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ABSTRACT

Modeling Arsenic Transformation in Clay Soils

by
Chao-Yi Chung

This project is designed to estimate the possible transformation forms of arsenic in clay soil. A computer model was established to simulate arsenic transformations. The amount of arsenic species adsorbed, dissolved, and the predominant soluble species are calculated by the model, which is mainly based on the Freundlich adsorption isotherm, solubility data collected by Keaton and Kardos, and pH-Eh diagram established by Ferguson and Garvis. The computer language used is Turbo PASCAL version 5.5.

The clay soil environment is considered to be in standard state: 25°C 1 atm. Environmental factors of the soil system which are accounted for by the model are moisture, pH and Eh. Soil moisture affect moderate soluble species, such as more than the very soluble species () and the relatively insoluble species (As_2S_3 , As_2S_5). The predominant soluble species is controlled by the pH-Eh condition.

Factors, which are not accounted for this model and also influence arsenic transformation are discussed and explained. Processes, such as biological conversion, evaporation and volatilization, are also possible processes in clay soil system and are not considered in current version of model, which are discussed in Chapter 3.

Solubility and adsorption approaches are applied in the model. However, these two approaches gives two opposite results. In the solubility approach, As_2O_3 , As_2O_5 , are very soluble. However, they are more adsorbed than dissolved in the adsorption approach. It is possible that $As(III)$ and $As(V)$ are highly soluble in soil water but also adsorbed largely when the presence of metal ions or other clay mineral functional groups. It is also possible that default n, k value are not good for this condition.

**MODELING ARSENIC
TRANSFORMATION IN CLAY SOILS**

by
Chao-Yi Chung

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This thesis is dedicated to
my parents

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CHAPTER 1

INTRODUCTION

Arsenic, a therapeutic agent used around in 400 BC., a well-known homicidal poison in the Middle Ages, is widely used as agricultural pesticide, herbicide, silvicide and fertilizer nowadays. It is also a ore smelting byproduct. As a result, arsenic may accumulate in soils. Soil arsenic could be uptaken from soils by plant and then by animal or it may drained to groundwater. Arsenic is considered hard to excrete from animal bodies and may accumulated in large amounts in animal bodies by biocondensation. It is a suspected carcinogen to human beings, but it is thought to be less toxic to animals [40].

Although regulations for arsenic have been established for human exposure in air and water, recent research suspects the internal cancer risk from arsenic to be significant [64]. According to its potential for increased human exposure and health risk, it is now one of the trace elements of major interest to EPA.

Arsenic toxicity depends largely on the degree of arsenic oxidation and its association with organic or inorganic species. The toxicity of arsenic in soils is related to its species bioavailabilities and mobilities. Therefore, it is important to know the transformation forms of arsenic in soils. Since arsenic is mainly bound to clay minerals, this project is so focused on arsenic transformation in clay soils.

The major tasks of the project are analyzing the most possible arsenic conversion processes in clay soils and establishing a computer model to predict the transformation forms of arsenic in clay soils. The physical, chemical and biological properties of clay soil and arsenic properties are discussed and used as modeling basis. In the model, environmental factors (such as temperature, moisture, pH-Eh) and initial arsenic quantities and species are input by the users, otherwise, the default values are generated by the model. The arsenic transformation forms and the concentration of each dominant form over a specific time period are simulated by the model as output.

From an engineering point of view, the specific forms of arsenic influence the feasibility of using specific technologies to remediate contamination. The accurate prediction of specific forms could help scientists to develop appropriate arsenic remediating methods. This project provides a way to evaluate arsenic contamination.

CHAPTER 2

RESEARCH OBJECTIVES

This project is designed to predict arsenic transformation forms in clay soil environment. It was accomplished in three stages. The first stage was determination of all possible reactions occurring in clay soil systems by a literature review. Classification of major environmental factors governing each reaction were determined in the second stage. Finally, the computer model prediction was the task in the third stage. Specific objectives of these stages are :

Stage 1. Determination of possible reactions :

1. Arsenic property study : Arsenic speciation, specific physical / chemical properties and biotoxicity.
2. Clay soil property study : Clay soil content, structure, functional group.
3. Compare previous studies and find out all possible reaction occurring in clay soil.

Stage 2. Classification of factors relating to each reaction :

1. Theoretical and practical information classification.
2. Evaluate the relationships between each factor and the favored reaction.

Stage 3. Modeling prediction of arsenic transformation:

1. Establishing computer model.
2. Compare modeling result with previous literature report.

CHAPTER 3

BACKGROUND

3.1 Arsenic Properties

Arsenic, long known as a toxic substance, was one of the most homicidal poisons of the Middle Ages [10]. Arsenic trioxide is a fine white powder that is tasteless and colorless; thus, it makes an excellent poison [24]. Nowadays, arsenic is regarded as a toxic trace element and also a suspected carcinogen that is of great concern to both nutritional scientists and toxicologists.

Widely distributed in the earth's crust, arsenic amounts vary from 0.1 to several hundred ppm - depending on the specific geology [13].

3.1.1. Physical and Chemical Properties

Free arsenic occurs only in small quantities and is usually associated with other metals in crystalline rocks and schists. Typically, arsenic exists in combined forms [41]. The major arsenical forms are oxides, sulfides, and complexes with other metals, such as orpiment (As_2S_3), arsenopyrites ($FeAs_2$), cobaltite ($CoAsS$), nickel glance ($NiAsS$) and arsenical pyrites ($FeAsS$) [41].

In its stable form, arsenic is a steel-gray, brittle, crystalline metalloid. It exhibits allotropy, the two other forms usually distinguished are yellow and black respectively [10]. Gray arsenic sublimates at 610°C with depolymerization without melting [60].

The element arsenic has an atomic number 33, atomic weight 74.91, and belongs to 5A group in the Periodic Table. Normal valence states of arsenic are 3 and 5, as in AsF_3 and AsF_5 [13]. It also has the possible coordination numbers of -3 (AsH_3), 4 ($As(CH_3)_4^+$) and 6 (AsF_6^-) [13, 41].

The compounds of arsenic have high biological activity. Among the numerous arsenic compounds are known substances that show powerful insecticidal, fungicidal, herbicidal,

and zoocidal effects. A common disadvantage of all the compounds of arsenic without exception is their high toxicity to man and domestic animals. Even some organoarsenic compounds that are relatively low in toxicity to warm - blooded animals are converted to toxic inorganic compounds when they undergo mineralization in animal organisms, in the soil, or in plants [46]. Fig. 1 indicates naturally occurring forms of arsenic and interactions among them. The major compounds of arsenic are briefly addressed below:

1. -Oxide: Arsenious oxide (As_2O_3) and arsenic oxide (As_2O_5) are the most important oxides. Arsenious oxide, known as white arsenic, tasteless and colorless, is sparingly soluble in water to produce arsenious acid $HAsO_2$ [32].

2. -Sulfide: Arsenic reacts with sulfur to form As_4S_3 , As_4S_4 , As_2S_3 and As_2S_5 . The sulfides As_4S_4 and As_2S_3 occur in nature. Hydrogen sulfide precipitates As_2S_3 and As_2S_5 from aqueous hydrochloric acid solutions of As (III) and As (V), respectively [60].

3. Hydrides: The most important hydride of arsenic is arsine (AsH_3). It is a colorless inflammable gas with a slight garlic - like odor, depositing arsenic on exposure to light and moisture. Arsine is only slightly soluble. Two additional arsenic hydrides are known: diarsine, stable at $-100^\circ C$, formed by decomposition of AsH_3 and triarsine, AsH_5 , which occurs in traces in the hydrolysis of an $MgPAs$ alloy [60].

4. Methylated arsines: In soils with high organic matter and in saturated (reducing) conditions, arsenates can form methylated arsines, which are more soluble in water, and trimethylated arsines which are volatile [6].

3.1.2. Biochemistry and Biototoxicity

Toxicology is the study of the nature and mechanism of toxic effects of substances on living organisms and other biological systems. It also deals with quantitative assessment of the severity and frequency of these effects in relation to the exposure of the organisms [40]. The assessment of health hazards of industrial chemicals, environmental pollution,

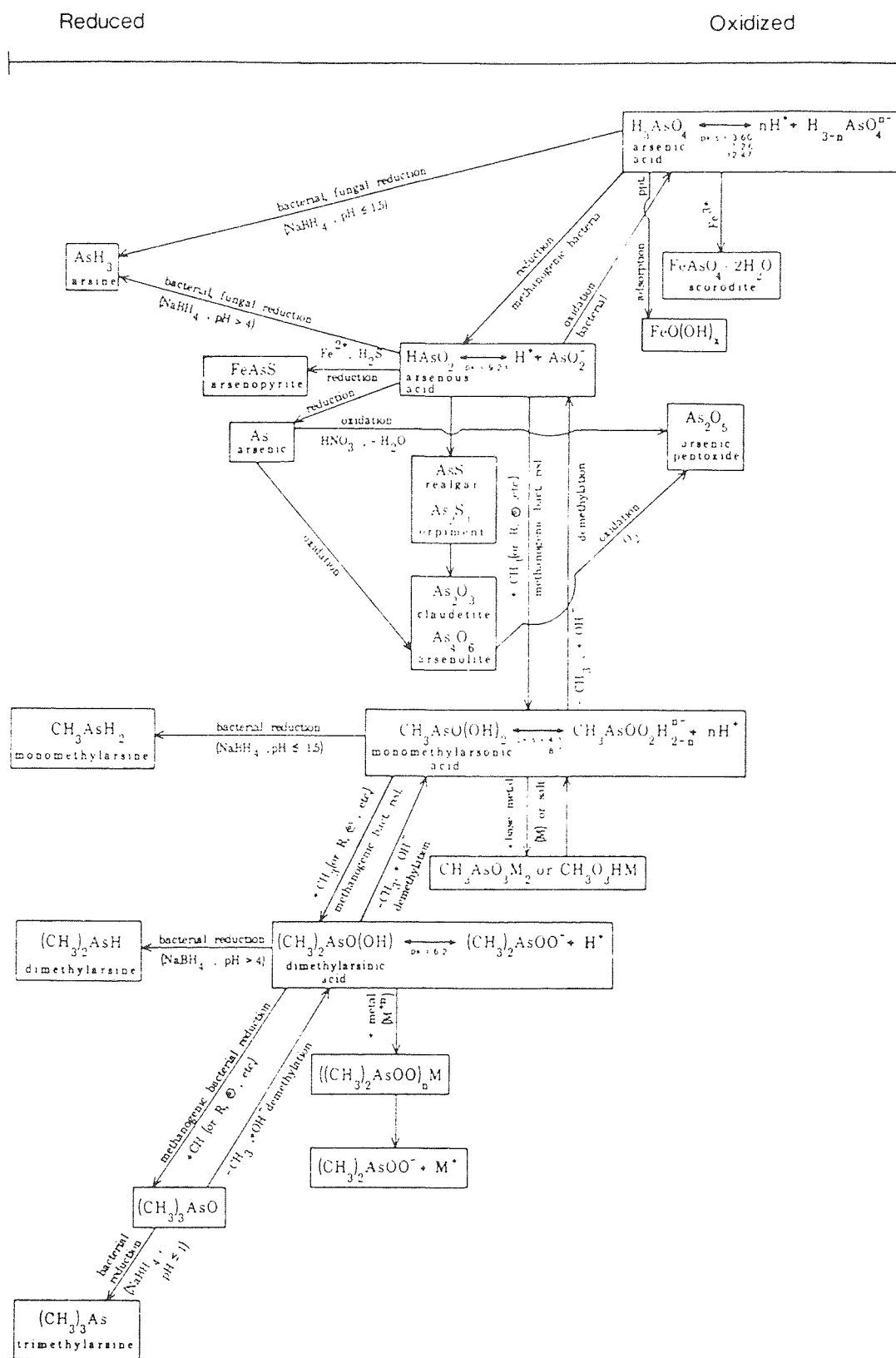


Figure 1. Forms of Naturally Occurring Arsenic Found in Natural Environment (Adapted from Welch et al, 1988, [69])

and other substances represents an important element in the protection of the health of the worker and members of communities [40]. Toxic effects, or simply toxicity, are greatly variable in nature, target organ, and mechanism of action. Table 1 listed the U. S. laws and their responsible agency.

Table 1 U.S. Laws that Have a Basis in Toxicology

Responsible agency	Law
Food and Drug Administration (FDA)	Federal Food Drug and Cosmetic Act
Environmental Protection Agency (EPA)	Federal Insecticide and Rodenticide Act Resource Conservation and Recovery Act Safe Drinking Water Act Toxic Substances Control Act
Consumer Protect Safety Commission (CPSC)	Consumer Protect Safety Act Federal Hazardous Substances Act
Occupational Safety and Health Administration (OSHA)	Occupational Safety and Health Act

(Adapted from Lu, F. C., 1991 [40])

All toxic effects result from biochemical interactions between the toxicants (and / or their metabolites) and certain structures of the organism [40]. Metabolism is the sum of all the chemical reactions which occur in the living cells of an organism, including synthesis and degradation reactions [Johnson, K. D. et al, 1981]. Absorption, distribution, excretion and biotransformation are main components of metabolism.

3.1.2.1. Metabolism

Although arsenic is not essential for human metabolism, due to its wide distribution in nature, it is constantly taken into the human body in very small quantities, and is therefore regarded by most authorities as a normal constituent of the body [10].

The major metabolism reaction is methylation to dimethylarsinic acid (cacodylic acid) and monomethylarsenic, thus detoxifying the arsenic. This is a first - order reaction, but can be saturated by large doses (USEPA 1980) [11]. It is generally accepted that most of the effects of arsenic are mediated via the reaction between the metal and thiol groups of various enzymes and cofactors such as glutathione [11].

The most significant antagonism to arsenic is the use of BAL ("British Anti-Lewisite", 2,3-dimercaptopropahol), as an antidote to arsenical poisoning. The highly reactive thiol groups form cyclic dithioarsenites, which are more stable than the protein - thiol arsenites, thus preventing the enzyme effects. Also, selenium is capable of reducing the carcinogenicity of arsenic, perhaps even eliminating it [11]. No synergisms are known [11].

Absorption can be highly dependent on the chemical form and (for inhalation) the physical form of the arsenic [11]. However, the common forms, particularly arsenic trioxide, are well absorbed by inhalation and essentially completely from the gastrointestinal tract [11]. Once absorbed, about four - fifths of the arsenic is stored and widely distributed to the tissues by the blood and quickly taken up by many tissues, but particularly by the liver, kidney, lungs spleen, skin [11, 10]. Most of the arsenic absorbed is accumulated in low level metabolic tissue such as hair and nails [41]. Bone and muscle have lower concentrations, but are major depots of the body burden of arsenic in addition to skins [11]. The total daily arsenic intake has been estimated to be of the order of 400 ~ 1000 μg [32]. Arsenic is excreted slowly in the urine, feces, and by the dermis as shed skin, hairs, and nails. The hair and nails may be used to detect past, discontinued exposure [11]. Guthmann and grass reported in 1933, the blood of normal woman contains 20 ~

100 μg of arsenic per 100g (0.2 ~ 1 ppb). Polissar et al (1989) published a result of multiple sampling as below:

Table 2 Median Arsenic Concentrations in Urine, Hair, Hand wash, and Personal Air Samples, by Sex and Age (Years), 1985 ~ 1986

	Urine, uncorrected (ppb)	Hair (ppm)	Hand wash $\mu\text{g}/\text{hand}$	Personal air monitor	
				Fine (ng/m^3)	Coarse (ng/m^3)
Male	9.6	2.7	1.00	12.4	3.7
Female	8.1	0.6	0.39	4.0	2.2
Age					
0-6	15.0	3.1	0.66	34.6	5.0
7-13	9.4	1.6	1.08	9.3	2.3
14-19	8.1	0.6	0.58	10.2	2.3
>20	7.8	0.6	0.38	4.0	3.0

(Adapted from Polissar et al, 1985, [52])

In their investigation, males had higher concentrations of arsenic than females, and children ages 0 - 6 had the highest concentrations of arsenic of any age group [52].

3.1.2.2 Toxic Effect

The toxicity of arsenic compounds depends largely on the oxidation state and whether arsenic is present in an organic form [69]. Usually, the toxicity is lower when arsenic is consumed as an organically-bound species [19]. From greatest to least, arsenic toxicity is as follows [69]: 1. arsenites (valence -3); 2. organo-arsine compounds, arsenites and

oxides (valence +3); 3. arsenates (+5); 4. arsonium metals and native arsenic (0). However, under some circumstances trimethylarsine is highly toxic. It has been identified as an important reservoir of arsenic in certain organisms, and has caused human poisoning through exposure in air. It is more soluble in hydrocarbons than water, which may account for its toxicity and for accumulation in certain organisms [19].

Arsenic toxicity is also related to individual species tolerance. It is also known that arsenic is toxic to higher plants, to all animals having central nervous systems, and to certain low organisms [41]. However, differ from other toxic element, arsenic is more toxic to human beings than to animals.

The toxic effects of arsenic are generally: (a) systemic vascular poisoning, a paralytic action on smooth and cardiac muscle and leading to hemorrhage; (b) mitotic poisoning, blockage of chromosomal mitotic metaphase during cellular division; and (c) protoplasmic poisoning, a combination with certain enzymatic sulfhydryl groups, which causes inhibition of various oxidative systems requisite in tissue respiration [45].

In acute poisoning, arsenic is a general protoplasmic poison acting upon various ferment processes, especially the phosphates, leading to diminished oxidation and tissue respiration [10]. The main symptoms are seen in the gastrointestinal system. These include throat constriction, difficulty in swallowing, chest pain, and may cause acute shock, weak pulse and breathing, resulting in immediate death or death from exhaustion in the following few days, often caused by cardiac failure [32, 11].

General symptoms of chronic poisoning are: weakness, nausea, and loss of appetite, with possibly some vomiting and diarrhea. General catarrh follows with hoarseness and mild bronchitis. Later general lassitude and sometimes jaundice supervene [32]. A well-known symptom of chronic poisoning is the onset of peripheral neuritis. The nerves in the limbs are affected, the feet and hands lose sensation and may lead to difficult in walking and controlled movement [32]. In certain parts of Taiwan and South Africa, the water may contain hundreds of milligrams per liter. In these area, the inhabitants may suffer from

dermal hyperkeratosis and hyperpigmentation. A more serious condition is gangrene of lower extremities, the black - foot disease, resulting from peripheral endarteritis [40].

Mutagenesis tests have been essentially negative, thus arsenic is not believed to cause genetic damage.

3.1.2.3. Tolerance of Arsenic

The National Interim Primary Drinking Water Regulations set the Maximum Contaminant Level (MCL) for arsenic in U. S. public water supplies at $50 \mu\text{g}/\text{l}$ [63]. In general, arsenic is not found in drinking water at levels exceeding this MCL. Well waters in the western U.S. and Alaska, however, may have much higher levels owing to the geochemical environment [63]. It has been estimated that there is an average daily intake of 10 - 12 μg of arsenic from drinking water in the U.S. [32]. The fatal dose is said to be in the region of 120 - 180 mg [32]. The smallest recorded dose is 2 g [10].

For animals, the ultimate L. D.₅₀ was less for the pure (39.4 mg kg^{-1}) than the crude preparation (42.9 mg kg^{-1}) [10]. The oral L. D.₅₀ for rats varies between 75 and 500 $\text{mg} \cdot \text{kg}^{-1}$ [10]. However, arsenic is carcinogenic in humans but not in animals [40].

3.1.3. Sources of Arsenic

The commonly identified arsenic - bearing minerals are realgar (AsS), orpiment (As_2S_3), arsenopyrite (FeAsS), claudetite (As_2O_3), arsenolite (As_4O_6), arsenic pentoxide (As_2O_5) and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Within this group of minerals, arsenopyrite probably is the most common arsenic mineral. It is found naturally in metal ore deposits and produced commercially as a byproduct during the processing of nonferrous metal ores [64].

Soil arsenic is usually bound to clay surfaces, and its mobility is a function of soil pH, phosphate levels, iron and aluminum content, and soil type. The mobile fraction, usually in the pentavalent form, is of concern in terms of movement to plants and water. Little reductive methylation occurs in most soils [63].

The largest use of arsenic is in the production of agricultural pesticides which includes herbicides, insecticides, desiccants, wood preservatives, and feed additives [64]. As of addition to alloys in amount 0.3 - 0.5 percent to increase hardening and heat resistance [10]. Some arsenical organic compounds also have therapeutic uses [10].

Inorganic forms of arsenic have commonly been used in the past in the production of agricultural pesticides, which includes herbicides, insecticides, desiccants, wood preservatives, and feed additives. Arsenic trioxide was the raw material for the older inorganic pesticides, including lead arsenate, calcium arsenate, and sodium arsenite. In more recent years, the production of organic arsenicals such as monosodium and disodium methanearsonate (MSMA and DSMA) and cacodylic acid have replaced many of the inorganic forms. More recently, arsenic and its derivatives have been used in the electronics industry [64, 24]. Appendix A lists the commonly used inorganic and organic arsenic species.

It is recognized that atmospheric emissions of arsenic from smelting operations constitute a major pollutant source. An estimated 4,500 metric tons of arsenic were released to the atmosphere in 1976 by primary nonferrous smelters, nearly 90% of this total was a result of copper production, Austin and Millward [7] demonstrated that *As* is significantly mobilized from the land to the troposphere by both natural processes and anthropogenic processes. In the latter case industrial emission accounts for about 30% of the present clay burden of *As* in the troposphere.

Arsine (AsH_3) is not an industrial product in the economic sense, but forms whenever nascent hydrogen is liberated in the proximity of trivalent arsenic. Since arsenic is present as a contaminant of many ores - zinc, lead, copper, antimony, gold, silver and tin - the formation of arsine occurs most frequently in the metallurgic industry, particularly from the action of acid on arsenic - bearing metal. It may also occur where the hydrogen ion is formed by hydrolysis, as in the reaction of moisture with calcium arsenide present as an impurity in ferrosilicon (Hake, 1910), in the process of wetting of aluminum and

phosphate dross (An, 1948; Spolyar and Harger, 1950); in lead refining (Wills, 1948; Banik, 1956); and in the purification of tin (Macaulay and Standly, 1956).

