

SPECIATION AND TOTAL DETERMINATION OF ARSENIC, CHROMIUM
AND SELENIUM IN FRESHWATER BODIES SEDIMENT

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*To my beloved husband and parent whose endless love and support
helped me get through all the obstacles.
Little Sufi and Faris;
always remind mama to work hard and achieve high.*

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ABSTRACT

Arsenic (As) is generally known for its toxicity while chromium (Cr) and selenium (Se) at the appropriate amount are essential elements to man and becomes quite toxic in excessive amount. Anthropogenic activities such as industrialization, agricultural and urbanization have led to the contamination of toxic elements into aquatic that finally end up in the sediment system. Environmental process such as diagenetic process causes the toxic elements to migrate from the bedrock materials into the sediment surface and lastly into the water column. This process has been recognized to be the factor of As contamination in well water in several countries such as Bangladesh, Taiwan, USA and Canada. A number of samples of freshwater sediments from identified rivers and lakes in Johor Bharu area had been analyzed to determine the concentration level of As, Cr and Se using neutron activation analysis (NAA) technique. Certified reference material (CRM) namely IAEA Soil-7, Marine Sediment Reference Material BCSS-1 and PACS -2 were applied to provide good quality assurance control during analysis. The results obtained show that the concentrations of As in the rivers and lakes sediment fall between 10 to 34 $\mu\text{g g}^{-1}$ and 18 to 62 $\mu\text{g g}^{-1}$, respectively. The concentrations of Cr in the rivers ranged between 27 $\mu\text{g g}^{-1}$ to 125 $\mu\text{g g}^{-1}$, while in the lake sediments the concentrations ranged between 173 $\mu\text{g g}^{-1}$ to 301 $\mu\text{g g}^{-1}$. The river sediment showed the Se concentration ranged between 0.56 $\mu\text{g g}^{-1}$ to 1.91 $\mu\text{g g}^{-1}$ and in lake sediment the concentration ranged between 0.31 $\mu\text{g g}^{-1}$ to 1.08 $\mu\text{g g}^{-1}$. The results of the As, Cr and Se concentrations were then compared to the 'background value' proposed by National Oceanic and Atmospheric Administration (NOAA), USA and several sediment quality guidelines. The As, Cr and Se concentrations were also correlated and normalized to iron content in order to evaluate and estimate the degree of contaminant enrichment in sediments. For speciation study, the inorganic species of As(III), As(V), Se(IV) and Se(VI) were studied by extracting the sediments using the microwave at the optimized time and power setting in the mild concentration of acid media. The As(III) and As(V) were preconcentrated and separated by ammonium pyrolydinedithiocarbamate (APDTC) into methyl isobutyl ketone (MIBK) while the Se(IV) and Se(VI) were separated after co-precipitation of sodium dibenzylidithiocarbamate (Na-DBDTC) with phenolphthalein. The efficiencies of all extraction procedures were determined using standard solutions and several CRM. The results showed that As(V) and Se(VI) were the dominant species in the river and lake sediments.

ABSTRAK

Arsenik (As) telah diketahui umum akan ketoksikannya sementara kromium (Cr) dan selenium (Se) pada amoun yang berpatutan merupakan unsur keperluan kepada manusia dan menjadi toksik pada amoun yang berlebihan. Aktiviti pencemaran seperti perindustrian, pertanian, perbandaran telah mendorong kepada pencemaran unsur toksik ke dalam akuatik yang akhirnya terkumpul dalam sistem enapan. Proses sekitaran seperti proses diagenetik menyebabkan unsur toksik bergerak dari bahan dasar ke dalam permukaan enapan dan akhirnya ke dalam turus air. Proses ini dikenalpasti sebagai faktor pencemaran As di dalam air telaga di beberapa negara seperti Bangladesh, Taiwan, Amerika dan Kanada. Beberapa sampel enapan sekitaran air tawar dari beberapa sungai dan tasik yang dikenalpasti di kawasan Johor Bharu telah dianalisis untuk menentukan kepekatan As, Cr dan Se menggunakan teknik analisis pengaktifan neutron. Bahan rujukan piawai antaranya, *IAEA Soil-7*, *Marine Sediment Reference Material BCSS-1* dan *PACS -2* telah digunakan untuk memberi kawalan kualiti jaminan yang baik semasa analisis. Keputusan yang diperolehi menunjukkan kepekatan As di sungai dan tasik masing-masing ialah 10 hingga 34 $\mu\text{g g}^{-1}$ dan 18 hingga 62 $\mu\text{g g}^{-1}$. Kepekatan Cr di sungai berjulat antara 27 $\mu\text{g g}^{-1}$ hingga 125 $\mu\text{g g}^{-1}$ manakala kepekataannya di dalam enapan tasik berjulat antara 173 $\mu\text{g g}^{-1}$ hingga 301 $\mu\text{g g}^{-1}$. Kepekatan Se di dalam enapan sungai berjulat antara 0.56 $\mu\text{g g}^{-1}$ hingga 1.91 $\mu\text{g g}^{-1}$ dan kepekataannya di dalam enapan tasik antara 0.31 $\mu\text{g g}^{-1}$ hingga 1.08 $\mu\text{g g}^{-1}$. Kemudian keputusan kepekatan As, Cr dan Se dibandingkan dengan 'nilai latar' yang dicadangkan oleh *National Oceanic and Atmospheric Administration (NOAA)*, Amerika dan beberapa panduan kualiti sedimen. Korelasi dan normalisasi kepekatan As, Cr dan Se kepada kandungan besi dijalankan untuk menilai dan menganggar pengkayaan bahan cemar di dalam enapan. Bagi kajian penspesiesan, spesies bukan organik As(III), As(V), Se(IV) dan Se(VI) ditentukan dengan mengekstrak enapan menggunakan gelombang mikro pada aras kecekapan masa dan kuasa yang telah ditetapkan di dalam media asid berkepekatan rendah. Pra-pemekatan dan pemisahan As(III) dan As(V) dijalankan dengan menggunakan ammonium pirolidineditiokarbamat (APDTC) di dalam metil isobutil keton (MIBK). Sementara Se(IV) dan Se(VI) dipisahkan selepas ko-pemendakan natrium dibenzilditiokarbamat (Na-DBDTC) dengan fenolftalein. Kecekapan semua prosedur pengekstrakan telah ditentukan dengan menggunakan larutan piawai dan beberapa bahan rujukan piawai. Keputusan menunjukkan As(V) dan Se(VI) adalah spesies yang dominan di dalam enapan sungai dan tasik.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	-	percent
°C	-	degree Celcius
$\mu\text{g g}^{-1}$	-	microgram per gram
$\mu\text{g mL}^{-1}$	-	microgram per mililiter
$\mu\text{g L}^{-1}$	-	microgram per liter
mg kg^{-1}	-	milligram per kilogram
mg L^{-1}	-	milligram per liter
g kg^{-1}	-	gram per koligram
ng m^{-3}	-	nanogram per meter cubic
pg m^{-3}	-	pikogram per meter cubic
μm	-	micrometer
mm	-	millimeter
min	-	minute
km	-	kilometer
kPa	-	kilopascal
M	-	mol
W	-	watt
APDTC	-	ammonium pyrolidinedithiocarbamate
AAS	-	atomic absorption spectrometry
AFS	-	atomic fluorescence spectrometry
BOD	-	biological oxygen demand
COD	-	chemical oxygen demand
CRM	-	certified reference material
DIBK	-	diethyl isobutyl ketone
DO	-	dissolved oxygen
DOE	-	Department of Environmental

