



Handbook of Arsenic Toxicology



Handbook of Arsenic Toxicology

Edited by
S. J. S. Flora



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*In the memory of my mother
Paramjit
who always told me,
'do not be successful but be valuable'*

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Foreword

Handbook of Arsenic Toxicology is a significant addition to the literature dealing with the toxicology of this very important metalloid. The chapters in this book are relevant to arsenic exposure via drinking water, the usual route of exposure of an estimated 200 million people in the world – many in developing countries. In Bangladesh, arsenic exposure is also more common through ingestion of food. Populations with high intake of rice and vegetables may also be at risk.

Arsenic is a recognized human carcinogen and it can also cause cardiovascular and metabolic disease. It is a unique toxicant to the respiratory system – the only one following ingestion that is associated with malignant and non-malignant respiratory diseases.

Arsenic for many years was known as the King of Poisons, and the Poison of Kings. It was the poison of choice for homicides because no chemical test was available to identify and measure it. Arsenic trioxide, As_2O_3 , was the highly favored poison form, because it is odorless, easily incorporated into food and drink, and before the development of the Marsh test, it was untraceable in the body. This chemical test was developed in about the 1830s after which time the number of homicides using arsenic compounds was greatly reduced.

The metabolism of inorganic arsenic has been carefully investigated during recent years. It was discovered surprisingly that inorganic arsenite was metabolized to the more toxic +3-methylated metabolites, methylarsonous acid (MMA^{III}) and dimethylarsinous acid (DMA^{III}). The latter compound is so toxic that it is wise to use a fume hood when working with it.

In his chapter on arsenical kidney toxicity, Bruce Fowler aptly points out that “the mitochondria are a major target organelle for arsenical toxicity with resultant inhibition of respiratory function, loss of ATP production, and generation of reactive oxygen species leading to altered cell signaling pathways, gene expression patterns, and induction of apoptosis.”

Many, but not all, chapters of this book are written by the new generation of arsenic investigators. They bring to the forefront many newer thoughts and information about the toxicity of compounds of this toxic metalloid. One cannot ignore, however, the contributions by some of the well-known established authors. The first chapter by Dr. Flora on the chemistry, occurrence and exposure to arsenic compounds sets the tone as to what is to come. Dr. D.N. Guha Mazumder is another highly respected investigator with a lengthy list of significant publications dealing with the human clinical effects of exposure to arsenic compounds.

One also needs to remember other highly respected investigators like Dr. Mariano Cebrian. Although he is not an author of a chapter in this book, he was among the earliest investigators of such research. His first arsenic paper was published in 1983, entitled *Chronic Arsenic poisoning in the North of Mexico*. This early paper is very relevant because it dealt with a human population and answered some questions dealing with arsenic toxicity. The paper also presented

new questions concerning arsenic exposure and human health and stimulated the entrance of other investigators into this previously neglected area of scientific investigation. The chapters of the present book expand these questions and answers.

With the number of people at risk today, it is surprising that no useful treatment of chronic arsenic toxicity for large populations has become available. Prevention and/or limiting exposure remain the only approaches, and the information supplied in this book is a great step forward in this area.

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Preface

I have been a chemical toxicologist for nearly 35 years. In this time, I have studied and evaluated the toxicities of toxic metals and the health effects produced by human exposure to metals.

Arsenic, a naturally occurring metalloid, is ubiquitously present in the environment. Arsenic is ranked first among toxicants posing a significant potential threat to human health based on known or suspected toxicity. This naturally occurring metalloid is a known poison, a co-carcinogen, and in lower concentrations has been shown to cause damage to almost all major organs including liver, lungs, bladder and brain. Currently, the permitted concentration of arsenic in water is 10 $\mu\text{g/L}$ (10 ppb). Yet, an estimated 100 million people worldwide are exposed to excessive amounts of arsenic via drinking water (in the ppm, not ppb, range). Many of these individuals obtain drinking water from unregulated sources (wells) or live in regions where arsenic levels are high, such as Bangladesh. Arsenic leaches from rock formations into water sources as the water table recedes, and hence exposure to high amounts of arsenic will continue to persist whilst the demand for clean water increases. This phenomenon particularly affects the Western region of the United States, where it is estimated that certain areas contain up to 3100 $\mu\text{g/L}$ arsenic (31 ppm) in drinking water, on par with levels reported in Taiwan, China, Bangladesh and India.

Although the largest number of people affected worldwide by the arsenic contamination of drinking water are in Bangladesh, the problem is not unique to that area. As early as 1960, scientists reported the link between various forms of cancer and arsenic in drinking water in Taiwan. Communities in North and South America, Europe, Asia and Australia also face the problem of arsenic-contaminated drinking water. The problem of arsenic-contaminated groundwater is found in communities throughout Canada and western USA that use groundwater as their source of drinking water. It is now almost certain that arsenic contamination is a worldwide problem; however, some of the most affected regions lie in the flood plains of the great rivers of Bangladesh, Nepal, and West Bengal, India. In Bangladesh alone, seventy million people are impacted. Problems associated with drinking groundwater were first noticed in Bangladesh by healthcare workers in the early 1990s. While the World Health Organization (WHO) and the Environmental Protection Agency (EPA) regulate water sources of arsenic, lack of strict regulations on food, beverages, and air quality can lead to increased arsenic exposure. Ingestion of arsenic activates metabolic pathways for excretion, resulting in a number of metabolites, some of which are more potent and toxic than the originally ingested inorganic form of arsenic.

Inorganic arsenic exposure of humans, by the inhalation route, has been shown to be strongly associated with lung cancer, while ingestion of inorganic arsenic by humans has been

linked to a form of skin cancer and also to bladder, liver, and lung cancer. The EPA has classified inorganic arsenic as a human carcinogen. This explosion of information in the recent years reflects the vast increase in number of researchers studying about the mechanisms of action of arsenic. The specific knowledge of the chemistry, biochemistry, toxicology, and epidemiology of arsenic is far greater than that for any other environmentally-occurring chemical carcinogen.

This book really began over 20 years ago, when I was confronted with the first of scores of instances in Uttar Pradesh, Maharashtra, West Bengal and Bihar in India, where individuals exposed to arsenic subsequently developed symptoms and effects that could notably be explained by the known toxicological effects. In some instances the exposures led to effects far in excess of what would be expected. In others, effects were noted following exposures to extremely low levels of arsenic; in even more instances the body organs targeted were not those known to be impacted by arsenic. I carried out number of studies during these years; a few of them with my colleagues in West Bengal. These studies led to one serious concern: that we do not have a safe, specific and effective chelating drugs in this part of the world, and those drugs available in the developed countries are largely ineffective against arsenic toxicity.

As time progressed, I began to think that the task was too big and a solution remained elusive. The breakthrough came when I got a reprint from Prof. M.M. Jones, Vanderbilt University in which his group synthesized and evaluated the efficacy of number of di- and monoesters of meso 2,3-dimercaptosuccinic acid (DMSA) with limited success against cadmium intoxication. There was a small but an interesting note on the top of the reprints written in red ink, where he asked me to try these esters against arsenic. This led me to my interest in arsenic poisoning and in particular searching for a new chelating agent. A review of the literature and our research group's own studies highlighted the shortcomings with DMSA, DMPS and BAL, and it was then hypothesized that monoesters of DMSA might be a better option to treat cases of arsenicosis.

I have attempted to bring together as comprehensive a group of scientists as possible in assembling this book. Whilst at first glance, the literature on arsenic toxicology seems exhaustive and systematic, this is not the case. There is no comprehensive and in-depth analysis of its effects on major organs, preventive and therapeutic measures; additionally, there are a few new topics where not much work has been undertaken but could be of potential future interest. This book thus promises to provide a comprehensive coverage of arsenic and its toxic effects, including its toxicokinetics, mode(s) of action, effects on all major organs and medical countermeasures. To my knowledge, this book perhaps is the first in-depth analysis of data on toxicology, risk assessment, and management. Included in these 28 chapters are detailed reviews of the many important mechanistic aspects of arsenic.

Chapters 1 and 2 provide an orientation and introduction to the subject of arsenic. The focus of these chapters is to provide an overview of various critical factors affecting arsenic chemistry, the natural and anthropogenic sources of exposure. The focus of Chapters 3 and 4 are risk assessment following arsenic exposure while Chapter 5 provides data for the removal of arsenic using activated alumina (AA) and modified AA adsorbents. Chapters 5 and 6 provide information on the general health effects of arsenic and the role of arsenic metabolites in

the toxic manifestation, respectively. Chapters 7–9 focus on various proposed modes of actions for arsenic, exposure pathways and toxicokinetics, various alterations in mediating genotoxic effects such as altered DNA repair, signal transduction, cellular proliferation, and altered DNA methylation. One of the major mechanisms of arsenic-induced toxic manifestation is oxidative stress. These chapters provide in-depth information regarding alterations at the biochemical level, detailed mechanisms of toxicity and oxidative injury, and the links between arsenic, oxidative stress and cancer. Chapter 10 discusses the gastrointestinal tract as one of the target organs of arsenic and a factor affecting its toxicity and the resultant risk assessments required. The authors suggest that arsenic species with higher toxicity degree than those ingested may appear in the intestinal lumen as a result of interactions with food components and from metabolism by enterocytes and micro biota. Also, the biotransformation may modulate arsenic intestinal absorption and therefore adverse effects.

Although arsenic impacts on the physiological cellular processes in numerous organ systems, the outcomes of its toxicity are usually first seen in the skin. The major focus of Chapter 11 is on skin manifestations from acute toxicity such as flushing, erythema, facial edema, acrodynia, urticarial, alopecia, loss of nails, and Mees lines visible on nails. The liver is the target organ of arsenic and many important various metabolizing reactions take place in liver, rendering it the most susceptible organ to any xenobiotic. Exposure to arsenic leads to various hepatic disorders, which has been discussed in Chapter 12. Arsenic, the only environmental toxicant has been linked to both malignant and non-malignant respiratory disease following ingestion, rather than inhalation, making arsenic a unique toxicant to the respiratory system. Chapter 13 suggests that chronic exposure to arsenic has been associated with the development of respiratory symptoms, impaired lung function and chronic lung disease. Chapter 14 provides an overview of information that arsenic disturbs various vital renal functions such as the excretion of nitrogenous waste products and maintenance of electrolyte balance, which leads to immediate effects on circulating blood and hence whole body. Chapter 15, 16, 17, and 19 make a strong argument for the potential role of arsenic in disrupting the normal functions of the central nervous system, thereby causing impairment of learning, concentration and short term memory. It also alters the release of various neurotransmitters. Since the brain is the most vital organ, it's important to fully understand the effect of arsenic intoxication and associated neuropathologies, which are discussed here.

Arsenic accumulates in the urinary bladder epithelium, causing activation of specific signaling pathways, leading to increased cell proliferation and increased incidence of urinary bladder tumors. Such manifestations are discussed in Chapter 18. Chronic arsenic exposure induces high oxidative stress which affect the structure and function of the cardiovascular system, resulting in cardiac anomalies such as arrhythmia and atherosclerosis. Moreover, newer technologies like the use of pluripotent stem cells could provide a better opportunity to study the effects of arsenic in a cell type-specific manner. Chapter 18 also briefly discusses emerging technologies that provide a new dimension to evaluate diseases.

Immunosuppression caused by arsenic is another major cause of cancer development in humans. Chronic exposure to arsenic has been shown to significantly compromise the host response to infection, thereby leading to development of fatal conditions. Chapter 21 provides

comprehensive information about such immunosuppressive effects. There have been many reports exhibiting significant relationship between arsenic exposure and adverse reproductive health outcomes such as stillbirths, low birth-weight, childhood stunting, neural tube defects and under-weight children. Chapter 22 specifically deals with various adverse effects of arsenic on reproductive system and potential mechanisms. Arsenic is classified as a human carcinogen and has been linked with various malignancies such as skin, lungs and liver. Chapter 23 specifically explores the association between arsenic exposure and cancer development and current mechanisms that have been proposed to contribute to such neoplastic processes. An association between chronic arsenic exposure and Type 2 diabetes is still inconclusive. Chapter 24 deals with the analysis of 27 studies including 15 cross-sectional, 4 case-control and 3 cohort studies. Authors conclude that their meta-analysis suggests that chronic arsenic exposure is likely to increase the risk of Type 2 diabetes. Chapter 25 attempts to highlight the advancement made so far in the development of arsenic biosensors – analytical devices that have high sensitivity, portability, small sample requirements and are easily used for quantitative and qualitative monitoring of various analytes.

Both chemical and synthetic medical countermeasures have been used against chronic arsenic poisoning. Chelating agents such as Dimercaprol and DMSA were found to be quite effective; however they are compromised with a few shortcomings. Extensive research in future is required to establish an effective drug against chronic arsenicosis. Also development of specific biomarkers is an important strategy. Chapter 26 focuses on available arsenic antidotes, their clinical uses, their drawbacks, side effects and the new developments in the area. Chapter 27 deals with recent progress on the mechanisms of arsenic uptake, toxicity, and detoxification in microbes and in plants. Chapter 28 provides information about arsenic concentration and biogeochemical cycle in marine environment (marine animals, bacteria, phytoplankton, etc).

