Puget Sound was removed by H_2O_2 , indicating that very little As was found in organic matter. Johnson and Hiltbold (1969) reported that no appreciable organic As was found in soils. Andreae (1979) and Walsh and Keeney (1975) reported that one major difference between phosphorus (P) and As in soils is that soils contain appreciable organic P and do not contain measurable levels of organic As. Arsenic adsorption studies with soils have generally shown that adsorption of all As species is independent of organic matter content of the soil (Jacobs et al., 1970; Wauchope, 1975). Boischot and Hebert (1948) pointed out, however, that organic matter fixed arsenate in small amounts under alkaline or neutral conditions, the amount of fixation being proportional to the amount of organic matter.

Despite the low amount of As associated with organic matter in soils and sediments, organic matter-As interactions in the water column can greatly influence the behavior of As. Organic fractionation (Waslenchuk, 1978; Waslenchuk and Windom, 1978) has shown that at least 40 percent of the As in river and estuarine waters in the southeastern United States is associated with the light ($< 10,000$ molecular weight) fraction of dissolved organic matter. Waslenchuk (1979) felt that this complexation of As by organics prevents adsorptive interactions between dissolved As and active solid-phase organic and inorganic materials.

Organic complexation is also a probable major factor responsible for the observed conservative behavior of As at the freshwater/saltwater estuarine interface (Waslenchuk and Windom, 1978).

The association of As species with soils apparently changes with time. Woolson and Kearney (1973) found that added cacodylic acid was initially distributed in the following soil fractions: water soluble >>Al > Fe > Ca. After 32 weeks, the distribution maintained the same order, although the water soluble fraction was substantially lower in As. In contrast, arsenate was largely present in the Fe and Al fractions. The continuing predominance of the water soluble fraction is possibly a consequence of the greater mobility of dimethylarsinic acid compared to other As species (Holm et al., 1979; Woolson and Kearney, 1973). Holm et al. (1979) and Wauchope (1975) have both reported that cacodylic acid is the least strongly adsorbed of all As species by soils and sediments.

Woolson et al. (1973) reported that 4-6 weeks was needed for equilibrium to be attained between water soluble As, Al-As, Fe-As, and Ca-As following addition of arsenate to soils. The higher the As application rate, the longer it took for the As forms to reach equilibrium. The percent Fe-As decreased as As level increased, percent Al-As remained relatively constant, percent water soluble As increased, and very little Ca-As was formed. The fixation of arsenate by Fe was apparently more important than fixation by Al at lower levels of applied As, while Al appeared to be responsible for adsorption at higher application rates (Woolson et al., 1973).

Time-dependent adsorption of As by soils and conversion to less soluble forms has been demonstrated (Jacobs et al., 1970; Woolson

et al., 1973. Woolson et al. (1973) found that soluble (ammonium acetate or ammonium chloride extractable) As decreased to a constant value after 4 months. Iron-arsenic continued to form even after the Al-As fraction had reached a maximum level and begun to decline (Woolson et al., 1973).

Arsenic Leaching from Sediment

Effect of Soil and Sediment Properties

The fate of sediment arsenic exposed to short- and long-term leaching is of great environmental significance. If leaching removes high amounts of As from the sediment, special precautions must be taken when dredging and disposing of such material. Brannon et al. (1980) have demonstrated that As in undisturbed, relatively noncontaminated (< 0.25 to $9 \mu\text{g As/g}$) sediments pose no long-term hazards to overlying water quality. In fact, arsenic in the water column was adsorbed by the sediments. Short-term release of As from relatively noncontaminated sediments (< 0.25 to $12.2 \mu\text{g As/g}$) under conditions simulating dredging and aquatic disposal has also been shown to be insignificant (Brannon et al., 1976, 1980). Leaching studies have not been conducted, however, using sediments that are highly contaminated with As.

Leaching of As from soils is influenced by the properties of the soil and the amount of added As. Arsenic leaching generally increases as the amount of added As increases (Arnott and Leaf, 1967; Johnson and Hiltbold, 1969). Soils low in Ca or Fe and Al leach higher amounts of As than soils high in these components (McGeorge, 1915; Tammes and de

Lint, 1969; Johnson and Hiltbold, 1969). Sandy soils leach higher amounts of As than more finely textured soils (Ehman, 1965; Dickens and Hiltbold, 1967; Tammes and de Lint, 1969; Hiltbold et al., 1974), presumably because both reactive Fe and Al usually vary directly with the clay content of soils (Woolson et al., 1971). Galba (1972b) found arsenate easiest to leach from calcareous soils. Desorption was closely related to chemical composition of the soil, especially with the ratio $\text{CaO} + \text{MgO}/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. The greater this ratio, the easier arsenates are desorbed (Galba 1972b). Kobayashi and Lee (1978) reported that extended extraction (77 days) with distilled water showed that highly calcareous sediments under oxygenated conditions yielded the least amount of As (25 percent of the total), and that highly organic sediments, again under oxic conditions, yielded the most (in excess of 60 percent). Sediments subjected to As loading could be expected to behave similarly.

Arsenic leached from soils can move downward with percolation water, especially on coarse-textured soils (Steevens et al., 1972). Tammes and de Lint (1969) observed a leaching half life of 6.5 ± 4 years for sandy soils in the Netherlands. Leaching may be quicker in sandy soils since water soluble As accumulates faster in sands than in clays despite the more rapid leaching of As from sands (Dorman et al., 1939). Even though As can be leached from soils, available evidence indicates that As will not move to great depths in the soil profile, even in sandy soils. Steevens et al. (1972) found that subsoil As concentrations increased to a depth of 38 and 68 cm for treatments of 90 and 180 kg

As/ha and 720 kg As/ha, respectively, during four cropping seasons. Hiltbold et al. (1974) recovered all of the As added as monosodium methanearsonate (MSMA) applied to the soil surface within 30 cm of the soil surface over a 6-year period, with no evidence of leaching into deeper zones.

Effect of Salinity

Wiklander and Alvelid (1951) found that increasing concentrations of all salts in water except phosphate suppress the leaching of arsenic from soils, the decrease generally being greater for the higher concentrations than for the lower ones. Increasing salt concentration evidently counteracts the desorption of arsenate ions, decreasing the arsenate concentration in solution with a corresponding increase in adsorbed arsenate (Wiklander and Alvelid, 1951). Gupta and Chen (1978) found, however, that increasing salinity reduced adsorption of arsenate on activated alumina and bauxite. Rates of arsenate and arsenite adsorption are slower in seawater than in fresh water, but the absolute adsorption was reduced by no more than 5 percent. Arsenite is less effectively adsorbed than arsenate, but arsenate adsorption is affected much more by chemical composition than is arsenite (Gupta and Chen, 1978). Huang (1975) has reported that the presence of NaCl in solution generally decreased As retention by the hydroxy-Al complexes of both biotite and potassium (K) depleted biotite. The effect of increased salt concentration, therefore, appears to be suppression to some extent of both adsorption and desorption, although the preceding results are somewhat contradictory.

Arsenic and Phosphorus Cycling

The chemistry of As is similar in many ways to that of other Group V elements (which includes P); but As is more labile than P, which is essentially covalent (Walsh and Keeney, 1975). This chemical difference between P and As is best illustrated by the fact that As undergoes oxidation-reduction and methylation reactions in the environment while P apparently does not undergo such reactions.

Despite these major differences, there are some similarities between the behavior of P and As in the environment. As with arsenic, Fe plays a major role in P retention by soils and sediment, although As compounds are more strongly adsorbed than P (Wauchope, 1975). Clement and Faust (1981) felt that this similar association with Fe reflected similar phosphate and arsenate chemistry. Clement and Faust (1981) felt that such similarities could result in arsenate and phosphate competing for bonding sites in muds, with the levels of either existing in the aqueous or solid phases depending on the relative amounts of each present in a system. This may well be the case, since phosphate addition to a soil will substantially suppress the adsorption of As (Livesey and Huang, 1981). Under similar aerobic conditions, increased release of As has also been noted when phosphate (300 mg P/l) was added to the system (Clement and Faust, 1981). The observed impact on arsenate adsorption of added phosphate was attributed to anion competition (Livesey and Huang, 1981), a factor which may also have caused increased As release when phosphate was added to a mud-water system.

Sediments and soils are not the only place where As and P compete. The structural similarity between arsenate and phosphate enables arsenate to substitute for phosphate in biochemical reactions and act as an uncoupler of mitochondrial oxidative phosphorylation (NAS, 1977).

Studies of algae have shown that arsenate competitively inhibits phosphate uptake by phytoplankton (Blum, 1966; Johnson and Burke, 1978). Sanders (1979) showed that arsenate is taken up readily by S. costatum and inhibits productivity at concentrations as low as 67 μM of As when the phosphate concentration is low. Phosphate enrichment ($>0.3 \mu\text{M}$) alleviates this inhibition. Planas and Healey (1978) reported that the principal effect of arsenate on the algal C. reinhardtii was as an inhibitor of phosphate uptake rather than as an uncoupler of phosphorylation.

The inhibition of phosphate uptake by arsenate appears to be a result of the competition for uptake sites. Sckerl (1968) showed that arsenate competes with P for uptake and transport in the cell. Arsenate enters yeast cells by competing with phosphate for permease sites during entry (Jung and Rothstein, 1965; Button et al., 1973). Despite competition between arsenate and phosphate, the overall As cycle in marine ecosystems is similar to the phosphate cycle, but the As regeneration time is much slower (Sanders, 1980).

This short review illustrates some of the similarities and differences between the behavior of P and As in the environment. Care should be taken in extrapolating the behavior of one from that of the other because of the differences between the environmental chemistry of As and

P, specifically the ability of As to undergo oxidation-reduction and methylation reactions.

Sources and Concentration of Sb

Natural

Antimony, like As, is a naturally occurring element. Onishi and Sandell (1955b) estimated that the amount of Sb in igneous rocks (and in the upper lithosphere) is 0.1 to 0.2 ppm. Boyle and Jonasson (1973) reported that the terrestrial abundance of Sb is on the order of 0.7 ppm. Heinrichs and Mayer (1977) reported Sb concentrations in two soils ranging from 0.4 to 0.7 ppm.

Antimony, found primarily in mineral ores, is derived principally from stibite, Sb_2S_3 (Braman and Tompkins, 1978). Shales containing organic matter, sulfides, and iron oxides also tend to be high in Sb (Onishi and Sandell, 1955b). Microbial oxidation of Sb_2S_3 in mineral ores and shales occurs in two stages during weathering (Layalikova and Shlain, 1974). The Sb_2S_3 is first oxidized to form Sb_2O_3 followed by further oxidation to yield Sb_2O_5 . Antimony weathering, based on Sb/As estimated weight ratios of from 0.1 to 0.23 (Onishi and Sandell, 1955b; Boyle and Jonasson, 1973), should be from 10 to 23 percent of the weight of As weathered.

Antimony concentrations in seawater have been reported to range from 0.13-0.57 $\mu\text{g Sb/l}$ (Portmann and Riley, 1966; Gilbert and Hume, 1973; Gohda, 1972). Antimony concentrations ranging from 0.2 to

1.7 $\mu\text{g/l}$ were reported in the Tonegama River in Japan (Nagatsuka and Yagaki, 1976). Andreae et al. (1981) reported total Sb concentrations ranging from 13.6 to 232.6 $\mu\text{g/l}$ in fresh, estuarine, and marine waters. Braman and Tompkins (1978) reported, however, that the average Sb concentration for both fresh and saline water samples determined by hydride generation was approximately 20 ng/l . The lower concentrations of Sb found in their study was attributed to the inability of hydride generation to detect insoluble antimony compounds such as Sb_2S_3 , Sb_2O_3 , or $(\text{CH}_3)_2\text{SbO}(\text{OH})$ (Braman and Tompkins, 1978; Parris and Brinckman, 1976), which may have been present.

Anthropogenic

Antimony is introduced into the environment by man's activities in much the same manner as As. Ragaini et al. (1977) reported that lead smelting operations in the Kellogg Valley of Idaho had resulted in soil Sb concentrations ranging from 5 to 260 $\mu\text{g/g}$. Greclius et al. (1975) reported that the major anthropogenic source of Sb to Puget Sound (1.52×10^6 kg Sb/yr) was a large copper smelter located near Tacoma. Antimony concentrations ranging from 0.46 to 0.64 $\mu\text{g/g}$ have been reported in Wyoming coals (Chadwick et al., 1975). When coal is burned, Sb is concentrated in fly ash discharged through the stack compared to fly ash collected by the precipitator (Lindberg et al., 1975). Antimony is also introduced into the environment from sewage and fertilizer (Papakostides et al., 1975; Grimans et al., 1977). It can therefore be seen that Sb concentrations in soils and sediments may be increased in localized areas by man's activities.

Chemistry of Sb

Recent studies have shown that Sb exists in the Sb(III) and Sb(V) forms and as methylantimony compounds in natural waters (Andreae et al., 1981; Byrd and Andreae, 1982). Andreae et al. (1981) reported results of Sb speciation analysis from 10 widely separated rivers and estuaries. Antimony (V) was the predominant species in all water samples, but Sb(III) was found in most samples and methylantimony compounds were consistently present in the marine and estuarine environment. The presence of the nonequilibrium Sb(III) and methylantimony compounds was attributed to biological and algal activity (Andreae et al., 1981). Byrd and Andreae (1982) reported that Sb(III) concentrations in the Baltic Sea exhibited a surface maximum which decreased to a midwater minimum followed by greatly increased Sb(III) concentrations in anoxic bottom waters. Methylstibonic acid was detected in all samples at an average concentration of 2.5 picomoles (Byrd and Andreae, 1982).

Greatly increased concentrations of Sb(III) in anoxic bottom waters (Byrd and Andreae, 1982) implicates microbial reduction as a source of Sb(III). Based on the limited data available (Latimer, 1952), reduction of Sb_2O_5 to Sb(III) in the form SbO^+ , at pH 7 and an SbO^+ activity of 10^{-6} should theoretically occur at approximately 140 mV. The existence of SbO^+ in the environment has not been demonstrated, but some form of Sb(III) is present (Andreae et al., 1981; Byrd and Andreae, 1982).

In seawater, Sb(OH)_6^- , $\text{SbCl}_2(\text{OH})_4^-$, and SbCl(OH)_5^- are probably the predominating Sb species (Newman, 1954; Sillen, 1961). The existence of

these negatively charged Sb species indicates that positively charged Fe and Al oxides associated with sediments should strongly adsorb Sb. The limited results available to date indicate that Sb does become associated with sedimentary Fe and Al oxides. Crecelius et al. (1975) have shown that 48 percent of the total Sb (0.28 to 1.82 µg/g) in three "noncontaminated" Puget Sound sediments was oxalate-extractable, thereby implying the Sb was associated with Fe and Al compounds.

Biological methylation of Sb should be possible because of the similarity between the chemistry of As and Sb (Parris and Brinckman, 1976). There is no obvious thermodynamic kinetic barrier to biomethylation of Sb. Andreae et al. (1981) have reported finding methylstibonic acid $(\text{CH}_3\text{SbO}(\text{OH})_2)$ and dimethylstibinic acid $((\text{CH}_3)_2\text{SbO}(\text{OH}))$ in natural waters, indicating that methylation of Sb in the environment is indeed occurring. Parris and Brinckmann (1976) postulated that if methylation of Sb should occur during biodegradation of items protected with Sb, the Sb could be put into a much more water soluble form, $(\text{CH}_3)_3\text{SbO}$.

The chemistry of other Sb compounds that could be produced via biomethylation have been studied by a number of investigators. Bamford and Newitt (1946) demonstrated that trimethylstibine is rapidly oxidized in the presence of oxygen. Trimethylstibine reacts six to eight times as fast as trimethylarsine in solutions of methanol exposed to air (Parris and Brinckman, 1976). Oxidation of trimethylstibine solutions under anhydrous conditions produces high yields of trimethylantimony oxide $((\text{CH}_3)_3\text{SbO})$ (Parris and Brinckman, 1976).

The limited data available on Sb indicate that Sb cycling in the environment may be similar to that of As. Byrd and Andreae (1982)

reported that Sb(III) concentration profiles in Baltic Sea waters followed a similar pattern to those of As(III). Andreae et al. (1981) suggested that the presence of Sb(III), As(III), methylantimony acids, and methylated As compounds in aerobic natural waters was probably due to similar mechanisms. The exact degree of similarity remains an area for future research.

MATERIALS AND METHODS

Sampling Areas

Sediment samples were obtained through the cooperation of personnel at the Waterways Experiment Station (WES) engaged in research on contaminated dredged sediments. Sampling site selection was predicated on obtaining some of the most highly contaminated sediments in the nation. The general geographical locations of the sediment sampling areas are shown in Figure 1. For a more detailed location of sediment sampling sites see Folsom et al. (1981).

Field Sampling Procedures

Dredged material samples were taken with clamshell or similar samplers. After sampling, the sediments were placed into new, 208- steel drums with polyethylene liners, sealed with airtight lids, and transported to WES. Upon arrival at WES the sediments in each drum were mechanically mixed, and a subsample (20 l) transferred to a polyethylene container which was then sealed and stored at 4°C until used in this study.

Controlled Eh-pH Incubation

In all controlled Eh-pH incubations, wet sediment was transferred to a 2.8-l wide mouth erlenmeyer flask. Sufficient distilled deionized

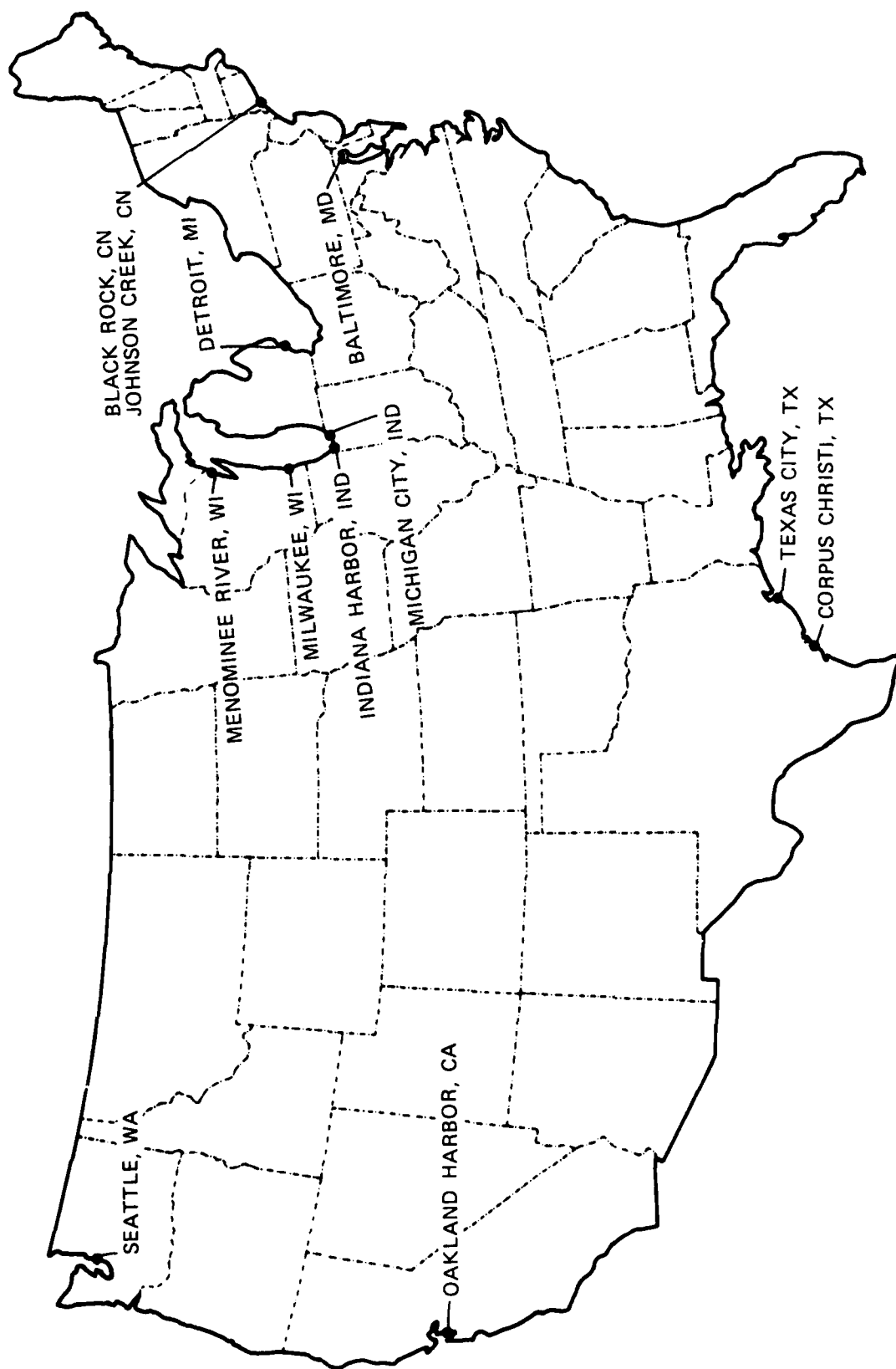


Figure 1. Map showing location of sampling areas.

water was added to each flask to produce a water-to-dry-sediment weight ratio of 15:1. The sediment-water mixtures were kept in suspension by continuous stirring with a magnetic stirrer. Sediment-water mixtures were equilibrated at $28 \pm 1^\circ\text{C}$ at a controlled Eh using the methods of Patrick et al. (1973), with some modifications. For each sediment-water mixture, Eh was monitored by a platinum electrode-calomel half cell connected to a pH-millivolt meter (Figure 2). The Eh desired for a particular incubation was set on a meter relay switch, which, by activating an air pump when the preset value was reached, prevented any further lowering of Eh. To help maintain anaerobic conditions and to act as a carrier for any volatile As or Sb compounds produced during the incubation, oxygen-free nitrogen gas was flushed through the system at a rate of approximately 15 ml/min. A combination pH electrode connected to a pH meter monitored pH. The desired pH was maintained by injecting either 1.0 N HCl or NaOH as necessary via syringe through a serum cap into the sediment-water mixture. Prior to beginning any experiment, sediment-water mixtures were allowed to incubate and stabilize at the chosen Eh-pH levels for 14 days prior to introducing any As or Sb compounds.

The first set of experiments investigated the effect of Eh and pH on leaching of native As and Sb in sediments from the Menominee River, Wisconsin; Indiana Harbor, Indiana; and Northwest Branch in Baltimore Harbor. Each sediment was incubated at four Eh levels (-150 mV, +50 mV, +250 mV, and +500 mV) and at three pH levels (pH 5.0, pH 6.5, and pH 8.0). Each Eh-pH combination was allowed to incubate for 1 week following stabilization at the chosen Eh-pH regime. Any volatile As or Sb compounds evolved were trapped in 20 ml of 0.005 M mercuric nitrate and

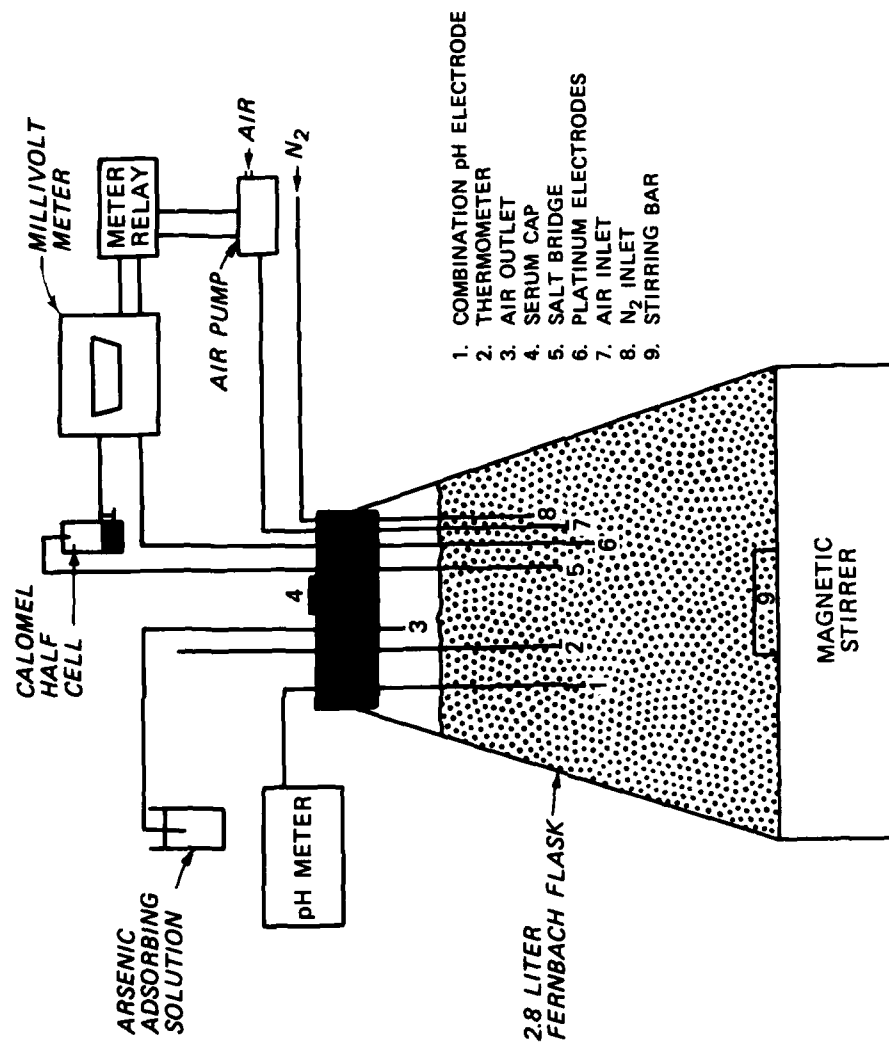


Figure 2. Redox potential and pH control apparatus for incubating sediment suspensions.

0.05 percent weight:volume nickelous nitrate prepared in 0.02 N nitric acid (Gupta and Chen, 1978).

The second set of experiments investigated the effect of Eh and pH on the mobilization and transformation of added As and Sb. As previously described, sediments from Texas City, Texas, were placed into the reactor units and allowed to stabilize at the chosen Eh-pH level for 14 days prior to any amendment. Each Eh-pH combination was replicated at two Eh levels (-150 mV and +400 mV) and three pH levels (pH 5.0, pH 6.5, and pH 8.0). Each Eh-pH combination was amended with 75 μ g of As(V)/g dry weight of sediment as sodium arsenate and 25 μ g Sb/g dry weight of sediment. The Sb amendment was prepared by dissolving Sb metal in HNO_3 .

Following 21 days of incubation, samples were withdrawn by syringe and the water soluble phase extracted and treated as previously described.

The third series of experiments investigated the effect of Eh and pH on the disodium salt of methylarsonic acid (DSMA) added to Texas City sediments. Each duplicated Eh-pH combination was amended with 35 μ g/g sediment dry weight of DSMA following stabilization at the chosen Eh-pH regime. Water soluble phase samples were taken and processed as previously described 2 hours after the amendment, then weekly for 5 weeks.

Samples were removed from each reactor for each Eh-pH combination and extracted using modifications of previously described selective extraction techniques (Brannon et al., 1976; Brannon et al., 1977). Sample handling and all steps in the water soluble and ammonium sulfate (exchangeable phase) extractions were conducted under an oxygen-free nitrogen atmosphere.

Water Soluble Phase

A 150-ml sample of the sediment-water mixture was taken by syringe and transferred to a 250-ml polycarbonate centrifuge bottle under an N_2 atmosphere. The bottle was sealed, then centrifuged at 9000 rpm ($13,000 \times g$) for 5 min. Following centrifugation the supernatant water was vacuum filtered under nitrogen through a 0.45- μ m pore-size membrane filter and immediately acidified to a pH of 1 with concentrated, ultrapure HCl. A 60-ml subsample to be used for As speciation analysis was immediately transferred to a polyethylene bottle and quick frozen at -60°C to prevent oxidation of As(III) to As(V), spurious losses of arsenite, and loss of methylated arsenicals (Andreae, 1979). The remainder of the sample was stored at 4°C until analyzed.

Exchangeable Phase

A separate 100-ml sample of the mixture was then removed by syringe and placed into an oxygen-free, tared, 250-ml centrifuge tube containing 24 ml of deoxygenated 5 N ammonium sulfate at pH 7. Dilution resulted in a 1 N ammonium sulfate extractant. A separate subsample was removed by syringe for determination of percent solids. The sediment suspensions were shaken mechanically for 1 hr, then centrifuged at 6000 rpm for 10 min, followed by vacuum filtration under oxygen-free conditions. The filtrate was acidified to pH 1 with concentrated, ultrapure HCl, and subsequently stored as described for the water soluble phase. This extractant also included metals from the water soluble phase. Specific concentrations of constituents in this extract (exchangeable) were therefore corrected for the mass of material found in the water soluble phase.

Easily Reducible Phase

The residue from the 1N ammonium sulfate extraction was washed once with 50 ml of N₂ sparged distilled deionized water and centrifuged at 6000 rpm for 5 min, and the liquid phase discarded. The remaining sediment residue was then blended, a 2-g (dry weight) subsample removed, and 100 ml of 0.1 M hydroxylamine hydrochloride - 0.01 M nitric acid solution (Chao, 1972) was added. The solid-to-extractant ratio was approximately 1:50. The mixture was mechanically shaken for 30 min and then centrifuged at 6000 rpm for 5 min; the extract was then filtered through 0.45- μ m pore-sized membrane filters.

Moderately Reducible Phase

The residue from the easily reducible phase was washed once with distilled water and centrifuged. The supernate was then discarded. Washed residue from the easily reducible phase was then extracted with 100 ml of oxalate reagent (0.1 M oxalic acid plus 0.175 M ammonium oxalate, pH 3.25). The mixture was mechanically shaken for 2 hours, then centrifuged at 6000 rpm for 10 min. The extract was then filtered through 0.45- μ m pore-sized membrane filters, transferred to polyethylene bottles, acidified with concentrated, ultrapure HCl to pH 2, then stored at 4°C.

Sediment Incorporation and Transformation of Added Arsenic and Antimony

Ten sediment samples from Indiana Harbor, site 3, Ind.; Menominee River, site 1, Wis.-Mich.; Detroit River, site 1, Mich.; Michigan City Harbor, site 3, Ind.; Milwaukee Harbor, Wis.; Oakland Inner Harbor,

site 3, Calif.; Black Rock Harbor, Conn.; Corpus Christi Ship Channel, site 1, Tex.; Seattle, Duwamish Waterway, site 3, Wash.; and Bridgeport Harbor (Johnson's Creek), Conn. were utilized. Sediment in each 20-ℓ container was first mechanically blended for 15 min. Subsamples (2000 g on a dry weight basis) were then transferred to each of three 3.8-ℓ, polyethylene containers with airtight lids. Sediment in each container was then amended with 20 g of cellulose (1 percent on a weight:weight basis) as a microbial energy source and the cellulose mechanically mixed with the sediment for 15 min. One container of each sediment was then sealed without further amendment, the second was amended with 75 µg As(V)/g dry weight from a 1000-mg/ℓ sodium arsenate solution, and the third amended with 75 µg Sb⁺³/g dry weight using a 1000-mg/ℓ solution of antimony potassium tartrate. Following thorough mechanical mixing of the added As and Sb with the sediment for 15 min, the containers were sealed and incubated for 45 days at 20 ± 0.5°C. At the conclusion of the incubation period, each sediment container was placed in a glove box under a nitrogen atmosphere. Each container was then opened and mechanically blended for 15 min. A subsample of approximately 200 ml of the blended sediment was then transferred to an oxygen-free, polycarbonate, 250-ml centrifuge bottle in the glove bag. The sediment interstitial water was then separated by centrifugation as previously described for the water soluble phase. A separate subsample (approximately 20 g dry weight) of each blended sediment sample was weighed into an oxygen-free, tared, 250-ml centrifuge tube containing 100 ml deoxygenated 1 N ammonium sulfate. A separate subsample was removed for determination of

percent solids. The extraction was then conducted as previously described for the exchangeable phase. Easily reducible phase and moderately reducible phase extractions were then conducted sequentially on the residue from the exchangeable phase as previously described. Total sulfides were determined on sediment subsamples by the Connell (1966) modification of the American Public Health Association (1980) method.

Short-Term Leaching

A subsample (40 g sediment dry weight) of wet sediment from each of the unamended, As amended, and Sb amended sediment anaerobic incubations previously described were transferred to 250-ml polycarbonate centrifuge tubes. Sufficient distilled-deionized water was then added to each centrifuge tube to bring the total volume of water to 160 ml. Each mixture was then aerated with compressed air for 5 min, shaken for 30 min, reaerated for 5 min, centrifuged at 6000 rpm for 10 min, and filtered through 0.45- μ m pore-size membrane filters. The conductivity and pH of the supernatant were determined on a small, disposable aliquot (15 ml) prior to filtration. The filtered portion of the sample was preserved by adding a few drops of ultrapure HCl followed by immediate freezing at -60°C .

