UNIVERSITI PUTRA MALAYSIA

HEAVY METALS CONTAMINATION IN PADDY WATER AND HEALTH RISK ASSESSMENT AMONG FARMERS IN TANJUNG KARANG

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BY

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ABSTRACT

HEAVY METALS CONTAMINATION IN PADDY WATER AND HEALTH RISK ASSESSMENT AMONG FARMERS IN TANJUNG KARANG

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Introduction: Tanjung Karang, Selangor is widely known for its paddy cultivation activity and was the third largest paddy field in Malaysia. The contamination of heavy metals in agriculture fields is commonly related to fertilizers as some fertilizers are known to contain certain heavy metals. Heavy metals do not undergo biodegradation and can accumulate in the environment and human body. Since paddy cultivation needs large amounts of water, this activity is one of the concerns. **Objective:** To determine the selected concentration heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in paddy water and assess their potential dermal health risks to farmers in Tanjung Karang. **Methodology:** The study was conducted at Kampung Sawah Sempadan in Tanjung Karang. 72 water samples were randomly collected from 24 paddy blocks consisting block A to X. The water samples were measured for in-situ water quality parameters such as temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and turbidity. The water samples were acidified with nitric acid and filtered through 0.45 μm membrane before injected into Inductively Coupled Plasma Mass Spectrometry (ICP-MS). 117 farmers were interviewed using questionnaires to obtain information for non-carcinogenic and carcinogenic dermal health risk assessments. **Results and Discussion:** As has the highest mean concentration (0.01 mg/L) followed by Zn (0.0084 mg/L), Cr (0.0045 mg/L), Ni (0.0026 mg/L), Cu (0.0024 mg/L), Pb (0.0016 mg/L) and Cd (0.000022 mg/L). All elements did not exceed the recommended concentration by Malaysia National Water Quality Standard (NWQS), Department of Environment and Food and Agriculture Organization (FAO). The average reading for temperature, pH, EC, DO and turbidity were 34.6 °C, 7.7, 260.2 μS/cm, 7.1 mg/L and 63.7 NTU respectively. The Hazard Quotient (HQ) for all selected heavy metals did not exceed 1 and Lifetime Cancer Risks (LCR) were between 1.78×10^{-6} to 4.06×10^{-6}. **Conclusion:** This study indicated that the pollution of selected heavy metals in the paddy water at Kampung Sawah Sempadan was minimum and the water is suitable to be used as irrigation water.

Keywords: Heavy metals, paddy water, agriculture, in-situ water quality parameters, health risk assessments

ABSTRAK

PENCEMARAN LOGAM BERAT DI DALAM AIR PADI DAN PENILAIAN RISIKO KESIHATAN DALAM KALANGAN PESAWAH DI TANJUNG KARANG

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Pengenalan: Tanjung Karang, Selangor adalah kawasan yang terkenal dengan aktiviti pertanian padi dan merupakan kawasan sawah padi yang ketiga terbesar di Malaysia. Pencemaran logam berat biasa dikaitkan dengan pengunaan baja kerana baja telah diketahui mengandungi beberapa logam berat. Logam berat tidak mengalami digradasi dan boleh berkumpul di persekitaran dan badan manusia. Oleh kerana tanaman padi memerlukan kuantiti air yang banyak, aktiviti ini merupakan salah satu kebimbangan. **Objektif:** Untuk menentukan kandungan beberapa logam berat (Cu, Cr, Zn, Ni, Pb, As and Cd) di dalam air padi dan menilai risiko kesihatan dermal kepada pesawah di Tanjung Karang. **Metodologi:** Kajian ini dijalankan di Kampung Sawah Sempadan di Tanjung Karang. 72 sampel telah diambil secara rawak daripada 24 blok padi yang terdiri daripada blok A hingga blok X. Parameter in-situ seperti suhu, pH, konduktiviti, oksigen terlarut dan kekeruhan telah diukur dan direkodkan di tapak pensampelan. Sampel air kemudiannya di tambah dengan asid nitrik dan di tapis menggunakan membran 0.45 μm sebelum dimasukkan ke dalam *Inductively Coupled Plasma Mass Spectrometry* (ICP-MS). 117 responden telah ditemubual menggunakan borang soal selidik untuk mendapatkan maklumat untuk penilaian risiko karsinogen dan risiko bukan-karsinogen. **Keputusan dan Perbincangan:** As mempunyai kandungan purata yang paling tinggi (0.01 mg/L) diikuti oleh Zn (0.0084 mg/L), Cr (0.0045 mg/L), Ni (0.0026 mg/L), Cu (0.0024 mg/L), Pb (0.0016 mg/L) and Cd (0.000022 mg/L). Kandungan semua elemen tidak melebihi kandungan maksimum oleh Standard Kualiti Air Malaysia, Jabatan Alam Sekitar Malaysia dan Food and Agriculture Organization (FAO). Bacaan purata bagi suhu, pH, konduktiviti, oksigen terlarut dan kekeruhan adalah 34.6 °C, 7.7, 260.2 μS/cm, 7.1 mg/L dan 63.7 NTU. *Hazard Quotient* (HQ) untuk semua logam berat tidak melebihi 1 and Risiko Kanser Sepanjang Hayat (LCR) adalah diantara 1.78×10^{-6} to 4.06×10^{-6}. **Kesimpulan:** Kajian ini mendapati pencemaran logam berat yang terpilih di dalam air sawah adalah minimum dan air itu sesuai digunakan sebagai pengairan.

Kata kunci: Logam berat, air padi, pertanian, parameter in-situ kualiti air, penilaian risiko kesihatan

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
Cd	Cadmium
Cr	Chromium
Cu	Copper
DAD	Dermal Absorbed Dose
DCR	Dermal Cancer Risk
DNA	Deoxyribonucleic acid
DO	Dissolved Oxygen
DOE	Department of Environment
EC	Electrical Conductivity
FAO	Food and Agricultural Organization
Fe	Iron
FLAA	Flame Atomic Absorption
GFAAS	Graphite Furnace Atomic Absorption
HDPE	High Density Polyethylene
Hg	Mercury
HNO_3	Nitric Acid
HQ	Hazard Quotient
IARC	International Agency for Research on Cancer
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

ICP-OES	Inductively coupled plasma optical emission spectrometry
K	Potassium
LCR	Lifetime Cancer Risk
Mn	Manganese
N	Nitrogen
Ni	Nickel
NIST	National Institute of Standards and Technology
NWQS	Malaysia National Water Quality Standard
P	Phosphorus
Pb	Lead
PPE	Personal Protective Equipment
RAIS	Risk Assessment Information System
RfD	Reference Dose
SF	Slope Factor
US EPA	United State Environmental Protection Agency
UV-VIS	Ultraviolet–visible
WHO	World Health Organization
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background

Agriculture is still one of the vibrant sectors of Malaysia's economy that contribute up to 12% of national gross domestic products despite the noticeable decline for the past few years. Malaysia's economy has been depending on agriculture over decade as Malaysia's products are exported worldwide. Agriculture, which is often labeled as the poor man's sector has slowly changing its pace towards a large-scale farming.

Paddy is the third most widely planted crop in Malaysia after oil palm and rubber. In the year 2013, 674,332 hectares were planted with paddy (Department of Agriculture Peninsular Malaysia, 2014). Paddy covered almost 97 percent of the total cultivated agricultural land in Malaysia together with other crops and plays a vital part in Malaysian diet as it is a staple food for Malaysians. Tanjung Karang is the third largest area of paddy field in Peninsular Malaysia and also known as 'the rice bowl of Selangor' (Fuad et al., 2012).

The growing of population has increased the demand for rice consumption. In order to fulfill this demand, Malaysia needs to sustain its production and increase the rice productivity. To sustain high productivity of crops, the application of large quantities of fertilizers is an important component. Contemporary farming with aimless utilization of agrochemicals such as fertilizers and pesticides, alongside tractor development, for higher yield profitability has contaminated the soils with toxic heavy metals (Liu et al., 2007; Hang et al., 2009).The increased use of metal-based fertilizer in agricultural could contribute to the incremental of heavy metals pollution in fresh water (Adefemi and Awokunmi, 2010).

Fertilizers are abundantly utilized as a part of agriculture and farming to supply essential macronutrients for crops, for example, nitrogen (N), phosphorus (P), potassium (K) and so forth. In the meantime, despite of the usefulness, fertilizers also can add to significant source contamination of toxic heavy metals such as arsenic (As), cadmium (Cd), lead (Pb), and others. The contamination of heavy metals in agriculture field is commonly related to fertilizers use as some fertilizers are known to contain certain heavy metals. Thus, the recent concern regarding the environmental contamination caused by heavy metals have started improvement of proper innovations and technologies to evaluate the vicinity and mobility of metals in soil, water, and wastewater (Tangahu et al., 2011).

The quality of water is essential for the human as it is directly linked with human health and concern (Prasad et al., 2014). Apart from heavy metals contamination, the water quality can also be assessed through in-situ water quality parameters such as turbidity, temperature, pH, salinity, electrical conductivity (EC), dissolved oxygen (DO), total suspended solid (TSS), total dissolved solids (TDS) and others. Davies et al. (2009) reported that in-situ water quality parameters have an important role to determine the accumulation of metals.

1.2 Problem Statement

Heavy metal contamination in soil and water due to increased agriculture activities, rapid urbanization, industrialization and mining activities had turned into a matter of worldwide concern (Singh et al., 2011; Krishna et al., 2013). An expected measure of 2.5 million tons of the agrochemicals are utilized as a part of agriculture around the world every year (Reddy et al., 2013).

The application of fertilizers by farmers especially chemical fertilizers such as urea fertilizers and compound fertilizers has contribute to the high concentration of the metals in the paddy field soil and water samples (Reddy et al., 2013). Fertilizers usually contain impurities such as heavy metals because they are not purified completely (Cakmak et al., 2010). Besides, mixed fertilizers are also one of the sources of heavy metal contamination in agriculture (Reddy et al., 2013).

These heavy metals will accumulate in soil and water as residue as they cannot be destroyed or degraded (Naveedullah et al., 2013). Most of the studies show that the prolong use of irrigation water that is contaminated with heavy metals increases the heavy metal concentration in soils beyond the acceptable limit. Consequently, the increasing of the heavy metals in soil also increases the plant's uptake of heavy metals (Shah et al., 2013)

Besides, heavy metals also have the ability to bio-accumulate in human body easily making them hazardous when exposed (Fenik et el., 2011). Human exposure to heavy metals have shown a significant increase as there are a dramatic increase of their use such as in industrial, agricultural, and domestic applications (Bradl, 2002).

Water itself is known as skin irritant (Tsai & Maibach, 1999) and occupations that involve wet work, including paddy rice farmers are therefore at risk. Shenoi et al. (2005) found a high prevalence of skin disease among paddy field farmers in southern India. A study on skin diseases among farmers using wastewater in rice cultivation area in Nam Dinh (Trang et al., 2007) found that agricultural work increased risk of skin diseases as farmers are required to have frequent contact with the wastewater and fertilizers.

In addition, according to the interview with the farmers at Kampung Sawah Sempadan, it was found that some of the farmers do not wear the appropriate and complete personal protective equipment (PPE) such as gloves and boots while handling

the paddy water, hence this may increase the risk of exposure to the heavy metals that present in the environment.

1.3 Research Justification

Agriculture has been attributed as largest contributor of non-point source pollution of surface water (Thorburn et al., 2003). Agrochemicals such as fertilizers and pesticides usually contain significant amounts of heavy metals and metalloids (Abdel-Haleem et al., 2001; El-Bahi et al., 2004). Heavy metals that have been identified in the polluted environment include As, Cu, Cd, Pb, Cr, Ni, Hg and Zn (Lone et al., 2008).

As rice is the staple food of more than half the world population, irrigation water is used in large quantities during the production of rice (Amin et al., 2011). Large amount of water is supplied to the crops from the seed germination to harvesting, making this activity one of the concerns (Arunakumara, Walpola & Yoon, 2013).

There are only limited numbers of studies reported the heavy metals contamination in paddy or agricultural water compared to the study of soil and crops. One study has been conducted by Reddy et al., (2013) on assessment of heavy metals and micronutrient of paddy field surface soil and water in paddy cultivated area. The study found that Cd concentration was significantly higher compared to the others and the association between the applications of fertilizers with the elevation of the higher reading of heavy metals and sediment had been confirmed. Another study conducted by Bambara et al. (2015) found that the concentrations of some heavy metals such as Cr,

Mn, Ni, and Hg in water samples in Loumbila water were higher than the Recommended Maximum Concentration for irrigation.

The unknown quality of irrigation water that is used in agricultural activities can be the cause of environment and vegetable pollution (Bambara et al., 2015). Since there are farmers in Tanjung Karang that do not wear appropriate and full PPE while working with paddy water, they are exposed to dermal contact with heavy metals that present in paddy water. Thus, it is important to assess the health risk that is imposed on the farmers by the exposure. This study is designed to investigate and create a better understanding on the concentration of heavy metals specifically in paddy water and to determine the carcinogenic and non-carcinogenic health risk associated with the respective heavy metals.