3.2 Clay Soil Properties

Soil is material found at the surface of the earth which sustains the vegetative cover on which all life animals depends. It has formed over time by the action of the climate and living organisms on the underlying geological parent material [45]. In general, the soils consist of a collection of solid particles with voids in between. The solid phase (about 50%) contains soil solids or particles of mineral or organic origin, whereas the voids can be filled either with water (25%), air (25%), or filled partly with both of them. Because of presence of more than one phase, the soil is actually a heterogeneous material [25, 23]. Fig. 2 shows the simplified skeleton of soil.

3.2.1. Soil Solids

Soil solids consists of both organic and mineral fractions. The inorganic fraction of the soil solids varies from less than 5% in organic soils (peat) to more than 90% in sandy soils. The mineral particles are derived from rocks and are of varying shapes and composition [25]. The organic fraction is derived from decaying plant and animal debris [45]. The chemical composition of particles varies from soil to soil [25]. Sec. 3.2.1.1 given more detailed description of soil components and soil classification. Soil mineralogy is discussed in Sec. 3.2.1.2.

3.2.1.1 Soil Composition and Classification

The mineral or inorganic fraction of the soil can be subdivided in terms of particle size into stones, sand, silt and clay [45]. In the Unified Soil Classification System, soils are generally classified as "coarse-grained (sands and gravels)", "fine grained (silt and clay)"

or "organic" [62]. The smallest grain that is larger than visible to the naked eye are called fine-grained [23]. There are no universally accepted size definitions but in general terms:

Table 3 Soil Classification

Soil	Size of Particle ^a	Plasticity ^b	Cohesion ^b
Stone	> 2 mm	X	X
Sand	0.06 ~ 2 mm	X	X
Silt	0.002 ~ 0.06 - 0.02	X	X
Clay	< 0.002 mm	√	√

^a Adapted from McRac, S. G., [45]

^b Adapted from Ghyllyal et al, [23]

The soil texture refers to the relative proportions of the sand, silt and clay. The textural triangle (Fig. 3) [45], includes the textural classes plotted from laboratory result, offers a practical classification method for soils.

The organic matter is most abundant nearest the surface, producing the black or dark brown colors of the topsoil which normally constitute 3 ~ 8% by weight. The underlying subsoil has less, around 1~2% and so is usually lighter in color [45]. Fresh plant or animal debris is progressively decomposed by soil micro - organisms, tending to a more or less stable end product called humus, a black amorphous substance which has lost all its original structure [45]. Humus is generally subdivided into three general classes: fulvic acid, humic acid and humin [15]. Table 4 listed briefly classification of these three parts.

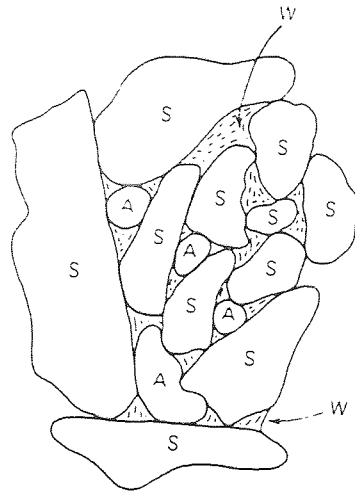


Figure 2 Soil Skeleton Containing Solid Particles (S) and Voids with Air (A) and Water (W) (Adapted from Holtz and Kovacs, 1981, [25])

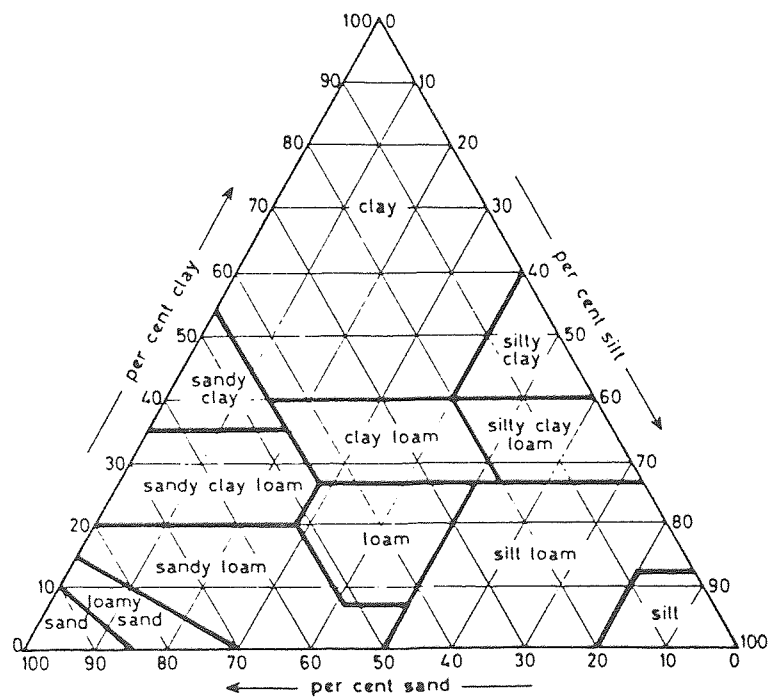


Figure 3 The Soil Textural Triangle, Relating Particle Size Distribution to Texture Classes (Adapted from McRea, 1988 [45])

Table 4 Classification of Humus

Humus	Molecular Weight	Solubility	
		Acid	Base
Fulvic acid	> 2,000	√	√
Humic acid	~ 300,000	X	√
Humin	Very high	X	X

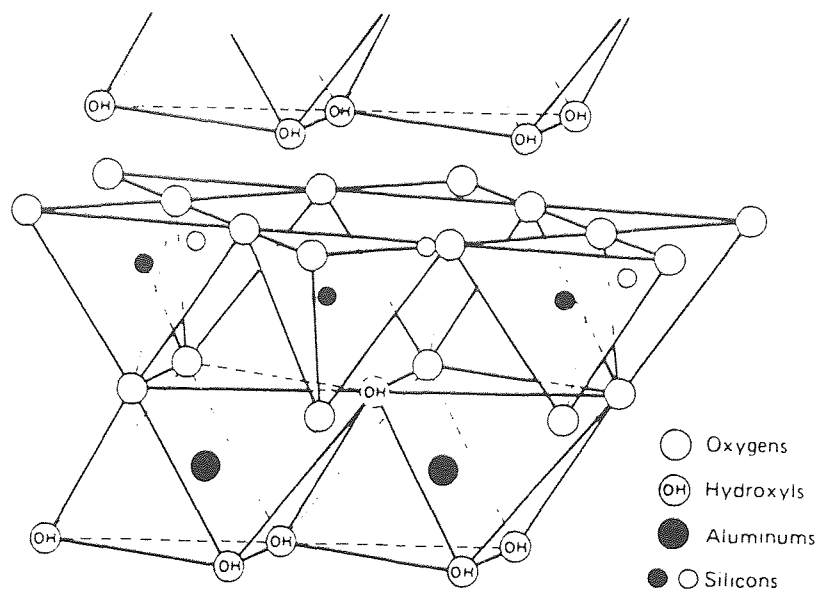
(Refer to Dragun, J. [15])

Humus is colloidal in structure. The typical humus colloid is comprised of (a) a central unit containing primarily *C* and *H*. (b) a colloidal surface comprised of carboxylic (*COOH*) and hydroxyl (*OH*) functional groups [15].

Carbon, hydrogen and oxygen along with eleven of the elements listed in Table B-1 (Appendix B): *Al*, *Ca*, *Fe*, *K*, *Mg*, *Mn*, *Na*, *P*, *S*, *Si* and *Ti*, constitute over 99 percent of the total elemental content of soil. The remaining one percent is comprised of elements known commonly as " trace elements " [15]. Arsenic is one of the trace elements.

3.2.1.2 Soil Mineralogy

Stones are generally rock fragments, and in most soils the sand and silt consist largely of grains of resistant minerals, chiefly quartz. The clay fraction is composed of extremely small crystalline particles of one or more members of a small group of minerals known as clay minerals which normally have silicate structures [44, 25]. Fig. 4 illustrates the typical chemical structures of clay minerals commonly found in soils of the U.S. [15].



Atomic structure of kaolinite (after Grim, 1959)

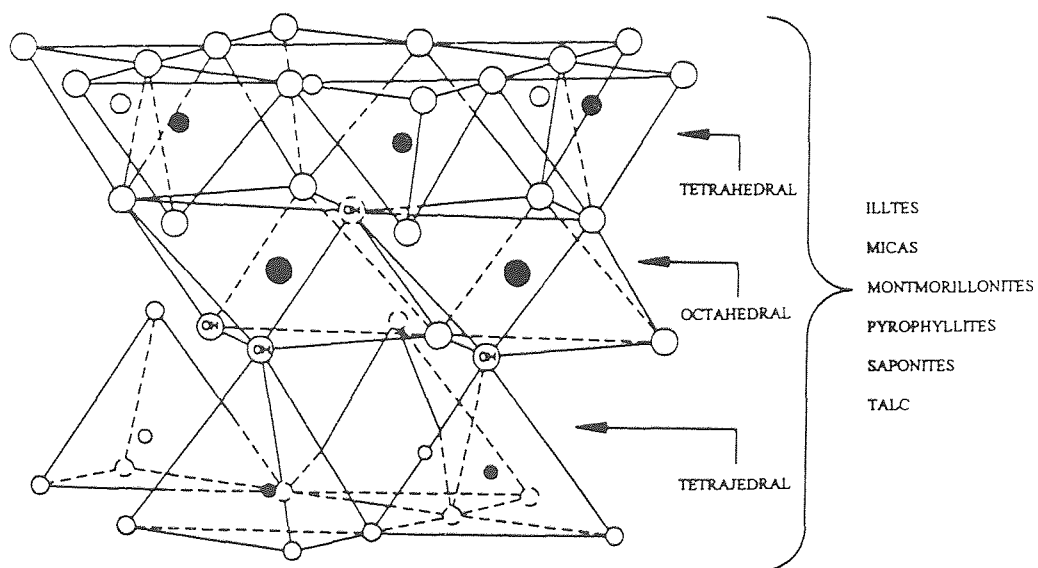


Figure 4 Structure of Clay Minerals Commonly Found in the U.S. Illites Micas Montmorillonites Pyrophyllites Saponites Talc Kaolinites Tetrahedral Octahedral Tetrahedral Octahedral (Adapted from Dragun, J. 1988, [15])

Soil clay minerals are comprised primarily of layers of tetrahedral and octahedral sheets. Each tetrahedral sheet is comprised of SiO_4 tetrahedra, while each octahedral sheet is comprised of aluminum oxyhydroxide octahedra. The typical clay minerals found in the U.S. soils are comprised of octahedral-tetrahedral sheets (i.e. 1:1 clays) and of tetrahedral-octahedral-tetrahedral sheets (i.e. 2:1 clays) [15].

If the octahedral sheets contained only Al^{3+} and if the tetrahedral sheets contained only Si^{4+} , the clays would be electrically neutral since the total number of positive and negative charges would be equal. However, when clays precipitate, the presence of insufficient amounts of Al^{3+} result in the substitution of Fe^{2+} and Mg^{2+} for Al^{3+} in the octahedral layer of some clays. Also, insufficient amounts of Si^{4+} in the tetrahedral layer of some clays. This substitution process of replacement is called isomorphous substitution and is responsible for the negative charges on clay mineral surfaces [15].

Humus is also responsible for the accumulation of cationic species of elements at soil surfaces. These negative charges on soil mineral surfaces are responsible for attracting and accumulating cationic species of elements of soil surfaces.

The total amount of cations adsorbed by these negative charges on a unit mass of soil is defined as the cation exchange capacity (CEC) of the soil. The CEC is usually expressed as milliequivalents (meq) per 100 grams of soil. The term milliequivalent is defined as one milligram of hydrogen or the amount of any other ion that will displace it. Clays and soils possess widely varying CEC's. Even soils with a given soil type can exhibit significant CEC variability (Refer to Appendix B: Table B-2) [15].

On the other hand, AEC is termed as the anion adsorption capacity by soil surface. These positive charges are responsible for accumulating at soil surfaces anionic species of elements such as phosphate and arsenic. In general, most soils possess a net negative charge; however, these are tropical soils that can obtain a net positive charge. As a general rule, the AEC of most the U.S. soils should be less than five percent of the CEC.

Since soils typically possess a significantly greater number of negative surface charges than positive ones, and since anions possess a net negative charge, repulsion between anions and soil surfaces can occur. This process is known as negative adsorption. The net effect of negative adsorption is the repulsion of anions from the water in the immediate vicinity of the soil surface and from narrow pores where water velocities are slow; as result, when leaching occurs, anions can migrate at a faster rate than they would if they were evenly dispersed throughout all water present in soil. This repulsion process is known as anion exclusion [15].

3.2.2 Soil Water

Soil water plays an important role in soil systems. Without it, there would be no weathering; nor would there be any organisms or accumulated water in the surface layers of the ground [27].

Between and within the structural units or peds is a network of pores of various sizes, which are filled mainly with water when the soil is wet and air when the soil is dry. The pores conduct water and air through the soil and provide an ideal growth environment for plant roots and the soil micro-organisms [45].

About half the volume of a soil is pore space. The volume of pores, i.e. the soil porosity or air capacity, can be calculated from the bulk density while bulk density is the weight of soil per volume and characteristically ranges from about 1.0 to 2.0 g / cm³.

$$\text{Porosity} = 100 - (\text{Bulk density} / \text{Particle density}) \times 100 \quad (3-1)$$

When soil is wetted, all the pores fill up with water, it is described as saturated. Under the action of gravity, however, water starts to drain out of the larger pores, the macropores larger than about 0.06 mm in diameter (unless there is some drainage impediment lower in the soil profile) and is replaced by air. This water is called

gravitational water and when all of it has drained away the soil is said to be at field capacity with a moisture content sometimes called its retained water capacity . The smaller pores retain water against gravitational removal mainly because of capillary forces and so is called the capillary water, held increasingly tightly the smaller the pores. The final physical category of soil water is the hygroscopic water which is held as a tight film near the particle surface. The amount of hygroscopic water, which is held by a soil is called its hygroscopic coefficient [45]. The various water states is illustrated in Fig. 5.

The soil water which plants draw on when current rainfall alone is not sufficient for their needs is called the available water. It corresponds to most but not all of the capillary water, since the gravitational water is considered to be too transitory, and the hygroscopic water (and some of the capillary water in the smallest pores) is too tightly bound [45]. Different soil texture poses different water retaining ability. Fig. 6 depicted the relationship between soil water availability and soil texture.

3.3 Physical / Chemical Conversion

Studies have demonstrated that the distribution and transformation of arsenic in soil systems is a complex process which is affected by a variety of physical and biogeochemical processes. Fig. 7 depicts these processes and interactions among them. Through these processes, arsenic is fixed, released and redistributed in soils. Reactions such as adsorption, precipitation and coagulation of arsenic compounds and complexes, bioaccumulation by biota, redox reaction and volatilization of many arsenic compounds are considered to govern arsenic transformations and distribution in soils [1]. These possible reactions are classified and divided into physical / chemical and biological parts, which are discussed in this and the following section, respectively. Table 5 indicates the physical / chemical processes that may occur in soils. Biological processes associated with arsenic conversion are shown in Table 13 which is in next section.

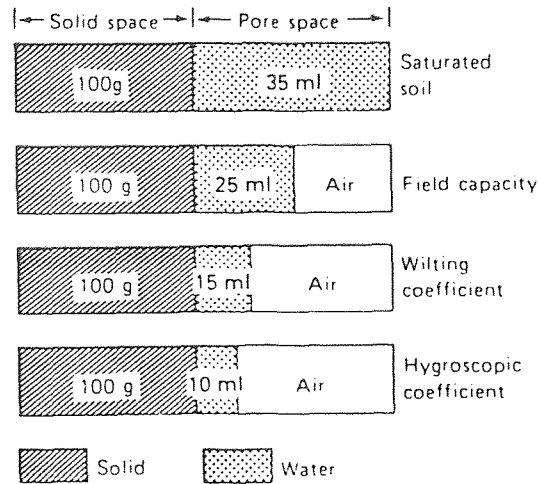


Figure 5 Typical Proportions of Solids, Air and Water in a Well -Structured Loamy Topsoil at Various Water States (Adapted from McRea, 1988 [45])

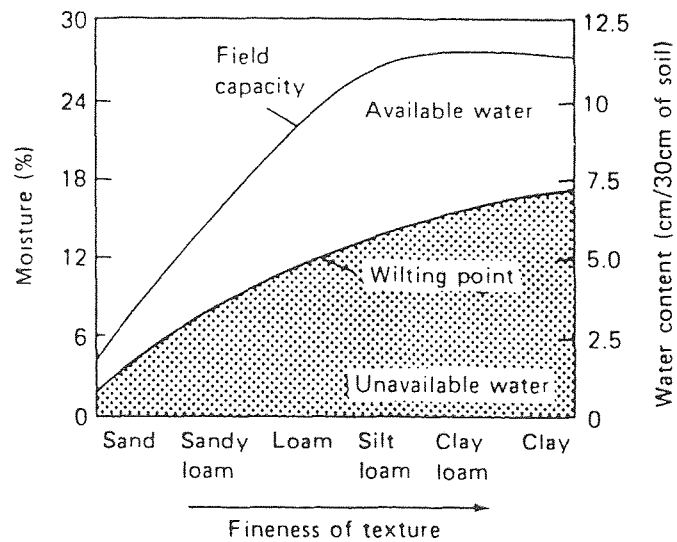


Figure 6 The Relationship between Soil Water Availability and Soil Texture (Adapted from McRea, 1988 [45])

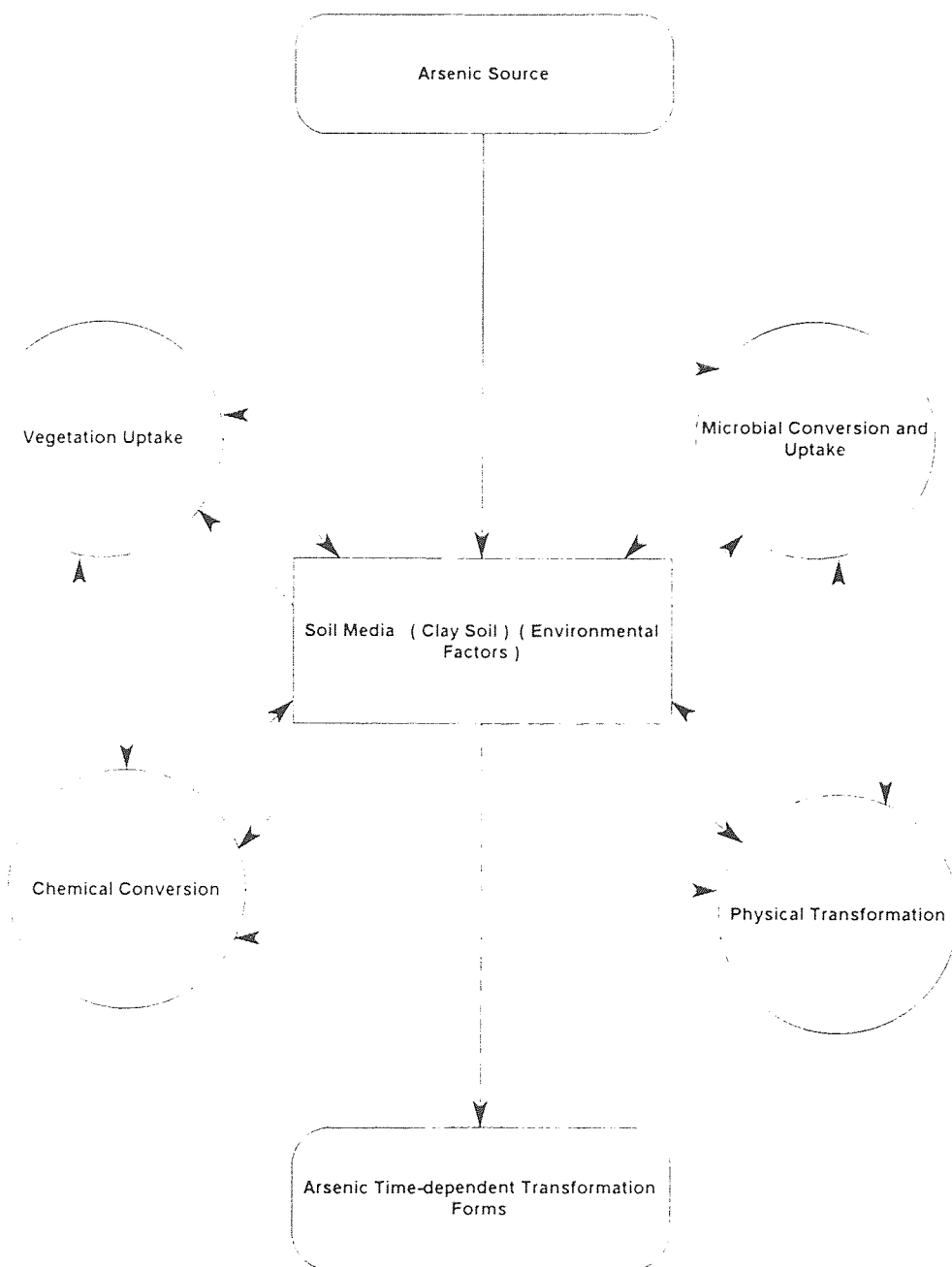


Figure 7 Interaction Network for Arsenic in Soil System

Table 5 Physical / Chemical Processes Associated with Arsenic Transformation and Distribution in Soil System

Type	No.	Reaction	Effect	Remark
Physical	1	Physical Adsorption	Fixation / Transformation	Detail in Sec. 3. 3. 1
	2	Precipitation	Fixation / Transformation	Considered with Adsorption (Description in Sec. 3.3.1, Mechanism in Sec. 3.3.2)
	3	Dissolution	Transformation	Detailed in Sec. 3. 3. 2
	4	Evaporation	Condensation	Discussed in Sec. 3.3.4
	5	Volatilization	Transformation / Translocation	Discussed in Sec. 3.3.4
	6	Drainage	Transportation	Not Considered in the Current Version of Model
	7	Diffusion	Transportation	Not Considered in the Current Version of Model
Chemical	8	Redox	Transformation	Detailed in Sec. 3.3.3
	9	Coprecipitation	Transformation / Fixation	Considered with Adsorption (Detailed in Sec. 3.3.1)
	10	Chemisorption	Transformation / Fixation	Considered with Adsorption (Detailed in Sec. 3.3.1)
	11	Ion Exchange	Transformation / Fixation	Considered with Adsorption (Detailed in Sec. 3.3.1)

3.3.1 Sorption Processes

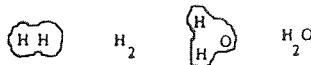
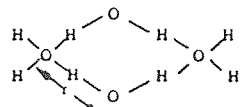
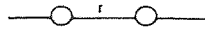
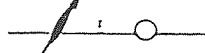
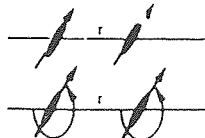
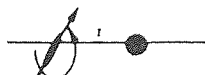
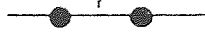
Sorption processes are defined as the accumulation of an element at the surface of soil particles with a decrease of the concentration of the dissolved element in water [15]. Sorption processes include adsorption, absorption, precipitation processes and coprecipitation with other elements. The phenomenon and mechanism of each process are discussed in Section 3.3.1.1 and 3.3.1.2 , respectively. Sec. 3.3.1.3 lists two arsenic sorption rate models and experimental data. Factors and phases associated with *As* sorption are compared in Sec. 3.3.1.4.