Incubated sediments from Indiana Harbor, Menominee River, Detroit River, Michigan City Harbor, and Corpus Christi Ship Channel were also subjected to additional short-term leaching. This additional leaching was conducted in an identical manner to the short-term leaching previously described except that four subsamples of each sediment treatment

were extracted with artificial seawater (Table 1) of varying salinities (5 ‰, 15 ‰, 25 ‰, and 35 ‰).

Long-Term Leaching

After the short-term leach with distilled-deionized water, the weight of decanted supernate was measured and replaced by an equal weight of distilled-deionized water. These samples were then mechanically shaken for one month while aerobic conditions were maintained in the suspension. At the end of the month, the suspensions were centrifuged at 6000 rpm for 10 min, followed by measurement of pH and conductivity on one aliquot and filtration and preservation of another aliquot as previously described for short-term leaching. The decanted supernate was replaced as previously described and the long-term leach continued, with monthly sampling, for five more months.

Incubated sediments from Black Rock Harbor were also leached under anaerobic and a combination of anaerobic/aerobic conditions. Additional 40-g sediment dry weight subsamples of Black Rock Harbor sediments from each treatment (none, As, Sb) were weighed into each of six 250-ml polycarbonate centrifuge tubes. Additional distilled-deionized water was then added to bring water volume to 160 ml. One triplicate set of samples was sealed and shaken mechanically under anaerobic conditions for three months. Sampling and replacement of distilled-deionized water were conducted monthly as previously described. The other triplicate set of samples was shaken for three months under alternating anaerobic/aerobic conditions (two weeks anaerobic/two weeks aerobic) for three

Table 1
Composition of Artificial Seawater
 (from Burkholder, 1963)

<u>Ingredient</u>	<u>Quantity</u>
Distilled water	1 l
NaCl	23.476 g
Na ₂ SO ₄	3.917 g
NaHCO ₃	0.192 g
KCl	0.664 g
KBr	0.096 g
H ₃ BO ₃	0.026 g
MgCl ₂ ·6H ₂ O	10.610 g
SrCl ₂ ·6H ₂ O	0.040 g
CaCl ₂ ·2H ₂ O	1.469 g
pH	7.2

months. Sampling and replacement of distilled-deionized water was conducted monthly as previously described at the end of the two-week aerobic segment of the leaching conditions.

Evolution of Volatile As and Sb Compounds

One-hundred gram subsamples of each incubated sediment treatment were added to 250-ml Erlenmeyer flasks. One hundred milliliters of distilled-deionized water was then placed on top of the resulting sediment layer. A stream of oxygen-free N_2 gas was bubbled through the water of each setup (Figure 3) for five weeks. Arsenic or Sb compounds that were evolved in the sediment water system were collected in 20-ml solutions of 0.005 M mercuric nitrate and 0.05 percent weight:volume nickelous nitrate prepared in 0.02 N nitric acid (Gupta and Chen, 1978). Absorbing solutions were changed and analyzed for As and Sb at weekly intervals. At the end of 5 weeks, the gas passing through the water above the sediment was changed to air, and the evolution of As and Sb compounds monitored for three weeks as previously described.

Analytical and Digestion Procedures

Arsenic

The concentrations of As(III), As(V), and total methylated As compounds were determined by a modification of the sequential volatilization hydride generation method originally described by Braman and Foreback (1973) and improved upon by Braman et al. (1977) and Andreae (1977). The modification involved analysis of total As, total inorganic As, and

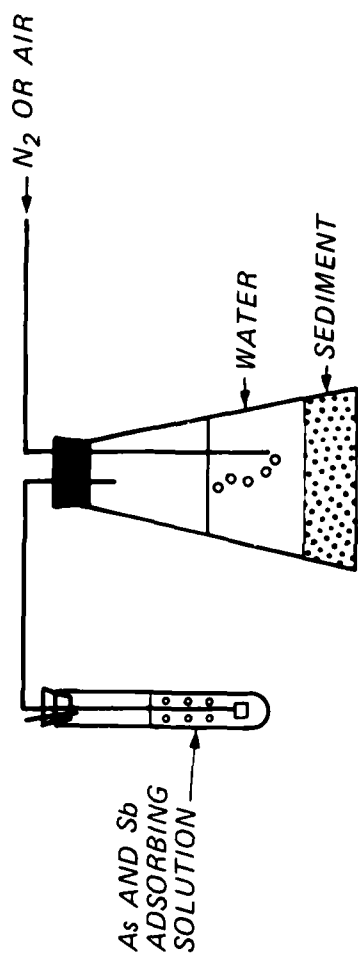


Figure 3. Apparatus for incubating submerged sediments.

As(V). Total As was first determined on the sample using a Perkin-Elmer model 503 atomic adsorption unit coupled to a Perkin-Elmer MHS-10 hydride generator. Total inorganic As was then determined on the sample by inserting a sulfuric acid trap in the line from the MHS-10 hydride generator to the atomic adsorption unit. The acid trap used was a Nesbitt adsorption bulb filled to a depth of 20 mm with concentrated H_2SO_4 . Additional acid causes backpressure in the MHS-10 system and results in disruption of the normal flow pattern. Concentrated sulfuric acid has been shown to quantitatively separate alkyl arsines (reduction products of organic As oxyacids) from inorganic arsines (Johnston, 1978). The efficiency of the sulfuric acid trap was verified by running standards and spiked samples containing from 10 to 100 ppb of As as methylarsonic acid, dimethylarsinic acid, and inorganic As through the system in the presence and absence of the sulfuric acid trap. Alkyl arsines which passed through the sulfuric acid trap were not detected (detection limits were <0.0005 mg/l), while inorganic arsines passed unaltered through the trap with no reduction in As detection limits. Concentrations of organic As compounds are determined from the difference between total As concentration and total inorganic As concentration.

Arsenate (As(V)) concentration was determined by a modification of the method of Andrae (1977); selective volatilization of As(III) from the sample followed by total inorganic As analyses. At a pH of 4 to 9 As(III) is the only form of inorganic As reduced to arsine (Braman and Foreback, 1973). At a pH of 6.5, only 0.2 percent of the arsenate present in a sample is reduced to arsine (Andrae, 1977). The pH of a sample aliquot (generally 1 ml or less) was adjusted to approximately

pH 6.5 with a Tris [tris (hydroxymethyl) aminomethane] buffer. The Tris buffer was similar to that used by Andreae (1977), 2.5 N in Tris and 2.4 N in HCl giving a pH of 6.2 after dilution to 0.05 N, except that HCl addition was stopped when pH 7.2 was reached. Following pH adjustment of the sample, 1 ml of 4.8 percent NaBH_4 solution was added, and argon gas slowly bubbled through the sample. When all added NaBH_4 had decomposed (6 hours), the sample was acidified and total inorganic As was again determined. This is a measure of As(V) since As(III) was removed from solution by treatment with Tris and sodium borohydride. The ability to selectively volatilize As(III) using this modification of the method of Andrae (1977) was verified by carrying standards and spiked samples containing from 10 to 100 $\mu\text{g}/\ell$ of As as As(III) (sodium arsenite solution), As(V) (sodium arsenate solution), and the methylated As compounds previously mentioned through the procedure both singly and in combination. Arsenite was not detected regardless of initial concentration and As(V) was quantitatively recovered in all cases.

Other Analytical Methods

Calcium, Fe, Mn, and Al concentrations were determined using direct flame aspiration with a Spectrometrics Spectraspan II ecelle grating argon plasma emission spectrophotometer. Antimony concentrations were determined with an isotope Zeeman shift atomic absorption spectrophotometer.

Total Digestion Procedure

One gram of oven-dried sediment was weighed into a 100-ml micro-Kjeldahl flask. Fifteen milliliters of concentrated HNO_3 was added; and

the mixture heated on a digestion rack until almost dry. Five milliliters of red fuming HNO_3 was added and the mixture again heated until almost dry. After cooling to room temperature, the mixture was diluted with 30 ml of 1.2 N HCl, filtered through Whatman No. 42 filter paper, and brought to a final volume of 50 ml.

Organic Matter

Organic matter was determined by weight loss on ignition at 550°C, a modification of the procedure in Standard Methods (American Public Health Association, 1980). Five grams of oven dry sediment was weighed to the nearest 0.1 mg and combusted at 550°C for 24 hours. After cooling to room temperature in a desiccator, the sample was reweighed and weight loss calculated.

Calcium Carbonate Equivalent

Calcium carbonate equivalent was determined on oven-dried sediments using gravimetric method No. 91-5 (Allison and Moodie, 1965).

Total Sulfur

Total sulfur was determined on oven-dried sediments using the LECO combustion method, application No. 103 (Laboratory Equip. Corp., St. Joseph, Mich.).

Particle-Size Distribution

Particle size was determined on air-dried sediments using the method of Day (1956) as modified by Patrick (1958).

Quality Control

Throughout the study, when a total experiment was not duplicated, at least one extract or incubation in ten was conducted in triplicate to assess the variability of the experimental procedure. For all chemical determinations, analysis of split samples, spiking of samples to determine percent recoveries, and analyses of National Bureau of Standards Reference Standards were conducted on every eighth sample to ensure consistent precision and accuracy.

Data Analysis

To test for overall differences, analysis of variance procedures were utilized (Steel and Torrie, 1960; Barr et al. 1976). Simple one-to-one correlations were determined using the least squares method. Multiple regression analysis was conducted using maximum R^2 improvement in a stepwise pattern. The procedure used was developed by the Statistical Analysis Systems (SAS) Institute (Barr et al., 1976). This technique looks for the "best" one-variable model, the "best" two-variable model, and so forth, to fit the input variables.

RESULTS AND DISCUSSION

Experimental and Analytical Variability

To evaluate the variability in the various experiments conducted, samples chosen at random were duplicated or triplicated in each series of studies. Mean coefficients of variation (CV) for water soluble phase parameters in the various experiments conducted during this study are presented in Table 2. For all determinations, experimental variability, which included variation between replicates, variation due to sample handling, and analytical variability, did not exceed 29 percent and was generally less than 20 percent. Mean CV's for parameters measured following selective sequential extraction of sediments are presented in Table 3. The CV's in Table 3 for selective extraction procedures are comparable to those reported for selective extraction procedures in other sediments (Brannon et al., 1977).

Analytical variability of split samples for Sb, As, As(V), and inorganic As are presented in Table 4. These CV's were derived by randomly selecting ten duplicate analyses conducted in the various chemical matrices used in the study. Every eighth sample in the study was analyzed in duplicate for all parameters. Analyses were very reproducible and had CV's comparable to those reported by other workers for analyses of various As compounds (Braman et al., 1977; Iverson et al., 1979; Denyszyn et al., 1978).

Table 2
Mean Coefficients of Variation (%) For Water Soluble Phase
Parameters in the Eh-pH, Short-Term Leaching, Long-Term
Leaching, and Anaerobic Incubation Studies

Experimental Procedure	Parameter Measured									
	Total As	As(V)	Inorganic As		Sb	Fe	Al	Mn	pH	Conductivity
Eh-pH Incubations	15.7	12.8	4.3		18.5	ND	ND	ND	ND	ND
Short-term Leach	14.8	29.0	19.1		3.40	ND	ND	ND	0.76	3.98
Long-Term Leach	18.2	13.0	25.1		2.96	ND	ND	ND	1.02	3.78
Anaerobic Incubation	15.2	BDL	9.0		0.00	19.8*	14.0*	12.1*	ND	ND

ND = Not Determined

BDL = All duplicated samples were below detection limit

* Computed from three separate incubations and extractions for 10 sediments

Table 3
Mean Coefficients of Variation (%) For Chemical Fractionation
Procedures Conducted on Replicate Experiments

Chemically Extractable Phase	Total		Inorganic				
	As	As(V)	As	Sb	Fe	Al	Mn
Exchangeable	19.7	BDL	19.7	6.9	17.4	BDL	9.5
Easily Reducible	13.8	ND	ND	6.8	10.1	17.7	5.4
Moderately Reducible	4.6	ND	ND	7.5	5.7	5.3	4.7

BDL = Below Detection Limits

ND = Not Determined

Table 4
Analytical Variability, Expressed As a Mean Coefficient of
Variation (%) of Ten Randomly Selected Samples

Sample Matrix	Total	As(V)	Inorganic	Sb
	As		As	
Water	2.99	8.87	6.77	4.33
Ammonium sulfate extractant	5.23	11.95	10.54	6.56
Hydroxylamine hydrochloride extractant	5.35	ND	ND	6.01
Oxalate extractant	2.97	ND	ND	1.22

ND = Not Determined

Transformation and Distribution of Arsenic in Sediments

Sediment Physical and Chemical Characteristics

Selected physical and chemical characteristics of ten sediments used in investigating the manner in which anaerobic sediments assimilate and transform added As(V) are presented in Table 5. The sediments exhibited a wide variety of particle size, ranging from nearly pure sand (91.4 percent) in Menominee site 1 sediment to nearly pure silt and clay in Corpus Christi (98.3 percent) and Milwaukee (96.6 percent) sediments. Total As concentrations were generally low, with only three sediments containing more than 10 $\mu\text{g/g}$ of total As. Iron, aluminum, organic matter, total sulfur, and calcium carbonate equivalent contents of the sediments generally exhibited a wide range of variation, with data for these parameters varying by factors of 6 to 50 among sediments.

As Speciation in Sediments

Concentrations of As(V), As(III), and organic As in amended and unamended sediment interstitial waters are presented in Figure 4. In both amended and unamended sediments, As(III) was generally the predominant form of inorganic As. Concentrations of As(V), As(III), and organic As were substantially higher in the interstitial water and exchangeable phase of amended sediments compared with unamended sediments (Tables 6 and 7). Addition of 75 $\mu\text{g/g}$ of As(V) to the sediments resulted in enrichment factors (amended conc./unamended conc.) as high as 72 for As(V), 3350 for As(III), and 1542 for organic As in the interstitial water. Similar enrichment factors were noted for exchangeable phase As species.

Table 5
Some Physical and Chemical Characteristics of the Sediments

Sediment	* % Sand > 50 μ m	* % Silt 2-50 μ m	* % Clay < 2 μ m	Total Sb μ g/g	* Total As μ g/g	* Total Fe mg/g	Total Al mg/g	CaCO ₃ * Equivalent %	* Organic Matter %	* Total Sulfur mg/g
Black Rock	36.7	51.2	12.1	2.1	3.6	19.4	12.0	0.4	16.4	14.8
Corpus Christi	1.7	85.8	12.5	1.6	10.2	10.7	14.9	7.4	8.9	5.0
Detroit	33.8	53.8	12.4	5.9	11.4	74.3	5.3	32.1	10.7	1.7
Indiana Harbor	38.8	46.6	14.6	17.5	37.5	291.3	2.8	18.2	6.6	1.6
Johnson Creek	17.5	74.1	8.4	7.1	2.6	24.9	17.0	1.3	14.2	14.3
Menominee l	91.4	5.7	2.9	0.5	4.1	7.0	1.8	7.6	2.7	0.3
Michigan City	47.5	42.9	9.6	11.8	2.3	29.8	5.5	21.1	13.0	3.8
Milwaukee	3.4	70.7	25.9	0.8	1.1	12.7	9.0	51.7	8.8	3.7
Oakland	65.4	18.3	16.3	1.2	2.7	15.4	14.7	0.2	2.0	2.3
Seattle	17.5	75.8	6.7	3.7	3.2	28.8	5.0	0.0	8.5	9.4

* Data from Folsom et al. (1981)

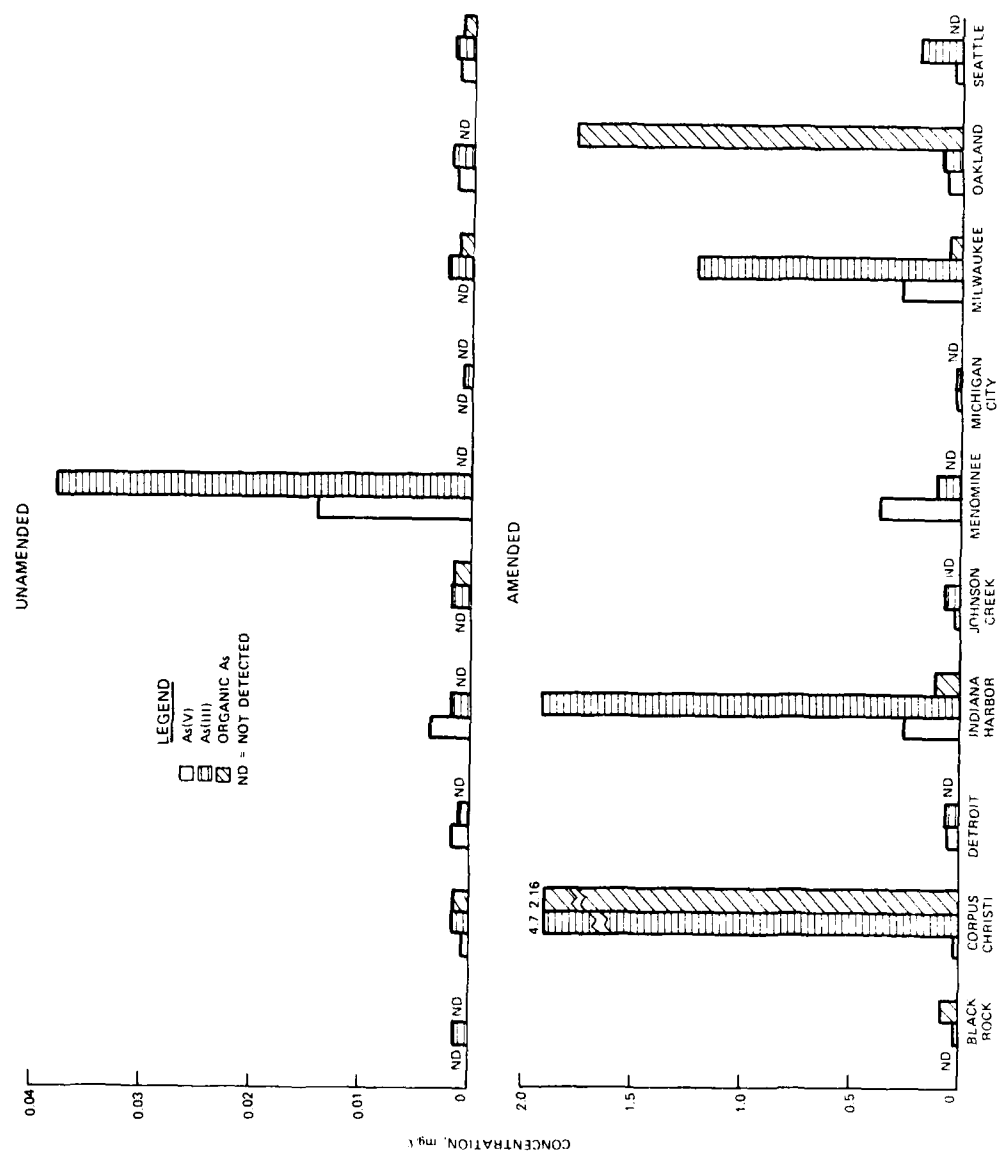


Figure 4. Concentration of various As species in the interstitial water of anaerobically incubated sediments (Note scale difference between graphs).

Table 6
Concentrations of As(V), As(III), and Organic As in the Interstitial Water
of Sediments Incubated Anaerobically for 45 Days

Sediment	As(V), $\mu\text{g/l}$		As(III), $\mu\text{g/l}$		Organic As, $\mu\text{g/l}$	
	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	ND	0.6	1.2	1.7	ND	83.0
Corpus Christi	0.5	22.0	1.4	4690.0	1.4	2160.0
Detroit	1.4	46.0	1.0	59.0	ND	ND
Indiana Harbor	3.6	259.0	1.8	1920.0	ND	110.0
Johnson Creek	ND	9.5	1.6	78.0	1.2	ND
Menominee	14.0	371.0	38.0	205.0	ND	ND
Michigan City	ND	82.0	0.7	68.0	ND	ND
Milwaukee	ND	275.0	2.1	1210.0	1.2	50.0
Oakland	1.3	67.0	1.9	83.0	ND	1770.0
Seattle	1.1	30.0	1.7	195.0	1.0	ND

ND = Not Detected

Table 7
Concentrations of As(V), As(III), and Organic As in the Exchangeable
Phase of Anaerobic Sediments

Sediment	As(V), $\mu\text{g/g}$		As(III), $\mu\text{g/g}$		Organic As, $\mu\text{g/g}$	
	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	0.013	NE	0.099	0.062	0.009	5.116
Corpus Christi	0.122	0.498	NE	12.199	0.023	NE
Detroit	0.004	0.301	0.009	0.263	NE	NE
Indiana Harbor	0.013	0.280	0.023	2.032	NE	NE
Johnson Creek	0.012	0.046	0.037	1.629	0.003	0.588
Menominee	0.043	0.064	0.099	0.492	NE	0.096
Michigan City	0.099	1.792	0.015	2.530	NE	NE
Milwaukee	0.004	0.141	0.014	0.703	NE	0.180
Oakland	NE	0.709	0.019	6.214	0.004	NE
Seattle	0.002	0.422	0.025	4.358	0.004	0.835

NE = None Extracted

Since the added As was in the As(V) form these results demonstrate that in the sediments studied, As(V) was reduced to As(III) under anaerobic conditions. The results also show that in five of the ten sediments, addition of As(V) resulted in accumulation of organic As in the sediment interstitial water under anaerobic conditions. The observed reduction of As(V) to As(III) and production of organic As occurred in sediments from both freshwater and saline areas; Black Rock, Corpus Christi, Johnson Creek, Oakland, and Seattle sediments were from saline environments.

Analytical results for native As are in agreement with those of other workers who have reported As(III) concentrations in anaerobic soils and sediments (Clement and Faust, 1981; Johnston, 1978; Andreae, 1979; Takamatsu et al., 1982) and water (McBride and Wolfe, 1971; Brunskill et al., 1980; Johnson and Pilson, 1975). The accumulation of As(III) following As(V) addition to sediments observed in this study is also in agreement with results of Brunskill et al. (1980) and Myers et al. (1973) who observed similar As reduction in sewage sludge. Addition of As(V) to the sediments did not affect the concentrations of Fe, Al, or Mn found in the interstitial water of the amended and unamended sediments. Reduction of Fe from Fe(III) to Fe(II) with subsequent dissolution of ferrous arsenate, a mechanism previously advanced to explain the increase in soluble As under anaerobic conditions (Kanamori, 1965; Deuel and Swoboda, 1972), therefore, played no part in the elevated concentrations of any As species in the amended sediments.

A portion of the organic As compounds found in the interstitial water were probably methylated As oxyacids. When organic As compounds have been found in aerobic and anaerobic environments, methylarsonic and

dimethylarsinic acid were reported to constitute the great majority of organic As (Braman, 1975; Andreae, 1979; Johnston, 1978; Takamatsu et al., 1982). Other organic As compounds have also been reported in the interstitial waters of anaerobic sediments and soils (Johnston, 1978; Takamatsu et al., 1982), although in much lower concentrations. The As compound reported in flooded soils by Takamatsu et al. (1982) was identified as $C_5H_7AsO_3H_2$, a molecule containing aliphatic hydrocarbon groups in place of a methyl group. Regardless of the composition of the organic As pool, the added As(V) that became part of the pool probably was reduced to As(III) prior to methylation or addition of a longer aliphatic carbon chain. Arsenic in methylated As oxyacids is present in the +3 and +1 valence states (Ehrlich, 1981).

It is highly unlikely that the organic As compounds in the sediment interstitial water were oxidation products of methylated arsines, a mechanism postulated by Wood (1974) and Ridley et al. (1977). During the incubation period of 45 days, and in all subsequent handling, sediments were not exposed to air; anaerobic conditions following incubation were verified by the presence of sulfides in all sediments.

There is strong reason to believe, therefore, that the organic arsenicals were formed under anaerobic conditions following reduction of As(V) to As(III). Direct methylation of arsenite or addition of other aliphatic hydrocarbon groups to As(III) is a more plausible mechanism than oxidation of methylated arsines for the accumulation of organic As compounds under the experimental conditions used in this experiment. These findings are in agreement with the biosynthetic pathway of dimethylarsine by methanobacteria (McBride and Wolfe, 1971). Although volatile As compounds were not measured in this phase of the study,

elevated concentrations of As(III) and soluble organic As, intermediates in the biosynthesis, were measured in the interstitial water and exchangeable phases.

Transformation of As(V) in Texas City Sediments

To determine the impact of oxidized and reduced conditions and pH on As(V) transformations in sediment, As(V) was added to Texas City sediment maintained at a specific Eh and pH. The Texas City sediment was high in clay content (26.9 percent), low in total Mn (57 $\mu\text{g/g}$), total As (0.55 $\mu\text{g/g}$), and total Fe (1.62 mg/g) content (B. L. Folsom, personal communication).

Unamended Texas City sediments were not subjected to the same incubations as As(V) amended sediments because of the low total As concentration. At the solid-liquid ratio (15:1) in the reactor units, solubilization of all sediment As would result in a total water soluble As concentration of only 0.035 mg/l , a minor amount compared to the amount of added As.

After stabilization of Eh-pH conditions in the sediment suspension, 4.75 mg/l (75 $\mu\text{g/g}$) of As(V) was added, and the mixture allowed to incubate for three weeks before sampling. Total water soluble As concentrations in Texas City suspensions are presented in Table 8. At pH 5.0 and 6.5, soluble As concentrations at -150 mV greatly exceeded those at +500 mV; at pH 8.0 the reverse was true. Under oxidized conditions, a maximum of 17.1 percent of the added As remained in solution compared to a maximum of 69.5 percent under reduced conditions. Arsenic(V) was present under reduced conditions only at pH 8.0 and as a minor portion (13.9 percent) of the total inorganic As (Figure 5). Under oxidized

Table 8

Water Soluble Total As (mg/l) in Texas City Sediment Suspensions

Redox Potential mV	pH		
	5.0	6.5	8.0
-150	2.50	3.30	0.18
+500	0.05	0.17	0.81

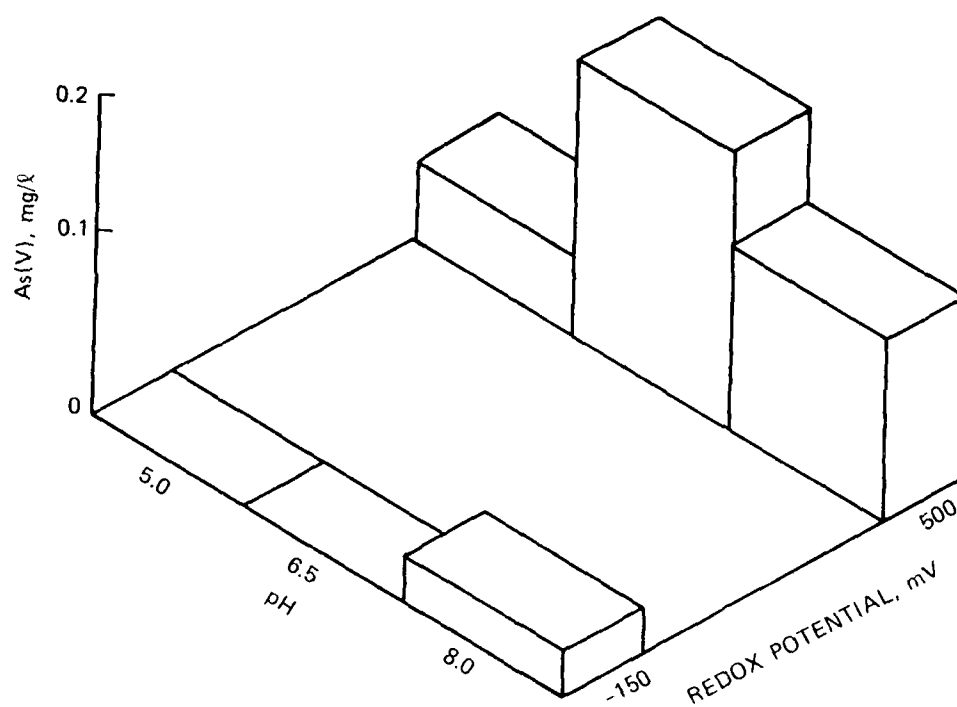


Figure 5. Influence of oxidation status and pH on water soluble As(V) in Texas City sediment suspensions.

conditions, As(V) was present in the interstitial waters at all pH's tested. Distribution of As(III) as a function of Eh and pH was the opposite of As(V) trends (Figure 6). Arsenic(III) was present at all pH's under reducing conditions, although much higher concentrations were reached at pH 5.0 and 6.5. Under oxidized conditions, As(III) was present only at pH 8.0. No organic As was found at any Eh-pH combination in Texas City sediment suspensions.

These results indicate that in Texas City sediments, in agreement with the 10 other sediments tested, addition of As(V) to sediments under anaerobic conditions will result in reduction of As(V) to As(III) and to accumulation of As(III). The higher concentrations of As(III) at pH 5.0 and 6.5 compared to pH 8.0 under reduced conditions are probably due to adsorption processes. Arsenite is less subject to adsorption under acidic conditions because the fraction of arsenite present in solution as an anion is small in acidic or weakly basic solution, but increases as the pH approaches 9.2 (Frost and Griffin, 1977). Maximum adsorption of arsenite has been reported at pH 9.2 for an anion exchange resin (Everest and Popiel, 1957), pH 7.0 for amorphous iron hydroxides (Pierce and Moore, 1980, 1982), and pH 9 (the limit of testing) for clay minerals (Frost and Griffin, 1977).

The distribution of As(V) in solution is also a possible consequence of adsorption processes. Maximum adsorption of arsenate by clay minerals, soils, and amorphous iron hydroxides has been reported to be in the pH range of 3.5 to 5.3. Soluble As(V) concentrations in Texas City sediment suspensions under both oxidized and reduced conditions were lower at pH 5.0 than at pH 8.0. The lack of soluble As(V) under

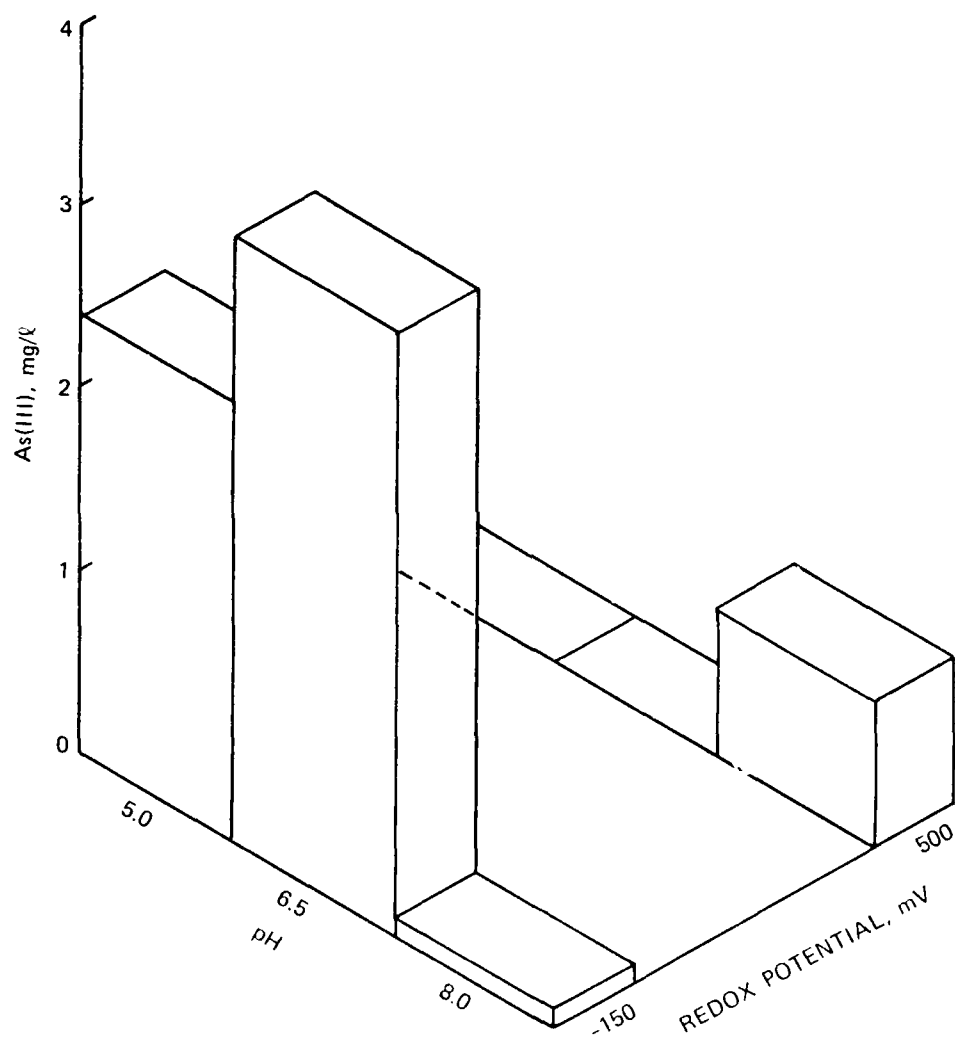


Figure 6. Influence of oxidation status and pH on water soluble As(III) in Texas City sediment suspensions.

reduced conditions at pH 5.0 and 6.5 may also have been due, however, to nearly complete reduction of all added As(V).

