QUANTIFICATION OF ARSENIC IN SOIL BY INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY

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FACULTY OF SCIENCE
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ABSTRACT

In this study, determination of arsenic in soil samples was done by Inductively Coupled Plasma – Optical Emission Spectrometry. Soil from five different locations with three sampling points was collected. The location chosen were garden, dam, beach, construction and agriculture areas. A standard method was used for the sample preparation using HotBlock^{TM} system. The highest arsenic concentrated found in the construction area (32.24 ± 0.02 mg/kg) and followed by agriculture (31.55 ± 0.03 mg/kg), garden (19.17 ± 0.02 mg/kg), dam (17.12 ± 0.01 mg/kg) and beach (1.73 ± 0.01 mg/kg).

ABSTRAK

Dalam kajian ini, penentuan arsenik dalam sampel tanah dijalankan dengan menggunakan *Inductively Couple Plasma – Optical Emission Spectrometry.* Sample tanah daripada lima lokasi yang berbeza dengan tiga titik persampelan diambil. Lokasi tersebut ialah kawasan kebun, empangan, pantai, kawasan pembinaan dan kawasan pertanian. Satu prosedur piawai telah digunakan untuk penyediaan sampel dengan menggunakan sistem HotBlock^{TM}. Kepekatan arsenik yang tertinggi adalah di kawasan pembinaan (32.24 ± 0.02 mg/kg) diikuti dengan kawasan pertanian (31.55 ± 0.03 mg/kg), kebun (19.17 ± 0.02 mg/kg), empangan (17.12 ± 0.01 mg/kg) dan pantai (1.73 ± 0.01 mg/kg).

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CONTENT

Page

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

APPENDIXES

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATION

^oC	degree Celcius
mL	mililitre
mg/L	miligram/ Litre
mg/kg	milligram/ kilogram
ng/L	nanogram/ Litre
µg/L	microgram/ Litre
g	gram
HCl	hydrochloric acid
HNO_3	nitric acid
cm	centimeter
AsO_3^{3-}	Arsenite
AsO_4^{3-}	Arsenate
IARC	International Agency for Research on Cancer
MSMA	Monosodium methyl arsenate
DSMA	Disodium methyl arsenate
nm	nanometer
As	Arsenic
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
SP1	Sampling Point 1
SP2	Sampling Point 2
SP3	Sampling Point 3
ppm	parts per million
K	Kelvin
r	correlation coefficient
N	number of samples
ATSDR	Agency for Toxic Substance and Disease Registry
t	statistic for confident limit
s	standard deviation
%	percentage

CHAPTER 1

INTRODUCTION

1.1 Soil

Soil is one of the three major natural resources other than air and water. It is one of the marvelous products of nature and without which there would be no life. According to Oxford Dictionary (2014), soil is the upper layer of earth in which plants grow, a black or dark brown material typically consisting of a mixture of organic remains, clay, and rock particles. In addition, soil is said to made up of a mixture of organic material and minerals (Saburchill, 2014). The organic matter comes from dead plants and many of the minerals come from the rocks underground. These rocks which are part of the lithosphere are referred as bedrock. These rocks are hidden because the plants grow on top of the soil and the rocks are found underground. Hence, it is clearly known that soil is made up of layers as shown in Figure 1.1

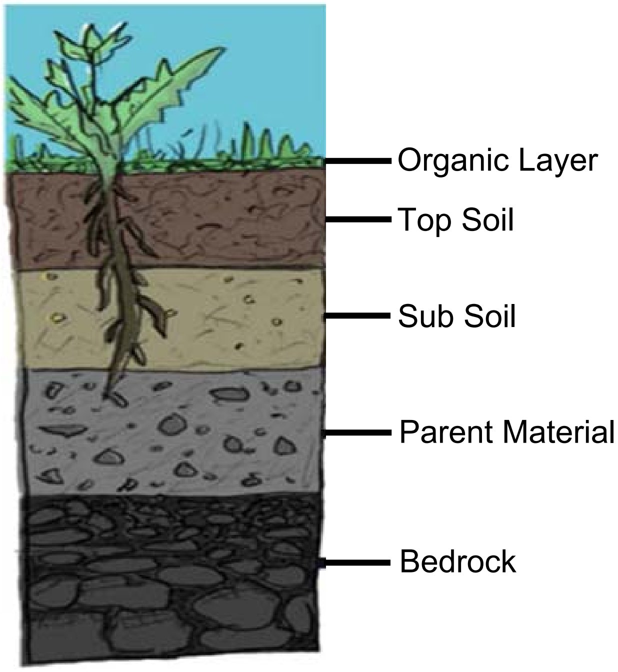


Figure 1.1 Cross section of soil (BLOGDIVVY, 2008)

1.2 Components of Soil

The main components in the soil are water, air, rocks, minerals, nutrients, organic matter, well decomposed organic matter which is known as humus and organisms. The proportion of each of these is important in determining the type of soil that is present. The relative proportions of these soil components vary with soil type and climatic conditions. For example, in a good garden soil the components are about 45% will be rock particle, 5% of organic matter, 25% of water and 25% of air (University of Illinois Board of Trustees, 2014).

1.3 Soil Formation

Soil formation or pedogenesis is the combined effect of chemical, physical, biological and anthropogenic processed working on soil parent material. Soil is said to formed when organic matter has accumulated and colloids are washed downward, leaving deposit of clay, humus, iron oxide, carbonate and gypsum (Wikipedia, 2014). These constituents are moved from one level to another by water and animal activity. As a result, layers form in the soil profile. The alteration and movement of materials within a soil causes the formation of distinctive soil horizons.

Soil formation is influenced by five classic factors that are intertwined in the evolution of a soil. These factors are parent material, climate, topography, organism and time (Michael, 2009; Natural Resource Conservation Service, 2013). The correlation between these factors can be executed by an example of the development of soil. It would begin with the weathering of lava flow bedrock which will produce the purely mineral-based parent material from which the soil texture forms. Soil development would proceed most rapidly from bare rock of recent flows in a warm climate under heavy and frequent rainfall. Under such conditions, plants become established very quickly on basaltic lava even though there is very little organic material. The plants are supported by the porous rock as it is filled with nutrient-bearing water that carries dissolved minerals from the rocks and guano.

Local topography of the rocks would hold fine materials and habour plant roots. The developing plant roots are associated with mycorrhizal fungi that assist in breaking up the porous lava and these means organic matter and a finer mineral soil accumulated with time (Van *et al*., 2006).

1.3.1 Parent Material

Parent material is the original underlying rock or mineral material from which a soil forms. The rocks can be igneous, sedimentary or metamorphic. Essentially the nature of parent rock in a particular region will affect the type of soil that develops. The soil forms as the parent material is chemically and physically weathered, transported, deposited and precipitated.

1.3.2 Climate

Effective precipitation and temperature are the principals of climate variables that influencing soil formation. Both variables highly affect the rates of chemical, physical and biological processes which involve in soil formation. The temperature and moisture both influence the organic matter content of soil through their effects on the balance between plant growth and microbial decomposition. Where else, mineral precipitation and temperature are the primary climatic influences on soil formation. The processes of weathering, leaching and plant growth will be maximized if warm temperature and abundant water presents at the same time (Wikipedia, 2014).

1.3.3 Topography

The topography is characterized by the inclination, elevation and orientation of terrain. Terrain is another important factor in soil development. Areas with many slopes in the land tend to have more freely drained soil as water can run off or percolate more rapidly. In contrast, flat areas of land can often be waterlogged because of the lack of gradient to promote lateral or sideway flows. Intermediate topography affords the best conditions for the formation of an agriculture productive soil.

1.3.4 Organism

Organisms in soil are microbes. The population is estimated to be around one billion cells per gram of soil but the number of species varies widely (Amber, 2008; Roesch *et al*., 2007). The total number of organisms and species can vary widely according to soil type, location and depth. Organisms such as plants, animals, fungi bacteria and human affect the soil formation (Wikipedia, 2014). Animals, soil mesofauna and micro-organism mix soil allowing moisture and gasses to move as they form burrows and pores. In the same way, plant roots open channels in soils. Microorganisms such as fungi and bacteria affect the chemical exchange between roots and soils and act as a reserve of nutrients. Human impact in soil formation is by removing vegetation cover with erosion as the result. Their tillage also mixes the different soil layers restarting the soil formation process as less weathered material is mixed with the more developed upper layers.

Earthworms, ants and termites mix the soil as they burrow and significantly affecting soil formation. In general, the mixing activities of animals sometimes called pedoturbation which tends to undo or counteract the tendency of other soil-forming processes to accentuate the differences among soil horizons. Termites and ants may also retard soil profile development by denuding large areas of soil around their nests leading to increased loss of soil by erosion. Large animals such as gophers, moles, and prairie dogs bore into the lower soil horizons bringing materials to the surface. Old animal burrows in the lower horizons often become filled with soil material from the overlying a horizon which creates profile features known as crotovinas (Wikipedia, 2014).

1.3.5 Time

Time is another factor that influencing the soil formation. Over time, soils evolve features that are dependent on the interplay of other soil forming factors. Soil is always changing. It takes about 800 to 1000 years for a 2.5 cm (1 inch) thick layer of fertile soil to be formed in nature (Wikipedia, 2014). For example, recently deposited material from a flood exhibits no soil development because there has not been enough time for the material to form a structure that further defines soil. The original soil surface is buried, and the formation process must begin anew for this deposit. Over a period of between hundreds and thousands of years, the soil will develop a profile that depends on the intensities of biota and climate. While soil can achieve relative stability of its properties for extended periods, the soil life cycle ultimately ends in soil conditions that leave it vulnerable to erosion. Despite the inevitability of soil retrogression and degradation, most soil cycles are long.