1.4 Conceptual Framework

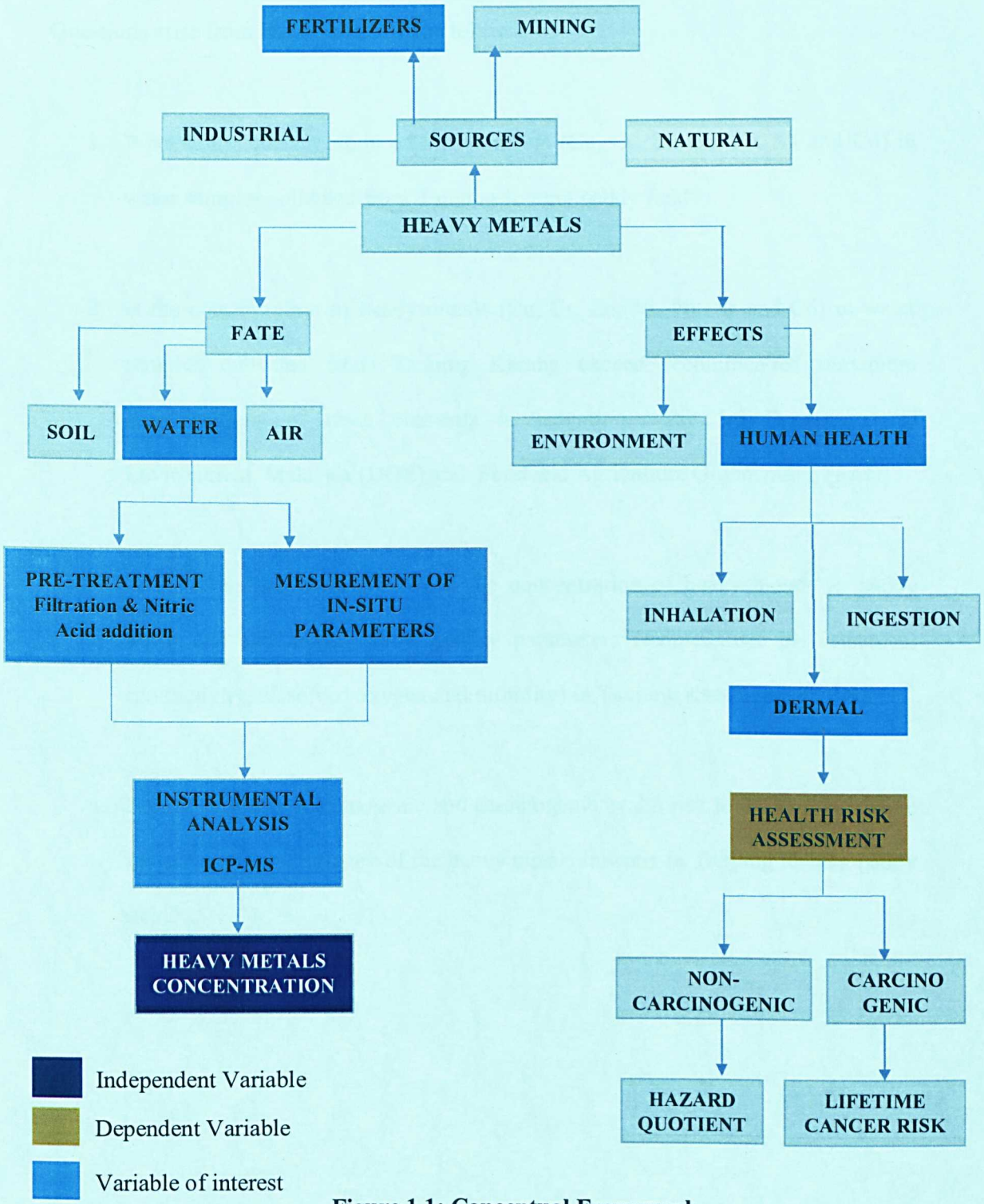

Figure 1.1: Conceptual Framework

1.5 Research Questions

Questions arise from this research are as follow:

1. What is the concentration of heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in water samples collected from Tanjung Karang paddy field?

2. Is the concentration of heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in water samples collected from Tanjung Karang exceed recommended maximum concentrations of trace elements in irrigation water by Department of Environment, Malaysia (DOE) and Food and Agriculture Organization (FAO)?

3. Is there any correlation between the concentration of heavy metals in paddy water and the in-situ water quality parameters (temperature, pH, electrical conductivity, dissolved oxygen and turbidity) in Tanjung Karang paddy field?

4. Is there any non –carcinogenic and carcinogenic health risk to the farmers due to the occupational exposure of the heavy metals in water in Tanjung Karang paddy field?

1.6 Hypothesis

There is a significant relationship between the concentrations of heavy metals in paddy water with the selected in-situ water quality parameters of paddy water at Tanjung Karang, Selangor.

1.7 Objectives

To determine the concentration of selected heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in paddy water and assess their potential dermal health risk to the farmers at Tanjung Karang.

The specific objectives are as follows:

1. To determine the concentration of heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in water samples collected from Tanjung Karang paddy field.

2. To compare the concentration of heavy metals (Cu, Cr, Zn, Ni, Pb, As and Cd) in water samples collected from Tanjung Karang with the recommended maximum concentrations of trace elements in irrigation water by Department of Environment, Malaysia (DOE) and Food and Agriculture Organization (FAO).

3. To determine the correlation between the concentrations of heavy metals in water samples with the in-situ water quality parameters (temperature, pH electrical conductivity, dissolved oxygen and turbidity) in Tanjung Karang paddy field.

4. To assess the carcinogenic and non-carcinogenic health risk of the farmers due to occupational exposure of heavy metals in paddy water.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals in Agriculture Water

Heavy metal is defined as any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Heavy metal is an inorganic pollutant which cannot be degraded to the less harmful components through biological or chemical processes. These cause heavy metals to accumulate in soil and in water bodies as a result of anthropogenic activities including agriculture and industrial discharge (Kabir et al., 2012). Dissolved metals are more toxic compared to particulate metals and the dissolved metal is dependent on several factors such as pH as well as presence of solids and organic matter (Ishaq & Khan, 2013).

Heavy metals can be accumulated and transferred by natural and anthropogenic sources. They are distributed to the environment through anthropogenic sources resulted from human activities such as industrial, mining, agriculture and transportation (Nazir et al., 2015).

A few researches had studied on the heavy metals in the agricultural and irrigation water and the results are varies. The concentrations of some heavy metals in Loumbila water had exceeded their respective permissible limits with the average

concentrations of Cr at 0.116 mg/L, Mn at 0.462 mg/L, Ni at 0.451 mg/L and Hg 0.034 mg/L (Bambara et al., 2015). However, in a study conducted by Mitsios, Golia & Tsadilas (2005), dissolved heavy metals in most cases, were not detectable in irrigation waters in Thessaly Region, Central Greece.

2.2 Heavy Metals and their Health Effects

As there is no effective excretion mechanism, heavy metals can be very harmful to the human body even in low concentrations (Ghosh et al., 2012). Metal pollution can affect the biological systems in harmful ways since it does not undergo biodegradation. Toxic heavy metals can be differentiated from other pollutants as they can be accumulated in living organisms, thus causing numerous diseases as well as disorders even when expose to lower concentrations (Pehlivan et al., 2009).

Exposure to copper can be from air, water, food, and by skin contact. Copper that dissolves in water can be carried in surface waters as copper compounds or as free copper and they are more likely bound to particles suspended in the water (ATSDR, 2004). Soluble copper compounds which are commonly used in agriculture are likely to threaten health. Dermal exposure to copper may cause contact dermatitis in some individuals (ATSDR, 1990). However, EPA does not classify copper as a human carcinogen because there are no adequate human or animal cancer studies.

Dermal exposure to chromium compounds can induce contact dermatitis or lesions. Deep ulcers or chrome holes can form if the symptoms are not treated

(Pedersen, 1982; Burrows, 1983). Skin contact to chromium can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted (Griswold & Martin, 2009). U.S. Air Force (1990) reported that dermal hypersensitivity reactions are elicited by both Cr (III) and Cr (VI) compounds.

Zinc is relatively harmless compared to the other heavy metals which shared similar chemical properties. Only exposure to high doses has toxic effects. Therefore, acute zinc intoxication is rarely observed (Plum et al., 2010). Based on the currently existing data, dermal exposure of zinc does not pose detrimental toxicological risk. Due to the lack of information, EPA has determined zinc is not classifiable as to its human carcinogenicity.

Nickel-induced contact dermatitis is well documented for humans and it is the most prevalent effects of nickel in humans (ATSDR, 1988). Nickel dermatitis produces erythema, eczema and lichenification of the hands and other areas of the skin that contact nickel (Nielsen et al., 1999). The most common harmful health effect of nickel in humans is an allergic skin reaction in those who are sensitive to nickel (Das, Das & Dhundasi, 2008). The metal is not only an allergen but also a potential immunomodulatory and immunotoxic agent in humans (Das & Buchner, 2007).

Lead is a toxic metal which can cause environmental contamination and health problems. It is a cumulative toxicant that affects multiple body systems, including the neurological, hematological, gastrointestinal, cardiovascular and renal systems (WHO, 2010). Carcinogenicity of inorganic lead and lead compounds have been evaluated,

however the data from human studies are inadequate for evaluating the potential carcinogenicity of lead (U.S EPA, 1989a).

Arsenic is a natural component of the earth's crust and is distributed widely in the environment. Long term arsenic exposure results in increased risk of carcinogenic and systemic health effects have been indicated by epidemiological studies (Tchounwou et al., 2012). Prolong exposure to high level of inorganic arsenic exhibit several symptoms include pigmentation, skin lesions and hyperkeratosis (Griswold & Martin, 2009).

Zhao et al. (1997) reported that arsenic may induce DNA hypomethylation, which facilitates aberrant gene expression and thus act as carcinogen. Direct dermatitis, allergenic hypersensitivity, and conjunctivitis have been associated with inorganic arsenic dusts in exposed workers (U.S. EPA, 1984). The International Agency for Research on Cancer (IARC) (1987) has classified arsenic and arsenic compounds as carcinogenic to humans.

Cadmium is a naturally occurring metal that is used in numerous chemical and industrial processes (Risk Assessment Information System, 1991). Cadmium is widely transported in the blood and body but accumulates primarily in the liver and kidneys (Goyer, 1991). Cadmium biological half-life in humans is about 10 to 35 years (WHO, 2008). However, according to ATSDR (1999) absorption of cadmium through the skin is not a significant route since only 0.5% of cadmium is absorbed by the skin.

2.3 In-situ water quality Parameters in Water

In-situ water quality parameters such as pH, dissolved oxygen, electrical conductivity and the available surface area for adsorption play an important role to determine the accumulation of metals (Davies et al., 2009). The importance of in-situ water quality parameters is to obtain the idea about the quality of water and to compare the results with standard values. Physical parameters are such as temperature, color, odour, pH, turbidity, TDS while chemical parameters include BOD, COD, dissolved oxygen, alkalinity, hardness and other characters (Patil et al., 2012).

The water temperature controls all chemical reaction rates, affects growth of fish, reproduction and immunity (Patil et al., 2012). Temperature has been noticed to have an influence on the chemical and biochemical reactions in water. Toxicity of heavy metals and the sensitivity of living organisms to toxic substances increase with high temperature (Momba et al., 2006). The change in temperature will change the density of water and it plays important role in the organism's metabolic activities (Prasad et al., 2014).

pH is an universal indicator and parameter which express the acidity and alkalinity of a solution (Prasad et al., 2014). Higher pH observed in water was attributed to increased photosynthetic activities of dissolved inorganic carbon by planktons (Iqbal et al., 2004). According to Gupta (2009) there was a positive correlation of pH with electrical conductivity and total alkalinity.

Electrical conductivity (EC) is the ability of water to conduct electric current (Prasad et al., 2014). Conductivity in water is due to ionization of dissolved inorganic solids and is a measure of total dissolved solids (Bhatt et al., 1999). According to Patil et al., 2012) and Prasad et al. (2014), there are significant correlation of conductivity with ten other in-situ water quality parameters such as temperature, pH, alkalinity, total hardness, calcium, total solids, total dissolved solids, chemical oxygen demand and chloride and iron concentration of water.

Dissolved oxygen (DO) in water gives some information either directly or indirectly such as bacterial activity, photosynthesis, nutrients availability, stratification and others (Vikal, 2009). There are several factors affecting oxygen content in natural waters which include input of atmosphere and photosynthesis and output from respiration, decomposition and mineralization as well as losses to atmosphere (Ishaq & Khan, 2013).

Turbidity is one of the obvious parameters to assess the quality and physical status of water. The factors that increase the turbidity of water are suspended particles, soil particles, discharged effluents, decomposed organic matters, total dissolved solids and the microscopic organisms which could interfere with the penetration of light (Ishaq & Khan, 2013). High turbidity is often associated with the raining season compared to dry season. Increased turbidity values during the raining season could be resulted from the increased surface runoff and erosion, through rain falls (Igbinosa, 2012). Ishaq & Khan (2013) also mentioned that the high turbidity observed during the monsoon might be due to heavy rainfall and flow of suspended particles.