The presence of As(III) in solution under oxidized conditions at pH 8.0 at a relatively high concentration (0.78 mg/l) when adsorption should be highest, indicates that aerobic reduction of As(V) may also be occurring. Others (Johnson, 1972; Heimbrook, 1974; Shariatpanahi and Anderson, 1981) have reported As(V) reduction by bacterial cultures under aerobic conditions. If such As(V) reduction is occurring under aerobic conditions, it is probably restricted to pH 8.0. Arsenite is much less subject to adsorption at pH 5.0 and 6.5, yet no soluble As(III) was observed.

Disappearance of Disodium Methanearsonate (DSMA)

Different Eh-pH conditions in Texas City sediment suspensions resulted in differences in initial adsorption of 2.22 mg/l (35 µg/g) of DSMA. Samples taken 2 hours following addition of DSMA to the reactor units revealed that relatively larger amounts of DSMA were adsorbed at pH 6 under oxidized conditions than at pH 8 (Table 9). At pH 5.93 essentially all methylarsonic acid exists as the univalent anion (Ferguson and Gavis, 1972). The 2 hours between addition of DSMA to the sediment-water suspension and initial sampling should have been more than sufficient for adsorption-desorption equilibrium to have been established. Anderson et al. (1978) reported that adsorption of arsenate and methanearsonic acid could be described by Langmuir isotherms, with each compound displaying similar adsorption rate constants. Adsorption rates for arsenate and methylarsonic acid should therefore

Table 9
Adsorption of DSMA from 2.64-ℓ Solutions Containing 2.22 mg/ℓ of
As and 63.3 g/ℓ of Texas City Sediments Under
Differing Eh and pH Conditions

Eh	pH	Equilibrium solution mg/ℓ As*	DSMA adsorbed	
			μg As per g	% total applied
+450	8.0	1.91	4.9	14.00
+450	6.0	1.29	14.7	42.01
-100	8.0	2.00	3.5	9.94
-100	6.0	1.85	5.9	16.71

*Means of duplicate suspensions, C.V. = 21.6

be similar. Adsorption of arsenate is known to be rapid, with from 50 to 90 percent of added arsenate adsorption completed within minutes (Anderson et al., 1976; Pierce and Moore, 1982).

Water soluble DSMA added to Texas City sediments generally decreased over time (Figure 7), the rates of disappearance apparently a function of the Eh-pH regime. The soluble organic As has been assumed to be DSMA for the duration of the incubation. The previous experiment demonstrated that no organic As is formed when As(V) is added to Texas City sediments. Holm et al. (1980) has also demonstrated that during degradation of methylarsonic acid, dimethylarsinic acid was not formed.

The disappearance of DSMA was apparently a demethylation reaction. Holm et al. (1980) has demonstrated that changes in As speciation did not occur in sterilized sediments. Von Endt et al. (1968) found that arsenate is the degradation product of methylarsonic acid. Holm et al. (1980) found good agreement between model predictions and experimental data of arsenate as the degradation product of methylarsonic acid. In our study inorganic As concentrations remained relatively constant or increased slightly over time (Figure 7). In general, under both oxidized and reduced conditions, inorganic As concentrations were higher at pH 3 compared to pH 6. The average concentration of inorganic As under oxidized and reduced conditions at pH 6.0 was 0.025 mg/l and 0.084 mg/l, respectively, compared to 0.344 mg/l and 0.140 mg/l, respectively, at pH 3.0.

The most substantial increase in inorganic As concentrations (0.19 mg/l) was found at pH 8.0 under oxidized conditions. Holm et al. (1980) found gains of approximately 2 mg/l As(V) during methylarsonic acid degradation, but their spike (19 mg/l) was considerably larger than

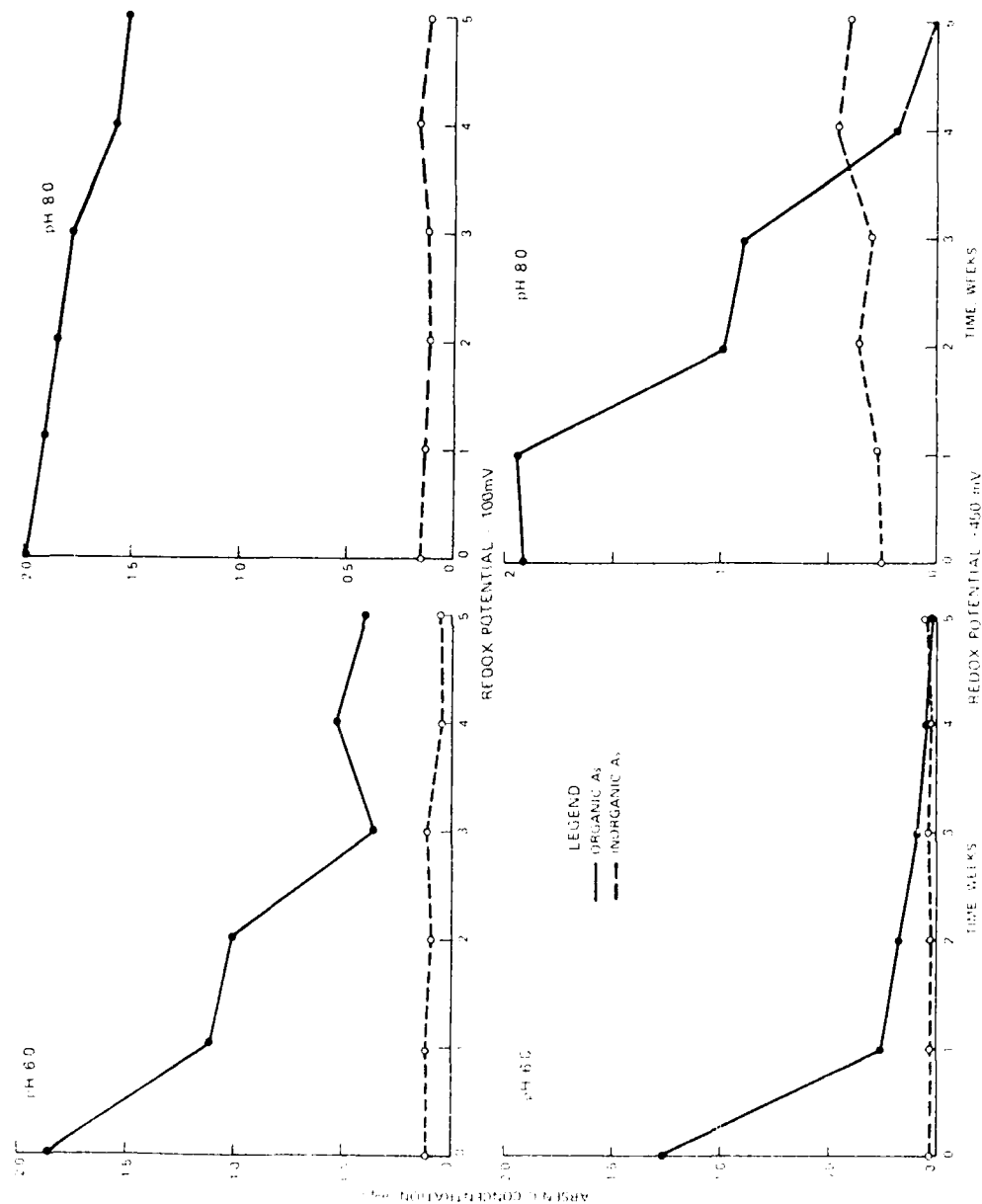


Figure 7. Influence of oxidation status and pH on water soluble added organic As in Texas City sediment suspensions.

the one used in this study (2.22 mg/l). At pH 6.0, arsenate adsorption is much more pronounced than at pH 8.0. Arsenate produced by degradation of DSMA at pH 6.0 may therefore have been rapidly adsorbed. At pH 8.0 under reduced conditions, very little DSMA disappeared from solution; very little arsenate was therefore produced. Only at pH 8.0 under oxidized conditions were degradation and adsorption-desorption conditions optimum for observing a buildup of inorganic As as DSMA disappeared.

Redox potential was maintained at -100 mV for the DSMA experiment instead of at -150 mV as in the previous experiment when As(V) was added to the sediment. Instead of a buildup of As(III) at -100 mV, however, As(III) concentrations were undetectable at pH 6.0 following four weeks of incubation and showed a marked decrease at pH 8.0. These data indicate that As(V) reduction may be favored at redox potentials lower than -100 mV.

Inorganic As concentrations at time 0 were higher in some treatments than solubilization of the entire amount of native sedimentary As could explain (a maximum of 0.035 mg/l). This indicates that some degradation of DSMA may have occurred immediately.

A plot of $\ln [\text{organic As}]_0 / [\text{organic As}]_t$ versus time t for each Eh-pH combination (Figure 8) resulted in a straight-line function. The straight line indicated first-order kinetics where decrease of organic As (DSMA) could be predicted as a function of time by:

$$\ln [\text{organic As}]_0 / [\text{organic As}]_t = Kt$$

where $[\text{organic As}]_0$ = initial concentration of DSMA

$[\text{organic As}]_t$ = concentration of DSMA at time t

K = first-order rate constant

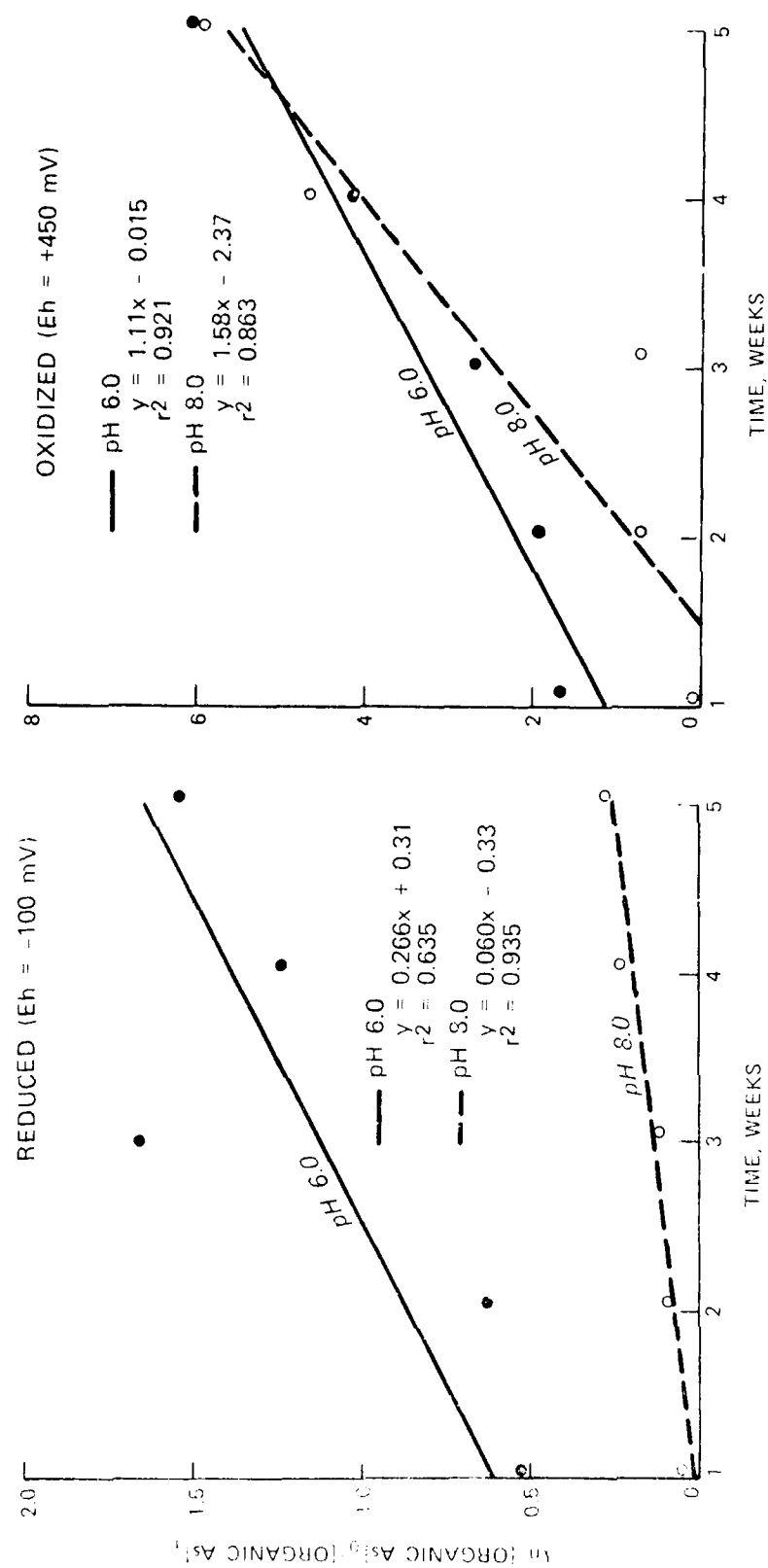


Figure 2. Linear regression equations describing disappearance of AsMA.

AD-A139 032

DREDGING OPERATIONS TECHNICAL SUPPORT PROGRAM
TRANSFORMATION FIXATION AND (U) ARMY ENGINEER
WATERWAYS EXPERIMENT STATION VICKSBURG MS

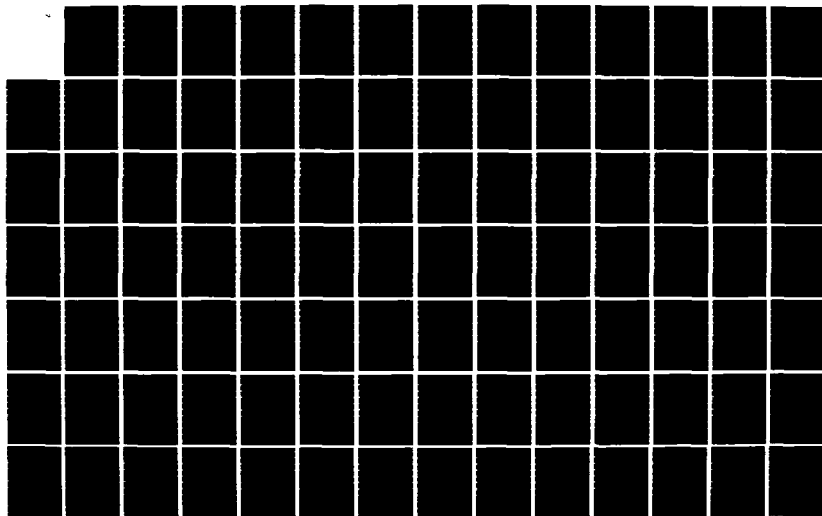
2/3

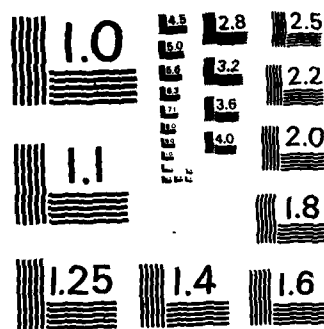
UNCLASSIFIED

JAN 84 WES-TR-D-84-1

J M BRANNON
F/G 13/2

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

First-order kinetics have also been shown by others (Hiltbold, 1975; Holm et al., 1980; Shariatpanahi et al., 1981) to adequately describe degradation of methylarsonic acid. Examination of the first-order rate constants in Figure 8 (slopes of the regression equations) showed that disappearance of DSMA from solution was slowest at pH 8.0 under reduced conditions and fastest at pH 8.0 under oxidized conditions. First-order rate constants for DSMA disappearance under oxidized conditions were 1.11 week^{-1} and 1.58 week^{-1} compared to rate constants of 0.06 week^{-1} and 0.266 week^{-1} under reduced conditions. These results indicate that the oxidation status of the sediment suspension strongly affected disappearance of DSMA (presumably via demethylation). Arsenic was not lost from the system as arsines; no As was detected in the arsenic adsorbing solution through which all gasses leaving the system were passed.

Short-Term As Releases

In some commonly encountered environmental situations such as disposal of dredged material and sediment resuspension by propellor wash or storms, direct mixing of bottom sediments with water will occur. The duration of such mixing is generally low (Wright et al., 1978; Lee, 1970), and is usually limited to minutes or days. The magnitude of short-term As releases and the factors influencing such releases are therefore of interest.

Distilled Water Leaching

Sediments previously incubated for 45 days under anaerobic conditions were leached with distilled water for 30 min. Arsenic leachate concentrations are presented in Table 10. In the short-term leachates, As(III) was the predominant As species found, with all but Indiana Harbor among the unamended sediments and Detroit, Menominee, and Indiana Harbor among the amended sediments containing greater than 50 percent As(III) in their leachates. Total As concentration in amended sediment leachates was highly correlated with exchangeable phase (EX) As concentrations ($r = 0.848$, $p < 0.01$). Total As concentrations in unamended sediment leachates were related to both interstitial water (IW) and EX As concentrations by the following equation: $\text{leachate As} = 1.50 \text{ IW As} + 0.16 \text{ EX As} + 0.007$ ($r^2 = 0.964$, $p < 0.01$).

Arsenic(III) concentrations in the short-term leachates were significantly ($p < 0.05$) correlated with interstitial water As(III) concentrations in amended ($r = 0.649$) and unamended ($r = 0.823$) sediments and also with exchangeable As(III) concentrations in amended ($r = 0.725$) and unamended ($r = 0.816$) sediments.

These results indicate that when anaerobic sediments from freshwater and saline environments are subjected to short-term mixing, As(III) will be the major As species released. The magnitude of the As(III) releases and total As releases are directly related to the amount of As(III) and total As in the sediment interstitial water and exchangeable phase. These results agree with previous findings that chemicals in the interstitial water and exchangeable phases are more mobile than other sediment phases (Brannon et al., 1977; Brannon et al., 1980).

Table 10
Concentration ($\mu\text{g/l}$) of As(V), As(III), Organic As, and
Total As in Sediment Distilled Water Leachates

Sediment	As(V)		As(III)		Organic As		Total As	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	0.6	33.0	8.0	310.0	ND	127.0	27.0	470.0
Corpus Christi	1.3	125.0	5.5	544.0	ND	ND	6.8	669.0
Detroit	ND	13.0	2.0	3.0	ND	2.0	2.0	18.0
Indiana Harbor	3.3	24.0	2.5	41.0	ND	27.0	5.8	92.0
Johnson Creek	ND	4.0	4.4	102.0	ND	64.0	4.4	170.00
Menominee	13.0	19.0	14.0	41.0	ND	37.0	27.0	92.0
Michigan City	0.9	16.0	2.5	40.0	ND	19.0	3.4	75.0
Milwaukee	0.5	17.0	1.4	31.0	ND	8.0	1.9	56.0
Oakland	ND	ND	3.0	83.0	ND	41.0	3.0	124.0
Seattle	ND	ND	6.7	256.0	ND	50.0	6.7	306.0

ND = Not Detected

The predominance of As(III) in short-term As releases from anaerobic sediments indicates that caution must be utilized when evaluating the environmental impact of such releases. Arsenic(III) is much more toxic than As(V) or methylated As compounds (Peoples, 1975).

To evaluate the impact of sediment properties on short-term As releases, distribution coefficients (K) were calculated as described by Houle and Long (1980). The distribution coefficient is $K = M_s/M_w$ where M_s is the mass of As in the sediment, expressed as $\mu\text{g As/g dry weight sediment}$ and M_w is the mass of As in the leachate, expressed as $\mu\text{g As/g dry weight of sediment}$.

Distribution coefficients for short-term release of As from unamended and amended sediments are presented in Table 11. Distribution coefficient values for total As ranged from 37.9 to 1425.0 in unamended sediments and from 31.8 to 1200.0 in amended sediments. Distribution coefficients were lower in amended compared to unamended sediments in seven out of the ten sediments, indicating that a higher fraction of the total sediment As had been released. Addition of As to sediments would therefore be expected to increase the percentage of sediment As available for short-term release.

Distribution coefficients following short-term leaching of unamended and amended sediments were related to total and extractable Fe as shown in Table 12. Distribution coefficients in unamended sediments were generally related to total Fe while those in amended sediments were also related to extractable Fe. This implies that added As, which generally composed the majority of sediment As, was adsorbed by more hydrous extractable Fe compounds. Native As may have been fixed or occluded by more crystalline Fe oxides. These results indicate that Fe,

Table 11
Arsenic Distribution Coefficients in Short-Term Leachates of Anaerobic Sediments

Sediment	As		As(V)		As(III)		Organic As	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	104.7	41.8	1500.0	595.5	112.5	63.4	ND	154.7
Corpus Christi	375.0	31.8	1961.5	170.4	463.6	39.2	ND	ND
Detroit	1425.0	1200.0	ND	1161.5	1425.0	7200.0	ND	10800.0
Indiana Harbor	1616.4	305.7	2840.9	1171.9	3750.0	686.0	ND	1041.7
Johnson Creek	147.7	114.1	ND	4850.0	147.7	190.2	ND	303.1
Menominee	37.9	215.0	78.9	1040.8	73.2	482.3	ND	618.0
Michigan City	169.1	257.7	638.9	1207.8	230.0	483.1	ND	1017.1
Milwaukee	144.7	339.7	550.0	1119.1	196.4	613.7	ND	2378.1
Oakland	225.0	156.7	ND	ND	225.0	234.0	ND	473.8
Seattle	119.4	63.9	ND	ND	119.4	76.4	ND	391.0

ND = Arsenic species not detected in leachate

Table 12
Correlations Between Short-Term Leachate As Distribution
Coefficients (K) and Sediment Properties

Sediment Properties	As		As(V)		As(III)		Organic As	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Total Fe	0.834**	0.224	0.750	-0.039	0.981**	0.149	†	0.097
Extractable Fe††	0.730**	0.866**	0.575	-0.101	0.453	0.894**	†	0.869**

** = p 0.01

† = No K available

†† = Sum of easily + moderately reducible phase Fe

in addition to its impact on As adsorption (Pierce and Moore, 1980, 1982), also strongly influences the short-term release of the various As species. Higher sedimentary Fe content will enhance the short-term retention of native As in sediments.

Saline Water

Five anaerobically incubated amended and unamended sediments were also leached with water of varying salinity. Concentrations of As(V), As(III), and organic As in amended sediment leachates are presented in Table 13. Arsenic(V) and As(III) concentrations in unamended sediment leachates are presented in Table 14; no organic As was leached from any of the unamended sediments. Alterations in leachate salinity did not impact leachate pH (Table 15). Higher concentrations of As(V), As(III), and organic As were released from amended compared to unamended sediments, but the impact of initial salinity on As leachate concentrations was minimal. In unamended sediments only, As(V) concentrations in 35 ‰ leachates were significantly ($p < 0.05$) higher than As(V) concentrations in distilled water leachates.

Results of this study indicate that varying the salinity of leachates had little impact on the short-term release of As species from sediments. Trends observed for Corpus Christi, the only saline sediment extracted, were similar to those observed for the other four freshwater sediments.

Results of short-term leaching with distilled water and water of varying salinity showed that addition of As to sediments resulted in increased As release, in agreement with previous findings (Arnott and Leaf, 1967; Johnson and Hiltbold, 1969). The relationship between

Table 13
Concentrations ($\mu\text{g}/\ell$) of As(V), As(III), and Organic As
in Saline Leachates of Amended Sediments

Sediment	As(V)				
	Salinity				
	0 ‰	5 ‰	15 ‰	25 ‰	35 ‰
Corpus Christi	125	200	103	178	138
Detroit	13	12	15	14	11
Indiana Harbor	24	25	68	54	98
Menominee 1	19	36	39	46	30
Michigan City	16	5	6	6	8

Sediment	As(III)				
	Salinity				
	0 ‰	5 ‰	15 ‰	25 ‰	35 ‰
Corpus Christi	544	450	507	582	609
Detroit	3	7	9	14	17
Indiana Harbor	41	30	26	41	18
Menominee 1	41	18	31	32	44
Michigan City	40	55	63	61	69

Sediment	Organic As				
	Salinity				
	0 ‰	5 ‰	15 ‰	25 ‰	35 ‰
Corpus Christi	ND	48	57	35	ND
Detroit	2	10	ND	ND	ND
Indiana Harbor	27	3	8	ND	6
Menominee 1	32	3	64	2	7
Michigan City	19	ND	ND	ND	ND

ND = Not Detected

Table 14
Concentrations ($\mu\text{g/l}$) of As(V) and As(III) in
Saline Leachates of Unamended Sediments

Sediment	As(V)				
	Salinity				
	0 ‰	5 ‰	15 ‰	25 ‰	35 ‰
Corpus Christi	1.3	1.5	2.4	3.9	6.7
Detroit	ND	0.7	0.8	0.6	ND
Indiana Harbor	3.3	2.2	4.3	2.3	4.0
Menominee 1	13.0	15.0	17.0	17.0	18.0
Michigan City	0.9	0.9	0.8	1.2	1.4

Sediment	As(III)				
	Salinity				
	0 ‰	5 ‰	15 ‰	25 ‰	35 ‰
Corpus Christi	5.5	4.3	3.2	1.8	1.0
Detroit	2.0	1.5	1.9	2.7	3.3
Indiana Harbor	2.5	4.0	2.0	4.0	3.3
Menominee 1	14.0	2.0	4.0	4.0	5.0
Michigan City	2.5	2.6	2.9	2.9	2.5

ND = Not Detected

Table 15
Effect of Salinity (°/oo) on Short-Term Leachate pH

<u>Sediment</u>	<u>Initial Salinity</u>				
	<u>0 °/oo</u>	<u>5 °/oo</u>	<u>15 °/oo</u>	<u>25 °/oo</u>	<u>35 °/oo</u>
Corpus Christi	8.4	8.4	8.3	8.3	8.2
Detroit	8.5	8.5	8.5	8.5	8.5
Indiana Harbor	6.8	6.8	7.0	6.9	7.0
Menominee 1	6.7	6.7	6.7	6.8	6.8
Michigan City	6.9	7.0	7.0	7.0	7.0

increasing Fe concentration and decreasing As releases also agrees with the findings of others (Tammes and de Lint, 1969; Johnson and Hiltbold, 1969).

The limited impact of leachate salinity on As release did not agree with the findings of Wiklander and Alvelid (1951) who reported suppression of As leaching by water of increasing salinity and Huang (1975) who reported the opposite for hydroxy - Al complexes of both biotite and K depleted biotite. Arsenic releases in the biotite studied by Huang (1975), however, were probably controlled by Al, a parameter that did not impact short-term releases in this study.

Upon mixing, short-term impacts of anaerobic sediments contaminated with As should be greatest when sediments are low in Fe and high interstitial water and exchangeable phase As. Releases of As(V), As(III), and organic As from sediment should be relatively insensitive to the salinity of the mixing water.

Leaching Under Controlled Eh-pH Conditions

Three additional sediments, some characteristics of which are described in Table 16, were subjected to one week of leaching under controlled Eh-pH conditions. One week of leaching, while too short to represent a "steady-state" or "equilibrium" concentration, nevertheless provides useful information on the concentration and speciation of As releases. No additional As was added to these sediments. A relatively short leaching period was chosen because of the destructive impacts of sediment sand on the Eh-pH incubation vessels.

Table 16
Some Physical and Chemical Characteristics of Sediments Leached
for One Week Under Specified Eh-pH Conditions
 (From Folsom et al., 1981)*

Sediment	% Sand* >50 μ m	% Silt* 2-50 μ m	% Clay* <2 μ m	Total Sb, μ g/g	Total* As, μ g/g	Total* Fe, mg/g
Menominee, Site 3	16.3	59.3	24.2	0.8	317.0	27.4
Baltimore Harbor	10.4	83.3	6.3	0.8	27.2	28.1
Indiana Harbor	38.8	46.6	14.6	17.5	37.5	291.3

Figures 9 and 10 present the distribution of various As species in the ammonium sulfate extractable fraction of sediments incubated for one week under controlled Eh-pH conditions. Statistical analyses showed that among sediments, As(V) and As(III) were higher at pH 8.0 than pH 5.0 and 6.5, regardless of Eh. This behavior would be expected of As(V) because adsorption of As(V) by soils, clay minerals, and amorphous iron hydroxides has been shown to peak in the pH range of 3.5 to 5.3 (Frost and Griffin, 1977; Galba, 1972a; Pierce and Moore, 1982). Johnston (1978) has also demonstrated that arsenate release from an anaerobic Moon silt loam soil peaked after 6 days. Arsenate concentrations should therefore be at a maximum in the sediment suspension.

Adsorption of As(III) by anion exchange resins, clay minerals, and amorphous iron oxides has been reported to increase as pH increases (Everest and Popiel, 1957; Frost and Griffin, 1977; Pierce and Moore, 1980, 1982). Results of this study, however, show that As(III) concentrations were highest at pH 8.0. This also contradicts results of work reported previously where higher concentrations of water soluble As(III) were found at pH 5.0 and pH 6.5 compared to 8.0 in anaerobic Texas City sediments following As(V) addition. Johnston (1978) has also reported that under anaerobic conditions, As(III) concentrations were higher at pH 7.5 compared to pH 5.0.

The concentrations of As(III) reached are not strictly due to leaching of sedimentary As(III). Johnston (1978) found that in anaerobic sediment slurries, high levels of As(III) (250 ppb) could be produced after only 4 days of incubation. In this study reduction of As(V) to As(III) was apparently occurring under both anaerobic and aerobic conditions. These findings are in agreement with those of other workers

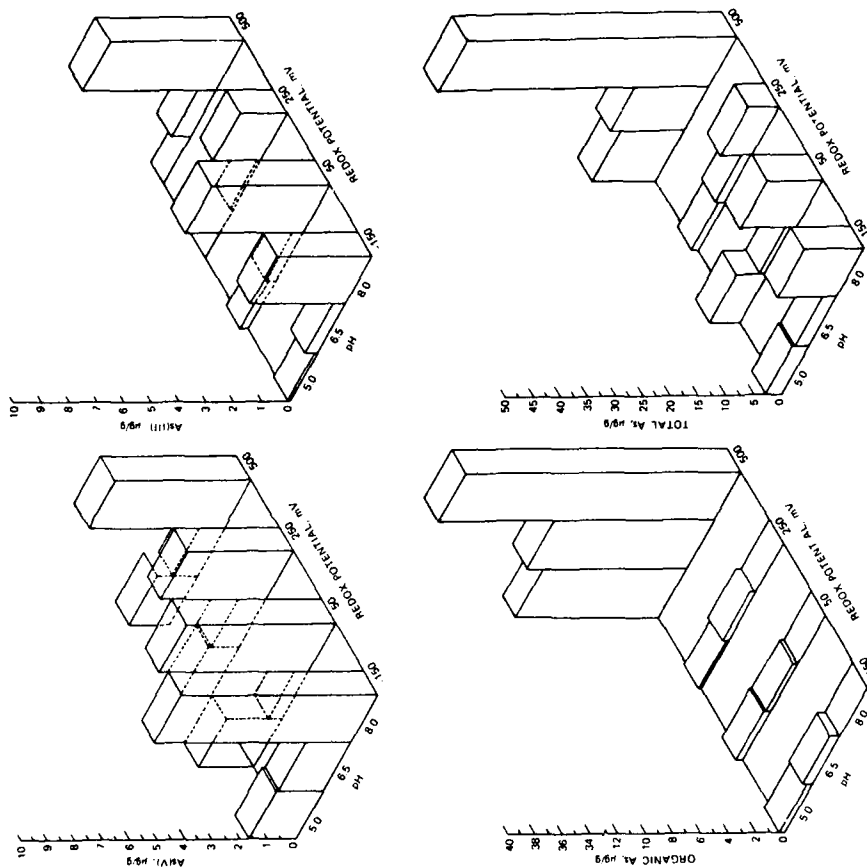
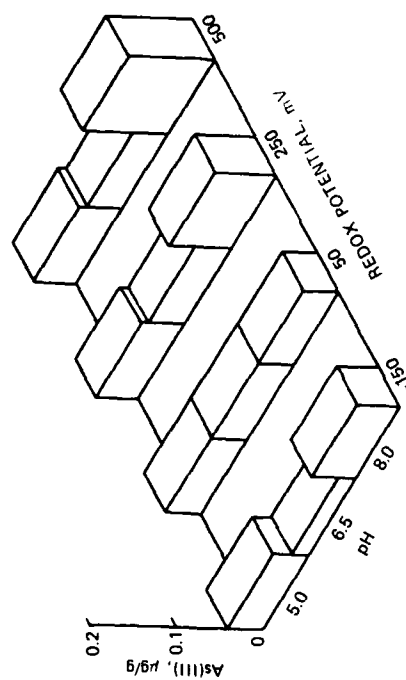
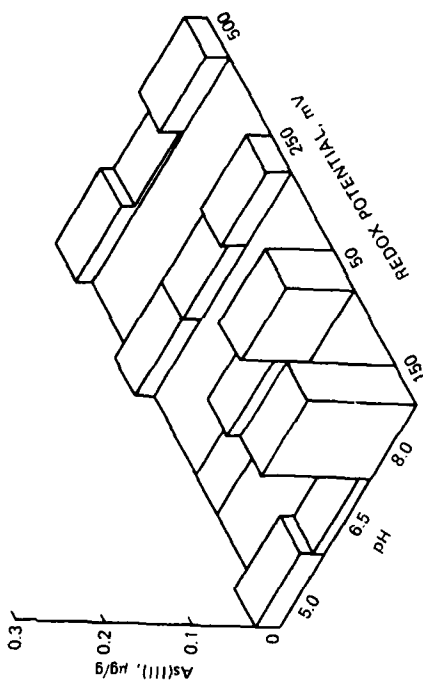


Figure 9. Influence of oxidation status and pH on short-term release of extractable As from Menominee 3 sediment suspensions.