1.4 Metals in Soil

Metals are defines as any element that has a silvery luster and is a good conductor of heat and electricity. Two third of elements found in nature are metals. According to the chemical definition, metals are elements and cannot be synthesized or degraded by biological or chemical processes though these processes can change chemical forms of metals. There are many terms used to describe and categorize metals which are trace metals, transition metals, micronutrients, toxic metals and heavy metals (Jaon & Bert). All soils naturally contain trace level of metals. Metals are contained in Earth crust and in parent rocks. The soil is formed by its weathering process. The average concentration of selected metals in soil are listed in Table 1.1

Table 1.1 Content of Various Elements in Soil (Lindsay, 1979)

Metals	**Selected Average for Soil (mg/kg)**	**Common Range for Soil (mg/kg)**
Al	71,000	10,000 – 300,000
Fe	38,000	7,000-550,000
Mn	600	20 – 3,000
Cu	30	2 - 100
Cr	100	1 -1,000
Cd	0.06	0.01 - 0.70
Zn	50	10 – 300
As	5	1.0 – 50
Se	0.3	0.1 – 2.0
Ni	40	5 – 500
Ag	0.05	0.01 – 5
Pb	10	2 – 200
Hg	0.03	0.01 – 0.3

The anthropogenic activities increase the quantity of metal in the environment. Metals are chemically very reactive in the environment which results in their mobility and bioavailability to living organism. Metals associated with the aqueous phase of soils are subject to movement with soil water. Immobilization of metals by mechanism of absorption and precipitation prevent the movement of the metals. Metal-soil interaction is such that when metals are introduced at the soil surface, downwards transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental condition over time such as degradation of the organic waste matrix, changes in pH, redox potential or soil solution composition due to various remediation schemes or to natural weathering processes also may enhance metal mobility (Joan & Bert, 1992).

Distribution, mobility, bioavailability and toxicity of metals depend not only on metal concentration but also on the form in which the metal exist. Chemical behavior of a metal element in the environment is possible only by identification all forms in which that elements can be found under different environmental conditions. Metal speciation is one of the most important properties that determine the individual behavior and toxicity of metal species in the environment. Chemical speciation of an element of an element refers to its specific from characterized by a different isotopic composition, molecular structure and electronic or oxidation state (Manouchehri *et al*., 2006).

Speciation is the process of identification and determination of different chemical and physical forms of elements present in a sample (Wang *et al*., 2006). Metals that occur in cationic forms have a higher ability of binding to negatively charged soil colloids and are thus less bioavailable but more easily accumulate in soil. Unlike cationic forms, the anionic forms that are mainly present in soil solution and are more bioavailable but are more readily leached form the soil.

1.5 Arsenic in Soil

Arsenic is a naturally occurring element that is widely distributed in the Earth's crust. Arsenic is classified chemically as a metalloid which has both properties of metal and a nonmetal. However it is frequently referred as metal. Arsenic occurs in two elemental form under ambient condition, which are steel grey coloured brittle metallic or a dark grey amorphous solid (ATSDR, 2007). It has a similar complex chemistry of phosphorus (CCME, 2001). Arsenic is about the 52nd most common chemical element on earth (BLOGDIVVY, 2008)

Arsenic occurs naturally in the environment and also has been used in many man made products. Over 200 arsenic containing minerals have been identified with approximately 60% being arsenates, 20% sulphides and sulphosalts and the remaining 20% including arsenides, arsenites and oxides (O'Neill, 1995).The most commonly occurring form is arsenopyrite which is an iron arsenic sulphide associates with many types of mineral deposits and especially those including sulphide mineralization (O'Neill,1995; Farago et al., 2003)

Arsenic forms in both organic and inorganic compounds after reacting with other elements. If arsenic reacts with carbon and hydrogen then it forms an organic compound but if it reacts with elements like oxygen, chlorine and sulfur, then it presents as inorganic compound. Most common valence states that arsenic can form are -3, +3 or +5 (ATSDR, 2007). Both inorganic and organic arsenic compound is toxic but inorganic arsenic compound to known as more toxic. This includes arsenite and arsenate with valence state of +3 and +5 respectively.

Arsenic is known as poisonous and toxic. Inorganic arsenic is thought to be the most toxic while most organic forms of arsenic are relatively less toxic (King County, 2014). Use of arsenic in many applications has been banned or phased out due to its known toxicity (ATSDR, 2007). Although few regulation has banned the use of arsenic but the occurrence of arsenic naturally is not avoidable.

The presence of arsenic in the environment can be due to both background and to anthropogenic sources. The soil environment is an important sink for arsenic compounds. Arsenic deposited in the soil may accumulate rapidly since it is only depleted slowly through plant uptake, leaching, methylation or erosion. Arsenic can be also released in soil by naturally weathering, industrial production and mining.

1.5.1 Arsenite and Arsenate

In typical surface soils, the most important inorganic forms of arsenic are arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) with the latter dominating under aerobic or oxidizing conditions (O'Neill, 1995; Kabata-Pendias and Mukherjee, 2007). The relationship between arsenate and arsenite in soil is complicated by the presence of clay minerals, iron and aluminium oxides, organic matter,microbial action, soil redox potential and pH (O'Neill, 1995; Kabata-Pendias and Mukherjee, 2007).These factors influence the relative stability of the two anions in solution and the rate of oxidation between the two forms in soil (Environment Agency, 2009).

Arsenite is considered to be more mobile in soils than arsenate and to be the main species at low pH under reducing condition (Kabata-Pendias and Mukherjee, 2007). Both arsenate and arsenite can adsorb to hydrated iron and aluminium oxides, clay and organic matter although phosphate has been shown to interfere with this (O'Neill,1995; IPCS, 2002). The role of aluminium oxides and hydroxides in arsenic adsorption is significant only in acidic soil (IPCS,2002).

1.5.2 Exposure of Arsenic to Humans

There are many ways that human can be exposed to arsenic since arsenic is found naturally in the environment. Through touching, ingestion, breathing and eye contact, arsenic can be exposed to humans. Arsenic can be exposed by digging, playing or gardening in the soil contaminated with arsenic. This touching as shown in Figure 1.2 exposure is normally faces by children and farmers. Through ingestion, children are exposed by unintentionally eating the arsenic contaminated soil while playing. Dust contaminated with arsenic could be brought into home from outside and human are exposed by breathing in the sawdust or burning smoke from wood treated with arsenic. The eye contact exposure is by contacting eye with air which brings the arsenic elements from the soil or sawdust or burning smoke.

Figure 1.2 Exposed arsenic in soil through touching

(Hawaii State Department of Health, 2010)

1.5.2.1 Health Effect

Long term exposure of inorganic arsenic mainly through drinking arsenic contaminated water, eating food prepared with this water and eating irrigated with arsenic rich water can lead to chronic arsenic poisoning. The immediate symptoms of acute arsenic poisoning include vomiting, abdominal pain and diarrrhoea. Other symptoms are blood in urine, cramping muscle and hair loss. The first symptoms of long term exposure to high levels of inorganic arsenic are usually observed in the skin and include pigmentation changes, skin lesions and hard patches on the palms and soles of the feet which are known as hyperkeratosis as shown in Figure 1.3. These occur after a minimum exposure of approximately five years and may be a precursor to skin cancer.

Figure 1.3 Hyperkeratosis (Disease Pictures, 2010)

In addition to skin cancer, long-term exposure to arsenic may also cause cancers of the bladder and lungs. The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans. Other adverse health effects that may be associated with long-term ingestion of inorganic arsenic include developmental effects, neurotoxicity, diabetes and cardiovascular disease. The final result of arsenic poisoning is coma and death

1.6 Objective

The objectives of this study are:

i) To quantify arsenic concentration in soil by using Inductively Coupled Plasma – Optical Emission Spectroscopy.

ii) To identify the highest arsenic content in soil among the five sampling locations.

CHAPTER 2

LITERATURE REVIEW

2.1 Brief Explanation on Literature Review

In this chapter, history of arsenic and murderous incident because of arsenic are discussed. Other than that, the properties of arsenic and various digestive techniques are explained. To further on, the previous research on arsenic in soil is also been briefly explained.

2.2 History of Arsenic

Arsenic has been discovered around 1250 by Albertus Magnus as shown in Figure 2.1. Arsenic is called differently in some languages. Arsenic known as arsenicum in Latin where else in Greek word it is arsenikon and the Arabic word Az-zernikh (Jeffson Lab, 2012). This trace metal has been used widely by the ancient Greek and Romans in earlier age.

Figure 2.1 Albertus Magnus (Dartmorth Toxic Metal, 2013)

In first century, a Greek physicians in the court of the Roman Emperor Nero described arsenic as a poison. Symptoms of arsenic poisoning were difficult to detect since they could mimic food poisoning and other common disorders. There could be no doubt about arsenic's efficacy as a single large dose which provoked violent abdominal cramping, diarrhea and vomiting often followed by death from shock (Dartmorth Toxic Metal, 2013).

Arsenic was the king of poison in middle ages and renaissance (Dartmorth Toxic Metal, 2013). At early of fourth century BC, mineral forms of arsenic were known (Dartmorth Toxic Metal, 2013). The Romans made considerable use of poisons in politics. In this same period a conspiracy was uncovered involving a group of women who schemed to poison men whose deaths would profit them in fourth century BC (Dartmorth Toxic Metal, 2013). In 82 BC, the Roman dictator and constitutional reformer Lucius Cornelius Sulla issued the Lex Cornelia probably the first law against poisoning in an attempt to stem what was becoming an epidemic of large-scale poisonings (Dartmorth Toxic Metal, 2013).

In the year of 1836, James Marsh, an English chemist perfected a sensitive and specific chemical test for arsenic and poisoners thereafter had little hope of escaping detection. Although the sinister use of arsenic decreased, certain commercial applications were found and various forms became common in the market place (Dartmorth Toxic Metal, 2013). At the mid of 1800, Mountaineers of central Austria (Styria) made a habit of consuming arsenic preparations once or twice a week as a general stimulant and tonic. They became known as "arsenic eaters" and some were reputed to have adopted the practice as a means of building up a tolerance against poisoning by their enemies (Dartmorth Toxic Metal, 2013).

Around 1900, a Germany pharmacologist named Paul Ehrlich became preoccupied with the violently poisonous nature of arsenic. Ehrlich however was convinced that the toxic potential of arsenic could be harnessed and used therapeutically as a treatment for diseases such as syphilis. Ehrlich patiently threaded his way through 604 different organic compounds of arsenic before he literally stumbled on number

605 to which he gave the grandiose name of Salvarsan. Salvarsan became the first drug that was safe enough to be given to humans and to be truly effective against the dread spirochete bacteria that causes syphilis. It was to be replaced immediately on the discovery of penicillin (Dartmorth Toxic Metal, 2013). Many other organic arsenical drugs were eventually introduced for use against various bacterial or parasitic infections, but few survived the introduction of antibiotics. One of the longest-lived medicinal preparations of arsenic was a solution of one-percent potassium arsenite called Fowler's Solution. Fowler's Solution was first used as a general tonic, but many reputable dermatologists felt it had value in the treatment of psoriasis (Dartmorth Toxic Metal, 2013).