EPA	-	Environmental Protection Agency
ETAAS	-	electro thermal atomic absorption spectrometry
GFAAS	-	graphite furnace atomic absorption spectrometry
HPLC	-	high performance liquid chromatography
HCl	-	hydrochloric acid
HClO ₄	-	perchloric acid
HF	-	fluoric acid
HNO ₃	-	nitric acid
H ₂ O ₂	-	hydrogen peroxide
H ₃ PO ₄	-	ortho phosphoric acid
H ₂ S	-	hydrogen sulfate
H ₂ SO ₄	-	sulfuric acid
IAEA	-	International Atomic Energy Agency
ICPMS	-	inductively coupled plasma mass spectrometer
MIBK	-	methyl isobutyl ketone
NAA	-	neutron activation analysis
Na-DBDTC	-	sodium diethyldithiocarbamate
NOAA	-	National Oceanic and Atmospheric Administration
NWQS	-	National Water Quality Standard
RSD	-	relative standard deviation
UV	-	ultra violet
WHO	-	World Health Organization

CHAPTER 1

INTRODUCTION

1.0 Research Background

Development in industrial and agricultural sectors as well as rapid increase of population and mining activities have adversely affected the quality of aquatic system. Industrial, domestic and municipal wastes that contain toxic contaminants including hazardous chemicals and pesticide residues may enter the aquatic environment and affect the natural system. Toxic contaminants such as heavy metals that are introduced into the aquatic system may also associate themselves with sediment components and can contribute to toxicity up to some extent.

The Department of Environment (DOE) had, in 2006, monitored about 146 river basins in Malaysia. Out of those 146 river basins, 69 river basins had been reported and categorized as polluted based on water quality parameter assessment of biochemical oxygen demand and ammoniacal-nitrogen ($\text{NH}_3\text{-N}$). The untreated and partially treated sewage and discharges from agro-based and manufacturing industries were the principal contributors to the major pollution in river system. Meanwhile, 42 rivers were recorded to be heavily polluted by earthwork and land clearing activities.

In the aquatic system, the sediment acts as a sink to a major number of contaminants. It also serves as an important medium for the transformation and migration of toxicants. Beyond this environmental system, the chemistry of some chemicals may have changed due to environmental, biological and physical

processes. Some chemicals are not biodegradable but may be biotransformed through food chain that reaches human beings where they ultimately result in chronic and acute ailments and illnesses.

Förstner and Wittmann (1983) grouped the existence of metals in water into two groups; inorganic and organic. Some of them might be soluble and others in particulate form. The metals in soluble state are present as ions, complex ions, chelate ions or molecule forms. The particulate metal form may occur as colloidal, precipitate or adsorbed to other constituents in the aquatic environment.

In natural waters, both inorganic and organic metals may undergo oxidation-reduction, precipitation-dissolution, adsorption-desorption or biochemical methylation reactions. All of these reactions control deposition, accumulation and mobilization of metals in the aquatic environment. These reactions do not only take place in the aqueous phase but also interact at the solid phase such as sediment, soil and geologic materials. Several metals can go through transformation and translocation by soil microbes and higher plants via their uptake mechanism.

According to Förstner (1983), aquatic solids are composed of a mixture of material inputs from various sources, including eroded rocks and soils, sewage and solid waste particles, atmospheric fallout and other formation in the aquatic system such as inorganic precipitates, biogenic matter, adsorbates on particles from solution, complexed and colloidal matter. During periods of reduced flow rates, suspended materials settle to the bed of the river, lake and sea, becoming partly incorporated into the bottom sediment.

Sediment analysis is particularly useful in detecting pollution sources and in the selection of critical sites for routine water sampling for contaminants that, on discharge to surface water, do not remain solubilized but are rapidly adsorbed by particulate matter (Simpson *et al.*, 2005). Local sources of pollution can be determined and evaluated with the lateral distribution analysis. Vertical sediment profiles are also useful, since they often uniquely preserve the historical sequence of pollution intensities and at the same time enable a reasonable estimation of background levels and the variation input of a pollutant over an extended period of time.

Since three decades ago, research aspect into sediment has become apparent from the fact that the sediments with their contaminants are in a constant interrelation with the liquid phases and organisms which means that the sediments themselves represent another environmental contaminant. Several problem areas with regard to the presence of contaminated sediment in the environment including the potential availability of the contaminants in the sediments for aquatic life, the behaviour of contaminants in soil and sediment with respect to potential pollution of groundwater and uptake of contaminants by plants from polluted sediments on agricultural land have been highlighted, studied and discussed extensively by scholars (Kubota, 1983; Thornton, 1983).

One of the well-known aquatic environmental studies ever conducted was conducted at The Great Lakes situated in United State and also in Canada region. The Great Lakes contain 20 % of the world's surface fresh water which cover more than 244,000 square kilometers of water (<http://epa.gov/greatlakes/index.html>). Contaminants are washed into the lakes via rivers and streams, or through pipes and discharge outlets. The lakes are also exposed to contaminants via atmospheric depositions. Contaminated sediments, primarily in harbors and industrialized segments of rivers and estuaries, contain pollutants that have been entering the lakes for decades. The sediment assessment study for metals, acid volatile sulfides, methylmercury, tributyltin, pesticides, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and dioxins were conducted to evaluate the nature and extent of bottom sediment contamination of The Great Lakes

(Schumacher, 1994). Studies conducted on sediment from this area have demonstrated that contaminated sediments are of great concern to humans and wild life that live in the Great Lake Basin. EPA's Great Lakes National Program Office has reported that polluted sediments are the largest major sources of contaminants in Great Lakes rivers and harbors which could eventually enter the food chain (EPA, 2004).

The introduction of elemental contaminants into the aquatic system has various sources. The source of contaminants could be originated from two origins; direct and indirect sources. The direct sources could be coming from natural processes like weathering and volcanic activity that contributes to the redistribution of metals from bedrock into the surface environment. Through the water system run-off and leaching process, the metals in solution form are introduced into lakes, rivers, groundwater and sea. The elements enrichment can be attributed to human activities such as industrial processing of ores and metals, agricultural, industrial and domestic wastes. The serious effects of mine, industrial and domestic effluents on water quality in river and lakes, as well as on the organism, have been known and studied for many years.

The indirect sources of contaminants could be originated from geochemical processes occurring in a particular system. The diagenesis process is a natural aquatic environmental process that contributes to the enrichment of toxic chemical in the sediment. This process may induce the vertical migration of multi oxidation state of element such as As from bottom of anoxic sediment to surface that can act as input of the toxic chemical to the water column. The diagenesis process may have developed in sediments of anoxic condition of the aquatic system occurring as a result of exhausted oxygen due to excessive utilization for degradation of biodegradable material such as municipal wastes. The diagenesis process usually occurs in marine, river, lake and ground water ecosystem which are highly contaminated by biodegradable materials such as sewage. Arsenic contamination in Bangladesh and North East India, are example of serious consequence of migration of multi oxidation state toxic element into water column in the anoxic sedimentary condition (McArthur *et al.*, 2004).