I intend that this book be useful for health scientists, including nutritionists and dietitians, pharmacologists, public health scientists, and colleges, epidemiologists, health workers and practitioners, agriculturists, botanists, healthcare professionals of various disciplines, policy-makers, and marketing and economic strategists. It is also designed for teachers and lecturers, undergraduates and graduates.

Finally, I am deeply indebted to all authors for their sincere and dedicated contributions to this book. I have tried to get all contributions written by specialists in the respective area; however, we have missed a few well-known names who expressed their inability due to various professional and personal commitments. The editor views these contributions as excellent summaries by some of the world's outstanding scientists/ researchers practitioners of arsenic toxicology and hope the readers will find them highly enlightening and useful. A special thanks to Molly McLaughlin, the project manager at Elsevier/Academic Press, who was a big support throughout the process and provided vital input in the preparation of this book.

Swaran J.S. Flora



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I am grateful to all of the contributors for taking the time and effort to complete these chapters in a thorough yet timely manner. In addition to the individual contributions of each of our chapter authors, who are recognized leaders in their respective areas of specialization, many other scientists from around the world have contributed extensively to our understanding of arsenic biochemistry and toxicology. I would like to acknowledge the work of all these contributors. Their efforts made it much easier to do my job of compiling and editing this book.

Many of us who are involved in research about arsenic find that our work is not just fascinating and compelling, but are drawn to this metalloid for its public health significance in the developing world. The daily exposure to arsenic in different parts of the world are manifold. In some countries, human exposure can exceed 3000 ppb and in parts of the developed world, the exposure is much less than 10 ng per day. Given this situation it is hoped that the understanding of basic mechanisms of the action of arsenic will lead to the design of effective prevention strategies for both the developed and developing world.

In addition to the contributors, several other scientists have also provided scientific substance for this book and they should be congratulated for their efforts, I also thank Molly McLaughlin, Editorial Project Manager at Elsevier/Academic Press for her extensive and excellent administrative support and unfailing help in the development of this book from its inception. This book would not have been physically possible without her tireless work and extraordinary skills. I am also grateful to the many people at Elsevier/Academic Press for their assistance, patience, and understanding in working with me to complete this book in a timely manner. A heartfelt thanks is also extended to Melissa Read at Elsevier/Academic Press for the fine production work.

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I dedicate this book to Gurpyari, my life-long companion, for her unconditional support in many projects. I also dedicate this book to my daughter Preeti, my son Ujjwal, and brother Govinder for providing me with reasons to fight for the protection of the environment and especially to my parents for their support during my studies and thereafter. I also dedicate this book to my mentor Dr S.K. Tandon (in memoriam) for his guidance, foresights and for opening my eyes to the science of toxicology.

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Arsenic: Chemistry, Occurrence, and Exposure

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1.1 Introduction

Arsenic, the king of poisons, has influenced the human population more than any other element or toxic compound for thousands of years. Today, millions of people are being chronically exposed to elevated doses of arsenic from air, food, water, and soil. Throughout the history of human progress, arsenic has been seen as a bizarre and frightful element. Toxic effects of arsenic are highly prevalent in both developed and developing countries. Arsenic toxicity has become a principal concern owing to the escalating contamination of air, water, and soil. It has the ability to readily change its oxidation state and bonding configuration, thus showing diverse chemical behavior in the environment and forming large numbers of organic and inorganic compounds. Specific electronic configurations of valence shells with filled s orbitals and half-filled p orbitals enable arsenic to easily donate electrons and overlap in covalent bonds. Naturally, arsenic forms bonds with oxygen and sulfur and generates large

numbers of oxides and sulfides. It is also capable of forming large numbers of bio-molecules as it forms stable bonding with the methyl group. The peculiar chemistry of arsenic is the basis for its dual action as a toxin and as a curative.

Drinking water and contaminated soils are the major means by which arsenic gains its entry into the food chain. Most of the arsenic compounds are readily soluble in water and so can easily enter water bodies such as rivers, lakes, and ponds, and by surface runoff. The main pathways of human exposure to arsenic are ingestion of drinking water, consumption of food, and inhalation of air. Among all sources, drinking water has been reported to be the main route of arsenic exposure around the globe [1,2]. Occupational exposure to arsenic is also very common in individuals working in wood preservation, desiccant, chemical warfare agent, pigment, drug and arsenic-based pesticide industries, and those involved in smelting and mining operations and residing in the vicinity of mining areas.

Prolonged exposure to arsenic leads to various dermatological, respiratory, neurological, and reproductive disorders and it is therefore referred to as a carcinogen and mutagenic agent [3,4]. The US Department of Health and Human Services in its 9th Report on Carcinogens listed arsenic compounds as human carcinogens. Arsenic exposure may cause severe health manifestations including cancers, melanosis (hyperpigmentation or hypopigmentation), hyperkeratosis (hardened skin), blackfoot disease (peripheral vascular disorder), gangrene, diabetes mellitus, hypertension, ischemic heart disease, etc. [5,6].

Due to increasing health concerns and adverse effects of arsenic on humans, US EPA in 2002 reduced the maximum permissible limit of arsenic in drinking water from 50 to 10 $\mu\text{g/L}$ [7]. Despite a number of corrective and preventive measures, the increase of arsenic contamination in ground water continued to develop with the addition of new areas to the list of arsenic-contaminated regions. In view of the global health issues associated with arsenic exposure, it has become essential to understand arsenic sources, geochemistry, interaction with water, and various mechanisms associated with arsenic release into the environment. This chapter deals with the occurrence of arsenic in air, water, and soil, and its chemistry in the entire medium along with its global distribution. The chapter also discusses a number of treatment methodologies for the effective removal of arsenic from ground water and to reduce the global arsenic burden.

1.2 Chemistry of Arsenic

1.2.1 Origin and History

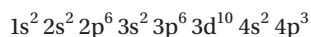
Arsenic has been known since ancient times in its sulfide form. The Greek philosopher Theophrastus knew about two arsenic minerals: bright yellow orpiment (As_2S_3) and red colored realgar (As_4S_4). Greek historian Olympiodorus of Thebes (5th century AD) was the first to obtain white arsenic (As_2O_3) by heating arsenic sulfide. The discovery of the element arsenic is attributed to Albertus Magnus, a German philosopher in the 1200s, who was the first to report the metallic behavior of arsenic. *De Mineralibus* described pure arsenic being obtained by the heating of orpiment with soap. Arsenic trioxide (As_2O_3), a by-product of copper refining, when mixed with olive oil and heated gives arsenic metal. Chinese scientist Tsao Kan-Mu studied

toxicity of arsenic compounds in the 1500s during the Ming dynasty and mentioned their use as pesticides in rice fields. The elemental name is believed to come from the Greek word *arsenikos* meaning potent. Arsenic ranks as the 20th most common element in Earth's crust, 14th in the sea, and 12th in the human body.

Humans have been using arsenic since ancient times both as a poison and a curative. It has also been used in pyrotechnics, metallurgy, warfare, and pigmentation, and for decoration. One of the most popular oxides of arsenic (arsenic trioxide) is a tasteless, odorless, white powder used in the past as a chemical warfare agent; however, green colored copper acetoarsenate was traditionally used in wallpapers as a pigment [8].

1.2.2 Atomic Structure and Bonding

Arsenic ranks 33rd in the periodic table, as part of the elements in Group 15, being a member of the nitrogen family. Its atomic number is 33 and its atomic weight is 74.921, placing it as heavier than iron, nickel, and manganese but lighter than silver, lead, or gold. The most stable and non-radioactive isotope of arsenic is arsenic-75 (^{75}As) with 33 protons and 42 neutrons inside the nucleus surrounded by 33 electrons in different energy shells. Other unstable and radioactive isotopes of arsenic are listed in Table 1-1. The isotopes are converted to stable elements by electron capture, electron emission, positron emission, neutron emission, and internal transition [9]. The electronic configuration of the stable form of arsenic, As(0), can be written as shown below to illustrate how the presence of five valence electrons allows arsenic to participate in chemical bonding, with an empty p orbital for electron occupation; this can also be illustrated by the electron dot model of arsenic (Figure 1-1).



The electronic configuration suggests that the first shell has two electrons, the second has eight electrons, the third has 18 electrons, while the fourth with five electrons is considered as

Table 1-1 Various Isotopes of Arsenic with their Decay Properties

Isotope	Mass	Mode of Decay	Half-life
^{68}As	67.9368	EC to ^{68}Ge	2.53 min
^{69}As	68.93228	EC to ^{69}Ge	15.2 min
^{70}As	69.93093	EC to ^{70}Ge	52.6 min
^{71}As	70.927114	EC to ^{71}Ge	2.72 d
^{72}As	71.926753	EC to ^{72}Ge	26.0 h
^{73}As	72.923825	EC to ^{73}Ge	80.3 d
^{74}As	73.923829	β^- to ^{74}Se ; EC to ^{74}Ge	17.78 d
^{76}As	75.922394	β^- to ^{76}Se	26.3 h
^{77}As	76.920648	β^- to ^{77}Se	38.8 h
^{78}As	77.92183	β^- to ^{78}Se	1.512 h
^{79}As	78.92095	β^- to ^{79}Se	9.0 min

Abbreviations used: min = minutes; d = days; h = hours; EC = electron capture; β^- = electron emission; As = arsenic; Ge = germanium; Se = selenium.

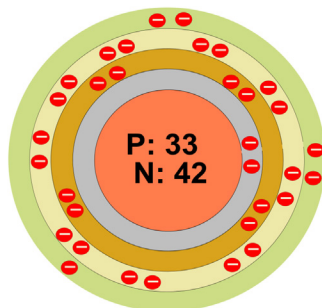


FIGURE 1-1 Electron dot model of arsenic (^{75}As) depicting number of protons (P) and neutrons (N) inside the nucleus and electrons (-) in various energy shells.

incomplete. In the fourth shell, the s orbital is completely filled and the p orbital is half filled, and therefore arsenic shows four common redox states: -3 , 0 , $+3$, and $+5$. Oxidation state -3 arises by the addition of three more electrons to the p orbital in order to complete the total of six electrons in this orbital. Elemental arsenic (^0As) equally shares its three electrons present in the 4p orbital with the other three surrounding arsenic atoms in a trigonal pyramidal structure and appears as a brittle gray metal. The $+3$ oxidation state forms when three electrons of the 4p orbital become more attracted towards a non-metal, usually oxygen or sulfur, whereas arsenic exhibits the $+5$ oxidation state when all the five electrons of the 4s- and 4p orbitals become more associated with the non-metal.

Table 1-2 lists selected physical properties of elemental arsenic, which suggest that the electronegativity of arsenic is greater than that of nitrogen and similar to that of phosphorus. Arsenic has a greater ability to lose electrons (oxidation potential) as compared to nitrogen and phosphorus, which increases the cationic character of arsenic and it thus can easily exhibit $+3$ and $+5$ oxidation states. Variable oxidation states of arsenic suggest that it can combine with many elements to form covalent compounds; however, in nature it most commonly bonds to oxygen and sulfur. Arsenic can occupy electrons in its bonding and anti-bonding orbitals and can exhibit the properties of ligands by sharing its valence electrons. Thus, it shows the ability to shift from an electropositive state (oxo-anions) to an electronegative state (metal arsenides). Arsenic in its pure form is a brittle, gray metal but in nature it is found with other metals, such as iron, copper, silver, and nickel as oxides and sulfides.

Arsenite is known to be more toxic and 25–60 times more mobile than arsenate [10]. In both oxidation states, it can combine with methyl groups to form organic species. Common organic species of arsenic are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). However, their natural occurrence is low compared to inorganic forms. Inorganic arsenicals are more toxic than organic arsenicals and the trivalent oxidation state is more toxic than the pentavalent oxidation state. Arsenic toxicity is also related to the rate at which it is metabolized and the degree to which it accumulates in the tissues. Generally, the As toxicity pattern is $\text{AsH}_3 > \text{As}^{3+} > \text{As}^{5+} > \text{RAs-X}$.