In 1940, Germans had developed an organic blistering war gas containing arsenic which was known by the code name of Lewisite (Dartmorth Toxic Metal, 2013) and in 1950s The toxicity of arsenic to insects, bacteria and fungi led to its use as a wood preservative (Rahman *et al.*, 2004).

In twentieth century, there were reports of death by arsenic containing cosmetics (Dartmorth Toxic Metal, 2013). At Early 20th century, lead hydrogen arsenate was a common insecticide on fruit trees. Later in middle of 20th century, monosodium methyl arsenate (MSMA) and disodium methyl arsenate (DSMA) are less toxic organic forms of arsenic. Both have replaced lead arsenate in agriculture which causes brain damage.

2.3 Murderous Incidents

Since Arsenic was discovered, many murderous incidents took place by using arsenic despite its beneficial use in many industries. Many people are affected by the misuse of arsenic in many areas. The murderous incident has took place since in middle ages but has reduced towards twentieth century since regulation has been introduced to protect the public.

In middle ages, in Italy the most widely accused of poisoners were the Borgias, Pope Alexander VI and his son, Cesare. As the Pope, Alexander VI appointed cardinals who were not only allowed but encouraged to increase their personal wealth through perquisites granted by the church. The nouveau riche pillar of propriety would then be invited to one or more sumptuous meals with the Borgias. There are those who say that arsenic actually improves the taste of wine. The Borgias made certain that their guest consumed as much of the doctored drink as possible. Following the inevitable and untimely death of the victim ownership of his property by church law reverted to his executioners. Pope died after consuming the wrong wine which used to poison others (Dartmorth Toxic Metal, 2013).

In between 1797 to 1803, Theodor Gottlieb Ursinus who is a high ranking Prussian civil servant and justice official was poisoned by his wife Charlotte Ursinus. She also has poisoned her aunt and her lover. Other than that, she also has attempted to poison her servant in 1803. Her sensational trial led to the first reliable method of identifying arsenic poisoning (Griffiths, 2009).

In 1878, two women were found murdered near their homes in New Haven, Conn. One had been savagely beaten and left in a wooded area and the body of the other was found floating in the water near an amusement park. Surprisingly, autopsies in both cases found that the women had been poisoned by enormous doses of arsenic (Dartmorth Toxic Metal, 2013).

In 1987, Claire Booth Luce became a victim of arsenic poisoning when was the United States ambassador to Italy because of the continual flaking of an arsenic based paint from the embassy dining room ceiling onto her dinners. She was forced to resign her position because of ill health brought on by that exposure (Dartmorth Toxic Metal, 2013)

Around 1990, the water supplies of much of the impoverished nation of Bangledesh consisted until recently of shallow wells that were often polluted by animal and human wastes. International efforts were mounted to provide better water supplies by digging deeper wells into aquifers. Many of these wells ended up tapping water from geologic formations naturally high in arsenic. Arsenic in groundwater is above 50 ug/L was found in 61 out of the total 64 districts in Bangladesh. This amount is 5 times higher than the concentration allowed by World Health Organization (WHO) for drinking water. As a result, thousands of people were poisoned (Utusan Malaysia Online, 2003; Dartmorth Toxic Metal, 2013).

In 1998, Arsenic was implicated in a sensational mass poisoning in Japan in which four people died and 40 were hospitalized. Arsenic trioxide had been added to pots of curried beef which were served at a village festival (Dartmorth Toxic Metal, 2013). Last not least, the report was in 2003. Residents of Kamisu, a town slightly north of Tokyo, complained of health problems and tests of their well water yielded levels of arsenic 450 times higher than mandated by government safety standards.(Utusan Malaysia Online, 2003)

2.4 Chemical and Physical Properties of Arsenic

The three most common arsenic allotropes are metallic gray (Chemicool, 2014), yellow and black arsenic but the stable form is a silver-gray which is brittle crystalline solid (Norman, 1998). It tarnishes rapidly in air and at high temperatures burns forming a white cloud of arsenic trioxide. Arsenic is a member of group V of the periodic table which combines readily with many elements. The metallic form is brittle and when heated it rapidly oxidizes to arsenic trioxide which has a garlic odor. The non metallic form is less reactive but will dissolve when heated with strong oxidizing acids and alkalis (Chisholm, 1911). The chemical and physical properties are shown in Table 2.1

Table 2.1 Chemical and Physical properties of Arsenic

Atomic number	33
Atomic mass	74.9216 g.mol $^{-1}$
Electronegativity according to Pauling	2.0
Density	5.7 g.cm^{-3} at 14°C
Melting point	814 °C (36 atm)
Boiling point	615 °C (sublimation)
Vanderwaals radius	0.139 nm
Ionic radius	0.222 nm (-2); 0.047 nm (+5); 0.058 (+3)
Isotopes	8
Electronic shell	[Ar] 3d^{10} 4s^{2} 4p^{3}
Energy of first ionisation	947 kJ.mol $^{-1}$
Energy of second ionisation	1798 kJ.mol $^{-1}$
Energy of third ionisation	2736 kJ.mol $^{-1}$
Standard potential	- 0.3 V (As^{3+}/ As)

2.5 Digestion Methods For Arsenic Analysis

Trace metals in soil have to undergo digestion before it could be analysed through spectroscopic techniques. Acid digestion which is known as wet digestion is an important step in trace metal analysis. Acid digestion procedures are employed for the determination of elements in solid subsequent to sampling and mechanical sample preparation in order to completely transfer the analytes into solution so that they can be introduced for the determination step in liquid form (BERGHOF,2000). Acids attack the matrix where these metals are embedded and solubilize heavy metals. The goal of every digestion process is the complete solution of the analytes and the complete decomposition of the soild (matrix) while avoiding contamination of the analytes (BERGHOF,2000).

Wet chemical digestion involves various mineral acids such as hydrochloric acid, nitric acid, hydrofluoric acid, sulfuric acid and perchloric acid. Combination of nitric acid with hydrochloric acid with the ratio of 1:3 is called aqua regia. Aqua regia is most preferable acid because of it can dissolve the so-called royal or noble metals, gold and platinum (Wikipedia, 2014) Using hydrochloric acid and nitric acid will enhance the visibility of trace metals in spectroscopy analysis. This digestion can be enhanced by using heating and digestion tools such as microwave digestion and HotBlock^{TM}.

Microwave digestion as shown in Figure 2.2 is a common technique used by elemental scientists to dissolve heavy metals in the presence of organic molecules prior to analysis by inductively coupled plasma, atomic absorption, or atomic emission measurements. This technique is usually accomplished by exposing a sample to a strong acid in a closed vessel and raising the pressure and temperature through microwave irradiation. This increase in temperature and pressure of the low pH sample medium increases both the speed of thermal decomposition of the sample and the solubility of heavy metals in solution. Once these heavy metals are in solution, it is possible to quantify the sample through spectroscopic techniques.

Figure 2.2 Microwave digestion (LabWrench, 2014)

HotBlock^{TM} as shown in Figure 2.3 function the same as microwave but it has advantages compare to microwave digestion. Digestion by using HotBlock^{TM} is fast, clean and most cost effective in performing metal digestion (Environmental Express, 2014). The heater mat in each block provides uniform heat distribution to all samples throughout the digestion process. Temperature stability allows all samples being digested to evaporate at a similar rate providing more uniform recoveries and preventing the opportunity for cross contamination (Environmental Express, 2014).

Figure 2.3 HotBlock^{TM} (Environmental Express, 2014)

2.6 Previous Research on Arsenic

Many research and quantification of arsenic has been conducted by using various techniques. For inorganic arsenic spectroscopic techniques been used but organic arsenic uses chromatograpic techniques. Most of the scientist interest was on inorganic arsenic because of its toxicity effect to human. Some of the researches are shown in Table 2.2

Table 2.2 Previous researches on arsenic in soil

Year	Researcher	Description
1999	Cristina *et al*	Atomic fluorescence determination of arsenic in soils after microwave-assisted distillation. In this study for inorganic arsenic, only hydrochloric acid been used but aqua regia been used for determining total arsenic
2009	Ji-Hyun *et al*	This research group has used double pulse-laser induced breakdown spectroscopy. In this techinique acid digestion is not been used. To verify this method, atomic absorption spectrometer with graphite furnace was used. For this verification method aqua regia and shaker been used for digestion of the soil.
2012	Anselimo *et al*	The soil samples were treated with a mixture of nitric acid, sulphuric acid and perchloric acid in the ratio of 6:3:1 and added hydrochloric acid were added. The heating tool to enhance the digestion was hot plate. In this study, Atomic Absorption Spectroscopy was used
2014	Jilei *et al*	This study was involved soil which underwent acid digestion where nitric acid, perchloride acid and hydrochloric acid with the ratio of 3:1:1. The mixture was digested using oven and electric heating board to evaporate the liquid. Then the sample was diluted to 10ml and analysed by using Inductivley Coupled Palsma-Optical Emission Spectroscopy.

CHAPTER 3

METHODOLOGY

3.1 Brief Explanation of Methodology

This study focuses on quantification of arsenic in soil. Soils samples from five different locations were collected and were under gone sample pre-treatment. After pre-treatment, the soils were digested at 95^{o}C with concentrated nitric acid and concentrated hydrochloric acid. This step followed by filtration and dilution and analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

3.2 Sampling

Sampling was done in five different locations which focused on human exposure of arsenic through soil. The places are garden, dam, beach, construction area and agriculture area. The soils were selected based on frequent human exposure to the soil. The soil was taken from the surface by using gardening tools. The soils were collected in a plastic container which is free from contamination.

Soil for garden was taken from a house from Selayang, Selangor. The soil for dam and beach was taken from *Empangan Batu Sungai Tua*, Selayang and Port Dickson, Negeri Sembilan respectively. MRT construction in Jalan Cheras represented the construction category and *Jabatan Pertanian Malaysia*, Ulu Langat district for agriculture.

In garden, human exposed to soil while gardening. This same goes to agriculture area but indirectly the arsenic in the soil is uptake by the plants. So not only the farmers exposed to arsenic through soil but also the consumers who eat the plant from the corps exposed indirectly. While in dam, human exposed to arsenic through soil by fishing activity carried by human. They have direct contact to the soil while sitting on the ground while fishing. In the other hand arsenic could leach out to the dam water which might effects the water supplied to the public and in the other hand, fishes could be contaminated by arsenic. This also well explained for beach. Human is much more exposed directly to the sand.