1.1 Problem Statement

In early civilizations, human culture and development were closely related to freshwater utilization in many aspects of life. Rivers and lakes were utilized for agriculture, transportation, daily usage and food resources. After the Industrial Revolution in early 19th century, rapid development in urbanization and industrialization took place including at some strategic areas close to the river or lake. Without proper planning, enforcement in environmental controlling, environmental education and awareness, man has allowed contaminants to enter the river and lake ecosystem. In Malaysia, most rivers and lakes are still providing raw water for daily consumption. But on the other hand, the contaminants entering the freshwater system are not deniable.

Health issue concerning freshwater especially for drinking purpose has always been a top priority in the nation. Rapid development in industrial and agricultural sectors as well as rapid increase of population has affected the quality of aquatic system adversely. Toxic contaminants such as arsenic, chromium and selenium introduced into aquatic system may also associate with sediments components as well and contribute to some extent of toxicity.

In the contaminated sediment, the chemistry of some contaminants may have changed due to environmental, biological and physical processes. Some contaminants are not biodegradable but may be biotransformed through food chain, thereby reaching human beings where they produce chronic and acute ailments. While, some other toxic contaminants released from the sediment bound enter the water column when the changes of the aquatic system environment occur such as decline in dissolved oxygen or pH.

1.2 Research Objectives

Sediment contamination issue is highly important in environmental concern. The sediment represents the largest reservoir for toxic contaminants within the aquatic system such as marine, river, lake and pond. The freshwater bodies such as river, lake and pond have great potential to be contaminated with toxic contaminant as they are situated inland closely to human settlement. Contamination of freshwater from anthropogenic activities or natural weathering may give hazardous impact toward drinking water consumption. The study and investigation of contaminants conducted at those stressful freshwater areas especially in sediments provides significant information regarding the possible sources of contaminant, mobility, and transportation behavioral, potential environmental and health risk particularly for some contaminants that have bioaccumulation capability.

The research objectives can be outlined as follows:

- a) To determine and quantify the total concentration of arsenic, selenium, chromium and iron in river and lake sediments using neutron activation analysis (NAA) technique.
- b) To compare the quality of sediments particularly of arsenic, selenium and chromium concentration with several international Sediment Quality Guidelines.
- c) To develop a suitable analytical method for inorganic speciation of As (III), As (V), Se (IV), and Se (VI) in sediment samples using neutron activation analysis (NAA) as a principal detection technique.
- d) To depict and compare the availability of arsenic, selenium, chromium, inorganic arsenic and selenium of the river and lake system used in this study.

1.3 Scope of Research

The main scope of research include sediment sampling at identified rivers and lake and collection of water parameter data such as pH, temperature and DO, analysis of sediment for the total concentration of arsenic, selenium, chromium and iron using nuclear analytical technique namely NAA and correlation study between the analysis results of arsenic, selenium and chromium to iron content.

The data of total arsenic, selenium and chromium concentration obtained were compared to several International Sediment Quality Guidelines. An effort to apply Enrichment Factor and Geoaccumulation Index for the purpose of evaluating and estimating the contamination impact in sediment has been taken and completed.

In addition, a speciation preparation method using microwave and preconcentration technique of inorganic arsenic and selenium species has been developed and arsenic, selenium, their respective species as well as chromium occurrence in two different environmental systems; river and lake, using statistical technique has been undertaken.

1.4 Man, Environment and Toxic Elements

The introduction of elemental contaminants into the aquatic system has various sources where the main point sources originate from anthropological activities and geochemical processes. Anthropogenic activities in industrial, agricultural, mining and transportation have led to many pathways of toxic elements into aquatic system and significantly contribute to the increase in contaminations of aquatic system. Some activities may include smelting process and fuel combustion via atmospheric fallout, pollution from leak, effluents, and land application of

sewage materials and leaching of garbage (Förstner and Whitman, 1983; MacDonald *et al.*, 2003). Several elements may also originate from the natural weathering process of underlying mineralized rock or associated overburden.

In water bodies, elemental contaminants are associated with the sediment underneath whereby sediments are often the ultimate repositories of contaminants leached to the environment. Toxic elements such as arsenic, cadmium, chromium, copper, mercury, selenium and other species tend to accumulate at the bottom of the sediment. The presence and addition of certain metals to sediments at such a level that would have harmful effects on organisms can be considered to constitute metal pollution. The compositions, quantities and the modes of these elemental inputs vary widely from one sediment to another and thus influence the contaminants behavior in affected sediments.

Aquatic organisms such as fishes, clams and mussels are among the species closely associated with sediment. Under polluted water conditions, these organisms can take up and accumulate metals present in the polluted sediment. Toxic elements are then able to enter aquatic biota through the food chain and this provides a great concern in human health perspective. Therefore, uptake of the contaminants by aquatic organisms has become a subject of interest by several researchers in which several organisms have been used as bio-indicators for assessing water pollution (Yusof *et al.*, 2004; Zanaton, 1994).

1.5 Arsenic

Arsenic is a metalloid that is widely distributed in the earth's crust at an average concentration of $2 \mu\text{g g}^{-1}$ (Merian, 1985). It ranks as the twentieth element in crustal abundance and has been listed to be contained in at least 23 most commonly naturally occurring minerals where the arsenargentite (Ag_3As) was first described back in 1795, (Azcue and Nriagu, 1994). Arsenic occurs mostly in rocks, soil, water and air.

WHO, in the Environmental Health Criteria 224 for Arsenic and Arsenic Compounds (2001), reported that the mean As concentrations in air from remote and rural areas range from 0.02 to 4 ng m⁻³. The mean total As concentrations in urban areas range from 3 to about 200 ng m⁻³ and much higher concentrations (> 1000 ng m⁻³) have been measured in the vicinity of industrial sources. Arsenic is widely distributed in surface freshwaters, and concentrations in rivers and lakes are generally below 10 µg L⁻¹, although the individual samples may range up to 5 mg L⁻¹ near anthropogenic sources. Arsenic levels in groundwater average about 1–2 µg L⁻¹ except in areas with volcanic rock and sulfide mineral deposits where As levels can be up to 3 mg L⁻¹. Concentrations of As in open ocean seawater are typically around 1–2 µg L⁻¹.

In sediments, the As concentration may range from 3 µg g⁻¹ to 4000 µg g⁻¹ with the higher levels occurring in areas of contamination or pollution (Mandal and Susuki, 2002). Background concentrations in soil range from 1 to 40 µg g⁻¹, with mean values often around 5 µg g⁻¹ (Burguera and Burguera, 1997; Chu, 1994). Arsenic concentration is considerably higher in sediment or soil than in earth crust, because of its accumulation during weathering and translocation in colloid fractions.

Elemental As is a member of Group 15 of the periodic table that includes nitrogen, phosphorus, antimony and bismuth. It has an atomic number of 33 and an atomic mass of 74.91. Arsenic can exist in four valency states: -3, 0, +3 and +5. Arsines and methylarsines are characteristic of As in the -3 oxidation state. Elemental As, As⁰ is formed by the reduction of arsenic oxide. Arsenic trioxide (As⁺³) is a product of smelting operations and is the material used in synthesizing most arsenicals. It is oxidized catalytically or by bacteria to arsenic pentoxide (As⁺⁵) or orthoarsenic acid (H₃AsO₄) (Eisler, 2000). Arsenic and its compounds occur in crystalline, powder, amorphous or vitreous forms.