INDIANA HARBOR



BALTIMORE HARBOR

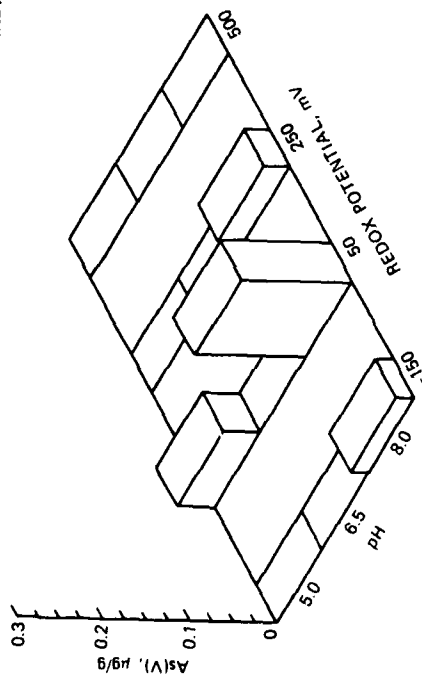
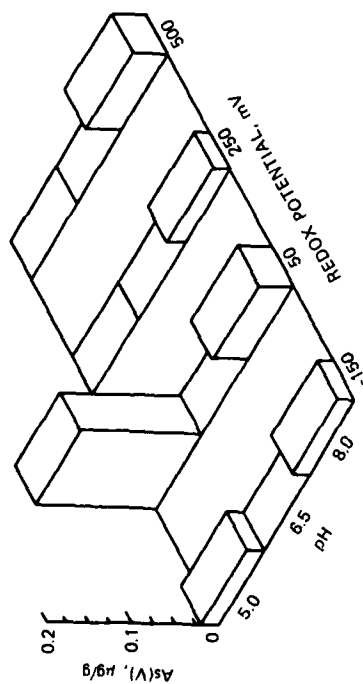


Figure 10. Influence of oxidation status and pH on short-term release of extractable As from Indiana and Baltimore Harbor sediment suspensions.

(McBride and Wolfe, 1971; Heimbrook, 1974; Shariatpanahi and Anderson, 1981; Myers et al., 1973) who have shown that reduction of As(V) by pure bacterial cultures occurs in both the presence and absence of oxygen.

It appears that the higher concentrations of As(III) extracted at pH 8.0 may have been due to removal of As(III) from the sediment exchange complex. The clear statistical trends exhibited in the ammonium sulfate extractable phase were not exhibited in the water soluble phase, but were present for exchangeable phase As(III) concentrations (Table 17), especially in Menominee 3 sediments where total As concentrations were high.

Concentrations of As species in the water soluble, exchangeable, and water soluble + exchangeable phases after one week of incubation are presented in Tables A1 through A3. The distribution of total As in the various sediment fractions (water soluble, water soluble + exchangeable, exchangeable, easily reducible, and moderately reducible) are presented in Tables A4 through A6. Iron and Al concentrations in the various fractions are presented in Tables A7 through A12. Water soluble Ca concentrations can be found in Table A13.

In sediments where organic As was detected, as in the case of Menominee site 3 and to a much lesser extent Baltimore Harbor, organic As was present in higher concentrations at an Eh of +500 mV. Organic As was detected at concentrations (0.01 $\mu\text{g/g}$) in Baltimore Harbor sediment suspended in pH 5.0 and an Eh of +500 mV and at pH 6.5 and an Eh of +250 mV (Table 3).

These results indicate that following one week's incubation under highly oxidized conditions, large amounts of organic As can be released from previously anaerobic sediment, especially those from Menominee. It

Table 17
Concentrations of Water Soluble Phase ($\mu\text{g}/\ell$) and Exchangeable
Phase ($\mu\text{g}/\text{g}$) As(III) as a Function of Eh and pH

Eh	pH	Indiana Harbor		Menominee 3		Baltimore Harbor	
		WS	EX	WS	EX	WS	EX
-150	5.0	1.1	0.03	ND	0.60	ND	0.03
-150	6.5	4.5	ND	37.0	NE	2.2	NE
-150	8.0	1.7	0.03	143.0	2.16	9.3	0.05
+50	5.0	14.0	ND	448.0	NE	14.0	NE
+50	6.5	4.5	ND	24.0	0.11	1.5	0.03
+50	8.0	3.5	0.01	114.0	2.68	ND	0.08
+250	5.0	1.7	0.04	17.0	NE	ND	0.02
+250	6.5	1.4	0.03	10.0	0.02	1.5	NE
+250	8.0	2.4	0.05	83.0	0.98	1.4	0.01
+500	5.0	ND	0.05	40.0	NE	ND	0.02
+500	6.5	2.2	0.02	27.0	0.44	ND	0.01
+500	8.0	3.9	0.07	87.0	3.78	ND	0.03

WS = Water Soluble As(III)

EX = Exchangeable Phase As(III)

ND = Not Detected

NE = None Extracted

is impossible from these data alone to judge if the extremely high concentrations of organic As (40.06 $\mu\text{g/g}$) were already present in the sediments or were formed by oxidation of more reduced arsines such as trimethyl arsine (Wood, 1974). Organic As was almost certainly present in the Menominee sediments because methylarsonic acid contaminated groundwater upwelling through the sediments is the main source of contamination (Anderson et al., 1978). Johnston (1978) found gradual accumulation of methylarsonic and dimethylarsinic acid under oxidized conditions in Barataria Bay sediment suspensions. He also noted high concentrations of a high boiling point As form, tentatively identified as trimethylarsine, on the second day of incubation.

Both leaching of organic As from the sediment and formation of additional As compounds by oxidation of arsines may have been occurring. It is difficult to comprehend how organic As concentrations at +500 mV can so greatly exceed that at other Eh levels in the absence of some type of in situ formation of organic As. However, the evidence for the presence of arsines is minimal. During the controlled Eh-pH leaching, arsine evolution from the sediment-water suspensions was not detected. In a separate arsine evaluation study, generation of volatile As compounds from amended sediments was minimal. Under anaerobic conditions Black Rock sediments released 23.9 $\mu\text{g As/m}^2$ and Michigan City sediments released 13.7 $\mu\text{g As/m}^2$. Volatile As compounds were not evolved from the other eight sediments under aerobic or anaerobic conditions. Arsenic losses from unamended sediments occurred primarily when the overlying water was aerobic (Table 18). An evolution rate of 6 $\mu\text{g As/m}^2/\text{week}$ could be detected in this experiment.

Table 18
Arsenic Losses ($\mu\text{g}/\text{m}^2$) from Unamended Sediments Whose
Overlying Water was Kept Anaerobic (Weeks 1-5)
and Aerobic (Weeks 6-8)

<u>Sediment</u>	<u>Treatment</u>	
	<u>Anaerobic</u>	<u>Aerobic</u>
Black Rock	18.0	9.0
Corpus Christi	ND	10.0
Detroit	20.4	17.2
Indiana Harbor	ND	7.2
Johnson Creek	ND	ND
Menominee I	ND	ND
Michigan City	ND	ND
Milwaukee	ND	7.9
Oakland	ND	11.0
Seattle	ND	17.1

ND = Not Detected

Long-Term As Releases

Leaching experiments were conducted with ten sediments to determine what As species would be released, the duration of the releases, the quantity of materials that would be released, and the sediment factors responsible for releases. This involved leachate analyses for the various As species initially (1/2 hour of shaking) and at subsequent monthly intervals for 6 months.

During the sampling procedure, any solids removed from the long-term leaching subsample by 0.45- μ m pore-size filtration were reintroduced into the incubation vessel with an appropriate quantity of As free distilled-deionized water. There were two reasons for this approach. First, it maintained a (relatively) constant solid to liquid ratio during the leaching period. Second, it provided the opportunity to extend the duration of the leaching study at any desired sampling frequency.

Prior to analyzing the leaching data, the movement of As species and Sb during the leaching period was expressed on a mass release basis. Net mass release is the change in the mass of chemical constituents in the water compared to the mass originally present in the same volume of water and was calculated using the method described by Plumb (1973). To calculate the total release of any one constituent, the following approach was used:

On sample day 1: $x \text{ released} = 160(x_1)$

On sample day 2: $x \text{ released} = 160(x_2) - (160 - y_1)(x_1)$

On sample day 3: $x \text{ released} = 160(x_n) - (160 - y_{n-1})(y_{n-1})$

where

x = species of interest

(x) = analytical concentration ($\mu\text{g/ml}$)

y = liquid remaining (ml) following sampling

subscript = sample day

A positive net mass release indicates movement of chemical constituents from the sediments into the water, and a negative value indicates the reverse process. Conversion of net mass release to a sediment dry weight basis was accomplished by dividing the mass of As or Sb released at each sampling period by 40 g, the dry weight of sediment used in each incubation.

Cumulative net mass release ($\mu\text{g/g}$) for a parameter at a specified sampling period is the summation of net mass releases for that specific parameter at a particular sampling period with all preceding net mass releases of that parameter. A cumulative release curve is obtained when such data are plotted as a function of sampling time.

Conductivity and pH

Leachate conductivity, summarized in Table 19, decreased markedly during the course of the experiment; a consequence of distilled-deionized water replacing leachate removed for analysis. On average, the initial leachate volume of 160 ml was replaced 5.84 times ($934 \text{ ml} \pm 47 \text{ ml}$) during the course of the experiment for the 10 sediments. The most dramatic reduction in leachate conductivity occurred following the initial half-hour leach at time 0. Leachate conductivities from saline sediments (Black Rock, Corpus Christi, Johnson Creek, Oakland, and Seattle) decreased most rapidly; conductivities at time 1 ranged from 7 percent to 26 percent of the conductivity measured at time 0.

Table 19
Average Conductivity ($\mu\text{mhos/cm}$) During
the Long-Term Leaching Tests

Sediment	Time, months						
	0	1	2	3	4	5	6
Black Rock Harbor	27800	7320	3270	2500	1390	1470	1930
Corpus Christi	28900	5760	2450	1720	870	750	510
Detroit River	1980	1510	1400	950	700	750	610
Indiana Harbor	1180	928	590	560	400	360	340
Johnson Creek	29700	6800	3060	1980	1070	730	1480
Menominee River	490	565	290	260	230	280	210
Michigan City	1470	1320	890	680	350	340	230
Milwaukee Harbor	890	1130	686	610	560	440	390
Oakland Harbor	28400	1990	680	310	150	125	80
Seattle	31900	4200	1930	1700	950	790	1210

Leachate pH changes, summarized in Table 20, were a possible consequence of the carbonate and sulfur content of the sediments. Sediments containing the lowest amounts of calcium carbonate equivalent (Table 5) were less buffered, and therefore less capable of withstanding processes such as sulfur oxidation that tend to lower pH. Total sulfur content of the sediments was significantly ($p < 0.02$) correlated ($r = 0.709$) with leachate pH after 6 months. Sediments containing greater than 7 percent CaCO_3 equivalent generally maintained a pH of approximately 7.0 or greater. Sediments low in CaCO_3 equivalent and high in total sulfur (Black Rock, Johnson Creek, and Seattle) generally attained the lowest leachate pH's.

Duration and Speciation of Long-Term As Releases

Total As. Cumulative net mass releases of As from unamended sediments during aerobic leaching are presented in Figure 11. Releases of sediment As were generally linear with the exception of Johnson Creek and Seattle sediments, where asymptotic limits on As releases were reached. Cumulative net mass releases of As from amended sediments during aerobic leaching (Figure 12) generally exhibited release patterns similar to that in unamended sediments. The similarity of release patterns was indicated by a highly significant ($p < 0.01$) correlation ($r = 0.609$, $n=70$) between amended and unamended net mass releases of As. In amended sediments, Black Rock, in addition to Johnson Creek and Seattle sediments, also reached an asymptotic limit on release.

These results indicate that in the majority of sediments, releases of As will persist for at least six months under agitated, aerobic conditions. Leaching conditions utilized in this study were designed to

Table 20
Average Leachate pH During the Long-Term Leaching Tests

Sediment	Time, months						
	0	1	2	3	4	5	6
Black Rock Harbor	8.0	7.1	6.7	5.9	6.8	5.7	5.4
Corpus Christi	8.4	7.9	7.8	7.5	7.8	7.3	7.2
Detroit River	8.5	8.3	8.4	8.3	8.4	8.3	7.9
Indiana Harbor	6.8	6.9	7.1	7.1	7.7	7.7	7.3
Johnson Creek	8.0	6.9	6.7	6.0	7.1	6.3	6.2
Menominee River	6.7	7.3	7.1	6.9	8.2	8.3	7.6
Michigan City	6.9	7.0	7.0	6.9	7.5	7.4	7.5
Milwaukee Harbor	6.8	7.6	7.4	7.5	7.4	7.2	6.9
Oakland Harbor	8.5	7.0	6.5	6.3	7.4	6.6	6.5
Seattle	8.2	6.6	6.3	5.5	5.3	4.5	4.1

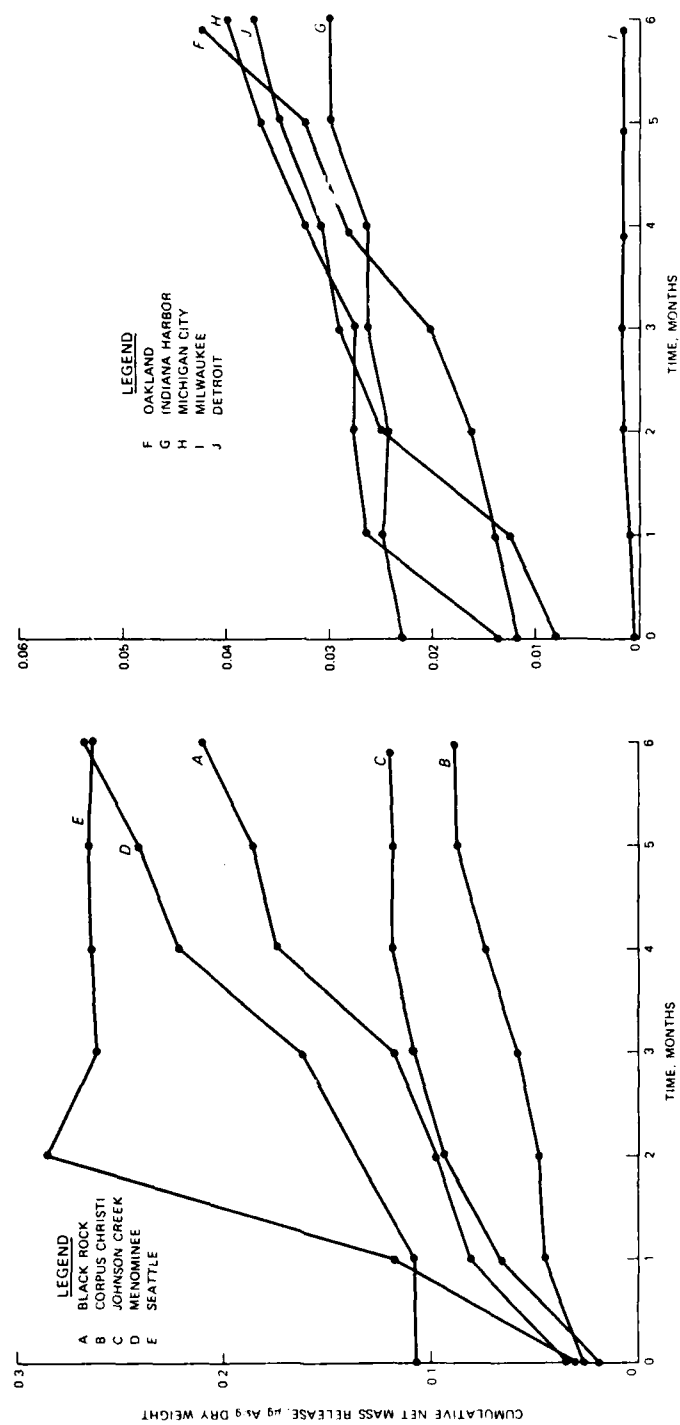


Figure 11. Cumulative As release from unamended sediments under aerobic conditions (Note scale difference between graphs).

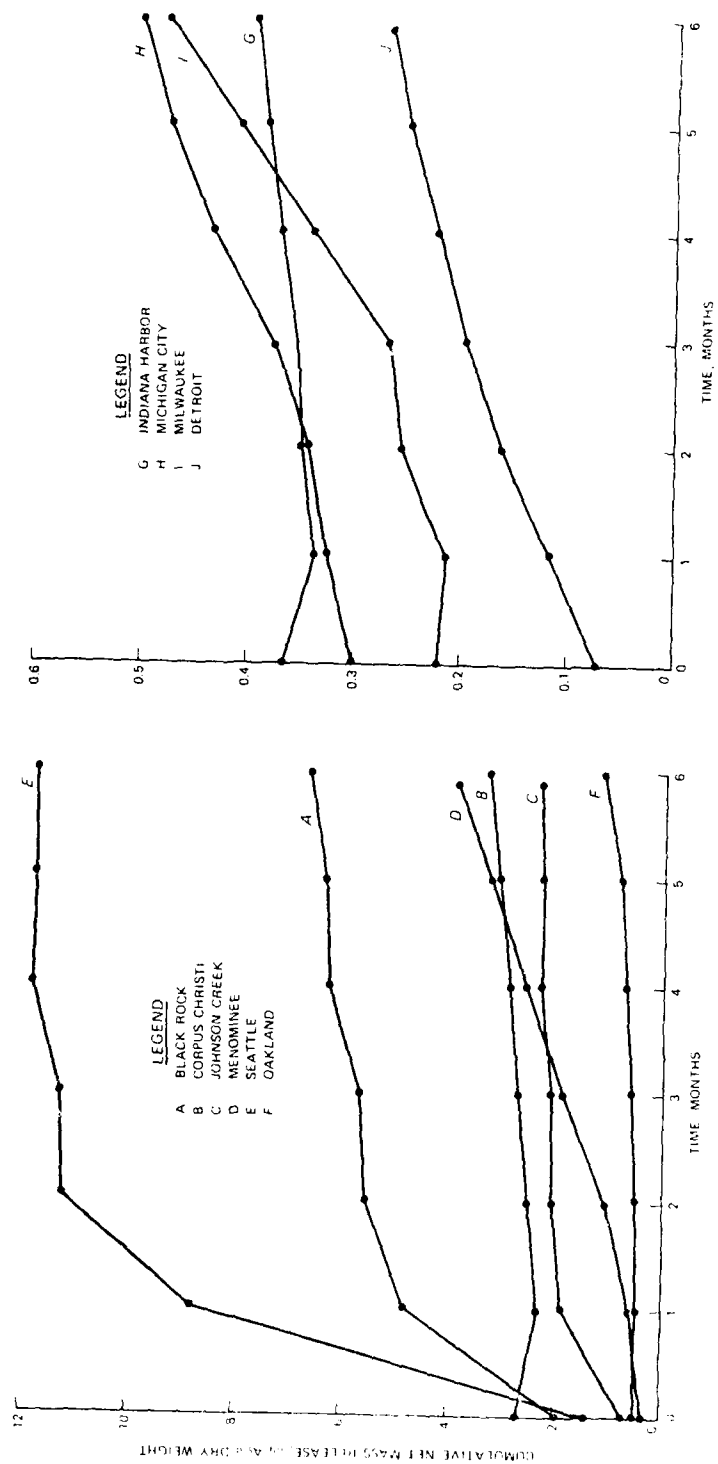


Figure 12. Cumulative As release from amended sediments under aerobic conditions (Note scale difference between graphs).

simulate a "worst case" situation where the entire mass of sediment was constantly exposed to the leaching solution and the liquid-front movement (i.e. as in a soil column) was static. Sediment particles may also have been abraded during leaching, making them more susceptible to extraction. However, even under these worst case conditions, asymptotic limits on releases, indicating that all As available for release had been released (Clement and Faust, 1981), were reached. The duration of release of the various As species will now be examined.

Arsenic(V). Cumulative net mass releases of As(V) from unamended (Figure 13) and amended (Figure 14) sediments were generally similar to releases of total As. Cumulative As(V) releases following six months of leaching were significantly ($p < 0.01$) correlated with total As releases in amended ($r = 0.981$) and unamended ($r = 0.906$) sediments. The general trends in the As(V) release patterns include low initial releases followed by linear releases. Asymptotic release patterns were noted, however, for Black Rock and Seattle among amended sediments and Johnson Creek, Seattle, and Indiana Harbor among unamended sediments.

Some sediments, such as Johnson Creek and Black Rock, exhibited asymptotic release in amended treatments and linear release in unamended treatments. One reason for this is that As(V) releases from amended sediments were an order of magnitude higher than unamended sediment releases, resulting in differences of scale that obscured minor releases from amended sediments. In amended sediments exhibiting asymptotic release, the added As contributed to large initial releases in the first month that rarely persisted following two months of leaching.

These results indicate that mixing anaerobic sediments with aerobic water should not result in large short-term (1/2 hour of mixing)

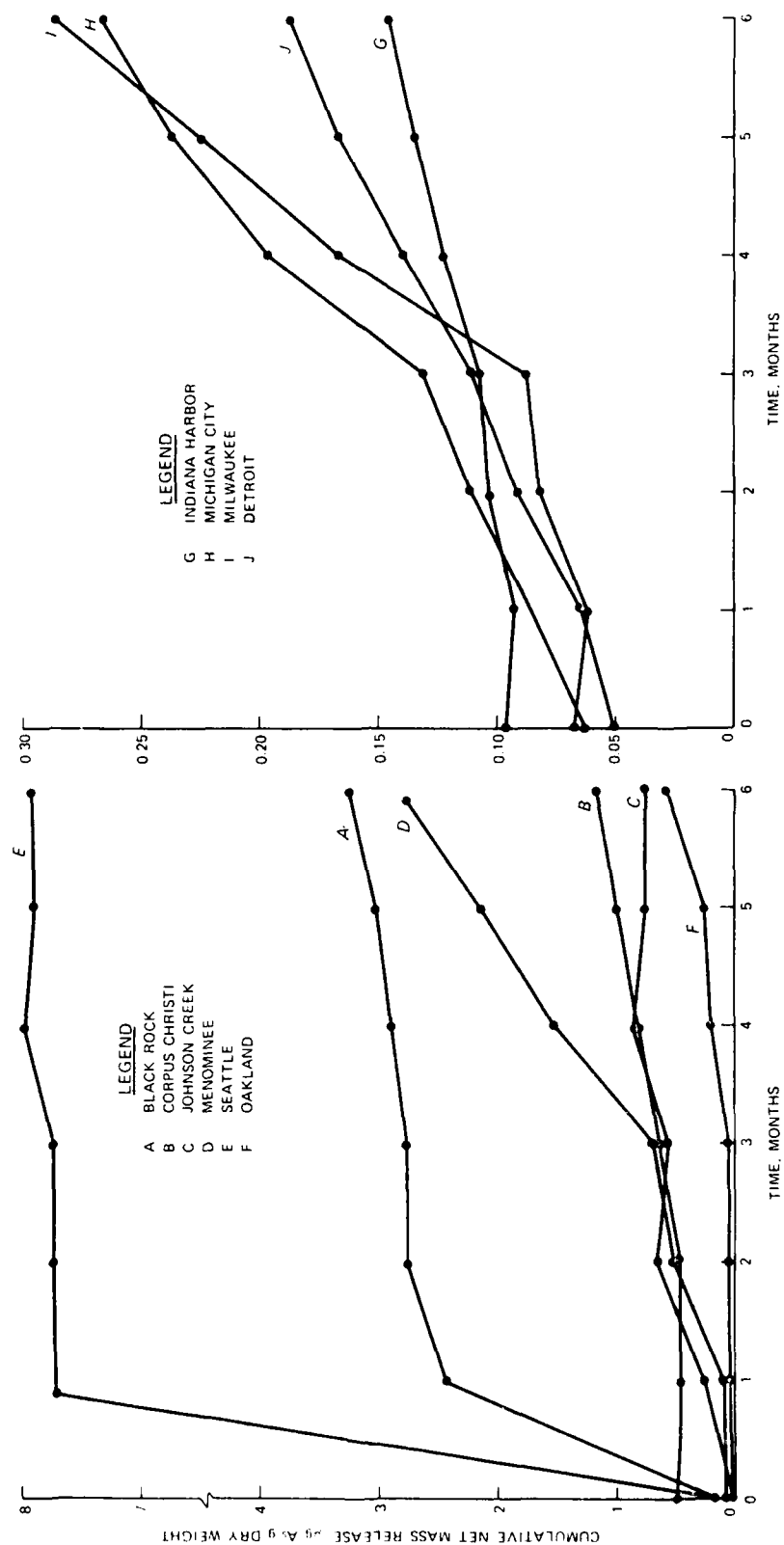


Figure 13. Cumulative As(V) release from amended sediments under aerobic conditions (Note scale difference between graphs).

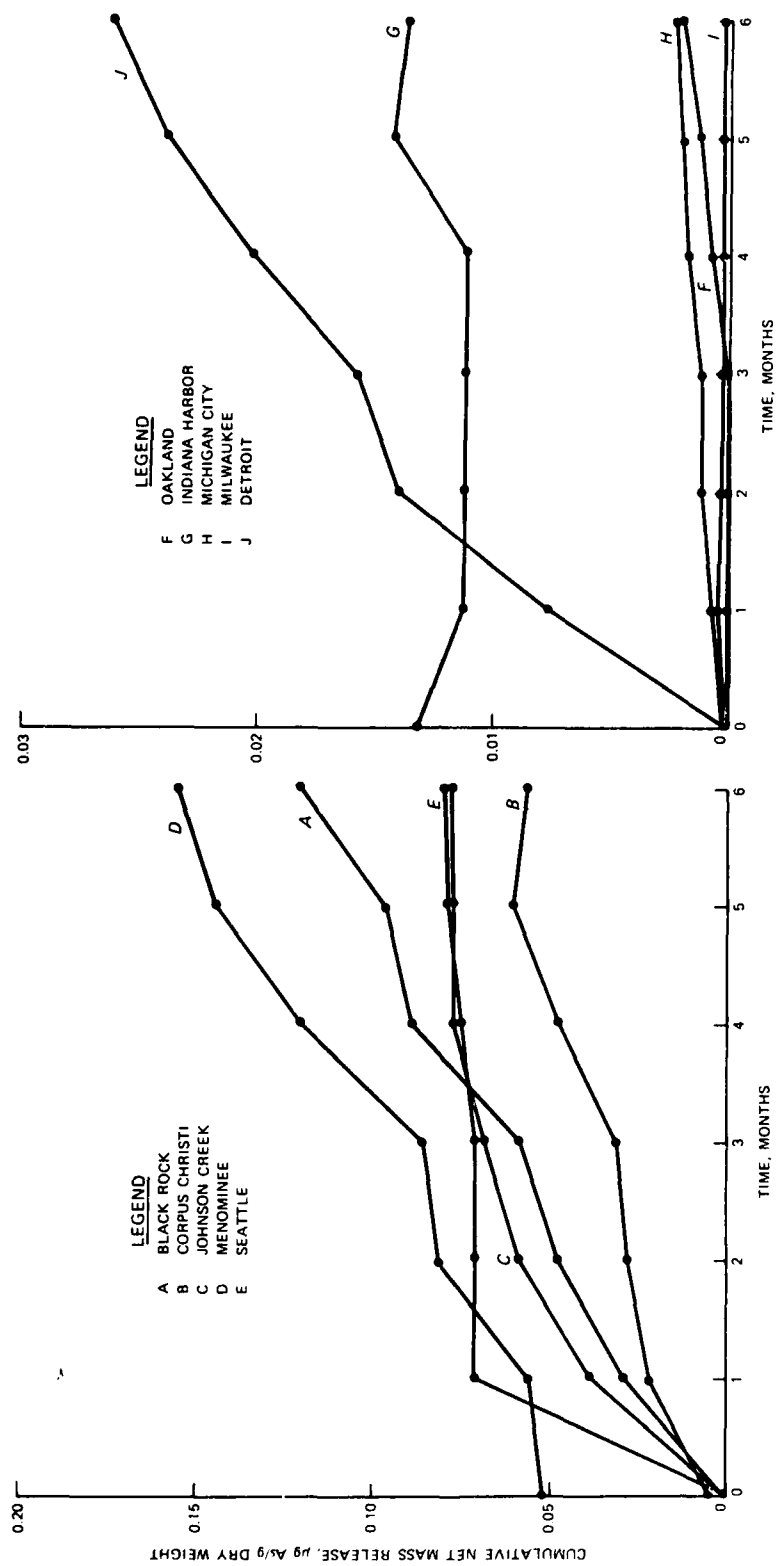


Figure 14. Cumulative As(V) release from unamended sediments under aerobic conditions (Note scale difference between graphs).

releases of As(V), even in sediments which have recently experienced a large influx of As(V). If the mixing is prolonged (one month or more), substantial releases of As(V) can be expected from some sediments. In other sediments, up to three months of mixing is required before substantial releases of As(V) will occur.

Arsenic(III). Cumulative As(III) releases from unamended (Figure 15) and amended (Figure 16) sediments differed substantially from that observed for total As and As(V). In most sediments, the majority of As(III) release occurred initially when anaerobic sediments were leached for 30 min. For sediments that released As(III) after the initial releases, substantial releases did not persist following the second month of leaching.

A number of recent papers (Oscarson et al., 1980; Oscarson et al., 1981a; Oscarson et al., 1981b) have demonstrated that Mn in lake sediments abiologically oxidized As(III) to As(V). If this process was occurring in our sediments, an inverse relationship between sediment manganese oxides and As(III) would be expected. This was indeed the case. The log of As(III) release was significantly ($p < 0.05$) correlated with easily reducible + moderately reducible (ERM/R) Mn in amended ($r = -0.772$) and unamended ($r = -0.751$) sediments. In addition, sediments from Black Rock, Johnson Creek, Oakland, and Seattle which contain less than 80 $\mu\text{g/g}$ of extractable Mn (easily + moderately reducible) were the only sediments other than unamended Michigan City sediments to release substantial amounts of As(III) after the initial releases.