3.3.1.1 Sorption Phenomenon

Sorption interactions generally operate among all phases present in any subsurface system and at the interface between these phases. Solutes which undergo sorption are commonly termed sorbates, the sorbing phase the sorbent, and the primary phase from which sorption occurs the solution or solvent. Two broad categories of sorption phenomena, adsorption and absorption, can be differentiated by the degree to which the sorbate molecule interacts with and is free to migrate between the sorbent phase. In adsorption, solute accumulation is generally restricted to a surface or interface between the solution and adsorbent [68]. In contrast, absorption is a process in which the solute is transferred from one phase to another and penetrates the sorbent phase by at least several nanometers. Dissolution is a common reaction among absorption processes.

Adsorption can be loosely defined to three categories by the interactions between sorbent and sorbate - physical, chemical and electrostatic adsorption according to the class of attractive force which predominates [68]. Some significant features of these different interactions and classes of adsorption are summarized in Table 6 [68]. Physical adsorption process have relatively weak binding forces than the others. The most general class of physical adsorption is the London dispersion forces type which have low adsorption heat generally of the order of 1 -2 kcal / mole [68]. Forces of greater intensity and longer

Table 6 Characteristic Interactions Associated with Categories of Adsorption

Category and Characteristic Interaction	Representation of Interaction	Interaction Range
CHEMICAL Covalent		Short Range
Hydrogen Bond		Short Range
ELECTROSTATIC Ion-Ion		$1/r$
Ion-Dipole		$1/r^2$
PHYSICAL Dipole-Dipole (Coulombic) (Keesom energy)		$1/r^3$
Dipole-Induced Dipole (Debye energy)		$1/r^6$
Instantaneous Dipole-Induced Dipole (London dispersion energy)		$1/r^6$

(Adapted from Weber et al, 1991 [68], which based on Israelachvili, 1985)

range exist between discrete entities which involve ion - ion or ion - dipole forces are called Electrostatic Adsorption [68]. Exchange phenomena, such as Ion Exchange, in which ions are attracted to a soil surface and displace another ion already present at the soil surface [15], are preceded by the electrostatic forces. The final category of sorption is chemical sorption or chemisorption. The bonds that form between solute molecules and specific surfaces are covalent bonds. Relatively large heats are involved in this type of sorption [68].

Precipitation is an additional variation of the process that occurs when a sufficiently high accumulation of solute exists at the interface to form a precipitate or some other type of molecular solute - solute association, e.g. a polymer or a micelle. It differs from adsorption in that precipitation results in formation of new and distinct three - dimensional phases, whereas adsorption takes place only at the adsorbent surface or solution - adsorbent interface [68]. Because adsorption process generally yield surface or interface concentrations of solutes greater than those in the bulk phase, it is possible for precipitation or association to occur on a surface in the absence of a solution phase reaction of the same type [68]. Although such association reactions are often classified as separate processes, they must in fact be preceded by adsorption or absorption. Under equilibrium conditions, precipitation rates are equal to dissolution rates. Thus, precipitation processes are discussed with dissolution processes and detailed in Sec. 3.3.2.

Coprecipitation is somewhat analogous to adsorption. When a sorbate or a particle entrapped in the interior of a particle of precipitate and then be sinked with the precipitate is known as Coprecipitation [12].

Above processes are briefly compared and listed in Table 7.

Table 7 Summary of Adsorption Phenomenon

Process	Representative Interaction / Reason	Dimension of Phase	Reference
Physical	London Dispersion Forces Columbic Forces	2	Weber, McGinley and Katz., 1991 [68]
Ion Exchange (Ligand Exchange)	Electrostatic Force	2	Weber, McGinley and Katz., 1991 [68]
Chemisorption	Covalent Bond	2	Weber McGinley and Katz., 1991 [68]
Precipitation	Concentration Exceed Solubility	3	Dragun, 1988 [15]
Coprecipitation			

3.3.1.2 Mechanisms

Physical adsorption (includes cation and anion adsorption), chemisorption and coprecipitation are discussed in this section. Precipitation is discussed later in Sec. 3.3.2 with dissolution.

3.3.1.2.1 Adsorption Mechanism

Physical adsorption and electrostatic adsorption are generally termed as adsorption. There are two categories of adsorption mechanisms-cation adsorption and anion adsorption. Arsenic adsorption falls into the latter [15]. Clay soil surfaces tend to possess net negative charges, however, soil surfaces are not homogeneous environment (refer to Section 3.2). Some locations on soil surfaces obtain a net positive charge which is responsible for accumulating anionic species of elements such as phosphate, arsenic, molybdate, selenite, sulfate, borate, silicic acid, fluoride, halides and nitrate [15]. Table 7 indicates the factors governing cation / anion adsorption in soil system and their contribution to arsenic adsorption, the more detailed descriptions of the mechanisms are discussed later in this section.

The clay minerals are a major constitute of clay soils. The following sections are focused on the clay soil adsorption. Although arsenic could also be adsorbed into the structure of other minerals such as carbonates, phosphates, sulfates, sulfides, and silicates, the sorption of these minerals is not be included in current version of the model due to the relatively small amounts.

1. Cation adsorption

The clay soil uptake capacity for cation is primarily governed by:

(1) *Broken bonds around the edges of the silicon - aluminum units*, which can be balanced by adsorbing cations. They occur predominantly on non cleavage surfaces and thus on vertical planes, in a position parallel to the c-axis of the layer. The number of

broken bonds and hence the adsorption capacity for cations increases as the particle size decreases and moreover, should be even further increased by lattice distortions which are in turn reflected in an appropriately diminished degree of crystallinity. This form of cation adsorption occurs chiefly for kaolinite [20].

(2) *Substitution of Si^{4+} by Al^{3+} in the tetrahedral layer and of Al^{3+} by divalent cations in the octahedral layer of the structural units of some clay minerals.* This process of substitution can leave behind unbalanced charges, which are then balanced by cations, in this instance predominantly on cleavage surfaces. Whereas substitution in a tetrahedral layer leads to an extremely strong bonding of cations and sometimes to their incorporation in fixed positions (e.g., potassium in mica), the substitution of Al^{3+} in the octahedral layers causes the balanced cations to be only loosely bonded. This results in their exchange under altered external conditions. Substitution of one of 400 *Si* atoms by *Al* in kaolinite creates 2 mEq / 100g cation exchange capacity.

The second type of cation bonding by substitution with the lattice is particularly significant for the minerals of the mica (illite) and chlorite groups [20].

(3) *Humic functional group dissociation:* Humus is colloidal in structure. The typical humus colloid is comprised of (a) a center unit containing primarily *H* and *C* , and (b) a colloidal surface comprised of carboxylic (*COOH*) and hydroxyl (*OH*) functional groups. These groups, when in the dissociated state, possess negative charges. These charges are responsible for accumulating cationic species of elements of soil surface [15].

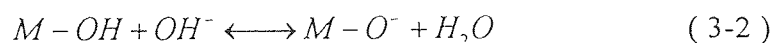
The pH value may control the adsorption possess of cations, such as heavy meals onto clay minerals. The H^+ ions compete with heavy metal cations for exchange site in the system, thereby partially releasing the latter [20].

2. Anion Adsorption

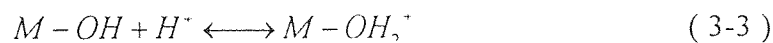
The second type of adsorption is anion adsorption, arsenic falls into this category [15, 6, 35]. The amount of anion adsorption by clay minerals is usually small compared to the

amount of cation exchange adsorption [21]. There are three different types of surfaces responsible for anion adsorption:

1. Oxide surfaces. Consider the oxide surface $M-OH$, where M signifies one of the elements such as Fe or Al , $-OH$ is hydroxyl group. $M-OH$ can develop either a positive or a negative charge. If the pH is high, then $M-OH$ will develop a negative surface charge due to H^+ dissociation from the $-OH$ group:



If the pH is low, then $M-OH$ will develop a positive surface charge by attracting H^+ :



As a result, when the clay surface poses a net positive charge, arsenic anions are adsorbed onto the clay surface, on the other hand, arsenic anions are released when the clay surface obtains negative charges. This pH dependent process explains why arsenic adsorption is affected by pH, Fe and Al concentration [15]. There is a mechanism about the change in the hematite surface with pH suggested by Singhet al.

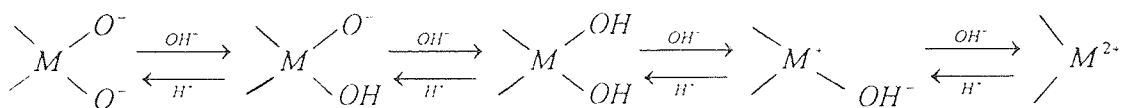


Figure 8 Change in the Surface of Hematite with pH (Singh et al., Water, Air, Soil Pollut., 42 , 373, 1988)

Adsorption of arsenate and arsenite onto hydrated ferric oxide surfaces occurs under oxidizing conditions over a wide pH range (pH 4-10). Fe - oxides have a positive surface charge up to pH 8.5 [42]. On the other hand, Fe - oxides obtained a negative surface charge and arsenic was thereby released under reducing conditions. An example of arsenate ligand exchange mechanisms is as follows:

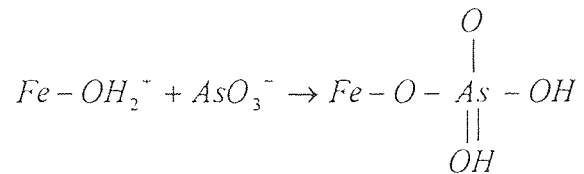
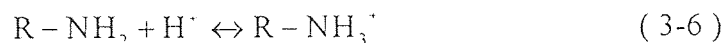
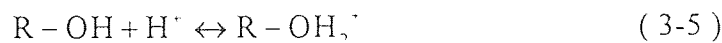


Figure 9 Arsenate Ligand Exchange Mechanism (Huang et al., 1980)

2. Edges of aluminosilicate clay minerals. If the edges of minerals contain ions that are not fully coordinated, these edges can adsorb H^+ and OH^- to form hydroxylated surfaces and behave in a manner similar to $M - OH$ [15].

Since all clay minerals have edges, they all participate to some extent in adsorbing anions. However, the 2:1 clay minerals have edges that comprise only about 1% of the total surface, therefore, these minerals do not extensively adsorb anions. But, the 1:1 clay minerals edges comprise a relative greater proportion of the total surface charge [15].

3. Organic matter. Soil organic matter possesses functional groups that adsorb H^+ and OH^- to form charged surfaces and behave in a manner similar to $M - OH$ [15].



3.3.1.2.2 Coprecipitation Mechanism

There are four types of coprecipitation: (1) Inclusion: This involves the mechanical entrapment of a portion of solution surrounding the growing particle. This type is normally significant only for large crystals. (2) Adsorption: Attachment of a particle onto the surface of precipitate. It is a major means of contaminant removal if the particles are small. (3) Occlusion: A particle is entrapped in the interior of a particle of precipitate. This type of coprecipitation occurs by adsorption of a contaminant onto the surface of a growing particle, followed by further growth of the particle to enclose the adsorbed contaminant.

(4) Solid - solution formation: A particle of precipitate becomes contaminated with a different type of particle that precipitates under similar conditions and is formed from ions whose size are nearly equal to those of the original precipitate [12].

3.3.1.2.3 Chemisorption Mechanism

Chemisorption is the formation of a covalent bond between an adsorbed element and a mineral surface [15]. For example, oxygen-containing arsenic anions penetrate the coordination shell of *Fe* atom, displace OH or OH₂ ligands from the surface and form direct covalent bonds with the structural cations (Hingston, 1981; Breeuwsma and Lyklema, 1971). Since the chemisorbed covalent bond is much stronger than the original physical or electrostatic bond, immobilization and fixation of arsenic results. This mechanism explains the partial irreversibility of arsenic adsorption by *Fe* oxides [6].

3.3.1.3 Phenomenological Model

The conceptual equation about the total concentration of any element, C_{Total} , in a soil is equal to [15]:

$$C_{Total} = C_{Fixed} + C_{Adsorbed} + C_{Water} \quad (3-7)$$

Where

C_{Fixed} = concentration of fixed element comprising part of the structure of clay and soil minerals, in mg element / kg soil.

$C_{Adsorbed}$ = concentration of element adsorbed onto the surface of soil minerals and onto organic matter exchange sites, in mg element / kg soil.

C_{Water} = concentration of element in soil water or groundwater in equilibrium with $C_{Adsorbed}$, in mg soluble element / kg soil.

C_{Fixed} represents the " immobile " fraction of C_{Total} which is precipitated or chemisorbed phases. The sum of $C_{Adsorbed}$ and C_{Water} represents the potentially mobile portion of C_{Total} .

However, since precipitation must be preceded by adsorption or absorption [68] and all the other processes mentioned above are possible [16]; Adsorption is generally defined as the accumulation of an element at the surface of a soil particle with a decrease in the concentration of the dissolved element in water [15, 16, 68] and referred to the sum of above processes. Therefore, Equation 3-7 could be rewritten as :

$$C_T = C_s + C_e \quad (3-7)$$

where

C_s = amount adsorbed by soil

C_e = amount exist in water

Since adsorption is such a complex process that involves an array of phenomena and environmental factors, phenomenological models are therefore typically used to simulate the adsorption phenomenon.

3.3.1.3.1. Adsorption Isotherm:

Models for characterizing the equilibrium distribution of a solute among the phases and interfaces of an environmental system under a fixed system temperature are termed "sorption isotherms" [68]. The equilibrium distribution system typically relates the amount sorbed per unit of sorbing phase or interfaces, and the amount retained in the solvent phase. Based on the assumption of Equation 3-8, the simplest approach is the linear model:

$$C_s = (K_d) C_e \quad (3-9)$$

where

K_d = adsorption (or distribution) coefficient

The observed K_d values of As (III) and As (V) are shown below [15]:

Table 8 Ranges for K_d for As in Soils and Clays

Arsenic Species	Observed Range (ml / g)	Mean ^a	Standard Deviation ^b
As (III)	1.0 - 8.3	1.2	0.6
As (V)	1.9 -18.0	1.9	0.5

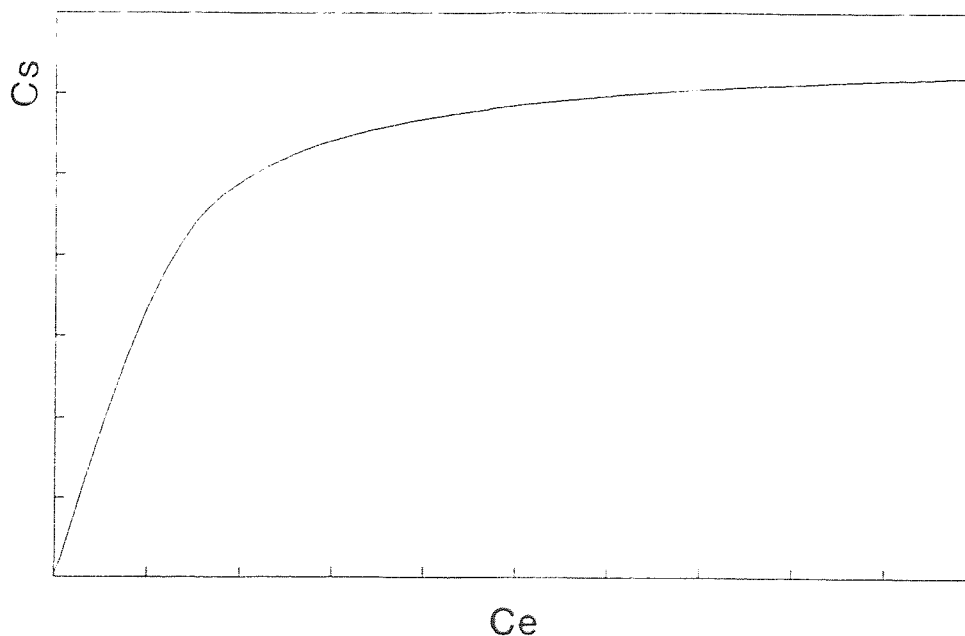
(Adapted from Dragun, J. The Soil Chemistry of Hazardous Materials [15]).

^a Mean of the logarithms of the observed values.

^b Standard deviation of the logarithms of the observed values.

However, arsenic does not fit linear equilibrium models [59], and many researchers [59, 16] have used non - linear equilibrium models to describe arsenic adsorption phenomenon.

There are many non - linear equilibrium isotherm have been made, but the L-Curve is used most frequently [15]: (Fig. 10)

**Figure 10** Non Linear Adorption Isotherm - L-Curve

The L-Curve is described mathematically by either the Freundlich or Langmuir equation [S2]. The Freundlich equation is usually expressed as [15,68]:

$$C_s = KC_e^n \quad (3-10)$$

where

C_s = amount adsorbed by soil

C_e = amount exist in water

K = adsorption capacity (constant)

n = adsorption intensity (constant)

The above equation can be expressed in logarithmic form:

$$\log C_s = n \log C_e + \log K \quad (3.11)$$

Constant n and k are empirically derived coefficients [68].

3.3.1.3.2. Adsorption Rate:

Chemical reaction rates depend on the nature of specific interactions that occur between the solute and sorbent in the sorption process. Physical sorption processes are generally rapid, with local (site) equilibrium being achieved within milliseconds or, at most seconds. The larger activation energies associated with other types of sorption (e.g. chemisorption) may, however, lead to slow rates. The fundamental basis for molecular characterization of reaction kinetics is the law of mass action, which states that the rate of an elementary homogeneous chemical reaction is directly proportional to the product of the masses (more rigorously, activities) of the reacting species [68]. While sorption reactions are clearly not homogeneous and rarely elementary, the sorption rates are calculated from experimental studies. There are two arsenic adsorption rate models suggested by Elkhatib et. al (1984) and McGeehan et. al (1992).

1. Elkhatab, Bennett and Wright (1984) use modified Freundlich equation to estimate arsenite adsorption rates:

$$X = K_a C_o t^{1/m} \quad (3-12)$$

where

X = sorbed *As* [mg*As*(III)kg⁻¹]

C_o = initial *As* (III) concentration [mg*As*(III)kg⁻¹]

t = reaction time (h)

K_a = sorption rate coefficient (h^{-1})

$1/m$ = constant

They found the initial reaction of *As* (III) with the soils was very rapid, more than 50% of the *As* (III) originally present was sorbed in the first 0.5 hour [17]. Their experimental data were fitted to their linear reaction rate. But they only have a short 2-h reaction period.

2. McGeehan, Naylor and Shafii (1992) used an iterative statistical program, PLATFOR, for performing linear - plateau regression analysis [44]. The fitted equation for describing arsenic adsorption rates can be evaluated by a computer program. Successive iterations set A equal to successively smaller observed values of X . At each iteration, the least square estimates of Eq. 3-13 along with the residual sum of squares and the coefficient of determination (γ^2) are calculated.

$$Y = \beta_0 + \beta_1 [\min (X, A)] \quad (3-13)$$

Where

β_0 = Intercept

β_1 = The slope of the line up to the point $X = A$

A = The largest observed value of X

The plateau model corresponding to the smallest residual mean is selected and the optimal plateau is indicated as Eq. 3-14.

$$Y = \beta_0 + \beta_1 [\min (X,A)] + \beta_2 [\max (X,A)-A] \quad (3-14)$$

Where

β_2 = The slope beyond the point of optimal plateau

In their observations, they found that adsorption of arsenite and arsenate were rapid initially and decreased with increasing equilibration time. The linear-plateau regression model provided a good fit for their *As* - adsorption data.

The above two models provide good approaches to deal with arsenic sorption rates. In addition, the batch scale arsenic adsorption experiments offer a general survey of sorption rates varied by species and sorbent. Generally arsenic sorption rates range from 2 hours to several days [44]. Table 9 lists results of previous *As* sorption studies.

3.3.1.4 Factors and Phases Associated with Arsenic Sorption Process

The adsorption of arsenic on clay depends on soil pH, texture, *Fe Al* organic matter, and the elapsed time after exposure [71]. As the soil's clay content increases, the arsenic amount adsorbed increases [71]. Table 10 lists the phases that may coprecipitate with or adsorb arsenic.

Extraction schemes show that most arsenic adsorbed in clay is bound to hydrous *Fe* oxide [53, 1, 72, 41]. Table 11 indicates factors associated with arsenic sorption processes. The more detailed discussions are recounted below.