Arsenic accumulation in soils and sediments may be due to the use of arsenical pesticides, application of fertilizers, irrigation, oxidation of volatile arsines in air, dust from the burning of fossil fuels and disposal of industrial, municipal and animal wastes (Prohaska and Stinger, 2005; Skonieczny and Hahn, 1978).

Historically, the use of arsenic-containing pesticides has left large tracts of agricultural land contaminated. Furthermore, soil treated with pesticides shows higher As concentration when compared to soil treated with herbicides, which are usually applied at lower rates (Prohaska and Stinger, 2005).

In the industry, elemental As is used as an additive in special alloys. Arsine is used in microelectronics and semiconductor industry. Some arsenic trioxide is used in the glass and ceramics industry as a decolorizing agent. Coal combustion and fuel burning contribute to As emission in the atmosphere. The degree of industrialization is also reflected in the amount of As in sewage sludge.

The presence of As ions in the environment particularly in drinking water is regulated by environmental and public health agencies or authorities. In Malaysia, according to Ministry of Health, the maximum permitted level of As in drinking water is 0.05 mg L^{-1} (Food Act 1983 (Act 281) and Regulations 2, 2000). Whereas, the provisional guideline value established for As according to Guidelines for Drinking-water Quality by WHO is 0.01 mg L^{-1} (WHO, 2004).

1.5.1 Geochemistry of Arsenic

The toxicity and mobility of As in the environment are dependent on the chemical form or species in which it exists. There are many As compounds of environmental importance. Representative marine As-containing compounds, of which some are found in terrestrial systems, are shown in Table 1.1; their molecular structures are shown Figure 1.1. Other inorganic As compounds of environmental significance are listed in Table 1.2.

Table 1.1: Naturally occurring inorganic and organic arsenic species. (WHO, 2001)
(see Fig. 1.1 for structures 1–22)

Name	Structure
Arsenate	1
Arsenite	2
Methylarsonic acid, MMA	3`
Dimethylarsinic acid, DMA	4
Trimethylarsine oxide	5
Tetramethylarsonium ion	6
Arsenobetaine, AB	7
Arsenocholine, AC	8
Dimethylarsinoylribosides	9 – 19
Trialkylarsonioribosides	20 - 21
Dimethylarsinoylrbitol sulfate	22

Arsenic (III) and (V) are the most often determined species in environmental water, soil and sediment, while organic As species are common constituents of biological tissue and fluids. Organic As, MMA and DMA can also be found in dissolved forms in the water column. Under oxidizing and aerated conditions, the predominant form of As in water and soil is As (V). Under reducing (acid and mildly alkaline) and waterlogged conditions, As (III) can become the predominant As 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. In brief, at moderate or high Eh, As can be stabilized as a series of pentavalent (arsenate) oxyanions, H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} . Figure 1.2 shows the speciation of As under varying Eh and pH.

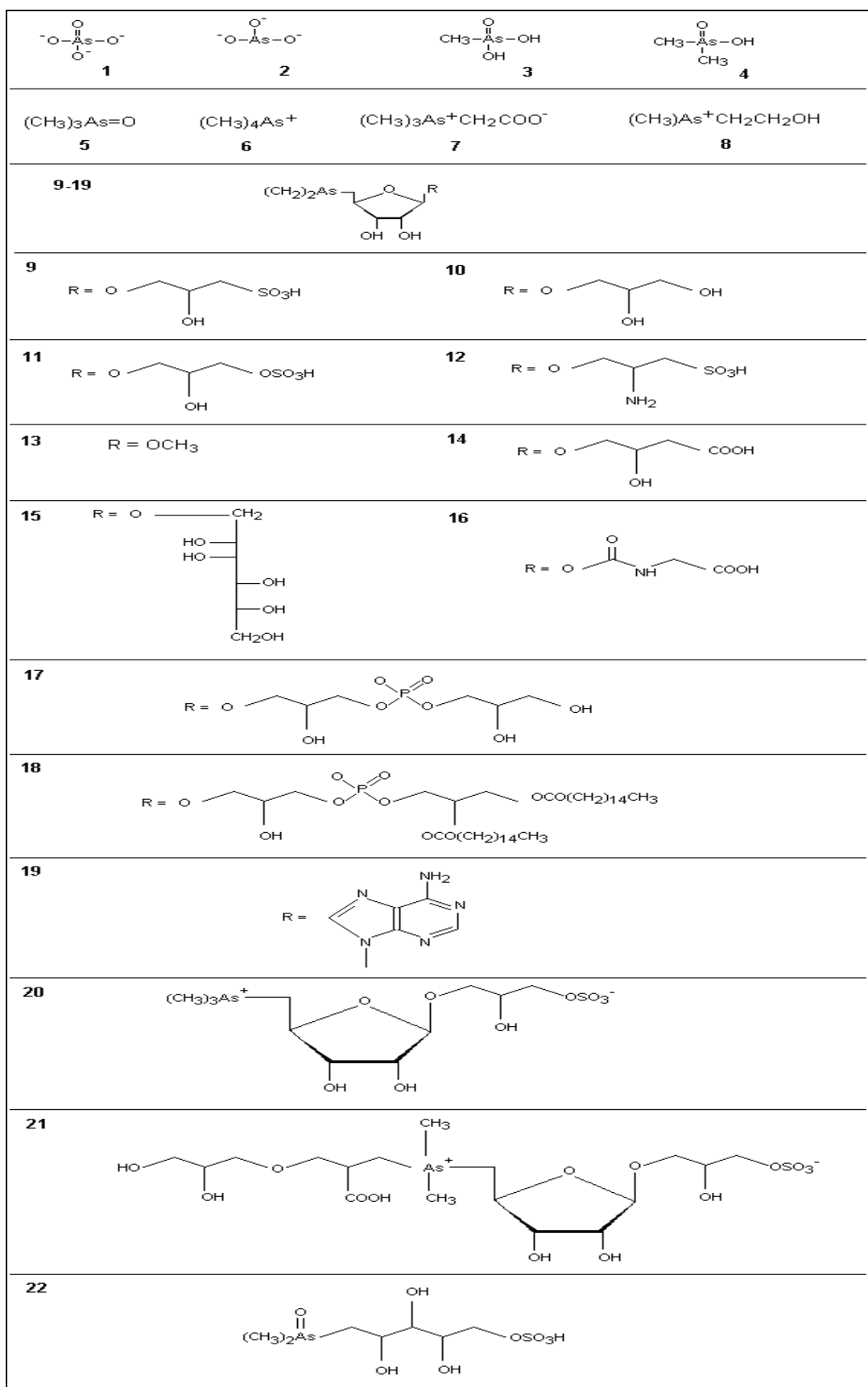


Figure 1.1: Structures of naturally occurring inorganic and organic arsenic species. (WHO, 2001)

Table 1.2: Inorganic arsenic species in the environment. (WHO, 2001)

Name	Synonyms	Formula
<i>Inorganic As, trivalent</i>		
As(III) oxide	As trioxide, arsenous oxide, white As	As ₂ O ₃ (or As ₄ O ₆)
arsenous acid	arsenious acid	HAsO ₂
As(III) chloride	As trichloride, arsenous trichloride	AsCl ₃
As(III) sulfide	As trisulfide orpiment, auripigment	As ₂ S ₃
<i>Inorganic As, pentavalent</i>		
As(V) oxide	As pentoxide	As ₂ O ₅
arsenic acid	<i>ortho</i> -arsenic acid	H ₃ AsO ₄
arsenic acid	<i>meta</i> -arsenic acid	HAsO ₃
arsenates, salts of <i>ortho</i> -arsenic acid		H ₂ AsO ₄ ⁻ , HAsO ₄ ²⁻ , AsO ₄ ³⁻

Arsenic solubility is low under oxidizing conditions and the more typical form of As is arsenate. At high pH or under reducing conditions, arsenate is reduced to soluble arsenite and the amount of arsenite increases significantly under strong reducing conditions. Under moderate reducing conditions, As solubility is controlled by iron oxy-hydroxides or manganese oxides (Barrachina *et al.*, 1999). With the presence of sulfide and under reducing conditions, it can lead to the precipitation of As₂S₃ in lake, river and marine sediments. The formation of sulfides in reducing conditions occurs simultaneously with the reduction of arsenate to arsenite. Figure 1.3 shows the transformation pathway of inorganic As in the environment.

