CHAPTER II

LITERATURE REVIEW

2.1 Properties of arsenic

Arsenic is classified as a metalloid element, with symbol As and atomic number 33 (Table 2.1). Arsenic distributes widely in the earth' curst and present at an average concentration of 2 mg.kg^{-1}. Its properties are similar to phosphorus and antimony, with oxidation state of -3, 0, +3, +5. Its atomic weight is 74.92158, melting point is 817 °C, and boiling point is 616 °C. The chemistry of arsenic is complex and there are many difference compounds of both inorganic and organic arsenic (Gomez-Caminero *et al.*, 2001).

Arsenic usually occurs in combination with one or more elements such as oxygen, chlorine, and sulfur and is referred to as inorganic arsenic. When arsenic occurs in combination with carbon and hydrogen, it is known as organic arsenic. It is important to make a distinction between inorganic and organic acid, since the inorganic form is usually more toxic than the organic form. Moreover, the inorganic form is more mobile than the organic form (Intarakuaunvetch, 1989).

Table 2.1 Chemical properties of arsenic (Jason, 2002)

Atomic Number: 33	Density: 5.72g.ml^{-1}
Atomic Weight: 74.92 16 amu	Melting Point: 1,091 K
Electron Configuration: [Ar] $3d'^{\circ}4s^{2}4p^{3}$	Boiling Point: 886 K
Valency: 3 and 5	Heat of Vaporization: 34.76kj.mol^{-1}
Coordination Number: 2, 3, 4, 5, 6	Heat of Fusion: N/A
Atomic Radius: 1.33 A	Specific Heat: 0.33J.gK^{-1}
Ionization Potential: 9.81 V	Crystal Shape: Rhombohedral
Bonding Radius: 1.2 A	Electro-negativity: 2.18

2.2 Occurrence of arsenic in the environment

2.2.1 Natural sources

Arsenic is naturally occurring element in the earth's crust. It is found widely distributed in nature approximately $5\text{x}10^{4}$ % of the earth's crust (McGraw-Hill, 1992). Arsenic is the main constituent of more than 200 mineral species, of which about 60%

are arsenate, 20% sulfide and sulfosalts and the remaining 20% include arsenides, arsenites, oxides and elemental arsenic. The most common arsenic minerals is arsenopyirte, FeAsS, and As is found associated with many types of mineral deposits especially those including sulphide mineralization. The concentration of associated arsenic can range from a few parts per million up to percentage quantities (O'Neill, 1990).

Arsenic is widely distributed in a large number of minerals. The highest mineral concentrations generally occur as arsenides of copper, lead, silver, or gold or as the sulfide. Major arsenic containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and opriment (As_2S_3). Oxidized forms of arsenic are usually found in sedimentary deposits. The elemental oxidation state, though stable in reducing environments, is rarely found (World Health Organization, 1981). Elemental arsenic is produced by reduction of arsenic trioxide (As_2O_3) with charcoal. As_2O_3 is produced as a by-product of metal smelting operations. Mining smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Historically, use of arsenic-containing pesticides had left large tracts of agricultural land contaminated. The use of arsenic in the preservation of timber has also led to contamination of the environment (Gomez-Caminero *et al.*, 2001).

Although the values shown are generally low, mineralized zones of sulfidic ores may contain much higher concentrations of arsenic; In the atmosphere, trace amounts of arsenic contain both inorganic and organic arsenic compounds (World Health Organization, 1981). Concentration of various types of igneous rocks ranges from < 1 to 15 mg $As.kg^{-1}$ with a mean value of 2 mg $As.kg^{-1}$. Similar concentrations (< 1-20 mg $As.kg^{-1}$) are found in sandstone and limestone. Significantly higher concentrations of up to 900 mg $As.kg^{-1}$ are found in argillaceous sedimentary rocks including shale, mudstone and slates. Up to 200 mg $As.kg^{-1}$ can be present in phosphorus rocks (O'Neill, 1990).

Arsenic not only occurs in earth's crust and atmosphere, but it also presents in water. In aquatic system, arsenic occurs in both inorganic and organic forms. The main organic species, methylarsenic acid and dimethylarsinic acid, are generally present in smaller amounts than the inorganic forms, arsenite and arsenate (World Health Organization, 1981).

Bowen (1979) referred by Alloway and Ayres (1997) reported that fresh water contains arsenic concentrations ranging from 0.2-230 $\mu g.L^{-1}$, in addition, arsenic in seawater is 0.5-3.7 $\mu g.L^{-1}$. The concentrations of arsenic in unpolluted surface water and groundwater are typically in the range of 1-10 $\mu g.L^{-1}$. Elevated concentrations in surface water and groundwater of up to 100-5,000 $\mu g.L^{-1}$ can be found in areas of sulfide mineralization.

2.2.2 Anthropogenic uses for arsenic and related sources of exposure

It is mainly through natural processes that humans come in contact with arsenic. It has been estimated that in the global cycling of arsenic, natural sources of arsenic added 45,000 t $As.year^{-1}$ to the atmosphere while anthropogenic sources added 28,000 t $As.year^{-1}$. Natural weathering of rocks and minerals are also the major source of groundwater arsenic concentrations. However, arsenic has been used extensively in the past and is still quite common in a number of manufactured products, processes and wastes and may thus interact with organisms (O'Neill, 1990).

Arsenic in products most commonly occurs today in pesticides, as a wood preservative (used in combination with chromium and copper in a preservative known as CCA) and as a growth nutrient for poultry and pigs. It may also be introduced today through herbicides, desiccants and fertilizers, the latter being indirectly imbued with arsenic. Recent worldwide estimates for the above report: 8000 ton $As.yr^{-1}$ as herbicides, 12000 ton $As.yr^{-1}$ as a cotton desiccant, 16000 ton $As.yr^{-1}$ as wood preservatives, 2-4 kg $As.ha^{-1}$ as pesticides with increases of up to three times this amount if dimethylarsenic acid is used, and 10-50 mg $As.kg^{-1}$ in livestock feed (Kabata and Pendias, 1984; O'Neill, 1990).

Arsenic has historically been used in products such as pesticides included; herbicides, rodenticides, fungicides, bactericides and parasiticides, defoliants, desiccants, pharmaceuticals, catalyst, corrosion-inhibitors, tanning agents, in semiconductors and to make light emitting diodes. It has also been used in the industrial processes of smelting, alloying for hardening lead and other metals and glass manufacturing to enhance the clarity of finished products (Ashworth, 1991; Lewis, 1998).

Arsenic has been commonly used in pesticides and herbicides over the past hundred years and has only recently been reduced approximately halved during the 1970s and 1980s. Popular forms included and still include lead arsenate, used as a pesticide in orchards, and sodium arsenite, used as the herbicide for aquatic weeds and as a defoliant for seed potatoes. The most toxic arsenical products in this category due to their possession of large percentages of soluble arsenic are sodium arsenate and arsenic trioxide which are typically used as herbicides (Kabata and Pendias, 1984; O'Neill, 1990). Though the use of arsenic-containing wood preservatives as copper chromium arsenate or ammonium copper arsenate has become quite prevalent (16,000 $t.yr^{-1}$), large-scale contamination derived from these sources does not appear to directly influence soil levels significantly; Though typical levels of contamination may be significant (10-220 $mg.kg^{-1}$) in the soil adjacent to treated wood, these levels decrease to background levels within a few centimeters. Besides direct contamination of soil near treated wood, arsenic may be introduced from this source via the combustion of treated wood. Proper disposal at hazardous landfill sites is recommended (O'Neill, 1990).

Animal studies involving rats, goats and miniature pigs have shown that arsenic is an essential micronutrient causing growth retardation, and elevated mortality in these animals fed an arsenic-deprived diet. An arsenic deficiency has not been proven in humans, however, due to low intake requirements theorized at 12 $\mu g.day^{-1}$ that are difficult for humans to avoid given arsenic's ubiquity the average human dietary intake for US adults has been estimated by the Food and Drug Administration to be from 25-35 $\mu g.day^{-1}$ with approximately 90% derived from seafood (Thornton and Farago, 1997).

Small amounts of organic arsenicals (10-50 mg $As.kg^{-1}$ feed) are added to the feed of turkeys, chicken and pigs. This arsenic is excreted with little chemical change and amounts are reflected in the manure of supplemented animals with concentrations of 30-40 $mg.kg^{-1}$ dry wt. having been found. These levels do not seem to significantly affect the arsenic content of crops grown in soils supplemented with this manure. Agricultural sources of arsenic contamination in soils have resulted in the following values in ppm: 2-26 in sewage sludge, 2-1200 in phosphate fertilizers, 0.1-24.0 in limestone, 2.2-120 in nitrogen fertilizers, 3-25 in manure and 22-60 in pesticides (Kabata and Pendias, 1984; O'Neill, 1990). Arsenic and related arsenicals are also introduced as a byproduct of a number of industrial processes. The smelting of ores to extract various metals especially, in descending order of arsenic quantity, copper, lead, gold and silver is a major source of arsenic contamination. Arsenic used to be purposefully obtained via its extraction from simple As-containing minerals but its prevalence as a byproduct of smelting is to such a degree that it has become the primary process toward As-ascertainment while mineral extraction has become secondary. Levels of arsenic per various unit metal smelted have been observed at 1.5 kg As.t^{-1} Cu, 0.4 kg As.t $^{-1}$ Pb and 0.65 kg As.t^{-1} Zn produced. Arsenic contamination via wind and re-deposition surrounding a single smelter has shown 21,000 mg As.kg^{-1} at 0.28 km, 10,000 mg As.kg^{-1} at 0.08 km and 600 mg As.kg^{-1} at 8 km. In addition to the levels of arsenic contributed to the atmosphere via coal combustion, arsenic is also found in the fly ash produced by coal combustion. Typical values range from 7-60 mg.kg^{-1} with highs sometimes exceeding 200 mg As.kg^{-1}. This byproduct is often used in the reclamation of land used for sand/gravel extraction. The solubility of the arsenic contained in fly ash is critical as it determines the potential for relatively rapid reintroduction or migration. Estimates of 4% soluble arsenic were determined for fly ash in the US using a high liquid/solid ratio.

Sewage sludge may also be a considerable source of arsenic contamination dependent on an area's degree of industrialization and pollution awareness, prevention with moderate to large contributions of arsenic derived from residential runoff rinsing atmospherically deposited arsenic as well as pesticide residues into treatment plants and industrial effluents containing highly variable arsenic concentrations, with metal-industry effluents sometimes contributing significant amounts as well as smaller amounts from phosphate detergents. Sludge of the UK have shown ranges of arsenic at 0-188 mg.kg^{-1} dry weight, lending to the addition of up to 30 times the contribution of phosphate fertilizers in the first 20 cm of soil if sludge is disposed of via land distribution. However, the application of sludge in the UK results in 2.5 t As.yr^{-1} while that of phosphate fertilizer delivers 6.1 t As.yr^{-1} (O'Neill, 1990).