2.4 Preservation and Pre-treatment of Water Samples

High Density Polyethylene (HDPE) bottles are commonly used in many studies to collect water for the determination heavy metals (Shuhaimi-Othman et al., 2008; Kavcar et al., 2009; Cidu et al., 2011). HDPE bottles were washed in 10% of nitric acid (HNO_3) in an ultrasonic bath for 15 minutes and were rinsed with distilled water (Prasad et al., 2014). According to Assubaie (2015), the bottles were washed by distilled deionized water and rinsed overnight in 10% HNO_3.

The bottles were dried in the oven, capped tightly and sealed in zip-locked bags before transported to the sampling site to avoid contamination from heavy metals in the external environment (Lim, Shaharuddin, & Sam, 2013). At the sampling site, before collection of water samples, the bottles were rinsed twice with the water that will be sampled (Bambara et al., 2015).

After collection, each water samples need to undergo preservation to prevent and retard the microbial as well as chemical changes of the samples after they are removed from their parent source. According to Method 3005 by EPA (1992) (Acid digestion of waters for total recoverable or dissolved metals for analysis by FLAA or ICP Spectroscopy), water samples should be acidified with the HNO_3 for preservation. A few drops of concentrated nitric acid were added to water samples to obtain pH around 2 (Assubaie, 2015). This is to prevent precipitation of metals and biological growth (Kramer, 1994; Eaton et al., 1995).

For dissolved metals, the samples should be filtered through a 0.45-μm filter membrane before acidification (EPA, 1992). During the transportation of samples to the laboratory, the samples were transported in a cooler box packed with dry ice and were protected from direct sunlight (Igbinosa, 2012). The samples were kept at 4° up until the analysis was conducted (Assubaie, 2015).

2.5 Analytical Methods to Determine Heavy Metals in Water Samples

There are variety of inorganic techniques such as AAS, ICP-OES, as well as ICP-MS that are available for determination of heavy metals (Baysal et al., 2013). ICP-MS, ICP-OES, AAS, UV-VIS spectrometer and Cyclic Voltammetry are the sophisticated instruments that were used for the determination of heavy metals in water.

Among all, Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and Graphite Furnace Atomic Absorption (GFAAS) are the most effective technique to determine the contamination of heavy metals in water as ICP-MS can determine up to 0.1μg/L of metal concentration in water (Reddy et al., 2012).

Many studies have reported the use of Atomic Absorption Spectrophotometer (AAS) to analyze the trace metals. However, due to the specific hollow cathode lamp that is used for every single element, multi-elements analysis cannot be performed. Therefore, each element should be determined one by one which make a qualitative analysis almost impossible (Baysal et al., 2013).

Bambara et al. (2015) used AAS to analyse the heavy metals such as cobalt (Co), chromium (Cr), iron (Fe), manganese (Mn), zinc (Zn), lead (Pb), nickel (Ni), cadmium (Cd), arsenic (As) and Mercury (Hg) in the vegetable and water samples. AAS was also used in the assessment of heavy metals (Cd and Pb) and micronutrients (Cu, Mn, and Zn) of paddy soil and water in India by Reddy et al. (2013). Another study by Liu et al. (2011) used AAS; PE-AA700 to detect Cu, Cr, Ni, Pb, and Cd in water samples.

On the other hand, ICP-MS is useful for determining multi-element analysis and is ideal for water. It uses plasma source to atomize the sample, and mass spectrometry used to detect the ions (Baysal et al., 2013). ICP-MS is commonly used in diverse research fields such as environmental, forensic sciences, food, material, chemical, semiconductor and nuclear industries (Ammann, 2007).

Reddy et al. (2012) in their study of heavy metals in surface and groundwater in India used Perkin-Elmer Sciex Elan 5000 ICP-MS to perform water analysis for As, Ni, Cr, Pb, Co, Se, Hg and Cd. In a study by Voica et al. (2012), ICP-MS was used to determine numbers of heavy metals in surface waters from Transylvania.

2.6 Legal Requirement and Guidelines of Heavy Metals in Water

In Malaysia, Environmental Quality Act 1974 is the act that regulates and related to the prevention, abatement, and control of pollution and enhancement of environment. One of the standards used for water in Malaysia is National Water Quality Standard (NWQS) by Department of Environment, Malaysia (DOE). Recommended Maximum

Concentration by Food and Agriculture Organization (FAO) was also referred to compliment the data which are not available in the DOE standard.

The recommended concentration of heavy metals in irrigation water for selected heavy metals in irrigation water (Class IV) by DOE and the Recommended Maximum Concentration by FAO are as follows:

Table 2.1: Recommended Concentration of Heavy Metals in irrigation water

Parameter	Concentration (mg/l) [a]	Concentration (mg/l) [b]
Cadmium (Cd)	0.01	0.01
Lead (Pb)	-	5.0
Arsenic (As)	0.1	0.1
Copper (Cu)	-	0.2
Zinc (Zn)	2.0	2.0
Nickel (Ni)	0.2	0.2
Chromium (Cr)	0.1	0.1

[a] Recommended Concentration of Heavy Metals in irrigation water (Class IV) by Department of Environment, Malaysia (DOE)
[b] Recommended Maximum Concentration of Heavy Metals in irrigation water by Food and Agriculture Organization (FAO)

2.7 Health Risk Assessment

Health risk assessment can be defined as methodological approach to identify, characterize, and analyze dose-response relationship of the chemicals toxicities to generate a numerical data (James, 1985). There are two types which health risk

assessment can be performed, which are qualitative risk assessment and quantitative risk assessment. Quantitative health risk assessment is used to estimate the potential health risk due to the exposure of carcinogenic or non-carcinogenic substances.

There are two categories for the potential chronic health risk, which are non-carcinogenic and carcinogenic risk. For the non-carcinogenic risk, there is a level of exposure below which no adverse effects will be observed known as threshold dose (USEPA, 1989). Non-carcinogenic risk can be calculated using Hazard Quotient (HQ). HQ is the ratio of exposure level to non-carcinogenic elements to the reference dose (RfD). According to United States Environmental Protection Agency (USEPA), if the value of HQ is less than one, then there is no significant risk of non-carcinogenic effects. However, if the values calculated exceed one, there may be a significant concern for potential non-carcinogenic health risk.

Carcinogenic health risk estimates represent the incremental probability that an individual will develop cancer over a lifetime as a result of a specific exposure to a carcinogenic chemical (USEPA, 1989b) and can be estimated using Lifetime Cancer Risk (LCR) equation.

CHAPTER 3

METHODOLOGY

3.1 Study Design

This study was classified as a cross-sectional study in which there is no intervention occurs. The concentrations of heavy metals compounds were quantified before their risks to the farmers were assessed.

3.2 Study Location

The study was conducted at Tanjung Karang, Selangor which is widely known for its paddy cultivation activity and the third largest paddy field in Peninsular Malaysia. The location is depicted in **Figure 3.1**. The study location was selected based on some criteria which are detailed out as follows:

i) Agriculture area with paddy cultivation as the main activity.

ii) The residents which will be the respondents are willing to give co-operation throughout the study.

iii) Short distance from the laboratory which preservation and analysis was conducted.

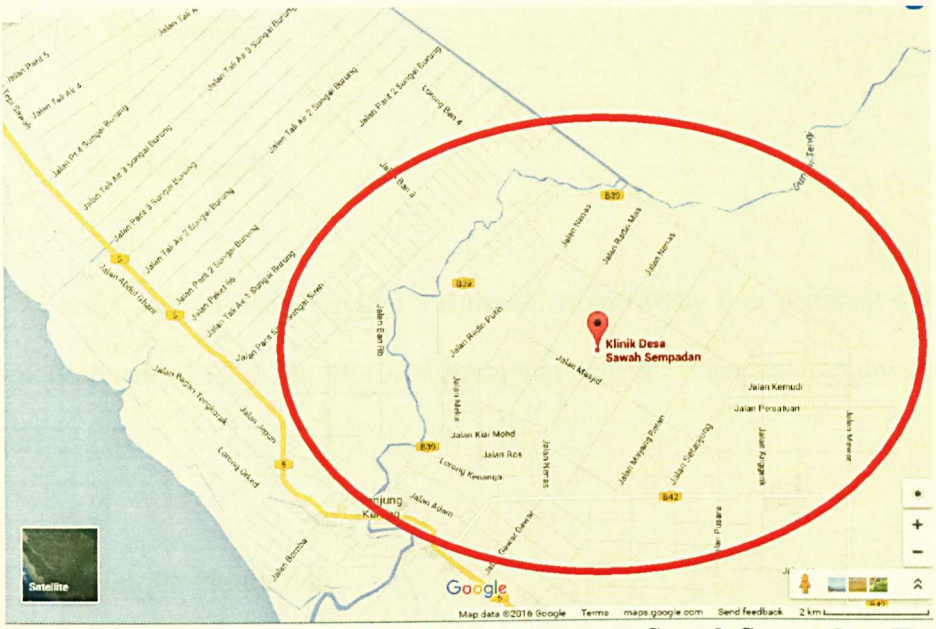

Figure 3.1: Location of the sampling sites at Kampung Sawah Sempadan, Tanjung Karang, Selangor

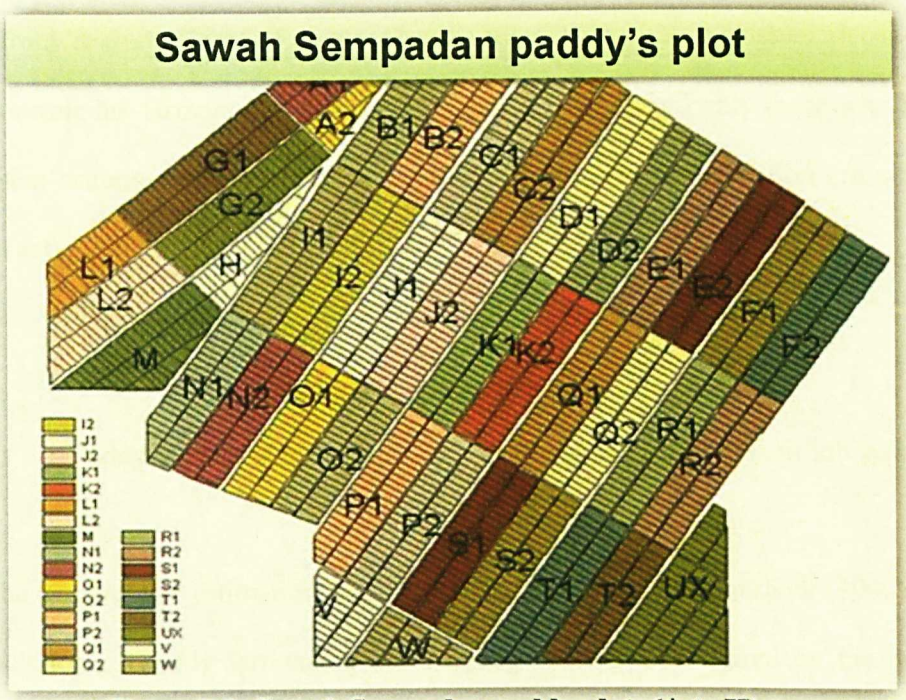

Figure 3.2: Sawah Sempadan paddy plots (A to X)

3.3 Sampling Technique

3.3.1 Water Sample

72 water samples were randomly collected from twenty four different blocks of paddy plots consist of Plot A to Plot X at Kampung Sawah Sempadan, Tanjung Karang, Selangor.

3.3.2 Sample Population

The sample frame in this study was the paddy farmers that were listed in the list acquired from Tanjung Karang Farmers Organization Office. The inclusive criteria were set to determine the farmers that can participate in this study and only those who fulfill the inclusion criteria were included in the study. Below are the inclusion criteria that have been set:

i) Paddy farmers within the age group of 18 to 70 years old

ii) Paddy farmers who work directly to the paddy water in their job task

The sample size estimation was calculated according to Lameshow (1990). The total population of paddy farmers in the Tanjung Karang as acquired by the district office of Tanjung Karang is approximately 7679, and the population of the paddy farmers in the study area (Kampung Sawah Sempadan) is 1147. Below is the calculation of the sample size:

$$N = \frac{[Z_{1-\alpha}\sqrt{2P(1-P)} + Z_{1-\beta}\sqrt{P_1(1-P_1)+P_2(1-P_2)}]^2}{P_1 - P_2} \quad \text{(Equation 3.1)}$$

Where,

N = Sample size

$Z_{1-\alpha} = 1.282$

$Z_{1-\beta} = 0.842$

$P_1 = 0.21$

$P_2 = 0.1$

$P = \frac{P_1 + P_2}{2}$

The value of prevalence P_1 is 0.21 according to Babic (2014) on the occupational allergic contact dermatitis and P_2 is 0.1 from the study by Anh et al. (2007) on dermatitis among farmers engaged in peri-urban aquatic food production in Hanoi, Vietnam.

$$N = \frac{[1.282\sqrt{2(0.155)(1-0.155)} + 0.842\sqrt{0.21(1-0.21)+0.1(1-0.1)}]^2}{0.21-0.1} \quad \text{(Equation 3.2)}$$

The minimum sample size will be rounded up to 20% to recover the loss of respondents throughout the study. Thus,

20% of 97

= 20 00

= 97 + 20

= 117 respondents

Thus, the total sample size population is 117.