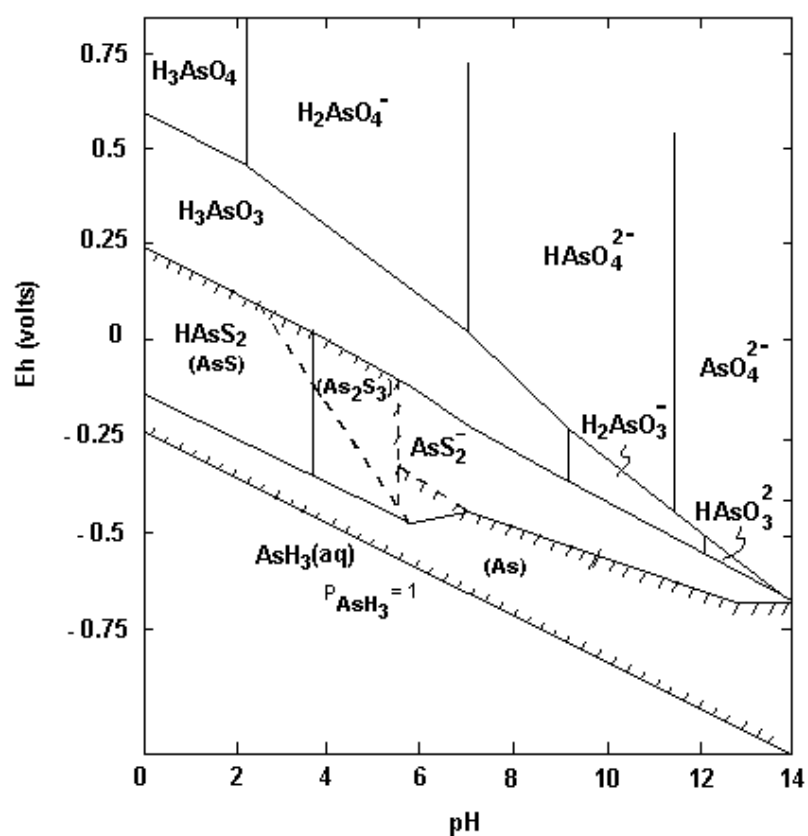


Figure 1.2: The Eh-pH diagram of arsenic in water at 25°C and one atmosphere (Kartinen and Martin, 1995 and WHO, 2001).

Arsenic is released into the atmosphere primarily as As₂O₃ and mainly adsorbed by particulate matters. 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, reconvert the As to non-volatile forms, which then settle back to the soil.

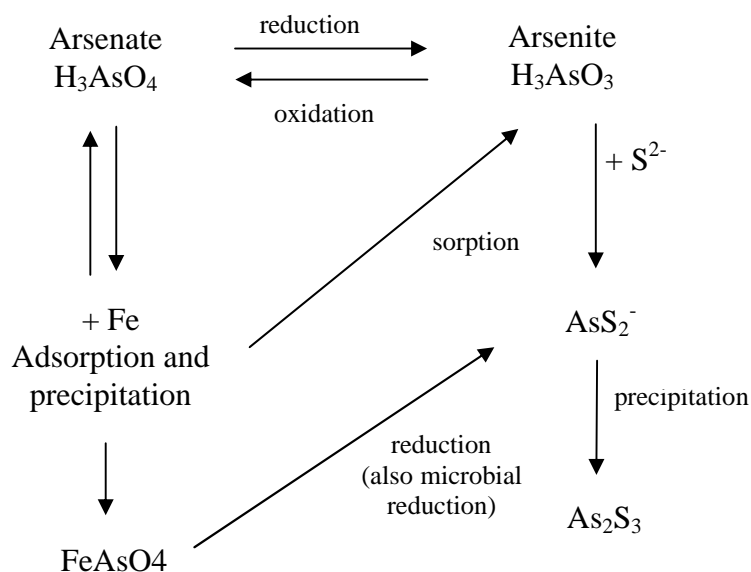


Figure 1.3: Simplified transformation pathway of inorganic arsenic in the environment (Prohaska and Stinger, 2005).

1.5.2 The Toxicology of Arsenic

Arsenic is a common environmental agent whose toxic properties have been known for centuries. Since ancient time, arsenicals have been used as agents of suicide and murder. Arsenic as a toxic, poisonous and killing agent was closely associated to the death of France's famous ruler, Napoleon Bonaparte.

Humans are exposed to many different forms of inorganic and organic As species in food, water and other environmental media. Each As form has different physicochemical properties and bioavailability. Zielhuis (1985) had classified at least three groups of As-compounds: i) inorganic water soluble compounds; ii) inorganic non- or low-solubility compounds and iii) organic As used to distinguish the metabolic models and health risks of arsenic-compounds in order to establish the quality standard or recommended limits of As.

The chemical forms and oxidation states of As are important with regards to their toxicity which is directly related to their mobility in water and body fluids. The toxicity of As compounds decreases in the following order; arsines > inorganic arsenites (As (III)) > arsenoxides > inorganic arsenates (As (V)) > organic pentavalent compounds > arsonium compounds > elemental As (Mandal and Susuki, 2002; Prohaska and Stingeder, 2005).

It appears that the stable, soluble inorganic arsenites and arsenates are readily absorbed by digestion tract, abdominal cavity and muscle tissue. Excretion of arsenate is faster than that for arsenite, mostly in urine (Förstner and Wittmann, 1983). Arsenate has a low order of toxicity than arsenite and does not inhibit any enzyme system due to its lack of affinity to hydroxo and thiol groups, but adenosine triphosphate (ATP) synthesis is inhibited by a AsO_4^{3-} by uncoupling oxidative phosphorylation and replacing the stable phosphoryl group. In contrast, arsenite inhibits thiol-dependent enzymes, binds to tissue protein as keratin disulfides in nails, hair and skin and retained in the body for a prolonged period.

Routes of As intake in vivo are considered respiratory for dust and fumes, and oral for As in water, beverages, soil, and food. People from many countries all over the world are suffering from the toxic effects of arsenicals as a result of natural groundwater contamination caused by industrial effluent and drainage problems. A number of As poisoning cases via contamination of groundwater in Argentina, Bangladesh, Chile, India, Taiwan and United State have also been reported (Mandal and Susuki, 2002). They also reviewed several As poisoning episodes from industrial sources and contamination in food and beverage all over the world.