Tailings or gangue from mining may also be significant sources of arsenic depending on the content of the original rock from which the mining occurs. Depending on the stability of the gangue, the arsenic contained therein is susceptible to significant distribution via wind-blown dust and may result in high levels of arsenic within the proximity determined by the settling distance of the dust. Arsenic's distribution in soil depth due to contamination from a metalliferous mine, beginning with a concentration of approximately 150 ppm at 0 cm, has been shown to decrease to about 8 ppm at 25 cm where concentrations remain roughly uniform to 50 cm and then to about 3 ppm down to 100 cm (Kabata and Pendias, 1984; O'Neill, 1990). Levels of arsenic average 50mg As/kg in oil shale used in the derivation of petroleum and nearly 100% remains in the byproduct shale. The build-up of arsenic is reported to be less severe in soils than in aquatic sediments unless contamination is due to lead arsenate. Possible reasons include, in soils, the opportunity for leaching as well as the formation, via microorganism metabolism, of volatile arsenicals with access to the atmosphere and, in aquatic sediments, the inhibition of arsenic mobility due to the presence and bonding potential of hydrated iron oxides and/or sulfides as well as arsenic's propensity to sorbs to particulate matter which tends to have long residence times in aquatic systems (O'Neill, 1990).

2.3 Speciation of arsenic

Arsenic is a ubiquitous element with metalloid properties. Its chemistry is complex and there are many difference compounds of both inorganic and organic arsenic (World Health Organization, 1981). Speciation determines how arsenic compounds interact with their environment. For example, the behavior of arsenate and arsenite in soil differs considerably. Movement in environmental matrices is a strong function of speciation and soil type. In a non-absorbing sandy loam, arsenite is 5-8 times more mobile than arsenate (Jason, 2002). Soil pH also influences arsenic mobility. At a pH of 5.8 arsenate is slightly more mobile than arsenite, but when pH changes from acidic to neutral to basic, arsenite increasingly tends to become the more mobile species, though mobility of both arsenite and arsenate increases with increasing pH (Jason, 2002). In strongly adsorbing soils, transport rate and speciation are influenced by organic carbon content and microbial population. Both arsenite and arsenate are transported at a slower rate in strongly adsorbing soils than in sandy soils (Gomez-Caminero *et al*, 2001).

Under oxidizing and aerated conditions, the predominant form of arsenic in water and soil is arsenate. Under reducing and waterlogged conditions (<200 mV), arsenite should be the predominant arsenic compounds. The rate of conversion is dependent on the Eh and pH of the soil as well as on other physical, chemical and biological factors (Gomez-Caminero *et al*, 2001).

2.3.1 Inorganic arsenic

Arsenite and arsenate are the most common inorganic compounds in the environment. Arsenic being components and of sulfidic ores, is weathering to form arsenate although arsenite may be formed under anaerobic conditions. Arsenate is the predominant form of arsenic in water.

2.3.1.1 Arsenite (As(III)) and arsenate (As(V))

Arsenite of the formulas MH_2AsO_3, M_2HAsO_3, and M_3AsO_3 are known. In these formulas, M represents a univalent metal cation or one equivalent cation. The alkali-metal arsenite are freely soluble in water, the alkaline-earth arsenite are condensed arsenates or arsenite, which are salts of polyarsenic or polyarsenous acids or a corresponding *meta* acid, are known in the solid state, such as disodium hydrogen arsenate, tetrapotassium diarsenate, and potassium m-arsenate. The arsenic-oxygen-arsenic bond in these compounds has extreme hydrolytic instability. It is therefore very unlikely that any species containing an arsenic-oxygen-arsenic group can be present in aqueous media in appreciable concentration (National Academy of Sciences, 1977).

Among the different species of As(V), $H_2AsO_4^-$ is dominant in the pH range 2 to 7, $H_2AsO_4^-$ is important between pH 7 to 11. Different forms of arsenic are presented in Table 2.2 and Figure 2.1.

2.3.2 Organic arsenic

A very large number of arsenic compounds that contain one or more arsenic-carbon bonds have been synthesized. The large variety of compounds is made possible by property of arsenic atom to bond from one to five organic groups, aromatic or aliphatic. The valences not used in bonding organic group can be linked to other atoms and groups. Such compounds may contain trivalent or pentavalent arsenic atoms or be derivatives of arsenic.

Table 2.2 The common inorganic and organic arsenic compounds
[World Health Organization, (1981)]

Name	Synonyms	Formula
Inorganic arsenic, trivalent		
Arsenic(III) oxide	Arsenic trioxide Arsenous oxide White arsenic	As_2O_3(or As_4O_6)
Arsenous acid		H_3AsO_3
Arsenenous acid	Arsenious acid	$HAsO_2$
Arsenites, salts of arsenous acid		$H_2AsO_3^{-}$, $HAsO_3^{2-}$, or AsO_3^{3-}
Arsenic(III) Chloride	Arsenic trichloride Arsenous trichloride	$AsCl_3$
Arsenic(III) sulfide	Arsenic trisulfide Orpigment, auripigment	As_2S_3
Inorganic arsenic, pentavalent		
Arsenic (V) oxide	Arsenic pentoxide	As_2O_5
Arsenic acid	Orthoarsenic acid	H_3AsO_4
Arsenenic acid	Metaarsenic acid	$HAsO_3$
Arsenates, salts of arsenic acid (ortho)		$H_2AsO_4^{-}$, $HAsO_4^{2-}$, or AsO_4^{3-}
Organic arsenic		
Methylarsenic acid	Methanearsonic	$CH_3AsO(OH)_2$
Dimethylarsinic acid	Cacodylic acid	$(CH_3)_2AsO(OH)$
Trimethylarsine oxide		$(CH_3)_3AsO$
Methylarsine		CH_3AsH_2
Dimethylarsine		$(CH_3)_2AsH$
Trimethylarsine		$(CH_3)_3As$

Methylated arsenic such as methylarsenic acid (MAA), dimethylarsenic acid (DMAA), trimethylarsine oxide (TMAO), and tetramethylarsonium ion are methyl derivatived. Small amounts of methylarsenic (MMA) and dimethylarsenic (DMA) are found in water, MMA generally present at higher concentrations than DMA. Furthermore, the methyl derivatives are found to be present in aquatic organisms and may concern with arsenic detoxification process.

2.4 Arsenic in environment

Arsenic is present in all soils, and the geologic history of a particular soil determines its arsenic content. The natural arsenic content in virgin soil varies from

0.1 to 0.4 ppm. The average is about 5-6 ppm, but it varies considerably among geographic regions. Soil overlying sulfide ore deposits commonly contain arsenic at several hundred parts per million; the reported maximum is 8,000 ppm (National Academy of Sciences, 1977). This arsenic may be present in unweathered sulfide minerals or in an inorganic anion state. The most common sulfide is arsenopyrite, although arsenosulfides of almost any metal cation can be found inorganic arsenate may be bound to iron and aluminum cations or oxides to any other cation present. Figure 2.1 showed summary of important inorganic, organic, and biological forms of arsenic in the environment.

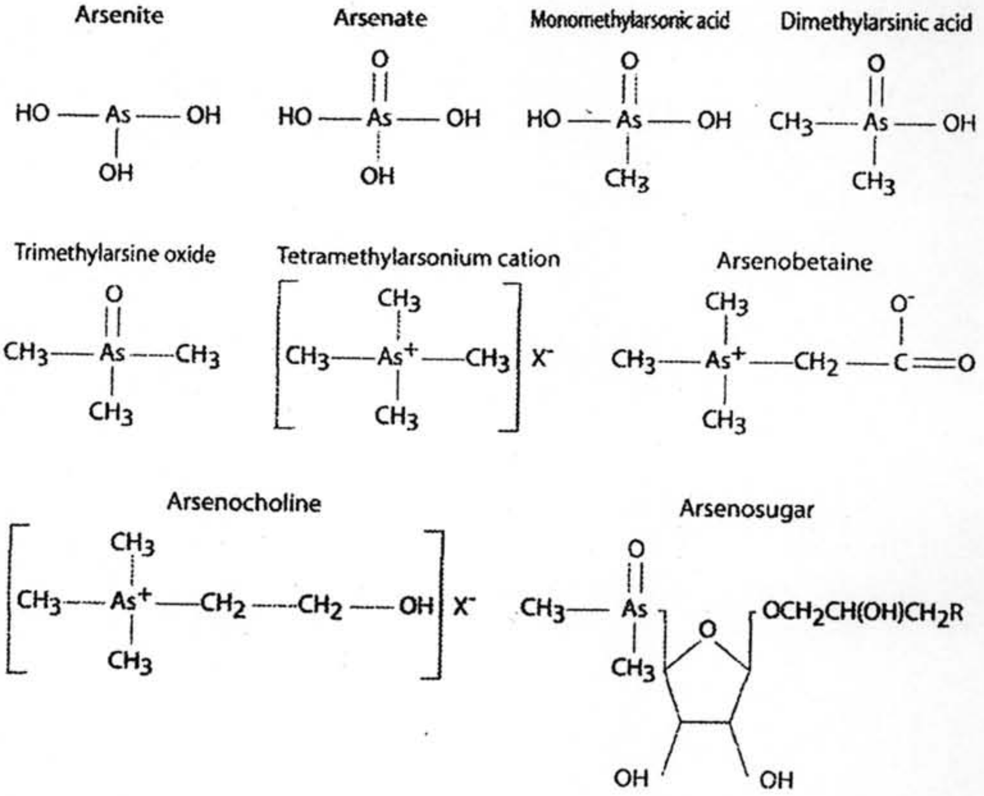

Figure 2.1 Summary of important inorganic, organic, and biological forms of arsenic in the environment (Peggy, 2006).