1. pH: pH influences soil anion exchange capacities (AEC) [22, 73] which is the total amount of anions adsorbed by positive charges on a unit mass of soil [15] and arsenic solubility (detailed in Sec. 3.3.2 Dissolution process). There is an example of pH influence

Table 9 Literature Review on Arsenic Adsorption Rate

Previous Research	Sorbate	Sorbent	Experimental Result
Anderson, et al, 1975 [4]	<i>As</i> (V)	Amorphous Aluminum Hydroxide	Over 90% adsorbed before sample be collected Reaction slowed greatly after 1 hour Reached equilibrium after 48 hours
Pierce and Moore ,1980 [51]	<i>As</i> (III)	Amorphous <i>Fe</i> -oxide	90% complete after 15 minutes stirring 99% after 2 hours
Livesey and Huang, 1981 [59]	<i>As</i> (V)	Soil	Rapid initially Leveled off after a 24 - hour reaction period 24 ~ 96 hours increment is very small
Elkhatib, et al, 1984 [17]	<i>As</i> (III)	Soil	More than 50% sorbed in half hour

Table 10 Phases Associated with Arsenic Sorption Process

Phase	Subphase	Previous Research
-Oxide	Hydrous	Leckie et al., 1980 ¹ Pierce and Moore 1980 [51]
	Iron Hydroxide	Leckie et al., 1980 ¹ Pierce and Moore 1980 [51]
	Iron Oxide (Amorphous)	Jacobs, Syers and Keeney, 1970 [28] Huang and Liaw, 1979 ² Wauchope, 1975 [67]
	Hydroxy - Aluminum	Huang, 1975 [26]
	Aluminum Hydroxide	Anderson, Ferguson and Gavis, 1976 [5]
	Aluminum Oxide (Amorphous)	Jacobs, Syers and Keeney, 1970 [28]
	Manganese Hydroxide	Oscarson et al., 1981, 1983 [50] Reuther, 1989 [53]
-Sulfide	Iron Sulfide	Moore, Ficklin and Johns, 1986 [49]
Clay Mineral		Frost and Griffin, 1977 [22]
Organic Matter		Wagemann, 1978 [66]

¹: Refer to Welch [69]²: Refer to Wauchope [67]

Table 11 Factors associated with *As* Sorption & Dissolution Process

Factor	Influence	Reason	Reference
Temperature	Arsenic solubility	Solubility is a function of temperature. As endothermic reaction, solubility increases with temperature increase while exothermic reaction, solubility decreases with temperature increases.	Dragun, 1988, [15]
pH-Eh	Arsenic species	Arsenic ionization and redox reaction are mainly controlled by pH.	Ferguson & Gavis, 1971, [19]
	Arsenic mobility	<i>As</i> (III) species has greater mobility than <i>As</i> (V) species. The speciation of <i>As</i> is affected by pH-Eh condition.	Xu, et al., 1988, [74]
	Soil <i>As</i> adsorption ability	Soil poses positive charge at pH below PZC ¹ , negative at pH above PZC. The positive is contributed <i>As</i> anion adsorption.	Frost, et al., 1977, [22] Xu, et al., 1988, [74]
<i>Fe</i>	Soil <i>As</i> adsorption ability	<i>As</i> sorption increasing as free iron oxide content increased.	Jacob, et al., 1970, [28] Elkhatib et al 1984 [16]
	Arsenic solubility	<i>Fe</i> oxide could coprecipitate arsenic and therefore reduce the arsenic concentration in soil water.	Ferguson & Gavis, 1971, [19] Forstner & Wittmann, 1977, [20]
	Arsenic Speciation*	Oxidize <i>As</i> (III) to <i>As</i> (V).	Aritola, et al., 1990, [6] Belzile, et al., 1989, [8]

Table 11 Factors associated with *As* Sorption & Dissolution Process (Continue)

Factor	Influence	Reason	Reference
<i>Mn</i>	Arsenic Solubility Arsenic Speciation	(Same as <i>Fe</i> does) Oxidize <i>As</i> (III) to <i>As</i> (V).	Forstner & Wittmann, 1977, [20] Oscarson, et al., 1981, [50] Aritola, et al., 1990, [6]
<i>Al</i>	Arsenic Adsorption	<i>As</i> could be adsorbed onto aluminum hydroxide surface.	Anderson, et al., 1976, [5] Huang, 1975, [26]
<i>P</i>	Arsenic Adsorption	Compete with <i>As</i> for adsorption site or isomorphous replacement.	Wagemann, 1977, [66]

* : Uncertain reaction

soil AEC: Iron oxide has a positive surface charge in most geologic environments and preferentially adsorbs anions like arsenic [19], however, when the pH value is higher, for example, goethite (Alpha-FeOOH) possesses a net negative charge above a pH of approximately 8.5 [15], which results in an electrostatic repulsion between the sorbent and the arsenic anion [69]. The pH changing point is referred to as the isoelectric point or the zero point of charge (ZPC) [15]. Different soils pose different ZPC.

Frost and Griffin [22] found that *As* (III) has an increase in adsorption as pH increases in the range from 3 to 9, while *As* (V) adsorbed from solution goes through a maximum at about pH 5. Fig. 11 and Fig. 12 show the arsenic adsorption ability as a function of pH.

Xu, Allard and Grimvall [74] pointed out that the adsorption of *As* (V) on the soil surface was primarily related to the surface charge of the soil, which is positive at pH below ZPC and negative at pH above ZPC, and the charge of the predominant *As* species in the aqueous phase. At pH values above the ZPC, there was a sharp drop in adsorption ability of clay materials. At pH values below the ZPC but above 2 to 3, adsorption was higher.

The experimental results of Everst and Popidl, and Yoshida et al. Showed that *As* (III) adsorption will increase with pH to a maximum at 9.2 [32].

Korte and Fernando [32] have an explanation for the apparent discrepancy: The pH of the ZPC can vary widely from as low as 2.0 to as much as 12.4, for example, Fe_3O_4 reportedly has ZPC of 6.5, while amorphous iron hydroxide (Fe(OH)_3) has a ZPC of 8.4. Aluminum hydroxide (Al(OH)_3) has a ZPC of 5 and aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$) a ZPC of 9.1. That is why different minerals pose different maximum adsorption capacities.

In soils and groundwaters, a low pH in combination with reducing conditions may favor the formation of *As* (III) species, which are more mobile than the corresponding *As* (V) species [74].

2. *Fe* and *Mn*: In soils and in particulate materials of the aquatic environment, *Fe* and *Mn* hydroxides or oxides commonly occur as coating on minerals and finely dispersed

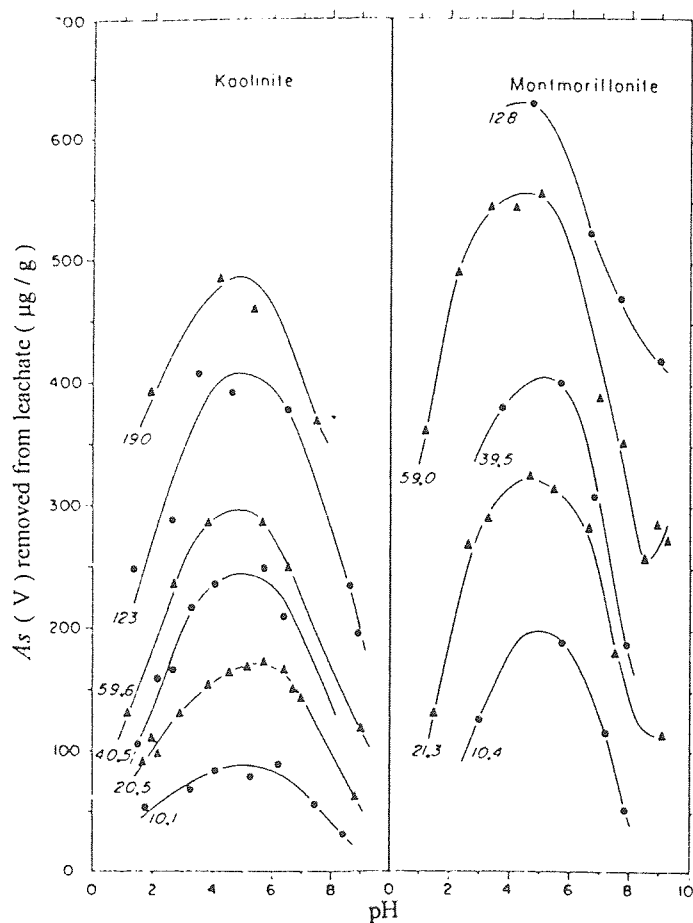
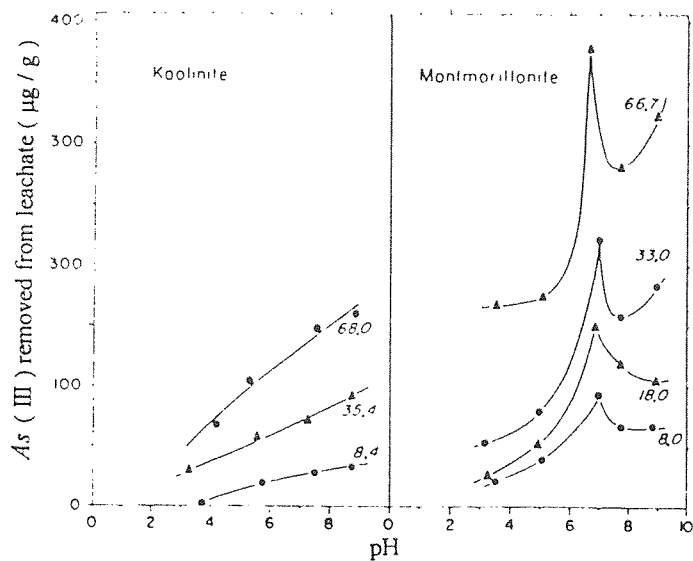


Figure 11 (upper) and Figure 12 (lower) The Amount of As (III) and As (V) Removed from DuPage Leachate Solutions by Kaolinite and Montmorillonite at 25°C Plotted as a Function of pH. Numbers Give the Initial Solution Concentration of As (III) As (V) in ppm. Each Data Point was Obtained by Using 4 g of Clay in a Total Solution Volume of 52.5 ml. (Adapted form Frost and Griffin [22])

particles. They can be present in X-ray amorphous, micro-crystalline and in more "aged" crystalline forms. The active forms exhibit high specific surface areas of up to $300 \text{ m}^2/\text{g}$ for MnO_2 and 230 to $320 \text{ m}^2/\text{g}$ for FeOOH [20].

With respect to the aquatic chemistry of iron oxides and hydroxides, $\text{Fe}(\text{OH})_3$, Fe_3O_4 (magnetite), amorphous FeOOH and $\alpha\text{-FeOOH}$ (goethite) are primarily to be considered. What are usually referred to as "hydrous ferric oxides" or "ferric hydroxides" are more likely to be poorly crystalline FeOOH . The mineralogy of Mn oxides is extremely varied and often taxonomically confusing. Because Mn can exist in soil as Mn^{2+} , Mn^{3+} , and Mn^{4+} , MnOOH species usually consist of mixtures of $\text{Mn}(\text{II})$ and $\text{Mn}(\text{IV})$ or $\text{Mn}(\text{III})$ [20].

Shnyukov (1963) observed that iron ores are always enriched with arsenic, owing to the high adsorptive capacity of the hydrous iron oxides, while arsenic is nearly absent from manganese ores. The fact that iron oxide has a positive surface charge in most geologic environments and preferentially adsorbs anions while manganese oxide is negatively charged and sorbs cations, has been cited as an explanation of such distributions of arsenic [19]. In addition, ferric arsenate is very insoluble while manganous arsenate and presumably manganic arsenate are much more soluble [19].

The ability of different soils to sorb As is related to the free iron oxide content. Arsenic sorption increases as the free iron oxide content increases [28]. Table 12 shows the amount of arsenic adsorbed at various free iron oxide contents.

The pH of the soil environment controls Fe adsorption, because in many cases the anions adsorbed by the Fe -oxides result from the dissociation of weak acids. The pH of the system controls the concentration of the ionic species being adsorbed and the surface charge of the oxide [16]. Under reducing conditions, oxygen is depleted and ferric iron (III) is reduced to soluble ferrous iron (II) and arsenic is released, which is a desorption process. The concentrations of both arsenic and iron increase in the interstitial water [2].

Table 12 Properties of Soils Used for Sorption and Fractionation Studies

Soil	Soil property							
	pH	Sand	Silt	Clay	Organic C	Free iron oxides*	Exchange - able Al	Total As
				%				meq/100g
Plainfield s	5.5	89.2	3.6	7.2	0.7	0.34	0.13	0.8
Waupun sicl	6.2	3.3	67.6	29.1	2.6	1.18	0.13	3.7
Superior cl	7.0	38.1	25.7	36.2	0.5	2.34	0.11	3.4

* Extracted by citrate-dithionite-bicarbonate.
(Adapted from Jacobs et al., 1970, [28])

The arsenic adsorption by iron is also influenced by exchangeable *K* and *Mg*. Iron oxides reportedly show a high selectivity for Mg^{2+} , and specific adsorption of this ion may subsequently interfere with arsenic adsorption and reduce its sorption rate [16]. Another competitive desorption of arsenic is phosphate which competes for available sorption sites.

Adsorption of arsenate and arsenite onto hydrated ferric oxide surfaces occurs under oxidizing conditions over a wide pH range (pH 4-10) [42]. Arsenate is considered to be much more strongly adsorbed than arsenite onto iron and aluminum hydroxide [30, 19, 56].

3. *Al*: Aluminum is another clay mineral associated with arsenic adsorption; however, bauxite and silicates are usually only moderately enriched in arsenic [19].

Hydroxyl- Al ions can be adsorbed on the external and interlamellar surfaces of micaceous mineral colloids (vermiculite, micas, and k-depleted micas) which are common in soils [26]. The dissociation of metal-oxide is responsible for anion adsorption.

Adsorption of arsenic on aluminum hydroxide can be interpreted in terms of electrostatic and chemical processes. When the pH is below ZPC, the surface of the arsenate-aluminum hydroxide complex is positive and adsorption of the anion is facilitated by coulombic attraction. Adsorption is limited only by the arsenic concentration or by the available sorption sites on the surface of the hydroxide. When the pH is greater than the ZPC, the surface of the complex is negative and specific anion adsorption must compete with coulombic repulsion [5].

The rate of arsenate adsorption on amorphous aluminum hydroxide is very fast in Anderson and co-workers' experiments [5]. Over 90% of the adsorption reaction takes place before a sample can be collected. The reaction was considered to have reached equilibrium after 48 hours. Adsorption is a linear function of pH between pH 8.5 ~ 4; When pH = 4 maximum adsorption occurs and pH = 8 no adsorption occurs [5].

Keaton and Kardos [30] found that alumina did not affect arsenic redox reactions.

3.3.2 Dissolution

When equilibrium is established, the precipitation rate equals to the dissolution rate. The elements A and B dissolved from mineral AB in water could be expressed as:



Where precipitation refers to the formation of an insoluble solid comprised of elements which were previously dissolved in water [15]. After equilibrium is established, the aqueous concentrations of A and B do not change but remain constant.

Solubility is a measurement of dissolution ability, which is a very important factor in estimating arsenic migration in the soil system. The soluble arsenic in soil water is associated to groundwater transport and plant uptake.

The arsenic solubility in soil water system is a function of temperature [15, 37], redox potential and pH [30, 29, 43, 72, 66], iron [53, 43, 30, 34, 72, 29, 56], manganese [43, 53], *Al* [73, 30], and *P* [30, 66] concentration. Also, it varies according to different arsenic species. The relationships between above factors and arsenic are discussed below:

1. Temperature Effect: The influence of temperature on solubility depends mainly on the total heat effects of the solution. If the heat of solution is endothermic, the solubility increases with an increase in temperature; if the heat of solution is exothermic, the solubility decreases with an increase in temperature, and if there is little thermal change, the solubility is influenced very little by change of temperature [55]. According to Linke's collection, arsenic trioxide As_2O_3 , arsenic pentoxide As_2O_5 , arsenic trisulfide As_2S_3 and arsenic pentasulfide As_2S_5 are endothermic reactions which solubility increase with temperature increase while arsine AsH_3 is exothermic reaction.

2. Eh-pH: Redox potential has long been considered an controlling factor in arsenic dissolution. The redox status of a soil refers to the presence or absence of electrons in soil. Redox reactions respond to electron pressure just as acid-base reactions respond to proton pressure [15]:



The redox relationship is commonly expressed as Eh, the redox potential [15]

$$Eh = pe (2.3 RT/F) \quad (3-18)$$

where

Eh = Redox potential, V

R = Gas constant, 0.001987 kcal/°K

T = Temperature, °K

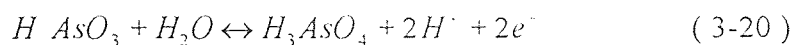
F = Faraday constant, 23.06 kcal/Vg equivalent

while

$$pe = 16.9 (Eh) \quad (3-19)$$

How Eh-pH condition affects the speciation and solubility of arsenic is not yet completely clear. Ferguson and Gavis [19] had made a widely adapted Eh-pH diagram (Fig. 13) for arsenic in a system including oxygen, H_2O and sulfur showing the predominant soluble species and the solids with solubilities low enough to occur in this system [19]. The arsenic oxides, As_2O_5 and As_2O_3 , are too soluble to appear in the diagram [29]. The diagram is suitable for predicting the predominant species of arsenic acid species (H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}), arsenious acid species ($HAsO_3$, $H_2AsO_3^-$ and $HAsO_3^{2-}$), realgar (As_4S_4), or piment (As_2S_3) and arsine (AsH_3). In oxic condition, arsenic oxides are predominant species while in anoxic environments, arsenic sulfides are the major soluble species.

The distribution of arsenic species ionized in waters can be predicted by the redox half-reaction and ionization fraction pKa. For example, As (III) dominates in reducing environments (low pH-Eh) while As (V) is predominant species in oxic conditions, the relationship between arsenic species and pH-Eh conditions can be expressed as thermodynamic equations based on redox-half reactions and derived from Gibbs's free energy. For example, the redox half-reaction of H_3AsO_3 and H_3AsO_4



result in a thermodynamic equation expressed like

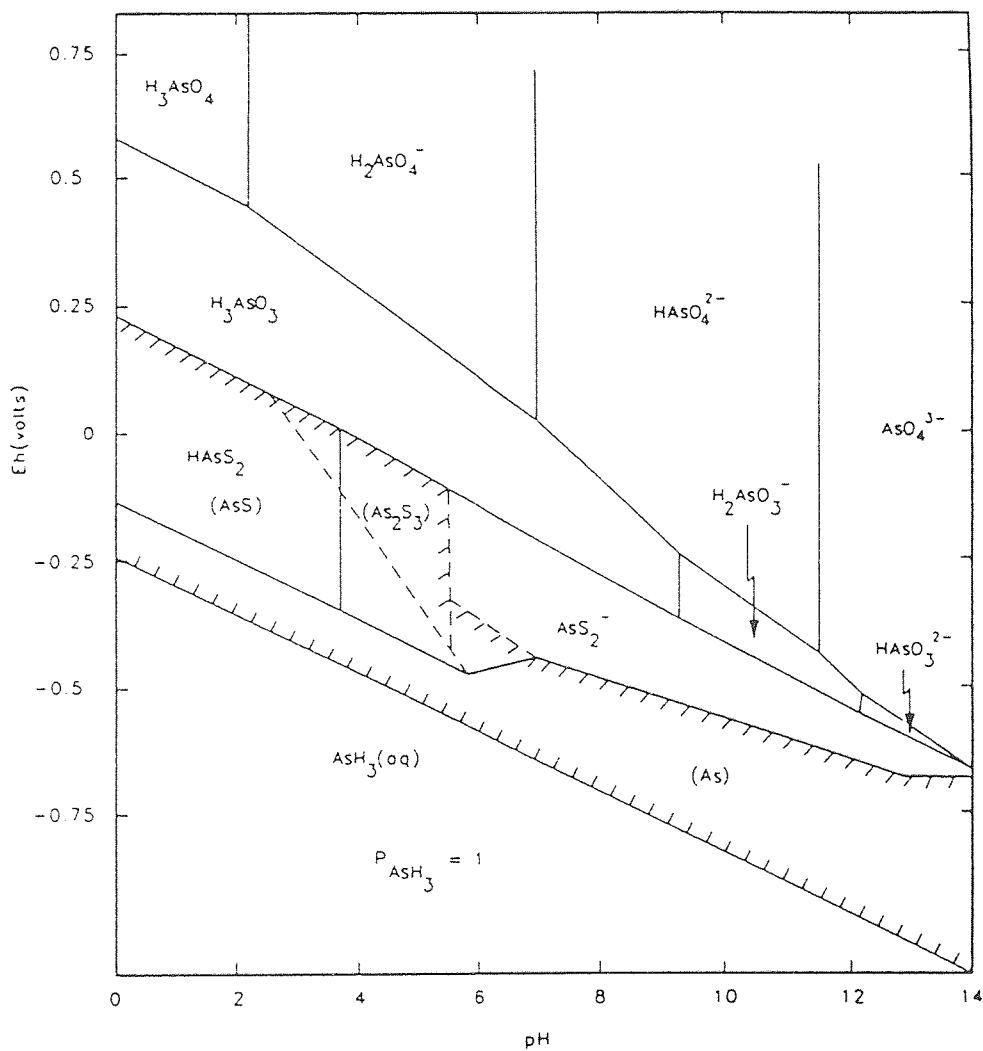


Figure 13 The Eh-pH Diagram for *As* at 25°C and 1 atm with Total Arsenic $2 \cdot 10^{-5}$ mol/l and Total Sulfur 10^{-3} mol/l.
(Adapted from Ferguson, J. F. and Gavis, J., Water Res., 6, 1259, 1972.)

$$\text{pH} + (2/3) \text{pe} = 7.35 \quad (3-21)$$

when $\text{pH} + (2/3) \text{pe} > 7.35$, the reaction goes to the right and the predominant species is H_3AsO_4 , otherwise, reaction goes to the left and H_3AsO_3 is predominant. The derivation of the thermodynamic equations is described in Appendix C. An experimental result about pH-Eh influence arsenic speciation and solubility was suggested by Masscheleyn, Delaune and Patrick [42].

- a. At higher soil redox levels (500 - 200 mv), arsenic solubility is low and the major part (65% -98%) of the arsenic in solution is present as As (V).
- b. Under moderately reduced soil conditions (0 - 100 mv), arsenic solubility is controlled by the dissolution of iron oxyhydroxides.
- c. Upon low reduction status (- 200 mv), the soluble arsenic content increased 13-fold as compared to 500 mv.

3. *Fe* and *Mn*: In addition to being adsorbed onto clay surfaces by *Fe*-oxide, arsenic can also be coprecipitated with *Fe* and *Mn* into metal ion precipitation [19] [2].

In groundwater, iron and manganese ions generally occur in reduced oxidation states in the forms of manganese (II) and iron (II). However, in the presence of dissolved oxygen in water the hydrous oxides of iron (III) and manganese (III / IV) are formed by oxidation of *Fe* (II) and *Mn* (II) [20, 2]. In anoxic conditions, iron sulfide replaced iron hydrous oxide as the predominant iron species, which also could precipitate arsenic and then form arsenopyrite (FeAsS) [56]. Fig. 14 shown the effect of iron on the solubility of *As* (III) and *As* (V).