McArthur *et al.* (2004) had carried out an extensive study on natural organic matter in sedimentary basin and its relation to As in anoxic groundwater. Water and sediment samples were collected from several wells in southern West Bengal. This investigation was aimed to explain the mechanism of As release to ground water by reductive dissolution of FeOOH. Human excreta in latrines penetrates the upper confining layer which has hydraulic continuity with the aquifer, may locally promote additional reduction of FeOOH and add to the As problem. Generally, the complete reduction of FeOOH contributes to high concentration of As (200-1180 $\mu\text{g L}^{-1}$).

Several epidemiological studies have shown that acute and chronic exposure to As can cause a variety of adverse health effects to humans such as dermal changes, respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenetic, and carcinogenic effects (Brown and Ross, 2002; Buchet, 2005; Leonard, 1985). Increased risks of lung and bladder cancer and arsenic-associated skin lesions have been reported to be associated with ingestion of drinking water at concentrations of As equal to and less than 50 $\mu\text{g L}^{-1}$ (WHO, 2001).

1.6 Selenium

Selenium is classified as a metalloid that lies between nonmetallic sulphur and metallic tellurium in Group 16 and between arsenic and bromine in Period IV of the Periodic Table. It has an atomic number of 34 and an atomic mass of 78.96. In physical state, Se occurs in grey metallic or red amorphous powder or vitreous form. Selenium can exist in four valency states: -2, 0, +4 and +6.

Selenium is an essential trace element to life. However at very low concentrations it can cause anomalies in organisms and at high concentrations it is toxic (Haygarth, 1994; Merian, 1985). Selenium exists at low abundance in the earth's crust with concentration of $0.05 \mu\text{g g}^{-1}$ (Haygarth, 1994). It is often associated with sulfur-containing minerals and usually accompanies sulfur in volcanic effluents which make the soils in the neighborhood of volcanoes tend to have enriched amounts of Se (Malisa, 2001; WHO, 2003b).

Selenium has vast potential use in the industries. Selenium exhibits both photovoltaic action, where light is converted directly into electricity, and photoconductive action, where the electrical resistance decreases with increased illumination. These properties make Se useful in the production of photocells and exposure meters for photographic use, as well as solar cells. Selenium is also able to convert alternating current electricity to direct current, and is extensively used in rectifiers. Below its melting point, Se is a p-type semiconductor and is finding many uses in electronic and solid-state applications such as in xerography for reproducing and copying documents (Lide, 2007).

Selenium is widely used in glass and ceramic industry for decolorizing and glazing. In heavy industry, it is used to improve the porosity of stainless steel casting and to improve the machinability of copper and copper alloy (Green and Turley, 1961). Selenium is also used as pigments in plastic and paint due to its resistant to heat, light and weathering. Selenium is an antioxidant, which makes it useful for inclusion in inks, mineral and vegetables oil, and lubricants (Haygarth, 1994). Early agricultural uses of Se compounds as pesticides were very limited and short-lived. The recent use of Se compounds as feed additives for the prevention of Se deficiency diseases in farm animals represents a source for environmental contamination (WHO, 1987). Selenium sulfide is used in shampoos as an anti-dandruff agent. Human activities, particularly mining, agricultural, petrochemical, and industrial manufacturing operations may result in environment contamination with Se.

The concentration of Se in igneous rocks is relatively low, usually much less than $1 \mu\text{g g}^{-1}$, and similar levels probably occur in metamorphic rocks. Sedimentary rocks, such as sandstone, limestone, phosphorite, and shales may contain from less than 1 and up to $100 \mu\text{g g}^{-1}$ of Se (WHO, 1987). The Se content in a soil may indicate, to some extent, the parent material from which the soil has been formed. Thus, in arid and semi-arid areas, soils with high Se content have been derived from sedimentary rocks, usually shales and chalks.

The range of soil Se content is typically from $0.1 \mu\text{g g}^{-1}$ to $2 \mu\text{g g}^{-1}$. But at seleniferous area, an average of Se concentration may be found to be between $45 \mu\text{g g}^{-1}$ and $80 \mu\text{g g}^{-1}$ (Quinn, 1985). In Great Lakes, USA, Se concentrations from bottom sediments range from $0.35 \mu\text{g g}^{-1}$ to $0.75 \mu\text{g g}^{-1}$. While, oceanic study for sediment samples reported that the Se concentrations range from $0.34 \mu\text{g g}^{-1}$ to $4.8 \mu\text{g g}^{-1}$ (Eisler, 2000). The concentrations of Se which are equal to or greater than $4.0 \mu\text{g g}^{-1}$ in sediments are a great environmental concern because of the potential for bioaccumulation in fish and wildlife (Derveer and Canton, 1997). Under natural conditions, the concentration of Se in water usually ranges from a few tenths to 2 or $3 \mu\text{g L}^{-1}$ (WHO, 1987). Surface waters seem much less likely to contain excessive levels of Se than ground waters. Selenium concentrations with levels exceeding $50 \mu\text{g L}^{-1}$ have been documented in groundwater, especially in areas with seleniferous soils, in sewage wastes, in irrigation drain water and in water of flyash settling ponds (Eisler, 2000).

The 2004 WHO International Standards for Drinking Water proposed a health-based guideline value of 0.01 mg L^{-1} for Se on the basis of human studies and following the recognition that biota accumulated Se from water. In Malaysia, under the Ministry of Health, the maximum permitted level of Se in drinking water is 0.01 mg L^{-1} (Food Act 1983 (Act 281) and Regulations 2, 2000).

1.6.1 Geochemistry of Selenium

The concentration of Se in soil depends on the parent material, topography, climate, age of soil and man activities (Frankenberger and Karlson, 1994). Inorganic Se species enter natural waters, groundwaters, soil and sediment from many sources. The two most common sources of Se in the environment include the weathering of rock and soils and organic compounds from decayed plant tissue and agricultural products (Koll, 1993). Selenium also enters the geochemical cycle through human activities which include agricultural drain water, sewage sludge, fly ash from coal-fired power plants, oil refineries and mining (Hamilton, 2004).

The fate of Se in natural environments is affected by many physical, chemical and biological factors, which are closely associated with changes in its oxidation state. The concentration and speciation availability of Se are associated with the pH, redox potential, solubility, complexing ability of soluble and solid ligands, and microbial interaction (Belzile *et al.*, 2000). Figure 1.3 shows the availability of Se species under varying Eh and pH. Changes in the valence state of Se from -2 (hydrogen selenide) through Se^0 (elemental selenium), +4 (selenite) and +6 (selenate) are associated with its geological distribution, redistribution and use. Most of the Se species found in soil and water are the inorganic selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) forms. Soluble selenates which occur in alkaline soil, are slowly reduced to selenites and are then readily taken up by plants and converted into organoselenium compounds, including selenomethionine, selenocysteine, dimethyl selenide and dimethyl diselenide.

At equilibrium, the typical form of Se in soil is elemental selenium. Referring to Figure 1.4 below, the biologically available Se is only present in relatively large amount in acidic areas or neutral soils and declines as the soils become more alkaline. The decline may be accelerated by active agricultural or industrial practices. In dry areas with alkaline soils and oxidizing conditions, elemental selenium and selenides in rocks and volcanic soils may oxidize sufficiently to maintain the availability of biologically active Se.