In guideline of World Health Organization (WHO), standard of arsenic contamination in soil (max. allowable) should not exceed 40 mg As.kg^{-1} soil (Gomez-Caminero *et al*, 2001). Arsenic (As) exists in the soil environment as arsenate, As(V), or as arsenite, As(III), both are toxic; however, arsenite is more toxic form and arsenate is the most common form (Federation Remediation Technologies Roundtable

(FRTR), 2007). The behavior of arsenate in soil seems analogous to that of phosphate because of their chemical similarity. Like phosphate, arsenate is fixed to soil, and thus is relatively immobile. Arsenite compounds are 4 to 10 times more soluble than arsenate compounds. Under anaerobic conditions, arsenate may be reduced to arsenite. Arsenite is more subject to leaching because of its higher solubility. (FRTR, 2007; Pickering *et al.*,2000)

Chemical forms of arsenic and their transformation in soil can be illustrated. Oxidation, reduction, absorption, dissolution, precipitation, and volatilization of arsenic reactions commonly occur. Mean total arsenic concentrations in air from remote and rural areas range from 0.02 to 4 ng.m^{-3}; much higher concentrations (>1,000 ng.m^{-3}) have been measured in the vicinity of industrial sources, although in some areas this is decreasing because of pollution abatement measures. Concentrations of arsenic in open ocean seawater are typically 1-2 μg.L^{-1}. Arsenic is widely distributed in surface freshwaters, and concentrations in rivers and lakes are generations in rivers and lakes are generally below 10 μg.L^{-1}. Although individual samples may range up to 5 mg.lit^{-1}near anthropogenic sources. Arsenic levels in groundwater average about 1-2 μg.lit^{-1} except in areas with volcanic rock and sulfide mineral deposits where arsenic levels can range up to 3 mg.kg^{-1}. Mean sediment arsenic concentrations range from 5 to 3000 mg/kg, with the higher levels occurring in areas of contamination. Background concentrations in soil range from 1 to 40 mg.kg^{-1}, with mean values often around 5 mg.kg^{-1}. Marine organisms normally contain arsenic residues ranging from < 1 to more than 100 mg.kg^{-1}, predominantly as organic arsenic species such as arsenosugar (macro-algae) and arsenobetaine (invertebrates and fish). Background arsenic concentrations in freshwater and terrestrial biota are usually less than 1 mg.kg^{-1} (fresh weigh). Terrestrial plants may accumulate arsenic by root uptake from the soil or by adsorption of airborne arsenic deposited on the leaves. Arsenic levels are higher in biota collected near anthropogenic sources or in areas with geothermal activity. Some species accumulate substantial levels, with mean concentrations of up to 3,000mg.kg^{-1} at arsenical mine sites (Gomez-Caminero *et al.*, 2001).

2.5 Arsenic environmental transportation and distribution

Most environmental transformations for arsenic appear to occur in the soil, in sediments, in plants and animals and in zones of biological activity in the oceans. Biomethylation and bioreduction are probably the most important environmental transformations of the element, since they can produce organometallic species that are sufficiently stable to be mobile in air and water. There major mode of arsenic biotransformation has been found to occur in the environment: redox transformation between arsenite and arsenate, the reduction and metheylation of arsenic, and the biosynthesis of organoarsenic compounds. These is biogeochemical cycling of compounds formed there processes (Gomez-Caminero *et al.*, 2001).

2.5.1 Arsenic in rock

Arsenic is generally uniformly distributed throughout major rock types. Most Igneous rock possesses arsenic concentrations ranging from <1-15 mg.kg^{-1}, with an overall average of 2 mg.kg^{-1}. Sedimentary rocks, especially finer grained argillaceous rocks; shale, mudstones and slates tend to contain much higher concentrations, ranging from <1- 900 mg.kg^{-1}. Arsenic is commonly found where iron or sulfide deposits exist. Arsenic has a propensity to bind to sulfur ligands and form precipitates. Consequently, arsenic precipitates of Fe and S may occur at elevated levels in sedimentary rock, in iron deposits and sedimentary iron ores, and in many mineralized areas. It is also in high concentration in manganese nodules. Arsenic has been shown to possess low organic affinities in various coal samples, though it was found in all organic fractions of the coal (Kabata and Pendias, 1984; O'Neill, 1990; Thornton and and Farago, 1997).

2.5.2 Arsenic in coal

Coal is a result of the accumulation and slow decay of plant remains in sedimentary strata. It undergoes *in situ* compaction under water with time, accompanied by biochemical processes such as decomposition due to bacterial action, dehydration, loss of volatile compounds (e.g. methane, higher hydrocarbons, carbon dioxide and nitrogen) and densification to form various ranks of coal depending on environmental conditions. In absence of atmospheric oxygen, the plant matter is further degraded by the action of anaerobic bacteria, which extract and utilize oxygen from organic molecules containing oxygen like lignin.

Arsenic, one of the potentially hazardous trace elements, is usually concentrated in the sulphidic minerals of coal. Many authors interpret the arsenic accumulation in terms of arsenic concentration during decay of plant matter in the humic layers. The arsenic content of coal samples worldwide is highly variable, with an average value around 5 $mg.kg^{-1}$ and extreme high values of up to 35,000 $mg.kg^{-1}$.

Since organic arsenic compounds are characteristic of living organisms, the question arises how they emerged in coal samples. Organic matter in coal originates from plants, which in general contain very little arsenic. Although arsenic compounds are rather stable under laboratory conditions, the stability of organic arsenic compounds under the harsh conditions during coal genesis is rather unlikely - even minor decomposition would result in total degradation of organoarsenic compounds over a period of millions of years. Purely abiogenic synthesis of organoarsenic compounds in an environment very rich in carbon in combination with long time periods and elevated temperatures can also not be excluded as suggested by fish for an oil shale environment (Mingshi *et al.*, 2005).

Arsenic in bituminous coal occurs primarily in pyrite and, to a lesser extent, in organic portions of the coal. A small fraction of this arsenic is emitted during coal combustion. Arsenic in coal occurs in two different forms, which vary depending upon the rank of the coal. In bituminous coals, arsenic occurs in the mineral pyrite, where it substitutes for sulfur in the pyrite structure. In lower-rank coals, arsenic occurs as part of an oxygenated complex. Under coal combustion flame conditions, both forms of arsenic can vaporize in the hot portions of the combustor. It then may undergo several additional transformation processes as the post-combustion gases cool. These processes include persistence as a vapor throughout the combustor and the air pollution control device, heterogeneous condensation on the surface of existing fly ash particles, dissolution in the alumino-silicate ash particles to form highly non ideal solution, heterogeneous chemical reaction with compounds on the surface of existing fly ash particles, and, ultimately, partition between the vapor phase and particulate fly ash.

Coal fired power stations are one of the largest anthropogenic contributors of trace elements to the environment. There is a growing environmental concern over the emissions, deposition, and management of the toxic trace elements released during combustion of coal. Trace elements in coal are present in very small concentrations of several parts per million, which can accumulate over time, if not managed in a sustainable way. Their occurrence and concentration vary between coals, primarily because of the geological variety of individual coal basins. Understanding their mobility, accumulation, and speciation is of vast importance as the specific compounds of the trace metals may have significant environmental impacts on human health and ecosystems. The oxidation state of the trace elements can determine its level of toxicity and carcinogenic potency. Therefore, speciation of the trace metals in coals and their combustion products is important for conducting comprehensive risk assessment of the trace metal emissions from coal based power plants and to further project their sustainable management options (Mingshi *et al.*, 2005).

2.5.3 Arsenic in water

There are many studies on the molecular forms of arsenic compounds in seawater have been reported into the concentration ratio arsenite/arsenate which is variable. The presence of arsenite compounds is the result of some reductive activity, which could be either biological or non-biological effect of dissolved organic matter on arsenate. The finding of methylarsenic acids in seawater and fresh natural water is evidence that arsenic goes through reactions other than simple oxidation or reduction. In both sea and fresh water, the occurrence of methylarsenic compounds is associated with phytoplankton activity. In fresh water, the level of methylarsenic compounds were especially high in locations where nutrients from fertilizers (presumably, also containing arsenic) had built up in lakes and ponds. Nevertheless, Sediment samples from two natural water environments did not unusually large amounts of methylarsenic compounds (World Health Organization, 1981).

Unpolluted freshwater typically ranges from 1-10 $\mu g.L^{-1}$ of arsenic. Levels may increase to 100-5000 $\mu g.L^{-1}$ near areas of high sulfide mineralization or up to $35 mg.L^{-1}$ in areas associated with hydrothermal activity. Under oxidizing conditions, arsenic exists in its pentavalent (arsenate) forms (above), high most reducing conditions, (acidic or mildly alkaline), Trivalent (arsenite) species, $HAsO_2$, dominate. The concentration of arsenic in solution depends on its co-precipitation with Fe, Ba, Co, Ni, Pb, and Zn. Arsenic sorbs to suspended particulate matter. Irrigation with water containing high levels of arsenic may increase soil levels via the build up of arsenic left behind as the water evaporates. This process has led to the increase of arsenic from 26 to150 µg.L^{-1} in a shallow aquifer. Similar to the reduction of arsenicals in soils, the shift in oxidation state in aqueous systems is a slow process, and species that do not correspond to given Eh/pH values may be found (O'Neill, 1990; Thornton and Farago, 1997). Figure 2.2 shows typical cycling and speciation of arsenic under different parameters in an aquatic system.

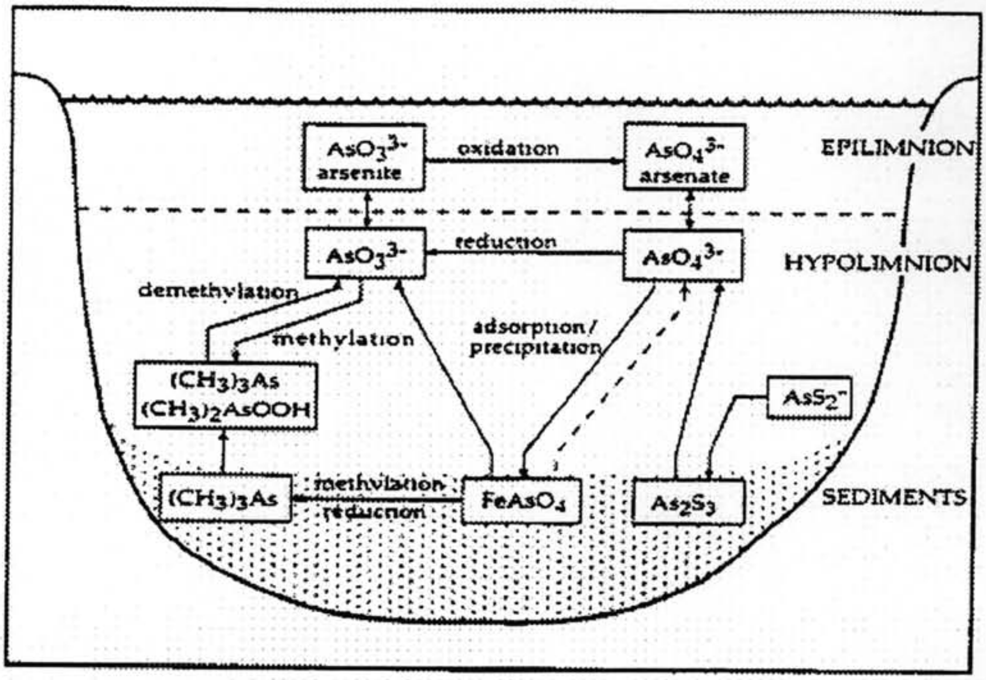

Figure 2.2 Arsenic speciation and cycling in an aquatic environment (Ringwood, 1996, refer by Jason, 2002)

2.5.4 Soil system

Parent materials underlying bedrock and weathered materials from other areas are the primary sources of arsenic in soil. The process of weathering may free arsenic from rock in the form of arsenious acid and arsenic acid salts. Generally, soils contain higher levels of arsenic than rocks (Kabata and Pendias, 1984; O'Neill, 1990). Unpolluted soils typically contain from 1- 40 mg.kg^{-1} of arsenic. Sandy soils and soils derived from granite may have lower concentrations while alluvial and organic soils may have much higher levels. The roasting of arsenic-containing sulfide ores and the burning of arsenic-containing coal leads to the emission of arsenic trioxide gas. The gas reacts with basic atmospheric oxides, such as alkaline earth oxides, to form arsenates that redeposit to the earth. Arsenic binds to ligands other than oxygen in soils, giving it stability when combined with a number of elements. In aerobic environments, ferric arsenate precipitates in soils. Soils containing the weathered products of pyrite have been observed to contain arsenic up to several hundred $mg.kg^{-1}$ via sorption to secondary iron oxides. Bauxites high in iron have shown As_2O_3 levels up to and above 500 $mg.kg^{-1}$ (O'Neill, 1990; Thornton and Farago, 1997).