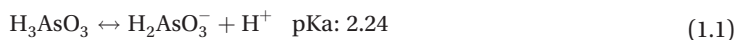
Table 1–2 Physical and Electronic Properties of Elemental Arsenic

Property	Value
Atomic number	33
Atomic mass	74.9216 g/mol
Appearance	Gray, brittle, non-metal flakes
Electronegativity according to Pauling	2.0
Density	5.7 g/cm ³ at 14°C
Molar volume	13.08 cm ³ /mole
Melting point	814°C (36 atm)
Boiling point	615°C (sublimation)
Specific heat	0.33 J/g K
van der Waals radius	0.139 nm
Ionic radius	0.222 nm (–2) 0.047 nm (+5) 0.058 (+3)
Isotopes	8
Electronic shell	[Ar] 3d ¹⁰ 4s ² 4p ³
Energy of first ionization	947 kJ/mol
Energy of second ionization	1798 kJ/mol
Energy of third ionization	2736 kJ/mol
Standard potential	–0.3 V (As ³⁺ /As)
Enthalpy of atomization	301.3 kJ/mole @ 25°C
Enthalpy of fusion	24.44 kJ/mole
Enthalpy of vaporization	34.76 kJ/mole
Electrical conductivity	0.0345 10 ⁶ /cmΩ
Thermal conductivity	0.502 W/cmK

1.2.3 Arsenic Oxidation and Reduction

Oxidation and reduction of arsenic mainly depend upon redox potential and pH conditions. In natural water bodies, arsenic predominantly exists as oxyanions of trivalent arsenite (As^{III}) or pentavalent arsenate (As^V). Under oxidizing conditions, the pentavalent form of arsenic predominates and the oxyanions' existence depends upon pH—at a pH less than 6.9, H₂AsO₄[–] predominates, while at a higher pH, HAsO₄^{–2} becomes dominating. Under reducing conditions at a pH less than 9.2, the neutral trivalent arsenic species H₃AsO₃ exists, which dissociates to form anions under high pH conditions only. Most often, more trivalent arsenic than pentavalent arsenic is found in reducing groundwater conditions, whereas the pentavalent arsenic prevails under oxidizing groundwater conditions. The stabilities of various arsenic species under different pH conditions are shown in [Figure 1-2](#), suggesting the significance of pH in the formation and occurrence of various forms of arsenic in natural water bodies. The dissociation reactions and corresponding equilibrium constants of H₃AsO₄ and H₃AsO₃ are as shown below:

Arsenite (As^{III})



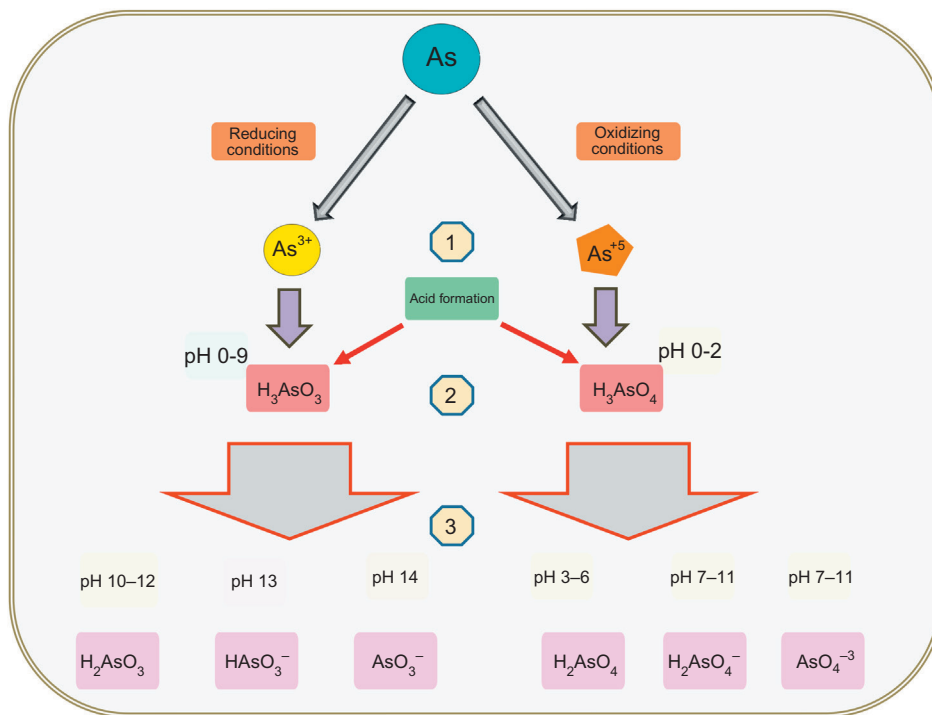
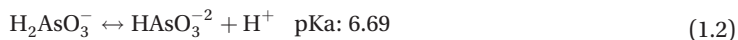
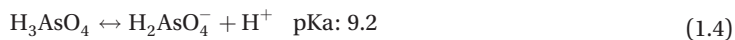


FIGURE 1–2 Pictorial depiction of (1) oxidation of arsenic under oxidizing and reducing conditions, (2) formation of acids by $\text{As}^{(+3)}/\text{As}^{(III)}$ and $\text{As}^{(+5)}/\text{As}^{(V)}$ under different pH conditions, and (3) dissociation of acids to oxyanions under various sets of pH conditions.



Arsenate (As^{V})



1.2.4 Arsenic Methylation

Methylation is a process of adding one or more methyl ($-\text{CH}_3$) groups to the chemical species. Bio-methylation plays an important role in the metabolism of inorganic arsenic and the mechanism involves alternate steps of two-electron reduction followed by oxidative addition

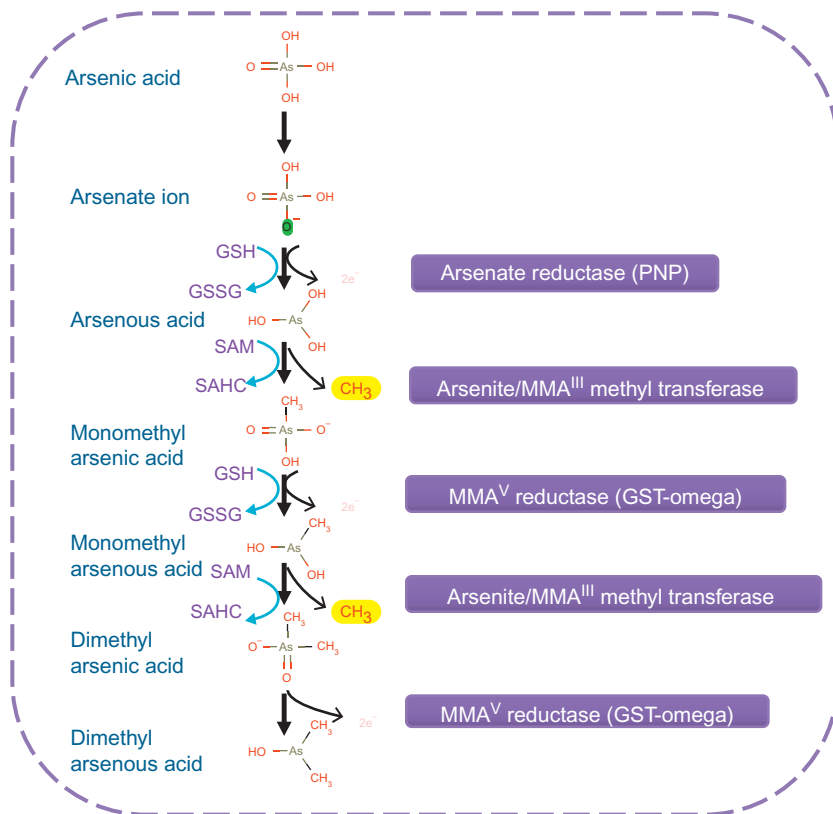


FIGURE 1-3 Biotransformation of inorganic arsenic in the mammalian system. Abbreviations: SAM—S-adenosylmethionine; SAHC—S-adenosylhomocysteine; GSH—reduced glutathione; GSSG—glutathione disulfide; PNP—purine nucleoside phosphorylase.

of a methyl group known as oxidative methylation [11]. Arsenate reduction can also occur non-enzymatically under low oxygen concentration or at pH 2 or lower. S-Adenosylmethionine, a methyl donor, methylates inorganic arsenic into monomethylarsonic acid (MMA) and then to dimethylarsinic acid (DMA). This reaction is catalyzed by methyltransferases in the presence of glutathione, which acts as a co-factor. It has been reported that arsenic methylation does not depend upon arsenic concentration in water [12]; rather it is assumed to be a detoxification mechanism of arsenic as, in organic form, arsenic cannot ionize readily to interact with bio-molecules and becomes less available for chemical and bio-chemical reactions [13]. The methylation process of arsenic via alternate reduction and oxidative methylation is depicted in Figure 1-3.

1.2.5 Historical and Modern Applications of Arsenic

Burning of coal in thermal power plants and disposal of fly ash, long-term mining and smelting of the sulfide ores, runoff from mine tailings, and application of pesticides and herbicides release

huge amounts of arsenic in to the biosphere. Additionally, arsenic is also used in the production of semiconductors, lead-acid batteries, and pesticides and herbicides, in the glass industry and copper refining industry, and in the hardening of metal alloys. Use of arsenic in wood preservation is very common and has increased significantly in the last few decades [14]. Wood may deteriorate by the attack of insects, fungi, bacteria, and animals, but can be protected by impregnating with CCA with the composition CuO (18.5%), Cr₂O₃ (47.5%), and As₂O₃ (18.5%). At one time, arsenic compounds such as lead arsenate, calcium arsenate, and sodium arsenate were used as pesticides for debarking trees, to control ticks, fleas, and lice, and in aquatic weed control. However, these applications have been banned due to the toxic effects of arsenic and later public awareness about food safety and environmental contamination [15].

1.3 Arsenic Minerals and Compounds

A mineral is a naturally occurring crystalline and inorganic solid. Arsenic minerals primarily include elemental arsenic, arsenolamprite, para-arsenolamprite, and nearly 320 other inorganic compounds. Arsenic minerals can be classified under five categories: elemental arsenic, arsenides, arsenosulfides, arsenites, and arsenates. Arsenides and arsenosulfides are commonly found associated with anoxic hydrothermal ore deposits, and with metamorphic and igneous rocks. When these minerals come in contact with water and oxygen, they are rapidly converted into arsenites and arsenates. Examples of arsenic minerals falling under the five categories are shown in Table 1-3.

1.3.1 Arsenosulfides

Arsenopyrite (FeAsS), orpiment (As₂S₃), and realgar (AsS/As₄S₄) are the most common arsenic sulfide minerals, occurring primarily in hydrothermal and magmatic ore deposits. Arsenic is commonly found in sulfide-bearing mineral deposits; especially with gold mineralization. Orpiment, due to its golden color, was used in ancient times as a pigment and dye, while realgar was a common red pigment for paints and dyes. Realgar decomposes in air to a yellow-orange compound para-realgar; consequently, old unrestored paintings have a yellow-orange tinge over a red color. Arsenic can exist in sulfide minerals either as a dominant mineral-forming element or as an impurity. Arsenic release into nature is a slow process as a result of mineral weathering; however, physical forces such as grinding, crushing, and pulverization from mining activities greatly increase the release rate. Arsenosulfides also combine with transition metals such as Co, Ni, and Cu to form a variety of other sulfides and sulfosalts [16].

In arsenic sulfides, elemental arsenic and sulfur are covalently bonded with different arrangements of As-S and As-As units. In arsenopyrite, each Fe atom is octahedrally coordinated by three As and three S atoms through edges and corners. In dimeric form $[(As-S)]^{-2}$ each As or S atom is tetrahedrally coordinated to three Fe atoms and one S-As atom. In the presence of water and oxygen, the arsenic present in arsenopyrite rapidly oxidizes to As⁺², As⁺³, As⁺⁵, and a precipitate in the form of scorodite (FeAsO₄·2H₂O) or amorphous Fe(III) arsenate [17].

Table 1–3 Examples of Arsenic Minerals Classified under the Five Categories

Group	Mineral	Formula
Elemental arsenic		
	Native arsenic	As
	Arsenolamprite	As
	Paraarsenolamprite	As
Arsenic sulfides		
	Arsenopyrite	FeAsS
	Cobaltite	CoAsS
	Orpiment	As ₂ S ₃
	Realgar	AsS/As ₄ S ₄
	Gersdorffite	NiAsS
	Enargite	Cu ₃ AsS ₄
Metal arsenides		
	Domeykite	Cu ₃ As
	Lollingite	FeAs ₂
	Nickeline or niccolite	NiAs
	Rammelsbergite	NiAs ₂
	Sperrylite	PtAs ₂
	Safflorite	CoAs ₂
Arsenite		
	Arsenolite	As ₂ O ₃
	Claudetite	As ₂ O ₃
	Sodium arsenite	NaAsO ₂
	Leiteite	ZnAs ₂ O ₄
	Reinerite	Zn ₃ (AsO ₃) ₂
	Gebhardite	Pb ₈ (As ₂ O ₅) ₂ OCl ₆
Arsenate		
	Johnbaumite	Ca ₅ (AsO ₄) ₃ (OH)
	Mimetite	Pb ₅ (AsO ₄) ₃ (Cl)
	Austinite	CaZn(AsO ₄)(OH)
	Scorodite	FeAsO ₄ ·2H ₂ O
	Erythrite	Co ₃ (AsO ₄) ₂ ·8H ₂ O

In realgar and its polymorphs As-As and S-S, dimers form a discrete molecular cage-like structure in which units are connected by van der Waals forces. Polymorphs of realgar, alacrinite (As₈S₉), and amorphous arsenic sulfide can also occur in hydrothermal deposits, volcanic emissions, intrusive igneous rocks, and hot springs. Realgar exists as high and low temperature polymorphs and at about 240°C α-realgar converts to β-realgar. α-Realgar in exposure to oxygen and sunlight converts to another polymorph, para-realgar.