3.4 Study Instrument

3.4.1 Questionnaire

The study instrument that was used in this study is the questionnaire. The questionnaire comprised of three sections namely Section A (personal information of the respondents), section B (exposure frequency and exposure duration to the heavy metals), and section C (personal hygiene and the use of personal protective equipment (PPE)).

The information obtained from this questionnaire was then incorporated into the equation to calculate the dermal risk exerted by the farmers. The questionnaire developed was based on Nordic Occupational Skin Questionnaire (2002) and Taneepanichskul et al. (2010). The sample of questionnaire can be referred in Appendix 1.

3.4.2 Water Sample Preservation and Analysis

In this study, the water samples collected from the paddy field at Tanjung Karang in the HDPE bottles were preserved and undergo pre-treatment before the analysis.

From the sampling field, all samples were transported to the laboratory in the cooler packed with ice. All samples were filtered through a 0.45-μm filter and acidified with nitric acid (HNO_3) (Fisher Scientific, USA) to a pH of 2 after the collection. The samples were kept in the chiller at 4°C in the laboratory before analysis of heavy metals concentration. The samples were preserved to ensure that significant changes in composition did not occur before the analysis.

The samples were injected into inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer Sciex Elan 9000, USA) for the determination of the concentration of Cu, Cr, Zn, Ni, Pb, As and Cd.

3.4.3 Measurement of In-Situ Water Quality Parameters

In-situ water quality parameters (pH of the water, temperature, electrical conductivity, dissolved oxygen and turbidity) were measured during sample collection by using the respective instruments.

Turbidity was measured using HACH 2100P Turbiditimeter, USA. pH was measured using Milwaukee Portable pH meter, USA and dissolved oxygen was measured using Eutech Instrument Cyberscan DO110 Dissolved Oxygen Portable meter (Thermo Fisher Scientific Inc, USA). EC and temperature were measured using Waterproof Portable Meter (CyberScan Series 600, USA). The water portable meter can measure the parameters simultaneously at a single time.

All parameters were measured and recorded on site to ensure that the data is accurate and precise according to the time of collection.

3.5 Statistical Analysis

Spearman correlation was used to find the association between the concentration of heavy metals in paddy water at Tanjung Karang paddy field and the in-situ water quality parameters (pH, electrical conductivity, dissolved oxygen and turbidity). Statistical Package for the Social Sciences (SPSS) version 22 was used to perform the statistical analysis.

3.6 Quality Control

The HDPE bottles that were used to collect the water samples were washed and soaked with 10% of nitric acid overnight. The bottles were rinsed with distilled water twice. Acid wash was done to remove any impurities or contaminants that present on the wall of the bottles.

The bottles were capped and tightly sealed in the zip lock bag before being transported to the site to avoid contamination of heavy metals from the external environment. During sample collection, the HDPE bottles were normalized by rinsing with the water sample and all samples were tightly sealed and kept in ice-packed cooler while transporting to the laboratory.

Blanks were carried throughout the entire sample preparation and analytical process for every batch of analytical samples. These blanks were useful in determining if samples were being contaminated and to obtain accurate measurement of heavy metals. For water sample analysis, ultrapure water was used as blank. The preparation of blank was similar as the method of preparing the sample to be analyzed but without adding the sample.

Graphs were plotted for each metal to construct the calibration curves. Calibration curve was obtained by the graph of concentrations of heavy metals against the intensities. Calibration curves for each heavy metal can be referred in Appendix 2. The linear regression coefficient (R^2) determined the range of linearity. The R^2 obtained must be more than 0.995 to ensure the accuracy of the results (Olmedo et al., 2010). The results for R^2 were recorded in Table 3.1

Table 3.1: The linear regression coefficient (R^2)

Analyte	Mass	Slope	Intercept	Regression Coeffcient (R^2)
Cu	62.930	14919.8199	0.000	0.9998
Cr	51.941	22939.6210	0.000	0.9991
Zn	65.926	4721.2498	0.000	0.9998
Ni	59.933	6798.8198	0.000	0.9999
Pb	207.977	24653.9447	0.000	0.9980
As	74.922	3623.5687	0.000	0.9999
Cd	110.904	5256.7269	0.000	0.9999

Instruments such as turbidity meter, pH meter, dissolved oxygen meter, water portable meter and weighing scale were operated according to the standard operation procedure of the equipment and were calibrated before used. All in-situ water quality parameters measurements were taken at the sampling location during the sampling period to ensure accuracy of the reading.

3.7 Health Risk Assessment Analysis

The risks for dermal exposure to heavy metals in paddy water were quantified under the present environmental conditions at Tanjung Karang. The risk characterizations for carcinogenic and non-carcinogenic effects were considered separately by using two different formulae.

3.7.1 Non-carcinogenic risks

The non-carcinogenic risk was calculated using Hazard Quotient (HQ) which is a ratio of exposure dose to the compounds-specific reference dose (RfD). The dermal RfD for the seven selected heavy metals were adjusted from oral toxicity factor. This adjustment accounts for the absorption efficiency in the critical study, which forms the basis of the RfD. The value for dermal RfD were adapted from the Risk Assessment Information System (RAIS) (2013), retrieved on April 2016 and were recorded as in Table 3.2.

Table 3.2: The dermal reference dose (RfD) for selected heavy metals

Compounds	RfD (mg/kg/day)
Copper (Cu)	1.2×10^{-2}
Chromium (Cr)	7.5×10^{-3}
Zinc (Zn)	6.0×10^{-2}
Nickel (Ni)	5.4×10^{-3}
Lead (Pb)	N/A
Arsenic (As)	1.2×10^{-4}
Cadmium (Cd)	5.0×10^{-6}

N/A = Not available

The dermal HQ was calculated by using the formula provided by the USEPA (2004).

The equation is as follows:

$$HQ = DAD / RfD \qquad \text{(Equation 3.3)}$$

Where,

DAD = Dermal Absorbed Dose (mg/kg-day)

RfD = Reference dose (mg /kg-day)

DAD is defined by the following equation (USEPA, 2004):

$$\frac{DA_{event} \times EV \times ED \times EF \times SA}{BW \times AT} \qquad \text{(Equation 3.4)}$$

Where,

DA_{event} = Absorbed dose per event (mg/cm^2-event)

SA = Skin surface area available for contact (cm^2)

EV = Event frequency (events/day)

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

BW = Body weight (kg)

AT = Averaging time (days)

DA_{event} is defined by the following equation (USEPA, 2004):

$$DA_{event} = K_p \times C_w \times t_{event} \qquad \text{(Equation 3.5)}$$

Where,

K_p = Dermal permeability coefficient of compound water (cm/hr)

C_w = Chemical concentration in water (mg/cm3)

t_{event} = Event duration (hr/event)

The skin surface areas (SA) for adult male adopted from the U.S EPA Exposure Factor Handbook (2011) were listed in Table 3.3.

Table 3.3: 50th Percentiles of Skin Surface Area for Adult Male

Area	50th Percentile (cm^2)
Hand	1070[b]
Feet	1370[b]
Hands and feet	2440[b]

The dermal permeability coefficient of compound water (K_p) were listed in Table 3.4.

Table 3.4: Water Dermal Permeability Coefficient (K_p)

Compounds	Water Dermal Permeability Coefficient (K_p) (cm/hr)
Copper (Cu)	1×10^{-3} [b]
Chromium (Cr)	1.14×10^{-3} [a]
Zinc (Zn)	3.19×10^{-4} [a]
Nickel (Ni)	3.06×10^{-4} [a]
Lead (Pb)	1×10^{-4} [b]
Arsenic (As)	1.62×10^{-3} [a]
Cadmium (Cd)	3.29×10^{-4} [a]

[a] U.S. EPA. Exposure Factors Handbook 2011 Edition (Final)
[b] USEPA Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) (2004)

3.7.2 Carcinogenic risks

Dermal cancer risk was estimated using Lifetime Cancer Risk (LCR) equation, which represent incremental probability that an individual will develop cancer over a lifetime as a result of exposure to a potential carcinogen. The slope factors were adapted from the RAIS (2013) retrieved on April 2016 as shown in Table 3.5.

Table 3.5: The dermal slope factor for selected heavy metals

Compounds	Dermal Slope Factor (mg/kg/day)
Copper (Cu)	N/A
Chromium (Cr)	N/A
Zinc (Zn)	N/A
Nickel (Ni)	N/A
Lead (Pb)	N/A
Arsenic (As)	3.66
Cadmium (Cd)	N/A

N/A = Not available

The dermal DCR was calculated by using the equation as follows:

$$\text{Dermal Cancer Risk} = \text{DAD} \times \text{SF} \qquad \text{(Equation 3.6)}$$

Where:

DAD = Dermal Absorbed Dose (mg /kg/day)

SF = Absorbed cancer slope factor (mg /kg/day)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Information on Questionnaire

The questionnaire used to interview the respondents consists of Section A, (personal information of the respondents), section B (exposure frequency and exposure duration to the heavy metals) and section C (personal hygiene and the use of PPE).

4.1.1 Socio-demographic background of respondents

The respondents involved in this study consist of 117 farmers who work in the Kampung Sawah Sempadan paddy field. The socio-demographic information of respondents was summarized in Table 4.1.

Table 4.1: Socio-demographic Information of Respondents (n=117)

Variables	Mean±SD	Minimum	Maximum
Age (years)	49.62±12.02	24	70
Weight (kg)	70.37±12.79	45	120
Height (m)	1.63±0.05	1.52	1.74
BMI (kg/m^2)	26.31±4.78	17.01	39.64

Variables	Category	Frequency	Percentage (%)
Gender	Male	117	100
Race	Malay	117	100

The respondent's age were ranged from 24 to 70 years old, with a mean of 49.62years old. The average weight of respondents was 70.37 kg and ranged from 45 to 120 kg. The average height of respondents was 1.63 m, minimum of 1.52 m and maximum of 1.74 m. The average Body Mass Index (BMI) of the respondents was 26.31 kg/m^2 with the range of 17.01 to 39.64 kg/m^2.

All respondents recruited in this study were male and Malay farmers as the majority of the population in the Kampung Sawah Sempadan are Malay.

4.1.2 Exposure of respondents to Heavy Metals

The information needed to assess the dermal health risk was obtained by interviewing the farmers. Information of farmer's exposure to heavy metals was recorded in Table 4.2.

Table 4.2: Information of farmer's exposure to heavy metals

Parameters	Average
t_{event} (hr/event)	2
Event frequency (events/day)	1
Exposure duration (years)	26
Exposure frequency (days/year)	220
Averaging time (days)	5791

t_{event} is the hour of contact to the heavy metals in paddy water per event. In this study, the average t_{event} was 2 hours. Event frequency (EF) refers to how many times the farmers involve in paddy cultivation activities in a day. The exposure duration (ED) is number of years the farmers have involved in the activity. In this case, the average ED for the respondents was 26 years. Exposure frequency (EF) refers to number of days per year of exposure and averaging time (AT) is the product of ED and EF.

4.1.3 Personal Hygiene and Use of Personal Protective Equipment (PPE)

The use of Personal Protective Equipment (PPE) plays an important role in protecting the farmers and minimizing the exposure to heavy metals in paddy water upon contact. The information on use of PPE among respondents was recorded in Table 4.3.

Table 4.3: Personal Hygiene and Use of Personal Protective Equipment (PPE) among Respondents

Variables	Categories	Frequency	Percentage (%)
Wash up/Shower after farming	Yes	95	81.2
	No	22	18.8
Change clothes after farming	Yes	112	95.7
	No	5	4.3
Use full PPE (boots and gloves)	Yes	43	36.8
	No	74	63.2

Based on the results obtained from the questionnaires, 81.2% of the farmers take a shower after farming as a routine of personal hygiene, while 18.8% do not immediately wash up. 95.7% of the respondents change the clothes they wear for farming every day or every time they go to the paddy field while only 4.3% of the respondents said that they recycle the same clothes for farming work. Out of 117 respondents, 43 respondents (36.8%) use full set of PPE which consist of boots and gloves, while the other 74 respondents (63.2%) do not wear sufficient protection.

4.2 Heavy Metals Concentration In Water Samples

In this study, twenty four paddy blocks were chosen as sampling points representing each blocks of Kampung Sawah Sempadan starting from block A to X. Three samples were collected at each plot and the concentration of seven heavy metals which are Cu, Cr, Zn, Ni, Pb, As and Cd were determined. The summarized results for concentration of selected heavy metals in water samples were listed in the Table 4.4.