For construction area, not the workers are exposed to arsenic in soil but also the people who stay around the construction area and who pass by the area. This could be direct contact of soil for the construction worker but for others it could be inhaling the dust from the construction soil.

Soil was collected at three different points for each sampling place. Each was labeled sampling point 1 (SP1), sampling point 2 (SP2) and sampling point 3 (SP3). The detailed explanation about the sampling at garden, dam, beach, construction area and agriculture area is represented by Table 3.1, Table 3.2, Table 3.3, Table 3.4 and Table 3.5 respectively.

Table 3.1 Sampling at garden area

Location : Garden in a house at Selayang, Selangor		
Sampling Point 1	Sampling Point 2	Sampling Point 3
		
Soil Collected		
		
Description on Sampling Point		
Planted small plants and introduce small amount of pesticides every 3 months once	Planted banana tree and introduce small amount of pesticides every 3 months once	Planted small plants and dead hamsters. Never introduced pesticide and consist of fish pond.

Table 3.2 Sampling at dam area

Location : *Empangan Batu Sungai Tua* (Selayang Dam)		
Sampling Point 1	Sampling Point 2	Sampling Point 3
		
Soil Collected		
		
Description on Sampling Point		
Near to the dam water and frequent fishing activity happens. Death fishes around this point were observed.	50 meters away from the water. Small plants been observed.	Near to the dam water and frequent fishing activity happens.

Table 3.3 Sampling at beach area

<table>
<tr><th colspan="3">Location : Port Dickson Beach, Negeri Sembilan</th></tr>
<tr><td>Sampling Point 1</td><td>Sampling Point 2</td><td>Sampling Point 3</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td colspan="3">Soil Collected</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td colspan="3">Description on Sampling Point</td></tr>
<tr><td>The place which children build sand castle and play with the sand. Adults have picnic activities.</td><td>A lot of crabs been observed. Near to the sea</td><td>The place which people will have a view of the sea</td></tr>
</table>

Table 3.4 Sampling at construction area

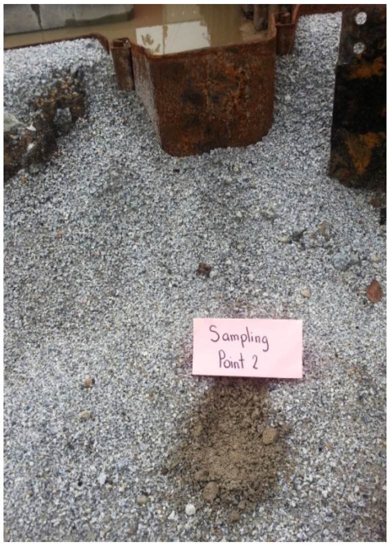
<table>
<tr><th colspan="3">Location : MRT Construction, Jalan Cheras</th></tr>
<tr><td>Sampling Point 1</td><td>Sampling Point 2</td><td>Sampling Point 3</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td colspan="3">Soil Collected</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td colspan="3">Description on Sampling Point</td></tr>
<tr><td>Near the fully built beam. A lot of rocks observed</td><td>Near half built beam. A lot of small rocks observed.</td><td>Between two fully built beams. A lot of small rocks observed.</td></tr>
</table>

Table 3.5 Sampling at agriculture area

Location : *Jabatan Pertanian Malaysia*, Ulu Langat District		
Sampling Point 1	Sampling Point 2	Sampling Point 3
		
Soil Collected		
		
Description on Sampling Point		
Newly planted vegetables Pesticide is introduced frequently	Planted Corn plant. Corns have not developed. Pesticide is introduced frequently	Planted corn planted. Corn has developed. Pesticide is introduced frequently

3.3 Sampling Pre-Treatment

The collected soils were air dried for two days. After drying it, the soil was sieved to remove the stones and rocks. This soil was then grounded by using mortar and pestle.

3.4 Sample Preparation

3.4.1 Apparatus and Material

In this analysis few apparatus and materials were used. This apparatus had been cleaned and dried before used. The apparatus and materials are

a) Beakers
b) Volumetric flasks (100ml)
c) Dropper
d) Pipettes
e) HotBlock^{TM} Digestion Tubes
f) Filter paper – Whatman No.41
g) Funnel
h) Thermometer
i) Hot plate
j) HotBlock^{TM}

3.4.2 Chemicals

In this analysis, only four chemicals were needed. The chemicals are

a) Concentrated nitric acid (HNO_3)
b) Concentrated hydrochloric acid (HCl)
c) Reagent water
d) 1000 ppm Arsenic stock solution

3.4.3 Procedure

1.0000 g ± 0.1 g of soil was weighed by using analytical balance which has a resolution of 0.1 mg. The soil weighed directly in digestion tube on a tared balance for better weighing. The tubes were labeled appropriately as shown in Table 3.6.

Table 3.6 Labeling of samples according to location

Points Location	Sampling Point 1		Sampling Point 2		Sampling Point 3	
	1	2	1	2	1	2
Garden	Garden (SP1)	Garden (SP1)*	Garden (SP2)	Garden (SP2)*	Garden (SP3)	Garden (SP3)*
Dam	Dam (SP1)	Dam (SP1)*	Dam (SP2)	Dam (SP2)*	Dam (SP3)	Dam (SP3)*
Beach	PD (SP1)	PD (SP1)*	PD (SP2)	PD (SP2)*	PD (SP3)	PD (SP3)*
Construction	MRT (SP1)	MRT (SP1)*	MRT (SP2)	MRT (SP2)*	MRT (SP3)	MRT (SP3)*
Agriculture	JPM (SP1)	JPM (SP1)*	JPM (SP2)	JPM (SP2)*	JPM (SP3)	JPM (SP3)*

2.5 mL of concentrated HNO_3 and 10.0 mL of concentrated HCl was added and the digestion tube was covered with reflux cap. This mixture was then heated and digested at 95 ± 5 ^oC using SC154 - 54-Well HotBlock™ (Environmental Express, USA) for 15 minutes.

The results mixture was filtered by Whatman No.41 filter paper and been collected in 100 mL volumetric flask. The filter paper was washed with 3 mL of approximately 95^oC concentrated HCl and followed by 20 mL of approximately 95^oC reagent water while the filter paper is in the funnel. The washing was collected in the same volumetric flask.

The filter paper was removed from the funnel and was placed in the same digestion tube and 5 mL of concentrated HCl was added into the digestion tube. Again the digestion tube covered with reflux cap was heated and digested at 95 ± 5 ^{o}C until the filter paper dissolved. Later the residue was filtered and collected in the same volumetric flask. The digestion tube and the reflux cap was washed with hot reagent water and filtered. The filtrate was allowed to cooled and diluted to the volume using reagent water. The sample is analysed by ICP-OES. The summarized method is in Appendix 1.

3.5 Instrumentation

3.5.1 ICP-OES

ICP-OES is one of the most powerful and popular analytical tools for the determination of trace elements in a myriad of sample type (Xiangdeng and Bradley,2000). The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radio frequency discharge (Xiangdeng and Bradley,2000). Liquid and gas samples can be introduced directly to ICP-OES while solid samples require extraction or acid digestion so that the analytes will be present in a solution.

In this analysis, ICP-OES used is PerkinElmer with the model of Optima 4300 DV as shown in Figure 3.1. For arsenic analysis, the wavelength setting was 193.696 nm and the internal temperature used was 6000 K. This high temperature is to vaporize the aerosol introduced by the nebulizer. To ensure the analytical quality, the calibration is carried out and checking on the quality control sample.

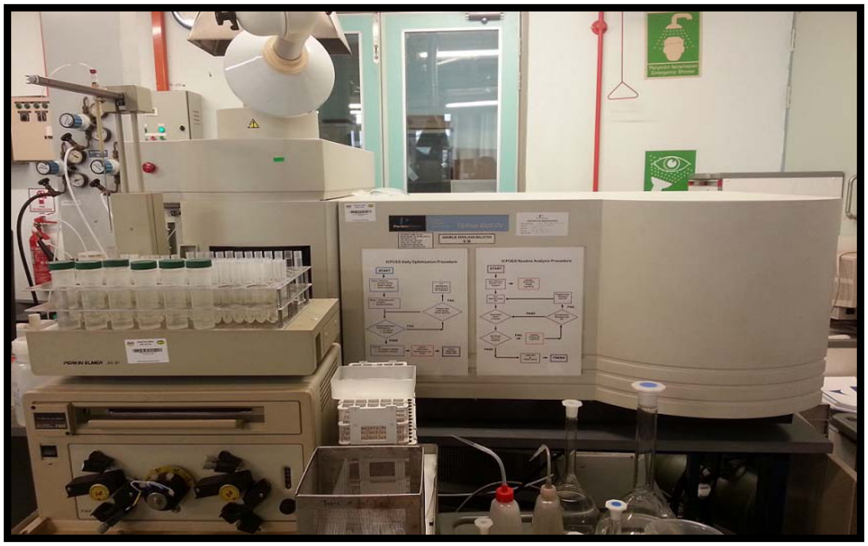


Figure 3.1 Optima 4300 DV ICP-OES (PerkinElmer, USA)

3.5.2 Calibration and Quality Control Standards

The blank standard was 10% of nitric acid which was prepared from the concentrated nitric acid. A series of arsenic calibration standards were prepared from 1000 ppm of arsenic by appropriate dilution using reagent water. The concentrations are 0.1, 0.5, 5, 20 ppm. The quality control was 5 ppm of arsenic standard.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Brief Explanation on Results and Discussion

In this chapter, soil selection and the observation during analysis is explained. The outcome from Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) is discussed accordingly and possibility of the arsenic contamination is briefly explained.

4.2 Observation During Analysis

The weighed soiled in the digestion tube carefully added with concentrated HNO_3 and concentrated HCl. This mixture gives a yellowish brown colour. The HotBlock^{TM} heated to 95 ± 5 ^{o}C before the digestion tube filled into the blocks. The mixture was heated and digested for 15 minutes as shown in Figure 4.1. During the heating process, there was brown fume observed. It indicates the oxidation occurs. For the sample from Jabatan Pertanian Malaysia, Ulu Langat district, formation of foam was observed while heating. This could be due to the high level of nitrogen contain in the soil. After the heating process, the mixture turned into dark yellowish colour except for the sample for Port Dickson Beach was light yellowish colour. The mixture was then filtered into 100 mL volumetric flask and washed with approximately 95^{o}C hot concentrated HCl and approximately 95^{o}C hot reagent water. This wash gives the analyte of interest goes into the flask. This completes the first digestion.