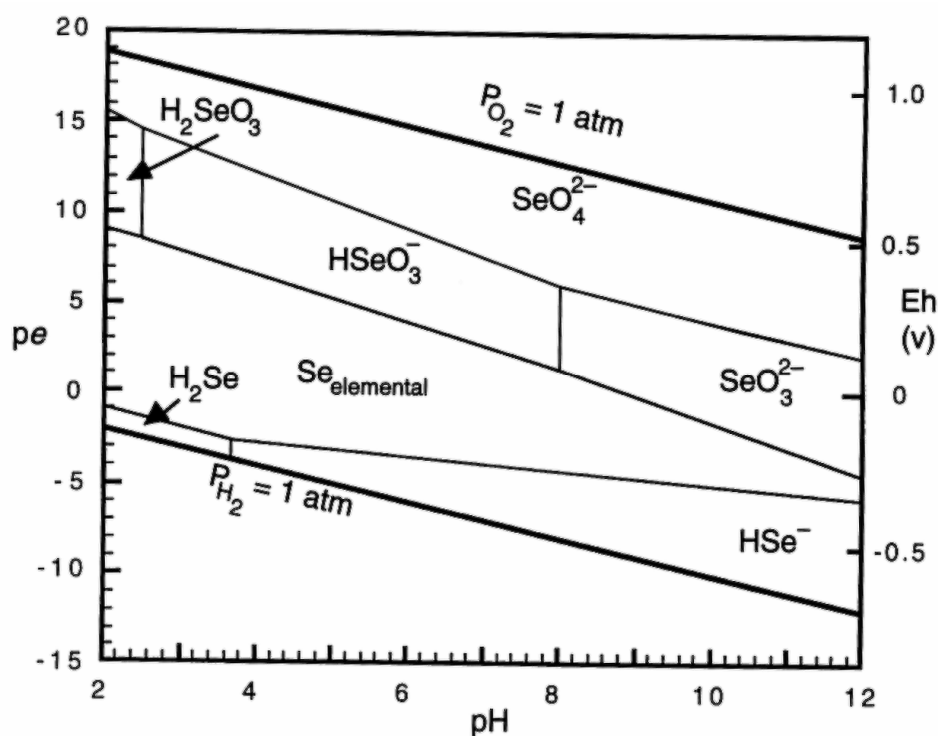


Figure 1.4: The Eh-pH diagram of selenium in water at 25°C and one atmosphere (Séby *et. al*, 2001).

Selenite (Se(IV)) would form mineral salts which are generally less soluble than selenate (Se (VI)) salts. Under acidic reducing conditions in soil, which may be waterlogged and rich in organic matter, elemental selenium and selenides are the dominant species. Elemental selenium, selenides and selenium sulfides are less biologically available for uptake. At high redox potential and in well-oxygenated alkaline soil, highly soluble selenate is the dominant species, and at neutral pH, selenite occurs in approximately equal concentrations to selenate. Selenate is stable in oxidized environments and is the form in which Se is most readily taken up by plants, which can cause great environmental concern.

1.6.2 The Toxicology of Selenium

The toxicity of Se depends on the biologically active oxidized forms of SeO_3^{2-} or SeO_4^{2-} (Uden, 2005). In oxidizing conditions or alkaline soil, Se may be sufficiently oxidized to maintain the availability of biological active forms that are readily absorbed by plants. In acidic or neutral soil, it tends to remain relatively insoluble and the amount of biologically active forms of Se available that can be absorbed by plants constantly decreases.

Selenium dioxide is the primary problem involved with most industrial exposure to the element as the oxide is easily formed when Se is heated. The dioxide itself forms selenious acid when it mixes water or sweat and becomes an irritant. Selenium compound released during fossil fuel combustion may pose an inhalation hazard to people. Most probable forms of Se released during combustion are selenious acid and elemental selenium. Acute poisoning through inhalation may occur in industry which produces Se dust and fumes, selenium dioxide and hydrogen selenide as the by products.

The considerable biological importance of Se was first recognized in the 1930s when it was discovered that certain well-defined and economically important farm animal diseases were actually the result of chronic Se poisoning. These animal diseases were restricted to agricultural areas in which large amounts of Se in the soil were available for uptake by the plants, which were then consumed by the animals. The farm animals showed severe signs of distress such as laboured breathing, abnormal movement and posture, prostration, and diarrhea. Death often followed within a few hours after the animals fell sick (WHO, 1987).

The capability of Se to accumulate in living tissue is a great concern as it can cause adverse health effect. The Se capability to accumulate in living tissue is due to its propensity to bioaccumulate within the base of food webs: from water and sediment to aquatic plants and aquatic invertebrates (Hamilton, 2004). Tinggi (2003) had summarized some effects of Se exposure to human. For an example, industrial exposures in the manufacture of Se rectifiers have caused hypochromic anemia and

leucopenia, and damaged the nails of long-term workers employed in the industry. There have been a number of reported cases of acute and subacute Se poisoning in humans as a result of accidental ingestion of selenic acid and vitamin tablets that contained high levels of Se. An ingestion of Se at high level is reported to cause gastrointestinal disturbances (vomiting, diarrhea), hair and nail changes, and neurologic manifestations. Examination of exposed individuals showed increased levels of Se in the blood and urine (WHO, 1987).

1.7 Chromium

Chromium has been identified both as an essential element and as a chemical carcinogen agent (Hoet, 2005). It is a transition element located in group 6 of the periodic table. It has an atomic number of 24 and an atomic mass of 51.996. Chromium demonstrates oxidation numbers of 2+, 3+, 4+, 5+, and 6+. Of these, the compounds of the trivalent chromium, Cr (III) are the most stable, the most abundant, less toxic and are mainly bound to organic matter in soil and aquatic environment. In acid media, hexavalent chromium, Cr (VI) compounds are strong oxidizing agent where Cr (VI) is readily reduced to Cr (III) at low pH.

Chromium and its compounds are widely used in the industrial, manufacturing and commercial sectors (Katz and Salem, 1994). In metallurgical industries, Cr is used as an alloying element that imparts the resistance to corrosion property to stainless steels by the formation of a thin, transparent and protective film of Cr_2O_3 . The film stability can be improved by increasing the Cr contents of the alloys and by the addition of nickel, molybdenum or other elements. Chromel is a nickel-chromium alloy used in the manufacture of resistance wire for electrical heaters and thermocouples.

Trivalent and hexavalent chromium compounds are widely used in manufacturing and industrial due to its chemical and physical properties. The colours of trivalent and hexavalent chromium compounds coupled with appropriate solubility characteristics make them the preferred pigments and colourants in the manufacture of paints, printing inks, floor coverings and vinyl sheeting. The inertness of the trivalent oxide makes Cr compounds useful as corrosion inhibitors and as agents for oxidizing and plating metals. The tendency of trivalent chromium to form complexes with basic oxygen and/or nitrogen atoms in protein makes it possible for the tanning of leathers to be completed in hours rather than in days. The leathers produced become more resistant to wear and heat. The oxidizing properties of hexavalent chromium compounds have found applications in the synthesis of organic dyestuffs. Chromium and its compounds have become ubiquitous in modern society.