Among the selected heavy metals, As has the highest mean concentration (0.01 mg/L), followed by Zn (0.0084 mg/L), Cr (0.0045 mg/L), Ni (0.0026 mg/L), Cu (0.0024 mg/L), Pb (0.0016 mg/L) and Cd (0.000022 mg/L). Compared to the Department of Environment, Malaysia (DOE) and Food and Agriculture Organization (FAO) standards, none of the heavy metal element had exceeded the maximum recommended value for irrigation water.

Table 4.4: *Heavy metal concentrations in paddy water and comparison with available standards (mg/L)*

	Cu	Cr	Zn	Ni	Pb	As	Cd
Mean	0.0024	0.0045	0.0084	0.0026	0.0016	0.01	0.000022
Standard Deviation	0.0012	0.0018	0.0044	0.0012	0.0009	0.0075	0.000014
25th Percentile	0.0016	0.0028	0.0059	0.0018	0.0011	0.0041	0.000012
Median	0.0021	0.0043	0.0081	0.0024	0.0015	0.0085	0.000019
75th Percentile	0.0031	0.0061	0.0110	0.0030	0.0019	0.0160	0.000028
Minimum	0.0011	0.0011	0.0011	0.0009	0.0007	0.0013	0.000007
Maximum	0.0063	0.0095	0.0221	0.0075	0.0064	0.0334	0.000103
Standards	0.2[b]	0.1[ab]	2.0[ab]	0.2[ab]	5.0[b]	0.1[ab]	0.01[ab]

[a] Recommended Concentration of Heavy Metals in irrigation water (Class IV) by Department of Environment (DOE)
[b] Recommended Maximum Concentration of Heavy Metals in irrigation water by Food and Agriculture Organization (FAO)

The average concentration of Cu in the paddy water was 0.0024 mg/L and sample X3 shows the maximum reading at 0.0063 mg/L. The mean concentration of Cr was 0.0045 mg/L with maximum concentration recorded at B3 (0.0095 mg/L). The average concentration of Zn was 0.0084 mg/L and the maximum concentration was 0.0221 mg/L from sample U1. Ni recorded an average concentration of 0.0026 mg/L with the maximum concentration of 0.0075 mg/L from sample C3. The mean concentration of Pb in paddy water was 0.0016 mg/L and the maximum concentration was recorded at sample I1 at 0.0064 mg/L. As shows the highest mean concentration among all heavy metals (0.01 mg/L) with the maximum concentration of 0.334 mg/L from sample T3. In this study, Cd shows the lowest mean concentration (0.000022 mg/L) among all heavy metals and the maximum level of Cd was from sample R1 at 0.000103 mg/L.

The average concentrations of the heavy metals assessed in this study were lower compared to the other studies. Reddy et al. (2013) reported the concentrations of Cd in paddy water were ranged from 1.4 to 5.8 mg/L, followed by Zn (0.1-0.2 mg/L), Cu (0.04 mg/L) and Pb (0.1-0.2 mg/L). The concentration of Cu, Zn, Cd and Pb recorded for mixed water that was used as irrigation water at Oasis farms, Saudi Arabia were 0.011 mg/L, 0.010 mg/L, 0.009 mg/L and 0.005 mg/L respectively (Assubaie, 2011). Results of heavy metal contamination in agricultural water in Dar es Salaam city, Tanzania indicate that the concentrations of Cr were ranged from 1.414 to 0.01 mg/L, Pb ranged from 0.113 and 0.083 mg/L and Cu ranged from 0.013 to 0.016 mg/L (Mwegoha & Kihampa, 2010).

However, the results of this study were consistent with a few similar studies, which the concentration of heavy metals assessed in the agricultural water did not exceed the permissible level. A study by Bambara et al. (2015) stated the average concentrations of heavy metals (Co, Cr, Fe, Mn, Zn, Pb, Ni, As, Hg) in Goudrin irrigation water were also less than FAO recommended limit. An assessment of the levels of some heavy metals in water of Alahsa Oasis farms, Saudi Arabia by Assubaie (2011) found that the levels of some heavy metals such as Mn, Fe, Zn and Pb in the water were in acceptable range and suitable for irrigation use. In another study by Reddy et al. (2013), the concentration of Cd, Pb, Zn, Mn, and Cu in the paddy water did not exceed the permissible limit of Indian standard.

The concentrations of heavy metals in all water samples were less than the recommended maximum level by DOE and FAO. Currently, Kampung Sawah Sempadan in Tanjung Karang is mainly active in paddy cultivation activity and there are no other anthropogenic activities such as industrial or mining around the area.

Since the concentrations of the selected heavy metals were low and did not exceed the available standards, the source of heavy metals in water samples was suggested from the natural source. Almost all types of water contain heavy metals, which result from the natural occurrence from the earth's surface (Newcomb and Rimstidt, 2002). Heavy metals that present naturally may enter into aquatic system through leaching of rocks, dust, and vegetation (Nazir et al., 2015). Under temperate weather, chemical elements were adsorbed in the topsoil or transported towards surface

water or groundwater when the primary crystalline structures of rock minerals were totally cleaved (Parth et al. 2011).

In this study, the concentration of Cd was the lowest which ranged from 0.000007 to 0.000103 mg/L. Cd concentration might be related to industrial activity, atmospheric emission and deposition of organic and fine grain sediments (Kahn et al., 1992). The concentrations of Cd reported in the water near the electroplating plant in China varies from 0.0015 mg/L to 0.0023 mg/L according to Liu et al. (2011). The absence of industrial or mining activities near the paddy field area at Kampung Sawah Sempadan may suggest the minimum presence of Cd in the paddy water.

Elevation of heavy metals pollution in agriculture is often reported with the use of wastewater as the irrigation source for the crops (Singh et al., 2004). Wastewater can increase the productivity of the crops but it also increases the concentration of heavy metals (Bambara et al., 2015). It is mostly used to irrigate the crops especially by those who experience water scarcity (International Water Management Institute, 2002). However, the use of municipal wastewater to irrigate the agricultural field is not common practice in Malaysia.

According to Abdullah & Mustapa (2015), the water used for the irrigation in the paddy field in Kampung Sawah Sempadan is from the Bernam River and it is the only source for irrigation supply in the area. This irrigation scheme is a run of the river without reservoir or dam and the paddy plots receive water directly from two tertiary

canals (Amin et al., 2011). This may suggest the low concentration of heavy metals in the paddy water is because of the water used to irrigate the paddy field is the river water.

4.3 In-Situ Water Quality Parameters

In-situ water quality parameters such as temperature, pH, electrical conductivity, dissolved oxygen and turbidity were measured during the samples collection at the sampling location. The results were summarized in Table 4.5.

Table 4.5: In-situ water quality properties of water and comparison with standard

	Temperature (°C)	pH	Electrical conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Turbidity (NTU)
Mean	34.6	7.7	260.2	7.1	63.7
Standard Deviation	1.8	0.6	104.7	0.6	21.4
25^{th} Percentile	33.4	7.2	190.9	6.7	48.6
Median	34.4	7.8	233.9	7.1	57.9
75^{th} Percentile	35.9	8.1	321.1	7.6	75.5
Minimum	30.4	6.5	113.5	6.0	30.2
Maximum	39.4	8.8	500.4	8.6	116.0
Standards*	Not available	5 - 9	6000	< 3	Not available

*In-situ water quality standard in irrigation water (Class IV) by Department of Environment (DOE)

Each the in-situ water quality parameters have their own importance and function in maintaining the water quality. The pH of the water samples in this study ranged from 6.5 to 8.8. The high pH levels may have caused by the precipitation of heavy metal to the sediments (Jorgensen, 1994). Prasad et al. (2014) mentioned in his study that the high pH of 8.8 indicates that rocks may be of alkaline origin. In this study, the pH for all samples were within the DOE acceptable range which are 5-9 for irrigation water.

The temperature of water samples during sampling recorded high values which ranged from 30.4°C to 39.4°C as the sampling was conducted during the sunny day and dry season of January. Thus, the temperature of the water was affected by the atmospheric temperature. The increased in temperature might be resulted from the absorption of heat from the sunlight of suspended particles that present in water (Igbinosa, 2012). The turbidity of water samples showed a great variation of reading with the minimum of 30.2 NTU and the maximum of 116.0 NTU. However, the standards for temperature and turbidity for irrigation water are not specified in the standard.

Electrical conductivity (EC) is a parameter that indicates the ability of water to conduct an electric current and higher value of EC is a good indicator of the presence of contaminants (Nazir et al., 2015). EC of water samples in the paddy filed were far below the DOE limit and is in agreement with the low concentration of heavy metals in the water.

Dissolved oxygen (DO) is one of the indicators for activity in the water. Lower DO indicates higher oxygen uptake by the organisms and by chemical processes. In this study, dissolved oxygen reading recorded in the paddy water samples ranged from 6.0 to 8.6 mg/L. For irrigational purpose, the recommended value for DO is below than 3, however this study found that the DO in all water samples were higher, thus indicating better water quality than the suggested standard for irrigation water.

4.4 Correlation of Heavy Metals Concentration and in-situ water quality parameters

The correlation of heavy metals concentration and in-situ water quality parameters were conducted by using non-parametric Spearman correlation. Table 4.6 shows the results of the correlation test.

The correlation coefficient (r) shows the strength of association between two variables. The greater coefficient value indicates a good relationship between two parameters (Agarwal & Agarwal, 2013). According to Patil & Patil (2010), direct relationship exists between two parameters when the decrease or increase of one parameter will exhibit the increase or decrease of another parameter.

Table 4.6 Correlation of Heavy Metal Concentrations and in-situ water quality parameters.

	Cu	Cr	Zn	Ni	Pb	As	Cd	Temperature	pH	EC	DO	Turbidity
Cu	1											
Cr	0.438**	1										
Zn	0.353**	0.28	1									
Ni	0.424**	0.238*	0.361**	1								
Pb	0.214	0.162	0.427**	0.206	1							
As	0.319**	0.37**	0.312**	0.279*	0.415**	1						
Cd	0.358**	0.416**	0.386**	0.448**	0.401**	0.484**	1					
Temperature	0.124	0.141	0.286*	0.071	0.381**	0.235*	0.13	1				
pH	0.208	0.329**	0.051	0.009	-0.01	0.447**	0.365**	0.258*	1			
EC	0.580	-0.008	0.000	0.072	-0.040	0.31	-1.470	-0.093	-0.080	1		
DO	0.350	-0.077	-0.066	-0.095	-0.396**	0.095	-0.226	-0.112	0.246*	0.230	1	
Turbidity	-0.104	0.001	-0.117	-0.083	0.011	-0.077	-0.237*	0.185	-0.286*	0.056	-0.006	1

*Correlation is significant at the 0.05 level (two-tail)
** Correlation is significant at the 0.01 level (two-tail)

Based on the Spearman correlation test on the heavy metals and in-situ water quality parameters all selected heavy metals showed positive correlation with each other. Cu showed a very significant positive correlation (at 0.01) with other heavy metals except Pb. Another similar study conducted by Reddy et al. (2013), Zn and Pb showed positive correlation with each other. However, Cu exhibited negative correlation with all the recorded metals. The significant positive correlation between the heavy metals suggests their common source of origin probably from the agrochemicals used in the paddy field (Reddy et al., 2013).

Temperature was the only in-situ water quality parameter that showed positive correlation with all heavy metals. However, it showed negative correlation with EC (-0.93) and DO (-0.112). The results were in consistent with another study conducted by Ishaq and Khan (2013) where all the metals recorded during the study had shown significant positive correlation with temperature and negative correlation between temperature with EC (-0.87) and DO (-0.89) respectively.

pH recorded a positive correlation with all metals except Pb. A negative correlation was observed for pH and EC (-0.080) and turbidity (-0.286) in this study. Other similar studies also recorded the negative correlation of pH and EC. Prasad et al. (2014) report a correlation coefficient (r) of -0.364 for pH and EC. There was a negative correlation with pH and EC among months, (r=-0.614, r=-0.586) in Euphrates River, Iraq (Hassan & Salman, 2010). Mohan et al. (2013) in his study reported r=-0.31 for pH and EC correlation.

EC had positive correlation with Cu, Zn, Ni, As, DO and turbidity while negative correlation were recorded for EC and Cr, Pb, Cd temperature and pH. Ishaq & Khan (2013) report almost a similar result of a 0.99 positive correlation for EC and DO and a negative correlation for EC and Cr (-0.41).

In this study, DO showed negative correlation with all metals (Cd, Zn, Cr, Ni, As) except Cu and Pb. In other similar study by Ishaq & Khan (2013), DO of water showed significant negative correlation with all the recorded metals (Cd, Zn, Cr, Ni, Co, Na, K, and Fe). Turbidity had negative correlation with most of the metals and other in-situ parameters.

4.5 Health Risk Assessment among Farmers

Heavy metals contaminations are important as they can pose potential toxicity to the environment and human (Vinodhini & Narayanan, 2008). Metals have the ability to accumulate in the human body system and cause damage to system organs (Lohani et al., 2008). Thus, it is important to assess the health risk of the people who are exposed to the heavy metals.