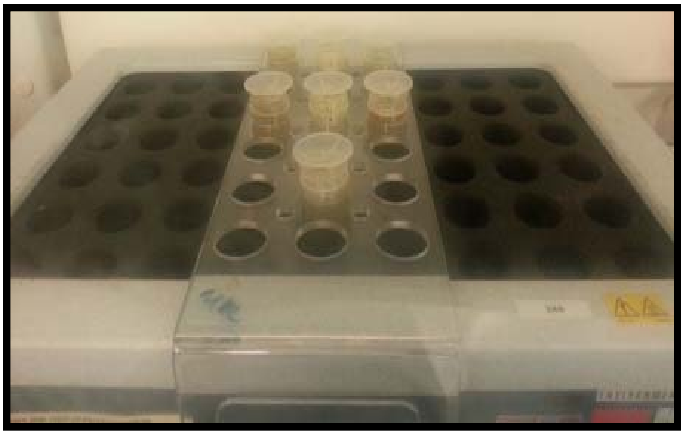
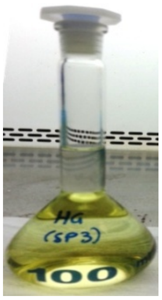
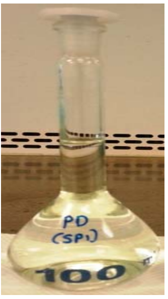
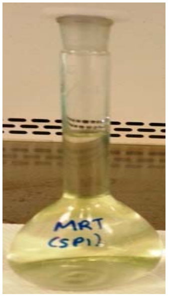


Figure 4.1 Digestion with SC154 - 54-Well HotBlock™ (Environmental Express, USA)

The second digestion includes the filter paper used for the first digestion. The filter paper was placed into the same digestion tube and added with concentrated HCl and heated and digested at 95 ± 5 °C until the filter paper dissolved. This process took approximately 15 minutes. This second digestion process is for extracting out all the left analyte of interest in the soil and the filter paper. This mixture is then filtered. The digestion tube and the reflux cap were washed with hot reagent water and filter into the same 100 mL volumetric flask. The filtrate is then diluted to volume after the filtrate cooled to room temperature. The samples are analysed by ICP-OES. The samples prepared are as shown in Table 4.1.

Table 4.1 Prepared samples from five different locations

Points Location	Sampling Point 1		Sampling Point 2		Sampling Point 3	
	1	2	1	2	1	2
Garden in a house at Selayang, Selangor						
Empangan Batu Sungai Tua (Selayang Dam)						
Port Dickson Beach, Negeri Sembilan						
MRT Construction Jalan Cheras						
Jabatan Pertanian Malaysia, Ulu Langat District						

4.3 Quantification by ICP-OES

4.3.1 Calibration and quality control

Before quantification of arsenic in the samples, the calibration is done with the concentration of 0, 0.1, 0.5, 5 and 20 ppm. Calibration is the process of evaluating and adjusting the precision and accuracy of measurement equipment. Blank calibration which is 0 ppm is carried out with 10% of nitric acid where else for 0.1, 0.5, 5 and 20 ppm is prepared from 1000 ppm Arsenic stock solution.

This calibration in presented by linearity graph. Evaluation of this graph is done by correlation coefficient, r. The value of are such that $-1 \leq r \leq +1$. The positive and negative signs are used for positive linear correlations and negative linear correlations respectively. In positive linear correlations, an *r* value of exactly +1 indicates a perfect positive fit and an *r* value of exactly -1 indicates a perfect negative fit for negative linear correlations (MathBits, 2000)

In this analysis reported value for r was 0.999992. This value shows a perfect fit for this Arsenic quantification analysis. The graph obtained is as shown in Figure 4.2 and the full report of calibration is as in Appendix V.

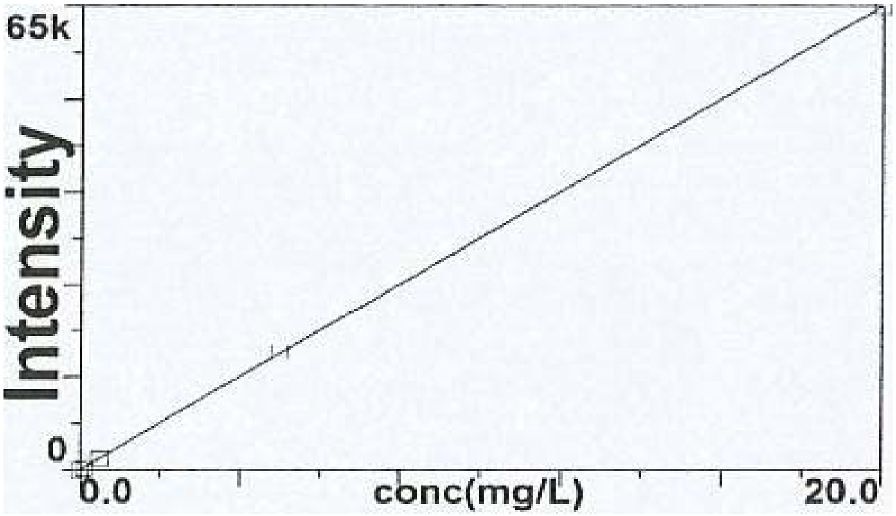


Figure 4.2 Linearity graph of calibration

The quality control which prepared was at 5 ppm was checked initially. The recovery was 97%. After the initial checking, quality control checks been done for every 20 interval of the samples. The recovery was from 100% to 101%. This shows the instrument was in good condition throughout the analysis process.

4.3.2 Quantification of Arsenic in Soil

Each sampling places was represented by three sampling point. One duplicate for each point was prepared. So for each sampling place number of samples, n, is equals to 6 (n=6). In total 30 soil samples from five different locations which were under gone sample pre-treatment and sample prepared were analysed by using ICP-OES. All the samples were quantified on the same day. All the results were calculated to the volume prepared is as shown in Appendix II. The calculation involved is

$$\text{Concentration of As (mg/kg)} = \frac{\text{Obtained concentration (mg/L) x 0.1 L (Volume prepared)}}{\text{Actual weight (kg)}}$$

Range of Arsenic concentration from n=6 is reported. The calculated arsenic concentration in five different locations is represented by Table 4.2. The raw data is attached as Appendix VI to XII. Other than the range of arsenic content, the average concentration with measurement uncertainty is also reported in Table 4.2. The calculation for average is as below:

$$\text{Average concentration of Arsenic (mg/kg)} = \frac{\sum \text{(concentration of arsenic, mg/kg)}}{N}$$

where N is number of sample

The calculation for measurement uncertainty is as below:

$$\text{Mesurement uncertainty (mg/kg)} = \sqrt{\sum(\text{standard deviation of sampling points})^2}$$

The standard deviations are as shown in Appendix III and the calculated values for mean and measurement uncertainty are shown in Appendix IV.

Table 4.2 Arsenic concentration from five different locations

Location	**Range of Arsenic concentration (mg/kg)**	**Average concentration ± measurement uncertainty (mg/kg)**
Garden in a house at Selayang, Selangor	2.77 to 41.74	19.17 ± 0.02
Empangan Batu Sungai Tua (Selayang Dam)	3.47 to 37.77	17.12 ± 0.01
Port Dickson Beach, Negeri Sembilan	0.43 to 4.22	1.73 ± 0.01
MRT Construction Jalan Cheras	9.18 to 73.43	32.24 ± 0.02
Jabatan Pertanian Malaysia, Ulu Langat District	12.50 to 47.08	31.55 ± 0.03

The highest arsenic contain in soil was found in construction area which was MRT Construction, Jalan Cheras. This followed by agriculture soil, garden soil, dam soil and beach which represented by *Jabatan Pertanian Malaysia* (Ulu Langat District), Garden in a house at Selayang (Selangor), *Empangan Batu Sungai Tua* (Selayang Dam) and Port Dickson Beach (Negeri Sembilan) respectively.

The construction, agriculture and garden areas show higher arsenic contain because there are no other route other than plant for the arsenic to leach out form the soil. This is different for the dam soil and the beach soil where the arsenic could leach out through plants, fishes and water (GreenFacts, 2014).

For MRT construction soil, the highest arsenic contain in soil is in sampling point two (SP2) with arsenic concentration from 30.36 to 73.43 mg/kg followed by sampling point three (SP3) and sampling point one (SP1) with arsenic concentration from 21.48 to 44.67 mg/kg and from 9.18 to 14.33 mg/kg respectively. The level of arsenic is high compared to a study which was conducted in Surfside construction in USA which shows 7.8 mg/kg (7News, 2014). The arsenic present from the construction side could be from the naturally occurring and man made product. The product such as cement and soil from mountains could be the main contribution to the arsenic contamination.

The soil from *Jabatan Pertanian Malaysia* (Ulu Langat District), is the second highest arsenic contain soil in this study. In this sampling place, SP2 (34.76 to 47.08 mg/kg) shows highest arsenic concentration and followed by SP3 (38.93 to 42.09 mg/kg) and SP1 (12.50 to 13.95 mg/kg). The presence of arsenic could be from the pesticides, herbicides, insecticide and fertilizer which have been used in this plantation. The obtained concentration is still low compared to the former lands in sugar cane cultivation in Hawaii. The concentration at the surface was 260 mg/kg (William, 2011). This is due to heavy usage of arsenic based herbiside, pesticide, insecticide and fertilizer in 1920s through 1940s (Hawai State Department of Health, 2010).

The garden soil in a house in Selayang is high compare to a garden in a school in Hawaii which contains 10.2 mg/kg (Roger, 2006). This concentration is due to the sugar cane plantation. The arsenic has spread out throughout the land since 1940s. The concentration of arsenic in the garden in Selayang is high because there are no heavy use of pesticide and herbicide as in the plantation. This could be the arsenic from the death hamster and small intake of arsenic by the small plants. In the other hand, the garden is in a small scale. The highest arsenic contain found in SP1 (19.88 to 41.74 mg/kg) and followed by SP3 (23.23 to 24.31 mg/kg) and SP2 (2.77 to 3.07 mg/kg).