It is well agreed that *Mn* (IV) is capable of oxidizing *As* (III) to *As* (V) [50, 8]. However, whether arsenite could be oxidize to arsenate by iron is still debatable. Oscarson et al [50], reported that only *Mn*-oxide can readily oxidize arsenite to arsenate, but Belzile et al [8] suggested iron oxyhydroxides also does so within a few days. Artiola et al [6]

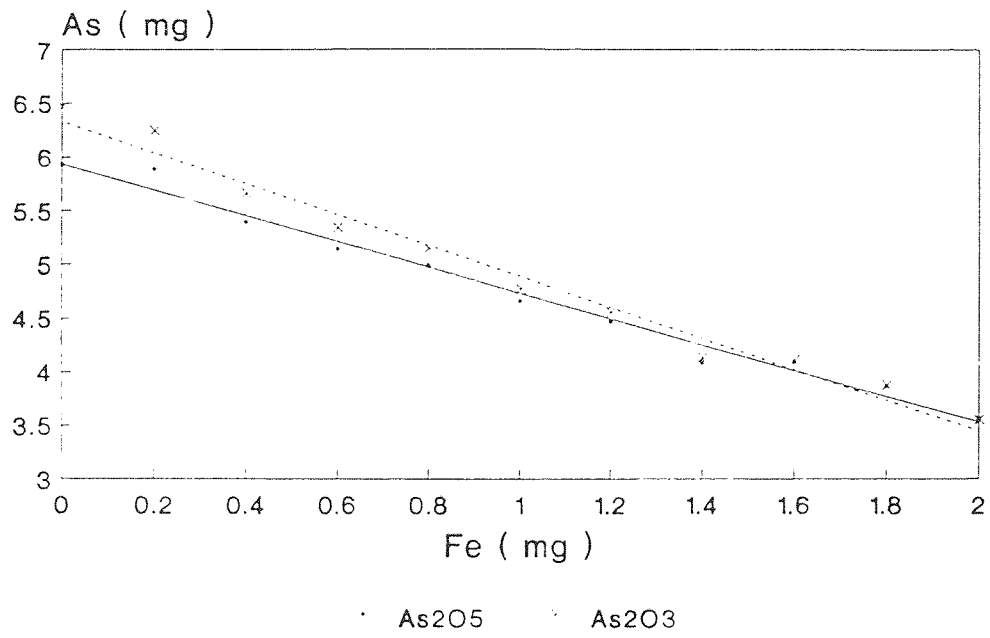


Figure14 The Effect of *Fe* Amount on the Solubility of As_2O_3 and As_2O_5

cited from EPA-540/2-84-003a and classified that ferrous sulfate oxidize *As* (III) and form stable, practically insoluble ferric arsenate.

3.3.3 Evaporation and Volatilization

Evaporation is the transfer of water from the liquid to the vapor state. Transpiration is the process by which plants remove moisture from soil and release it to the air as vapor. Nearly two-thirds of the precipitation that reaches the land surfaces of the earth is returned to the atmosphere by evapotranspiration [38]. The rate of evaporation from a water surface is proportional to the difference between the vapor pressure at the surface and the vapor pressure in the overlying air (Dalton's law). But, in soil systems, the evaporation loss from soil cannot exceed the water available in the soil [38]. Evaporation in soil systems results in the loss of water and then reduces the amount of arsenic dissolved in soil water thus forming condensed arsenic.

The evaporation rate from water surfaces can be expressed by empirical equations based on turbulence theory [38], such as:

$$E = 0.00241 (P_{v_s} - P_{v_8}) V_8 \quad (3-22)$$

where

E = Evaporation rate (inches per day)

P_{v_s} = Vapor pressure at the water surface (inches of mercury)

P_{v_8} = Vapor pressure 8m above water surface

V_8 = Wind Velocity 8m above water surface (miles per day)

Evaporation rate can also be estimated by energy - balance methods [38]:

$$E = \frac{H_i - H_o - \Delta H}{\rho [\lambda (1 + R)]} \quad (3-23)$$

while

$$R = \frac{0.61 P_{atm} (T_s - T_a)}{1000 (P_{V_s} - P_{V_a})} \quad (3-24)$$

where

H_i = Total heat input to the lake

H_o = The heat leaving the lake (reflected, back radiation and heat content of the overflowing water)

ΔH = The change in heat content of the reservoir water

ρ = Density of the evaporated water

λ = The latent heat of evaporation

R = Ratio of the heat used for evaporation

T_s = Surface temperature (°C)

T_a = Air temperature (°C)

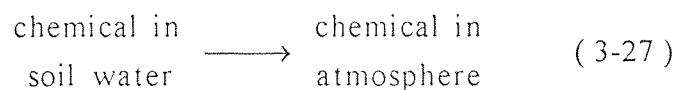
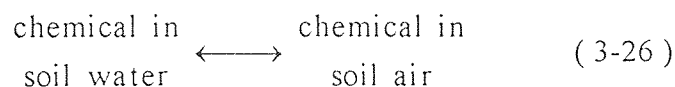
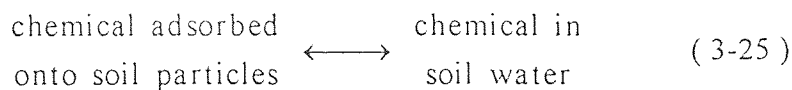
P_{V_s} = Surface pressure (millibars)

P_{V_a} = Air pressure (millibars)

The oldest method of estimating lake evaporation is by use of evaporimeters or evaporation pans [38]. However, the above equations are evaporation estimates of evaporation from water surfaces not soil. Soil consists of heterogeneous materials, and the evaporation from soil is associated with soil structure and available water content, which are much more complex than evaporation from water surfaces.

Volatilization is the process whereby liquids and solids vaporize and escape to the atmosphere. Organic compounds that readily volatilize are known as VOCs (volatile organic compounds). The physics of this phenomenon is very similar to gas adsorption, except the net flux is out of the water surface [38].

The rate at which an organic chemical will move through soil air and volatilize into the atmosphere is controlled by the following equilibria [15]:



The rate at which a chemical volatilizes from soil is affected by many factors, such as soil properties, chemical properties, and environmental conditions [61]. The factors that influence chemical volatilization can be classified into three categories: (1) movement away from the evaporating surface into the atmosphere; (2) changes in the vapor density of the chemical, and (3) changes in the rate of movement to the evaporating surface [61].

There are many methods have been established to estimate organic chemical evaporation, each is applied to a specific environmental condition [61].

Natural volatilization of arsenic from the land surface yields vapor pressures of about 1.3×10^{-11} torr for As_2O_3 (1.71×10^{-14} atm). Biological methylation has been shown to be another volatilization process for *As* [7].

3.4 Biological Conversion

Organisms affect the distribution of arsenic by accumulating, transporting and transforming it [19]. Plants and microorganism uptake arsenic from soils and accumulate it in their bodies, then, translocate arsenic or transform it. The possible reactions associated with arsenic transformation by microbes are discussed in Sec.3.4.1. Plant uptake

conversion of arsenic is described in Sec. 3.4.2. Table 13 briefly listed these biological conversions.

3.4.1 Microbial Uptake and Conversion

There are several microbe mediated reactions that have been considered by biogeochemists: redox transformation among arsenite, arsenate and arsine [56, 13, 21], biosynthesis of complex organoarsenic compounds and subsequent degradation [56, 13]. Among the various microorganisms, bacteria, fungi, and planktonic algae are the species that have been found to possess the ability to transform or convert arsenic [13, 4].

3.4.1.1 Redox Reactions

The possible redox reactions among arsenic species are:

1. Oxidation of arsenite to arsenate
 - a. Turner (1943) isolated 15 strains (5 species) of arsenite-oxidizing bacteria which were provisionally characterized as three *Pseudomonas*, one *Xanthomonas*, and one *Achromobacter* [13].
 - b. Phillips (1976) and Osborne (1976) isolated 34 different strains of arsenite-oxidizing *Pseudomonas* from sewage and classified into two main groups: *Pseudomonas fluorescens-arsenoxydans* and *Pseudomonas acidovorans-fluorescens-arsenoxydans* [13].
 - c. Freeman et al., (1986) found the mixed microbial cultures of Lake Ohakuri (New Zealand) are able to oxidize arsenite to arsenate under aerobic conditions but unable to do that in anaerobic conditions [21].
2. Reduction of arsenate to arsenite

Table 13 Biological Conversion

Type	No.	Reaction	Effect	Remark
Microbial Uptake & Conversion	1	Microbial Redox Reaction	Transformation / Translocation	Detailed in Sec. 3.4.1
	2	Microbial Methylation	Transformation / Translocation	Detailed in Sec. 3.4.1
Vegetation Uptake	3	Vegetation Uptake	Translocation / Transformation	Detailed in Sec. 3.4.2

- a. *Pseudomonas fluorescens*, a common aquatic bacterium, carries out this reduction under aerobic conditions, activated sewage sludge does so under anaerobic conditions (Myers, et al., 1973) [13].
- b. Crecelius (1977) found wine yeast also reduces arsenate [13]
- c. Freeman et al., (1986) investigated Lake Ohakuri, (New Zealand) and found that mixed microbial cultures reduce arsenate to arsenite under both aerobic and anaerobic conditions. Four species of sediment fungi were isolated and were found capable of reducing *As* (V) to *As* (III) [21].
- d. Johnson (1972) used as aerated mixed culture of bacteria from water and found that the phosphate concentration steadily decreased during the experiment, but the total arsenic concentration remained constant, indicating no accumulation by the bacteria.

3. Reduction of arsenate to arsine

Cheng and Focht (1979) found arsine could be produced by the addition of sodium arsenate to glucose enriched soils (3 diverse samples). Two bacteria, *Pseudomonas* and *Alcaligenes*, were isolated from the soil and shown to be arsine producers under anaerobic conditions (*He* atmosphere; supplementary nitrate or nitrite is essential).

Only traces of arsine are produced from unriched cultures [13].

3.4.1.2 Methylation / Demethylation

Certain fungi, yeasts and bacteria are known to methylate arsenic to gaseous derivatives of arsine [19] and methylated arsine. There is an instance of methylation of arsine gas. Cheng and Focht (1979) found that some soils and the isolated soil bacteria, *Pseudomonas* and *Alcaligenes*, release arsine from arsenite under anaerobic conditions [13]. However, this reaction forms arsine which is more toxic than arsenite and arsenate and since it is a gas, it is more likely to emit to the atmosphere.

The most common methylarsenic species are: monomethylarsonate (MMA), monomethylarsonic acid (MMAA), dimethylarsenate (DMA), dimethylarsenic acid (DMAA), trimethylarsine (TMA) and trimethylarsine oxide (TMAO). These are also known as organoarsenicals.

Although many microorganisms isolated from mixed cultures have been proved capable to methylate arsenic, it is still debatable about whether microbes methylate arsenic in the natural soil system. The arguments and debate are listed below:

1. Methylation occurred in nature soil environment:

- a. Ferguson and Gavis (1972): Methylmetabolism occurred only under aerobic conditions [19].
- b. Wood (1974): Arsenic compounds are reduced and methylated by anaerobes to give dimethylarsine and trimethylarsine as volatile products of extreme toxicity. Fortunately, these arsenic compounds are readily oxidized to give products less toxic, such as cacodylic acid. However, cacodylic acid has been shown to be an intermediate in the synthesis of dimethylarsine from arsenic salts [70].
- c. Ebdon et al., (1987) found MMAA, but no DMAA in soil pore waters [13].

2. Methylation did not occur in natural environment

- a. Andreae (1979) investigated the arsenic concentration profiles with depth in the pore waters of three sediment cores collected in the deep northeast Pacific and the continental borderland off southern California and found no methylarsenicals in both the oxic and anoxic sediments [13].
- b. Aggett and O'Brien [3]: Neither methylarsenic acid nor dimethylarsenic acid has been found in lake interstitial waters. (Lake Ohakuri, New Zealand).

3. Other explanations and debates

- a. Cullen and Reimer [13] classified previous researches and made conclusion as: methylarsenicals will only be found in interstitial water when the total arsenic concentrations are elevated.
- b. Aggett and O'Brien (1985) [3] analyzed the experimental results of Ferguson and Gavis [19], Wood [70] and their own indicating that methylation may occur only under high organic content condition.
- c. methylarsenicals come from other sources than microbial methylation: man-made methylarsenicals contamination [3], or decomposition of organic matter [13]
- d. Even the methylation did occur, the methylarsenic concentrations are controlled by a balance between methylation and demethylation (Craig, 1985) [13].

3.4.2 Vegetation Uptake

The processes of plant uptake, translocation, accumulation, and biodegradation of toxic chemicals are important in assessing the environmental risks involved in the use of the chemicals [36]. The feasibility of plant uptake of arsenic from soils is related to the arsenic mobility. The forms in which mobilized trace elements are held in soils for uptake by plants include: (1) in solution, in ionic or combined form, in which case they can be removed from the soil by water extraction; (2) as readily exchangeable ions in inorganic or organic exchangeable complexes, extractable by neutral salts such as ammonium acetate; (3) as more firmly bound ions in the exchange complexes, extractable by dilute acetic acid or a chelating agent such as EDTA; (4) in insoluble organic or organo-mineral complexes, extractable by EDTA, (5) incorporated in precipitated oxides or other insoluble salts, extractable by vigorous extractants such as acid ammonium oxalate; (6) in secondary minerals in a fixed form [47]. The proportion of a trace element present in any one form

depends on the nature and amount of the clay minerals and the organic matter and on the pH-Eh of the soils, as well as on the element properties [47].

The plant root draws its supply of nutrients from the soil zone in its immediate neighborhood. Mitchell [47] demonstrated a plant uptake model that illustrates the steps involved between the weathering of minerals or decomposition of organic residues and uptake by plant (shown in Fig. 15).

Under low arsenic levels (40 - 50 ppm total *As* or 5 ppm *As* by extraction), suggested by Woolson et al [73], a positive plant growth response is predicted. Conversely, growth reduction was significant under high arsenic levels. Since plant uptake ability varies from species to species, only global estimation of plant uptake of arsenic is possible. Biogenic interactions between the dissolved and particulate phases were calculated from a primary productivity uptake of 2×10^{-7} Kt C y^{-1} , with 90% recycled in the mixed layer and 7% dissolving in deep waters (Menzel, 1974). The equivalent arsenic fluxes were calculated from the productivity rates with an *As* concentration of 10 ppm in marine plankton (Onishi, 1969; Sanders and Windom, 1980), to yield a biogenic uptake of 500 Kt *As* y^{-1} [7].

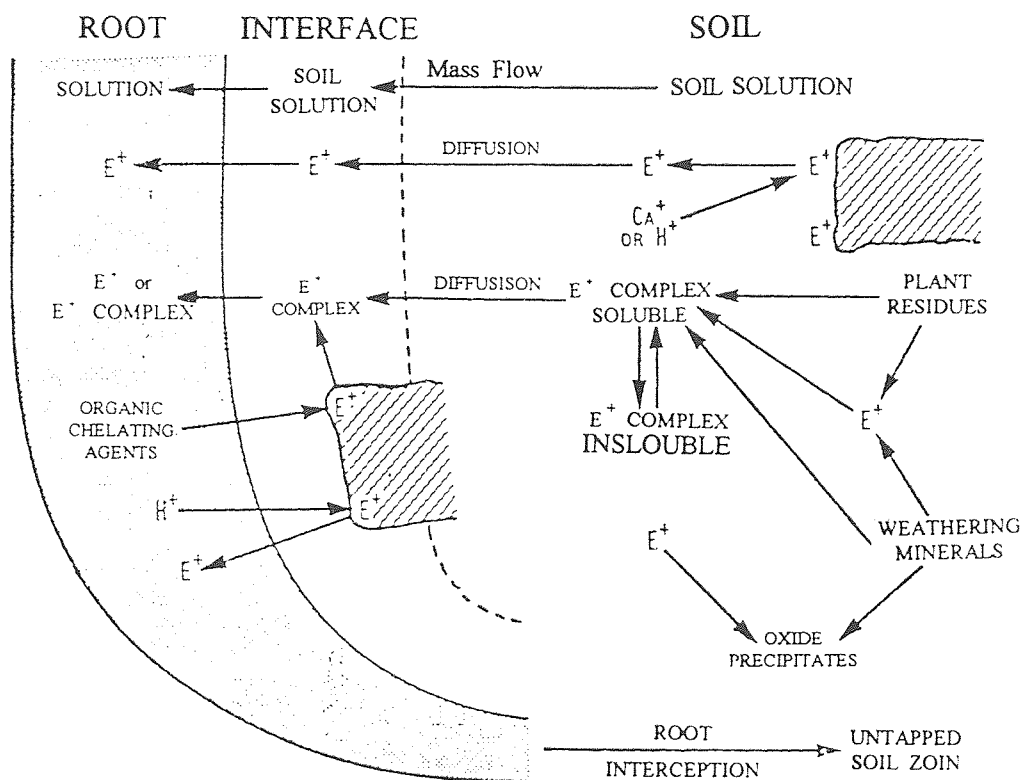


Figure 15 The Principle Processes Operative in the Transfer of Trace Elements from the Soil to the Plant Root

The general symbol E^+ is used to represent any trace element cation that can participate in the particular process illustrated. A complementary diagram could be procedure to illustrate anionic processes.

(Adapted from Mitchell, 1972, [47])

CHAPTER 4

RESEARCH APPROACH

4.1 Description of Model

A computer model was developed to estimate the dominate form of arsenic in clay soils after a certain user-designated time. The speciation of arsenic and concentration of dominant arsenic species are computed based on inputs of environmental factors and the specific reactions. The specific reactions considered in the model are listed in Table 5 and discussed in Chapter 3. The environmental factors are listed below:

Table 14 Environmental Factors Included in Model

Clay Soil Content	Other Environment Factors
Porosity (%)	Temperature
Moisture (%)	pH
<i>Al</i> Content (%)	Eh
<i>Fe</i> Content (%)	
<i>Mn</i> Content (%)	

The computer language utilized is PASCAL. Owing to its well-organized structure, PASCAL can be easily programmed to deal with those complex reactions occurring in the model. The whole process of the computer modeling is presented in the Computer Flowchart in Fig. 16.

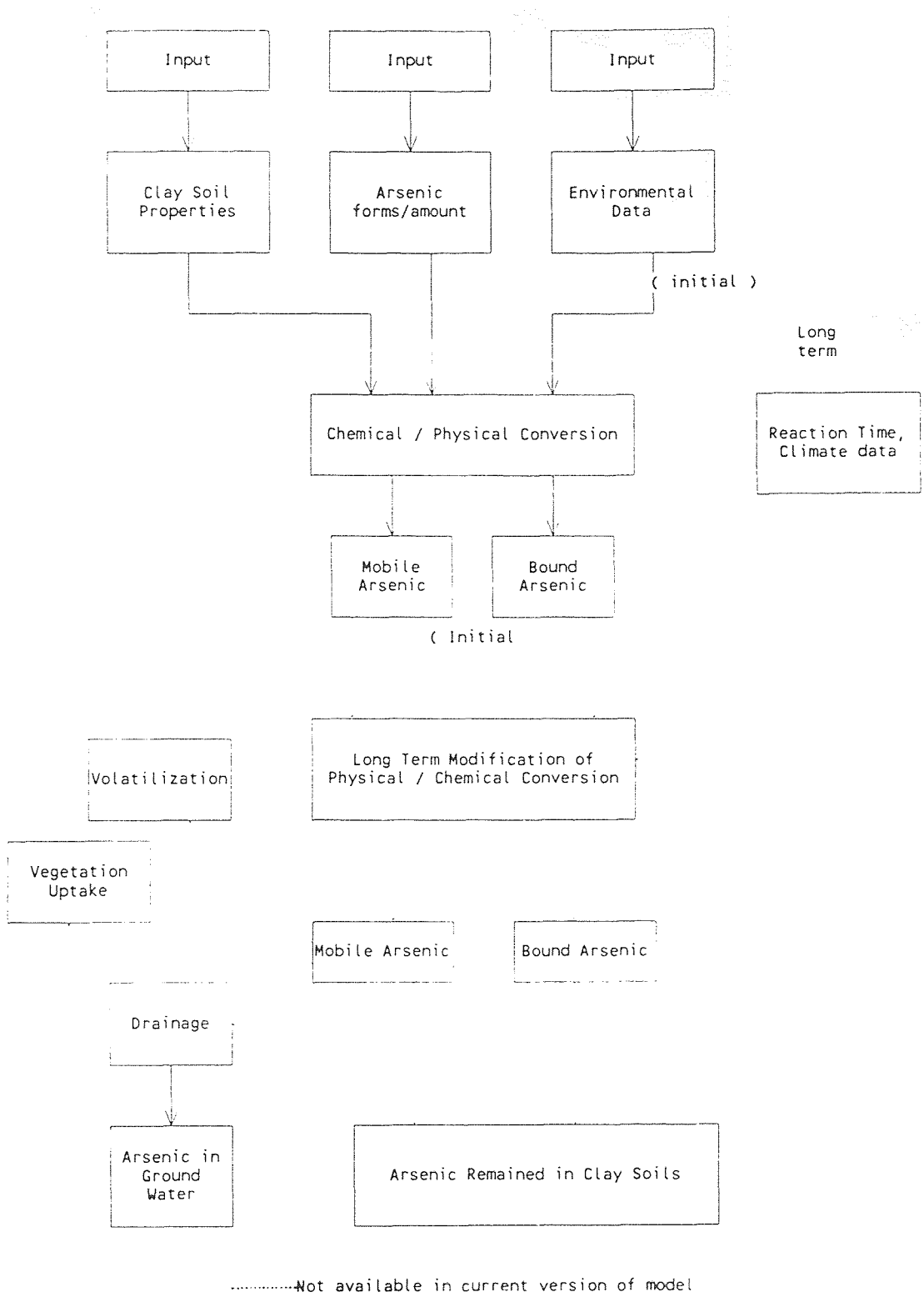


Figure 16 Computer Process Flowchart

4.2 Modeling Assumptions and Approaches

The main reactions related to arsenic distribution in soil systems are: adsorption, dissolution, redox reactions, volatilization and biological uptake. Based on the theories discussed in Chapter 3, volatilization and biological uptake both are time-dependent processes and exert less influence in the initial contamination period compared to the physical and chemical processes. The physical and chemical reactions occur relatively fast (from less than a second to several days) and change little after equilibrium has been established. As a result, the initial arsenic transformation can be regarded as controlled by physical and chemical processes. The long term speciation is and then influenced by organisms and volatilization; and it may also influenced by physical and / or chemical factors. The modeling process is hereby divided into two parts. One is initial physical and chemical reactions, the other is time - dependent biological combined with physical and chemical processes.