Sediments, especially those high in Mn, should release As(III) only initially when mixed with aerobic water. Sediments continually mixed or

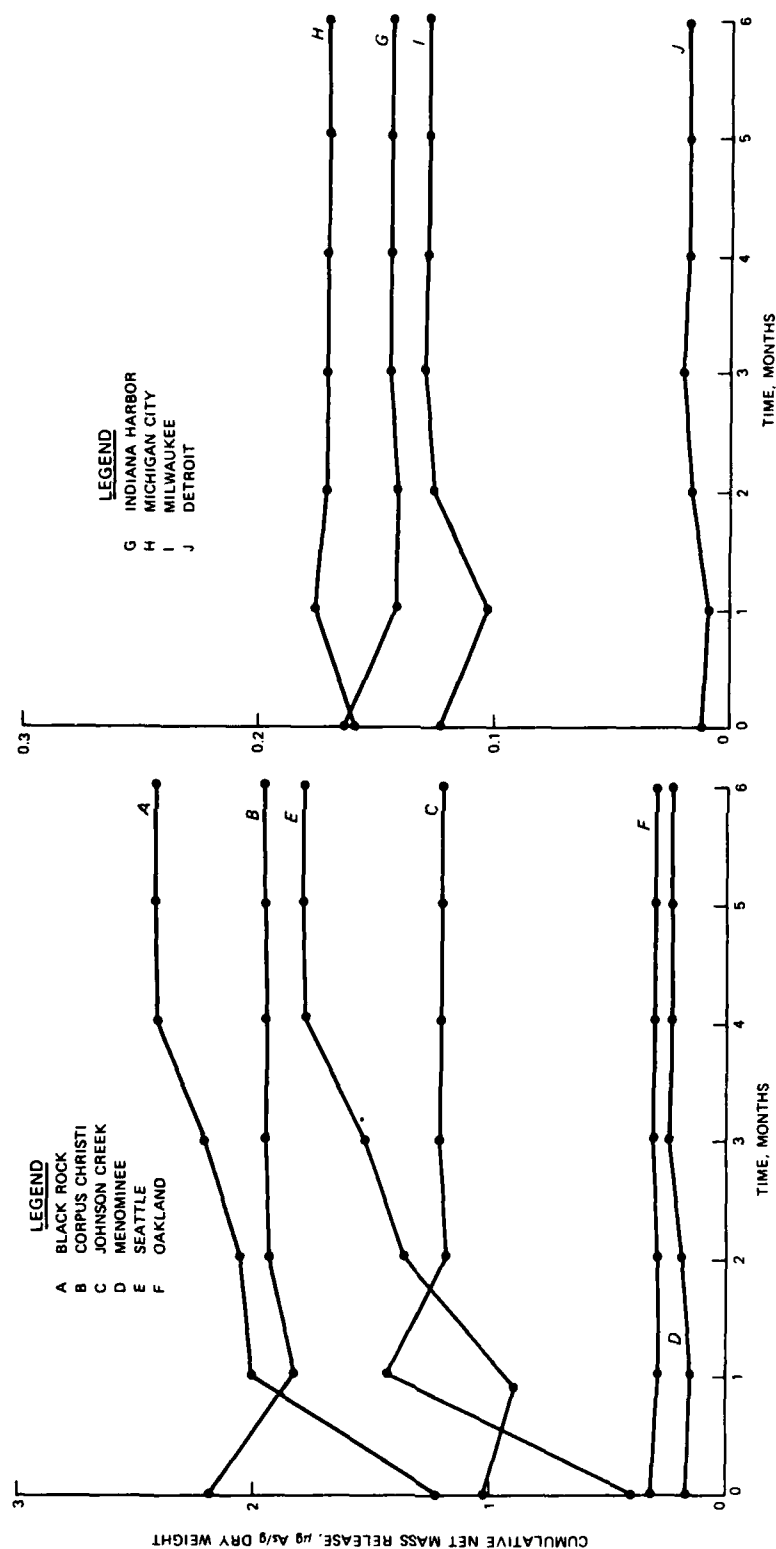


Figure 15. Cumulative As(III) release from amended sediments under aerobic conditions
(Note scale difference between graphs).

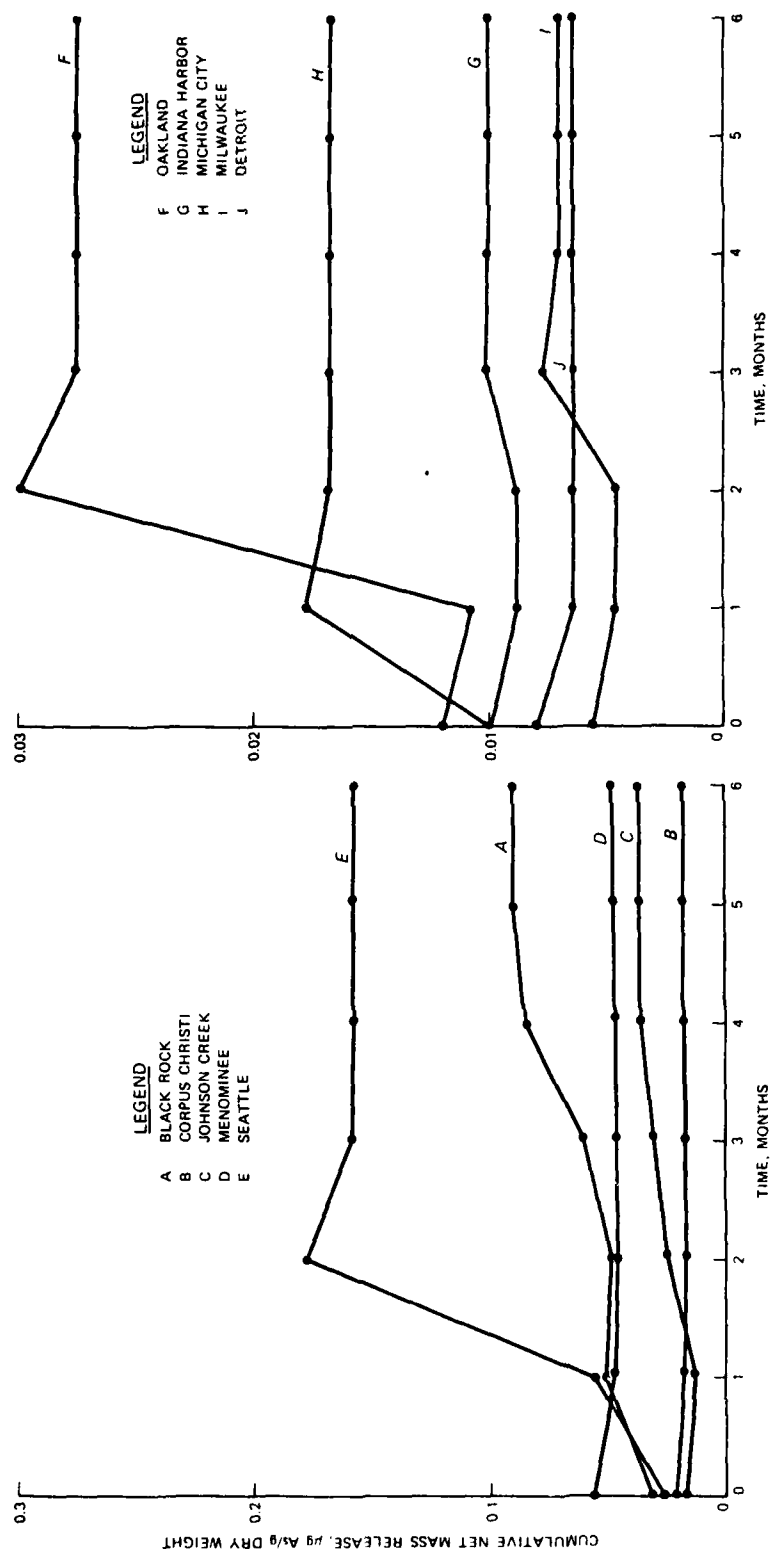


Figure 16. Cumulative As(III) release from unamended sediments under aerobic conditions
(Note scale difference between graphs).

leached with aerobic water should exhibit minimal releases of As(III) following initial release.

Organic As. Measurable amounts of organic As were found in leachates of all As(V) amended sediments and in 80 percent of unamended sediments. Other than substantial initial release, organic As losses from amended sediments generally occurred following the first month of leaching, notably in Black Rock, Menominee, and Seattle sediments (Figure 17). Following the first month of leaching, unamended Menominee and Seattle sediments released substantially more organic As than the other sediments (Figure 18). The substantial release of organic As by both amended and unamended sediments indicates continued production during the leaching period. Except for Menominee 1, sediments which released substantial amounts of organic As following the first month also continued to release As(III). Oscarson et al. (1981b) has postulated that the abiotic oxidation of As(III) to As(V) by sediments would tend to counteract the methylation process since methylation of inorganic arsenicals is essentially a reduction reaction. Except for trends noted in Menominee 1 sediments, results of this study are consistent with the observation of Oscarson et al. (1981b). Menominee sediments, however, are contaminated with organic As (Anderson et al., 1978) and may have been releasing adsorbed organic As compounds. Release of adsorbed organic As could not account for the large difference (0.96 $\mu\text{g/g}$) in organic As release between amended and unamended organic As release. It is therefore highly likely that organic As was being produced in Menominee 1 sediments, possibly without an As(III) precursor.

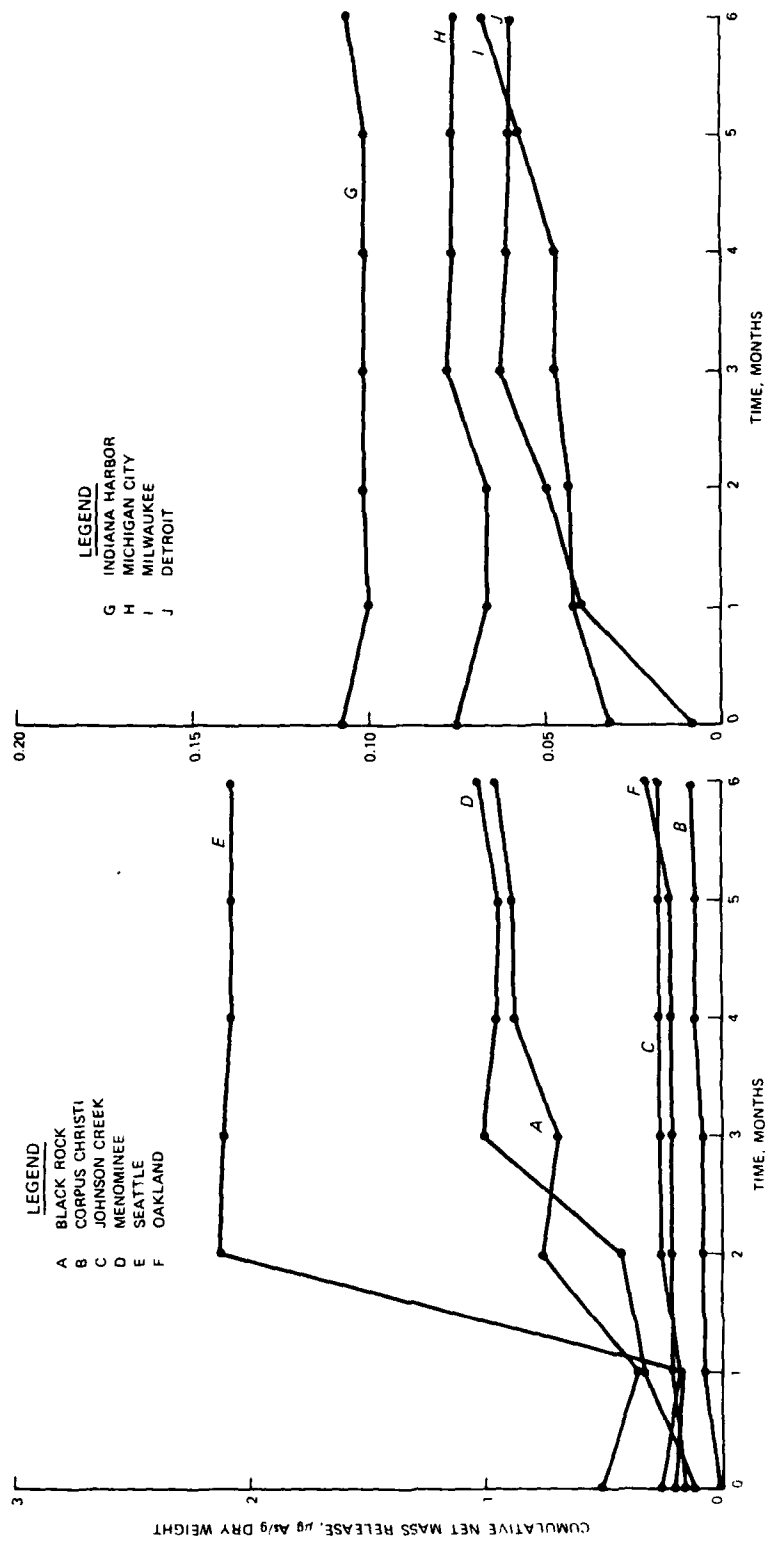


Figure 17. Cumulative organic As release from amended sediments under aerobic conditions (Note scale difference between graphs).

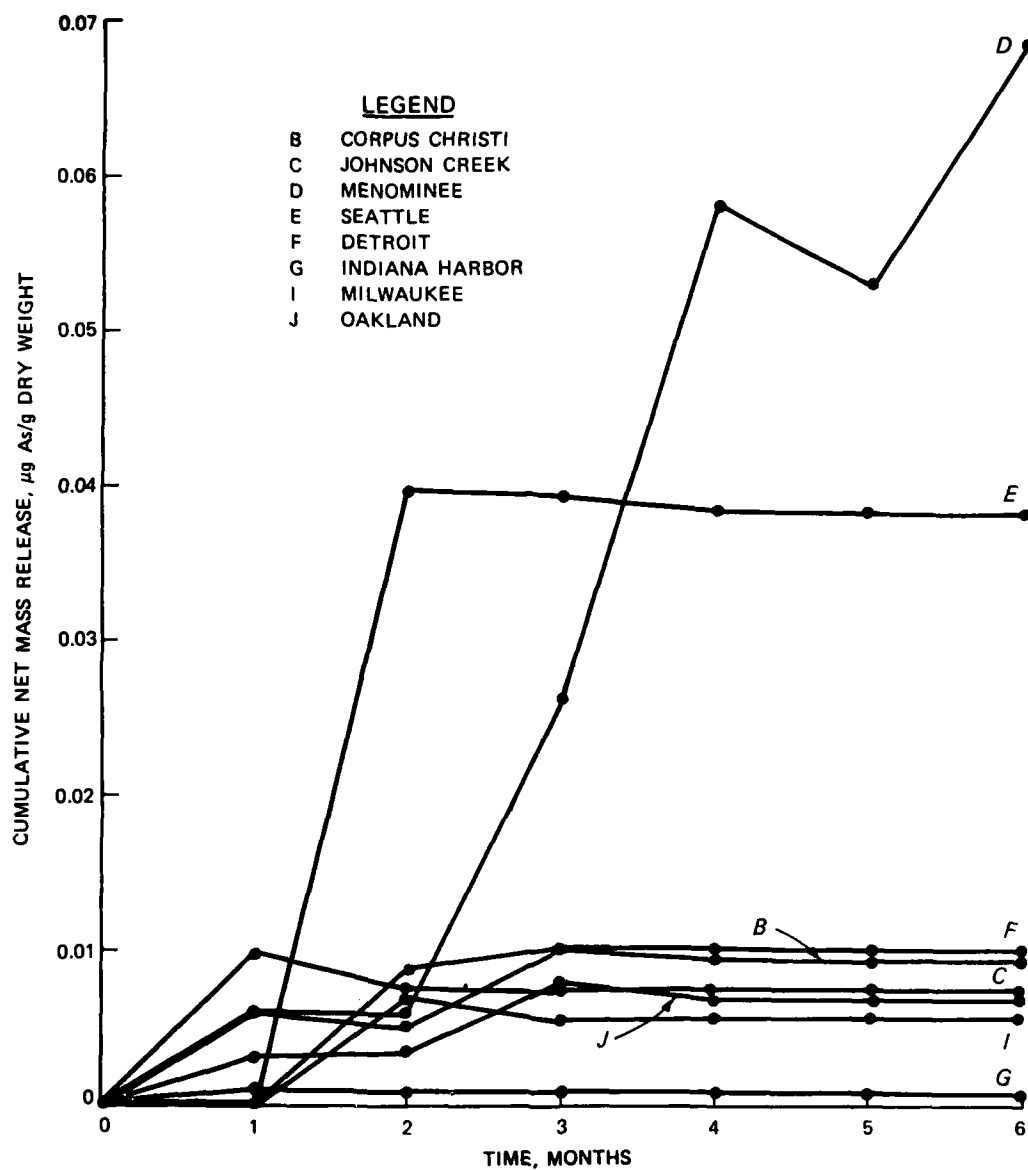


Figure 18. Cumulative organic As release from unamended sediments under aerobic conditions.

Phasing of As Releases

Examination of release curves for amended and unamended sediments revealed that release of the various As species was phased at intervals throughout the leaching period. Trends observed in Menominee 1 sediments (Figure 19) were representative of trends in other sediments. Releases of As(III) were highest initially but were superceded by releases of As(V) and organic As at the end of six months leaching. Releases of organic As roughly paralleled that of As(V) for three months after which no further substantial releases of organic As were noted. In general, As(III) release predominated initially, followed by As(V) and organic As releases in the first three months. The final three months of leaching were characterized by almost exclusive release of As(V).

At the conclusion of six months of leaching, As releases were in the order As(V) > As(III) > organic As in approximately 70 percent of the sediments (Table 21). Initial As(III) releases exceeded As(V) releases in 90 percent of the sediments and organic As releases in all sediments. At the conclusion of leaching, organic As releases exceeded As(III) releases in 20 percent of the unamended sediments and 40 percent of the amended sediments.

Long-term leaching results agreed with results of the short-term leaching studies and the literature (Arnott and Leaf, 1967; Johnson and Hiltbold, 1969) in that added As resulted in increased As releases. Releases of total As during long-term leaching under agitated conditions greatly exceeded long-term releases previously reported under quiescent conditions (Brannon et al., 1980). Previous long-term leaching studies have not determined release of the various As species.

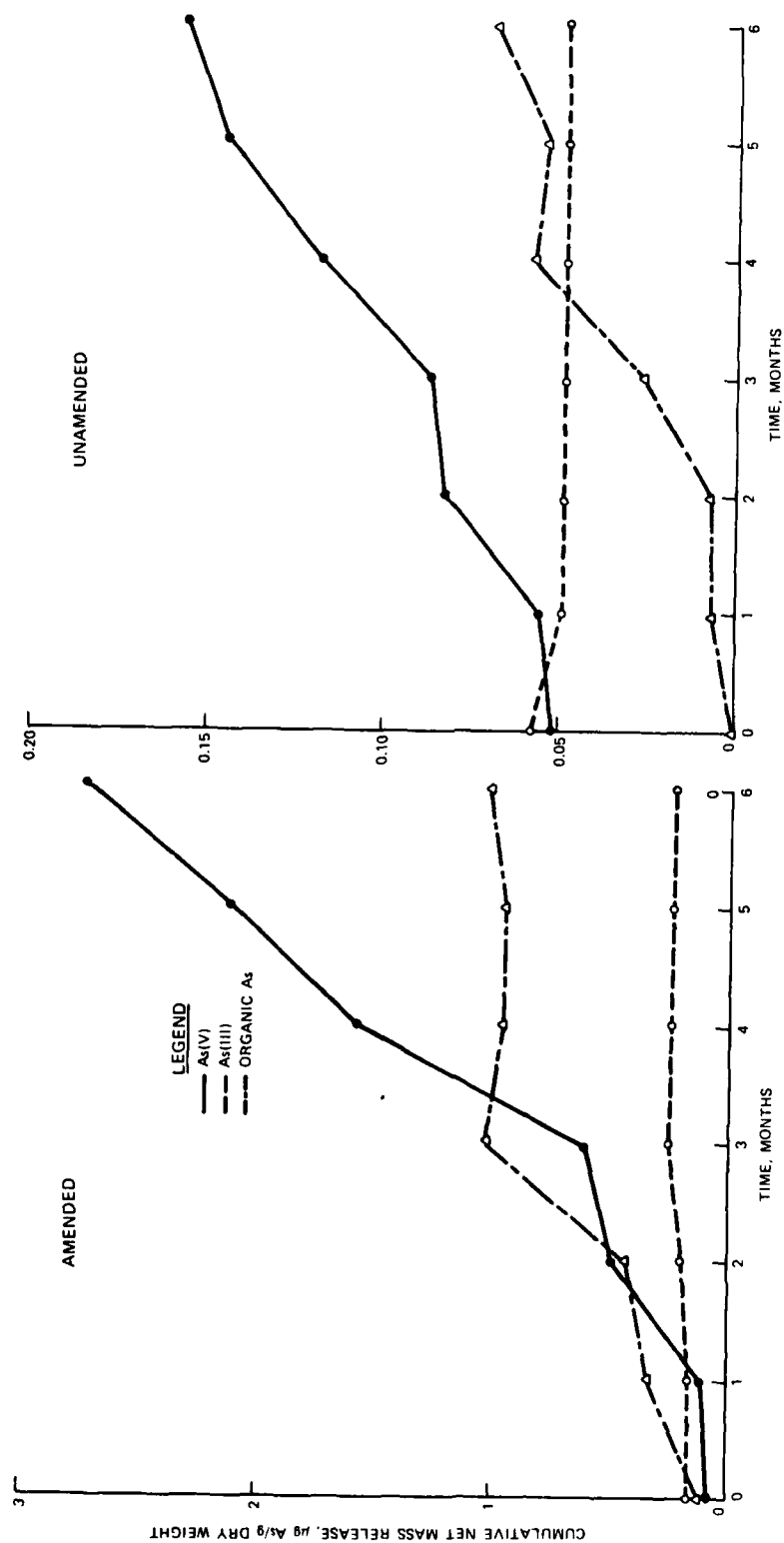


Figure 19. Cumulative As release from Menominee sediments under aerobic conditions
(Note scale difference between graphs).

Table 21
Leaching of As(V), As(III), and Organic As as a
Percentage of Total As Leached

Sediment	As(V) % of Total		As(III) % of Total		Organic As % of Total	
	U	A	U	A	U	A
Black Rock	57.55	48.95	42.45	36.60	0.00	14.46
Corpus Christi	67.86	35.47	22.62	60.55	11.90	39.76
Detroit	68.42	70.37	15.79	7.41	26.32	22.22
Indiana Harbor	46.67	37.50	36.67	37.50	13.33	27.50
Johnson Creek	65.29	33.04	30.58	54.02	6.61	12.05
Menominee 1	57.99	70.51	17.84	6.15	25.65	26.41
Michigan City	57.50	52.94	42.50	33.33	0.00	15.69
Milwaukee	23.53	60.42	41.18	33.33	35.29	14.58
Oakland	53.49	48.33	65.12	25.83	16.28	26.67
Seattle	29.59	67.17	59.18	15.23	14.61	17.60

U = Unamended

A = Amended

When an anaerobic sediment is resuspended or moved to an aerobic environment, substantial changes in the speciation of As releases over time can be expected. Over a prolonged period, As(V) will probably be the major constituent released, although release of As(III) will predominate initially. Since As(V) and organic As compounds are less toxic than As(III) (Peoples, 1975), As leached under aerobic conditions from initially anaerobic sediments will become less toxic as time of leaching increases. Leachate releases should therefore be carefully controlled during the first few months when the potential for release of As(III) is greatest.

Impact of Varying Environmental Conditions on Long-Term Leachate Composition

Varying the environmental conditions a sediment is exposed to will affect long-term As releases. Alternating two-week periods of anaerobic and aerobic leaching with sampling following the aerobic period resulted in the almost exclusive release of As(V) in amended and unamended Black Rock sediments (Figure 20). Conversely, leaching under anaerobic conditions resulted in the almost exclusive release of As(III) in amended and unamended sediments. Releases of As from amended and unamended sediment followed similar trends within a treatment. Arsenic releases from unamended Black Rock sediments under aerobic conditions (0.12 $\mu\text{g/g}$) were similar to As releases from Black Rock sediments under anaerobic/aerobic (0.14 $\mu\text{g/g}$) and anaerobic (0.15 $\mu\text{g/g}$) conditions, even though the releases under aerobic conditions included an additional initial leach. Arsenic releases from amended sediments were much greater under aerobic conditions, primarily due to the initial leach at time 0, during which

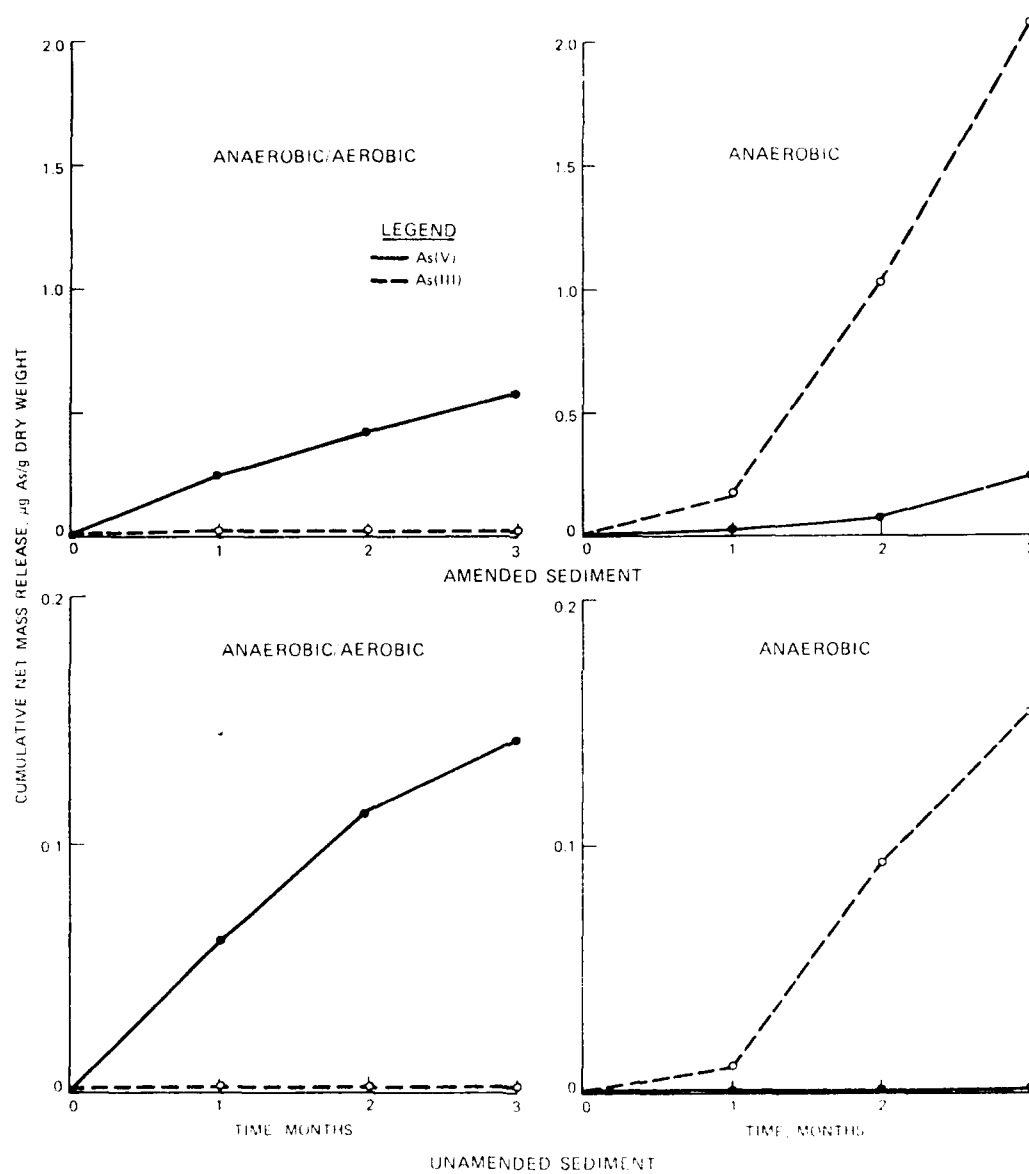


Figure 20. Cumulative As release from Black Rock sediments under anaerobic/aerobic and anaerobic conditions (Note scale difference between graphs).

1.88 $\mu\text{g/g}$ of As was released. Results indicated that As(III) releases could be curtailed by alternating anaerobic/aerobic conditions. Such conditions would be found in an area subject to intermittent flooding. Organic As was not formed under either anaerobic/aerobic or anaerobic conditions, contrary to results observed in aerobic leaches of quiescent Black Rock sediments.

Under environmental conditions where an anaerobic sediment is in intimate contact with anaerobic water, releases of As(III) to the water column should occur. Organic As may also be released if it is produced under anaerobic conditions in the sediment. Anaerobic sediment-water contact commonly exists in reservoirs during periods of temperature stratification. Lis and Hopke (1973) showed that in the hypolimnion of Chautauqua Lake, New York, As releases from sediments occurred more readily under low dissolved oxygen conditions.

Fixation and Retention of As by Sediment

Operationally defined selective extraction techniques and adsorption studies have been used to identify factors responsible for As retention by soils and sediments (Brannon et al., 1976; Woolson et al., 1971; Crecelius et al., 1975; Galba, 1972b; Misra and Tiwari, 1963a,b). Such studies give little information on long-term chemical changes, but may provide insight into leaching potential and short-term adsorption processes (Wauchope, 1975).

In this study, selective extraction techniques before and after leaching in combination with analyses of As releases were utilized as a more direct measure of the leaching potential of native and added As.

Procedures for computing long-term net mass releases have been described previously.

Arsenic Distribution in Sediments

Following 45 days of anaerobic incubation, the great majority of added As (75 μ g As/g dry weight sediment) was associated with the sediment solid phase (Table 22). All sediments, with the exception of Corpus Christi which adsorbed only 77.3 percent of added As, adsorbed at least 98.6 percent of the added As. All sediments incubated contained some total sulfides, with concentrations ranging from 19 to 2677 μ g sulfide/g dry weight. Sulfide concentrations were significantly ($p < 0.05$) correlated ($r = 0.694$) with sediment total sulfur concentrations. Sediment pH ranged between 6.5 and 8.5 following incubation.

Unamended and amended sediments were subjected to sequential selective extraction at the conclusion of anaerobic incubation. Total As concentrations in the various chemically extracted phases are presented in Table 23. All chemically extracted phases in the amended sediments were enriched with As compared to unamended sediments. In unamended sediments, the majority of As extracted (71.1 percent to 99.4 percent) was acid oxalate extractable (moderately reducible phase). This agrees with findings of others (Grecelius et al., 1975; Clement and Faust, 1981) that acid oxalate extractable As is the major reservoir of sediment As. The moderately reducible phase extractant used in this study is reported to preferentially attack poorly crystallized oxides of Fe, Al, and Mn while having little effect on more crystalline oxides (McKeague and Day, 1966; Jacobs et al., 1970). Poorly crystalline

Table 22
Total Sulfide Concentration and pH of Sediments
Following Anaerobic Incubation

<u>Sediment</u>	<u>Total Sulfide</u> <u>μg/g</u>	<u>pH</u>	<u>% As</u> <u>Adsorbed</u>
Black Rock	2677	7.1	99.8
Corpus Christi	184	6.9	77.3
Detroit	28	8.5	99.9
Indiana Harbor	1929	6.9	98.6
Johnson Creek	1621	7.1	99.8
Menominee 1	19	6.5	99.7
Michigan City	936	6.8	99.6
Milwaukee	77	6.7	97.9
Oakland	687	7.3	98.6
Seattle	1214	7.0	99.6

Table 23

Total As Concentrations in the Interstitial Water, Exchangeable,
Easily Reducible, and Moderately Reducible Phases of Sediments
Incubated Anaerobically for 45 Days

Sediment	Interstitial water, mg/l		Exchangeable, $\mu\text{g/g}$		Easily Reducible, $\mu\text{g/g}$		Moderately Reducible, $\mu\text{g/g}$	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	0.0012	0.0853	0.11	5.24	0.05	2.67	5.25	59.00
Corpus Christi	0.0033	6.8700	0.15	12.70	0.55	10.14	1.55	34.30
Detroit	0.0024	0.1050	0.01	0.56	0.51	4.42	8.25	60.00
Indiana Harbor	0.0054	2.3000	0.04	2.31	1.75	14.00	7.00	40.50
Johnson Creek	0.0028	0.0870	0.05	2.26	0.59	6.77	7.11	51.00
Menominee 1	0.0520	0.5760	0.14	0.65	1.22	19.70	5.55	14.40
Michigan City	0.0007	0.1500	0.02	4.32	0.56	8.52	4.40	61.00
Milwaukee	0.0033	1.5400	0.02	1.03	0.09	2.60	0.94	20.50
Oakland	0.0032	1.9200	0.02	6.92	0.17	8.48	1.35	9.65
Seattle	0.0038	0.2250	0.03	5.62	0.20	3.86	6.05	43.70

metals in the moderately reducible phase may therefore be active adsorption sites for added As compounds. The general nature of the exchangeable and easily reducible extractants and their mode of attack on sediments has been detailed elsewhere (Engler et al., 1977).