Three different situations were considered regarding to the use of PPE and the skin surface area that are exposed to the heavy metals in the paddy water. The first situation is where the farmers wear gloves but do not wear the boots, hence exposing the feet to the paddy water. Second situation is where farmers wear boots but do not wear the gloves and exposing the hands to the paddy water. Meanwhile, the third situation is

where the farmers do not wear both gloves as well as boots thus exposing hands and feet to the paddy water that contain heavy metals.

The risks were categorized into non-carcinogenic and carcinogenic and the effects were considered for each heavy metal by calculating HQ and LCR respectively. The HQ and LCR for each heavy metal were listed in the Table 4.7.

Table 4.7: Hazard Quotient (HQ) and Lifetime Cancer Risk (LCR) of farmers

Heavy metals	Hand exposure		Feet exposure		Hands and feet exposure	
	HQ	LCR	HQ	LCR	HQ	LCR
Cu	6.0×10^{-6}	N/A	7.69×10^{-6}	N/A	1.37×10^{-5}	N/A
Cr	2.04×10^{-5}	N/A	2.62×10^{-5}	N/A	4.66×10^{-5}	N/A
Zn	1.34×10^{-6}	N/A	1.71×10^{-6}	N/A	3.12×10^{-6}	N/A
Ni	4.42×10^{-6}	N/A	5.66×10^{-6}	N/A	1.01×10^{-5}	N/A
Pb	N/A	N/A	N/A	N/A	N/A	N/A
As	4.05×10^{-3}	1.78×10^{-6}	5.19×10^{-3}	2.28×10^{-6}	9.26×10^{-3}	4.06×10^{-6}
Cd	4.36×10^{-5}	N/A	5.54×10^{-5}	N/A	9.87×10^{-5}	N/A

N/A= Not applicable

The farmers in Kampung Sawah Sempadan exposed to the paddy water for average 2 hours per day depending on the weather, the area of paddy field they worked on and the peak season. The average event frequency (EF) is the average frequency of farmers involves in paddy cultivation activities per day. In this study, the average EF is 1. Most of the farmers work in the paddy field early in the morning. However, it is also depending on the weather.

The average exposure duration of the respondents was 26 years. Since the range age for the respondents were 24 to 70, the durations they had involved in paddy cultivation activities were different. Majority of the respondents are full time farmers while some of them have another job and only involve in the paddy cultivation activities as part time and started to become farmers at the late age. The paddy cultivation activities take 110 days per season with 2 seasons per year which make up the exposure frequency of 220 days/year.

The average body weight of the respondents was 70.3 kg and almost similar to the body weight that were recommended by USEPA which are 70 kg. For dermal exposure to water, 50th percentile body surface area values are used to estimate contact rates (USEPA, 1989). The skin surface areas were considered based on the area that the farmers were exposed while handling the paddy water. The areas are feet and hands as some of the farmers do not wear the appropriate PPE such as boots and gloves.

The HQ calculated for feet exposure, hands exposure and for both hand and feet exposures were less than 1 for each selected heavy metals. According to USEPA, the

value of HQ less than one indicates that there is no significant risk of non-carcinogenic effects Although the average exposure duration exposed to heavy metals were as high as 26 years, the risk is not significant as the concentration of heavy metals in the paddy were in lower concentrations.

Other studies also reported no significant non-carcinogenic and carcinogenic health risk due to dermal exposure of heavy metals in water. According to Naveedullah et al. (2013), the mean dermal HQ due to exposure to the metals in the watershed of the Siling Reservoir were found to be less than unity for both winter and summer seasons (2.95×10^{-4} and 2.21×10^{-6}). Another study by Hadzi et al. (2015) reported the dermal HQ for Cr, Hg and Cd from the mining and the pristine sites below 1.

Among the selected heavy metals, only As has the reported dermal RfD, thus the LCR was only calculated for As. The LCR calculated were in the range of 1.78×10^{-6} to 4.06×10^{6} shows the carcinogenic risk are in the acceptable risk level of 10^{-4} to 10^{-6} thus do not pose significant life cancer risk to the farmers.

However, Hadzi et al. (2015) reported dermal LCR for As above 1×10^{-6} in both pristine and mining sites, indicating a carcinogenic threat to the local residents. Addo et al. (2015) reported a carcinogenic risk for As with the LCR of 2.42×10^{-5} in their study on health risk assessment of groundwater from open-wells in the vicinity of a cement factory at Akporkloe, Southeastern Ghana.

The significant cancer risks due to As exposure in both studies may be resulted from the elevated level of As due to anthropogenic activities around the study areas which are mining and cement factory. On the other hand, As concentrations in the paddy water at Tanjung Karang is low and do not exceed the permissible standard, thus do not pose carcinogenic risk to the farmers who are exposed.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The present study showed the selected heavy metals in the paddy water at Kampung Sawah Sempadan present in lower concentration and did not exceed the recommended concentration of heavy metals in irrigation water by DOE and FAO.

The concentration of Cu in the paddy water range from 0.0011 mg/L to 0.0063 mg/L, Cr ranged from 0.0011 mg/L to 0.0095 mg/L, Zn recorded readings from 0.0011 mg/L to 0.0221 mg/L, Ni has a range of 0.0009 mg/L to 0.0075 mg/L, Pb in paddy water has the minimum concentration of 0.0007 mg/L and the maximum concentration was recorded at 0.0064 mg/L, As ranged from 0.0013 to 0.0334 mg/L and Cd with the range of 0.000007 mg/L to 0.000103 mg/L. As recorded the highest mean concentration of all assessed metals (0.01 mg/L) while Cd recorded the lowest mean concentration (0.000022 mg/L)

The in-situ water quality parameters (temperature, pH, EC, DO and turbidity) recorded were also in the permissible range of DOE (2008). This study indicated that the pollution of selected heavy metals in the paddy water at Kampung Sawah Sempadan was minimum and the water is suitable to be used as irrigation water.

The HQ calculated for all selected heavy metals were below than 1 thus indicate that the risk of non-carcinogenic dermal exposure to heavy metals in paddy water among farmers were negligible. There is also no significant carcinogenic risk for arsenic exposure as the LCR obtained is 1.78×10^{-6} to 4.06×10^{-6}.

There are several limitations of this study that should be considered to improve on further research. The source of heavy metals contamination in the paddy water is not well considered and scientifically tested thus it cannot be certain that the heavy metals pollution are caused by the use of agrochemicals such as fertilizers or pesticides. Therefore, further study on the possible sources of heavy metals that present in the paddy water and the association with the heavy metals concentration is needed.

The health risk assessment of the farmers was only quantified for dermal exposure of heavy metals. Another exposure pathway that are possible for heavy metals exposure in paddy water is oral exposure. This route was not assessed in this study as the likelihood of the accidental ingestion of the water is low compared to the dermal exposure in this case. However, if the oral exposure happens, the concern is higher than the dermal exposure. Thus the consideration of this pathway in the further study is recommended.

Another limitation of this study was only As was quantified for carcinogenic risk. Cancer slope factors for other selected heavy metals were not available for dermal exposure. Thus, the carcinogenic risks for other heavy metals that were classified as carcinogen were not quantified.

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Appendix I

UPM

UNIVERSITI PUTRA MALAYSIA

JABATAN KESIHATAN PEKERJAAN & PERSEKITARAN
FAKULTI PERUBATAN DAN SAINS KESIHATAN
UNIVERSITI PUTRA MALAYSIA

PENILAIAN PENDEDAHAN KEPADA PENCEMARAN LOGAM BERAT DI DALAM AIR PADI DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG.

ARAHAN SOALAN:

1. Borang soal selidik ini mengandungi **Tiga (3)** bahagian iaitu:

   Bahagian A : Maklumat Diri
   Bahagian B : Pendedahan kepada Logam Berat
   Bahagian C : Penggunaan Kelengkapan Pelindung Diri

2. Anda diminta menjawab semua soalan yang ada dalam buku soalan ini
3. Buku soalan ini hendaklah dikembalikan kepada pengkaji setelah selesai menjawab

Appendix I

PENDEDAHAN KEPADA LOGAM BERAT DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

KEGUNAAN PENYELIDIK

BAHAGIAN A: MAKLUMAT DIRI

1. Umur: ..... Tahun

2. Jantina:

☐ Lelaki
☐ Perempuan

3. Bangsa:

☐ Melayu
☐ Cina
☐ India
☐ Lain-lain (sila nyatakan): .....

4. Berat: ..... kg
5. Jisim berat badan ..... kg/m^2
6. Adakah anda merokok?

☐ Ya
☐ Tidak

BAHAGIAN B: PENDEDAHAN KEPADA LOGAM BERAT

6. Pekerjaan sekarang: .....
7. Tempoh bekerja di tempat sekarang: ..... bulan/ tahun
8. Adakah anda mandi selepas ke tempat kerja?

☐ Ya
☐ Tidak

SULIT

PENDEDAHAN KEPADA LOGAM BERAT DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

KEGUNAAN PENYELIDIK

9. Adakah anda menukar pakaian kerja setiap hari?

	Ya
	Tidak

10. Nyatakan kekerapan anda mengendalikan atau terdedah kepada air padi:

..... kali/ hari
atau
..... kali/ minggu
atau
..... kali/bulan
atau
..... kali/ tahun

BAHAGIAN C: PENGGUNAAN KELENGKAPAN PELINDUNG DIRI

11. Adakah anda menggunakan alat pelindung diri semasa bekerja?

	Ya
	Tidak

12. Apakah jenis kelengkapan pelindung diri yang digunakan semasa bekerja?

a. But	
c. Baju kalis air	
e. Sarung tangan	
f. Cermin mata	
g. Topeng	
h. Penutup kepala	

SULIT

Appendix I

PENDEDAHAN KEPADA LOGAM BERAT DALAM KALANGAN PESAWAH DI KAMPUNG SAWAH SEMPADAN, TANJUNG KARANG

KEGUNAAN PENYELIDIK

13. Jika "Ya", berapa kerapkah anda memakai kelengkapan pelindung diri?

a. Sentiasa (setiap kali turun ke sawah)	
b. Hampir sentiasa (2-4 kali seminggu)	
c. Jarang (sekali seminggu)	
d. Sangat jarang (kurang daripada 4 kali sebulan)	

14. Kekerapan anda menukar kelengkapan pelindung diri:

a. Setiap hari	
b. Seminggu sekali	
c. Dua minggu sekali	
d. Sebulan sekali	
e. Lain-lain (sila nyatakan)	

-Tamat soal selidik-

SULIT

Appendix II

Table 1: Concentrations and intensities of absorbance of heavy metals

Heavy metals	Concentration (µg/L)	Intensity
Cu	1.560	26548.856
	6.439	104220.873
	12.549	205567.786
	24.682	389417.815
	49.228	742271.408
Cr	1.560	20342.678
	6.552	145700.985
	12.958	324359.254
	25.009	626745.542
	49.595	1213335.490
Zn	1.560	13147.068
	6.045	33047.808
	12.224	62616.385
	24.679	121697.973
	49.581	238493.086
Ni	1.560	8848.356
	6.350	44224.888
	12.536	88095.957
	24.875	172202.729
	49.637	336285.956
Pb	1.560	39233.455
	6.377	188524.572
	12.569	377935.818
	24.544	699613.835
	49.190	1377087.159
As	1.560	5635.831
	6.278	23472.616
	12.507	46841.428
	24.845	91473.663
	49.890	182411.956
Cd	1.560	6606.748
	6.364	34549.927
	12.546	68875.790
	24.795	132842.280
	49.902	265800.927