Part 1. Initial physical and chemical processes

As discussed in Chapter 3, the total arsenic distribution in soil system can be simplified as Equation 3-8 : $C_t = C_s + C_e$ where C_t = Total arsenic, C_s = Arsenic adsorbed, C_e = Arsenic in water, which indicates that arsenic is either adsorbed by soil or exists in soil water. Then, assume the transformation of each species is affected by environmental factors, such as temperature, pH - Eh, other ions (*Fe, Mn, Al, and / or S, P*). The arsenic distribution can be evaluated from either adsorption experiments or dissolution theories / experiments. As mentioned before, adsorption is a complex process, which includes several reactions, so it can not be expressed as simple theoretical equations so far. The environmental factors that influence arsenic transformation are described in the adsorption and dissolution approaches separately.

Part 2. Time dependent reactions

Since there are many debatable reactions and insufficient information, it is unable to predict the time - dependent reactions in the current version of model. Detailed discussed in Sec. 4.2.2.

4.2.1 Initial Reactions - Immediate Reactions

As discussed before, the initial physical / chemical reactions are mainly governed by adsorption and dissolution : $C_T = C_s + C_e$ (Equation. 3-8). Once the initial total arsenic amount C_{Total} and arsenic adsorbed (by soil) C_{Soil} or arsenic dissolved (in soil water) C_{Water} are known, the other items can be evaluated. Therefore, there are two methods to approach the equilibrium equation, one is from adsorption and the other is from dissolution.

4.2.1.1 Adsorption

The Freundlich isotherm : $C_s = K C_e^n$ (3-10) and $C_T = C_s + C_e$ (3-8) are used for estimating arsenic distribution. If C_T and n, K are known, the C_s, C_e could be derived from the above equations.

From

$$C_T = C_s + C_e \quad (3-8)$$

$$\Rightarrow C_e = C_T - C_s \quad (4-1)$$

and the logarithmic form of equation 3-10:

$$\log C_s = n \log C_e + \log K \quad (3-11)$$

replace C_e by $C_T - C_s$

$$\Rightarrow \log C_s = n \log(C_T - C_s) + \log K \quad (4-2)$$

$$\left(\text{ or } \ln C_e = n \ln(C_i - C_s) + \ln K \right) \quad (4-3)$$

If n and k are known, C_s , C_e could be evaluated by Trial and Error method.

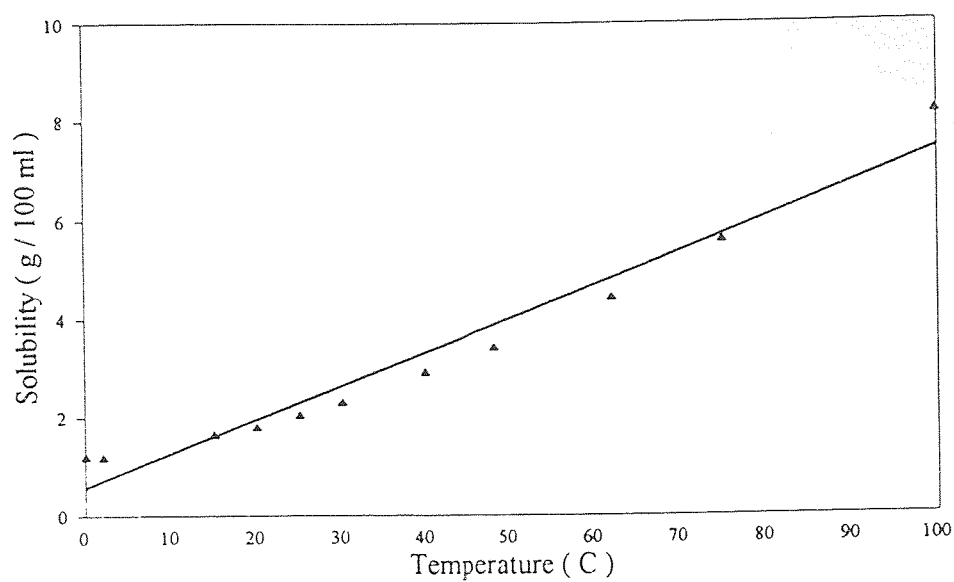
In this model, C_T , n and k are input by the user, then C_s and C_e are generated by computer trial and error approach. If the user doesn't input n and k value, the computer uses a default value set in the program. The default values are based on the average soil distribution coefficients discussed in Sec. 3.3.1.2.1, while for $As(III)$, $n = 1$, $K = 1.2$; for $As(V)$, $n = 1$, $K = 1.9$.

4.2.1.2 Dissolution

The solubility of arsenic species could be acquired from previous experimental data, and the predominant soluble species could be evaluated by pH - Eh diagram. Since the species energy information could be found so far are only in the environment of temperature at 25 °C, therefore the soil environment are set in 25°C. The modification of solubility - temperature relationship are discussed in Appendix C - 3.

4.2.1.2.1 Solubility Varied by Temperature

Based on Linke's solubility data, which are a collection of experimental results of solubility vs. temperature varied by species, the relationship between solubility of each arsenic species and temperature can be calculated by linear regression. There are five species among the collection are commonly used in industry and agriculture (refer to Appendix A commonly used arsenic compound), which are arsenic trioxide (As_2O_3), arsenic pentoxide (As_2O_5), arsenic trisulfide (As_2S_3), arsenic pentasulfide (As_2S_5) and arsine (AsH_3). Therefore, the regressed relationship of these five species are used in the modeling. From Fig. 17 to Fig. 21 are the original experimental data and the linear regression lines of arsenic compounds v.s. temperature. The numerical experimental data and statistical



▲ Experimental Data

Figure 17 Solubility of As_2O_3 Varied by Temperature

Temp As₂O₃ g/100ml H₂O

Regression Output:

0	1.21	Constant	0.583165476
2	1.2	Std Err of Y Est	0.476256665
15	1.66	R Squared	0.956298857
20	1.81	No. of Observations	11
25	2.05	Degrees of Freedom	9
30	2.31		
39.8	2.93	X Coefficient	0.068436052
48.2	3.43	Std Err of Coef.	0.004876557
62	4.45		
75	5.62		
98.5	8.18		

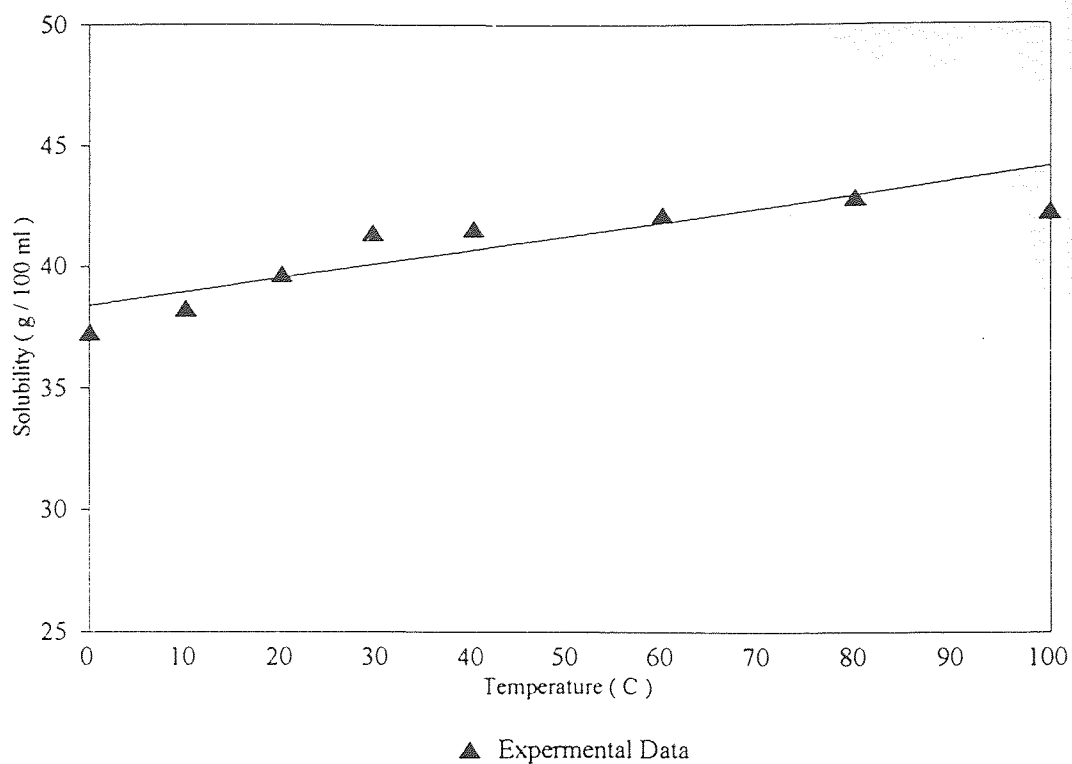


Figure 18 Solubility of As_2O_3 Varied by Temperature

Temp.	As ₂ O ₃ g/100mlH ₂ O	Regression Output:	
0	37.3	Constant	38.39926
10	38.3	Std Err of Y Est	0.91768
20	39.7	R Squared	0.848349
29.5	41.4	No. of Observations	8
40	41.6	Degrees of Freedom	6
60	42.2	X Coefficient(s)	0.057455
80	42.9	Std Err of Coef.	0.009917
100	43.3		

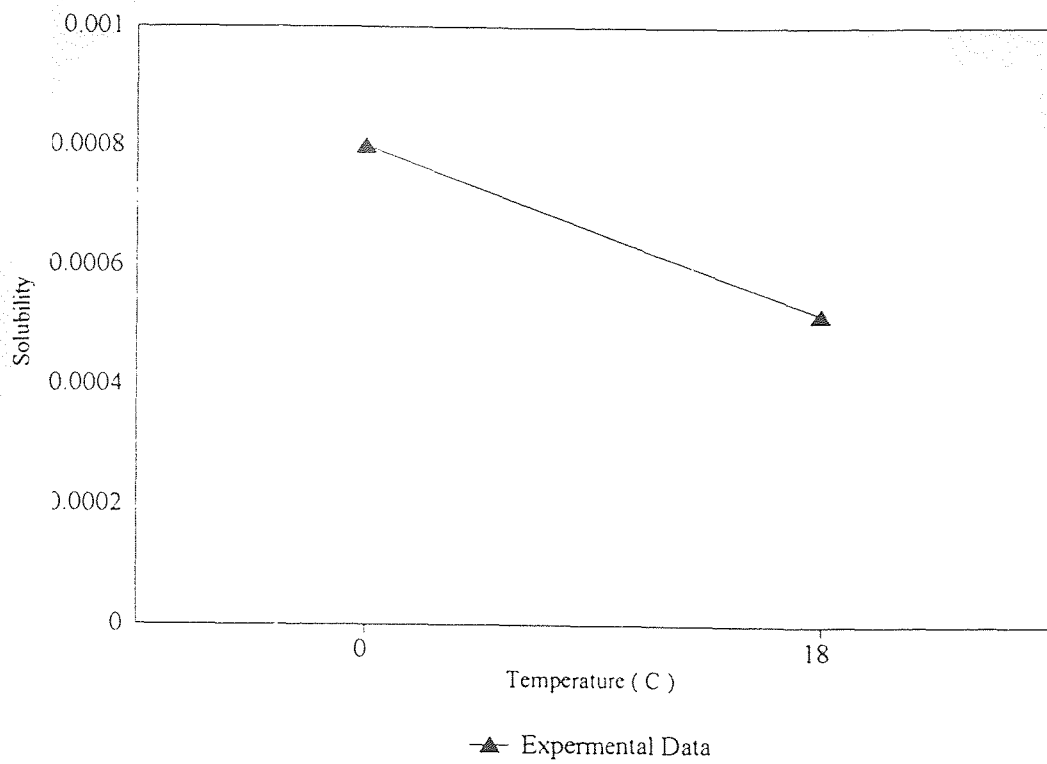


Figure 19 Solubility of As_2S_3 Varied by Temperatrue

Temp.	As_2S_3 g/l
0	0.0008
18	0.00052

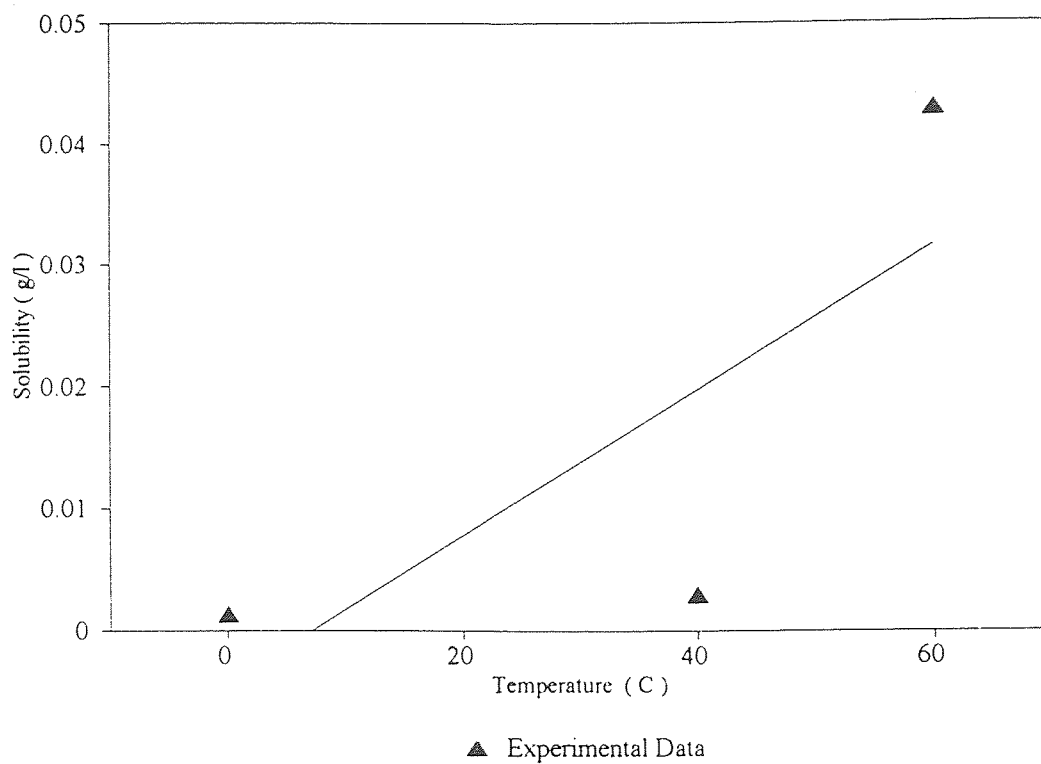


Figure 20 Solubility of As_2S_3 , Varied by Temperatruue

Temp.	As ₂ S ₃ g/l	Regression Output:	
0	0.00136	Constant	-0.00424
40	0.003	Std Err of Y Est	0.020943
60	0.043	R Squared	0.605651
		No. of Observations	3
		Degrees of Freedom	1
		X Coefficient(s)	0.000601
		Std Err of Coef.	0.000485

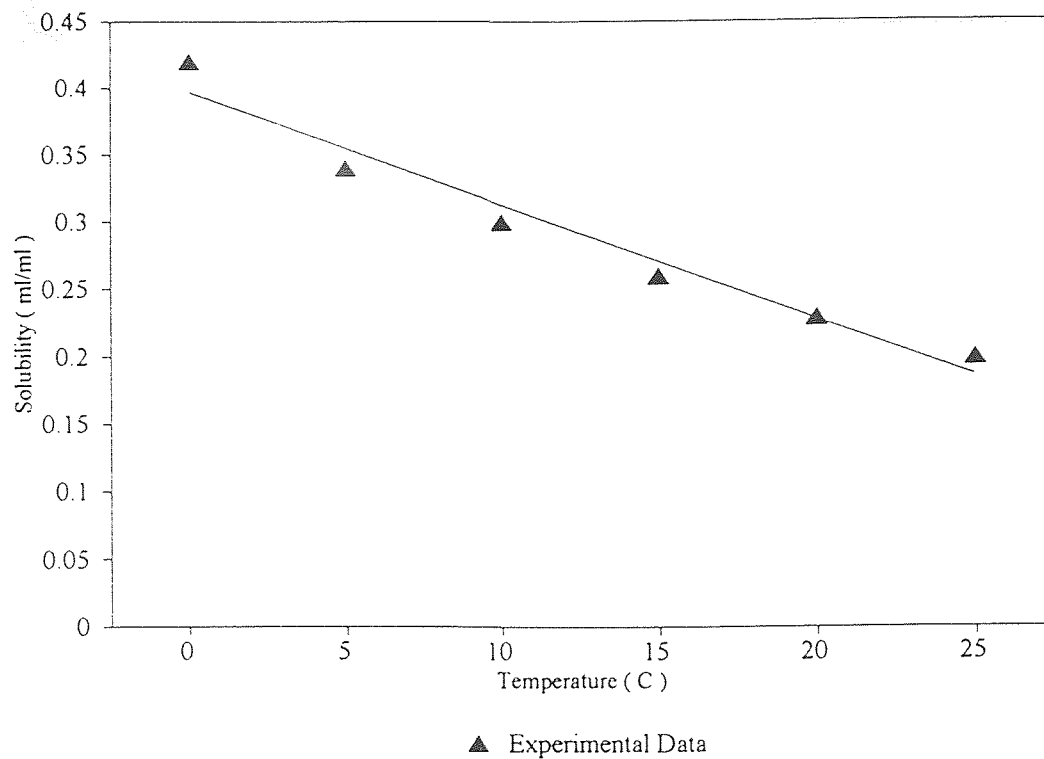


Figure 21 Solubility of AsH_3 Varied by Temperature

Temp.	AsH3 ml/ml	Regression Output:	
0	0.42	Constant	0.396667
5	0.34	Std Err of Y Est	0.017416
10	0.3	R Squared	0.962182
15	0.26	No. of Observations	6
20	0.23	Degrees of Freedom	4
25	0.2	X Coefficient(s)	-0.0084
		Std Err of Coef.	0.000833

references, such as coefficients, constants and standard errors, are shown below each graph.

From the linear regression, the relation equations at evaluated are:

$$1. As_2O_3 \text{ (g/100 ml } H_2O \text{)} = 0.068436 \times \text{Temperature (} ^\circ\text{C)} + 0.583165 \quad (4-4)$$

$$2. As_2O_3 \text{ (g/100 ml } H_2O \text{)} = 0.057454 \times \text{Temperature (} ^\circ\text{C)} + 38.39926 \quad (4-5)$$

$$3. As_2S_3 \text{ (g/l } H_2O \text{)} = -0.00028 \times \text{Temperature (} ^\circ\text{C)} + 0.0008 \quad (4-6)$$

$$4. As_2S_3 \text{ (g/l } H_2O \text{)} = 0.0006 \times \text{Temperature (} ^\circ\text{C)} - 0.00423 \quad (4-7)$$

$$5. AsH_3 \text{ (ml/ml)} = -0.0084 \times \text{Temperature (} ^\circ\text{C)} + 0.396666 \quad (4-8)$$

4.2.1.2.2 pH-Eh

Based on redox half-reactions and Gibbs free energy data, the thermodynamic equations between arsenic species can be evaluated (refer to Appendix C-2).

The pH-Eh effect can be combined with temperature influences according to the Thermodynamic Equation.

$$\Delta G = \Delta G^\circ + RT \ln K \quad (4-9)$$

where

G = Gibbs Free Energy, kcal

ΔG = Free Energy Change

ΔG° = Standard Free Energy of Formation

R = Gas Constant = 1.9872 cal Deg⁻¹ mole⁻¹

T = Absolute Temperature, °k

K = Equilibrium Constant

when system is equilibrium, $\Delta G = 0$, then

$$\Delta G^\circ = -RT \ln K$$

However, since the ΔG° , K and Eh would varied by temperature change, like:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4-10)$$

where

ΔH = Enthalpy change

and

$$pe = \frac{F}{2.3 RT} Eh \quad (4-11)$$

but the ΔG° available so far, are only ΔG° at 25°C, 1 atm. Therefore, the soil environment is set at 25°C, 1 atm in this version of model. The redox-half reactions and thermodynamic equations are calculated and listed in Table 15.

4.2.2 Time - Dependent Reactions

Time - dependent reactions here are Evaporation, Volatilization and biological conversions accompanied with physical/chemical conversions varied by environment changing. However, these reactions are associated with many unknown or uncertain reactions and need supportive experimental data to establish the model, so these reactions not included in this version of model. The difficulties of simulation are described below:

1. Evaporation (soil water):

Interstitial water evaporation is related to soil structure, available water content, temperature and vapor pressure. The soil - evaporation equation is needed for modeling.

Table 15 Redox-Half Reactions and Thermodynamic Equations for the Ferguson and Gavis Arsenic Eh-pH diagram (25°C, 1 atm)

Line No.	Redox-Half Reactions	Thermodynamic Equations
1.	$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+$	pH = 2.2
2.	$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$	pH = 6.97
3.	$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+$	pH = 11.5
4.	$H_3AsO_3 \leftrightarrow H_2AsO_3^- + H^+$	pH = 9.24
5.	$H_2AsO_3^- \leftrightarrow HAsO_3^{2-} + H^+$	pH = 12.1
6.	$H_3AsO_3 + H_2O \leftrightarrow H_3AsO_4 + 2H^+ + 2e^-$	pH + pE = 9.93
7.	$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_4^- + 3H^+ + 2e^-$	pH + 2 / 3 pE = 7.35
8.	$H_3AsO_3 + H_2O \leftrightarrow HAsO_4^{2-} + 4H^+ + 2e^-$	pH + 1 / 2 pE = 7.25
9.	$H_2AsO_3^- + H_2O \leftrightarrow HAsO_4^{2-} + 3H^+ + 2e^-$	pH + 2 / 3 pE = 6.6
10.	$H_2AsO_3^- + H_2O \leftrightarrow AsO_4^{3-} + 4H^+ + 2e^-$	pH + 1 / 2 pE = 7.8
11.	$HAsO_3^{2-} + H_2O \leftrightarrow AsO_4^{3-} + 3H^+ + 2e^-$	pH + 2 / 3 pE = 6.4
√ 12.*	$SO_4^{2-} + 8H^+ + 8e^- \leftrightarrow S^{2-} + 4H_2O$	pH + pE = 4.5
12.*	$H_2S + 4H_2O \leftrightarrow SO_4^{2-} + 10H^+ + 8e^-$	pH + 4 / 5 pE = 4.1
12.*	$HS^- + 4H_2O \leftrightarrow SO_4^{2-} + 9H^+ + 8e^-$	pH + 8 / 9 pE = 3.8
12.*	$H_2S \leftrightarrow H^+ + HS^-$	pH = 6.9
13.	$AsH_3 \leftrightarrow As + 3H^+ + 3e^-$	pH+pE-1/3 log AsH ₃ = -4.03
14.	$O_{2(g)} + 4H^+ + 4e^- \leftrightarrow 2H_2O$	pH+pE+1/4 log O ₂ = 20.8

* Uncertain reaction; Discussed in Appendix C-2.