In orpiment (As₂S₃), molecular units are present in chain form and connected by bridging S atoms and cross-linked by van der Waals attraction forces. Both the minerals realgar and

orpiment are stable over a wide range of temperature; however, orpiment possesses a greater stability range due to reduced sulfur fugacity [18].

Oxidation of arsenopyrite is the widespread mechanism for the distribution of arsenic into the environment. Arsenopyrite is formed under high temperature and a reductive environment, such as areas around buried plant roots or other nuclei of decomposing organic matter. Pyrite readily oxidizes in aerobic conditions with the formation of iron oxides and traces of arsenic. Arsenic is also found associated with phosphate minerals; however, the concentrations are less than those of oxide and sulfide minerals. By substituting Si^{4+} , Al^{3+} , Fe^{3+} , and Ti^{4+} arsenic can also be found associated with many other minerals; however, the concentrations are comparatively less.

Other arsenosulfides of transition metals are also known and the most common are enargite (Cu_3AsS_4), cobaltite (CoAsS), and gersdorffite (NiAsS). Enargite is orthorhombic thioarsenate where each arsenic atom is coordinated with four sulfur atoms as $(\text{AsS}_4)^{-3}$ [19]. Below 300°C enargite is converted to its polymorph luzonite with tetragonal geometry.

1.3.2 Metal Arsenides

A large number of metal arsenides are known and generally can be considered as metal alloys with the formula MAs_n , where M is a metal and $n = 1, 2, \text{ or } 3$. In these compounds arsenic exists in a negative oxidation state; however, bonding is strongly covalent and the compounds are semiconducting in nature. The well-known semiconductor is GaAs while other arsenides can be formed with Fe, Co, Ni, and Cu. Naturally occurring common metal arsenides are domeykite (Cu_3As), lollingite (FeAs_2), nickeline or niccolite (NiAs), nickel-skutterudite (Ni,CoAs_3), rammelsbergite (NiAs_2), safflorite (CoAs_2), and sperrylite (PtAs_2).

In skutterudite, each Co atom or any other divalent metal atom is surrounded by six arsenic atoms in octahedral mode, while in lollingite each Fe atom is coordinated with six arsenic atoms in orthorhombic geometry [20]. Another important metal arsenide is GaAs, which is synthetic in nature and each arsenic atom is coordinated by four Ga atoms [21]. It has various applications as a semiconductor in solar cells, light emitting diodes (LEDs), laser windows, etc. Other synthetic arsenides are indium (III) arsenide (InAs) and mixed indium gallium arsenide (InGaAs) with similar applications.

1.3.3 Arsenites

The most common arsenites are polymorphs of As(III) oxides, arsenolite (As_2O_3 , isometric), and claudetite (As_2O_3 , monoclinic), with similar thermodynamic stability, while claudetite is thought to be slightly more stable at standard conditions [18]. These oxides occur naturally as secondary weathering products of arsenic sulfides and industrially during combustion of arsenic-bearing minerals and coal in gaseous form, which upon condensation gives the powdered form of white As_2O_3 . The structure of arsenolite consists of $\langle\text{As}_4\text{O}_6\rangle$ cages, while in claudetite each arsenic atom is surrounded by three oxygen atoms in a trigonal pyramidal structure. Arsenic trioxides are moderately soluble in water and have been used industrially as pigments

and pesticides for a long time. The solubility of arsenite salts is largely due to the type of cation in the compound. The most soluble are the alkali arsenites, whereas metal arsenites are the least soluble.

1.3.4 Arsenates

Arsenates are usually considered a subclass of the phosphate mineral group owing to the similarity in size and charge of the phosphate and arsenate anionic unit. In arsenate, the unit $(\text{AsO}_4)^{-3}$ is either tetrahedrally or octahedrally coordinated to transition metal or alkaline earth metal with anions (OH^- , Cl^- , and F^-) for charge balancing. Similarly to phosphate minerals arsenate minerals also occur in a variety of soil and oxidized environments with a range of waters of hydration. During the period of the 1870s - 1970s arsenates of copper, lead, and calcium were extensively used as herbicides and insecticides and significantly increased the environmental burden of arsenic. As_2O_5 is rarely found in nature; however, it was synthesized and widely used at one time in the production of copper arsenate, a wood preservative. As_2O_5 decomposes at 315°C to As_4O_6 and O_2 . In water it can dissolve to form various species, H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} , depending upon the pH of the solution.

1.4 Organoarsenicals

In organoarsenic compounds arsenic combines easily with carbon to form various organic compounds with one or more As-C bonds and is widely used in agriculture and plant protection agents. A wide variety of organoarsenic compounds are found naturally in the environment as a consequence of bio-methylation and other biosynthetic pathways. They can be grouped into aliphatic and aromatic organoarsenic compounds. The most common classes of natural organoarsenic compounds are methylated forms of arsenite and arsenate. These can be generated by replacing a hydroxyl ($-\text{OH}$) ligand by a methyl group ($-\text{CH}_3$). The structures of major organoarsenic compounds are depicted in [Figure 1-4](#). By the replacement of one or more methyl or hydroxyl groups around arsenic by other organic moieties such as sugars, lipids, or cyclic groups, a wide variety of arsenic-bearing organic compounds are generated. Major aliphatic organoarsenic compounds methane-arsenic acid and dimethylarsenic acid were at one time used as fungicides, herbicides, and desiccants. On the other hand, aromatic organic arsenicals such as arsanilic acid have been used as corrosion inhibitors for iron and steel, and as additives for motor fuel, agricultural bactericides, herbicides, and fungicides. In organoarsenicals arsenic can exist in three oxidation states: As(I), As(III), and As(V). Compounds of oxidation state As(I) feature three bonds to As but only an As-As single bond and are used in antisyphilitic drugs such as Salvarsin and Neosalvarsan. Arsenic (V) compounds show the general formula $\text{RAsO}(\text{OH})_2$ or $\text{R}_2\text{AsO}(\text{OH})$ ($\text{R} = \text{alkyl or aryl}$). Monomethylarsonic acid ($\text{CH}_3\text{AsO}(\text{OH})_2$) and dimethylarsinic acid, commonly known as cacodylic acid ($((\text{CH}_3)_2\text{AsO}_2\text{H})$), figure prominently throughout the chemistry of organoarsenic compounds. Arsenic (III) compounds are prepared by alkylation of AsCl_3 and its derivatives

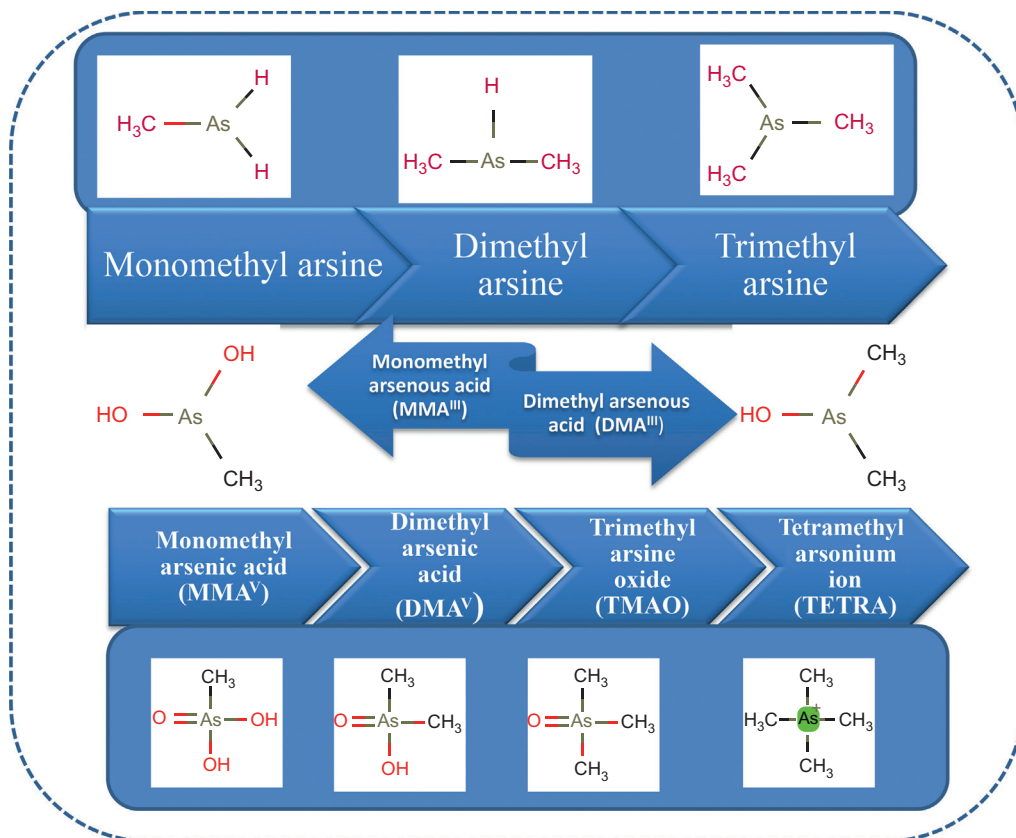


FIGURE 1-4 Structure of major methylated organoarsenic compounds.

using organolithium and Grignard reagents [22], e.g., methylarsenic dichloride (CH_3AsCl_2), dimethylarsenic chloride ($(\text{CH}_3)_2\text{AsCl}$), and trimethylarsine ($(\text{CH}_3)_3\text{As}$). Reduction of these chloride derivatives produces hydrides, such as dimethylarsine ($(\text{CH}_3)_2\text{AsH}$) and methylarsine (CH_3AsH_2). Trimethylarsine and triphenylarsine are symmetrical organoarsenic (III) compounds, commonly used as ligands in coordination chemistry.

1.4.1 Organoarsenicals in the Food Chain

Inorganic arsenic and its compounds enter the food chain and metabolize through a methylation process known as bio-methylation in the presence of specific enzymes related to vitamin B_{12} . The organic compound arsenobetaine is found in some marine foods such as fish and algae, and is considered a non-toxic form of organoarsenic compound. Carbohydrates bound to arsenic known as arsenosugars are found especially in seaweeds, and if lipid is bound to arsenic an arsenolipid is formed [23].

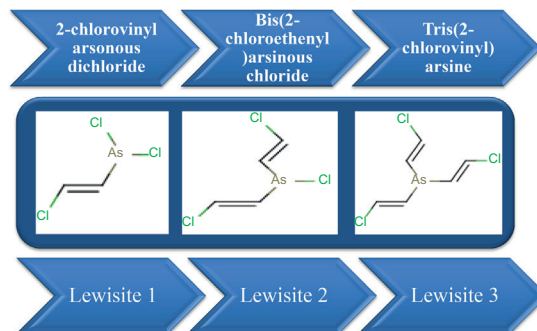


FIGURE 1-5 Structure of three different Lewisites illustrating the number of chlorine atoms in each that are responsible for its reaction with bio-molecules.

1.4.2 Organoarsenicals in Chemical Weapons

Lewisite (2-chloroethenylarsinous dichloride), an organoarsenic compound initially manufactured in the USA and Japan as a chemical weapon, acts as a blister agent and lung irritant. It is synthesized by the addition of arsenic trichloride to acetylene in the presence of a suitable catalyst. It is usually found as a mixture of 2-chlorovinylarsinous dichloride (Lewisite 1) as well as *bis*(2-chloroethyl)arsinous chloride (Lewisite 2) and *tris*(2-chlorovinyl)arsine (Lewisite 3) (Figure 1-5). It diminishes energy metabolism of the human body by inhibiting activity of pyruvate dehydrogenase necessary for the generation of ATP via converting pyruvate to acetyl-CoA. Sequentially, nervous pathology arises as the nervous system essentially depends on glucose as a catabolic fuel. It can easily penetrate ordinary clothing and rubber, and causes immediate pain and itching on skin with a rash and swelling, which convert to large, fluid-filled blisters after approximately 12 hours. Eye exposure causes stinging and strong irritation to blistering and scarring of the cornea. Sufficient absorption causes systemic poisoning leading to liver necrosis or death.

1.4.3 Methylation in Mammals

In mammals, methylation of inorganic arsenic compounds occurs in the liver, via the activity of methyltransferases, to $(\text{CH}_3)_2\text{As}^{\text{III}}\text{OH}$ (dimethylarsinous acid) and $(\text{CH}_3)_2\text{As}^{\text{V}}(\text{O})\text{OH}$ (dimethylarsinic acid). The source of the methyl groups is methionine, in the form of S-adenosyl methionine in the process of detoxification of inorganic arsenicals [24]. When the liver's methylation capacity is inhibited by the excess exposure to inorganic arsenic compounds, an imbalance occurs, which has deleterious effects on various organs and leads to carcinogenesis.