The Selayang dam is the second least contaminated soil in this study. SP3 (35.33 to 37.77 mg/kg) has the highest arsenic contain compare to SP2 (10.55 to 10.63 mg/kg) and followed by SP1 (3.47 to 4.97 mg/kg). This could be from the death fish and human activity around the place. This arsenic level is high compared to Tanzania dam. As the study conducted by Norwegian University of Life Sciences, amount of arsenic is 111 µg/L to 1142 µg/L (Mining Watch Canada, 2009). This high concentration is due to the human activity which pollutes the dam soil.

The least arsenic concentrated soil was the beach soil which is known as sand. The arsenic could easily leach out to the sea so the arsenic was not detected in SP2 where the instrument is not sensitive enough to detect the very low concentration of the arsenic. The SP2 is nearby the sea. There is also a possibility of arsenic intake by the crabs which found in SP2. The highest contain arsenic found in SP1 (0.54 to 4.22 mg/kg) where many human activities such as games, picnic and building sand castle were observed. In SP3 (0.43 mg/kg), there was less human activities so the amount of arsenic is lesser compare to SP1. The arsenic content in the Dunga beach, Kenya was ranging from 11.1 to 14 ng/g (Anselimo *et al*, 2012). In Port Dickson beach SP1 and SP3 reports higher arsenic level compare Dunga beach.

According to *Agency for Toxic Substances and Disease Registry (ATSDR),* 2007, minimum risk level for oral exposure to inorganic arsenic is 0.005 mg/kg/day for approximately 14 days or less and 0.0003 mg/kg/day for chronic duration which is 365 days. No minimum risk level for acute duration, intermediate duration or chronic duration were derived for inorganic arsenic or organic arsenic compounds which exposed through inhalation.

Long term oral exposure to low levels of inorganic arsenic may cause dermal effects such as hyperpigmentation and hyperkeratosis, corns and warts. Other than that, peripheral neuropathy characterized by a numbness in the hands and feet may progress to a painful “pins and needles” sensation. There may also be an increased risk of skin cancer, bladder cancer and lung cancer (ATSD, 2007).

Construction workers who work in the MRT construction, Jalan Cheras could be exposed to arsenic directly from soil through oral by allowing the soil dust to go through their mouth. Other than that, construction workers could unintentionally eat the arsenic contaminated soil. The workers might experiencing the initial stage of effects of arsenic exposure such as corns, warts, vomiting, abdominal pain, diarrrhoea, blood in urine, cramping muscle and hair loss. If this continues and no prevention action taken, the workers might have cancer in the future.

Arsenic also can be orally consumed indirectly through plant, animals and drinking water. Arsenic in living organism is from the soil. If the soil contains high level of arsenic, so the uptake of arsenic by the plant and other living organism such as fish will be high. The starting point of arsenic contamination is from the soil and the concentration increases dramatically by using products contain arsenic such as herbiside, pesticide, insecticide and fertilizer. Arsenic from soil also can also leach out to water which can be water supply area. High concentration of arsenic can lead to contamination of groundwater. This will affect the daily drinking water. Treatment has to be done to remove the arsenic before the water can be supplied to household. This will cost a lot of money.

Although the arsenic level been reported is terrifying but only partial amount of the arsenic will be consumed directly and indirectly by humans, plants, aquatic living organisms and water. The initial concentration of arsenic in soil will eventually be reduced throughout the food chain (Imamul *et al*., 2006). This is by indirectly arsenic consumption by humans.

Consuming arsenic contaminated product could put high risk in arsenic effects. Without having any knowledge on the effects, people cannot identify the initial symptoms of arsenic contamination which can lead to cancer in long term exposure .Some awareness and precaution steps should be taken into count to minimize the exposure of arsenic to humans and other living things.

CHAPTER 5

CONCLUSION

In this study, soil from garden in a house at Selayang (Selangor), *Empangan Batu Sungai Tua* (Selayang Dam), Port Dickson Beach (Negeri Sembilan), MRT Construction, Jalan Cheras and *Jabatan Pertanian Malaysia* (Ulu Langat District) is sampled are successfully quantified for arsenic concentration with using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The highest range for arsenic concentration is in MRT Construction, Jalan Cheras soil with the concentration of 32.24 ± 0.02 mg/kg. The second highest arsenic content is in *Jabatan Pertanian Malaysia* (Ulu Langat District) soil with arsenic concentration of 31.55 ± 0.03 mg/kg. This followed by the soil from a garden in a house at Selayang (Selangor) and *Empangan Batu Sungai Tua* (Selayang Dam) with arsenic concentration of 19.17 ± 0.02 mg/kg and 17.12 ± 0.01 mg/kg respectively. The least arsenic content soil was form Port Dickson Beach (Negeri Sembilan) which gives concentration of 1.73 ± 0.01 mg/kg. Arsenic level in the studied soils is high and the contact with arsenic through soil in a long term will gives negative impacts to the human’s health.

CHAPTER 6

SUGGESTION

In this study, five locations were studied on arsenic in surface soil. In this study, MRT construction contains the highest concentration of arsenic. For future studies, it is suggested the study can be focused to construction area only. The study can be extended to quantification of arsenic in air in the construction area. The arsenic in air can be from the soil dust or particulates which will be in the air during hot days. To study the amount of arsenic consumed directly or indirectly by the construction workers, the hair samples and blood samples from the randomly picked construction workers could be done. This study can be conducted after three months so that the arsenic which metabolite in the construction worker’s hair and blood could be studied. In addition a survey on health condition of the construction workers can be done to know the arsenic effect on their health.

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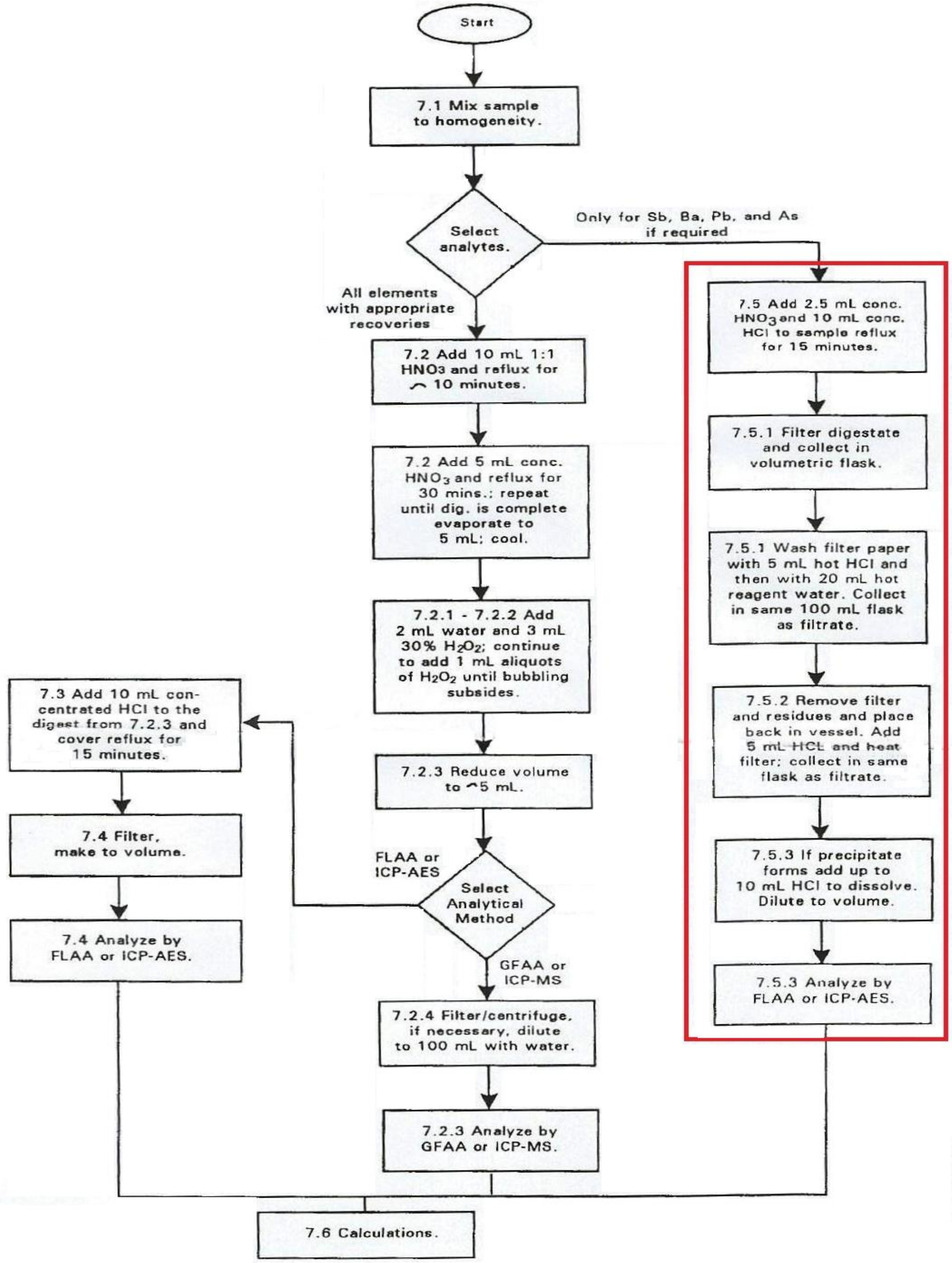
APPENDIXES

APPENDIX I

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS



APPENDIX II

Sample ID	Actual Weight of Soil (g)	Weight of Soil (kg)	Concentration of As (mg/L)	Concentration of As in 0.1L (mg/kg)
Garden (SP1)	1.0026	0.0010	0.4185	41.7415
Garden (SP1)*	1.0017	0.0010	0.1991	19.8762
Garden (SP2)	1.0022	0.0010	0.0308	3.0732
Garden (SP2)*	1.0016	0.0010	0.0277	2.7656
Garden (SP3)	1.0006	0.0010	0.2433	24.3154
Garden (SP3)*	1.0003	0.0010	0.2324	23.2330
Dam (SP1)	1.0010	0.0010	0.0497	4.9650
Dam (SP1)*	1.0012	0.0010	0.0347	3.4658
Dam (SP2)	1.0008	0.0010	0.1064	10.6315
Dam (SP2)*	1.0003	0.0010	0.1055	10.5468
Dam (SP3)	1.0018	0.0010	0.3784	37.7720
Dam (SP3)*	1.0018	0.0010	0.3539	35.3264
PD (SP1)	1.0027	0.0010	0.0054	0.5385
PD (SP1)*	1.0019	0.0010	0.0423	4.2220
PD (SP2)	1.0036	0.0010	Not Detected	Not Detected
PD (SP2)*	1.0028	0.0010	Not Detected	Not Detected
PD (SP3)	1.0016	0.0010	Not Detected	Not Detected
PD (SP3)*	1.0014	0.0010	0.0043	0.4294
MRT (SP1)	1.0022	0.0010	0.0920	9.1798
MRT (SP1)*	1.0014	0.0010	0.1435	14.3299
MRT (SP2)	1.0007	0.0010	0.7348	73.4286
MRT (SP2)*	1.0006	0.0010	0.3038	30.3618
MRT (SP3)	1.0018	0.0010	0.2152	21.4813
MRT (SP3)*	1.0012	0.0010	0.4472	44.6664
JPM (SP1)	1.0000	0.0010	0.1250	12.5000
JPM (SP1)*	1.0003	0.0010	0.1395	13.9458
JPM (SP2)	1.0007	0.0010	0.4711	47.0770
JPM (SP2)*	1.0000	0.0010	0.3476	34.7600
JPM (SP3)	1.0000	0.0010	0.4209	42.0900
JPM (SP3)*	1.0001	0.0010	0.3893	38.9261