Chromium is found in all phases of environment, including air, water, rock and soil. Almost all of the sources of Cr in the earth's crust are in the trivalent state. The concentration of Cr in rocks varies from an average of $5 \mu\text{g g}^{-1}$ in granitic rocks, to an average of $1800 \mu\text{g g}^{-1}$ in ultrabasic and serpentine rocks (WHO, 1988). Weathering of rocks produces Cr complexes that are almost exclusively in the trivalent state. In most natural soils, Cr occurs in low concentrations of an average of $5 \mu\text{g g}^{-1}$. The highest concentrations of Cr which are at 125 g kg^{-1} are always found in serpentine soils (Shanker *et al.*, 2005). In freshwater, Cr concentrations generally range from 0.1 to $117 \mu\text{g L}^{-1}$ whereas the values for seawater range from 0.2 to $50 \mu\text{g L}^{-1}$ (Shanker *et al.*, 2005). Chromium concentration varies widely in the atmosphere, from background concentration of 5 to 7 pg m^{-3} in air samples from remote areas such as Arctic to at least 2 to 4 times higher concentration in urban areas than background concentrations (WHO, 2003a).

As a guideline, the WHO (2004) recommended a maximum level of $50 \mu\text{g L}^{-1}$ Cr in drinking water. In Malaysia, the quality criteria for drinking water is set under the Food Act 1983 (Act 281) and Regulations 2 (2000) and the maximum permitted value for total Cr is $50 \mu\text{g L}^{-1}$. Due to the fact that the health effects are determined largely by the oxidation state, WHO (2003a) proposed a different guideline values for chromium (III) and chromium (VI). However, the available toxicological data mainly in the study of carcinogenicity of Cr (VI) is yet not enough to support the derivation of a new value.

1.7.1 Geochemistry of Chromium

Chromium compounds are highly varied and widely distributed in the occupational, domestic and natural environments. Environmental Cr concentrations reflect the element's distribution in air, water, soil, plants and animals from both anthropogenic and natural sources. Chromium compounds are released from minerals containing Cr during the physical, chemical and biological weathering processes by which rocks are abraded or dissolved. Once released, the Cr compounds can be transported as wind or waterborne particulates. Volcanism is an alternative to weathering for the release of Cr compounds.

The combustion of large quantities of coal and oil is also the major anthropogenic source of environmental Cr. Emissions from Cr chemical manufacturing facilities, from many cooling towers, and steel mills are other major sources of airborne Cr. Industrial and domestic wastes are also dispatched to landfills for disposal. Sewage sludge compost piles and steel mill slag heaps are additional wastes to be considered as potential sources of Cr for the contamination of soil and groundwater.

The distribution of compounds containing Cr (III) and Cr (VI) depends on the redox potential, pH, the presence of oxidizing or reducing compounds, the kinetics of the redox reactions and formation of Cr (III) complexes or insoluble Cr (III) salts (WHO, 2003a). In soils, Cr (III) predominates. In the environment, Cr (VI) occurs mostly as CrO_4^{2-} or HCrO_4^- and Cr (III) as $\text{Cr}(\text{OH})^{2+}$. Figure 1.5 shows dissolved Cr species under varying pH and Eh.

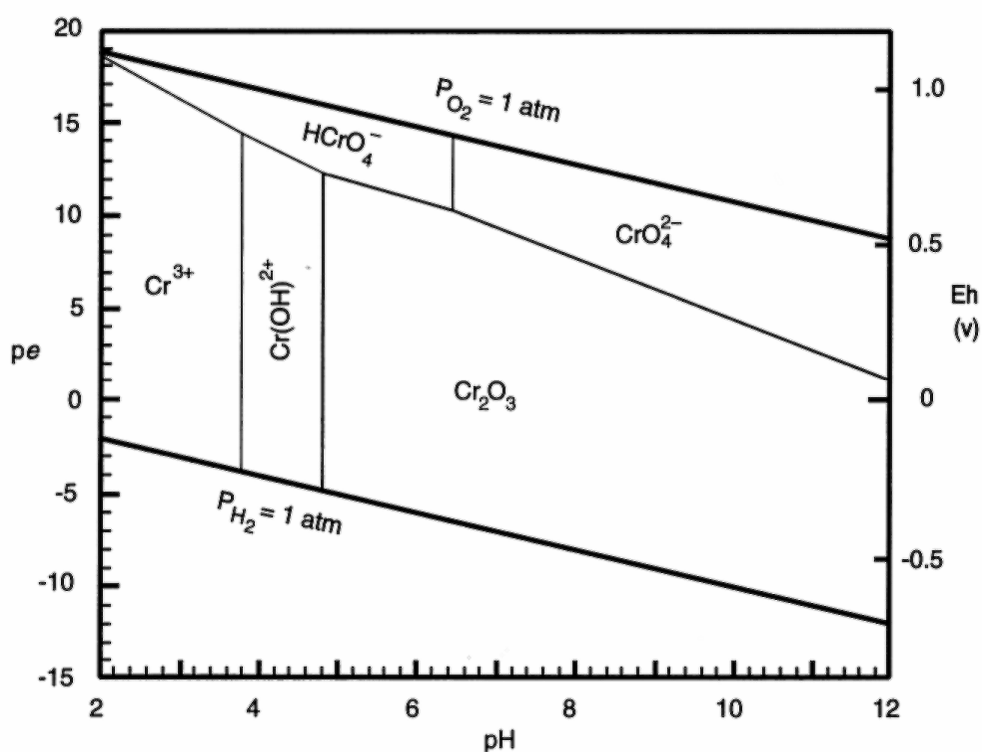


Figure 1.5: The Eh-pH diagram of chromium in water at 25°C and one atmosphere (Beverkog and Puigdomenech, 1997).

Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water, Cr will be absorbed by sediments and become immobilized. Only a small part of the Cr that ends up in water will eventually dissolve. Chromium (VI) can easily be reduced to Cr (III) by organic matter. It is a moderately strong oxidizing agent and will react with organic matter or other reducing agents to form Cr (III). Therefore, in surface water rich in organic content, Cr (VI) will exhibit a much shorter lifetime (EPA, 1998). In water, Cr (III) is a

positive ion that forms hydroxides and complexes and is adsorbed at relatively high pH values. In surface waters, the ratio of Cr (III) to Cr (VI) varies widely, and relatively high concentrations of the latter can be found locally. In general Cr (VI) salts are more soluble than those of Cr (III), making Cr (VI) relatively mobile (WHO, 2003a).

1.7.2 The Toxicology of Chromium

The importance of Cr is underscored by knowledge that it is an ubiquitous, naturally occurring element usually found in rocks, minerals and geological emissions. Chromium in excess amounts can be quite toxic, depending upon the chemical species of Cr and the route of exposure (Crouse *et al.*, 1983). Exposure to Cr can occur from the large amounts of Cr released into the environment from the industries, mining and processing of chromites ores. Moreover, Cr may make its way into the human body from dietary intake and drinking water.

Chromium is not known to accumulate in the bodies of fish, but high concentrations of Cr, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals, Cr can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation (WHO, 1988).

Chromium (III) is an essential nutrient for humans and Cr deficiency may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much of Cr (III) can cause adverse health effects as well, for instance skin rashes. Chromium (VI) compounds are, in general, more toxic than Cr (III) compounds with regards to acute and chronic oral toxicity, dermal irritancy and allergy, systemic effects, cytotoxicity, genotoxicity and carcinogenicity (Katz and Salem, 1994). Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. Some epidemiological data suggest that an excess of lung cancer has also occurred in the chromate-pigment industry (WHO, 1988). People who

smoke tobacco also have a higher chance of exposure to Cr. When present as a compound in leather products, it can cause allergic reactions, such as skin rash. Inhalation of Cr (VI) can cause nose irritations and nosebleeds.