Trivalent forms of arsenic tend to predominate in reducing soil conditions. However, the reduction of arsenate (+5) to arsenite (+3) is slow and soil levels may be under kinetic control. The pentavalent forms of arsenic acid (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$ and AsO_4^{-3}) predominate at normal soil pH values of 4-8. Eh values of less than +300 mV at pH = 4 and –100 mV at pH = 8 (in the absence of complexing species and methylating organisms) tend toward the thermodynamic stability of arsenous acid (H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{-2}$) of the trivalent oxidation state. Similar to the reduction of arsenicals in soils, the shift in oxidation state in aqueous systems is a slow process, and species that do not correspond to given Eh/pH values may be found (O'Neill, 1990; Thornton and Farago, 1997). Figure 2.3 summarizes arsenic speciation in soil under various combinations of redox potential and pH.

Inorganic arsenicals may also change oxidation states (solely or in combination with the inorganic processes described above) via metabolism by soil microorganisms, including yeasts and bacteria. This metabolism occurs on the surfaces of soil particles or suspended particles in aqueous environments. Resulting products under aerobic conditions may be monomethylarsonic acid ($CH_3AsO(OH)_2$), dimethylarsinie acid (or cacodylic acid, $(CH_3)_2AsO(OH)$) and trimethylarsenic oxide ($(CH_3)_3AsO$), and under anaerobic conditions, volatile and highly toxic and flammable methylarsine gases: trimethylarsine ($(CH_3)_3As$) and dimethylarsine ($(CH_3)_2AsH$). (Trimethylarsine gas is spontaneously flammable in air (Chapman *et al.*, 1984).

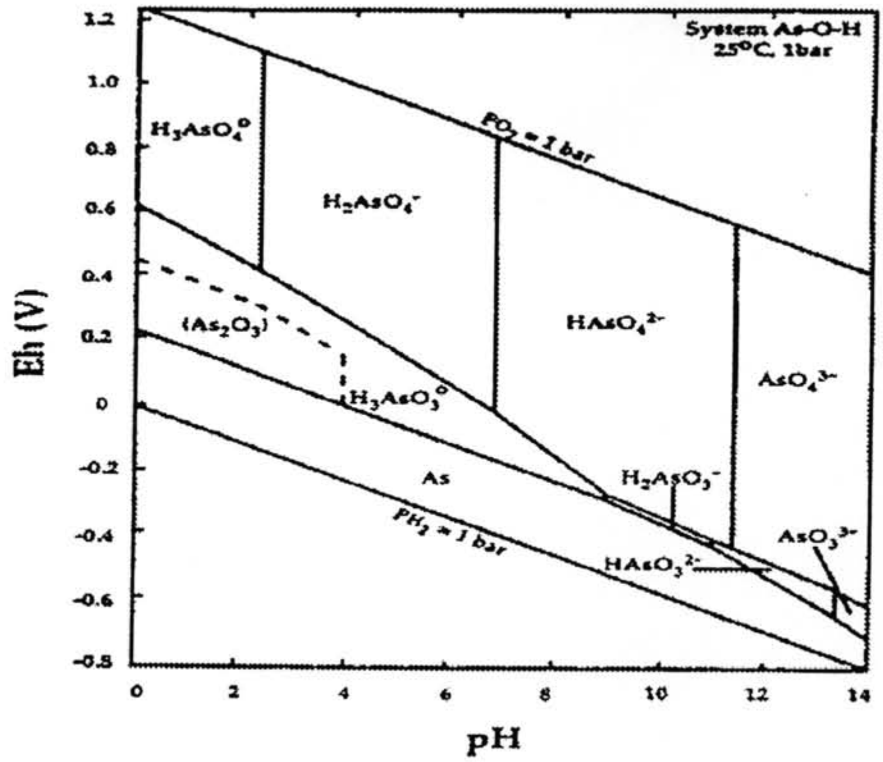

Figure 2.3 Arsenic stability diagram for 25 °C, 1 atmosphere (Ringwood, 1996, refer by Jason, 2002).

This biomethylation, however, depends on the microorganisms, soil conditions and arsenic species present. Some microorganisms can methylate a wide variety of arsenicals within a broad range of pH values while others are much more limited in their methylating capacity for various arsenicals at varying pH values (Kabata and Pendias, 1984; O'Neill, 1990; Thornton and Farago, 1997).

Clay minerals, organic matter and the presence of iron and aluminum oxides interfere with arsenic's oxidation rates and solubility and, consequently, leaching rates. Vice versa, arsenic's oxidation states largely govern its soil reactions with the above factors. Mobility is dependent on the stability of the parent minerals and the electrochemical properties of the elements involved. Reducing environmental conditions are shown to allow arsenic medium mobility with variable potential. Strongly adsorbed arsenic in soils is unlikely to ever become desorbed, with accumulation occurring over time. Arsenic absorbed to Fe and Al is the exception to this, becoming available if these soils are hydrolyzed with the reduction of soil potential.

Studies regarding the sorption mechanisms for arsenate and arsenite upon soil minerals have theorized three main mechanisms. One mechanism, predominantly with Fe and Al oxides, involves the entire surface of the oxides having bonding sites with uniform attraction toward arsenicals. This surface attraction may explain a small percentage of total bound arsenic (for example, up to 0.5 mmol As(III).g^{-1} $Fe(OH)_3$). A second mechanism may explain larger percentages by the ability of hydrated arsenic ions to freely diffuse throughout loose and hydrated Fe and Al compounds (for example, greater than 50mmol As(V).g^{-1} $Fe(OH)_3$). Soil pH values are critical for these mechanisms in terms of sorption capacity, with maximum sorption at pH = 4 for pentavalent arsenicals ($H_2AsO_4^-$ the dominant species) and pH 7 for trivalent arsenicals as H_3AsO_3. Overall, pentavalent arsenicals have shown a greater capacity for sorption than trivalent arsenicals. A third theory has been used for soils containing a diversity of mineral types, each with their own attraction energies and quantities of surface hydrated oxides of Fe, Mn and Al. Humic acids also possess sorptive abilities toward arsenic with maximum sorption of pentavalent arsenicals occurring at pH = 5.5 and that of trivalent arsenicals at higher pH values with a more varied relationship with regard to humic acid type. Monomethylarsonates are sorbed to soil components similarly to pentavalent arsenicals while dimethylarsinates are less strongly sorbed.

Arsenic in the presence of sulfide in soils at low redox potentials tends to form arsenic sulfide minerals, however, it is rare for soils to possess sulfides as they are rapidly leached out as sulfate due to the tendency for soils to possess high redox potentials. This is not the case in aqueous sediments where lower redox potentials allow for the presence of sulfide that can form the precipitate As_2S_3 in the presence of arsenic. These precipitates are susceptible to greater solubility in the form of oxidized sulfates if water is drained and sediments are aerated. Generally, arsenic sorption is directly inversely proportional to soil particle size, in that as particle sizes decrease, arsenic sorption increases. Arsenic concentrations of some acid sulfate soils in Canada have shown concentrations in the clay at 4 times the amount in the silt fraction.

It is important to note that our knowledge of the properties of trace heavy metals in soils, including arsenic, is far from complete and much conflicting or perplexing evidence exists from studies and from what has been observed in nature. Much uncertainty remains as to the ultimate fate of arsenic given any soil. A complete and universal understanding of microbial methylation as well as arsenic's mobility from solid to gaseous phase and solid to solution phase does not exist (Kabata and Pendias, 1984; O'Neill, 1990)

2.5.5 Arsenic in air

Arsenic is emitted into the atmosphere by high temperature processes such as coal-fired power generation plants, burning vegetation and volcanism. Natural low-temperature biomethylation and reduction to arsines also release arsenic into the atmosphere. Arsenic is released into the atmosphere primarily as As_2O_3 and exists mainly adsorbed on particulate matter. These particles are dispersed by the wind and are returned to the earth by wet or dry deposition. Arsines released from microbial sources in soils or sediments undergo oxidation in the air, reconverting the arsenic to non-volatile forms, which settle back to ground. Dissolved forms of arsenics in the water column include arsenate, arsenite, methylarsonics acid (MMA) and dimethylarsinic acid (DMA). In well-oxygenated water and sediments, nearly all arsenic is present in the thermodynamically more stable pentavalent state (arsenate). Some arsenite and arsenate species can inter-charge oxidation state depending on redox potential (Eh), pH and biological processes. Some arsenic species have an affinity for clay mineral surfaces and organic matter and this can affect their environmental behavior. There is potential for arsenic release when there is fluctuation in Eh, pH, soluble arsenic concentration and sediment organic content. Weathered rock and soil may be transported by wind or water erosion. Many arsenic compounds tend to adsorb to soils, and leaching usually results in transportation over only short distances in soil (Gomez-Caminero *et al.*, 2001).

Atmospheric arsenic is thought to make up a substantial portion of the global arsenic cycle due to the high volatility of various arsenicals. Thirty-five percent of atmospheric arsenic is estimated to be derived from low temperature volatilization, making this process the primary contributor to atmospheric arsenic concentration. However due to the affinity of arsenic to particulate matter; it is estimated that only 7% of atmospheric arsenic exists in the gaseous phase while the remainder is associated with the particulate phase. Several varying atmospheric estimates have been made, the most recent of which maintains an overall arsenic load of 73,540 ton $As.yr^{-1}$ with a ratio of natural to anthropogenic sources of 60:40. Other estimates have reported 18800 ton $As.yr^{-1}$, 31,400 ton $As.yr^{-1}$ with a ratio of 25:75 and 296,470 ton As.yr^{-1} with a ratio of 70:30. Volcanic activity is the second-leading natural contributor to atmospheric arsenic. Anthropogenic sources are dominated by copper smelting making up 40% of the total, followed by the combustion of coal with 20%. These two sources vary widely in relation to a population's degree of industrialization coupled with that country's natural arsenic content of the copper ore and coal deposits, as well as their efficiency in pollution control. Overall atmospheric deposition of arsenic in rural areas has been estimated at 0.8-5.5 mg.m^{-2}.yr^{-1}. Given an average deposition rate of 1.0 mg.m^{-2}.yr^{-1}, an average soil content of 10 mg.kg^{-1}As and a soil density of 1.4 g.cm^{-3}, the average increase in mass due to arsenic is estimated at 0.15% in the first 5 cm of soil in these areas with a value of 0.1% annually after being corrected for subsequent losses to volatilization. The world mass increase average due to deposition using these figures has been estimated at 0.05% for the Northern Hemisphere and 0.02% for the Southern Hemisphere (O'Neill, 1990).