1.5 Arsenic Mobilization in the Environment

Arsenic is mobilized in the environment via various natural processes such as weathering of rocks, hydrothermal and geothermal activities, biological activities, and a range of

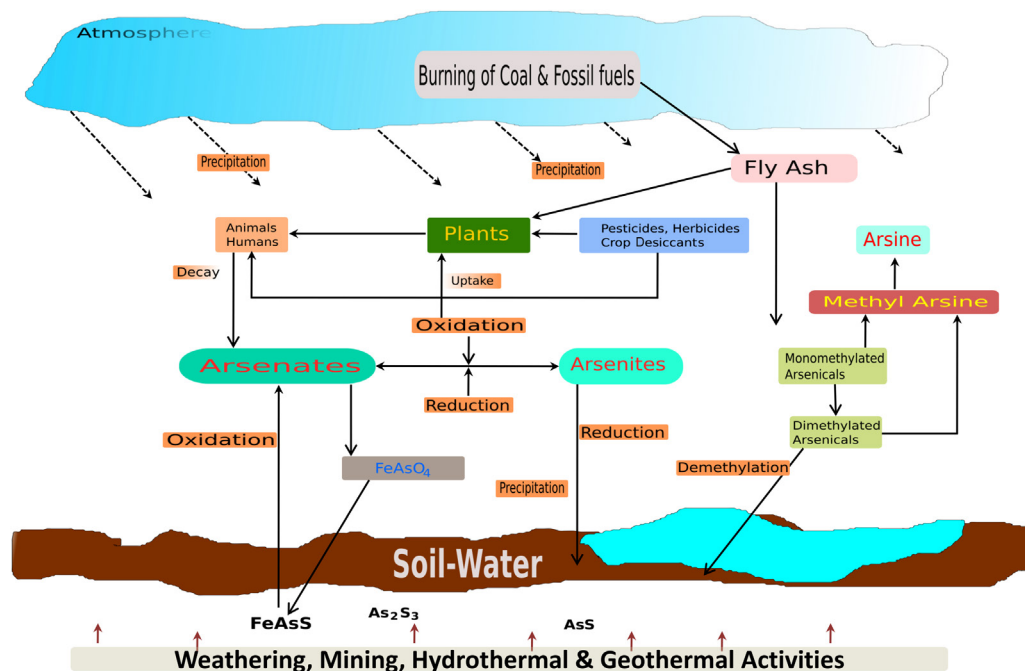


FIGURE 1-6 Arsenic mobilization in air, water, and soil. Arsenic accumulation via weathering and mining, and oxidative dissolution of arsenic-bearing mineral releases to the soil. Arsenic undergoes reduction, methylation, demethylation, and precipitation reaction and finally returns to soil and forms arsenic-rich sediments. Industrial processes, burning of coal, and use of pesticides release arsenic into the atmosphere. None of the various species of arsenic escapes from the environment; rather they continue to cycle from one species to another and from one medium to another.

anthropogenic activities. Widespread anthropogenic activities include mining, combustion of fossil fuels, use of arsenical pesticides, herbicides and crop desiccants, and the use of arsenic as an additive to livestock feed, particularly for poultry (Figure 1-6). Arsenic may enter the human body through drinking water, inhalation, and diet, but above all drinking water probably possesses the greatest menace to human health. Drinking water contains arsenic at various concentrations depending on the source. However, ground water holds the highest concentration of arsenic owing to various natural and human activities.

1.5.1 Aqueous Chemistry of Arsenic

Arsenic is ubiquitously present in the aquatic environment with concentrations near $0.62\ \mu\text{g/L}$ in river water and $0.5\text{--}3.0\ \mu\text{g/L}$ in ocean water [25]. Based on redox conditions and pH, arsenic can exist in all possible oxidation states +5, +3, 0, and -3, among which As(III) and As(V) are the most dominating in aqueous systems [26]. Various forms of arsenic are distributed in the environment; the most common species are listed in Table 1-4.

Arsenic readily forms oxyanions in both oxidation states As(III) (H_3AsO_3) and As(V) (H_3AsO_4), and becomes mobile in the pH range of 6.5-8.5 usually found in ground water.

Table 1–4 List of Various Arsenic Species and their Chemical Formulae

Name	Abbreviation	Chemical Formula
Arsenite, arsenous acid	As ^{III}	As(OH) ₃
Arsenate, arsenic acid	As ^V	AsO(OH) ₃
Monomethylarsonic acid	MMA ^V	CH ₃ AsO(OH) ₂
Monomethylarsonous acid	MMA ^{III}	CH ₃ As(OH) ₂
Dimethylarsinic acid	DMA ^V	(CH ₃) ₂ AsO(OH)
Dimethylarsinous acid	DMA ^{III}	(CH ₃) ₂ AsOH
Trimethylarsine oxide	TMAO	(CH ₃) ₃ AsO
Trimethylarsine	TMA ^{III}	(CH ₃) ₃ As
Arsenobetaine	AsB	(CH ₃) ₃ As ⁺ CH ₂ COO ⁻
Arsenocholine	AsC	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH
Tetramethylarsonium ion	Me ₄ As ⁺	(CHM ₃) ₄ As ⁺
Dimethylarsinoyl ethanol	DMAE	(CHM ₃) ₂ AsOCH ₂ CH ₂ OH

At this pH range, most of the toxic trace metal ions remain in solution form and precipitate or co-precipitate with an increase in pH as an oxide, hydroxide, carbonate, or phosphate. In contrast, oxyanion-forming elements such as arsenic, chromium, and selenium also exist in solution at higher pH values. Among all oxyanion-forming elements arsenic is unique in terms of its relative mobility over a wide range of redox conditions. Other oxyanion-forming elements such as Se, Cr, U, Mo, and V remain mobile under oxidizing conditions only and become immobilized in a reducing environment due to stronger adsorption or reduction to metallic form. On the other hand, arsenic oxyanions remain mobile under both oxidizing and reducing conditions.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation in aqueous systems. The redox potential of arsenic oxyanions is such that arsenite becomes stable in aqueous form under moderately reducing conditions (+300 mV at pH 4 to – 200 mV at pH 9) while arsenate is stable in oxidized aqueous solutions [18]. Under oxidizing conditions and low pH (less than 6.9), arsenic exists as As(V) and H₂AsO₄⁻ species dominate, while at higher pH due to ionization of one more proton, HAsO₄⁻² exists predominantly. In reducing conditions and pH less than 9.2, the neutral arsenite species H₃AsO₃ predominates. The structural configuration of arsenous acid (As³⁺) reveals that arsenic has three pyramidal bonds with a lone pair of electrons occupying the fourth arm of a tetrahedron (Figure 1–4). It has been suggested spectroscopically that in solution form also, arsenite retains its pyramidal structure [27]. Arsenous acid showing a pKa of 9.23 dominates in natural aqueous solution, while deprotonated forms can exist under alkaline conditions. The geometry of arsenic acid suggests a regular tetrahedron, which can easily donate protons under alkaline conditions to form the stable arsenate (AsO₄)⁻³ anion, which resembles the orthophosphate (PO₄)⁻³ anion and shows competitive chemical behavior in natural water systems. The adsorption and desorption behavior of arsenic on mineral surfaces plays an important role in regulating its aqueous concentration in various water systems. In the presence of reduced sulfur, arsenic exists in solution form as sulfides, while under reducing conditions these sulfides (As₂S₃, AsS) become precipitated. Arsenic species are also affected by temperature, such as in hydrothermal fluids from shallow-water islands; the

dominant species between pH 5 and 7 is trivalent $\text{As}(\text{OH})_3$, whereas at higher temperature and pressure in deep-water systems the H_2AsO_4^- arsenate species predominates. Moreover, at high temperature and high concentration of Fe and S, orpiment and claudetite preferentially precipitate. Thio-arsenic species are also possible in sulfide-rich hydrothermal systems; such thio-arsenates were reported in the geothermal waters of the Yellowstone National Park [28].

1.5.2 Redox-Dependent Mobilization of Arsenic

Redox reactions are of great significance for controlling the behavior of many chemical species in natural water systems, including arsenic. Thermodynamic equilibrium suggests that under strongly reducing conditions As(V) should dominate over As(III); however, this is not necessarily followed in all natural systems where other redox couples also influence arsenic oxidation/reduction. In oxygenated water, the As(V)/As(III) ratios should be of the order of 10^{15} – 10^{26} , which remain stable for a period of days or weeks due to slow oxidation reactions. It has been suggested that the As(V)/As(III) ratio can be used as a reliable redox indicator in groundwater systems [29]. Experimental studies suggested that oxidation of As(III) becomes slow under acidic conditions (pH 5), while at pH 8–12.5 the reaction accelerates. The rate of As(III) oxidation increases in the presence of manganese oxide, which is evident by the fact that it can reduce the half-life of As(III) from 1–3 years to 10–20 minutes. Oxidation reaction is independent of the concentration of dissolved oxygen; however, it is controlled by surface reactions such as photochemical oxidation and reduction triggered by titanium-containing particles [30].

1.5.3 Microbial-Dependent Mobilization

Redox reaction of As(III)/As(V) is also catalyzed by microorganisms; thus sterile water samples are less susceptible to speciation changes. Arsenite in geothermal water in the southwest USA was found to oxidize rapidly with a rate constant of less than 0.3 hours. Arsenate reduced rapidly in Mono Lake, CA, in the presence of bacteria with rate constant ranging from 0.02 to 0.3 per day [31]. Methylated arsenic species also readily oxidized chemically and biologically.

1.6 Sources of Arsenic in the Biosphere

Arsenic is a natural constituent of Earth's crust and ranks 20th in abundance in relation to the other elements; it is found in approximately 320 mineral forms in rocks. Arsenic can enter terrestrial and aquatic environments via both natural geologic processes and anthropogenic activities. Natural occurrence of arsenic depends upon various processes such as weathering of rocks and sediments, hydrothermal and geothermal activities, dissolution of sulfide minerals, forest fire, and wind-blown dust [32]. Anthropogenic sources of arsenic include mineral processing, glass manufacturing, wood preservation, pesticide production and uses, leaching through landfill or waste, and production of coal and petroleum products and their processing. Anthropogenic sources of arsenic are responsible for its release into the atmosphere via emission due to copper smelting and coal combustion and into the hydrosphere and lithosphere through all types of waste [33]. Major natural and anthropogenic sources of arsenic

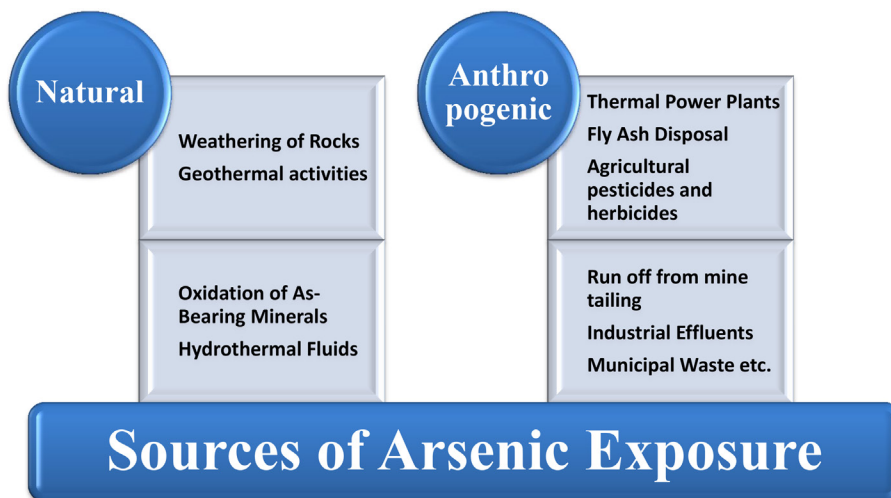


FIGURE 1–7 Major natural and anthropogenic sources of arsenic entry in to the environment.

are depicted in [Figure 1–7](#). The detailed process of arsenic release from various sources is discussed in subsequent sections.

1.6.1 Arsenic in Rocks and Soils

Historically, the concentration of arsenic in Earth’s crust was reported to be 2 mg/kg and subsequently it was estimated in various forms of rocks and soils. Indisputably, the arsenic burden has increased at a tremendous rate on planet Earth and varies according to the types of rocks, sediments, and soils. In igneous rocks, arsenic concentrations vary from 1.5 to 5.9 mg/kg with the major contributor being volcanic material generating high-arsenic water [34]. Metamorphic rocks generally show less than 5 mg/kg arsenic with the exception of pelitic rocks containing unusually high concentrations, 18 mg/kg. In sedimentary rocks, arsenic concentrations range between 5 and 10 mg/kg. Argillaceous deposits have a high arsenic concentration (13 mg/kg) probably owing to enhanced sulfide mineral, oxides, clays, and organic matter. Iron-rich rocks, phosphorites, coal, and bituminous deposits are enriched with exceptionally high arsenic concentration ranges of between 100 and 900 mg/kg [35].