APPENDIX III

Sample ID	Measured Standard Deviation from ICP-OES
Garden (SP1)	0.00672
Garden (SP1)*	0.01274
Garden (SP2)	0.00535
Garden (SP2)*	0.00212
Garden (SP3)	0.00944
Garden (SP3)*	0.00518
Dam (SP1)	0.00567
Dam (SP1)*	0.00032
Dam (SP2)	0.00208
Dam (SP2)*	0.00164
Dam (SP3)	0.00391
Dam (SP3)*	0.00284
PD (SP1)	0.00352
PD (SP1)*	0.00323
PD (SP2)	Not Detected
PD (SP2)*	Not Detected
PD (SP3)	Not Detected
PD (SP3)*	0.00196
MRT (SP1)	0.01089
MRT (SP1)*	0.00692
MRT (SP2)	0.00726
MRT (SP2)*	0.00654
MRT (SP3)	0.00596
MRT (SP3)*	0.01039
JPM (SP1)	0.01671
JPM (SP1)*	0.00123
JPM (SP2)	0.00639
JPM (SP2)*	0.00930
JPM (SP3)	0.01224
JPM (SP3)*	0.00933

APPENDIX IV

Location	Average concentration of As (mg/kg)	Measurement uncertainty (± mg/kg)
Garden in a house at Selayang, Selangor	19.17	0.02
Empangan Batu Sungai Tua (Selayang Dam)	17.12	0.01
Port Dickson Beach, Negeri Sembilan	1.73	0.01
MRT Construction Jalan Cheras	32.24	0.02
Jabatan Pertanian Malaysia, Ulu Langat District	31.55	0.03

APPENDIX V

Calib

Method: ASekitar 15 metal
Result: vicky140523a

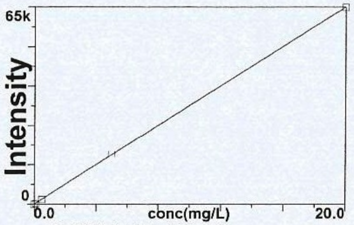
Cd 226.502

1

Cr 267.716

2

As 193.696



Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999992

3

Pb 220.353

4

Cu 324.752

5

Mn 257.610

6

Calib

Method: ASekitar 15 metal
Result: vicky140523a

Ni 231.604

7

Sn 189.927

8

Zn 213.857

9

B 249.677

10

Fe 259.939

11

Ag 328.068

12

APPENDIX VI

```
Method: ASekitar 15 metal                  Page   1                 Date: 5/23/2014 3:07:41 PM

==========================================================================================
Analysis Begun

Start Time: 5/23/2014 11:28:06 AM              Plasma On Time: 5/23/2014 9:17:06 AM
Logged In Analyst: Administrator               Technique: ICP Continuous
Spectrometer: Optima 4300 DV, S/N 077N0111403  Autosampler: AS-91

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\ICP\Data\Sample Information\
                         Result 2014\140523avicky.sif
Batch ID: 140523avicky
Results Data Set: vicky140523a
Results Library: C:\Documents and Settings\All Users\PerkinElmer\ICP\Data\Results\Results.mdb

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 1                                Autosampler Location: 1
Sample ID: Calib Blank 1                       Date Collected: 5/23/2014 11:28:24 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:

------------------------------------------------------------------------------------------
Mean Data: Calib Blank 1
                   Mean Corrected                            Calib
Analyte               Intensity     Std.Dev.   RSD      Conc. Units
As 193.696              68.3          15.06  22.05%     [0.00] mg/L

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 2                                Autosampler Location: 2
Sample ID: Standard 1                          Date Collected: 5/23/2014 11:31:32 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:   60                                Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: Standard 1
                   Mean Corrected                            Calib
Analyte               Intensity     Std.Dev.   RSD      Conc. Units
As 193.696             323.1           8.53   2.64%      [0.1] mg/L

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 3                                Autosampler Location: 3
Sample ID: Standard 2                          Date Collected: 5/23/2014 11:34:42 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:   60                                Auto Dilution Factor: 1
```

```
Method: ASekitar 15 metal                  Page   2                 Date: 5/23/2014 3:07:41 PM

------------------------------------------------------------------------------------------
Mean Data: Standard 2
                   Mean Corrected                            Calib
Analyte               Intensity     Std.Dev.   RSD      Conc. Units
As 193.696             1640.1         10.52   0.64%      [0.5] mg/L

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 4                                Autosampler Location: 4
Sample ID: Standard 3                          Date Collected: 5/23/2014 11:37:52 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:   60                                Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: Standard 3
                   Mean Corrected                            Calib
Analyte               Intensity     Std.Dev.   RSD      Conc. Units
As 193.696            16497.6         89.03   0.54%      [5.0] mg/L

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 5                                Autosampler Location: 5
Sample ID: Standard 4                          Date Collected: 5/23/2014 11:40:49 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:   60                                Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: Standard 4
                   Mean Corrected                            Calib
Analyte               Intensity     Std.Dev.   RSD      Conc. Units
As 193.696            65012.3        499.75   0.77%     [20.0] mg/L

------------------------------------------------------------------------------------------
Calibration Summary

Analyte        Stds.  Equation          Intercept     Slope   Curvature    Corr. Coef.   Reslope
As 193.696       4    Lin, Calc Int          53.0      3250     0.00000       0.999992

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                 Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                      MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 6                                Autosampler Location: 6
Sample ID: QC 1                                Date Collected: 5/23/2014 11:44:47 AM
Analyst:                                       Data Type: Original
Initial Sample Wt:                             Initial Sample Vol:
Dilution:                                      Sample Prep Vol:
Wash Time:  120                                Auto Dilution Factor: 1
```

APPENDIX VII

```
Method: ASekitar 15 metal                    Page   3                Date: 5/23/2014 3:07:41 PM

-----------------------------------------------------------------------------------------------
Mean Data: QC 1
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696               15755.2      4.831 mg/L          0.0204      4.831 mg/L          0.0204   0.42%
   QC value within limits for As 193.696  Recovery = 96.62%
All analyte(s) passed QC.

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 7                                     Autosampler Location: 20
Sample ID: DI                                       Date Collected: 5/23/2014 11:47:46 AM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: DI
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 -14.2    -0.0207 mg/L         0.00417    -0.0207 mg/L         0.00417  20.19%

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 8                                     Autosampler Location: 21
Sample ID: Soil Trial                               Date Collected: 5/23/2014 11:50:58 AM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: Soil Trial
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 -43.2    -0.0296 mg/L         0.00270    -0.0296 mg/L         0.00270   9.10%

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 9                                     Autosampler Location: 22
Sample ID: Garden (SP1)                             Date Collected: 5/23/2014 11:54:12 AM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: Garden (SP1)
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                1413.2     0.4185 mg/L         0.00672     0.4185 mg/L         0.00672   1.61%
```

```
Method: ASekitar 15 metal                    Page   4                Date: 5/23/2014 3:07:41 PM


===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 10                                    Autosampler Location: 23
Sample ID: Garden (SP1)*                            Date Collected: 5/23/2014 11:57:10 AM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: Garden (SP1)*
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 700.0     0.1991 mg/L         0.01274     0.1991 mg/L         0.01274   6.40%

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 11                                    Autosampler Location: 24
Sample ID: Garden (SP2)                             Date Collected: 5/23/2014 12:00:09 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: Garden (SP2)
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 153.2     0.0308 mg/L         0.00535     0.0308 mg/L         0.00535  17.34%

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===============================================================================================
Sequence No.: 12                                    Autosampler Location: 25
Sample ID: Garden (SP2)*                            Date Collected: 5/23/2014 12:03:08 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------------
Mean Data: Garden (SP2)*
                    Mean Corrected          Calib.                         Sample
Analyte                Intensity      Conc. Units       Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 143.0     0.0277 mg/L         0.00212     0.0277 mg/L         0.00212   7.64%

===============================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba
```

APPENDIX VIII

```
Method: ASekitar 15 metal                    Page   5              Date: 5/23/2014 3:07:41 PM

===========================================================================================
Sequence No.: 13                                 Autosampler Location: 26
Sample ID: Garden (SP3)                          Date Collected: 5/23/2014 12:06:07 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Garden (SP3)
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 843.9   0.2433 mg/L        0.00944     0.2433 mg/L         0.00944  3.88%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 14                                 Autosampler Location: 27
Sample ID: Garden (SP3)*                         Date Collected: 5/23/2014 12:09:06 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Garden (SP3)*
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 808.5   0.2324 mg/L        0.00518     0.2324 mg/L         0.00518  2.23%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 15                                 Autosampler Location: 28
Sample ID: Dam (SP1)                             Date Collected: 5/23/2014 12:11:59 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Dam (SP1)
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 214.5   0.0497 mg/L        0.00567     0.0497 mg/L         0.00567 11.42%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 16                                 Autosampler Location: 29
Sample ID: Dam (SP1)*                            Date Collected: 5/23/2014 12:14:51 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1
```

```
Method: ASekitar 15 metal                    Page   6              Date: 5/23/2014 3:07:41 PM

-------------------------------------------------------------------------------------------
Mean Data: Dam (SP1)*
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 165.7   0.0347 mg/L        0.00032     0.0347 mg/L         0.00032  0.94%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 17                                 Autosampler Location: 30
Sample ID: Dam (SP2)                             Date Collected: 5/23/2014 12:17:44 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Dam (SP2)
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 398.7   0.1064 mg/L        0.00208     0.1064 mg/L         0.00208  1.96%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 18                                 Autosampler Location: 31
Sample ID: Dam (SP2)*                            Date Collected: 5/23/2014 12:20:37 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Dam (SP2)*
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                 395.8   0.1055 mg/L        0.00164     0.1055 mg/L         0.00164  1.56%

===========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

===========================================================================================
Sequence No.: 19                                 Autosampler Location: 32
Sample ID: Dam  (SP3)                            Date Collected: 5/23/2014 12:23:31 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------
Mean Data: Dam  (SP3)
                  Mean Corrected        Calib.                          Sample
Analyte                Intensity    Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                1282.9   0.3784 mg/L        0.00391     0.3784 mg/L         0.00391  1.03%
```