2.5.6. Arsenic in plants

The tissue of edible plants reflects low levels of arsenic, often at or below the limits of detection, even when grown in arsenic-contaminated soils. Overall, however, arsenic uptake is specific to plant specie. Plants grown in smaller particle soils in clays and silts with higher clay-mineral and Fe/Al contents will contain less arsenic than when grown in larger particle soils i.e. sands or sandy barns when all soil types contain the same arsenic concentrations. This trend follows that of the soil characteristics described above in that smaller particles and Fe/Al oxides sorb arsenic more strongly than in other instances. Plant uptake of arsenic may bypass the soil-root route by absorption through foliage of airborne, arsenic-containing residues from arsenic-pesticides, however, overall plant concentrations remain low (O'Neill, 1990).

Though quantities of arsenic uptake vary widely relative to species, arsenic levels in terrestrial plants are generally much lower than that of their soils, while some aquatic macrophytes may accumulate arsenic levels similar to that of their sediments that concentrations over 1000 mg As.kg^{-1} fresh weight have been observed. Grasses inhabiting piles of arsenic-contaminated up to 26,530 mg.kg^{-1} spoil piles from old arsenic mines in England have shown arsenic levels up to 3,460 mg.kg^{-1} dry weight and those in some urban soils at 20 mg As.kg^{-1} possessed levels at 3 mg As.kg^{-1} dry weight. Crops grown in dredged spoil at 8 mg As.kg^{-1}showed the following results in descending order of relative concentration factors obtained on a dry weight comparison; radish; 1.0 > grass; 0.33 > lettuce; 0.26 > carrot; 0.17 > potato tuber; 0.07 > spring wheat grain; 0.04. Arsenic uptake is also dependent on arsenic species. Studies with bean roots have shown the following uptakes in descending order with the species most assimilated: arsenate > arsenite > monomethylarsonate > dimethylarsinate. It is theorized that arsenic uptake is performed passively with the uptake of water (Kabata and Pendias, 1984; O'Neill, 1990).

Arsenic available to plants tends to increase at pH values of 5.5 and below, corresponding to acidities in which Fe and Al oxides become more soluble, however, there is evidence to support increased arsenic uptake in lettuce grown in higher pH soils. Arsenic values were 3-4 times higher in lettuce grown in soil with a pH = 8 than in pH 6. Arsenic's phytotoxicity is largely dependent on plant specie mainly the specie's ability to translocation arsenic to less sensitive areas or decrease absorption, soil characteristics and water availability. Translocation moves arsenic throughout the plant i.e. from plant to grain and occurs throughout plant tissues, but the highest concentrations in plants grown in highly contaminated soils exist in older leaves and roots. Five different sources have labeled concentrations of arsenic as "phytotoxically excessive" at 50, 25, 30, 20 or 15 ppm dry weight. Beans are one of the most sensitive plants to arsenic. Due to the low assimilation of arsenic in terrestrial plants from their soils, arsenic uptake in vegetative consumers is also low and most of the arsenic ingested by grazing livestock is derived directly from the ingestion of the soil itself (Kabata and Pendias, 1984; O'Neill, 1990).

2.6 Effects of arsenic on human and on other organisms in the environment

The concentration of arsenic in soil varies widely, generally ranging from about 1 to 40 parts of arsenic to a million parts of soil (ppm) with an average level of 5 ppm. However soils in the vicinity of arsenic-rich geological deposits, some mining and smelting sites, or agricultural areas where arsenic pesticides had been applied in the past may contain much higher levels of arsenic. The concentration of arsenic in natural surface and groundwater is generally about 1 $\mu g.L^{-1}$ but may exceed 1,000 $\mu g.L^{-1}$ in mining areas or where arsenic levels in soil are high. In guideline of World Health Organization (WHO), arsenic concentration in drinking water should not exceed 0.05 $mg.l^{-1}$. Besides, Environmental Protection Agency has also established a maximum contaminant level of 0.05 $mg.l^{-1}$.

Arsenic in drinking water set by countries and other organizations are variable to harmful of arsenic, many governmental organizations in Thailand have also allowed arsenic contaminated in drinking water should not more than 0.05 $mg.l^{-1}$. Arsenic contamination not only is determined in drinking water standard, but it also is set for food. In Thailand, Ministry of Public Health has established arsenic contaminant level of 2 $mg.l^{-1}$ in food (Jutithepharak *et al.*, 1988).

Non-occupational human exposure to arsenic in the environment is primarily though the ingestion of food and water. Of these, food is generally the principal contributor to the daily intake of total arsenic. In some areas arsenic in drinking-water is a significant source of exposure to inorganic arsenics. The daily intake of total arsenic from food and beverages is generally between 20 and 300 $\mu g.day^{-1}$. In workplaces with up-to-date occupational hygiene practices, exposure generally dose not exceed 10 $\mu g.m^{-3}$ (8-h time-weighted average (TWA)) (Gomez-Caminero *et al.*, 2001).

2.6.1. Toxicology

Arsenic toxicity is largely dependent on the concentration of soluble arsenic in the environment; sorbed arsenic is largely unavailable. Each arsenical possesses a different level of toxicity and a hierarchy of toxicity exists among them. Arsenic in its gaseous state, arsine gas, is the most toxic and trivalent arsenicals are more toxic than pentavalent arsenicals. Of its trivalent forms, arsenic trioxide (As_2O_3) predominates in nature, while the other compounds (salts or arsenious acid) are more toxic. Due to its insolubility in water, and, thus, bodily fluids, the metallic form of arsenic is thought to be nontoxic, and the toxicity of organic forms is low (Goldfrank, 1994; Lippmann, 2000).

Arsenic can be absorbed through gastro-intestinal (GI), respiratory, and dermal routes. Solubility greatly affects the absorption of inorganic arsenic salts. The absorptive rate exceeds 80-90% for most trivalent and pentavalent arsenicals according to human and animal studies. Chronic exposure may occur in populations through drinking water supplies with higher levels more likely in areas with higher concentrations of arsenic in the soil or air. Symptoms include hyperkeratosis that localized overgrowth of the outermost layer of skin, white striae of the cutica, cardiovascular irregularities, myocardial ischemia that is inadequate blood supply to the heart, hypertension, liver dysfunction, hematological changes, blackfoot disease, Raynaud's syndrome that is abnormal spasms of blood vessels causing diminished blood supply (MedTerms, 2007), skin epithelima, and other cancers (Lippmann, 2000).

Chronic ingestion of low levels of arsenic yields high concentrations in the hair, nails and skin, tissues rich in the amino acid cysteine. Chronic accumulation also occurs in lungs, heart, uterus, skin, bone, muscle and in the fetus, as arsenic is trans-placentic. Dermal absorption through intact skin into the body is minimal but prolonged topical exposure may cause skin irritation, which may promote systemic absorption. Mucous membrane absorption can be significant and administration via enema has resulted in finality. Chronic arsenic exposure via inhalation may result in lesions to the skin and mucous membranes, as well as alterations of the nervous and respiratory systems. Ultimately, lung cancer may result. The metabolism of inorganic arsenicals occurs via methylation. Each subsequent methylated product is less reactive and easier to eliminate from the body via renal excretion due to higher water solubility and lower lipid solubility. Miniscule amounts of arsenic arc eliminated via sweating and skin. Trivalent and pentavalent arsenicals possess different mechanisms of toxicity. Primarily, trivalent arsenic (As(III)) inhibits the citric acid cycle and final adenosine triphosphate (ATP) production. This ability suggests that primary poisoning from acute exposure is due to the rapid cessation of organ function. The toxicity of arsenate (As(V)) is due in part from its transformation to arsenite (As(III)) in the body, however it works to decrease ATP production also. Treatments for arsenic poisoning include dialysis and the administration of chelating agents such as British antilewisite (BAL or $C_3H_5OS_2$) (Goldfrank, 1994; Lippmann, 2000).

2.6.2. Carcinogenicity and teratogenicity

The carcinogenicity of arsenic has not been conclusively established and its role in carcinogenesis has not been defined. Laboratory studies utilizing rodents have consistently yielded higher incidences of pulmonary tumors and/or carcinomas and lymphocytic leukemia and malignant lymphomas. In humans, epidemiological studies have shown inorganic arsenic to be carcinogenic, showing higher incidences of respiratory, skin and liver cancers and correlations to neoplasms of the lymphatic and hematopoietic tissues and cancers of the GI tract (Opresko, 1992; Lippmann, 2000).

The contradictions (not discussed here) between the results of animal and human studies indicate that arsenic is a co-carcinogen rather that a primary carcinogen. Pentavalent arsenic has been shown to inhibit host-resistance factors, possibly increasing the chances of developing cancer due to other agents. Cancer susceptibility may also be increased via DNA repair inhibition due to As or a theorized depletion of selenium concentrations in the body. Teratogenic effects have not been extensively studied but exposures to arsenic have been correlated with a variety of fetal effects in ewes and hamsters. Teratogenic effects have not been exhibited in humans (Lippmann, 2000).

2.6.3. Genotoxicity and mutagenicity

Arsenic has shown genotoxic effects in many bacterial cells, demonstrating strong clastogenic (causing breaks in chromosomal compounds (CancerWEB, 2007) effects that exhibit damage to DNA synthesis and DNA itself. Positive results were obtained with $NaAsO_2$, As_2O_4, $AsCl_3$, As_2O_3, and the organoarsenical dimethyldithiocarbamate, while other organic arsenicals, such as sodium methyl arsenate and calcium methyl arsenate, showed negative results. Non-bacterial studies determined that non-lethal doses of AsO_2^- had clastogenic effects in mammalian somatic cells. There exists a linear dose-response curve for both trivalent and pentavalent arsenic for total chromosomal aberration frequency (Lippmann, 2000).

2.7 Phytoremediation

Phytoremediation is the direct use of living green plants for *in situ*, or in place, risk reduction for contaminated soil, sludge, sediments, and ground water, through contaminant removal, degradation, or containment. Growing and, in some cases, harvesting plants on a contaminated site as a remediation method is an aesthetically pleasing, solar-energy driven, passive technique that can be used to clean up sites with shallow, low to moderate levels of contamination. This technique can be used along with or, in some cases, in place of mechanical cleanup methods (U.S. Environmental Protection Agency,1998).