Marine deposits due to higher sulfur content contain arsenic at greater concentrations compared to non-marine deposits. Historically, the average concentration of arsenic in deep-sea sediments was estimated to be approximately 40 mg/kg. The most important arsenic minerals in the oceanic crust are cobaltite (CoAsS), loellingite-safflorite ($\text{FeS}_2(\text{Co,Fe})\text{As}_3$), luzonite (Cu_2AsS_4), tennantite ($\text{Cu}_{10}(\text{Fe,Zn})_2\text{As}_4\text{S}_{13}$), claudetite, and elemental arsenic, principally intergrown with elemental gold [36]. In oceanic sediments, arsenic is usually concentrated in fine-grain sediments, particularly those rich in organic matter, sulfide minerals, phosphate, or iron oxides [37]. Elevated arsenic concentrations were found in river sediments in India, from the

Ganges plain ranging between 1.2 and 2.6 mg/kg, from the Brahmaputra river (between 1.4 and 5.9 mg/kg), and from the Meghna river (between 1.3 and 5.6 mg/kg) [38].

Availability of metals to organisms is not only dependent upon the total amount of a metal present in the soil, but also on the nature of chemical bonding of the metal with the soil particles. Arsenic concentration in soil also varies between 5 and 10 mg/kg, with peats and bog soils having higher values (13 mg/kg) due to increased pervasiveness of sulfide minerals under reduced conditions. The presence of arsenic in soils primarily depends upon geological reactions. However, it is also greatly enhanced by smelting and fossil fuel combustion, mining activity, and use of pesticides and phosphate fertilizers. Previously in orchard soils, the concentration of arsenic was reported in the range of 366–732 mg/kg due to excessive application of arsenical pesticides. Arsenic occurs in soils mainly as arsenate, AsO_4^{3-} , under oxic conditions. This form of arsenic is strongly adsorbed onto clays, oxides/hydroxides of Fe and Mn (AlAsO_4 and FeAsO_4), and organic matter. In alkaline and calcareous soils, the main form is $\text{Ca}_3(\text{AsO}_4)_2$. Arsenic leaching from surface soil becomes higher in sandy soil due to weak sorption. The amount of sorption depends upon arsenic concentration, contact time, and concentration of Fe and manganese in the soil. The mobility of As in soils is increased under reducing conditions such as flooded soils. An increase in pH also increases the mobility of the arsenic apparently by bringing about a change from Al and Fe arsenates to calcium arsenate. Bacteria are also important in increasing the mobility of arsenic as they increase the bio-methylation of arsenic, the compounds formed being comparatively mobile forms of arsenic. Various factors regarding the mobilization of arsenic in the soil are presented in Figure 1–8. The natural occurrence of arsenic-bearing minerals may significantly enrich the soil concentration of arsenic. Soils in the vicinity of gold mines as well as gold processing wastes often contain elevated concentrations of arsenic [39]. As mentioned above, arsenic accumulation in soil not only occurs

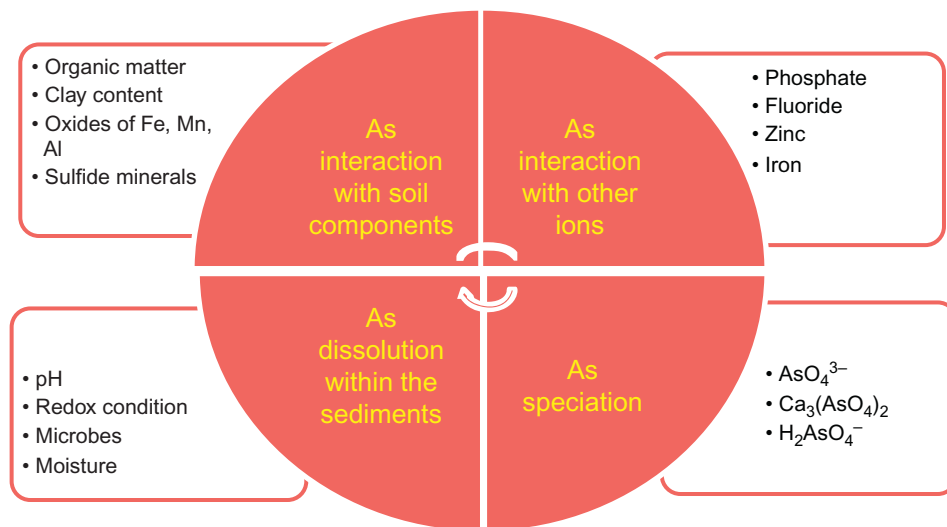


FIGURE 1–8 Various factors affecting arsenic mobilization in soil.

via natural sources but also from anthropogenic sources such as mining, airborne emissions, waste discharges from metal processing facilities, burning of fossil fuels, use of wood preservatives, and agricultural application of arsenical pesticides [40].

Since the beginning of the industrial revolution, the most common human-contributing sources leading to the introduction of trace metals into the soil have included disposal of industrial effluents, sewage sludge, mining, landfills, and use of agricultural chemicals [41]. Arsenic contamination of soils may cause loss of vegetation, groundwater pollution, and arsenic toxicity in plants, animals, and humans [42]. The chemistry and behavior of arsenic is determined by arsenic speciation rather than its total amount. Conversion of the arsenic forms is also affected by different soil factors, such as soil reaction, oxidation–reduction state, microbial activity, organic matter content, etc. Wood impregnation releases considerable amounts of arsenic into the soil in the vicinity of the impregnation plant. To carry out the processing, chiefly arsenic pentoxide (As_2O_5) is used, which is easily dissolved in water (65.8 g/L). Another method of wood impregnation is by pressure treatment with chromated copper arsenate (CCA). In many countries use of CCA for wood preservation has already been banned.

The bio-availability of arsenic in soil depends upon physical and chemical properties of soil and water such as pH, redox conditions, presence of precipitating, complexing, and sorbing agents, and mineralogical composition of the soil and its grain size. In addition, climatic, hydrogeological, and geomorphological activities also influence the mobility and availability of arsenic. Arsenic leached in the pentavalent form is able to form anions, such as H_2AsO_4^- , of a strong acid, with pKa values of 2.24, 6.94, and 11.5, which adsorb most effectively at low pH. Consequently, its mobility is fairly low in acidic soils with high clay or oxide content.

1.6.2 Arsenic in the Atmosphere

In 1936 James Svoboda first described mass eradication of honeybee families (Tisin's disease) as a most sensitive ecological indicator of arsenic pollution in air [43]. The phenomenon was observed in the vicinity of various smelters and power plants that burned arsenic-containing coal. In the atmosphere, arsenic concentration increases from smelting, fossil-fuel combustion, and volcanic activity.

Arsenic emission depends upon its concentration in raw material, quality of fuel or waste, production procedure, temperature, pressure, gas composition, and gas cleaning equipment. Due to specific evaporation–condensation processes at high temperatures, arsenic partially or entirely evaporates into the atmosphere. The diameter of arsenic particles dispersed in the atmosphere was typically found to be $1\ \mu\text{m}$, suggesting efficient movement with wind and air [44]. Combustion of fossil fuels releases arsenic to the atmosphere with typical levels of 0.1–80 mg/kg (dry) for coal and biomass fuels, and up to 500 mg/kg (dry) for sewage sludge.

Airborne arsenic is transferred to water bodies by wet or dry precipitation and increases aqueous concentration. Atmospheric arsenic arising from coal burning has been cited as a major cause of lung cancer in parts of China and India; exposure is known to be lethal from direct inhalation from domestic coal fires [45].

1.6.2.1 *Arsenic Emission due to Burning of Coal*

Coal is a natural source of arsenic and primarily responsible for the release of arsenic into the air, via smoke stacks during coal combustion, and into soil and water via combustion of products, mainly fly ash. India has the world's fourth largest reserves of coal and the third largest coal excavator, after the United States and China, serving the electricity demands of the nation. Electricity generation is mainly dependent upon coal-based thermal power plants. In eastern India, coal combustion is one of the major sources of anthropogenic arsenic emission into the biosphere. Coal contains both inorganic and organic forms of arsenic; however, its enrichment is related to sulfide mineralization, either syngenetic or epigenetic [46]. The arsenic-bearing sulfides are epigenetic and contain high concentrations of arsenic, whereas pyrites are syngenetic containing very low arsenic levels [47]. Release of arsenic during coal combustion depends upon various factors such as initial concentration in the parent coal, design and operating conditions of the furnace, and combustion temperature. During low temperature combustion (1000–1200°C) AsO and As₂O₃ escape in the gaseous phase, while at high temperature (1200–1600°C) only As₂O₃ is released.

1.6.2.2 *Arsenic Dissipation from Fly Ash*

Fly ash is produced in substantial amounts around the world and contributes as a potential and significant anthropogenic source of arsenic [48]. During combustion of coal in thermal power plants, the main part of the initial arsenic evaporates into the atmosphere in the gaseous phase. Most of the organic arsenic, pyrite, and some micro-minerals also escape into the atmosphere in the gaseous phase and only a minor part of arsenic remains in bottom ash. The escaping arsenic is captured by fly ash and collected by an electrostatic precipitator. This suggests that the atmospheric emission of arsenic in solid and gaseous phases is rather minor and most of the arsenic ends up with fly ash. Upon cooling, the combustion gases are adsorbed onto fly ash particles and their concentration becomes comparatively higher in particles less than 10 μm due to high surface area. Particles of less than 1 μm when inhaled may be deposited in the pulmonary tissue of the respiratory tract and enter the blood. Release of arsenic from fly ash produces air, soil, and water pollution. Excessive amounts of arsenic over permissible levels have been reported in the soil, tubewell, and surface water near thermal power plants. Arsenic associated with fly ash ends up in ground water through leaching and adversely affects water quality. Reports suggest that arsenic is highly leachable in fly ash as it occurs as a surface precipitate [49]. Arsenic concentration increases with time in ground water from acidic to alkaline fly ash leaching. However, under alkaline conditions, after attaining a maximum level concentrations start declining with time. Many factors such as pH, concentration of Ca/Mg, reducing or oxidizing conditions, leaching time, temperature, and anionic constituents (sulfate and phosphate) strongly influence leaching of arsenic from fly ash [50].

The extent of the arsenic in fly ash depends on both the mineralogy and particle size distribution of the coal and combustion temperature. Arsenic concentrations in fly ash generally range from 2 to 440 mg/kg and sometimes can be as high as 1000 mg/kg depending upon the concentration in the original coals, the combustion methods, and combustion temperature [49]. The toxicity of arsenic when present with fly ash depends upon its state, mobility, and

Table 1–5 Various Forms of Arsenic Present in Fly Ash

Name of Species	Formula
Arsenopyrite	FeAsS
Arsenic trioxide	As ₂ O ₃
Calcium orthoarsenate	Ca ₃ (AsO ₄) ₂
Scorodite	FeAsO ₄ ·2H ₂ O
Thallian arsenian pyrite	(Fe,Tl)(S,As) ₂

availability in the biosphere. Arsenic concentration was found to be higher in hollow spherical particles (low density) than in compact spherical particles (high density) [51]. The concentration of arsenic in fly ash also depends upon sulfur content of the coal and is found higher in those feed coals with high sulfur content. The pH of fly ash also influences concentration and species of condensed arsenic. In an acidic medium, fly ash contains more Si, thus occurring as Fe₃[AsO₄]₂, while in alkaline medium due to an increase in Ca concentration it is present as Ca₃[AsO₄]₂. Arsenic is captured by calcium-bearing minerals and hematite, and forms a stable complex with Ca or Fe in fly ash. It has been reported that arsenic is largely present in Ca-rich fly ash as Ca₃(AsO₄)₂ and Ca₂As₂O₇ because Ca can react with arsenic vapor and capture the metal in water-insoluble forms as As(V) [52]. Fly ash may contain various forms of arsenic depending upon pH condition, particle size, and presence of other minerals, as summarized in Table 1-5.

1.6.3 Arsenic in Various Water Resources

1.6.3.1 Rain Water

Arsenic enters the atmosphere in various ways including volcanic emissions, marine aerosols, burning of fossil fuels, and industrial pollution, and is then reversed in the form of precipitation. It is estimated that anthropogenic sources of atmospheric arsenic emission contribute to about 30% of global arsenic release. Concentrations of arsenic in rainfall were found to be very high: approximately 0.5 µg/L in the areas affected by smelting operation, power plants, soil dust, and burning of coal. In copper smelting areas, the average arsenic concentration was found to be 16 µg/L. Nevertheless, rainfall contributes little arsenic to surface and groundwater bodies. In rain water the most dominant species of arsenic are As₂O₃ near smelters and coal burning areas, AsH₃ near landfills, and reducing soils and arsenate near marine aerosols. The reduced form of arsenic undergoes oxidation in the presence of atmospheric SO₂ and O₃.

1.6.3.2 River and Lake Water

Arsenic concentration in river water depends upon bedrock lithology, base flow contribution, surface recharge, and industrial or sewage effluents. Increased concentrations of arsenic are found in areas where water flows into surface water from surrounding rocks and increases the pH and alkalinity of resultant water. A high concentration of arsenic was found in the Loa River Basin of northern Chile ranging from 190 to 21,800 µg/L, which correlated well with high salinity of water [53]. Increased arsenic concentrations of 114 µg/L was also reported in river waters

in central Argentina owing to increased pH conditions [54]. A higher concentration of arsenic (1100 µg/L) has been observed in Sugar Creek, South Carolina, downstream of an industrial complex. Arsenic concentration also increases in river water due to mining activities such as mine waste and mill tailing. A high arsenic concentration (200–300 µg/L) was found in surface water affected by tin and gold mining activities [55].