In As amended sediments, the moderately reducible phase generally remained the largest reservoir of sediment As, containing from 38.5 percent to 92.3 percent of the As extracted. Arsenic concentration in the moderately reducible phase was significantly correlated ($p < 0.05$) with moderately reducible phase Al in both unamended ($r = 0.652$) and amended ($r = 0.874$) sediments. Aluminum, Fe, and Mn concentrations in the various chemically extractable phases are presented in Tables B1, B2, and B3, respectively. Moderately reducible phase Fe and As in both the amended and unamended sediments had a correlation coefficient of only 0.52, very similar to the coefficient of 0.54 reported by Clement and Faust (1981) for oxalate extractable As and Fe.

Despite the low degree of correlation with Fe, both Al and Fe were probably playing a role in As retention by the moderately reducible phase. Both Fe and Al have been implicated as soil and sediment components responsible for adsorption of both inorganic and organic As compounds (Jacobs et al., 1970; Woolson et al., 1971; Wiklander and Fredricksson, 1946; Wauchope, 1975; Akins and Lewis, 1976; Woolson et al., 1973; Livesey and Huang, 1981). In addition, Clement and Faust (1981) have determined that only 60 percent of the As extracted by oxalate in Tulpehocken Creek sediment was inorganic As; the remainder was organic. Extraction of mixed As species from the solid phase has been shown to result in differing extraction efficiencies for each As species

(Iverson et al., 1979), greatly complicating the situation. The presence of organic As compounds in the moderately reducible phase, coupled with the prospect of differing extraction efficiencies, may explain why poor correlations between moderately reducible phase Fe and As exist when all available evidence implicates sediment Fe as an important As sink. In fact, not all As added to sediments in this study was recovered; recoveries ranged from a high of 96.0 percent in Corpus Christi sediments to a low of 32.9 percent in Milwaukee sediments.

Sediment Properties and Long-Term As Releases

Total As net mass releases from unamended and amended sediments following six months leaching are summarized in Tables 24 and 25, respectively. Total As losses in unamended sediments ranged from 0.017 to 0.273 $\mu\text{g As/g}$ compared to losses of from 0.268 to 11.818 $\mu\text{g As/g}$ in amended sediments. Net mass releases of As from amended and unamended sediments were significantly correlated ($r = 0.845$, $p < 0.01$), indicating that the same sediment properties may have been controlling releases of native and added As.

To determine the effect of sediment properties on the partitioning of As between sediment and leachate, a distribution coefficient (K) was used. The coefficient selected, the chromatographic distribution coefficient, is defined as the concentration of a species in the solid phase divided by the concentration in the liquid phase (Houle and Long, 1980). Such a distribution coefficient does not apply solely to adsorption, but to all equilibria causing retention or displacement. For K to be a properly dimensionless constant, concentration units in sediment and solution must be the same (Houle and Long, 1980).

Table 24
Total Net Mass Release ($\mu\text{g/g}$) of As, As(V), As(III), and
Organic As From Unamended Sediments During
Six Months of Aerobic Leaching

<u>Sediment</u>	<u>As</u>	<u>As(V)</u>	<u>As(III)</u>	<u>Organic As</u>
Black Rock	0.212	0.122	0.090	0.000
Corpus Christi	0.086	0.057	0.019	0.010
Detroit	0.042	0.026	0.006	0.010
Indiana Harbor	0.030	0.014	0.011	0.004
Johnson Creek	0.124	0.079	0.037	0.008
Menominee	0.273	0.156	0.048	0.069
Michigan City	0.040	0.023	0.017	0.000
Milwaukee	0.017	0.004	0.007	0.006
Oakland	0.058	0.023	0.028	0.007
Seattle	0.276	0.079	0.158	0.039

Table 25
Total Net Mass Release (ug/g) of As, As(V), As(III), and
Organic As From As Amended Sediments During
Six Months of Aerobic Leaching

<u>Sediment</u>	<u>As</u>	<u>As(V)</u>	<u>As(III)</u>	<u>Organic As</u>
Black Rock	6.644	3.247	2.434	0.963
Corpus Christi	3.268	1.156	1.979	0.133
Detroit	0.268	0.188	0.019	0.061
Indiana Harbor	0.398	0.146	0.145	0.107
Johnson Creek	2.224	0.744	1.212	0.268
Menominee	4.020	2.749	0.241	1.030
Michigan City	0.515	0.267	0.171	0.077
Milwaukee	0.485	0.287	0.130	0.068
Oakland	1.209	0.583	0.308	0.318
Seattle	11.818	7.937	1.801	2.080

To obtain such K values, total As concentrations ($\mu\text{g/g}$) in unamended sediments were divided by cumulative net mass release ($\mu\text{g/g}$) following six months leaching. In amended sediments, K values were obtained by dividing the sum of total As concentration ($\mu\text{g/g}$) and $75 \mu\text{g/g}$ of As (the amount of sediment amendment) by the cumulative net mass release of As from sediments so amended. Values of K for amended and unamended sediments are summarized in Table 26. A high K value signifies that more of the total sediment As was retained as compared to a sediment with a lower K value.

Correlations between the distribution coefficients (K) for As and sediment properties in unamended and amended sediments are summarized in Table 27. These results indicate that both extractable and total Fe were significant factors affecting the retention of As by sediments during leaching. Under different leaching conditions such as less agitation or shorter exposure to leaching, the absolute amount of As leached from sediment would differ from that reported in this study. The relative amounts of As leached, however, should not change to any great extent. Sediments high in total Fe would be expected to release less native As than sediments low in Fe. For sediments to which As(V) has been added, CaCO_3 equivalent concentration and extractable Fe, in addition to total Fe, are important sediment constituents controlling the release of As.

It is not surprising that sediment Fe is such an important sediment constituent influencing the retention of sediment As. Iron oxides and hydroxides strongly adsorb As compounds (Pierce and Moore, 1980, 1982; Wiklander and Alvelid, 1951; Gupta and Chen, 1978; Ferguson and Anderson, 1974). Iron and Al compounds have also been demonstrated to

Table 26
Arsenic Distribution Coefficients (K) Following Six Months of Aerobic Leaching

Sediment	As		As(V)		As(III)		Organic As	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	17.0	11.8	29.5	24.2	40.0	32.3	--	81.6
Corpus Christi	121.4	26.1	178.9	73.7	536.8	43.1	1020.0	640.6
Detroit	300.0	318.8	438.5	459.6	1900.0	4547.4	1140.0	1416.4
Indiana Harbor	1250.0	282.7	2678.6	770.5	3409.1	775.9	9376.0	1051.4
Johnson Creek	21.5	34.7	32.9	104.3	70.3	64.0	325.0	289.6
Menominee	15.2	20.3	26.3	28.8	85.4	328.2	59.4	76.8
Michigan City	57.5	152.5	100.0	289.5	135.3	452.1	--	1003.9
Milwaukee	64.7	158.2	275.0	265.2	157.1	585.3	183.3	1119.1
Oakland	62.8	64.8	117.4	133.3	96.4	252.3	385.7	244.3
Seattle	12.0	6.6	40.5	9.9	20.3	43.4	82.1	37.6

Table 27

Correlations Between the Distribution Coefficient (K) of Various As
Species and Sediment Properties Following Six Months Leaching

Sediment Properties	Amended K Values				Unamended K Values			
	As		Organic As		As		Organic As	
	As	As(V)	As(III)	As	As	As(V)	As(III)	As
Total Fe	0.666*	0.881**	0.214	0.425	0.989**	0.986**	0.935**	0.983**
CaCO ₃ Equivalent	0.679*	0.517	0.488	0.832**	0.189	0.207	0.279	0.095
Extractable Fe [†]	0.755*	0.557	0.903**	0.625*	0.343	0.272	0.576	0.279

* p < 0.05

** p < 0.01

† Sum of Easily + Moderately Reducible Phases

be the major sink for added As in aerobic soils (Johnson and Hiltbold, 1969; Woolson et al., 1971; Jacobs et al., 1970; Fordham and Norrish, 1974).

In unamended sediments, As distribution coefficients following leaching were related to total Fe. In amended sediments, distribution coefficients for As, As(III), and organic As were also related to extractable As, a relationship also noted for short-term releases of added As. These results indicate that long-term partitioning of most added As was being influenced by the extractable Fe species of lower crystallinity. Native As, however, appeared to have been intimately associated with more crystalline Fe oxides.

Our studies have demonstrated that aerobic leaching causes significant changes in sedimentary Fe and As phases. Following leaching, sediments were subjected to selective extraction procedures utilized prior to leaching. Arsenic concentrations in the moderately reducible phase showed significant increases following leaching in both unamended and amended sediments (Table 23). This increase in As concentration was paralleled by a decrease in easily reducible Fe and an increase in moderately reducible Fe (Table 29).

Prior to leaching, 60.7 percent of the added As had been found in the exchangeable, easily reducible, and moderately reducible phases. Following leaching, 92.1 percent of the added As was accounted for, including the average As release of 3.07 $\mu\text{g As/g}$ of amended sediments.

The increase in moderately reducible Fe and decrease in easily reducible Fe following six months of aerobic conditions was apparently due to formation of more crystalline Fe oxides that were resistant to extraction by hydroxylamine hydrochloride, a weak reducing agent. Lee

Table 28
Mean Concentrations of As in Ten Sediments Before and After
Six Months of Aerobic Leaching

Parameter	Treatment	Exchangeable μg/g		Easily Reducible μg/g		Moderately Reducible, μg/g	
		Unamended	Amended	Unamended	Amended	Unamended	Amended
As	Before	0.05	3.9	0.8	7.9	4.8	39.4
	After	0.02	0.3*	0.5	6.4	8.1*	67.9*
As(V)	Before	0.02	0.43	ND	ND	ND	ND
	After	0.01	0.26	ND	ND	ND	ND
As(III)	Before	0.03	3.05	ND	ND	ND	ND
	After	0.00	0.03*	ND	ND	ND	ND
Organic As	Before	0.00	0.68	ND	ND	ND	ND
	After	0.00	0.06*	ND	ND	ND	ND

ND = Not Determined

* Significant difference between before and after concentrations at $p < 0.05$ level

Table 29
Mean Concentrations of Selected Chemical Parameters
From Ten Sediments Before and After Six
Months of Aerobic Leaching

<u>Parameter</u>	<u>Treatment</u>	<u>Easily</u> <u>Reducible, $\mu\text{g/g}$</u>	<u>Moderately</u> <u>Reducible, $\mu\text{g/g}$</u>
Fe	Before	2437.7	11949.9
	After	1173.7*	15699.2*
Al	Before	61.5	1635.4
	After	374.2	1532.1
Mn	Before	155.1	189.6
	After	231.9	113.6

* Significant difference between before and after concentrations at
 $p < 0.05$ level

(1970) reviewed the literature on the role of Fe oxides in the aquatic environment and found that the crystallinity of hydrous Fe oxide precipitates increased with time. The increase in mean As concentration in the moderately reducible phase was apparently related to the increased crystallinity and concentration of Fe in this phase.

Under aerobic conditions, As will become associated with sediment phases, such as the moderately reducible phase, that are inherently less mobile in the aquatic environment (Brannon et al., 1977, 1980). This shift of As to the moderately reducible phase appears to accompany a shift of Fe from the easily reducible to the moderately reducible phase. Such a shift can explain why native As distribution coefficients following leaching were related to total Fe instead of the more hydrous extractable Fe compounds.

The impact of sediment CaCO_3 equivalent on retention of As during leaching is somewhat ambiguous. Woolson et al. (1971) has reported that Al and Ca bound As may predominate if the amount of "reactive" Al or Ca is high and "reactive" Fe is low. In our sediments, however, there was no systematic variation between sediment total Fe concentration and CaCO_3 equivalent. It is therefore likely that sediment CaCO_3 was affecting long-term releases in a more indirect manner, such as alteration of leachate pH. Calcium carbonate tends to buffer pH (Stumm and Morgan, 1970), preventing large pH variations from occurring during leaching. As discussed previously, sediments low in CaCO_3 equivalent content generally had lower leachate pH's than sediments high in CaCO_3 . Leachate pH strongly affects the adsorption-desorption behavior of the various As species (Frost and Griffin, 1977; Everest and Popiel, 1957;

Pierce and Moore, 1980, 1982; Galba, 1972a) and may well affect microbial transformation of As compounds. Support for such an effect is provided by the strong relationship between CaCO_3 equivalent and the organic As distribution coefficient because production of organic As during the leaching was apparently a microbially mediated transformation.

Antimony Behavior in Sediments

Distribution of Sb in Sediment

In unamended sediments, essentially all Sb extracted was in the moderately reducible phase (Table 30). This was also true of Sb amended sediments except for Menominee 1, Milwaukee, and Oakland, where the majority of extractable added Sb was recovered in the easily reducible phase. Recovery of added Sb ranged from 100 percent in Michigan City sediments to 38 percent in Indiana Harbor sediments. Antimony concentrations in the moderately reducible phase were significantly ($p < 0.05$) correlated with moderately reducible phase Al in both unamended ($r = 0.724$) and amended ($r = 0.707$) sediments. These results indicate that Al in addition to Fe, the major constituent of the moderately reducible phase, was affecting fixation of Sb by sediments. These results agree with those reported by Greclius et al. (1975) for Puget Sound sediments.

To investigate the effect of Eh-pH conditions on soluble Sb concentrations, 1600 $\mu\text{g/l}$ of Sb was added to Texas City sediment suspensions. After three weeks, higher concentrations of water soluble Sb were present at +500 mV compared to -150 mV (Figure 21). The absence of high Sb

Table 30

Total Sb Concentration in the Interstitial Water, Exchangeable,
Easily Reducible, and Moderately Reducible Phases of
Sediment Incubated Anaerobically for 45 Days

Sediment	Interstitial water, mg/l		Exchangeable, $\mu\text{g/g}$		Easily Reducible, $\mu\text{g/g}$		Moderately Reducible, $\mu\text{g/g}$	
	Unamended	Amended	Unamended	Amended	Unamended	Amended	Unamended	Amended
Black Rock	ND	0.04	ND	NE	ND	7.2	5.3	59.0
Corpus Christi	ND	0.86	ND	0.91	ND	*	1.6	34.3
Detroit	ND	0.04	ND	0.24	0.5	9.6	8.3	60.0
Indiana Harbor	ND	0.14	ND	0.51	ND	10.0	7.0	40.5
Johnson Creek	ND	0.04	ND	0.30	ND	10.7	7.1	51.0
Menominee I	ND	0.03	ND	1.71	ND	17.9	5.6	14.4
Michigan City	ND	0.02	ND	0.25	0.7	23.1	4.4	61.0
Milwaukee	ND	0.03	ND	0.26	ND	27.7	0.9	20.5
Oakland	ND	0.75	ND	0.30	ND	20.8	1.4	9.7
Seattle	ND	0.03	ND	0.22	ND	0.3	6.1	43.7

ND = Not detected

NE = None extracted

* Sample lost

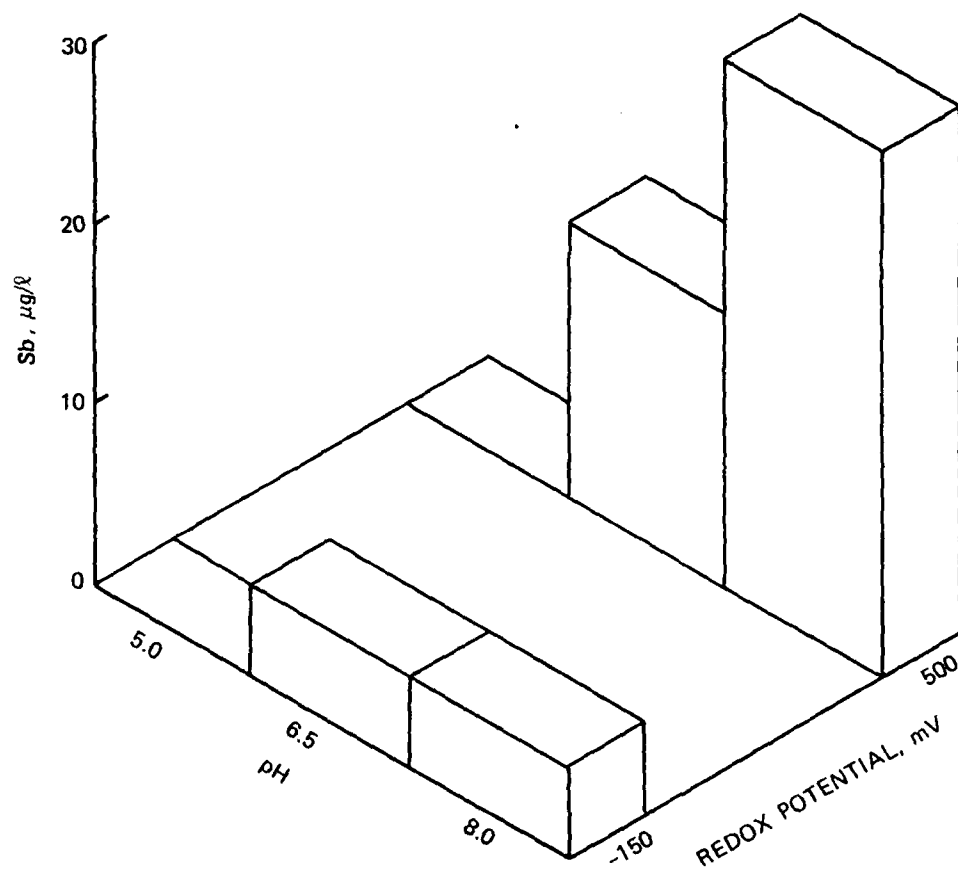


Figure 21. Influence of oxidation status and pH on water soluble Sb concentrations in Texas City sediment suspensions.

concentrations under reduced conditions may indicate that reduction of Sb(V) to Sb(III) was not occurring or that the adsorption properties of Sb(III) differed from that of As(III). High concentrations of As(III) were noted in Texas City sediment suspensions under reduced conditions. The distribution of Sb somewhat resembled that of As(V) in these sediments. Higher concentrations of Sb were noted under oxidized conditions and at higher pH values.

Short-Term Leaching

Antimony concentrations in amended sediment leachates were much higher than leachate concentrations in unamended sediments (Table 31). These results are not unexpected because of the highly soluble form of Sb (antimony potassium tartrate) added to the sediments. Values of the distribution coefficient (K) are also presented in Table 31. Antimony distribution coefficients in amended sediments were significantly ($p < 0.05$) correlated with extractable Fe ($r = 0.662$) and CaCO_3 equivalent ($r = 0.753$). This indicates that although moderately reducible phase A1 and Sb concentrations were related in the sediments, Fe and CaCO_3 were responsible for retention of added Sb during short-term leaching.

To examine the effects of salinity on Sb leachate concentrations, five of the ten sediments were leached with water of varying salinity. In amended sediments, the salinity had no significant impact on leachate Sb concentrations (Table 32). In unamended sediments, Sb concentrations in saline leachates of Detroit and Michigan City sediments were significantly higher than Sb concentrations in distilled water leachates.

Table 31
Antimony Concentration ($\mu\text{g}/\ell$) in Short-Term Leachate
and Value of the Distribution Coefficient (K)

Sediment	Unamended Sediment		Amended Sediment	
	Concentration $\mu\text{g}/\ell$	K	Concentration $\mu\text{g}/\ell$	K
Black Rock	nd	+	2570	7.8
Corpus Christi	nd	+	276	69.4
Detroit	nd	+	174	120.4
Indiana Harbor	nd	+	382	53.7
Johnson Creek	nd	+	3530	5.8
Menominee 1	nd	+	650	31.0
Michigan City	nd	+	544	36.8
Milwaukee	nd	+	257	73.8
Oakland	nd	+	4040	4.7
Seattle	34.0	44.9	4780	4.2

+ K cannot be computed when no Sb is released.

Table 32
Total Water Soluble Sb Concentrations ($\mu\text{g}/\ell$) from Amended
and Unamended Sediments Leached with Water of
Varied Initial Salinity

Sediment	Initial Salinity of Leaching Water, ‰									
	0		5		15		25		35	
	U	A	U	A	U	A	U	A	U	A
Corpus Christi	ND	2760	ND	3270	ND	3150	ND	2900	ND	2810
Detroit	ND	174	9	185	9	186	9	198	10	198
Indiana Harbor	ND	382	ND	393	ND	465	ND	538	ND	636
Menominee	ND	647	ND	684	ND	746	ND	855	ND	855
Michigan City	ND	544	11	521	13	591	14	676	15	749

U = Unamended

A = Amended

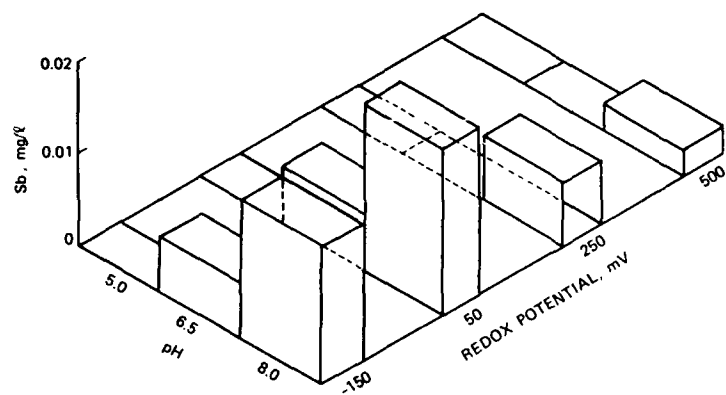
ND = Not detected

These results indicate that disposal of some freshwater sediments in saline environments may result in increased desorption of Sb. This would probably not hold true for saline sediments; Corpus Christi, the only saline sediment tested, did not desorb Sb when leached with saline water.

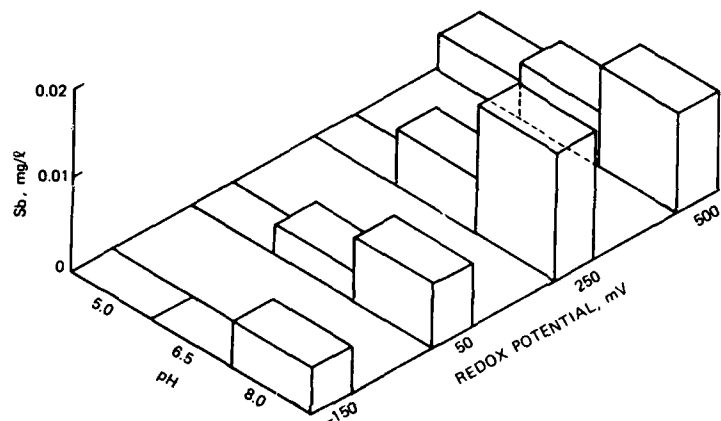
Water soluble Sb concentrations in three sediments following one week's leaching under controlled Eh-pH conditions are presented in Figure 22. Antimony concentrations in all chemically extracted sediment phases are summarized in Tables C1 through C3. The Sb concentrations showed a strong overall resemblance to the distribution patterns of added Sb in Texas City sediments. Statistical analyses revealed that, among sediments, water soluble Sb concentrations at pH 8.0 were higher than water soluble Sb concentrations at pH 6.5 or pH 5.0.

These results indicate that higher amounts of Sb will be mobilized into water soluble form under basic compared to acidic conditions. No clear concentration trends were evident for Eh. During the short term (less than one week) there would probably be no impact on Sb concentrations due to the oxidation-reduction status of the sediment. This supposition is given credence by results of the following longer term study with Black Rock sediments.

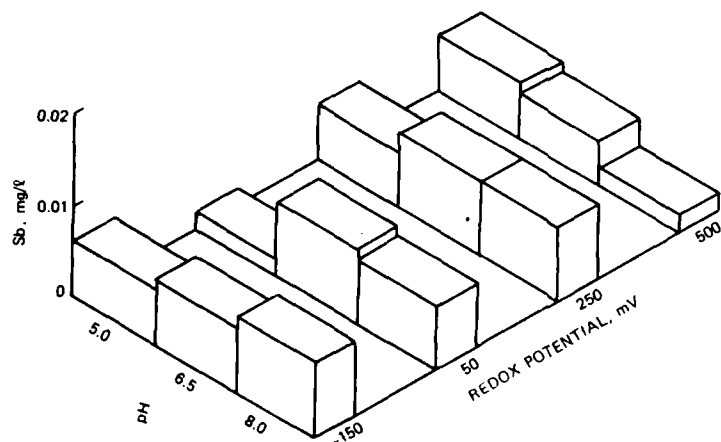
Black Rock sediments were leached for three months under anaerobic and anaerobic/aerobic conditions (Table 33). Anaerobic/aerobic conditions included two weeks anaerobic and two weeks aerobic incubation in a monthly cycle. Antimony release under both environmental conditions was slight with no significant differences in net mass release. No Sb releases were detected from unamended Black Rock sediments.



BALTIMORE HARBOR



INDIANA HARBOR



MENOMINEE RIVER

Figure 22. Influence of Eh and pH on short-term releases of Sb from sediment suspensions.

Table 33
Cumulative Net Mass Release of Sb ($\mu\text{g/g}$) from Amended
Black Rock Harbor Sediments Leached Under Anaerobic
and Anaerobic/Aerobic Conditions

Leaching Conditions	Time, Months		
	1	2	3
Anaerobic	0.005	0.008	0.009
Anaerobic/Aerobic	0.005	0.005	0.005

Antimony Volatization

Cumulative sediment Sb losses by volatization from Sb amended sediments are summarized in Figure 23. No loss of Sb was detected in unamended sediments; Sb evolution rates of $8 \mu\text{g}/\text{m}^2/\text{week}$ could be detected. Release of volatile Sb compounds, presumably some form of stibine, was most pronounced in the first week of anaerobic incubation when five sediments released detectable amounts of Sb. No further releases were subsequently noted in three of the sediments.

Corpus Christi sediments released substantial amounts of volatile Sb following two weeks of anaerobic incubation, averaging $0.74 \mu\text{g}/\text{m}^2/\text{week}$ Sb release from week 2 to 5. When incubation conditions were shifted to aerobic, both Corpus Christi and Milwaukee sediments released additional Sb following a two-week lag period.

These results demonstrate that volatile Sb compounds can be lost from sediments to which Sb has been added. Releases of Sb have been demonstrated to occur when the water overlying the sediment was anaerobic or aerobic. This implies that volatile Sb compounds can be formed under anaerobic or aerobic conditions or pass through an oxidized sediment layer following production in the anaerobic sediment zone.

Long-Term Sb Releases

Cumulative Sb releases were either linear or asymptotic (Figure 24). Unlike As releases, Sb releases from unamended sediments differed substantially from releases observed in Sb amended sediments. For example, amended Menominee sediments released $24.26 \mu\text{g Sb/g}$ of sediment compared to no releases from unamended Menominee sediment containing

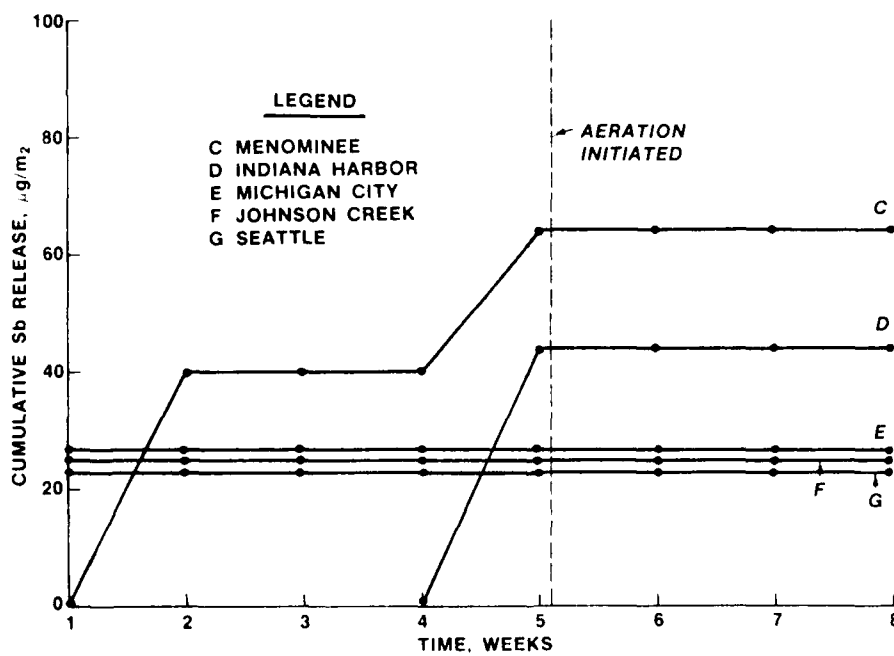
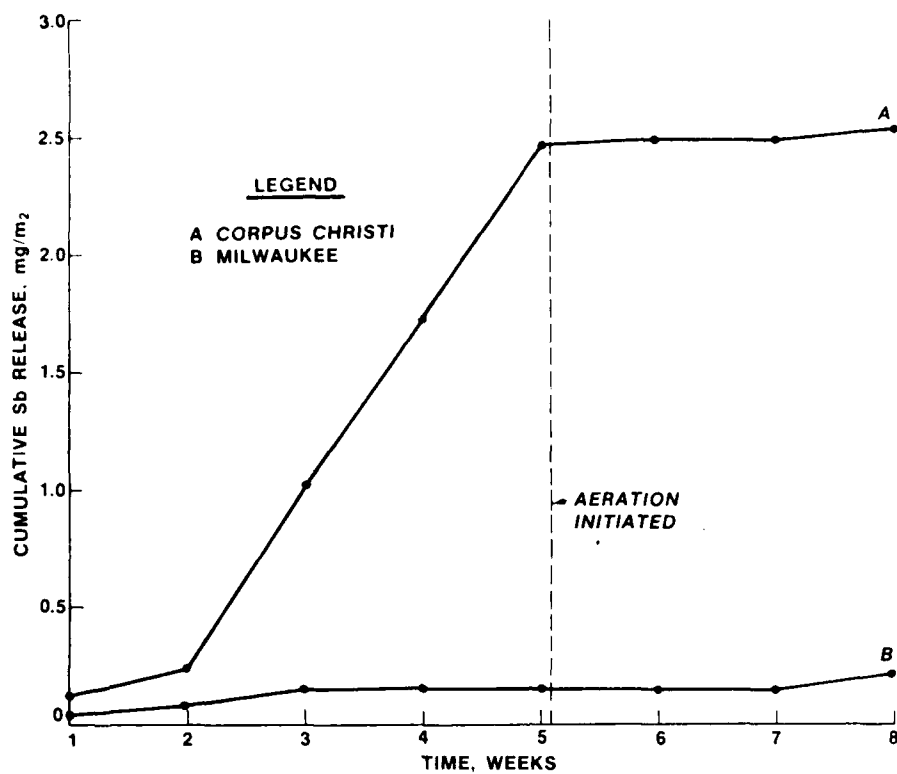


Figure 23. Cumulative releases of volatile Sb compounds from Sb amended sediments (Note scale difference between graphs).

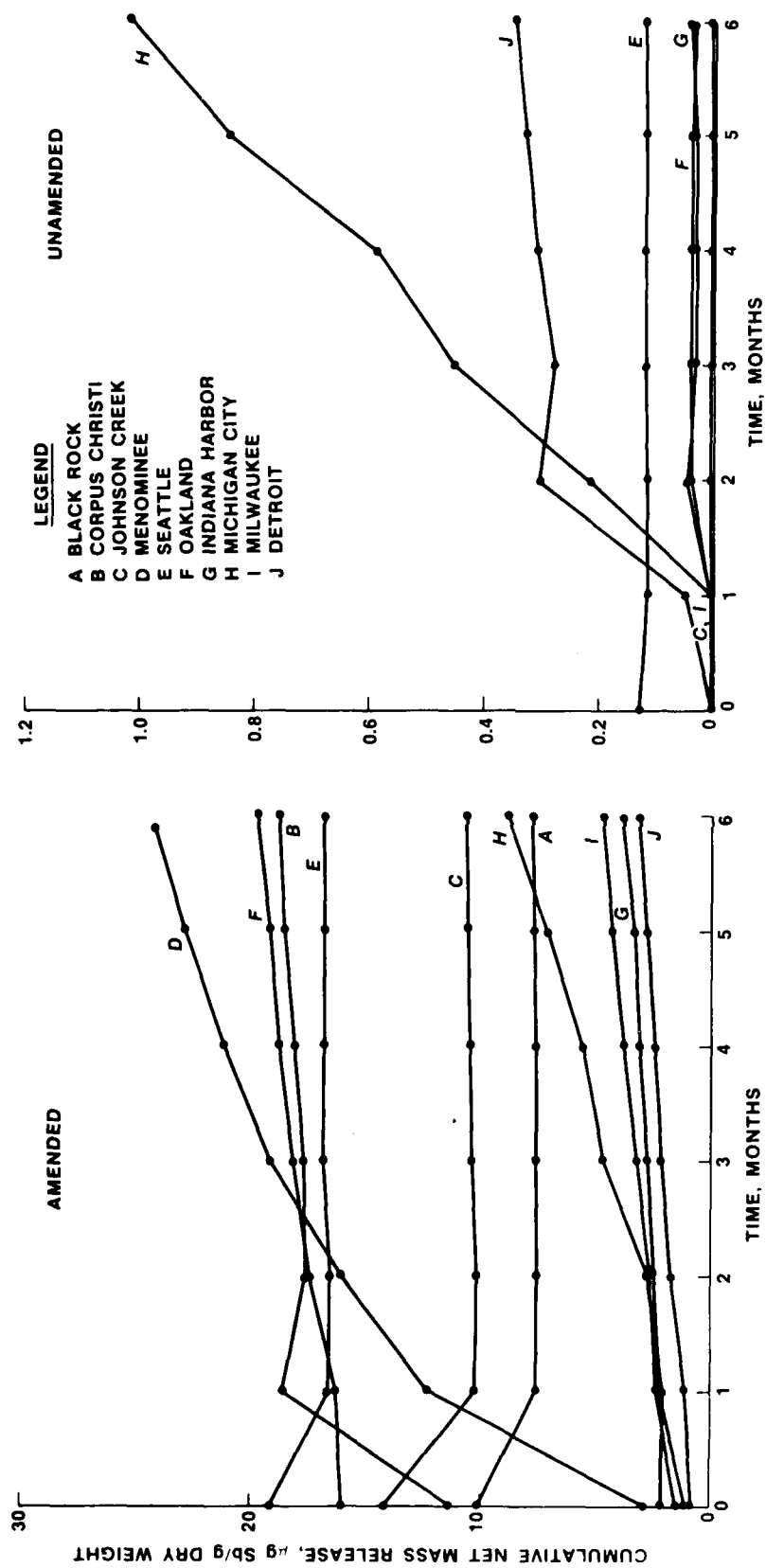


Figure 24. Cumulative Sb releases from sediments under aerobic conditions (Note scale difference between graphs).