Phytoremediation of metals is a cost-effective "green" technology based on the use of specially selected metal-accumulating plants to remove toxic metals, including radionuclides, from soils and water. Phytoremediation takes advantage of the fact that a living plant can be compared to a solar driven pump, which can extract and concentrate particular elements from the environment. The metals targeted for phytoremediation include lead, cadmium, chromium, arsenic and various radionuclides. The harvested plant tissue, rich in accumulated contaminant, is easily and safely processed by drying, ashing or composting and disposing in landfill. The volume of toxic waste produced as a result is generally a fraction of that of many current, more invasive remediation technologies, and the associated costs are much less. Some metals can be reclaimed from the ash, which further reduces the generation of hazardous waste and generates recycling revenues. This new technology can be used to clean up metals, pesticides, solvents, explosives, crude oil, polyaromatic hydrocarbons, and landfill leachates. Phytoremediation has been studied extensively in research and small scale demonstrations, but full-scale applications are currently limited to a small number of projects (Raskin, 1994; U.S. Environmental Protection Agency, 1998).

Arsenic is removed from soil by moving up into plant roots, stems, and leaves. The plant is then harvested and disposed of and the site replanted until the arsenic in the soil is lowered to acceptable level.

2.7.1 Phytoremediation can be used to clean up contamination in several ways (Ellen *et al.*, 2005):

Phytovolatilization:

Plants take up water and organic contaminants through the roots, transport them to the leaves, and release the contaminants as a reduced of detoxified vapor into the atmosphere.

Microorganism stimulation:

Plants excrete and provide enzymes and organic substances from their roots that stimulate growth of microorganisms such as fungi and bacteria. The microorganisms in the root zone then metabolize the organic contaminants.

Phytostabilization:

Plants prevent contaminants from migrating by reducing runoff, surface erosion, and ground-water flow rates. "Hydraulic pumping" can occur when tree roots reach ground water, take up large amounts of water, control the hydraulic gradient, and prevent lateral migration of contaminants within a ground water zone.

Phytoaccumulation/extraction:

Plant roots can remove metals from contaminated sites and transport them to leaves and stems for harvesting and disposal or metal recovery through smelting processes.

Phytodegradation by plants:

Organic contaminants are absorbed inside the plant and metabolized (broken down) to non-toxic molecules by natural chemical processes within the plant.

2.7.2 The advantages of phytoremediation

The advantages of using metal accumulating plants to remove arsenic from contaminated soil as follows (Raskin, 1994)

1. Plants can transform toxic arsenic forms to less or non-toxic forms
2. Low cost to work and maintenance
3. Ability to treat contaminated areas *in situ*
4. Ability to apply with other treatment technologies

2.7.3 The suitable plants for remediation of heavy metals should have the following characteristics:

1. High metal accumulated in their shoot
2. High biomass especially in shoot
3. Widely distribution and can grow in high metal contaminated land
4. Short life span and life cycle
5. High propagation
6. High growth rate

2.7.4 Uptake of arsenic by plants

The uptake of arsenic by plants was studied in various plants. In common with most trace elements, the degree of uptake varies widely from species to species. The degree of uptake and concentration of arsenic species absorbed by bean roots was arsenate > arsenite > monomethylarsenate > demethylarsinate, with toxicity being directly proportional to the root concentration (O'Neill, 1990). Besides, the uptake of arsenic and other heavy metals by chosen crops was studied by (Tlustos *et al.*, 1997) that showed the difficulties to get positive effect of remediation treatment application in soil neutral in pH, high clay and organic matter content. Figure 2.4 showed phytoremidiation of Arsenic in plant

In addition, there is data indicates that when each soil type contains similar As concentrations, lower level are found in plants grown on clays and silts with their higher clay mineral and Fe/Al oxide content, than in plants growing on lighter soils such as sands or sandy loam (O'Neill, 1990).

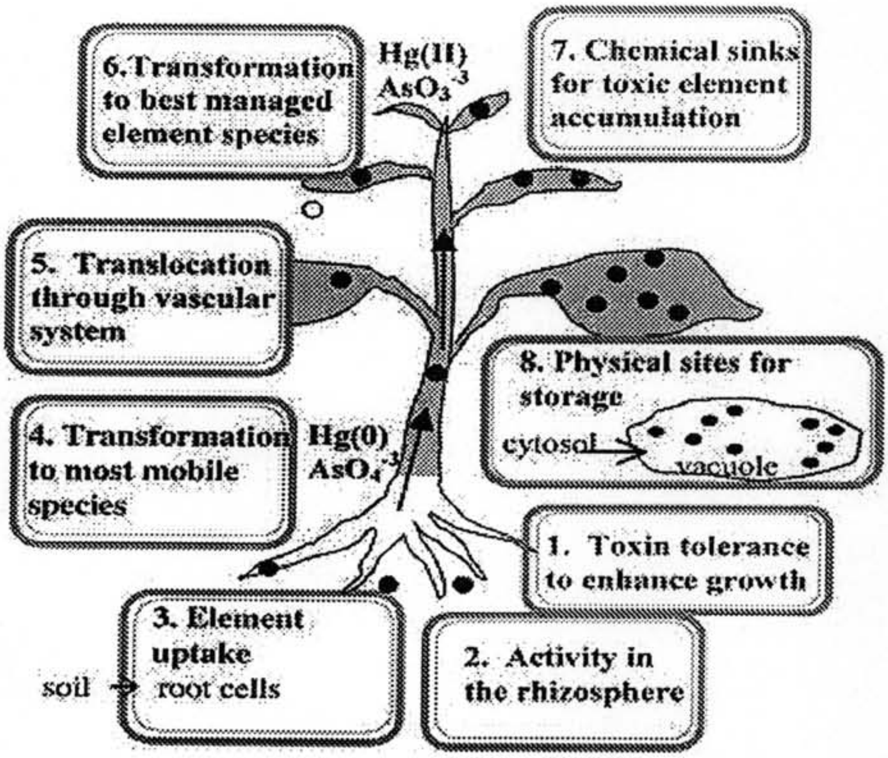

Figure 2.4 Phytoremediation of arsenic in plant (Meharg and Hartley-Whitake, 2002).

2.7.5 Arsenic and plants relationship

Arsenic is chemically similar to phosphorus, an essential plant nutrient; it behaves very much like phosphate in the plant-soil system that it can substitute for phosphorus in plant nutrition, but it is phytotoxic. Arsenate can enter into reactions in place of phosphorus, thereby becoming a toxicant. There is strong evidence that arsenate is normally absorbed in a manner similar to the phosphate uptake mechanism (National Academy of Sciences, 1977; Bieleski and Ferguson, 1983; Nriagu, 1994).

Arsenic is ubiquitous in the plant kingdom. The concentration varies from less than 0.01 to about 5 ppm (dry-weight basis). Differences in arsenic content probably reflex species differences in plants and, in larger sence and environment in a particular geographic region. Plants growing in arsenic- contaminated soils generally have higher residues than plants grown in normal soils. Arsenic concentrations are less than 5.0 ppm (dry weight) or 0.5 ppm (fresh weight) for untreated vegetation. Whereas treated plants may have much higher concentrations. However, values for some non-treated plants are as high as or higher than those of plants that were treated with arsenic or grown in arsenic- contaminated soil. Natural variations among plants, plant species, available soil arsenic, and growing conditions are all responsible in part for these discrepancies. There appears to be little chance that animals would be poisoned by consuming plants that contain arsenic residues from contaminated soils, because plants injury occurs before toxic concentrations could appear. Arsenic accumulates in plants growth on soils contaminated by arsenic is not readily translocated to shoots, most is found in the roots. In order for plant levels to reach 1 mg $As.kg^{-1}$ on a fresh weight basis, soil levels must exceed 200-300 mg $As.kg^{-1}$ (Aten *et al.*, 1980; National Academy of Sciences, 1977).

The relationship between the soil arsenic and growth of plants depends on the forms and availablility of the arsenic. The toxicity of arsenic varies with its form and valencies, its toxic order being AsH_3 > As (III) > As(V) > organic As (National National Academy of Sciences, 1977; Nriagu, 1994).

Arsenite and arsenate are the major forms of arsenic in toxication and these anions are readily taken up by plants (Schmoger and Grill, 2000). The bioaccumulation of arsenic by plants may provide a means of removing this element from contaminated soil and water (Pickering *et al.*, 2000). According to the data from which studied the biochemical fate of arsenic taken up by Indian mustard (*Brassica* *juncea*), suggest that arsenate enters the roots as a phosphate analog possibly via the phosphate transported mechanism and is promptly reduced to arsenite. And little arsenic is transported to the aboveground tissues, but the addition of the arsenic chelator dimercaptosuccinate to the hydroponic growth solution caused significant amounts of arsenic to move into the shoot, perhaps offering a way of removing arsenate from contaminated soil (Pickering *et al.*, 2000).

When arsenic in solution penetrates the cuticle and enters the apoplast system (the nonliving cell-wall phase), it bathes external surface of the plasmolemma of the symplast. This is the location of at least some of the enzymes of the living plant. One of the first symptoms of injury is wilting, caused by loss of turgor, and this immediately suggests an alteration in membrane integrity. Reactions of trivalent arsenic with sulfhydryl enzymes could well explain the effects of membrane degration- injury and eventually death. In general, arsenates are less toxic than arsenites. The arsenate symptoms involve chlorosis, but not rapid loss of turgor (at least in the early expression of toxicity), and the contact action of the arsenates is more subtle. Arsenate is known to uncouple phosphorylation. Thus, the couple phosphorylation of adenosine diphosphate (ADP) is abolished, the energy of adenosine triphosphate (ATP) is not available, and the plant must slowly succumb (National Academy of Sciences, 1977).

2.8 *Canna* sp.

***Canna* sp.** (or **Canna lily**, although not a true lily) is a genus of nineteen species of flowering plants, the only genus in the family Cannaceae. The plants are large tropical and subtropical perennial herbs with a rhizomatous rootstock. The broad, flat, alternate leaves, that are such a feature of this plant, grow out of a stem in a long narrow roll and then unfurl. The leaves are typically solid green but some cultivars have glucose, brownish, maroon, or even variegated leaves. The three sepals and three petals are seldom noticed, they are small and hidden under extravagant stamens. What appear to be petals are the highly modified stamens or staminodes. The staminodes number (1–) 3 (–4) (with at least one staminodal member called the labellum, always being represented. A specialized staminode, the stamen, bears pollen from a half-anther. A somewhat narrower, 'petal' is the pistil which is connected down to a three-chambered ovary. The flowers are typically red, orange, or yellow or any combination of those colours, and are aggregated in inflorescences; in spikes, clusters, or in panicles (thyrses). The wild species often grow to 2-3+ meters but there is a wide variation in size among cultivated plants; numerous cultivars have been selected for smaller stature. *Canna* sp. grow from swollen roots, correctly known as rhizomes, which store starch, and this is the main attraction of the plant to agriculture, having the largest starch particles of all plants (Wikipedia Encyclopedia, 2007). Figure 2.5 showed *Canna* sp.