Appendix II

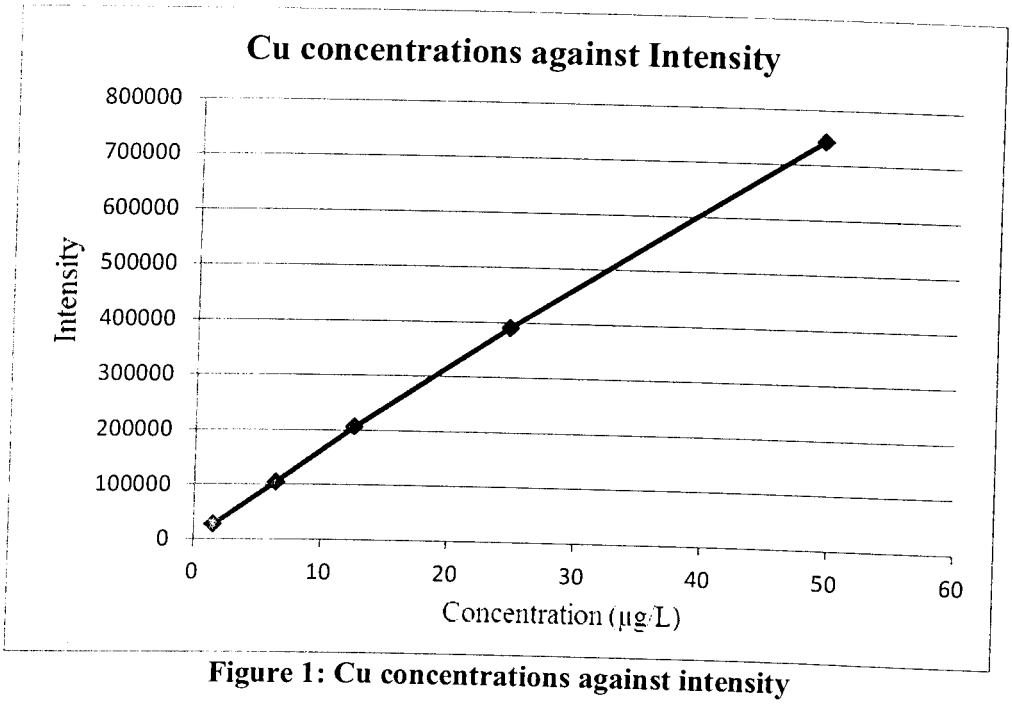

Figure 1: Cu concentrations against intensity

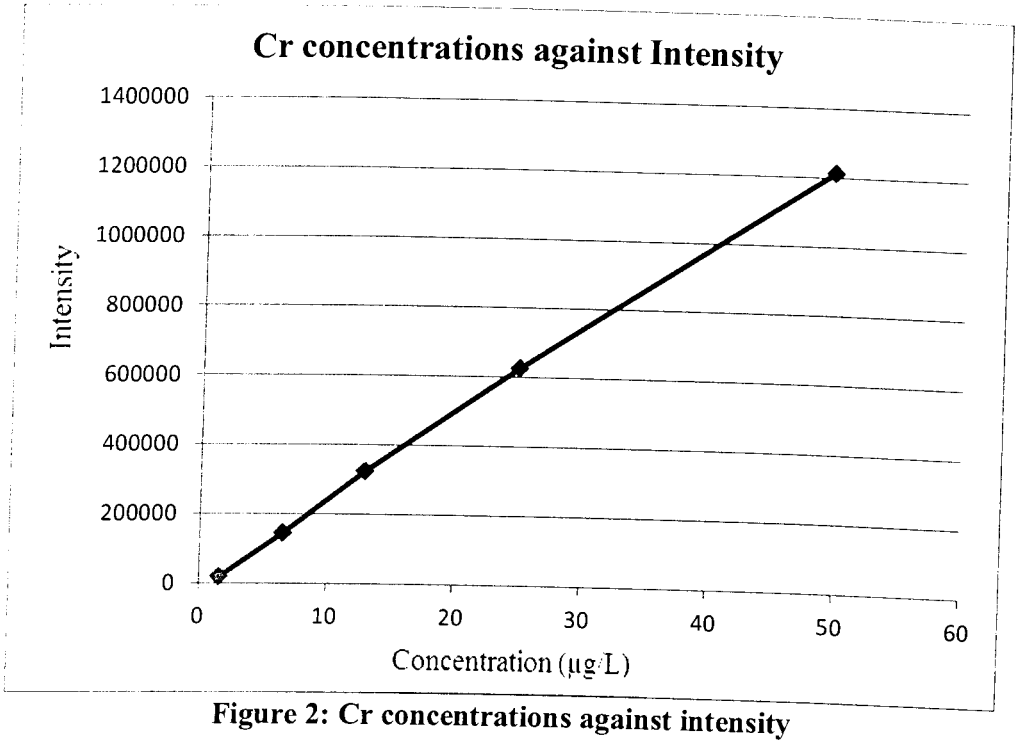

Figure 2: Cr concentrations against intensity

Appendix II

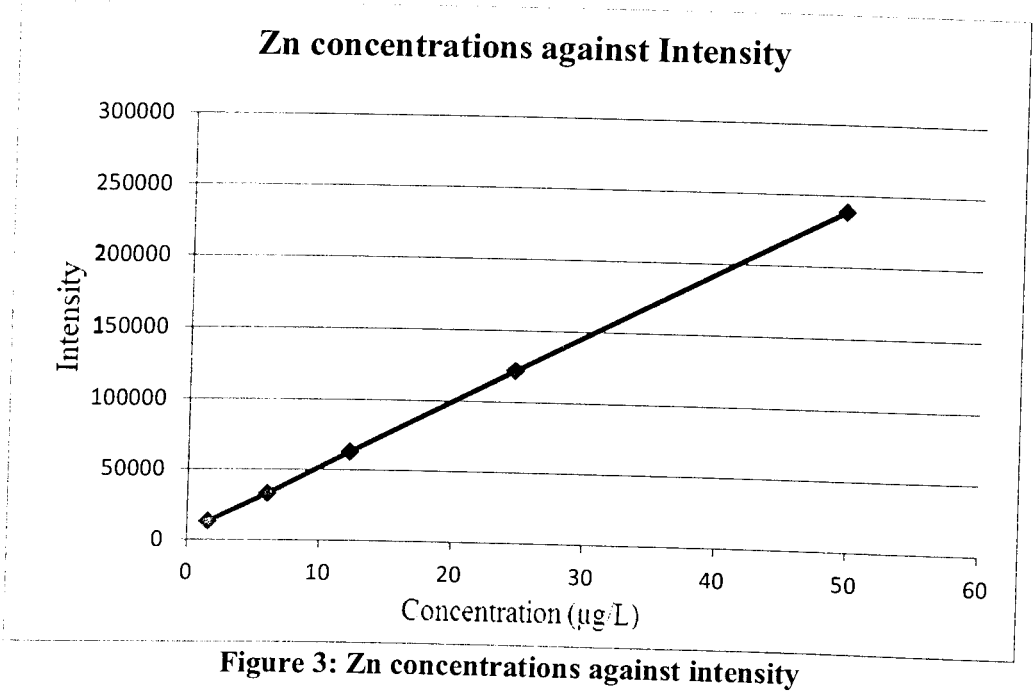

Figure 3: Zn concentrations against intensity

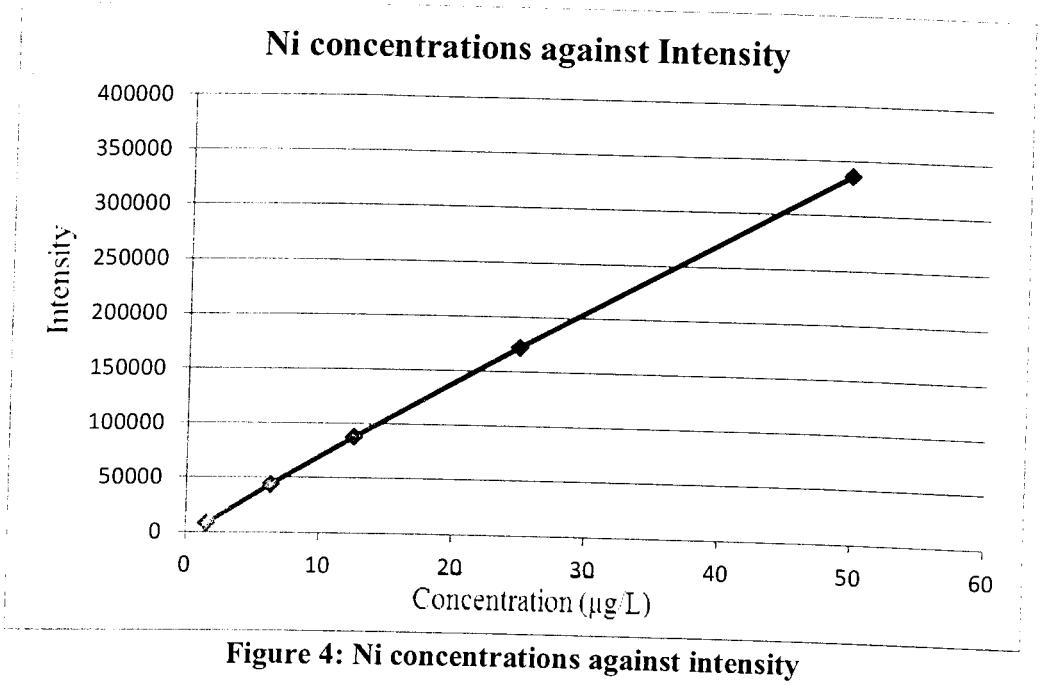

Figure 4: Ni concentrations against intensity

Appendix II

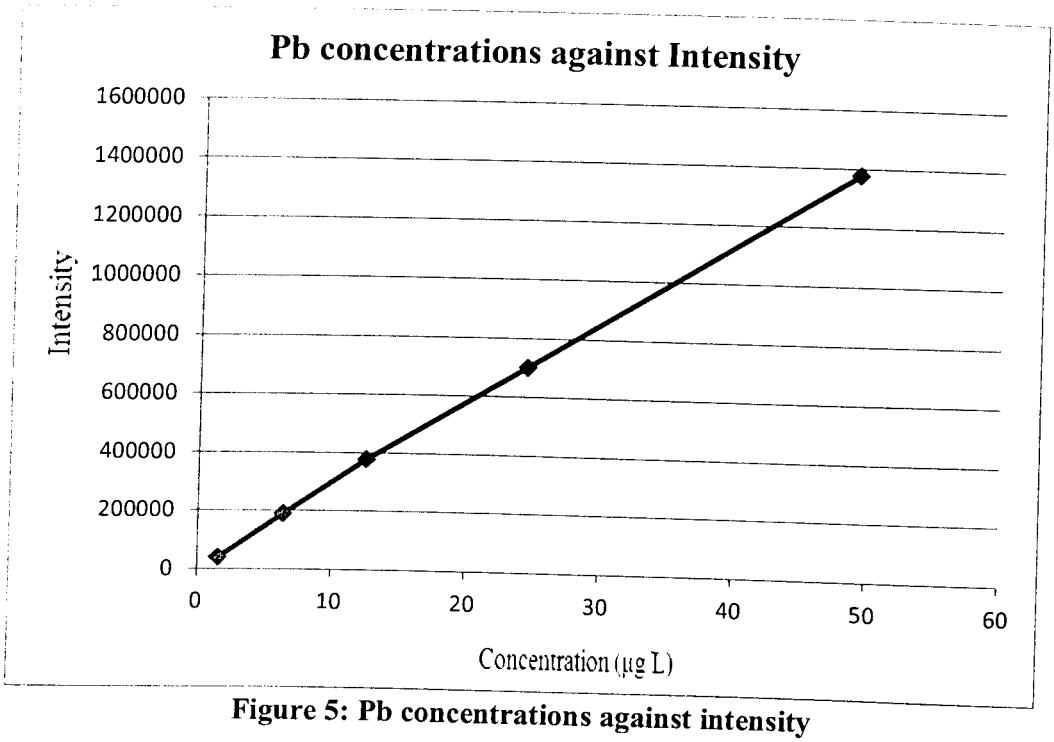

Figure 5: Pb concentrations against intensity

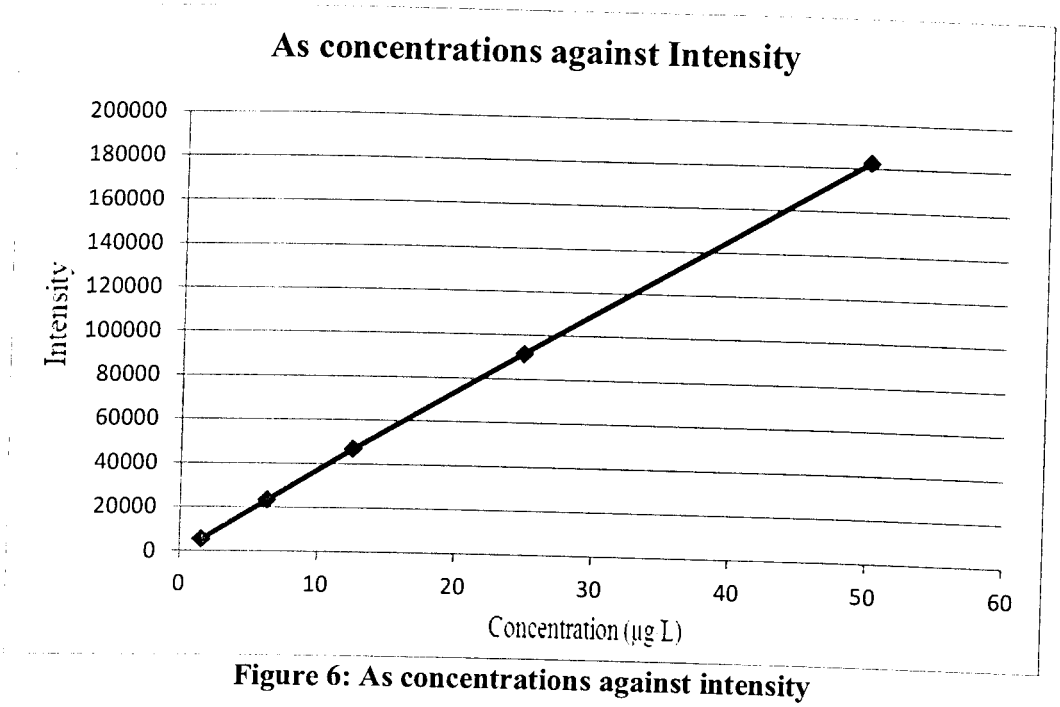

Figure 6: As concentrations against intensity

Appendix II

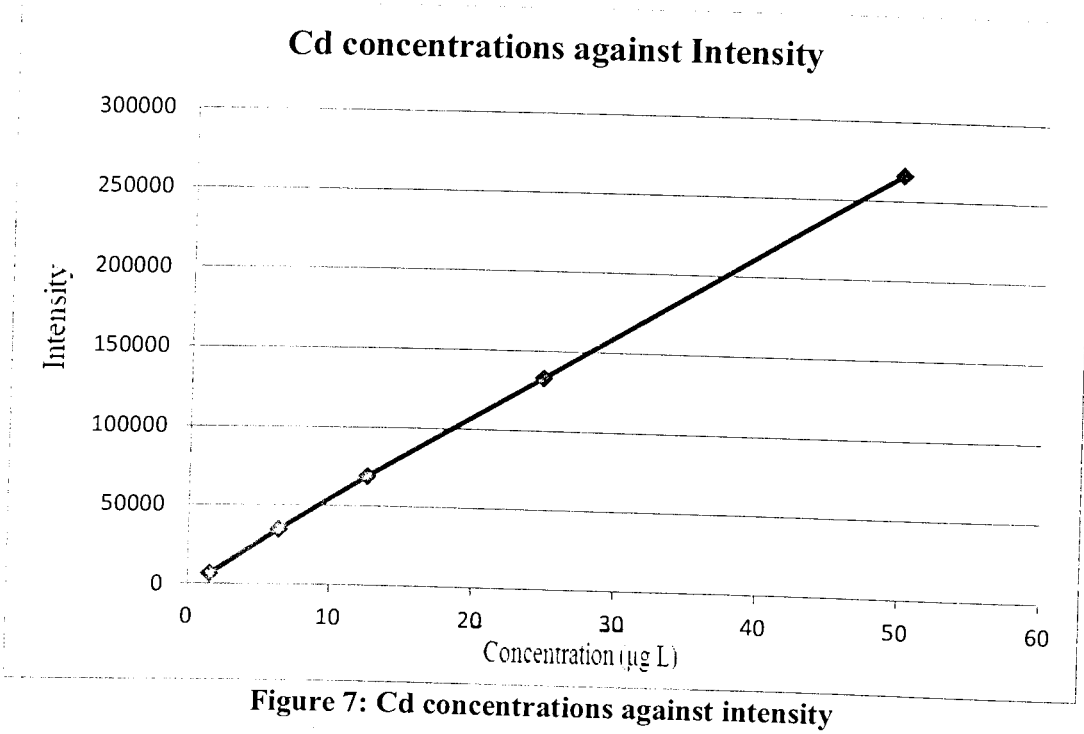

Figure 7: Cd concentrations against intensity

Appendix III

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1640a

Trace Elements in Natural Water

This Standard Reference Material (SRM) is intended for use in evaluating methods used in the determination of trace elements in fresh water. SRM 1640a consists of acidified spring water with mass fractions and mass concentrations assigned for 29 elements, 22 of which were gravimetrically added. The solution contains nitric acid at a volume fraction of approximately 2 %. A unit of SRM 1640a consists of 250 mL of solution in a high-density polyethylene (HDPE) bottle sealed inside an aluminized Mylar pouch.

Certified Values and Uncertainties: The certified values for 22 elements in SRM 1640a are given expressed in mass fraction units and mass concentration units in Tables 1 and 2, respectively. A NIST certified value is a value in which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been fully investigated or taken into account [1].

Each certified mass fraction value given in Table 1 is the average of the value calculated from the gravimetric preparation and the value determined using either inductively-coupled plasma optical emission spectroscopy (ICP-OES) or inductively-coupled plasma mass spectrometry (ICP-MS), adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See "Instructions for Use" for more information regarding transpiration.) The magnitude of the transpiration adjustment (0.11 %) is based upon the results of unpublished NIST studies of transpiration rates of similar HDPE bottles sealed inside similar aluminized Mylar pouches, and is such that the actual mass fraction is expected to be equal to the certified mass fraction value approximately halfway through the certification period. Each expanded uncertainty, U, in Table 1 is calculated as $U = ku_c$, where k is the coverage factor for the appropriate degrees of freedom (df) and a 95 % level of confidence (k and df are also given in Table 1) and u_c is the combined standard uncertainty calculated according to the ISO Guide [2]. The value of u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES or ICP-MS analysis, method bias [3], and the transpiration adjustment.

Each certified mass concentration value given in Table 2 is calculated from the corresponding certified mass fraction value in Table 1 through multiplication by the density of the SRM 1640a solution. Each expanded uncertainty, U, in Table 2 is calculated as $U = ku_c$, where k is the coverage factor for the appropriate degrees of freedom (df) and a 95 % level of confidence (k and df are also given in Table 2) and u_c is the combined standard uncertainty calculated according to the ISO Guide [2]. The value of u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the certified mass fraction value and the solution density.

Expiration of Certification: The certification of **SRM 1640a** is valid within the measurement uncertainty specified, until **05 August 2020**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 1640a was provided by M.R. Winchester of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 08 June 2010
See Certificate Revision History on Last Page

SRM 1640a

Appendix III

This SRM was prepared by T.A. Butler, L.L. Yu, and M.R. Winchester of the NIST Analytical Chemistry Division. The ICP-OES analyses were performed by T.A. Butler, J.L. Molloy, and M.R. Winchester of the NIST Analytical Chemistry Division. The ICP-MS analyses were performed by J.L. Molloy, T.A. Butler, L.L. Yu, and M.R. Winchester of the NIST Analytical Chemistry Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Reference Values and Uncertainties: The reference values for seven elements in SRM 1640a are given expressed in mass fraction units and mass concentration units in Tables 3 and 4, respectively. Reference values are non-certified values that are best estimates of the true values. However, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [1].

The reference mass fraction values and expanded uncertainties given in Table 3 are calculated using the same approach employed for the certified mass fraction values (see explanation above), including the use of the transpiration adjustment, except that each reference mass fraction value is based solely upon analysis using either ICP-OES or ICP-MS and uncertainty components are limited to those associated with the analysis and the transpiration adjustment. The reference mass concentration values and expanded uncertainties given in Table 4 are calculated using the same approach employed for the certified mass concentration values (see explanation above), except that they are calculated using the reference mass fraction values in place of the certified mass fraction values.

NOTICE AND WARNING TO USERS

CAUTION: This SRM is an acidic solution. All appropriate safety precautions, including use of gloves during handling, should be taken.

INSTRUCTIONS FOR USE

The SRM should be shaken before use to remix water that may have condensed on the inner surfaces of the bottle. To help prevent contamination, pipettes or other labware should **NOT** be inserted into the bottle. Instead, a portion of the solution should be decanted into another clean, dry container for use. Unused portions should not be returned to the SRM bottle.