Due to high evaporation rate, weathering of volcanic rocks, and geothermal activities, high arsenic concentrations are also found in lake water. Arsenic concentrations of 10–20 mg/L in Mono Lake in California, USA, was reported below the pH range of 9.5–10 [56]. Thermal stratification in lake water also affects arsenic concentration and is found to be increased at depths up to 10 m due to increasing ratio of As(III) to As(V) and influx of mining contaminated water. The concentration of As(III) becomes higher in summer due to depleted dissolved oxygen levels and increased biological productivity in the deeper lake water. In lake and river waters, As(V) is generally the dominant species, varying according to seasonal variation, redox conditions, temperature, and biological activity. During summer As(III) can be detected in water due to biological reduction of As(V). In the thermally stratified Mono Lake, under hypersaline and hyperalkaline conditions, As(V) was found in the upper oxic layer and As(III) in the lower reducing layer [31]. The ratio of organic arsenic species also increases in summer due to enhanced methylation reaction catalyzed by microbial activity, and the most common organic forms that exist in water are DMA^V and MMA^V [57].

1.6.3.3 *Sea and Estuarine Water*

In open sea water the average arsenic concentration varies around 1.5 µg/l; however, in estuaries it is more variable (0.1–4 µg/L) due to various river inputs, salinity, and redox gradient. Increased arsenic concentration was observed in the Krka Estuary in Croatia with increased salinity from 0.13 to 1.8 µg/L dominated by As(V) [58]. In sea water arsenate (As(V)) dominates over arsenite (As(III)) and their ratio exists in the range of 10–100 µg/L. At seawater pH (7.5–8.2), As(V) exists as HAsO_4^{2-} and H_2AsO_4^- , while As(III) exists as the neutral species H_3AsO_3 . Organic arsenical also exists in seawater as a result of methylation reactions by phytoplankton. In seasonally anoxic estuarine waters, variations in the relative proportions of As(III) and As(V) can be large. In marine and estuarine waters, organic forms are usually less abundant but are often detected and depend upon temperature and variation in aquatic biota [59].

1.6.3.4 *Ground Water*

Concentrations of arsenic in water bodies depends upon the source of arsenic and local geochemical conditions varying more than four orders of magnitude. Among all the sources of arsenic the greatest range and highest concentrations are found in groundwater due to considerable mineral water interactions and favorable conditions for arsenic mobilization and accumulation. Governments, external agencies, academic institutions, and private research and development centers are making determined efforts to identify increasing concentrations of arsenic worldwide. There are many countries in the world where the arsenic concentration in drinking water was found to be more than the World Health Organization (WHO) permissible value (10 µg/L) [60]. Over the past two or three decades, the occurrence of high concentrations of arsenic in drinking

water has been recognized as a major public health concern in various parts of the world; apparently, there are areas where the concentration still needs to be recognized. Early identification of arsenic-affected areas can serve as a milestone for the remediation program and to provide safe drinking water. In ground waters, the ratio of As(III)/As(V) varies to a great extent due to variation in redox conditions, sources of water, and environmental conditions. Arsenic mobility in surface and ground water is dependent upon five factors: (1) redox reactions; (2) adsorption and desorption; (3) competitive adsorption (ion exchange); (4) solid phase precipitation and dissolution; and (5) biological activity. These processes are regulated by redox potential, pH, chemical composition of the system, competing anions, aquifer minerals, and reaction kinetics [61].

1.6.4 Arsenic in Dietary Products

1.6.4.1 *Plants and Crops*

The presence of arsenic in soil adversely affects growth of plants and the effects depend upon the chemical form and availability of As. The toxicity of arsenic varies in the following order as per its oxidation state and form: $\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{organic As}$. Arsenic availability to plants depends upon soil texture and is found to be high in coarse-textured soils with less colloidal material and little ion exchange capacity, while the concentration is low in fine-textured soils that are high in clay, organic material, iron, calcium, and phosphate. The average arsenic concentration naturally occurring in the soil worldwide is 10 mg/kg. In arsenic-contaminated soil, the uptake of arsenic by plants was found to significantly increase, particularly in vegetables and edible crops [62]. Uptake of arsenic follows a different mechanism for the two oxidation states, As(III) and As(V). As(V) is taken up via a phosphate uptake system in plants due to the similarity of As(V) to phosphate [63]. Therefore, phosphate supplementation has been suggested to reduce arsenic uptake because of competition between phosphate and As(V).

1.6.4.2 *Rice and Other Food Items*

It is reported that 40% of arsenic in the human body comes from the food chain [64]. Arsenic intake via food varies from 17 to 291 $\mu\text{g}/\text{day}$ in different countries. Seafood accounts for 60–96% of the total dietary intake of arsenic, mostly in the form of arsenobetaine and arsenosugars, relatively non-toxic forms of arsenic [65]. Other food sources are vegetables, mushrooms, grains, milk, chicken, and beef, which account for inorganic arsenic consumption [66]. In non-arsenic endemic regions, the principal sources of inorganic arsenic in the diet are rice and chicken, which results in the accumulation (55–97 ng/g) of methylated arsenic compounds [67]. Herbal medicines and seaweed are also important sources of arsenic, e.g., Hijiki seaweed has high levels of inorganic and organic arsenic [68].

Rice is the major crop in India and covers about 23% of the country's total irrigated land for its production. Nearly 42% of the total food grain production is rice in India and West Bengal is one of the major rice producing states covering an area of 5,900,000 ha. In West Bengal, a huge amount of the population is dependent upon water for irrigation purposes but it is found to be contaminated with arsenic. For the cultivation of rice during lean periods an enormous amount of ground water is used, which leads to oxidative decomposition of pyrite to form Fe^{+2}

Table 1–6 Concentration of Arsenic in Different Rice Varieties

Rice Variety	Origin	Total As ($\mu\text{g/g}$)
Basmati white	India	0.05
Long grain	America	0.26
Long grain	Bangladesh	0.13
Long grain	Europe	0.18

and Fe^{+3} sulfate and sulfuric acid, responsible for arsenic mobilization. In South East Asian countries, rice is grown mostly under waterlogged lowland conditions in which the physical and chemical condition of the soil affects the mobilization of arsenic and its uptake by rice [69].

In West Bengal, villagers living in arsenic-contaminated areas largely depend upon rice for their calorific intake [63]. The concentration of arsenic varies according to rice species and is summarized in Table 1–6. Due to the high arsenic levels found in paddy rice, such rice has been considered an important source of arsenic intake and risk is increased if it is cooked in arsenic-polluted water due to chelation of arsenic to the rice starch/bran [70]. According to WHO, the permissible limit of arsenic in rice and other food items has been reported as between 1.0–2.0 mg/kg and 2 mg/kg [71].

1.6.4.3 Tobacco

Cigarette smoking is a well-established risk factor for carcinogenesis. The chemical agents associated with cigarette smoke are classified as group I carcinogens and include benzene, polycyclic aromatic hydrocarbons (PAHs), cadmium, arsenic, nickel, chromium, 2-naphthylamine, vinyl chloride, 4-aminobiphenyl, and beryllium [72]. In the United States, arsenic levels in tobacco rose from 12 mg/g in the 1930s to over 50 mg/g in the 1950s. By the 1970s, in response to policy efforts, arsenic levels reduced to 1 mg/g of tobacco, which further declined in subsequent years [73]. Arsenic exposure due to tobacco smoking has been prevalent in Asian countries due to the smoking of handmade cigarettes, especially bidis [74].

1.7 Arsenic in Hydrothermal and Geothermal Fluids

1.7.1 Arsenic Occurrence in Hydrothermal Fluids

The concentration of arsenic in the world's oceans is usually high and governed by various factors such as riverine input, weathering and sedimentation on the sea floor, water exchange between atmosphere and sea, inputs of volcanic gases, and hydrothermal fluids. The dwelling time of arsenic in the oceans is assumed to be between 32,000 and 63,000 years with an average concentration of 1.7 $\mu\text{g/L}$.

In the past 25 years, active hydrothermal systems, polymetallic mineral deposits, and robust biological communities have been discovered including sediment-free and sediment-covered ocean ridges, the East Pacific rise, mid-Atlantic ridges, rifted continental margins,

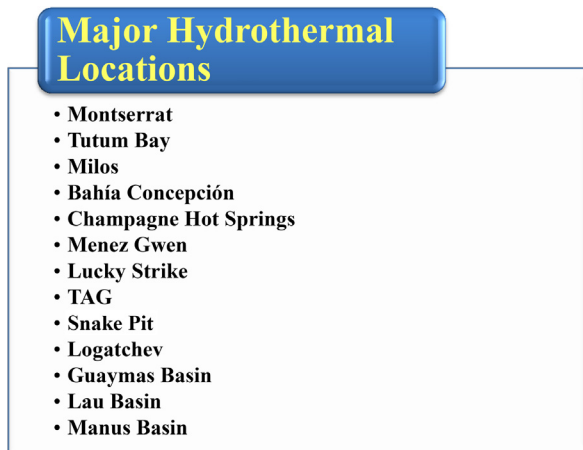


FIGURE 1–9 Major hydrothermal locations distributed worldwide contributing significantly to the environmental arsenic burden.

Table 1–7 Comparison between Shallow and Deep Water Systems

Property	Shallow Water	Deep Water
Depth	Less than 200 m	More than 200 m
Photosynthesis rate	High due to benthos and phytoplanktons	None takes place
Water source	Meteoric and sea water	Sea water
Temperature	Up to 100°C	Above 400°C

volcanic arcs, back-arc basins, and seamounts. Major hydrothermal locations worldwide are listed in [Figure 1–9](#). Chemical analyses of hydrothermal fluids and suspended particles from submarine systems reveal that arsenic and other metals are effectively mobilized from the oceanic crust and sedimentary, transported to the sea floor, and concentrated in surface mineral deposits. Hydrothermal fluids emerging at the sea floor are known to contain considerable amounts of dissolved transition metals and toxic elements due to water/rock interaction at elevated temperatures and potentially magmatic degassing. Arsenic concentrations in hydrothermal fluids are 2–500 times higher as compared to seawater concentrations.

The chemistry of hydrothermal fluids is chiefly governed by physicochemical variables, phase separation, depth and temperature, rock lithology, water/rock interaction, and heat gradient [75]. Cold and dense water percolates downward and is heated up to 400°C, and hot water rises upwards due to resilience. Hydrothermal systems can be divided into shallow and deep water based on their depth, and systems at a depth of 200 m are considered deep water systems [76]. Comparison of shallow and deep water systems is summarized in [Table 1–7](#).

In shallow water systems, photosynthetic organisms can absorb arsenate from the surrounding sea water owing to its similarity to phosphate [77]. Arsenate is converted to arsenite

and then further to methylated species, which are again converted and detoxified to different arsenosugars. These arsenosugars are further converted to the less toxic arsenobetaine in higher marine organisms.

1.7.2 Arsenic Concentration in Shallow and Deep Hydrothermal Systems

Some shallow and deep water hydrothermal systems are listed in [Figure 1–7](#). Montserrat Island in the Caribbean, located at the northern end of the inner arc consisting mainly of andesitic rocks, showed a large increase in shallow water hydrothermal discharge near its western coast after a volcanic eruption in July 1995 [78]. The springs showed alarmingly high concentrations of arsenic (3600 µg/L) after the eruption, followed by a steady decline.

Another shallow-water hot springs in Tutum Bay located 150 m offshore along the southwest part of Ambitle Island (Papua New Guinea), shows temperatures up to 98°C in 5–10 m of water. The sediments in this region consist mainly of feldspar, hornblende, pyroxene, magnetite, and weathering product coated with hydrous ferric oxide [79]. Arsenic concentrations in the water range from 750 to 1050 µg/L, while in ferric oxide they reach up to 50,000 mg/kg.

Milos, another hydrothermal site situated in the central Hellenic volcanic arc, showed arsenic concentrations as high as 2900 µg/L in Paleochori Bay, whereas concentrations were even higher (up to 5850 µg/L) in Spathi Bay, known to be the highest in a hydrothermal system. At Milos, hydrothermal fluids have been divided into two groups, one with high chlorine containing less arsenic and the other with low chlorine but supplemented with more arsenic [80].

Bahia Concepcion located in the Gulf of California, covered by a marine and continental sedimentary layer, contains hydrated ferric oxide enriched with high concentrations of arsenic up to 50,000 mg/kg [81]. Champagne hot springs located near the island of Dominica in the Caribbean consist mainly of medium-K calc-alkaline andesites and hydrothermal hydrated ferric oxide, augmented with arsenic concentrations up to 1880 mg/kg [82].

Various shallow water systems differ in terms of temperature, pH, H₂S content, redox state, fluid pressure, iron concentration, and gas fugacity, which seem to be responsible for leaching of arsenic from host rock and its transportation in hydrothermal fluid. Aquifers with high temperature, low pH, and high H₂S content show high concentrations of arsenic, perhaps due to higher leaching capacity and phase separation. Phase separation generates a low chlorine vapor phase in which arsenic partitioning is high pertaining to dominance of uncharged arsenic species and SH⁻ complexation [83].