(Chemical reactions are adapted from Ferguson [19] and Seyler [56])

√: equation chosen.

2. Volatilization (arsenic)

Volatilization is related to arsenic species, species vapor pressure, soil structure and temperature. Since volatilization is varied by species, it is a more complex process than water evaporation. Volatilization model is needed for estimation.

3. Microbial redox reaction

Only certain species of microbes can reduce arsenic (detailed in Sec. 3.4.1), so whether the microbial redox reaction occurs depends on the existence and the amount of the arsenic - redoxing microbes. However, it is hard to distinguish if the redox reaction is done by microbial or chemical way, so the microbial redox reaction is included in chemical redox reactions.

4. Microbial methylation

As discussed in Sec. 3.4.1.2, the whether microbial methylation happens in soil system is still debatable.

5. Plant uptake

Plant uptake processes are associated with soil structure and plant species, which need experimental data to establish plant uptake model.

CHAPTER 5

RESULTS AND DISCUSSION

The model provides two different ways to estimate arsenic transformation forms. In the first part, after the user inputs porosity, moisture, pH, Eh, soil information and the initial amount of 5 arsenic species: As_2O_3 , As_2O_5 , As_2S_3 , As_2S_5 and AsH_3 , the model will generate the soluble and adsorbed amount of these five species and the predominant soluble transformed species transformed from the above soluble species. This estimation is based on solubility-experimental data and pH-Eh diagrams which are derived from Gibbs' free energy theory.

The second part of the model is the adsorbed and soluble amount estimation. But it predicts the total As (III) and As (V) instead of specific species. The Freundlich isotherm is used in the simulation. According to $C_s = K C_e^n$, the C_s (adsorbed) and C_e (exist in water) can be estimated after the user inputs n and k values. If the user did not input the n and k values the n and k values would be generated by the computer based on the mean value [15].

5.1 Model Output (Screen)

The following pages are the modeling output shown in the screen, and cases of result.

5.2 Model Limitation

The first part of the model is applied only under the standard conditions (25°C, 1 atm), because of the unavailability of the entropy information of arsenic species under other environmental conditions. However, the natural soil environment is usually under lower temperature conditions (around 15 ~ 20°C).

*** Arsenic Transformation Model ***

This program is used to estimate the possible SPECIES and AMOUNTS of Arsenic (As) after a period of reaction time in Clay soils.

The following information should be inputted by the user :

1. Clay Soil Information
2. Environmental Factors
3. Initial information of Arsenic (Forms, Amounts)

If some of these data are NOT inputted, the model will generate default values based on previous experimental results.

<< Press ENTER to Continue >>

(Screen 1)

Part I. Solubility Approach

1. Please input clay soil information

Porosity -- ____ % (Hint : Clay soil porosity less than 50 %)

Moisture -- ____ % (Hint : Clay soil moisture less than 25 %)

2 Please input environmental factors

(Assume soil is in standard status: 25 C, 1 atm)

pH -- _____ (Hint: pH = 0 to 14)

Eh -- _____ (volts) (Hint: Soil Eh = -1 to 1)

<< Press ENTER to Continue >>

(Screen 2)

3. Please input initial arsenic species information

As₂O₃ ___ (mg/ 1/1000 cubic m)As₂O₅ ___ (mg/ 1/1000 cubic m)As₂S₃ ___ (mg/ 1/1000 cubic m)As₂S₅ ___ (mg/ 1/1000 cubic m)AsH₃ ___ (ml/ 1/1000 cubic m)

<< Press ENTER to Continue >

(Screen 3)

The arsenic transformation forms are :

Forms	Adsorbed	Soluble	Gas
-------	----------	---------	-----

As₂O₃As₂O₅As₂S₃As₂S₅AsH₃

Predominant soluble form is : _____

<< Press ENTER to Continue or ESCAPE to Stop >>

(Screen 4)

Part II. Adsorption Approach

According to Freundlich isotherm ($C_s = K * (C_e)^n$)

Please input initial total arsenic value

$C_t =$ ___ (mg) (Assume $C_t > 1$ mg)

Please input As(III) / As(V) ratio (%)

As(III) ___ (%)

As(V) ___ (%)

Please input n, K value (Input "999", for the default value)

	As(III)	As(V)
n =	_____	_____
K =	_____	_____

<< Press ENTER to Continue >>

(Screen 5)

The distribution of As is :

Forms	Cs	Ce
___ As(III)	___ (mg)	___ (mg)
___ As(V)	___ (mg)	___ (mg)

<< Press ENTER to RETURN to DOS >>

(Screen 6)

Computer Output Case 1

Porosity : 35.00 Moisture : 15.00 pH : 7.00 Eh : 1.00

Initial As₂O₃, As₂O₅, As₂S₃, As₂S₅ and AsH₃: 10.00 mg/l

Part I.	Form	Adsorbed	Soluble
Equilibrium	As ₂ O ₃	0.00	10.00
Equilibrium	As ₂ O ₅	0.00	10.00
Equilibrium	As ₂ S ₃	9.94	0.06
Equilibrium	As ₂ S ₅	8.38	1.62
Equilibrium	AsH ₃	0.00	10.00

Predominant Form : HAsO₄(-2) 31.68 mg

Part II Ct : 20.00 As(III) : 50.00 % As(V) : 50.00 %

As(III) : n = 1.0, K = 1.2; As(V) : n = 1.0, K = 1.9

As(III) 5.45 (mg) (adsorbed) 4.55 (mg) (soluble)

As(V) 6.55 (mg) (adsorbed) 3.45 (mg) (soluble)

Computer Output Case 2

Porosity : 35.00 Moisture : 15.00 pH : 5.00 Eh : 1.00

Initial As₂O₃, As₂O₅, As₂S₃, As₂S₅ and AsH₃: 10.00 mg/l

Part I.	Form	Adsorbed	Soluble
Equilibrium	As ₂ O ₃	0.00	10.00
Equilibrium	As ₂ O ₅	0.00	10.00
Equilibrium	As ₂ S ₃	9.94	0.06
Equilibrium	As ₂ S ₅	8.38	1.62
Equilibrium	AsH ₃	0.00	10.00

Predominant Form : HAsO₄(-2) 31.68 mg

Part II Ct : 20.00 As(III) : 50.00 % As(V) : 50.00 %

As(III) : n = 2.0, K = 1.2; As(V) : n = 2.0, K = 1.9

As(III) 7.50 (mg) (adsorbed) 2.50 (mg) (soluble)

As(V) 7.95 (mg) (adsorbed) 2.05 (mg) (soluble)

Computer Output Case 3

Porosity : 35.00 Moisture : 25.00 pH : 5.00 Eh : 0

Initial As₂O₃, As₂O₅, As₂S₃, As₂S₅ and AsH₃: 10.00 mg/l

Part I.	Form	Adsorbed	Soluble
Equilibrium	As ₂ O ₃	0.00	10.00
Equilibrium	As ₂ O ₅	0.00	10.00
Equilibrium	As ₂ S ₃	9.89	0.11
Equilibrium	As ₂ S ₅	7.31	2.69
Equilibrium	AsH ₃	0.00	10.00

Predominant Form : H₃AsO₃ 32.80 mg

Part II Ct : 20.00 As(III) : 80.00 % As(V) : 20.00 %

As(III) : $n = 0.4$, $K = 1.2$; As(V) : $n = 0.4$, $K = 1.9$

As(III) 3.32 (mg) (adsorbed) 12.68 (mg) (soluble)

As(V) 2.33 (mg) (adsorbed) 1.67 (mg) (soluble)

Computer Output Case 4

Porosity : 35.00 Moisture : 25.00 pH : 9.00 Eh : 0

Initial As₂O₃, As₂O₅, As₂S₃, As₂S₅ and AsH₃: 100.00 mg/l

Part I.	Form	Adsorbed	Soluble
Equilibrium	As ₂ O ₃	0.00	100.00
Equilibrium	As ₂ O ₅	0.00	100.00
Equilibrium	As ₂ S ₃	99.89	0.11
Equilibrium	As ₂ S ₅	97.31	2.69
Equilibrium	AsH ₃	0.00	10.00

Predominant Form : HAsO₄(-2) 302.80 mg

Part II Ct : 100.00 As(III) : 50.00 % As(V) : 50.00 %

As(III) : $n = 0.2$, $K = 1.2$; As(V) : $n = 0.2$, $K = 1.9$

As(III) 2.60 (mg) (adsorbed) 47.40 (mg) (soluble)

As(V) 4.08 (mg) (adsorbed) 45.92 (mg) (soluble)

The second significant limitation is, in the first part, the input arsenic species are limited in some specific species (As_2O_3 , As_2O_5 , As_2S_3 , As_2S_5 and AsH_3), since the solubility data of these species are the only data collected so far.

In the natural soil environment, the presence of metal ions significantly affects the solubility of arsenic, because arsenic might coprecipitate with metal ions. However, these factors are not included.

As for the second part of model, the estimation is based totally on the Freundlich isotherm equation, which does not consider the environmental factors such as temperature, pH-Eh or metal ions.

5.3 Discussion of Results

1. In the first part of model, As_2O_3 , As_2O_5 and AsH_3 shown having high solubility which are almost dissolved in the amount of 10 mg and 100 mg. Arsenic sulfide have relatively low solubility and almost all adsorbed in the amount of 10 mg and 100 mg..
2. The thermodynamic calculation of predominant arsenic species shown applied to the pH-Eh diagram.
3. In the second part, soil arsenic adsorption ability are mainly depend on n value. But it seem that arsenic (III) and (V) are almost adsorbed by using the default value of n. k. But, when the n value are as low as 0.2 or less the result of part II is similar to which of part I.
4. Comparing the results of above two parts, it is confusing about these two opposite results. It seemed that As (III) and As (V) should almost dissolved in soil water according to their high solubility. However, based on the practical value of n and k, As (III) and As (V) should almost adsorbed by soil. It is interesting to find out which approach is more correct. It is possible that arsenic have high solubility but also could be largely adsorbed when the metal ions or some other clay mineral functional groups presents. Or, it might also possible that the default n, k are not applied to this condition.

CHAPTER 6

CONCLUSIONS

The project details possible processes which influence arsenic transformation occurring in soil system. It provides classification of relative theories and comparison of previous studies, which is useful for advance arsenic researches.

A model was developed to assist in evaluating the arsenic transformation in Clay soil. Arsenic can be evaluated using solubility and redox relationships. It can also be evaluated using relationship.

1. In the first part of model - dissolution approach, As_2O_3 , As_2O_5 and AsH_3 are very soluble species. and As_2S_3 and As_2S_5 are relative too insoluble to dissolve in soil water.
2. Soluble species are highly depends on pH-Eh condition.
3. In the second part of model, adsorption approach, $As(III)$ and $As(V)$ are almost adsorbed based on practical value of n, k. But, when n is as low as 0.2 or less, arsenic are almost dissolved in water.

CHAPTER 7

Recommendation For Further Research

The computer prediction is based on known theoretical equations or practical data. For establishing a more accurate model, more information is needed. The following areas are suggested for further research to build a more powerful model :

1. How is arsenic solubility affected by metal ions ?

Arsenic might coprecipitate with metal ions and therefore reduce the solubility of arsenic in soil water. Metals such as *Fe*, *Mn*, *Ca* commonly exist in clay soil systems and influence arsenic solubility. However, there are no previous studies focus on this topic.

2. How is arsenic sorption ability varied by clay soil content ?

Many researchers discuss arsenic adsorption as a function of soil content, for example : *Fe*, *Al*, *Mn*. However, this information needs to be classified into some quantitative equations for modeling. Also, it is a lack of experimental data considering organic and sulfide content of soil.

3. Microbial conversion research

As discussed in Sec. 3.4.1, microbial reactions are quite complex. Some researchers found it did not affect arsenic transformation, but some others suggested it is a controlling factor. More research is needed to clarify this issue.

4. Volatilization research

Since some gaseous arsenic are more toxic than the solid arsenic and volatilization, it is also an important process that happens in soil systems. The volatilization studies are recommended for further research.

APPENDIX A

COMMONLY USED ARSENIC COMPOUNDS

Table A-1 Arsenic Compound Used in Industry, Agriculture and Medicine

Arsenic compound	Formula	Known as	Uses
Arsenic	As		Alloying additive Electronic devices, i.e. transistor, etc. Veterinary medicines
Arsenic pentoxide	As_2O_5	Arsenic oxide Boliden salts	Chemical intermediate Defoliant Wood preservative
Arsenic trioxide	As_2O_3	Arsenic Arsenolite White arsenic Arsenious oxide	Insecticides and fungicides Glass Chemicals Anti-fouling paints Taxidermy Timber preservation
Arsenic trichloride	$AsCl_3$	Butter of arsenic	Pharmaceuticals and chemicals
Arsine	AsH_3		Stabilizing selenium in transistors
Calcium arsenate	$Ca_3(AsO_4)_2$		Insecticide, herbicide and larvicide
Cooper arsenite	$CuHAsO_3$	Scheele's green	
Cooper aceto-arsenite	$3CuOAs_2O_3Cu(OOCCH_3)$	Paris green	Larvicide
Orpiment	As_2S_3		Depilatory-firework-pigment

Table A-1 Arsenic Compound Used in Industry, Agriculture and Medicine (Continued)

Arsenic compound	Formula	Known as	Uses
Potassium arsenate	KH_2AsO_4	Macquer's salt	Preservation of hides Textile printing Fly papers
Potassium arsenite	$KH(AsO_2)_2$	Fowler's solution	Veterinary medicine
Realgar	As_2S_2		Pigment Depilatory
Lead arsenate	$PbHAsO_4$		Insecticide, herbicide, and growth regulator
Sodium arsenate	Na_2HAsO_4 Na_3AsO_4	Wolman salts	Wood preservative Calico printing Insecticide Weedkiller
Sodium arsenite	$NaAsO_2$		Herbicides Pesticides Corrosive inhibitor Chemical intermediate Fluorescent lamps
Magnesium arsenate	$Mg_3(AsO_4)_2$	Atoxyl	trypanicide
Sodium arsanilate	$NH_2C_6H_4AsO(OH)(ONa)$		Pharmaceuticals manufacture

(Adapted from Kipling, M.D. 1977 [32])

APPENDIX B

BASIC SOIL CONTENT INFORMATION

Table B-1 Native Soil Concentrations of Various Elements

Element	Concentration (ppm)	
	Typical Range	Extreme Limits
Ag	0.1-5.0	0.1-50
Al	10,000-300,000	-
As	1.0-40	0.1-500
B	2.0-130	0.1-3000
Ba	100-3,500	10-10,000
Be	0.1-40	0.1-100
Br	1.0-10	-
Ca	100-400,000	-
Cd	0.01-7.0	0.01-45
Ce	30-50	-
Cl	10-100	-
Co	1.0-40	0.01-500
Cr	5.0-3,000	0.5-10,000
Cs	0.3-25	-
Cu	2.0-100	0.1-14,000
F	30-300	-
Fe	7,000-550,000	-
Ga	0.4-300	-
Ge	1.0-50	-
Hg	0.01-0.08	-
I	0.1-40	-
K	400-30,000	-
La	1.0-5,000	-
Li	7.0-200	1.0-3,000
Mg	600-6,000	-
Mn	100-4,000	1.0-70,000
Mo	0.2-5.0	0.1-400
Na	750-7,500	400-30,000
Ni	5.0-1,000	0.8-6,200
P	50-5,000	-

Table B-1 Native Soil Concentrations of Various Elements (Continued)

Element	Concentration (ppm)	
	Typical Range	Extreme Limits
Pb	2.0-200	0.1-3,000
Ra	$10^{-6.5}$ - $10^{-5.7}$	-
Rb	20-600	3.0-3,000
S	30-10,000	-
Sb	0.6-10	-
Sc	10-25	-
Se	0.1-2.0	0.01-400
Si	230,000-350,000	-
Sn	2.0-200	0.1-700
Sr	50-1,000	10-5,000
Th	0.1-12	-
Ti	1,000-10,000	400 - > 10,000
U	0.9-9.0	<250
V	20-500	1.0-1,000
Y	10-500	-
Zn	10-300	3.0-10,000
Zr	60-2,000	10-8,000

(Adapted from Dragun, 1988 [15])

Table B-2 General Range for the Cation Exchange Capacities of Soil Clays, Soil Organic Matter, and Several Soil Types

		CEC (meq/100 grams)
Soil	Clays	
	Chlorite	10-40
	Illite	10-40
	Kaolinite	3-15
	Montmorillonite	80-150
	Oxides and Oxyhydroxides	2-6
	Saponite	80-120
	Vermiculite	100-150
Soil	Organic Matter	>200
Soil	Type	
	Sand	2-7
	Sandy Loam	2-18
	Loam	8-22
	Silt Loam	9-27
	Clay Loam	4-32
	Clay	5-60

(Adapted from Dragun, 1988 [15])

APPENDIX C

CALCULATION OF SOLUBILITY EQUATIONS

Table C Gibbs's Free Energies of formation for Arsenic Species at 25°C, and 1 atm (ΔG° , kcal mole⁻¹)

Species	State	ΔG°	Reference
H_3AsO_4	aq.	-184.0	19
$H_2AsO_4^-$	aq.	-181.0	19
$HAsO_4^{2-}$	aq.	-171.5	19
AsO_4^{3-}	aq.	-155.8	19
H_3AsO_3	aq.	-154.4	19
$H_2AsO_3^-$	aq.	-141.8	19
$HAsO_3^{2-}$	aq.	-125.3	19
$HAsS_2$	aq.	-11.61	19
AsS_2^-	aq.	-6.56	19
AsS	s	-16.81	19
As_2S_3	s	40.25	19
As	s	0	19
AsH_3	aq.	23.80	19
AsH_3	g	16.50	19
As_2O_3	s	-140.8	19
As_2O_5	s	-186.9	19
H_2O	aq.	-56.69	72
HS^-	aq.	3.01	72
H_2S	g	-7.892	72
H_2S	aq.	-6.54	72
SO_4^{2-}	aq.	-177.34	72
H^+		0	72
e^-		0	72

C-1 Thermodynamic Equation Used:

1. Gibbs free energy equation:

$$\Delta G = \Delta G^\circ + RT \ln K$$

where

G = Gibbs Free Energy, kcal

ΔG = Free Energy Change

ΔG° = Standard Free Energy of Formation

R = Gas Constant = 1.9872 cal Deg⁻¹ mole⁻¹

T = Absolute Temperature, °k

K = Equilibrium Constant

when system is equilibrium, $\Delta G = 0$, then

$$\Delta G^\circ = -RT \ln K$$

2. $\Delta G^\circ = -nF E_h^\circ$

where

n = Number of Electrons involved in the reaction

F = the Faraday, 23.06 Kcal (volt eq)⁻¹

E_h° = Standard Electrode Potentials

3. $pE = F E_h / (2.3 R T)$

C-2. Calculation and Equations of Mathematical Equations

Line 1. $H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+$

$$pH = - \log K \quad (C-1)$$

$$\begin{aligned} \Delta G^\circ &= \Delta G_{H_2AsO_4^-} - \Delta G_{H_3AsO_4} \\ &= -181.0 - (- 184.0) \\ &= 3 \text{ kcal mole}^{-1} \end{aligned}$$

By

$$\Delta G = -RT \ln K$$

$$\begin{aligned} \Rightarrow \ln K &= \Delta G / -RT = 3 / (1.9872 \times 10^{-3} \times 298) \\ &= -5.06 \end{aligned}$$

$$\Rightarrow \log K = (1 / 2.3) * \ln K = -2.2$$

$$\begin{aligned} \Rightarrow \log K &= (1 / 2.3) * (-5.06) \\ &= 2.2 \end{aligned}$$

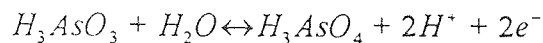
Substitute $\log K = -2.2$ to (C-1), get

$$\text{pH} = 2.2$$

Line 2 ~ Line 5

Same method as above

Line 6



$$2 \text{pH} + 2 \text{p}\epsilon = - \log K$$

$$\Rightarrow \text{pH} + \text{p}\epsilon = - (1/2) \log K \quad (\text{C-2})$$

$$\begin{aligned} \Delta G &= \Delta G_{H_3AsO_4} - \Delta G_{H_3AsO_3} - \Delta G_{H_2O} \\ &= -184 - (-154.4) - (-56.69) \\ &= 27.09 \end{aligned}$$

$$\Delta G = -RT \ln K$$

$$\begin{aligned} \ln K &= (\Delta G / -RT) \\ &= 27.09 / (1.9872 \times 10^{-3} \times 298) \\ &= -45.73 \end{aligned}$$

$$\begin{aligned} \Rightarrow \log K &= (1 / 2.3) \ln K \\ &= -19.89 \end{aligned}$$

Substitute $\log K = -19.89$ to C - 2, we get

$$\text{pH} + \text{p}\epsilon = - (1/2) (-19.89)$$

$$\Rightarrow \text{pH} + \text{p}\epsilon = 9.93 \quad (\text{C-3})$$

(check Eh-pH diagram)

since $p\varepsilon = FE / (2.3 RT) = 16.9 E^\circ \quad (25^\circ\text{C})$

then C - 3 could be rewritten to :

$$\text{pH} + 1 / 16.9 \text{ Eh} = 9.93$$

$$\text{pH} = 0 \quad \text{Eh} = 0.59$$

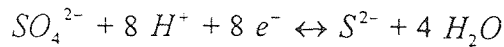
$$\text{pH} = 2.2 \quad \text{Eh} = 0.46$$

Line 7 ~ Line 11 Same as Line 6

Line 12

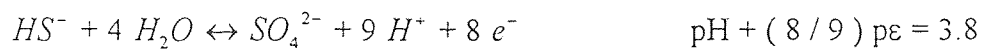
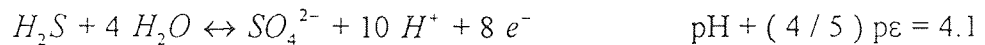
The upper boundary of arsenic sulfides with arsenious acid.