Figure 2.5 *Canna* sp.

2.9 *Cyperus papyrus* (L.)

Family name: Cyperaceae Common names: Papyrus (Eng.); Papirus (Afr.); the bulrush of the Bible. *C. papyrus* is a stately aquatic member of the sedge family. The plants are easily cultivated and suitable for medium to large water features, especially in warmer climates. The most conspicuous feature of the plants are the bright green, smooth, rounded culms (flowering stems) which are up to 40 mm thick at the base and may be up to 5 m tall in ideal conditions. Each is topped by a dense cluster of thin, bright green, shiny stalks, which resemble a feather duster when young. The stalks elongate later and bend gracefully downward under their own weight so that the cluster becomes almost spherical in shape. During summer these stalks bear small brown spikelets (groups of flowers) and eventually numerous tiny dark brown fruits are borne in the axils of glumes (tiny scales). The culms are connected by stout horizontal rhizomes which creep along the substrate under water and are anchored by numerous roots. The younger parts of the rhizome are covered by red-brown, papery, triangular scales, which also cover the base of the culms and represent reduced leaves. It is therefore incorrect to describe the plants as leafless. Similar brown papery structures (termed bracts) occur at the tops of the culms below the clusters of thin stalks (Wikipedia Encyclopedia, 2007).

Papyrus is estimated to range from subtropical to tropical desert to wet forests, tolerating annual temperatures of 20-30°C and pH of 6.0 - 8.5. Papyrus flowers in late summer, and prefers full sun to partly-shady conditions. Like most tropical plants, it is sensitive to frost. Figure 2.6 showed *C. papyrus* (L.).

Figure 2.6 *Cyperus papyrus* (L.)

2.10 *Colocasia esculenta* (L.)

This plant, commonly known as Elephant-ear, grows well at either high or low altitude, in swamp, marshes, and other muddy shallow water areas. Optimum growth occurs in hot, humid areas. This large shore plant grows in riprap areas of reservoirs .The plant will reach 3-7 feet or 1-2 m tall with leaf blades reaching up to 2 feet or 60 cm long, but occasionally reaches a height of over 2-m under ideal conditions. It is a showy plant for use around water features. The flower is a spathe that grew to 15 inches 35 cm long. Its large stiff leaves, 40-90 cm long, are thick in texture, ovate with a cordate base, and always peltate (Sripen, 1992).

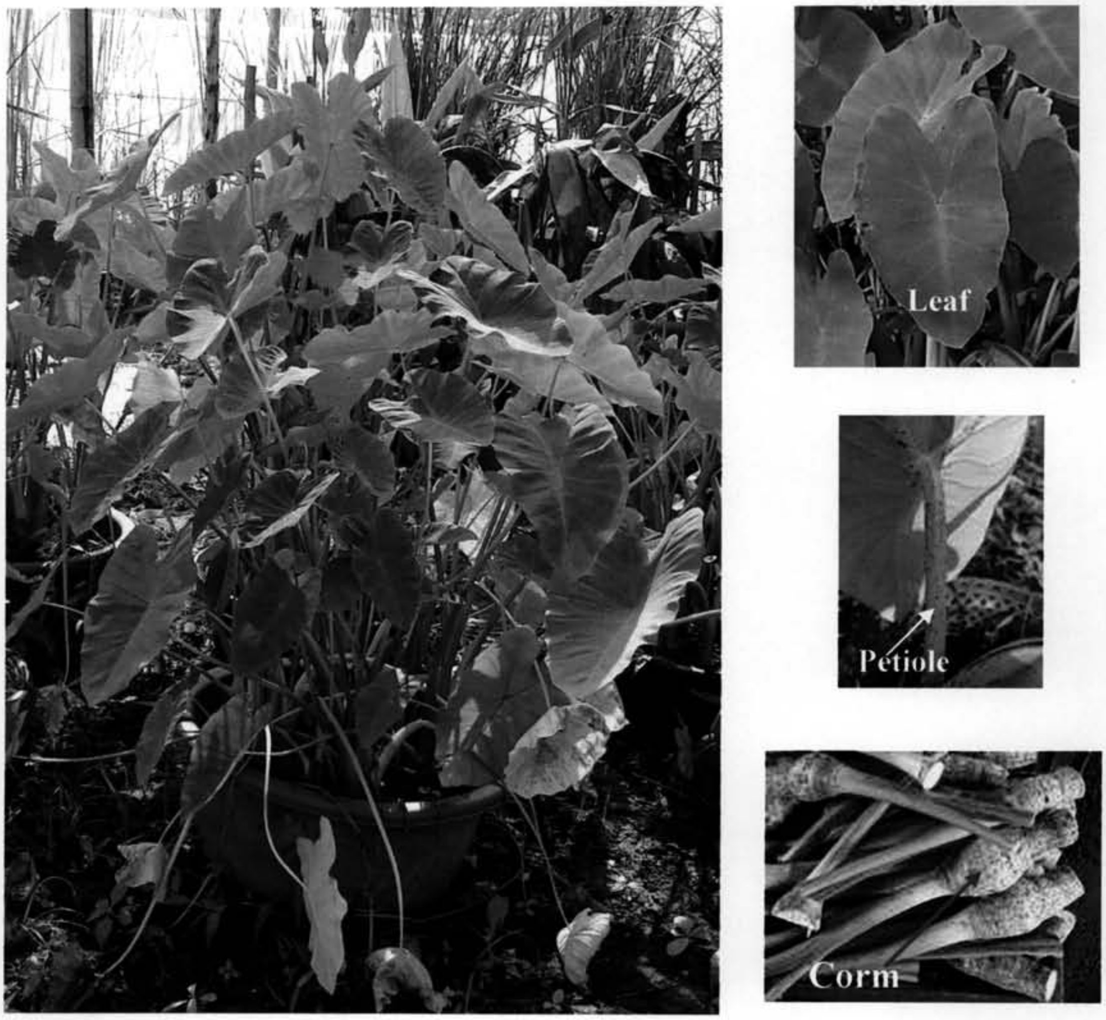

Figure 2.7 *Colocasia esculenta* (L.)

The inflorescence is much shorter than the petioles with the staminate flowers occupying the upper three-quarters and pistillate flowers the lower quarter section of a short cylindric crowded spedix. The pale yellow spathe is ovatelanceolate shaped usually with enrolling margins. The fruit of elephant-ear is an oblong berry containing numerous viable seeds. Reproduction also occurs by the production of stolons (Steve, 2007).

C. esculenta need full sun to partial shade, with a rich, well-drained soil and abundant water. In the greenhouse, using a soil mix with equal parts of peat moss, loam and sand, or per lit. The tubers are planted 3-5 inches or 7 to 13 cm deep and should be at least 4 feet or 1.2 m apart. The plants should be kept moist at all times and fertilized weekly during the growing season. When grown near aquatic settings, they can be planted in several inches of water and will spread quite quickly. Plants grown in containers need to be re-potted on a yearly basis or at the end of the growing season. The tuber should be lifted and stored for the winter. Figure 2.7 showed *C. esculenta* (L.).

2.11 *Typha angustifolia* (L.)

Typha is a genus of about eleven species of monocotyledonous flowering plants in the monogeneric family, Typhaceae. Cattails or bulrushes are wetland plants, An erect, rhizomatous, semiaquatic or aquatic, perennial herb, typically 1 to 7 m tall, but *T. minima* is smaller: 0.5-1 m, with spongy, strap-like leaves and starchy, creeping stems (rhizomes) (Wikipedia Encyclopedia, 2007).

Leaves are erect, linear, flat, basal, very narrow, and flattened; ¼"-½" wide and 3'-6' tall and 12-16 leaves arising from each vegetative shoot. Stems are stout, erect, 3'-6'. Rhizomes are stout, produced at the leaf base, up to 27" in length and typically ¾"-1½" in diameter. Flower is structure a dense, fuzzy, cylindrical spike on the end of stem, with a distinct gap of 1"-3" of naked stem between the upper, male portion or staminate and the lower, female or pistillate portion. Both male and female sections are roughly the same length. Male flowers lighter brown; female flowers often green during bloom turning dark brown during seed maturation; individual blossoms minute and closely packed on spike. Bloom May-June. Fruits are cigar-shaped and 2"-6" long, with soft, downy seeds. Seed is a tiny nutlet, about 1 mm long, with downy hairs underneath (Earl, 2007).

Almost anywhere soil remains wet, saturated, or flooded most of the growing season, including. wet meadows, marshes, fens, pond and lake margins, floating bog mats, seacoast estuaries, roadside ditches, irrigation canals, oxbow lakes, and backwater areas of rivers and streams. Tolerates have continuous inundation, seasonal drawdown, and brackish waters. Where Common Cattail and Narrow Leaf Cattail are found together, they are frequently segregated by water depth, with Common Cattail found in shallow water and Narrow Leaf Cattail in deep water, usually more than 2½' deep. A dominant component of early is successional stages in wetlands. It rapidly colonizes exposed wet mineral soils, as it produces an extremely high number of wind and water dispersed seeds. It is also an early successional species occupying the water's edge on floating bog mats. In some situations with constant water levels, maintains relatively stable communities. Forms dense are nearly single species communities in shallow, freshwater marshes (Earl, 2007). Figure 2.8 showed *T. angustifolia* (L.).

Rhizome

Figure 2.8 *Typha angustifolia* (L.)

2.12 There are 6 parts of literature that related to the research. There are as follows;

There was the study on variation in arsenic accumulation-hyperaccumulation in fern and their allies. A range of fern species (45) and their allies, *Equisetum* and *Selaginella* species and *Psilotum nudum* were screened for their ability to hyperaccumulate arsenic. *Pteris* genus, which is not hyperaccumulate arsenic, *Pteris straminea*, and *tremula* (Andrew, 2003).

Arsenic in wetland vegetation was studied on available, phytotoxicity, uptake and effects on plant growth and nutrition. In wetland surface sediments of Louisiana, arsenic concentration is elevated because of cotton desiccants and of organic arsenicals as herbicides in rice-producing areas, and petroleum hydrocarbon recovery operations. The uptake, potential bioavailable and phytotoxicity of As to an important wetland plant species, *Spartina alterniflora* are grown in hydroponic conditions. Arsenic carsenicals and MMAA were mainly accumulated in roots, while DMAA was readily translocated to shoots. Arsenic chemical form and concentration significantly affected macro- and micro-nutrient concentration in plant tissue (Carbonell *et al.*, 1998).

2.12.1 Phytoremediation of arsenic

In New Zealand, Watercress is consumed as a vegetable, The Waikato river and some other aquatic systems in Taupo volcanic zone, have elevated arsenic concentrations due to geothermal activity. Robinson *et al.*, (2003) studied about uptake of arsenic by New Zealand watercress (*Lepidium sativum*). Arsenic concentrations were above the WHO limit. It is recommended that watercress from the Waikato river, or other areas with elevated water arsenic concentrations, should not be consumed.