5.6 $\mu\text{g/g}$ of moderately reducible phase Sb. Substantial amounts of Sb (0.35 $\mu\text{g/g}$) were released, however, from unamended Detroit sediments even though amended Detroit sediments released the least Sb of all amended sediments.

Cumulative net mass releases of Sb, percentage losses of extractable (easily + moderately reducible phase) and added Sb, and Sb distribution coefficients are summarized in Table 34. Antimony amended sediments lost from 3.61 percent to 32.34 percent of added Sb during leaching. Unamended sediments lost from 0.00 percent to 22.65 percent of extractable Sb.

Antimony distribution coefficients (K) in amended sediments were correlated with extractable Fe ($r = 0.841$, $p < 0.01$) and CaCO_3 equivalent ($r = 0.665$, $p < 0.05$). These results were very similar to those obtained for release of total As, indicating that As and Sb releases may be regulated by similar sediment properties.

Sediment Sb also behaved similar to As following leaching. Easily reducible phase Sb in amended sediments decreased significantly following leaching while moderately reducible phase Sb increased (Table 35). Moderately and easily reducible phase Fe behaved in a similar manner. In these same sediments, moderately reducible phase As in both amended and unamended sediment increased significantly following leaching.

The decrease in easily reducible phase Fe and increase in moderately reducible phase Fe indicates that sediment Fe was more resistant to extraction with a mild reducing agent following aerobic leaching. Decreased easily reducible phase Fe concentrations and increased moderately reducible phase Fe are symptomatic of sediment Fe becoming more crystalline following prolonged exposure to air (Lee, 1970).

Table 34
Antimony Net Mass Release ($\mu\text{g/g}$), Losses (%), and Distribution Coefficient (K)
Following Six Months of Aerobic Leaching

Sediment	Net Mass Release, $\mu\text{g/g}$		Sb Losses, %		K	
	Unamended	Amended	Unamended*	Amended**	Unamended	Amended
Black Rock	ND	7.93	0.00	10.57	--	10.1
Corpus Christi	ND	18.94	0.00	22.25	--	4.0
Detroit	0.35	3.05	3.99	3.61	25.4	27.5
Indiana Harbor	0.05	3.81	0.63	5.03	155.6	21.5
Johnson Creek	0.01	10.71	0.08	14.27	1183.3	7.7
Menominee I	ND	24.26	0.00	32.34	--	3.3
Michigan City	1.16	8.86	22.65	10.28	4.4	9.0
Milwaukee	0.01	4.78	0.67	6.36	150.0	15.9
Oakland	0.04	19.74	2.86	26.27	35.0	3.9
Seattle	0.13	16.96	2.07	22.44	48.4	4.8

ND = Not detected

* % Loss = Net Mass Release/Extractable Sb X 100

** % Loss = Amended - Unamended Mass Release/75 $\mu\text{g/g}$ X 100

Table 35
Mean Concentrations of Fe and Sb Among Ten Sediments Before and After
Six Months of Aerobic Leaching

Parameter	Treatment	Exchangeable, $\mu\text{g/g}$		Easily Reducible, $\mu\text{g/g}$		Moderately Reducible, $\mu\text{g/g}$	
		Unamended	Amended	Unamended	Amended	Unamended	Amended
Sb	Before	BDL	0.5	0.1	20.3	0.8	25.3
	After	0.03	0.5	0.1	3.3*	2.3	55.9*
Fe**	Before	ND	ND		2438		11950
	After				1174*		15699*

ND = Not Determined

BDL = Below Detection Limit

* Significant difference between before and after concentrations at $p < 0.05$ level

** Amended means are for before and after treatments

If increased surface area due to particle abrasion during mechanical shaking had occurred to any significant extent, element concentrations in all extractants would be expected to increase in the after treatment, a phenomenon that was not observed.

These results illustrate the strong influence of sediment Fe on fixation of Sb. Not only does Fe affect short- and long-term Sb releases, but it also acts to fix Sb in the sediment. Aerobic conditions in sediments would be expected to render Sb less available to leaching by gradual incorporation into less mobile sediment phases.

SUMMARY AND CONCLUSIONS

Arsenic

Interstitial water and exchangeable phase concentrations of As(V), As(III), and organic As were monitored in ten As(V) amended sediments and unamended sediments following 45 days of anaerobic incubation. Results indicated that As(III) was a major component of total interstitial water and exchangeable phase As in sediments containing only native As. In sediments to which As(V) had been added, high accumulations of interstitial water and exchangeable phase As(III) were found, indicating that reduction of As(V) to As(III) was occurring in a wide range of anaerobic sediments. In five of the ten sediments, addition of As(V) also resulted in accumulation of organic As in the interstitial water. Direct methylation of As(III) or addition of other aliphatic hydrocarbon groups to As(III), rather than oxidation of methylated arsines, is a plausible mechanism for the accumulation of organic As compounds under the anaerobic conditions of this experiment.

Concentrations of water soluble As(V), As(III), and organic As were also monitored following three weeks of incubation under varying controlled Eh-pH conditions in Texas City sediment slurries containing added As(V). Under reduced conditions (-150 mV) at pH 5.0 and 6.5, from 53 percent to 70 percent of the added As(V) was recovered as As(III). Under oxidized conditions (+500 mV), As(III) was detected indicating that aerobic reduction of As(V) may also have been occurring.

Incubation of Texas City sediment⁺ suspensions amended with disodium methanearsonate (DSMA) under controlled Eh-pH conditions resulted in decreased water soluble DSMA concentrations over time. Rates of disappearance were apparently a function of the Eh-pH regime of the sediment slurry. DSMA disappeared from solution at a more rapid rate under oxidized compared to reduced conditions and was accompanied by accumulation of inorganic As at pH 8.0 under aerobic conditions. Disappearance of DSMA from solution followed first-order kinetics.

Results of short-term leaching (30 min) of anaerobically incubated unamended and As amended sediments with distilled water and water of varying salinity showed that addition of As to sediments resulted in increased As release. In both amended and unamended sediment, As(III) was the predominant As species released. During mixing of short duration, releases of As(III) and total As should be greatest when sediments are low in Fe and high in interstitial water and exchangeable phase As and As(III). High total Fe concentrations enhance the short-term retention of native As while higher concentrations of more hydrous extractable Fe compounds enhance the retention of added As. Releases of As(V), As(III), and organic As from sediment were shown to be relatively insensitive to the salinity of the mixing water.

Three sediments containing no added As were subjected to one week of leaching under controlled Eh-pH conditions. Higher concentrations of extractable (water soluble + exchangeable) As(V) and As(III) were found at pH 8.0 than at pH 5.0 and 6.5, regardless of Eh. Detection of As(III) under oxidized conditions was further evidence that reduction of As(V) to As(III) was occurring under oxidizing as well as under anaerobic conditions. In sediments where organic As was detected, most

notably Menominee, organic As was present in higher concentrations in the leachate under highly oxidizing conditions ($E_h = +500$ mV) than reduced conditions. Leaching of organic As from the sediment and formation of additional organic As during the week of aerobic incubation were the postulated sources of organic As.

Release of volatile As compounds from sediment slurries under varying E_h -pH conditions and from sediments overlain by anaerobic or aerobic water was minimal. The maximum As release, noted under anaerobic conditions, was only $23.9 \mu\text{g As/m}^2$ during a five-week period. These results indicate that release of volatile arsenicals from either aerobic or anaerobic sediment suspensions on quiescent sediments should not pose any potential environmental hazard.

Long-term leaching experiments were conducted with ten sediments to determine what As species would be released, the duration of the releases, the quality of materials that would be released, and the sediment factors affecting releases. This involved leachate analyses for the various As species initially (1/2 hour of shaking) and at subsequent monthly intervals for six months.

In the majority of sediments tested, long-term releases under agitated, aerobic conditions persisted during the entire leaching period. Sediments amended with As(V) consistently released greater amounts of As than sediments containing no added As. Arsenic(III) releases generally predominated initially, followed by As(V) and organic As releases in the first three months. The final three months of leaching were characterized by almost exclusive release of As(V). At the conclusion of six months of leaching, As releases were in the order As(V) > As(III) > organic As in approximately 70 percent of the sediments.

Long-term (3 months) leaching of Black Rock sediments under alternating two-week periods of anaerobic and aerobic leaching with sampling following the aerobic period resulted in the almost exclusive release of As(V). Conversely, leaching under anaerobic conditions resulted in the nearly exclusive release of As(III). Releases of native and added As followed similar trends within a given treatment.

These long-term leaching results suggest that soluble As releases from sediments are potentially more harmful during the first months of aerobic leaching or at any time under anaerobic conditions. This is due to the higher toxicity of As(III) compared to As(V) and organic As.

At the conclusion of the anaerobic incubation of unamended and As amended sediments (45 days), sequential selective extraction results showed that the majority of native and added As was generally found in the moderately reducible phase (acid oxalate extractable). Poorly crystallized oxides of Fe, Al, and Mn are preferentially attacked by the moderately reducible phase extractant. Long-term aerobic leaching, however, caused significant changes in both sedimentary Fe and As phases. Arsenic concentrations in the moderately reducible phase of both amended and unamended sediments showed significant increases following leaching. This increase in As concentration was paralleled by a decrease in easily reducible Fe and an increase in moderately reducible Fe. This change in Fe distribution apparently resulted from formation of more crystalline Fe oxides during the six months of aerobic leaching. Arsenic is therefore not only lost from the system during aerobic leaching, but the As remaining is predominately concentrated in a more immobile sediment phase. This remaining sedimentary As should be highly resistant to further aerobic leaching.

Long-term net mass releases of As from unamended and amended sediments were significantly correlated, indicating that similar sediment properties as well as similar chemistry of added and native As may have been controlling releases. Arsenic distribution coefficients between sediment and water following six months of aerobic leaching were related to both extractable (easily + moderately reducible) and total Fe. For sediments to which As(V) has been added, CaCO_3 equivalent concentration and extractable Fe, in addition to total Fe, are important sediment components controlling the release of As.

Antimony

Sediments containing native and added Sb were subjected to similar experimental incubation, extraction procedures, and short- and long-term leaching as in the As experiments. Speciation of Sb was not examined however, so that only total Sb concentrations are available.

In ten unamended and Sb amended sediments, the majority of extractable Sb was found in the moderately reducible phase following 45 days of anaerobic incubation. Correlation analyses revealed that Al in addition to Fe, the major constituent of the moderately reducible phase, was influencing fixation of Sb by sediments. Levels of Sb in the interstitial water and exchangeable phases were higher in sediments amended with Sb than in unamended sediments.

Following three weeks of incubation under various Eh-pH conditions, concentrations of water soluble Sb in Sb amended Texas City sediments were highest at pH 8.0 under oxidized conditions. Antimony distribution patterns in the water soluble phases of three sediments incubated for

one week under various Eh-pH conditions showed a strong resemblance to the distribution patterns of added Sb in Texas City sediments. Sediment pH appeared to have a much greater impact on Sb mobilization than redox potential.

At the conclusion of six months aerobic leaching, significant changes were found in both sedimentary Fe and Sb phases. Antimony concentrations in the moderately reducible phase of amended sediments increased while easily reducible phase Sb decreased. Increased Sb concentrations in the moderately reducible phase were paralleled by increased Fe concentrations in the moderately reducible phase. This behavior was similar to that noted for As and indicated that Sb had shifted to more immobile sediment phases during aerobic leaching.

Long-term (six months) releases of Sb were much higher from Sb amended sediments than from sediments containing no added Sb. In most sediments, the majority of Sb release occurred early in the leaching experiment. Net mass release of Sb following six months of leaching was directly related to extractable Fe and CaCO_3 equivalent concentration, some of the same factors that affected As release. These results suggest that Sb release from contaminated sediment is more likely to occur during the first few months of aerobic leaching.

Short-term releases of Sb were higher from amended than from unamended sediments. Antimony releases from Sb amended sediments were related to extractable Fe and CaCO_3 equivalent concentrations. Short-term release of native Sb from freshwater sediments were enhanced by leaching with saline water. This trend would probably not hold true for saline sediments; Corpus Christi, the only saline sediment tested, did not desorb additional Sb when leached with saline water.

Seven out of ten Sb amended sediments released volatile Sb compounds during anaerobic incubation. Two of these sediments released additional Sb under aerobic conditions. This observation indicates that release of volatile Sb compounds from sediments subjected to recent inputs of Sb may be cause for concern.

The main conclusion to be drawn from this portion of the study is that Sb behavior in sediments is very similar to As behavior. Notable exceptions to this general similarity are the pronounced release of volatile Sb compounds from Sb amended sediments and the increased release of Sb from some freshwater sediments leached with saline water. The behavior of As and Sb were otherwise similar during short- and long-term leaching experiments. The properties affecting short- and long-term releases and fixation of these two elements by sediments were also similar.

REFERENCES

- Akins, M. B. and R. J. Lewis. 1976. Chemical distribution and gaseous evolution of arsenic - 74 added to soils as DSMA - 74 As. Soil Sci. Soc. Am. J., 40:655-658.
- Albert, W. B. and C. H. Arndt. 1931. Concentration of soluble arsenic as an index of arsenic toxicity to plants. South Carolina Agr. Exp. Sta. 44th Ann. Rep., pp 47-48.
- Alexander, M. 1977. Introduction to Soil Microbiology. John Wiley and Sons, New York.
- Allison, L. E. and C. D. Moodie. 1965. Carbonate. In Black, C. A. (ed.), Methods of Soil Analysis, American Society of Agronomy Monograph No. 9, pp 1388-1389.
- American Public Health Association 1980. Standard Methods for Examination of Water and Wastewater. 15th ed., N.Y.
- Anderson, M. A., J. F. Ferguson, and J. Cavis. 1976. Arsenate adsorption on amorphous aluminum hydroxide. J. Colloid. Interface Sci., 54:391-399.
- Anderson, M. A., T. R. Holm, D. G. Iverson, and R. R. Stanforth. 1978. Mass balance and speciation of arsenic in the Menominee River, Wisconsin. Project Rep. 6. U.S. EPA Environ. Res. Lab., Athens, Georgia.
- Andreae, M. O. 1977. Determination of arsenic species in natural waters. Anal. Chem., 49:820-823.
- Andreae, M. O. 1978. Distribution and speciation of arsenic in natural waters and some marine algae. Deep - Sea Res., 25:391-402.
- Andreae, M. O. 1979. Arsenic speciation in seawater and interstitial waters: The influence of biological-chemical interactions on the chemistry of a trace element. Limnol. Oceanogr., 24:440-452.
- Andreae, M. O. and D. K. Klumpp. 1979. The biosynthesis and release of organo-arsenic compounds by marine algae. Environ. Sci. Technol., 13:738-741.
- Andreae, M. O., J. F. Asmode' P. Foster, and L. Von't dack. 1981. Determination of antimony (III), antimony (V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. Anal. Chem., 53:1766-1771.
- Angino, E. E., L. M. Magnuson, T. C. Waugh, O. K. Galle, and J. Bredfeldt. 1970. Arsenic in detergent: Possible danger and pollution hazard. Science, 168:389-390.

Arnott, J. T. and A. L. Leaf. 1967. The determination and distribution of toxic levels of arsenic in a silt loam soil. Weeds, 15:121-124.

Bamford, C. H. and D. M. Newitt. 1946. Physical and chemical properties of organo-metallic compounds. Part III. The oxidation of Boron and Antimony alkyls. J. Chem. Soc., :695-701.

Barr, A. J., J. H. Goodnight, J. P. Sall, J. T. Helwig. 1976. A users guide to SAS 76. SAS Institute Inc., Raleigh, N.C.

Blasco, F., C. Gaudin, and R. Jean Jean. 1971. Absorption des ions arseniate par les Chlorelles. Reduction partielle de l'arsenate en arsenite. In Hehd, C. R. (ed), Stances Acad. Sci. Ser. D Sci. Nat., 273:812-815.

Blum, J. J. 1966. Phosphate uptake by phosphate-starved Euglena. J. Gen. Physiol., 49:1125-1137.

Bohn, H. L. 1976. Arsenic Eh-pH diagram and comparisons to the soil chemistry of phosphorus. Soil Sci., 121:125-127.

Boischot, P. and J. Hebert. 1948. Fixation des arseniates par le sol. Annales Agronomiques, 18:426-448.

Bottino, N. R., E. R. Cox, E. J. Irgolic, S. Maeda, W. J. McShane, R. A. Stockton, and R. A. Zingaro. 1978. Arsenic uptake and metabolism by the alga Tetraselmes chui. In Brinckman, F. E. and J. M. Belloma (eds.), Organometals and Organometalloids. American Chemical Society, Washington, D.C., pp 116-129.

Bowen, H. J. 1966. Trace Elements in Biochemistry. Academic Press, New York, London, pp 280.

Boyle, R. W. and I. R. Jonasson. 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. Geochem. Explor., 2:251-296.

Braman, R. S. 1975. Arsenic in the environment. In Woolson, E. A. (ed.), Arsenical Pesticides. Amer. Chem. Soc. Symp. Ser., No. 7:108-123.

Braman, R. S. and C. C. Foreback. 1973. Methylated forms of arsenic in the environment. Science, 182:1247-1249.

Braman, R. S. and M. A. Tompkins. 1978. Atomic emission spectrometric determination of antimony, germanium, and methylgermanium compounds in the environment. Anal. Chem., 50:1088-1093.

Braman, R. S., D. L. Johnson, C. C. Foreback, J. M. Ammons, and J. L. Bricker. 1977. Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds. Anal. Chem., 49:621-625.

- Brannon, J. M., R. M. Engler, J. R. Rose, P. G. Hunt, and I. Smith. 1976. Distribution of toxic heavy metals in marine and freshwater sediments. In Krenkel, P. A., J. Harrison, and J. C. Burdick, III (eds.), Dredging and its Environmental Effects, Proceedings of the Specialty Conference, Mobile, Ala., American Society of Civil Engineers, New York.
- Brannon, J. M., R. H. Plumb, Jr., and I. Smith. 1980. Long-term release of heavy metals from sediments. In Baker, R. A. (ed.), Contaminants and Sediments, Vol 2, Ann Arbor Science, Ann Arbor, Mich., pp 221-266.
- Brannon, J. M., J. R. Rose, R. M. Engler, and I. Smith. 1977. The distribution of heavy metals in sediment fractions from Mobile Bay, Alabama. In Yen, T. F. (ed.), Chemistry of Marine Sediments, Ann Arbor Science, Ann Arbor, Mich., pp 125-149.
- Brenchley, W. E. 1914. On the action of certain compounds of zinc, arsenic, and boron on the growth of plants. Annals Bot., 28:283-301.
- Brunskill, G. J., B. W. Graham, and J. W. M. Rudd. 1980. Experimental studies on the effect of arsenic on microbial degradation of organic matter and algal growth. Can. J. Fish. Aqu. Sci., 37:415-423.
- Burkholder, P. R. 1963. Some nutritional relationships among microbes of sea sediments and waters. In Oppenheimer, C. H. (ed.), Symposium on Marine Microbiology, Thomas, Springfield, Ill., pp 133-150.
- Button, D. K., S. S. Dunker, and M. L. Morse. 1973. Continuous culture of Rhodotorula rubra: Kinetics of phosphate arsenate uptake, inhibition and phosphate limited growth. J. Bacteriol. 113:599-611.
- Byrd, J. T. and M. O. Andreae. 1982. Distribution of arsenic, antimony, and tin species in the Baltic Sea (Abstract). Trans. Amer. Geophy. Union, 63:71.
- Chadwick, R. A., R. C. Rice, C. M. Bennett, and R. A. Woodruff. 1975. Sulfur and trace elements in the Rosebud and McKay coal seams, Colstrip field, Montana. Mont. Geol. Soc., Annual Field Conference, Guideb. 22:167-175.
- Challenger, F. 1945. Biological methylation. Chem. Rev., 36:315-361.
- Chao, T. T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am. Proc., 36:764-768.
- Cheng, C.-N., and D. D. Foelt. 1979. Production of arsine and methylarsines in soil and culture. App. Environ. Micro., 38:494-498.
- Clement, W. H. and S. D. Faust. 1981. The release of arsenic from contaminated sediments and muds. J. Environ. Sci. Health, A16:87-122.

- Connell, W. E. 1966. The reduction of sulfate to sulfide under anero-
bic soil conditions. M.S. Thesis, Louisiana State University, Baton
Rouge.
- Cox, D. P. 1974. Microbial methylation of arsenic. Symposium on the
Review of Arsenical Pesticides, 168th Nat'l. Meeting, American Chemical
Society, Atlantic City, N.J.
- Cox, D. P. 1975. Microbiological methylation of arsenic. In Woolson,
E. A. (ed.), Arsenical Pesticides, Amer. Chem. Soc. Symp. Ser.
No. 7:81-96.
- Cox, D. P. and M. Alexander. 1973. Production of trimethylarsine gas
from various arsenic compounds by three sewage fungi. Bull. Environ.
Cont. Toxic., 9:84-88.
- Crecelius, E. A., M. H. Bothner, and R. Carpenter. 1975. Geochem-
istries of arsenic, antimony, mercury, and related elements in sediments
of Puget Sound. Env. Sci. Tech., 9:325-333.
- Day, P. R. 1956. Report of the committee on physical analyses
(1954-1955). Soil Sci. Soc. Am. Proc., 20:167-169.
- Denyszyn, R. B., P. M. Grohse, and D. E. Wagoner. 1978. Sampling and
atomic absorption spectrometric determination of arsine at the $2 \mu\text{g}/\text{m}^3$
level. Anal. Chem., 50:1094-1096.
- Deuel, L. E. and A. R. Swoboda. 1972. Arsenic solubility in a reduced
environment. Soil Sci. Soc. Amer. Proc., 36:276-278.
- Dickens, R. and A. E. Hiltbold. 1967. Movement and persistence of
methanearsonates in soil. Weeds, 15:299-304.
- Dorman, E., F. H. Tucker, and R. Coleman. 1939. The effect of calcium
arsenate upon the productivity of several important soils of the cotton
belt. Amer. Soc. Agron., 31:1020-1028.
- Edmonds, J. S. and K. A. Francesconi. 1981. The origin and chemical
form of arsenic in the school whiting. Mar. Poll. Bull., 12:92-96.
- Ehman, P. J. 1965. Effect of arsenical build-up in the soil on subse-
quent growth and residue content of crops. Proc. S. Weed Conf.,
18:685-687.
- Ehrlich, H. L. 1981. Geomicrobiology. Marcel Dekker, Inc. New York.
- Engler, R. M., J. M. Brannon, J. Rose, and G. Bigham. 1977. A prac-
tical selective extraction procedure for sediment characterization. In
Yen, T. F. (ed.), Chemistry of Marine Sediments, Ann Arbor Science, Ann
Arbor, Mich., pp 163-171.
- Epps, E. A. and M. B. Sturgis. 1939. Arsenic compounds toxic to rice.
Soil Sci. Soc. Am. Proc., 4:215-218.

- Everest, D. A. and W. J. Popiel. 1957. Ion-exchange studies of solutions of arsenites. J. Chem. Soc.:2433-2436.
- Ferguson, J. F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res., 6:1259-1274.
- Ferguson, J. F. and M. A. Anderson. 1974. Chemical forms of arsenic in water supplies and their removal. In Rubin, A. J. (ed.), Chemistry of Water Supply, Treatment and Distribution, Ann Arbor Science, Ann Arbor, Mich., pp 137-158.
- Fleischer, M. 1973. Cycling and control of metals. Proceedings of an environmental resources conference, National Environmental Research Center, Cincinnati.
- Folsom, B. L., C. R. Lee, and D. J. Bates. 1981. Influence of disposal environment on availability plant uptake of heavy metals in dredged material. U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., Technical Report EL-81-12. 151 pp.
- Fordham, A. W. and K. Norrish. 1974. Direct measurement of the composition of soil components which retain added arsenate. Aust. J. Soil Res., 12:165-172.
- Frost, R. R. and R. A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J., 41:53-57.
- Galba, J. 1972a. A study of sorption of arsenates in soils. III. Effects of pH values of soil solution on the intensity of sorption of arsenates. Polnohospodarstvo, 18:1055-1061.
- Galba, J. 1972b. Desorption of arsenates under water. Polnohospodarstvo, 18:945-952.
- Gilbert, T. R. and D. N. Hume. 1973. Direct determination of bismuth and antimony in sea water by anodic stripping voltammetry. Anal. Chem. Acta., 65:451-459.
- Gohda, S. 1972. Activation analysis of arsenic, copper, and antimony in sea water. Bull. Chem. Soc. Japan, 45:1704-1708.
- Grimanis, A. P., M. Vassilaki-Grimani, G. B. Griggs. 1977. Pollution studies of trace elements in sediments from the upper Saronikos Gulf, Greece. J. Radioanal. Chem., 37:767-773.
- Gupta, S. K. and K. Y. Chen. 1978. Arsenic removal by adsorption. J. Wat. Poll. Cont. Fed., 50:493-506.
- Harrison, J. B. and V. E. Berkheiser. 1982. Anion interactions with freshly prepared hydrous iron oxides. Clays Clay Min., 30:97-102.
- Healy, T. W., A. P. Herring, and D. W. Fuerstenau. 1966. J. Colloid Interface Sci., 21:435-444.

- Heimbrock, M. E. 1974. Microbial transformation of inorganic arsenic compounds. Ph.D. dissertation: Colorado State Univ., Fort Collins, Colorado, 1-122.
- Heinricks, H. and R. Mayer. 1977. Distribution and cycling of major and trace elements in two central European forest ecosystems. J. Environ. Qual., 6:402-407.
- Hess, R. E. and R. W. Blanchar. 1976. Arsenic stability in contaminated soils. Soil Sci. Soc. Am. J., 40:847-852.
- Hess, R. E. and R. W. Blanchar. 1977. Dissolution of arsenic from waterlogged and aerated soil. Soil Sci. Soc. Am. J., 41:861-865.
- Hiltbold, A. E. 1975. Behavior of organoarsenicals in plants and soils. In Woolson, E. A. (ed.), Arsenical Pesticides. Amer. Chem. Soc. Symp. Ser. No. 7:53-69.
- Hiltbold, A. E., B. F. Hajek, and G. A. Buchanan. 1974. Distribution of arsenic in soil profiles after repeated applications of MSMA. Weed Sci., 22:272-275.
- Holm, T. R., M. A. Anderson, D. G. Iverson, and R. S. Stanforth. 1979. Heterogeneous interactions of arsenic in aquatic systems. In Jenne, E. A. (ed.), Chemical Modeling in Aqueous Systems. ACS Symposium Series No. 93, American Chemical Society, Washington, D.C. pp 711-736.
- Holm, T. R., M. A. Anderson, R. R. Stanforth, and D. G. Iverson. 1980. The influence of adsorption on the rates of microbial degradation of arsenic species in sediments. Limnol. Oceanogr., 25:23-30.
- Houle, M. J. and D. E. Long. 1980. Interpreting results from serial batch extraction tests of wastes and soils. In Shultz, D. (ed.), Disposal of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium at Chicago, Ill., Mar 17-20, EPA-600/9-80-010, pp 60-81.
- Howard, A. G., M. H. Asbab-Zavar, and S. Apte. 1982. Seasonal variability of biological arsenic methylation in the estuary of the River Beaulieu. Mar. Chem., 11:493-498.
- Huang, P. M. 1975. Retention of arsenic by hydroxy-aluminum on surfaces of micaceous mineral colloids. Soil Sci. Soc. Am. Proc., 39:271-274.
- Hurd-Karrer, A. M. 1939. Antagonism of certain elements essential to plants toward chemically related toxic elements. Plant Physio., 14:9-29.
- Iverson, D. G., M. A. Anderson, T. R. Holm, and R. R. Stanforth. 1979. An evaluation of column chromatography and flameless atomic absorption spectrophotometry for arsenic speciation as applied to aquatic systems. Env. Sci. Tech., 13:1491-1494.

- Jacobs, L. W., J. K. Syers, and D. R. Keeney. 1970. Arsenic sorption by soils. Soil Sci. Soc. Am. Proc., 34:750-754.
- Johnson, D. L. 1972. Bacterial reduction of arsenate in seawater. Nature, 240:44-45.
- Johnson, D. L. and M. E. Pilson. 1975. The oxidation of arsenite in seawater. Environ. Lett., 8:157-171.
- Johnson, D. L. and R. M. Burke. 1978. Biological mediation of chemical speciation II. Arsenate reduction during marine phytoplankton blooms. Chemosphere, 8:645-648.
- Johnson, D. L. and R. S. Braman. 1975. Alkyl- and inorganic arsenic in air samples. Chemosphere, 6:333-338.
- Johnson, L. R. and A. E. Hiltbold. 1969. Arsenic content of soil and crops following use of methanearsonate herbicides. Soil Sci. Soc. Am. Proc., 33:279-282.
- Johnston, S. W. 1978. Behavior of indigenous arsenic in flooded soils and sediments. MS Thesis, Dept. of Marine Sciences, Louisiana State Univ., Baton Rouge, La.
- Jung, C. and A. Rothstein. 1965. Arsenate uptake and release in relation to the inhibition of transport and glycolysis in yeast. Bio-Chem. Pharmacol., 14:1093-1112.
- Kanamori, S. 1965. Geochemical study of arsenic in natural waters, Part 3, The significance of ferric hydroxide precipitate in stratification and sedimentation of arsenic in lake waters. Research Laboratory, Faculty of Science, Nagoya Univ., pp 46-57.
- Kanamori, S. and K. Sugawara. 1965. Geochemical study of arsenic in natural waters, Part 2, Arsenic in river water. Research Laboratory, Faculty of Science, Nagoya Univ.:36-45.
- Keaton, C. M. and L. T. Kardos. 1940. Oxidation-reduction potentials of arsenate-arsenite systems in sand and soil mediums. Soil Sci., 50:189-206.
- Kobayashi, S. and G. F. Lee. 1978. Accumulation of arsenic in sediments of lakes treated with sodium arsenite. Env. Sci. Tech., 12:1195-1200.
- Latimer, W. M. 1952. Oxidation Potentials. 2nd ed. Prentice Hall, Inc., Englewood Cliffs, New Jersey. 392 pp.
- Layalikova, N. N. and L. B. Shlain. 1974. Formation of minerals of antimony (V) under the effect of bacteria. Izv. Akad. Nauk. SSSR, Ser. Biol., 3:440-444.