Ferguson and Gavis [19] suggested this boundary is determined entirely by the reduction of $S_{(s)}$ and SO_4^{2-} to $-2 S$. The reaction could be written as follow:



$$\text{pH} + p\varepsilon = 4.5$$

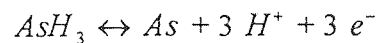
But Seyler and Martin [6] proposed that SO_4^{2-} / H_2S is the controlling couple of redox potential. Thus, the boundary reactions are:



However, they have very similar Eh results when pH value are substituted. In this model, the Ferguson's equation is chosen because it is simpler.

Line 13

The lower boundary between the arsenic sulfides and *As* metal.



$$\text{pH} + p\varepsilon - (1 / 3) - \log pAsH_3 = (-1 / 3) \log K \quad (C-4)$$

$$pAsH_3 = 1 \quad (\text{known})$$

$$\Delta G = - \Delta G_{AsH_3(g)} = - 16.5 \text{ kcal / mole}$$

$$\Delta G = -RT \ln K$$

$$\begin{aligned} \Rightarrow \ln K &= (\Delta G) / (-RT) \\ &= - 16.5 / - (1.9872 \times 298) \\ &= 27.86 \end{aligned}$$

$$\begin{aligned} \Rightarrow \log K &= (1 / 2.3) \ln K \\ &= 12.1 \end{aligned}$$

Substitute $\log K = 12.1$ to C-4, get

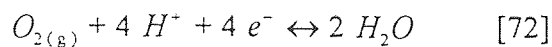
$$\text{pH} + \text{p}\epsilon - (1 / 3) \log pAsH_3 = - 4.03$$

since $pAsH_3 = 1$ then

$$\text{pH} + \text{p}\epsilon = - 4.03$$

Line 14

Water solubility boundary line (upper)



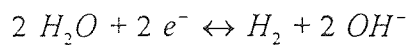
$$\text{pH} + \text{p}\epsilon + (1 / 4) \log P_{O_2} = 20.8$$

at $P_{O_2} = 0.21 \text{ atm}$

$$\text{pH} + \text{p}\epsilon = 20.6$$

Line 15

Water solubility boundary line (lower)



$$\text{p}\epsilon = -14 + (1 / 2) \log P_{H_2} + \text{pOH}$$

when $P_{H_2} = 1$

$$\text{p}\epsilon = -14 + \text{pOH}$$

$$\Rightarrow \text{p}\epsilon = -14 + (14 - \text{pH})$$

$$\Rightarrow \text{p}\epsilon + \text{pH} = 0$$

C-3 Equations Modification

The Ferguson and Gavis's diagram only showed soluble *As* species at 25°C. Since ΔG , K and Eh would varied by temperature change, modification of equations are necessary for temperature different than 25°C. Since

$$\Delta G = - RT \ln K$$

$$\text{and } \ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [57]$$

where

$$\Delta H = \text{Enthalpy change}$$

$$\Rightarrow \ln k_1 - \ln k_2 = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

use the known value of $T = 25^\circ\text{C}$

$$\Rightarrow \ln k_2 = \ln k_{25} - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

If $\Delta G'$ or ΔH° were inputed, the $\log k$ could be derived.

Also, the Eh is changed by temperature change in the following manner:

$$pe = \frac{F}{2.3 RT} Eh \quad [57]$$

C-4 Modeling Setup

Step 1.

Determine whether arsenic is soluble.

1. Water solubility boundary line (upper) Line 14

pH + pe > 20.8 insoluble

$$\text{pH} + \text{p}\epsilon < 20.8$$

2. Water solubility boundary line (lower) Line 15

$$\text{pH} + \text{p}\epsilon > 20.8 \quad \text{soluble} \quad \text{Step 3}$$

$$\text{pH} + \text{p}\epsilon < 20.8 \quad \text{insoluble} \quad \text{Step 2}$$

Step 2.

Insoluble *As* → check Arsenic is in metal / form (*As*) or transform to Arsine (*AsH₃*)

Metal / Arsine boundary Line 13

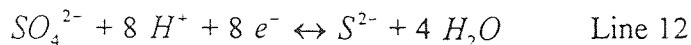
Assume $\text{p}AsH_3 = 1$

$$\text{pH} + \text{p}\epsilon > -4.03 \quad \text{Metal (As)} \quad \text{Step 3}$$

$$\text{pH} + \text{p}\epsilon < -4.03 \quad \text{Arsine (AsH}_3\text{)} \text{Step 2}$$

Step 3.

Soluble *As* → check *As* in Oxide or Sulfide status use equation:



$$\text{pH} + \text{p}\epsilon > 4.5 \quad \text{Arsenic acid / Arsenious acid} \text{ Step 4}$$

$$\text{pH} + \text{p}\epsilon < 4.5 \quad \text{Arsenic sulfide}$$

Step 4.

Check Arsenic acid / Arsenious acid

Case pH of

0 - 2.2 check Line 6

$$\text{pH} + \text{p}\epsilon > 9.93 \quad H_3AsO_4$$

$$\text{pH} + \text{p}\epsilon < 9.93 \quad H_3AsO_3$$

2.2 - 6.97 check Line 7

$$\text{pH} + (2/3) \text{p}\epsilon > 7.35 \quad H_2AsO_4^-$$

$$\text{pH} + (2/3) \text{p}\epsilon < 7.35 \quad H_3AsO_3$$

6.97 - 9.2 check Line 8

$$\text{pH} + (1/2) \text{p}\epsilon > 7.25 \quad HAsO_4^{2-}$$

$$\text{pH} + (1/2) \text{p}\epsilon < 7.25 \quad H_3AsO_3$$

9.2 - 11.5	check Line 9
$\text{pH} + (2/3) \text{p}\epsilon > 6.6$	HAsO_4^{2-}
$\text{pH} + (2/3) \text{p}\epsilon < 6.6$	H_2AsO_3^-
11.5 - 12.1	check Line 10
$\text{pH} + (1/2) \text{p}\epsilon > 7.8$	HAsO_4^{2-}
$\text{pH} + (1/2) \text{p}\epsilon < 7.8$	H_2AsO_3^-
else	check Line 11
$\text{pH} + (2/3) \text{p}\epsilon > 6.4$	HAsO_4^{2-}
$\text{pH} + (2/3) \text{p}\epsilon < 6.4$	HAsO_3^{2-}

APPENDIX D

COMPUTER PROGRAM

```
{      Computer  Model  of  Arsenic  Transformation      }
{      In          Clay          Soil          }

Program  Transformation  ( Ini_As, Output );
Uses     Crt;
Const   Maxnumber = 100;
        Temperature = 25;
        F = 23.06;           { Faradays' Constant }
        R = 1.9872 * 0.001;  { Universal Gas Constant }
        K = 273;            { Absolute Temperature 0 C }
        n1 = 1;             { Adsorption Intensity Constant }
        K3 = 1.2;           { As(III) Adsorption Capacity Constant }
        K5 = 1.9;           { As(V) Adsorption Capacity Constant }

Type    Data =
        Record
            Formula : String;           Status      : Char;
            Initial  : Real;             Coefficient : Real;
            Soluble  : Real;             Constant    : Real;
            Adsorbed: Real;              Modification: Integer;
            Other    : Real;

        End;

        Information = Array [ 1..Maxnumber ] of Data;

Var

        Ini_As : Text;                  Species : Information;
        Porosity, Moisture, pH, Eh : Real;
        Flag : Boolean;                  X, Y : Integer;

Procedure  Introduction;                { Introduce the Program }
```

```
Begin                                { Called By Procedure 'Input_Data' }
  GotoXY (14,3);                      { Controlling Display }
  Writeln ( ' * * *   Arsenic   Transformation   Model   * * * ');
  Writeln;
  Writeln;
  Write ( ':7, 'This program is used to estimate the possible ');
  Writeln ( ' SPECIES   and');
  Writeln;
  Write ( ' AMOUNTS of Arsenic   (As)   after a specific of reaction');
  Writeln ( ' time in Clay');
  Writeln;
  Writeln ( ' soils. ');
  Writeln;
  Write ( ':7, ' The following information should be input by ');
  Writeln ( ' the user : ');
  Writeln;
  Writeln (':13, '1. Clay Soil Information ');
  Writeln;
  Writeln (':13, '2. Environmental Factors ');
  Writeln;
  Writeln (':13, '3. Initial information on Arsenic(Forms, Amounts)');
  Writeln;
  Write (':7, 'If some of these data are NOT input, the ');
  Writeln ( 'model will ');
  Writeln;
  Write ( ' generate default values based on previous experimental');
  Writeln ( ' results. ');
  Writeln;
  Write (':3, '<< Press ENTER to Continue >>');
```

End;

```

                                { Input / Import Initial As & Environ. Data }
Procedure  Input_Data ( Var  Porosity, Moisture, pH, Eh : Real;
                        Var  Species : Information );

Var  I : Integer;

Begin                                { Called By Main Program }
  Introduction;                       { Introduce the Program }
  While ( Readkey <> Chr (13) ) Do    { Controlling Cursor }
    GotoXY ( WhereX, WhereY );
  ClrScr;                             { Clear Screen }
  { --- Input Clay Soil Information and Environmental Factors --- }
  GotoXY ( 5,5 );                     { Controlling Display }
  Writeln ('1. Please input clay soil information');
  Writeln;
  Write ('':7, 'Porosity --      &');
  Writeln ('':8, '( Hint : Clay soil porosity less than 50 % )');
  Writeln;
  Write ('':7, 'Mositure --      &');
  Writeln ('':8, '( Hint : Clay soil moisture less than 25 % )');
  Writeln;
  GotoXY ( 5,13);
  Writeln ('2. Please input environmental factors');
  Writeln;
  Writeln ('':7, '(Assume soil is in standard state: 25 C, 1 atm )');
  Writeln;
  Writeln;
  Writeln ('':7, 'pH --', '':20, '( Hint: pH = 0 to 14 )' );
  Writeln;
  Writeln ('':7, 'Eh -- (volts)', '':7, '( Hint: Soil Eh = -1 to 1 )');
  GotoXY ( 21,7 ); { X := 21; Y := 7; Fix_Screen (X,Y); }
  Readln ( Porosity );

```

```
While ( Porosity > 50 ) or ( Porosity < 0 ) Do
Begin
  GotoXY ( 21,7 );
  Writeln ( '   ' );
  GotoXY ( 21,7 );
  Readln ( Porosity );
End;

GotoXY ( 21,9 );
Readln ( Moisture );
While (Moisture > Porosity) or (Moisture > 25) or (Moisture < 0) Do
Begin
  GotoXY ( 21,9 );
  Writeln ( '   ' );
  GotoXY ( 21,9 );
  Readln ( Moisture );
End;

Moisture := ( Moisture / 100 );
GotoXY ( 15,18 );
Read ( pH );
While ( pH > 14 ) or ( pH < 0 ) Do
Begin
  GotoXY ( 15,18 );
  Writeln ( '   ' );
  GotoXY ( 15,18 );
  Readln ( pH );
End;

GotoXY ( 15,20 );
Readln ( Eh );
While ( Eh > 1 ) or ( Eh < -1 ) Do
Begin
```

```

GotoXY ( 15,20 );
Writeln ( ' ' );
GotoXY ( 15,20 );
Readln ( Eh );

End;

Writeln;

Writeln;

Write (':3, '<< Press ENTER to Continue >>');

While ( Readkey <> Chr (13) ) Do      { Controlling Cursor }
    GotoXY ( WhereX, WhereY );

ClrScr;                               { Clear Screen }

{ --- End of Clay Soil Information and Environmental Factors --- }
    { --- Input arsenic information --- }

Assign ( Ini_As, 'a:Ini_As.Txt');
Reset ( Ini_As );
While Not Eof ( Ini_As ) Do
Begin
    For I := 1 to 5 Do
    With Species [I] Do
    Begin
        Readln (Ini_As, Formula);
        Readln (Ini_As, Status);
        Readln (Ini_As, Coefficient);
        Readln (Ini_As, Constant);
        Readln (Ini_As, Modification);
    End;
End;

GotoXY ( 5,3 );
Writeln ('3. Please input initial arsenic species information ');
For I := 1 to 5 Do

```

```

With Species [I] Do
Begin
  GotoXY ( 8, 6+(I-1)*2 );
  IF ( Status = 'S' ) Then
    Writeln(Formula,':',(14-length(Formula)),'(mg/ 1/1000 cubic m)')
  Else
    Writeln(Formula,':',(14-length(Formula)),'(ml/ 1/1000 cubic m)');
End;

For I := 1 to 5 Do
With Species [I] Do
Begin
  Gotoxy ( 18, 6+(I-1)*2 );
  Read ( Initial );
End;
Writeln;
Writeln;
Write ('':3,'<< Press ENTER to Continue >>');
While ( Readkey <> Chr (13) ) Do      { Controlling Cursor }
  GotoXY ( WhereX, WhereY );
  ClrScr;                               { Clear Screen }
End;                                     { --- End of arsenic information --- }

Procedure Dissolution ( Var Species:Information; Moisture:Real );
Var   I : Integer;                       { Check Dissolved / Adsorbed }
      Solubility, Temp : Real;

Begin
  For I := 1 to 5 Do
  With Species [I] Do
  Begin
    Solubility := ( Coefficient*Temperature+Constant )*Modification;
    Temp := Solubility * 1000 / 1000 * Moisture;
  End;
  End;
End;

```

```

IF ( Initial > Temp ) Then
    Soluble := Temp
Else
    Soluble := Initial;
Adsorbed := 0;
Other := 0;
IF ( Status = 'S' ) Then
    Adsorbed := Initial - Soluble
Else
    Other := Initial - Soluble;
End;
End;

Procedure Pre_Form ( Var Species:Information; pH, Eh:Real );
Var
    pE, Sum_Soluble : Real;          I : Integer;
    Predominant : String;
Begin
    pE := ( F / (2.3 * R * (K+Temperature) )) * Eh;
    IF ( (pH+pE) < 0 ) Then          { Lower water solubility boundary line }
        Begin
            IF ((pH+pE) > -4.3) Then          { Metal As / Arsine }
                Predominant := 'Metal As '
            Else
                Predominant := 'Arsine (AsH3)';
        End
    Else                               { Soluble As }
        Begin
            IF ((pH+pE) < 4.5) Then          { Oxide / Sulfide }
                Predominant := 'Arsine Sulfide '

```

```
Else                                     ( As(III) acid / As(V) acid )
Begin
  IF ( pH < 2.2 ) Then
    Begin
      IF ((pH+pE)>9.93) Then
        Predominant := 'H3AsO4 '
      Else
        Predominant := 'H3AsO3 '
      End
    End
  Else IF ( (pH > 2.2) and (pH < 6.97)) Then
    Begin
      IF ((pH+(2/3)*pE)>7.35) Then
        Predominant := 'H2AsO4(-) '
      Else
        Predominant := 'H3AsO3 '
      End
    End
  Else IF ( (pH > 6.97) and (pH < 9.2)) Then
    Begin
      IF ((pH+(1/2)*pE)>7.25) Then
        Predominant := 'HAsO4(-2) '
      Else
        Predominant := 'H3AsO3 '
      End
    End
  Else IF ( (pH > 9.2) and (pH < 11.5)) Then
    Begin
      IF ((pH+(2/3)*pE)>6.6) Then
        Predominant := 'HAsO4(-2) '
      Else
        Predominant := 'H2AsO3(-) '
      End
    End
  End
```



```

Else IF ( (pH > 11.5) and (pH < 12.1)) Then
  Begin
    IF ((pH+(1/2)*pE)>7.8) Then
      Predominant := 'AsO4(-3) '
    Else
      Predominant := 'H2AsO3(-) '
    End
  Else
    Begin
      IF ((pH+(2/3)*pE)>6.4) Then
        Predominant := 'AsO4(-3) '
      Else
        Predominant := 'HAsO3(-2) '
      End;
    End;
  End;

  End;

Sum_Soluble := 0;
For I := 1 to 5 Do
  With Species[I] Do
    Sum_Soluble := Sum_Soluble + Round(Soluble*10000)/10000;
    Species[6].Formula := Predominant;
    Species[6].Adsorbed := 0;
    Species[6].Soluble := Sum_Soluble;
  End;

Procedure Output ( Var Species : Information );
Var I : Integer;
Begin
  GotoXY ( 5, 2 );
  Writeln ( ' The arsenic transformation forms are : ' );
  GotoXY ( 8, 4 );

```

```

Writeln ( ' Forms      Adsorbed      Soluble      Gas' );
For I := 1 to 5 Do
With Species[I] Do
Begin
  GotoXY ( 9, 5+I*2 );
  Write ( Formula );
  GotoXY ( 26, 5+I*2 );
  Write ( Adsorbed:6:4 );
  GotoXY ( 46, 5+I*2 );
  Writeln ( Soluble:6:4 );
  GotoXY ( 62, 5+I*2 );
  Writeln ( Other:6:4 );
End;

Writeln;
Write ( '-----' );
Writeln ('-----');
Writeln;
Writeln ( ':8, 'Predominant soluble form is :' );
Writeln;
Writeln ( ':8,Species[6].Formula,':29,Species[6].Soluble:6:4 );
Writeln;
End;

Procedure N_K ( Ct, n, K : Real;   Var   Cs, Ce : Real );
Var   J : Integer;
      Index, Temp : Real;

Begin
  Index := Ct;
  Temp := 0;
  For J := 1 to Round(Ct*100) Do

```

```

Begin
    { LnCs -n* Ln(Ct-Cs) = LnK }
    IF (Index > ABS( Ln(J/100)- n*ln(Ct+0.0001-J/100)-ln(k))) Then
        Begin
            Index := ABS( Ln(J/100)- n*ln(Ct+0.0001-J/100)-ln(k));
            Temp := J/100;
        End;
    End;

    Cs := Temp;

    Ce := Ct - Cs;
    { Ct = Cs + Ce }

End;

Procedure Adsorption ( Var Flag : Boolean );
Var
    I, J, L : Integer;
    Decimal, Cs, Ce, Ct, Index, Temp, Ratio : Real;
    n_3, n_5, K_3, K_5 : Real;

Begin
    ClrScr;
    GotoXY ( 5, 3 );
    Writeln (':20,'Additional Checking');
    Writeln;
    Writeln (':8,'According to Freundlich isotherm ( Cs=K*(Ce)^n)' );
    Writeln;
    Writeln (':8,'Please input initial total arsenic value');
    Writeln;
    Writeln ( ': 12, 'Ct =          (mg)   ( Assume Ct > 1 mg )' );
    Writeln;
    Writeln (':8,'Please input As(III) / As(V) ratio (%)');
    Writeln;
    Writeln (':12,'As(III)          (%)');
    Writeln;
    Writeln (':12,'As(V)          (%)');

```

```
Writeln;
Write (':8,'Please input n, K value');
Writeln (':2,'( Input "999", for the default value )');
Writeln;
Writeln (':25,'As(III)',':8,'As(V)');
Writeln;
Writeln ( ': 12, 'n = ' );
Writeln;
Writeln ( ': 12, 'K = ' );
GotoXY ( 20, 9 );
Readln ( Ct );
GotoXY ( 25, 13);
Readln ( Ratio );
GotoXY ( 25, 15 );
IF ( ( Ratio - Trunc(Ratio) ) > 0 ) Then
    L := 2
Else
    L := 0;
Writeln ( (100-Ratio):2:L );
GotoXY ( 30, 21 );
Readln ( n_3 );
GotoXY ( 42, 21 );
Readln ( n_5 );
IF ( n_3 = 999 ) Then
    Begin
        n_3 := n1;
        GotoXY ( 30, 21 );
        Writeln ( n_3:2:1 );
    End;
IF ( n_5 = 999 ) Then
```

```
Begin
    n_5 := n1;
    GotoXY ( 42, 21 );
    Writeln ( n_5:2:1 );
End;

GotoXY ( 30, 23 );
Readln ( K_3 );
GotoXY ( 42, 23 );
Readln ( K_5 );
IF ( K_3 = 999 ) Then
    Begin
        K_3 := K3;
        GotoXY ( 30, 23 );
        Writeln ( K_3:2:1 );
    End;
IF ( K_5 = 999 ) Then
    Begin
        K_5 := K5;
        GotoXY ( 42, 23 );
        Writeln ( K_5:2:1 );
    End;

Writeln;

Write (':3,' << Press ENTER to Continue >>');
While ( Readkey <> Chr (13) ) Do { Controlling Cursor }
    GotoXY ( WhereX, WhereY );

ClrScr; { Clear Screen }

GotoXY ( 8, 3 );

Writeln ('The distribution of As is :');

Writeln;

Writeln;
```

```

Writeln ('':8,'Forms','':14,'Cs','':17,'Ce');
Writeln;
N_K ( Ct*(Ratio/100), n_3, K_3, Cs, Ce );
Writeln ('':8,'As(III)','':10,Cs:4:2,' (mg)','':9,Ce:4:2,' (mg)');
Writeln;
N_K ( Ct*(1-Ratio/100), n_5, K_5, Cs, Ce );
Writeln ('':8,'As(V)','':12,Cs:4:2,' (mg)','':9,Ce:4:2,' (mg)');
Writeln;
Writeln;
Flag := False;
Write ('':3,'<< Press ENTER to RETURN to DOS >>');
While ( Readkey <> Chr (13) ) Do
    GotoXY ( WhereX, WhereY );
End;
{ ..... Main Program ..... }
Begin
    TextColor ( Yellow );      { Setting Foreground Color }
    TextBackground ( Blue );   { Setting Background Color }
    ClrScr;                    { Clear Screen }
    Input_Data ( Porosity, Moisture, pH, Eh , Species ); { Input Data }
    Dissolution ( Species,Moisture ); { Calculate Species Solubility }
    Pre_Form ( Species,pH,Eh );      { Evaluate Predominant Species }
    Output ( Species );             { Modeling Output }
    Write ('':3,'<< Press ENTER to Continue or ESCAPE to Stop >>');
    Flag := True;
    While Flag Do
        Case ( Readkey ) of
            Chr (27) : Flag := False;
            Chr (13) : Adsorption ( Flag );      { Adsorption Isotherm }
        Else

```

```
        GotoXY ( WhereX, WhereY );  
  
    End;  
  
    TextBackground ( Black );           { Return to original color }  
  
    Clrscr;  
  
End.  
  
{ ..... End of Main Program ..... }  
□
```

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