In the Kemerovo region, Russia, The uptake of heavy metals, As, and Sb by aquatic plants growing in industrial collection ponds of metal mining industry was studied. Cu, Pb, Cd, Zn, As, and Sb are the major pollutants in these plant habitats. Analysis of fresh platyphyllous cattail acid extracts has demonstrated that As and Sb present a serious threat to human and animal health, as they are capable of entering food chains in large amounts (Hozhina *et al.*, 2001).

2.12.2 Translocation and transformation of arsenic in plants

The research conducted on arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. Elevation of arsenic levels in soils causes considerable concern with respect to plant uptake and subsequent entry into wildlife and human food chains. Arsenic speciation in the environment is complex, existing in both inorganic and organic forms, with inter-conversion between species regulated by biotic and abiotic processes. To understand and manage the risks posed by soil arsenic it is essential to know how arsenic is taken up by the roots and metabolized within plants (Andrew and Whitaker, 2003).

Entering the root, arsenic can be translocated to different parts of plant. Most studies are more concerned with accumulation of arsenic in agricultural products. (O'Neill,1990). In general roots contain higher level than stem, leaves or fruit (Tlustos *et al.*, 1998), also indicated that roots were the dominant part in arsenic uptake. The transformation from arsenate to arsenite resulted in monomethylarsenic acid and dimethylarsinic acid being present due to microbial activity, in addition, the transformations indicated by microorganism in the highly contaminated soil lead to detoxification.

Weihua *et al.* (2001) studied arsenic speciation and distribution in an arsenic hyperaccumulating plant. Phytoremediation, an emerging, plant based technology for the removal of toxic contaminants from soil and water, has been receiving renewed attention. Speciation and distribution of arsenic in the plant can provide important information helpful to understanding the mechanisms for arsenic accumulation, translocation, and transformation. The results of this study demonstrate the ability of Brake fern (*Pteris vittata*) as an arsenic hyperaccumulator. It transfers arsenic rapidly from soil to aboveground biomass with only minimal arsenic concentration in the roots. The arsenic is found to be predominantly as inorganic species; and it was hypothesized that the plant uptakes arsenic as arsenate (As(V)) and arsenate was converted to arsenite (As(III)) within the plant.

2.12.3 Effects of phosphorus for arsenic uptake

The development of proteoid roots under phosphorus deficiency by white lupin (*Lupinus albus*) may result in increase arsenate uptake, as arsenate is a phosphate analogue. This together with its high biomass product, rapid growth and ability to survive in soil with low phosphate and nitrogen contents, low pH and high metal contents make them an interesting species to investigate with respect to revegetation, and possibly also for long-term phytoremediation, of arsenic contaminated soils (Elvira *et al.*, 2003).

Arsenic contaminated soil and water vary with pH and concentrations of arsenic and phosphorus for hyperaccumulator *Pteris vittata L.* to optimize plant growth and maximize arsenic removal from contaminated sites, especially water. Plant biomass and uptake of P and arsenic were impacted by all the three factors. The fern had a relatively high biomass and P uptake at low pH/low arsenic or high pH/high arsenic. The results suggested that optimum plant growth could be achieved by adjusting pH corresponding to As levels in the growth media, and maximum plant As hyperaccumulation by maintaining minimum P concentrations with medium $pH \leq 5.21$ (Tu and Ma, 2003).

2.12.4 Total arsenic and arsenic speciation analysis

A new system is for the spectrophotometric determination of arsenic in environmental and biological samples was proposed for the determination of traces of arsenite. The method involves bleaching of the pinkish red colored dye, Rhodamine-B, by the action of iodine which is released by the reaction between potassium iodate and arsenic in slightly acidic medium (Ajai, *et al.*, 2000).

Analytical methods for inorganic arsenic in water were reviewed. Inorganic arsenic, a term which encompasses both As (III) and As (V) species, constitutes the highest toxicological risk associated with arsenic in water in contrast to the organic arsenic species. Different determination methods of inorganic arsenic have been developed over 40 years providing timely and efficient risk assessments of inorganic arsenic contamination world wide (Hung *et al.*, 2004).

Overview of speciation chemistry of arsenic; studied on the speciation of arsenic in environmental and biological samples are a subject of current interest. Because of the low level of arsenic species in real samples and many problems related with its speciation remain unresolved (Kumaresan and Riyazuddin, 2001).These studies, which have been approached in many different ways, would lead to knowledge that is determinant in the understanding of the cycle of this element in the environment and of its physiological and toxicological behavior in the living organisms. Sueli and Maria, (2001), investigated about selective reduction of arsenic species by hydride generation-atomic absorbtion spectrometry and sample storage and arsenic determination in natural waters. Total arsenic, arsenite, arsenate, and dimethylarsinic acid (DMA) were selectively determined in natural waters by hydride generation-atomic absorption spectrometry, using sodiumtetrahydroborate(III) as reductant but in different reduction media.

Considerable analytical progresses have been made toward arsenic speciation analysis over the last decade. Hyphenated techniques involving a highly efficient separation and a highly sensitive detection have become the techniques of choice. The methods based on high-performance liquid chromatography separation with inductively coupled plasma mass spectrometry, hydride generation atomic spectrometry, and electrospray Mass Spectrometry detection have been shown most useful for arsenic speciation in environmental and biological matrices (Zhilong *et al.*, 2002).

2.12.5 Effect of arsenic for human and environment

There was a report on arsenic toxicity and accumulation in turnip (*Lycopersicum esculentum*), arsenic affected by arsenic chemical speciation. Arsenic uptake by turnip, growing under soil less culture conditions, was studied. Both organic arsenicals showed a higher upward translocation than their inorganic counterparts, contributing to the greater phytotoxicity and lower dry matter productions of these organic treatments. If turnip plants are exposed to a large pulse of arsenic, as growth on contaminated nutrient solutions, they will accumulate residues at levels that are unacceptable for animal and human consumption (Angel *et al.*, 1999).

Effects on and Accumulation by tomato plants, the uptake of arsenic species by *Lycopersicum esculentum,* growing under soil less culture conditions, was studied. The phytoavailablility and phytotoxicity were primarily determined by the arsenic species. Both MA and DMA showed a higher upward translocation than arsenite and arsenate, and treatments with MA and DMA clearly reduced plant growth and fruit yield. When tomato plants are exposed to high concentrations of arsenic in nutrient solutions, they may uptake arsenic to the concentrations unacceptable for human food (Burlo *et al.*, 1999).

2.12.6 Arsenic study in Thailand

Efficiency of arsenic removal from contaminated soil by *Vetiveria zizanioides* and *Vetiveria nemoralis* were studied (Dhitivara, 2000). This studied in difference concentration of arsenic and it was found that growth of both species was not affect by arsenic. In addition, *V. zizanioides* had number of plants per clump and diameter of clump *V. zizanioides* than of *V. nemoralis*. In contrast, the height and dry weight of *V. nemoralis* was higher than *V. zizanioides*. Accumulation of arsenic in roots was higher than in leaves. Amount of arsenic accumulation in *V. zizanioides* was more than in *V. nemoralis*. In addition, arsenic removal efficiency by two species increased by exposed time.

The remediation measure taken by government was to drill deep wells and extract clean water from limestone at 50 m deep hydrologists, environmental scientists and chemists from the Department of Mineral Resources also investigated the possibility of arsenic removal from soil and groundwater (Intrasuta, 1991).

Efficiency of arsenic removal from soil by *C. esculenta* (Dark violet and green) was investigate growth rate of *C. esculenta* in arsenic contaminated soils, to determine the level of arsenic accumulation in parts of *C. esculenta*, and to compare arsenic removal efficiency from soil by *C. esculenta.* The efficiency of both *C. esculenta* was not different; in addition, all parts of the experiment can survive under arsenic concentration ranged from 0-150 mg.As.kg^{-1}.Consequently, *C. eculenta.* are more appropriate for Thailand and should be recommended for soil improvement in case of arsenic contamination (Jampanil, 2000).

Phytoextraction of arsenic from contaminated soil by *C. esculenta*; (taro and wild taro) were studied and compared the accumulation of arsenic in *C. esculenta* among different concentrations of arsenic in soil and study the efficiency of ethylenediaminetetraacetic acid (EDTA) solution to enhance the accumulation of arsenic in both plant species. The results indicate that both plants could grow well in concentration of 100 and 200 mg.As.kg^{-1}soil. Amount of arsenic accumulated in root was more than in corm, petiole, and lamina, respectively. And the research shows that the accumulation of arsenic in both plants can be enhanced through the application of EDTA to the soil (Tambamroong, 2002).

The potential of Thai indigenous plant species for the phytoremediation of arsenic contaminated land was studied by Visoottiviseth *et al.* (2002). To assess the potential of the native plant species for phytoremediation, plant and soil samples were collected from two areas in Thailand that have histories of arsenic pollution from mine tailings. The areas were the Ron Phibun District, Nakorn Si Thammarat province) and Bannang Sata District, Yala province, and samples were taken in 1998 and 1999 and analysis for total arsenic by atomic absorption spectrophotometry. Arsenic concentrations in soil ranged from 21 to 14,000 $\mu g.g^{-1}$ in Ron Phibun, and from 540 to 16,000 $\mu g.g^{-1}$ in Bannang Sata. The criteria used for selecting plants for phytoremediation was: high arsenic tolerance, high bioaccumulation factor, short life cycle, high propagation rate, wide distribution and large shoot biomass.

A new broke out that people in some villages of Ron Phibun, Nakhon Sri Thammarat Province were suffering from Bowen's disease or basal cell cerinoma or simply known as skin cancer. Drinking arsenic contaminated water causes this disease. The symptoms among the disease are recognized as spots on skin, palm and sole which are prevalent among the people in 12 villages and vicinity areas of tin mines. Results of investigation showed that the arsenic in water came from dissolution of arsenopyrite accumulated in placer deposits and water from ore dressing plants by floatation process. Arsenic contamination covered a broad area, more or less following the pathways of both surface and groundwater flows. Thus, high concentrations of arsenic can be found in soil, plants, and in water from dug wells. However, the disease is not contagious and providing clean water can do protection (Budinas *et al.*, 1987).

Environmental fluxes of arsenic from lignite mining and power generation in northern Thailand was investigated. The excavated lignite, fly ash, stream sediment and surface water survey were carried out to determine the arsenic distribution in the mining area. Arsenic-rich overburden waste and fly ash pile are scattered throughout the lignite mining area and these have increase the nearby streams. Arsenic concentration was highest in residual part of the stream sediments. The highest arsenic concentration were 515 $mg.kg^{-1}$ in borehole lignite, 312 $mg.kg^{-1}$ in fly ash, 5,213 $mg.kg^{-1}$ in reservoir bottom sediment, 325 $\mu g.l^{-1}$ in mine sump water, and 8 $\mu g.l^{-1}$ in Mae Moh reservoir water (Vladimir and Kanitta, 2002).