The Mid-Atlantic Ridge (MAR) is a deep hydrothermal region occupied by two hydrothermal systems, Menez Gwen and Lucky Strike, which are both similar in rock composition and fluid geochemistry. The systems were found to be poor in chlorine and iron, while rich in gaseous components [84]. Menez Gwen hydrothermal discharge, located at a depth of 840–865 m with a temperature around 285°C, had an arsenic concentration found to be 18.5 µg/L, while Lucky Strike at a temperature range of 170–324°C had an arsenic concentration of 4.3–24 µg/L [85]. Another hydrothermal field in the MAR region is TAG, discovered in 1972, and, further towards the south, the Snake Pit hydrothermal system was identified. Both systems were found

to be chlorine rich with TAG showing low arsenic ($0.8\ \mu\text{g/L}$) and Snake Pit in the range of 3.2 to $14.2\ \mu\text{g/L}$ [86].

East Pacific Rise spreads 9000 km in the Pacific Ocean with various hydrothermal regions studied in different sections, primarily Guaymas Basin located in the central Gulf of California characterized by 2000 m water depth. The basin is set apart with a temperature of up to 315°C , highly reducing conditions, and arsenic concentration in the range of $21.1\text{--}80.5\ \mu\text{g/L}$ [87]. The area possesses a high sedimentation rate of organic and carbonate-rich material, which undergoes pyrolysis at high temperature to release NH_4^+ ions in the fluid [88].

Deep-water hydrothermal springs also occur in back-arc basins with a high temperature gradient and a different chemical composition from those of mid-ocean ridges [89]. The fluid is characterized by very low pH (≈ 2), high amounts of dissolved metals (Mn, Zn, Cu, and Pb), and the presence of rocks like dacites and andesites [90]. The most common back-arc basin is Lau Basin located between the remnant Lau Ridge and the active Tofua volcanic arc with 1700–2000 m water depth [91]. At low pH and with high chlorine, arsenic concentration lies in the range of $450\text{--}825\ \mu\text{g/L}$.

Another hydrothermal system is Manus Basin located at the New Britain Trench, active in 1650 to 2500 m water depth [92]. Hydrothermal systems from back-arc basins show higher values than those from mid-ocean ridges. Higher arsenic concentration could be due to transportation of high amounts of dissolved iron leading to precipitation and incorporation of arsenic into iron sulfides.

1.7.3 Arsenic Occurrence in Geothermal Systems

High temperature geothermal systems occur throughout the world generally in one of three tectonic plates. The edge of the Pacific plate is defined by geothermal fields in New Zealand, Papua New Guinea, the Philippines, Indonesia, Japan, Kamchatka, Alaska, western USA, Mexico, Central America, and Chile. Other geothermal systems are Earth's "hot spots," such as in Hawaii, Yellowstone, and the Azores. The presence of arsenic in geothermal fluids has been known since the mid-19th century. Geothermal fluid arsenic concentrations are usually three orders of magnitude higher than those in uncontaminated surface and ground waters. Arsenic concentrations in the thermal fields of Yellowstone National Park range from 0.1 to $10\ \text{mg/kg}$, a range that is observed in most active geothermal fields. On the other hand, extremely high arsenic concentrations (more than $20\ \text{mg/kg}$) were found in geothermal well fluids. Arsenic is a ubiquitous component of geothermal systems and occurs together with other elements such as mercury, antimony, selenium, thallium, boron, lithium, and fluoride [93]. In geothermal areas, arsenic contamination occurs via two main processes: (1) natural contamination where the geothermal waters reach the surface as natural springs and then mix with surface water flows or shallow groundwater bodies used by humans for both irrigation and drinking water supply; and (2) human exploitation of geothermal waters as an energy resource causing mobilization of arsenic and other heavy metals contained in the geothermal waters to reach the surface and then contaminate surface and shallow groundwater bodies.

Arsenic concentrations in natural geothermal systems exceed permissible limits, and in some parts such as West Yellowstone, the concentration reached as high as 2000 $\mu\text{g/L}$. The population in these areas shows symptoms of chronic arsenic poisoning such as skin lesions and malignant growth [94]. River systems receive geothermal fluids that accumulate arsenic in aquatic plants, a notable source of exposure.

Geothermally active areas came into existence due to the emergence of hot water and steam at the Earth's surface and development of high geothermal gradient. The elevation in temperature is related to volcanic or magmatic activity, metamorphism, faulting, and radioactivity. Deeply circulating hot fluids are of low density and rise through the host rock, while cold water from the water table moves downward to recharge ground water. The chemical composition of geothermal fluid is regulated by fluid temperature and host rock composition. At high temperature, water behaves as an excellent solvent and can dissolve various ionic crystalline minerals forming new hydrated materials. At high temperature due to enhanced water/rock interaction, various elements such as Li, Rb, Cs, B, and Cl leach into solute. The concentration of dissolved gases such as CO_2 and H_2S are also a function of mineral solubility, especially carbonate and sulfide minerals. When geothermal fluid rises through the crust, pressure decreases and fluid separates into two phases, steam and water. Geothermally active areas can be divided into two groups: (1) hot water springs with neutral pH, rich in chloride and silica; and (2) steam vents of acidic pH, which are sulfate rich and susceptible to microbial oxidation of sulfuric acid. Geysers and carbonate-rich springs are also hot water discharges, but include steam heating and steam-phase mixing, respectively.

The development of geothermal fields for power generation increases the rate and volume of geothermal water reaching the surface. Geothermal sites used for power generation require substantial amounts of water to be extracted. During the separation of steam and water in geothermal power generation, arsenic is retained in the waste bore water and creates a number of problems in its disposal [95]. It becomes essential to re-instill thermal waste to its reservoir in order to prevent contamination of cold water. The geothermal springs are also used as swimming pools and hot spas, both for local residents and for tourists.

1.7.4 Arsenic Speciation and Deposition in Geothermal Fluids

According to water chemistry, geothermal waters can be classified into two main categories: (1) neutral Cl-SO_4^{-2} water; and (2) acid- SO_4^{-2} water. The former system has a high concentration of chlorine (263–1337 mg/L) with arsenic concentration ranges from 1 to 890 $\mu\text{g/L}$ while the latter has a low concentration of Cl (1.19 to 6.9 mg/L) and a low concentration of arsenic (0.8–660 $\mu\text{g/L}$) [96].

The behavior of arsenic in geothermal systems and surface water environments can be interpreted using thermodynamic data. In most hydrothermal fluids, arsenic is expected to be transported as arsenous acid (H_3AsO_3), which forms by the dissolution of orpiment at acidic to neutral pH and a wide range of temperatures [97]. Orpiment solubility increases with temperature, however, independent of pH under acidic or acid neutral conditions and then increases with pH.

In sulfide-rich hydrothermal fluids, arsenic exists as thioarsenite complexes, a group of covalently bonded arsenic–sulfide complexes that may or may not include oxygen. Orpiment solubility increases with pH and sulfide concentration but is less affected by temperature changes below 200°C. When rising geothermal fluid is exposed to atmospheric oxygen or mixed with another oxidizing fluid, such as a shallow ground water, arsenous acid (As^{+3}) oxidizes to arsenate (H_2AsO_4^- or HAsO_4^{2-}). Oxidation to arsenate occurs very rapidly in hot spring overflows and receiving streams and rivers. Various geothermal waters such as found in Yellowstone National Park, on the island of Dominica, in the Valles Caldera (New Mexico), and Massive Central (France) are likely to contain mostly As(V), due to strong oxidizing conditions. Hot springs formed from reservoir fluids contain mainly As(III), whereas that with acid sulfate and bicarbonate is enriched with As(V).

1.7.5 Biogeochemical Fate of Arsenic in Hydro- and Geothermal Systems

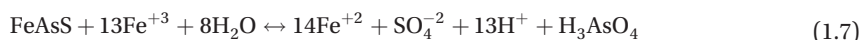
The biogeochemical fate of arsenic at submarine hydrothermal sites is less well known. Average arsenic concentrations in soft tissues of mussels (40 ppm) from the Mid-Atlantic Ridge are higher than those of mussels (2–20 ppm) from coastal environments. In contrast, shrimp recovered from the Mid-Atlantic Ridge have a lower arsenic content (13 ppm) compared to shrimp (15 ppm) from surface waters and coastal zones [98]. The high levels of arsenic (up to 70 ppm) in gill tissues and digestive tracts of these organisms were found mostly in the form of arsenobetaine and arsenosugars, suggesting assimilation of arsenic through the activity of symbiotic bacteria and by filtration of Fe oxyhydroxide particles. The presence of arsenic-bearing sulfosalt minerals proustite (Ag_3AsS_3) and pearceite ($\text{Ag}_{16}\text{As}_2\text{S}_{11}$) in filamentous bacteria from northern Gorda Ridge located off the coast of Oregon and northern California is a further indication that microorganisms play a key role in the chemistry of arsenic in submarine hydrothermal environments. Thermophilic bacteria and cyanobacteria in hot spring bio-films also facilitate the formation of silica, silicates, carbonates, and oxide minerals in sinter deposits and indicate enrichment of arsenic along with other elements such as Sb, P, and Zn [99].

1.8 Arsenic Release from Mining and Mineral Processing

1.8.1 Oxidation of Arsenic Sulfide and Industrial Ore Leaching

High concentrations of arsenic and other heavy metals such as Cd, Fe, Pb, Ni, and Zn are commonly present in acid mine drainage (AMD) effluents chiefly due to oxidation of arsenopyrite. AMD is polluted water, and contains high levels of iron, aluminum, and sulfuric acid. Arsenic is one of the priority pollutants associated with AMD, especially from gold mining operations [100]. Mining activities accidentally accelerate physical weathering of pyrite by grinding up the

ore and then oxidation of pyrite takes place. The presence of pyrite in sulfide-rich coals also plays a major role in the generation of acid rain and AMD.



Fe^{2+} and H^+ are released after oxidation of pyrite and move to the surface and ground water, where Fe^{2+} is oxidized to Fe^{3+} in the presence of dissolved oxygen in water. Fe^{3+} can further hydrolyze in water and precipitate as $\text{Fe}(\text{OH})_3$, which releases more H^+ into the water. In addition, iron-(oxy)hydroxysulfates often precipitate in iron-rich, acid-sulfate waters, under acidic conditions [101]. Under such conditions, soluble Fe^{3+} reacts readily with more pyrite and oxidizes it due to the action of acidophilic chemolithotroph bacteria, particularly *Acidithiobacillus ferrooxidans* [102].

The dissolution of the most common arsenic sulfide minerals orpiment and arsenopyrite follows the same mechanism and largely depends upon pH. Orpiment dissolution increases linearly from acidic to alkaline conditions [103], whereas arsenopyrite dissolution is minimal at near neutral pH and increases towards acidic and alkaline conditions [104]. Orpiment dissolution is controlled by weak van der Waal forces. At alkaline pH, due to absorption of hydroxide ion (OH^-) at the mineral surface, van der Waals forces becomes weak and two species can be formed, S-As-S and S-As-S-OH [105]. These species release arsenite and sulfide followed by recombination to thioarsenites and oxidation to thioarsenates in solution. In sulfide-deficient solutions, arsenite dominates at pH 2-8; however, in anoxic, sulfide-rich solutions, thioarsenite ($\text{AsO}_x\text{S}_x^{-3}$) has been proposed to pre dominate [106]. The formation of mono- ($\text{AsO}_3\text{S}^{-3}$), di- ($\text{AsO}_2\text{S}_2^{-3}$), and trithioarsenate (AsOS_3^{-3}) was proposed upon dissolution of orpiment at neutral pH [107].

Dissolution of arsenopyrite releases iron along with arsenic and sulfur, which also influence arsenic mobility and formation of thioarsenic species. Initially, Fe^{+2} , S^{-2} , and As^- species are released from the mineral surface and undergo oxidation at alkaline pH to form iron-arsenic oxide or hydroxide surface coating to prevent further release of arsenic [108,109]. The presence of iron and rapid formation of iron sulfides leave no or little free sulfide for thioarsenate formation.

Under acidic conditions, neither mineral forms thioarsenate because at low pH thioarsenic species transform quantitatively to arsenite or precipitate as amorphous arsenic sulfide minerals [110]. At highly alkaline conditions, thioarsenite transforms to arsenite due to competitive ligand exchange of SH^- vs. OH^- groups. Monothioarsenate is stable towards reduction; however, di- and trithioarsenate are reduced to arsenite (As(III)). It has been postulated that thioarsenates once released by mineral dissolution might have higher mobility compared to arsenites and arsenates and may increase arsenic burden in natural or mining-impacted environments.

Release of arsenic from arsenopyrite is also enhanced in the presence of hydrogen peroxide (H_2O_2), a common constituent of rain water [111]. Hydrogen peroxide is a stronger oxidizing agent compared to molecular oxygen. It can also generate more potential oxidizing agent