- Lee, G. F. 1970. Factors affecting the transfer of materials between water and sediments. Literature Review No. 1, Eutrophication Information Program, University of Wisconsin, Madison, Wis.
- Lindberg, S. E., A. W. Andren, R. J. Raridon, and W. Fulkerson. 1975. Mass balance of trace elements in Walker Branch watershed: Relation to coal-fired steam plants. Environ. Health Perspect., 12:9-18.
- Lis, S. A. and P. K. Hopke. 1973. Anomalous arsenic concentrations in Chautauqua Lake. Environ. Letters, 5:45-51.
- Livesey, N. T. and P. M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci., 131:88-94.
- McBride, B. C. and R. S. Wolfe. 1971. Biosynthesis of dimethylarsine by Methanobacterium. Biochem., 10:4312-4317.
- McBride, B. C. and T. L. Edwards. 1977. Role of the methanogenic bacteria in the alkylation of arsenic and mercury. In Drucker, H. and R. Wilding (eds.), Biological Implications of Metals in the Environment. ERDA Symposium Series 42. Springfield, Va. National Technical Information Service, pp 1-19.
- McGeorge, W. T. 1915. Fate and effect of arsenic applied as a spray for weeds. J. Agric. Res., 5:459-463.
- McKeague, J. A. and J. H. Day. 1966. Dithionite - and oxalate - extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46:13-22.
- Misra, S. G. and R. C. Tiwari. 1963a. Studies on arsenite-arsenate system adsorption of arsenate. Soil Sci. Plant Nutr., 9:10-13.
- Misra, S. G. and R. C. Tiwari. 1963b. Studies on arsenite-arsenate adsorption on soils. Ind. J. App. Chem., 26:117-121.
- Myers, D. J., M. E. Heimbrook, J. Osteryoung, and S. M. Morrison. 1973. Arsenic oxidation state in the presence of microorganisms: Examination by differential pulse polarography. Env. Letters., 5:53-61.
- Nagatsuka, S. and Y. Yagaki. 1976. Activation analyses of trace elements in the Tonegawa water system. Bunseki Kiki, 14:583-592.
- National Academy of Sciences. 1977. Arsenic. Washington, D.C. 332 pps.
- Neal, C., H. Elderfield, and R. Chester. 1979. Arsenic in sediments of the North Atlantic ocean and the eastern Mediterranean Sea. Mar. Chem., 7:207-219.
- Newman, H. M. 1954. Antimony (V) species in hydrochloric acid solution. J. Am. Chem. Soc., 76:2611.

- Onishi, H. and E. B. Sandell. 1955a. Geochemistry of arsenic. Geochem. et Cosmochem. Acta, 7:1-33.
- Onishi, H. and E. B. Sandell. 1955b. Notes on the geochemistry of antimony. Geochem. et Cosmochem. Acta, 8:213-221.
- Osborne, F. H. and H. L. Ehrlich. 1976. Oxidation of arsenite by a soil isolate of *Alcaligenes*. J. Appl. Bacteriol., 41:295-305.
- Oscarson, D. W., P. M. Huang, and W. K. Liaw. 1980. The oxidation of arsenite by aquatic sediments. J. Environ. Qual., 9:700-703.
- Oscarson, D. W., P. M. Huang, and W. K. Liaw. 1981a. Role of manganese in the oxidation of arsenite in freshwater lake sediments. Clays Clay Min., 21:219-225.
- Oscarson, D. W., P. M. Huang, C. Defosse, and A. Herbillon. 1981b. Oxidative power of Mn (IV) and Fe (III) oxides with respect to As (III) in terrestrial and aquatic environments. Nature, 291:50-51.
- Papakostides, G., A. P. Grimanis, D. Zafiropoulos, G. B. Griggs, and T. S. Hopkins. 1975. Heavy metals in sediments from the Athens sewage outfall area. Mar. Poll. Bull., 6:136-139.
- Parks, G. A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals: Isoelectric point and zero point of charge. In Gould, R. F. (ed.), Equilibrium Concepts in Natural Water Systems. Advan. Chem. Series No. 67:121-160.
- Parris, G. E. and F. E. Brinckman. 1976. Reactions which relate to environmental mobility of arsenic and antimony. II. Oxidation of trimethylarsine and trimethylstibine. Env. Sci. Tech., 12:1128-1134.
- Patrick, W. H., Jr. 1958. Modification of method of particle size analysis. Soil Sci. Soc. Am. Proc., 22:366-367.
- Patrick, W. H., Jr., B. G. Williams, and J. T. Moraghan. 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Sci. Soc. Am. Proc., 37:331-332.
- Penrose, W. R., H. B. S. Conacher, R. Black, J. C. Meranger, W. Miles, H. M. Cunningham, and W. R. Squires. 1977. Implications of inorganic/organic interconversion on fluxes of arsenic in marine food webs. Environ. Health Persp., 19:53-60.
- Peoples, S. A. 1975. Review of arsenical pesticides. In Woolson, E. A. (ed.), Arsenical Pesticides, Amer. Chem. Soc. Symp. Ser. No. 7:1-12.
- Pierce, M. L. and C. B. Moore. 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. Env. Sci. Tech., 14:214-216.

- Pierce, M. L. and C. B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res., 16:1247-1253.
- Pilson, M. E. Q. 1974. Arsenate uptake and reduction by Pocillopora verrucosa. Limnol. Oceanogr., 19:339-341.
- Planas, D. and F. P. Healey. 1978. Effects of arsenate and growth and phosphorus metabolism of phytoplankton. J. Phycol., 14:337-341.
- Plumb, Jr., R. H. 1973. A study of the potential effects of the discharge of taconite tailings on water quality in Lake Superior. Ph.D. Thesis, University of Wisconsin, Madison, Wis.
- Portmann, J. E. and J. P. Riley. 1966. The determination of antimony in natural waters with particular reference to sea water. Anal. Chem. Acta., 35:35-41.
- Ragaini, R. C., H. R. Ralston, and N. Roberts. 1977. Environmental trace metal contamination in Kellogg, Idaho near a lead smelting complex. Env. Sci. Tech., 11:773-781.
- Reed, J. F. and M. B. Sturgis. 1936. Toxicity from arsenic compounds to rice on flooded soils. J. Am. Soc. Agron., 28:432-436.
- Ridley, W. P., L. J. Dizikes, and J. M. Wood. 1977. Biomethylation of toxic elements in the environment. Science, 197:329-332.
- Sanders, J. G. 1979. The concentration and speciation of arsenic in marine macro-algae. Est. Coast. Mar. Sci., 9:95-99.
- Sanders, J. G. and H. Windom. 1980. The uptake and reduction of arsenic species by marine algae. Est. Coast. Mar. Sci., 10:555-567.
- Schuth, C. K., A. R. Isensee, E. A. Woolson, and P. C. Kearney. 1974. Distribution of ¹⁴C arsenic derived from [¹⁴C] cacodylic acid in an aquatic ecosystem. J. Agr. Food Chem., 22:999-1003.
- Sckerl, M. M. 1968. Translocation and metabolism of MAA-carbon-14 in johnsongrass and cotton. Ph.D. Thesis, Univ. of Arkansas, Fayetteville, 72 pp.
- Scudlark, J. R. and D. L. Johnson. 1982. Biological oxidation of arsenite in seawater. Est., Coast. Shelf Sci., 14:693-706.
- Shariatpanahi, M. and A. C. Anderson. 1981. Effect of sodium arsenate on microbial growth in a chemostat. J. Environ. Sci. Health, B16:283-291.
- Shariatpanahi, M., A. C. Anderson, A. J. Englande, A. A. Abdelghani, and R. F. Wilkinson. 1981. Rate studies on the biotransformation of mono-sodium methanearsonate. J. Environ. Sci. Health, 16B:35.

- Shnyukov, E. F. 1963. Arsenic in the cimmerian iron ores of the Azov-Black Sea region. Geokhimiya, pp 87-93.
- Sillen, L. G. 1961. Arsenic. In Sears, M. (ed.), Oceanography. Invited lectures presented at the International Oceanographic Congress, New York, 1959, Washington, D.C., American Association for the Advancement of Science, p 574.
- Small, H. G., Jr. and C. B. McCants. 1962. Residual arsenic in soils and concentration in tobacco. Tobacco Sci., 6:34-36.
- Sollins, L. V. 1970. Arsenic and water pollution hazard. Science, 170:871.
- Steel, R. G. D. and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill Book Co., Inc. New York.
- Steevens, D. R., L. M. Walsh, and D. R. Keeney. 1972. Arsenic phytotoxicity on a plainfield sand as affected by ferric sulfate or aluminum sulfate. J. Environ. Qual., 1:301-303.
- Strohal, P., D. Huljev, S. Lulic, and M. Picer. 1975. Antimony in the coastal marine environment, north Adriatic. Est. Coast. Mar. Sci., 3:119-123.
- Stumm, W. and J. J. Morgan. 1970. Aquatic Chemistry. Wiley-Interscience, New York.
- Takamatsu, T., H. Aoki, and T. Yoshida. 1982. Determination of arsenate, arsenite monomethyl-arsenate, and dimethylarsinate in soil polluted with arsenic. Soil Sci., 133:239-246.
- Tammes, P. M. and M. M. de Lint. 1969. Leaching of arsenic from soil. Neth. J. Agric. Sci., 17:128-132.
- Turner, A. W. 1949. Bacterial oxidation of arsenite. Nature, 164:76-77.
- Turner, A. W. and J. W. Legge. 1954. Bacterial oxidation of arsenite. Aust. J. Biol. Sci., 7:452-476, 496-503, 504-514.
- Vandecaveye, S. C. 1943. Growth and composition of crops in relation to arsenical spray residues in the soil. Proceedings of the Sixth Pacific Science Congress of the Pacific Science Association. Vol. 6, Los Angeles, Calif., University of California Press, pp 217-223.
- Von Endt, D. W., P. C. Kearney, and D. D. Kaufman. 1968. Degradation of monosodium methanearsonic acid by soil microorganisms. J. Agric. Food Chem., 16:17-20.
- Walsh, L. M. and D. R. Keeney. 1975. Behavior and phytotoxicity of inorganic arsenicals in soils. In Woolson, E. A. (ed.). Arsenical Pesticides. Amer. Chem. Soc. Symp. Ser. No. 7:1-12.

- Waslenchuk, D. G. 1978. The budget and geochemistry of arsenic in a continental shelf environment. Mar. Chem., 7:39-52.
- Waslenchuk, D. G. 1979. The geochemical controls on arsenic concentrations in southeastern United States rivers. Chem. Geol., 24:315-325.
- Waslenchuk, D. G. and H. L. Windom. 1978. Factors controlling the estuarine chemistry of arsenic. Est. Coast. Mar. Sci., 7:455-464.
- Wauchope, R. D. 1975. Fixation of arsenical herbicides, phosphate, and arsenate in alluvial soils. J. Env. Qual., 4:355-358.
- Wedepohl, K. H. (ed.). 1969. Handbook of Geochemistry. Springer-Verlag, Berlin, Vol II, ch. 33.
- Wiklander, L. and L. Fredriksson. 1946. Die sorption von natriumarsenat und natriumarsenit durch hoden und syntetische eisen-und aluminiumoxyde. Acta Agric. Suecana, 1:345-376.
- Wiklander, L. and S. Alvelid. 1951. Solubility of arsenate in synthetic systems and soils. Annals Royal Agric. Coll. Swe., 17:342-354.
- Wilson, F. H. and D. B. Hawkins. 1978. Arsenic in streams, stream sediments, and ground water, Fairbanks area Alaska. Env. Geol., 2:195-202.
- Winchester, J. W. and G. D. Nifong. 1970. Water pollution in Lake Michigan by trace elements from pollution aerosols fallout. The Univ. of Mich., College of Eng., Dept. of Oceanography and Meteorology. Techn. Progress Rep. 3:1-12.
- Wong, P. T. S., Y. K. Chan, L. Luxon, and G. A. Bengert. 1977. An unpublished paper from the 11th annual conference on trace substances, Columbia, Missouri, June 7-9.
- Wood, J. M. 1974. Biological cycles for toxic elements in the environment. Science, 183:1049-1052.
- Woolson, E. A. 1975. Bioaccumulation of arsenicals. In Woolson, E. A., (ed.), Arsenical Pesticides, Amer. Chem. Soc. Symp. Ser. No. 7:97-107.
- Woolson, E. A. 1976. Abstracts of 16th meeting, Weed Sci. Soc. Am., p 91.
- Woolson, E. A. and A. R. Isensee. 1981. Soil residue accumulation from three applied arsenic sources. Weed Sci. Soc. Am. J., 29:17-21.
- Woolson, E. A. and P. C. Kearney. 1973. Persistence and reactions of ¹⁴C-cacodylic acid in soils. Env. Sci. Tech., 7:47-50.
- Woolson, E. A., A. R. Isensee, and P. C. Kearney. 1977. Distribution and isolation of radioactivity from ⁷⁴As-arsenate and ¹⁴C-methanearsonic acid in an aquatic model ecosystem. Pestic. Biochem. Physiol., 6:261-269.

Woolson, E. A., J. H. Axley, and P. C. Kearney. 1971. The chemistry and phytotoxicity of arsenic in soils: I. Contaminated field soils. Soil Sci. Soc. Am. Proc., 35:938-942.

Woolson, E. A., J. H. Axley, and P. C. Kearney. 1973. The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorus. Soil Sci. Soc. Amer. Proc., 37:224-259.

Wrench, J., S. W. Fowler, and M. Y. Unlu. 1979. Arsenic metabolism in a marine food chain. Mar. Poll. Bull., 10:18-20.

Wright, T. D., D. B. Mathis, and J. M. Brannon. 1978. Aquatic disposal field investigations Galveston, Texas offshore disposal site, Evaluative summary. U.S. Army Engineer Waterways Experiment Station, Technical Report D-77-20, Vicksburg, Miss.

APPENDIX A: EFFECT OF LEACHING UNDER CONTROLLED Eh-pH
CONDITIONS ON SEDIMENT CHEMICAL CONSTITUENTS

Table A1

Effect of Controlled Eh-pH Leaching on the Distribution and Chemical Form of
Arsenic in the Water Soluble Fraction of Sediment Suspensions

Eh	pH	Indiana Harbor			Menominee River			Baltimore Harbor		
		As(V) µg/l	As(III) µg/l	Organic As, µg/l	As(V) µg/l	As(III) µg/l	Organic As, µg/l	As(V) µg/l	As(III) µg/l	Organic As, µg/l
-150	5.0	1.8	1.1	3.5	77.0	nd*	135.0	1.7	nd	nd
50	5.0	10.0	14.0	nd	326.0	448.0	874.0	13.0	14.0	nd
250	5.0	1.4	1.7	nd	67.0	17.0	100.0	1.0	nd	nd
500	5.0	2.5	nd	nd	52.0	40.0	672.0	1.1	nd	nd
-150	6.5	nd	4.5	3.9	65.0	37.0	110.0	nd	2.2	nd
50	6.5	nd	4.5	nd	22.0	24.0	60.0	1.9	1.5	nd
250	6.5	0.8	1.4	nd	44.0	10.0	70.0	nd	1.5	nd
500	6.5	nd	2.2	nd	39.0	27.0	850.0	nd	nd	nd
-150	8.0	0.7	1.7	nd	339.0	143.0	560.0	11.0	9.3	nd
50	8.0	0.8	3.5	nd	136.0	114.0	260.0	30.0	nd	nd
250	8.0	1.9	2.4	nd	176.0	83.0	280.0	5.8	1.4	nd
500	8.0	1.3	3.9	1.0	208.0	87.0	5440.0	1.2	nd	18.0

* Not detectable

Table A2
Effect of Controlled Eh-pH Leaching on the Distribution and Chemical Form of
Arsenic in the Exchangeable Phase of Sediment Suspensions

Eh	pH	Indiana Harbor			Menominee River			Baltimore Harbor		
		As(V) µg/g	As(III) µg/g	Organic As, µg/g	As(V) µg/g	As(III) µg/g	Organic As, µg/g	As(V) µg/g	As(III) µg/g	Organic As, µg/g
-150	5.0	ne*	0.03	ne	0.87	0.60	ne	ne	0.03	ne
50	5.0	0.05	ne	ne	ne	ne	ne	0.03	ne	ne
250	5.0	ne	0.04	ne	0.47	ne	0.01	ne	0.02	ne
500	5.0	ne	0.05	ne	0.97	ne	4.56	ne	0.02	0.01
-150	6.5	ne	ne	ne	0.99	ne	0.58	ne	ne	ne
50	6.5	ne	ne	ne	0.33	0.11	0.17	ne	0.03	ne
250	6.5	ne	0.03	ne	0.60	0.02	0.36	ne	ne	0.01
500	6.5	ne	0.02	ne	0.47	0.44	2.99	ne	0.01	ne
-150	8.0	0.01	0.03	ne	4.23	2.16	ne	ne	0.05	ne
50	8.0	0.04	0.01	ne	3.75	2.68	ne	ne	0.08	ne
250	8.0	0.01	0.05	ne	2.22	0.98	ne	ne	0.01	ne
500	8.0	0.03	0.07	ne	1.47	3.78	ne	ne	0.03	ne

* Not extracted

Table A3
Effect of Controlled Eh-pH Leaching on the Distribution and Chemical Form of
Ammonium Sulfate Extractable Arsenic in the Sediment Suspensions

Eh	pH	Indiana Harbor			Menominee River			Baltimore Harbor		
		As(V) -g/g	As(III) -g/g	Organic As, -g/g	As(V) -g/g	As(III) -g/g	Organic As, -g/g	As(V) -g/g	As(III) -g/g	Organic As, -g/g
-150	5.0	0.02	0.04	nd*	1.67	0.60	0.38	nd	0.03	nd
50	5.0	0.14	0.04	nd	1.98	3.09	0.39	0.04	nd	nd
250	5.0	nd	0.05	nd	1.06	nd	0.15	nd	0.02	nd
500	5.0	nd	0.05	nd	1.47	nd	10.15	nd	0.02	0.01
-150	6.5	nd	0.02	nd	1.59	0.03	0.65	nd	0.01	nd
50	6.5	nd	0.04	nd	0.52	0.32	0.30	nd	0.04	nd
250	6.5	nd	0.04	nd	1.02	0.11	0.51	nd	0.02	0.01
500	6.5	nd	0.04	nd	0.90	0.74	11.76	nd	0.01	nd
-150	8.0	0.02	0.05	nd	7.15	3.39	nd	0.02	0.12	nd
50	8.0	0.04	0.04	nd	5.68	4.30	nd	0.13	0.08	nd
250	8.0	0.02	0.07	nd	3.83	1.74	0.16	0.03	0.03	nd
500	8.0	0.04	0.10	nd	4.23	4.93	40.06	nd	0.03	nd

* Not detectable

Table A4
Effect of Controlled Eh-pH Leaching on the Distribution of
Total Arsenic in Indiana Harbor Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water soluble, $\mu\text{g/g}$	6.4	24.0	3.1	2.5	8.4	4.5	2.2	2.2	2.4	4.3	4.3	6.2
Ammonium sulfate extractable, $\mu\text{g/g}$	0.7	0.18	0.05	0.05	0.02	0.04	0.04	0.04	0.07	0.08	0.09	0.14
Exchangeable, $\mu\text{g/g}$	0.03	0.06	0.04	0.05	ne*	ne	0.03	0.02	0.04	0.05	0.05	0.09
Easily reducible, $\mu\text{g/g}$	3.5	5.2	2.9	1.5	1.6	2.1	1.2	0.9	1.1	3.5	0.5	0.5
Modorarily reducible, $\mu\text{g/g}$	34.5	34.0	34.3	41.5	35.5	35.0	42.0	41.5	32.5	37.0	42.0	36.5

* None extracted

AD-A139 032

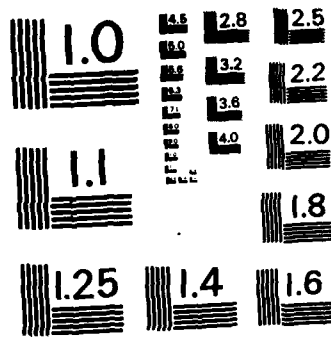
DREDGING OPERATIONS TECHNICAL SUPPORT PROGRAM
TRANSFORMATION FIXATION AND. (U) ARMY ENGINEER
WATERWAYS EXPERIMENT STATION VICKSBURG MS J M BRANNON
JAN 84 WES-TR-D-84-1 F/G 13/2

3/3

UNCLASSIFIED

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Table A5

Effect of Controlled Eh-pH Leaching on the Distribution of
Total Arsenic in Menominee River Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	250	500	-150	50	250	500	500
Water soluble, $\mu\text{g/l}$	135.0	874.0	100.0	672.0	110.0	60.0	70.0	850.0	5440.0
Ammonium sulfate extractable, $\mu\text{g/g}$	2.65	5.46	1.21	11.62	2.27	1.14	1.64	13.40	49.22
Exchangeable, $\mu\text{g/g}$	1.48	ne*	0.47	5.53	1.58	0.61	0.98	3.90	5.25
Easily reducible, $\mu\text{g/g}$	28.8	48.1	39.2	49.4	44.3	44.4	45.2	66.2	60.7
Moderately reducible, $\mu\text{g/g}$	645.0	605.0	742.5	605.0	486.0	428.0	497.5	420.5	459.0

* None extracted

Table A6
Effect of Controlled Eh-pH Leaching on the Distribution of
Total Arsenic in Baltimore Harbor Sediment Suspensions

Chemical Fraction	pH 5.0				pH 6.5				pH 8.0			
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water soluble, $\mu\text{g/l}$	1.7	27.0	1.0	1.1	2.2	3.4	1.5	<0.5	20.0	30.0	7.2	19.2
Ammonium sulfate extractable, $\mu\text{g/g}$	0.03	0.04	0.02	0.03	0.01	0.04	0.03	0.01	0.14	0.21	0.06	0.03
Exchangeable, $\mu\text{g/g}$	0.03	0.03	0.02	0.03	0.00	0.03	0.02	0.01	0.05	0.08	0.01	0.03
Easily reducible, $\mu\text{g/g}$	3.2	3.6	2.8	1.3	2.0	2.4	1.7	1.1	1.2	2.2	1.2	1.3
Moderately reducible, $\mu\text{g/g}$	26.5	23.8	33.7	39.5	27.8	30.8	41.3	34.8	33.5	29.1	31.6	36.1

Effect of Controlled Eh-pH Leaching on the Distribution of Iron in Indiana Harbor Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0				
	-150	50	500	-150	50	500	-150	50	500		
Water soluble, mg/l	321	386	84.5	0.5	2.8	0.4	0.1	0.2	0.3	0.1	
Ammonium sulfate extractable, µg/g	2633	3885	1009	9.8	70.7	9.5	0.8	1.3	2.3	1.3	
Exchangeable, µg/g	ne*	561.0	281.0	5.2	49.6	6.6	0.3	ne	ne	0.2	
Easily reducible, mg/g	4.5	4.6	4.3	3.5	3.9	4.2	3.8	3.2	3.3	2.8	2.3
Moderately reducible, mg/g	125	125	129	124	121	122	129	123	121	124	124

*** None extracted**

Table A8
Effect of Controlled Eh-pH Leaching on the Distribution of
Iron in Menominee Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	500	-150	50	500	-150	50	500
Water soluble, $\mu\text{g/l}$	0.3	52.2	0.6	0.6	0.1	0.4	0.1	0.1	0.3
Ammonium sulfate extractable, $\mu\text{g/g}$	7.5	153.0	9.5	24.0	2.1	14.7	2.9	3.7	27.3
Exchangeable, $\mu\text{g/g}$	4.1	ne*	3.9	18.2	1.0	10.1	2.2	1.2	23.1
Easily reducible, mg/g	1.4	1.8	1.9	1.4	1.0	1.1	1.0	1.3	0.9
Moderately reducible, mg/g	149	138	167	150	132	124	169	140	161

* None extracted

Table A9
Effect of Controlled Eh-pH Leaching on the Distribution of
Iron in Baltimore Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	250	500	-150	50	250	500	500
Water soluble, $\mu\text{g/l}$	0.9	233.0	13.1	3.7	0.1	0.1	0.5	0.3	0.3
Ammonium sulfate extractable, $\mu\text{g/g}$	19.0	2693.0	187.0	12.0	1.3	0.7	174.0	0.9	1.6
Exchangeable, $\mu\text{g/g}$	11.0	917.0	72.1	ne*	0.3	ne	ne	ne	ne
Easily reducible, mg/g	3.8	2.4	3.8	2.8	2.8	2.6	2.5	2.6	2.4
Moderately reducible, mg/g	151.0	124.0	161.0	202.0	153.0	158.0	142.0	160.0	207.0

* None extracted

Table A10
Effect of Controlled Eh-pH Leaching on the Distribution of
Aluminum in Indiana Harbor Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	500	-150	50	500	-150	50	500
Water soluble, $\mu\text{g/l}$	102	33	404	299	19	9	245	22	500
Ammonium sulfate extractable, $\mu\text{g/g}$	5.01	0.64	6.97	6.63	0.13	0.14	0.61	0.27	0.38
Exchangeable, $\mu\text{g/g}$	4.14	0.35	3.49	3.84	ne*	0.06	ne	0.06	ne
Easily reducible, $\mu\text{g/g}$	280	270	332	527	243	285	307	356	188
Moderately reducible, $\mu\text{g/g}$	5900	5950	5850	5950	5850	6475	5700	6350	5850

* None extracted

Table All
Effect of Controlled Eh-pH Leaching on the Distribution of
Aluminum in Menominee Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	500	-150	50	500	-150	50	500
Water soluble, $\mu\text{g/l}$	177	53	524	48	75	110	58	60	43
Ammonium sulfate extractable, $\mu\text{g/g}$	2.31	4.28	5.74	0.06	1.23	2.96	0.95	0.80	2.81
Exchangeable, $\mu\text{g/g}$	0.48	3.76	2.05	0.06	0.56	2.23	0.42	ne*	2.24
Easily reducible, $\mu\text{g/g}$	394	79	78	18	20	61	22	27	45
Moderately reducible, $\mu\text{g/g}$	3135	3720	3500	3230	3115	2365	4300	3700	4155

*** None extracted**

Table A12
Effect of Controlled Eh-pH Leaching on the Distribution of
Aluminum in Baltimore Harbor Sediment Suspensions

Chemical Fraction	pH 5.0				pH 5.5				pH 8.0			
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water soluble, $\mu\text{g/l}$	579	282	983	3920	19	76	25	27	192	600	229	85
Ammonium sulfate extractable, $\mu\text{g/g}$	25.00	8.00	29.00	175.00	0.39	0.44	0.41	3.03	1.18	0.35	0.21	0.40
Exchangeable, $\mu\text{g/g}$	19.50	5.50	20.60	184.60	0.23	ne*	0.20	2.83	ne	ne	ne	ne
Easily reducible, $\mu\text{g/g}$	873	897	751	857	848	890	737	802	360	485	724	676
Moderately reducible, $\mu\text{g/g}$	1320	1215	1235	1325	1335	1360	1360	1360	1645	1235	1303	1340

* None extracted

Table A13
Effect of Controlled Eh-pH Leaching on the Distribution of Calcium in
the Water Soluble Fraction of Sediment Suspensions

Sediment	pH 5.0			pH 6.5			pH 8.0		
	-150	50	250	500	-150	50	250	500	500
	----- mg Ca/l -----								
Indiana Harbor	1580	1390	1610	1420	1410	1340	1510	1340	950
Menominee River	1900	2300	2760	1830	1220	1330	1760	1290	1180
Baltimore Harbor	103	146	124	182	89	96	111	171	122

APPENDIX B. DISTRIBUTION OF VARIOUS CHEMICAL CONSTITUENTS
IN SEDIMENTS FOLLOWING ANAEROBIC INCUBATION

Table B1
Aluminum Concentration in the Interstitial Water, Exchangeable,
Easily Reducible, and Moderately Reducible Phases of
Sediments Incubated Anaerobically for 45 Days

<u>Sediment</u>	<u>Interstitial Water, mg/l</u>	<u>Exchangeable μg/g</u>	<u>Easily Reducible, μg/g</u>	<u>Moderately Reducible, μg/g</u>
Black Rock	0.23	0.36	24.6	2772
Corpus Christi	0.30	0.24	14.9	670
Detroit	0.02	0.37	23.2	3765
Indiana Harbor	0.25	0.16	19.1	890
Bridgeport	0.26	0.33	7.7	2210
Menominee 1	0.23	0.12	91.0	286
Michigan City	0.26	0.42	13.6	2186
Milwaukee	0.20	0.43	23.6	555
Oakland	0.21	0.05	194.8	349
Seattle	0.27	0.38	170.4	2671

Table B2
Iron Concentration in the Interstitial Water, Exchangeable,
Easily Reducible, and Moderately Reducible Phases of
Sediments Incubated Anaerobically for 45 Days

<u>Sediment</u>	<u>Interstitial Water, mg/l</u>	<u>Exchangeable μg/g</u>	<u>Easily Reducible, μg/g</u>	<u>Moderately Reducible, μg/g</u>
Black Rock	4.2	70.7	7841.8	15500
Corpus Christi	1.7	3.8	38.9	3537
Detroit	0.5	8.1	346.0	57917
Indiana Harbor	44.3	127.4	3637.3	18350
Bridgeport	1.1	16.3	3497.2	100
Menominee 1	65.5	101.9	753.0	970
Michigan City	59.2	378.1	1662.1	14506
Milwaukee	27.0	204.3	162.2	5983
Oakland	3.2	8.2	2241.3	2542
Seattle	3.2	20.8	4203.0	95

Table B3

Manganese Concentration in the Interstitial Water, Exchangeable,
Easily Reducible, and Moderately Reducible Phases of
Sediments Incubated Anaerobically for 45 Days

<u>Sediment</u>	<u>Interstitial Water, mg/l</u>	<u>Exchangeable μg/g</u>	<u>Easily Reducible, μg/g</u>	<u>Moderately Reducible, μg/g</u>
Black Rock	1.2	3.7	40.0	42.8
Corpus Christi	9.1	39.6	266.3	130.7
Detroit	0.1	14.6	410.0	948.3
Indiana Harbor	1.3	4.6	205.3	256.3
Bridgeport	0.5	1.2	18.6	19.8
Menominee 1	14.2	28.2	79.7	20.7
Michigan City	2.5	14.7	216.2	189.9
Milwaukee	1.7	15.4	245.3	176.3
Oakland	2.4	3.9	50.3	20.7
Seattle	0.9	1.6	19.7	27.3

APPENDIX C. EFFECT OF LEACHING UNDER CONTROLLED
Eh-pH CONDITIONS ON SEDIMENT ANTIMONY

Table C1
Effect of Controlled Eh-pH Leaching on the Distribution of
Antimony in Indiana Harbor Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	250	500	-150	50	250	500	500
Water soluble $\mu\text{g/l}$	<3.0	<3.0	<3.0	4.0	<3.0	3.0	6.0	6.0	11.0
Ammonium sulfate extractable, $\mu\text{g/g}$	nd*	0.03	0.04	0.10	0.04	0.07	0.12	0.10	0.21
Exchangeable, $\mu\text{g/g}$	ne**	0.03	0.04	0.06	0.04	0.04	0.07	0.04	0.10
Easily reducible, $\mu\text{g/g}$	nd	nd	nd	nd	nd	nd	0.2	0.2	nd
Moderately reducible, $\mu\text{g/g}$	8.3	7.2	7.3	7.5	5.4	5.6	7.4	7.6	7.2

* Not detected

** None extracted

Table C2
Effect of Controlled Eh-pH Leaching on the Distribution of
Antimony in Menominee River Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0		
	-150	50	250	500	-150	50	250	500	500
Water soluble $\mu\text{g/g}$	6.0	2.0	6.0	6.0	7.0	8.0	8.0	7.0	8.0
Ammonium sulfate extractable, $\mu\text{g/g}$	0.08	0.02	0.05	nd*	0.12	0.10	0.11	0.04	0.10
Exchangeable, $\mu\text{g/g}$	0.13	ne**	ne	ne	0.06	0.03	0.04	ne	0.03
Easily reducible, $\mu\text{g/g}$	nd	nd	nd	nd	nd	nd	nd	nd	nd
Moderately reducible, $\mu\text{g/g}$	1.5	1.9	2.0	1.9	1.7	1.7	1.5	1.5	1.9

* Not detected

** None extracted

Table C3

Effect of Controlled Eh-pH Leaching on the Distribution of
Antimony in Baltimore Harbor Sediment Suspensions

Chemical Fraction	pH 5.0			pH 6.5			pH 8.0				
	-150	50	250	-150	50	250	-150	50	250	500	
Water soluble $\mu\text{g/l}$	<3.0	<3.0	<3.0	6.0	6.0	<3.0	<3.0	15.0	18.0	7.0	3.0
Ammonium sulfate extractable, $\mu\text{g/g}$	nd*	nd	nd	nd	0.06	0.06	nd	0.17	0.16	0.07	0.03
Exchangeable, $\mu\text{g/g}$	ne**	ne	ne	ne	0.01	0.06	ne	0.04	0.01	0.01	0.01
Easily reducible, $\mu\text{g/g}$	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Moderately reducible, $\mu\text{g/g}$	3.5	3.0	3.7	5.1	3.2	4.0	4.2	4.0	4.0	3.8	3.6

* Not detected

** None extracted

END

FILMED

4-84

DTIC