APPENDIX IX

```
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 20                                 Autosampler Location: 33
Sample ID: Dam (SP3)*                            Date Collected: 5/23/2014 12:26:26 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: Dam (SP3)*
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                  1203.2   0.3539 mg/L        0.00284      0.3539 mg/L        0.00284  0.80%
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 21                                 Autosampler Location: 6
Sample ID: QC 1                                  Date Collected: 5/23/2014 12:29:20 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: QC 1
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                 16253.0    4.984 mg/L         0.0099       4.984 mg/L         0.0099  0.20%
   QC value within limits for As 193.696  Recovery = 99.68%
All analyte(s) passed QC.

==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 22                                 Autosampler Location: 34
Sample ID: PD (SP1)                              Date Collected: 5/23/2014 12:32:17 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: PD (SP1)
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                    70.5   0.0054 mg/L        0.00352      0.0054 mg/L        0.00352 65.25%
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba
```

```
==========================================================================================
Sequence No.: 23                                 Autosampler Location: 35
Sample ID: PD (SP1)*                             Date Collected: 5/23/2014 12:35:27 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: PD (SP1)*
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                   190.4   0.0423 mg/L        0.00323      0.0423 mg/L        0.00323  7.65%
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 24                                 Autosampler Location: 36
Sample ID: PD (SP2)                              Date Collected: 5/23/2014 12:38:22 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: PD (SP2)
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                   -67.4  -0.0371 mg/L        0.00523     -0.0371 mg/L        0.00523 14.11%
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 25                                 Autosampler Location: 37
Sample ID: PD (SP2)*                             Date Collected: 5/23/2014 12:41:33 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
Wash Time:   60                                  Auto Dilution Factor: 1

------------------------------------------------------------------------------------------
Mean Data: PD (SP2)*
                    Mean Corrected        Calib.                          Sample
Analyte                  Intensity    Conc. Units      Std.Dev.       Conc. Units       Std.Dev.   RSD
As 193.696                   -22.7  -0.0233 mg/L        0.00371     -0.0233 mg/L        0.00371 15.91%
==========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                   Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                        MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

==========================================================================================
Sequence No.: 26                                 Autosampler Location: 38
Sample ID: PD (SP3)                              Date Collected: 5/23/2014 12:44:45 PM
Analyst:                                         Data Type: Original
Initial Sample Wt:                               Initial Sample Vol:
Dilution:                                        Sample Prep Vol:
```

APPENDIX X

```
Method: ASekitar 15 metal                Page   9             Date: 5/23/2014 3:07:41 PM

Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: PD (SP3)
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                    32.6   -0.0063 mg/L       0.00197     -0.0063 mg/L        0.00197  31.32%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 27                              Autosampler Location: 39
Sample ID: PD(SP3)*                           Date Collected: 5/23/2014 12:47:56 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: PD(SP3)*
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                    66.9    0.0043 mg/L       0.00196      0.0043 mg/L        0.00196  46.07%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 28                              Autosampler Location: 40
Sample ID: MRT (SP1)                          Date Collected: 5/23/2014 12:51:08 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: MRT (SP1)
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                   352.2    0.0920 mg/L       0.01089      0.0920 mg/L        0.01089  11.83%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 29                              Autosampler Location: 41
Sample ID: MRT (SP1)*                         Date Collected: 5/23/2014 12:54:05 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: MRT (SP1)*
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                   519.4    0.1435 mg/L       0.00692      0.1435 mg/L        0.00692   4.83%
```

```
Method: ASekitar 15 metal                Page  10             Date: 5/23/2014 3:07:41 PM

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 30                              Autosampler Location: 42
Sample ID: MRT (SP2)                          Date Collected: 5/23/2014 12:57:03 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: MRT (SP2)
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                  2441.2    0.7348 mg/L       0.00726      0.7348 mg/L        0.00726   0.99%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 31                              Autosampler Location: 43
Sample ID: MRT (SP2)*                         Date Collected: 5/23/2014 1:00:02 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: MRT (SP2)*
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                  1040.4    0.3038 mg/L       0.00654      0.3038 mg/L        0.00654   2.15%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

====================================================================================
Sequence No.: 32                              Autosampler Location: 44
Sample ID: MRT (SP3)                          Date Collected: 5/23/2014 1:03:00 PM
Analyst:                                      Data Type: Original
Initial Sample Wt:                            Initial Sample Vol:
Dilution:                                     Sample Prep Vol:
Wash Time:    60                              Auto Dilution Factor: 1

------------------------------------------------------------------------------------
Mean Data: MRT (SP3)
                      Mean Corrected        Calib.                        Sample
Analyte                  Intensity     Conc. Units      Std.Dev.      Conc. Units       Std.Dev.   RSD
As 193.696                   752.4    0.2152 mg/L       0.00596      0.2152 mg/L        0.00596   2.77%

====================================================================================
Method Loaded
Method Name: ASekitar 15 metal                Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                     MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba
```

APPENDIX XI

```
Method: ASekitar 15 metal                 Page  11                 Date: 5/23/2014 3:07:41 PM

=========================================================================================
Sequence No.: 33                                    Autosampler Location: 45
Sample ID: MRT (SP3)*                               Date Collected: 5/23/2014 1:05:59 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: MRT (SP3)*
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696             1506.5     0.4472 mg/L       0.01039     0.4472 mg/L       0.01039   2.32%

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 34                                    Autosampler Location: 46
Sample ID: JPM (SP1)                                Date Collected: 5/23/2014 1:08:58 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: JPM (SP1)
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696              459.2     0.1250 mg/L       0.01671     0.1250 mg/L       0.01671  13.37%

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 35                                    Autosampler Location: 47
Sample ID: JPM (SP1)*                               Date Collected: 5/23/2014 1:11:50 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: JPM (SP1)*
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696              506.5     0.1395 mg/L       0.00123     0.1395 mg/L       0.00123   0.88%

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 36                                    Autosampler Location: 6
Sample ID: QC 1                                     Date Collected: 5/23/2014 1:14:43 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1
```

```
Method: ASekitar 15 metal                 Page  12                 Date: 5/23/2014 3:07:41 PM

-----------------------------------------------------------------------------------------
Mean Data: QC 1
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696            16368.6      5.020 mg/L        0.0166      5.020 mg/L        0.0166   0.33%
   QC value within limits for As 193.696  Recovery = 100.39%
All analyte(s) passed QC.

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 37                                    Autosampler Location: 48
Sample ID: JPM (SP2)                                Date Collected: 5/23/2014 1:17:41 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: JPM (SP2)
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696             1584.3     0.4711 mg/L       0.00639     0.4711 mg/L       0.00639   1.36%

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 38                                    Autosampler Location: 49
Sample ID: JPM (SP2)*                               Date Collected: 5/23/2014 1:20:33 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: JPM (SP2)*
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
As 193.696             1182.9     0.3476 mg/L       0.00930     0.3476 mg/L       0.00930   2.68%

=========================================================================================
Method Loaded
Method Name: ASekitar 15 metal                      Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                           MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=========================================================================================
Sequence No.: 39                                    Autosampler Location: 50
Sample ID: JPM (SP3)                                Date Collected: 5/23/2014 1:23:26 PM
Analyst:                                            Data Type: Original
Initial Sample Wt:                                  Initial Sample Vol:
Dilution:                                           Sample Prep Vol:
Wash Time:   60                                     Auto Dilution Factor: 1

-----------------------------------------------------------------------------------------
Mean Data: JPM (SP3)
                  Mean Corrected        Calib.                       Sample
Analyte              Intensity     Conc. Units      Std.Dev.     Conc. Units      Std.Dev.   RSD
```

APPENDIX XII

```
As 193.696              1421.0      0.4209 mg/L      0.01224      0.4209 mg/L      0.01224    2.91%

=================================================================================================
Method Loaded
Method Name: ASekitar 15 metal                         Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                              MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=================================================================================================
Sequence No.: 40                                       Autosampler Location: 51
Sample ID: JPM (SP3)*                                  Date Collected: 5/23/2014 1:26:19 PM
Analyst:                                               Data Type: Original
Initial Sample Wt:                                     Initial Sample Vol:
Dilution:                                              Sample Prep Vol:
Wash Time:   60                                        Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------------
Mean Data: JPM (SP3)*
                   Mean Corrected          Calib.                          Sample
Analyte               Intensity       Conc. Units      Std.Dev.       Conc. Units      Std.Dev.   RSD
As 193.696              1318.3       0.3893 mg/L      0.00933       0.3893 mg/L      0.00933   2.40%

=================================================================================================
Method Loaded
Method Name: ASekitar 15 metal                         Method Last Saved: 2/5/2014 2:50:34 PM
IEC File:                                              MSF File:
Method Description: Cd, Cr, As, Pb, Cu, Mn, Ni, Sn, Zn, B, Fe, Ag, Al, Se, Ba

=================================================================================================
Sequence No.: 41                                       Autosampler Location: 6
Sample ID: QC 2                                        Date Collected: 5/23/2014 1:29:13 PM
Analyst:                                               Data Type: Original
Initial Sample Wt:                                     Initial Sample Vol:
Dilution:                                              Sample Prep Vol:
Wash Time:   60                                        Auto Dilution Factor: 1

-------------------------------------------------------------------------------------------------
Mean Data: QC 2
                   Mean Corrected          Calib.                          Sample
Analyte               Intensity       Conc. Units      Std.Dev.       Conc. Units      Std.Dev.   RSD
As 193.696             16443.7        5.043 mg/L       0.0344       5.043 mg/L        0.0344   0.68%
   QC value within limits for As 193.696  Recovery = 100.86%
All analyte(s) passed QC.
```