The accuracy of trace element analysis is limited by contamination, especially at the microgram per kilogram (or microgram per liter) level. All apparatuses should be scrupulously clean, and only high-purity reagents should be employed. Sampling and manipulations, such as evaporations, should be done in a clean environment, such as a Class-100 clean hood.

The mass concentration values and uncertainties given in Tables 2 and 4 were calculated from the mass fraction values and uncertainties in Tables 1 and 3, respectively, taking into account the anticipated range of density values of the SRM solution in the temperature range 17 °C to 27 °C. Therefore, the mass concentration values and uncertainties given in the tables are valid when the SRM solution is used within a temperature range of 22 °C ± 5 °C. A more precise estimate of the mass concentration for a given temperature can be obtained by multiplying the mass fraction value by the accurately measured density of the solution at that temperature. The uncertainty associated with a mass concentration value calculated in this way can be estimated by combining the uncertainty components for the mass fraction value and the measured density following the ISO Guide [2].

Transpiration: The certified and reference values given in Tables 1 through 4 account for the effects of transpiration that may occur *prior to the first opening of the sealed pouch by the SRM user*. After the SRM bottle has been removed from the pouch, the rate of transpiration will rise, resulting in gradual increases in the mass fractions (and concentrations) of the elements. *It is the responsibility of the user of this SRM to account for this effect.* One approach is to weigh the SRM bottle both before and after each use. Mass loss observed during storage can be utilized to correct for transpiration. In order to minimize transpiration, the SRM bottle should be stored tightly closed and sealed inside an airtight container. The user should set a maximum shelf-life for a partially used SRM bottle commensurate with accuracy requirements.

Appendix III

PREPARATION OF MATERIAL

SRM 1640a was prepared at NIST using only high-purity reagents. An acid-cleaned HDPE tank of 2 kL capacity was filled with a known mass of commercially available spring water and enough concentrated nitric acid to adjust the acid volume fraction to approximately 2 %. After thorough mixing with a precleaned recirculating pump, a preliminary ICP-MS analysis was performed to determine the levels of the 29 elements of interest. The levels of the 22 elements to be certified were gravimetrically adjusted to target values by additions of aliquots of known masses of the SRMs in the SRM 3100 series of single-element standard solutions. For each of these elements, the target value was approximately 80 % of the Maximum Contaminant Level (MCL) listed in either the National Primary Drinking Water Regulations or the National Secondary Drinking Water Regulations maintained by the United States Environmental Protection Agency (*EPA*) [4], or approximately the mass fraction that was present in SRM 1640 Trace Elements in Natural Water, whichever was less. After addition of the aliquots and thorough mixing, the SRM solution was packaged in acid-cleaned HDPE bottles of 250 mL capacity and sealed inside aluminized Mylar pouches.

Table 1. Certified Values for Elements in SRM 1640a Expressed in Mass Fraction Units [a]

Element	Mass Fraction (µg kg)			*k*	*df*
Aluminum	52.6	±	1.8	2.069	23
Antimony	5.064	±	0.045	2.365	7
Arsenic	8.010	±	0.067	1.980	120
Barium	150.60	±	0.74	1.984	98
Beryllium	3.002	±	0.027	2.060	25
Boron	300.7	±	3.1	2.365	7
Cadmium	3.961	±	0.072	2.365	7
Chromium	40.22	±	0.28	2.021	40
Cobalt	20.08	±	0.24	2.447	6
Copper	85.07	±	0.48	2.228	10
Iron	36.5	±	1.7	2.447	6
Lead	12.005	±	0.040	1.970	227
Manganese	40.07	±	0.35	2.201	11
Molybdenum	45.24	±	0.59	2.017	43
Nickel	25.12	±	0.12	2.026	37
Selenium	19.97	±	0.16	2.228	10
Silver	8.017	±	0.042	2.086	20
Strontium	125.03	±	0.86	2.179	12
Thallium	1.606	±	0.015	2.365	7
Uranium	25.15	±	0.26	2.145	14
Vanadium	14.93	±	0.21	2.447	6
Zinc	55.20	±	0.32	2.010	49

[a] Certified mass fraction values are the equally weighted means of results from gravimetry and ICP-OES or ICP-MS adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See "Instructions for Use" for more information.) The magnitude of the transpiration adjustment (0.11 %) was selected so that the actual mass fractions are expected to be equal to the corresponding certified values approximately halfway through the certification period. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, the ICP-OES or ICP-MS analysis, method bias [3], and the transpiration adjustment. The coverage factor (*k*) for each analyte is determined from the Student's *t*-distribution corresponding to the degrees of freedom (*df*) and a 95 % level of confidence.

Appendix III

Table 2. Certified Values for Elements in SRM 1640a Expressed in Mass Concentration Units[1]

Element	Mass Concentration[2] (µg/L)			k	df
Aluminum	53.0	±	1.8	2.064	24
Antimony	5.105	±	0.046	2.262	9
Arsenic	8.075	±	0.070	1.977	142
Barium	151.80	±	0.83	1.976	151
Beryllium	3.026	±	0.025	2.045	29
Boron	303.1	±	3.1	2.306	8
Cadmium	3.992	±	0.074	2.365	7
Chromium	40.54	±	0.30	2.008	51
Cobalt	20.24	±	0.24	2.365	7
Copper	55.75	±	0.51	2.120	16
Iron	36.8	±	1.8	2.447	6
Lead	12.101	±	0.050	1.965	517
Manganese	40.39	±	0.36	2.160	13
Molybdenum	45.60	±	0.61	2.013	46
Nickel	25.32	±	0.14	2.001	59
Selenium	20.13	±	0.17	2.160	13
Silver	8.081	±	0.046	2.040	31
Strontium	126.03	±	0.91	2.120	16
Thallium	1.619	±	0.016	2.306	8
Uranium	25.35	±	0.27	2.120	16
Vanadium	15.05	±	0.25	2.365	7
Zinc	55.64	±	0.35	1.995	68

[1] Certified mass concentration values are calculated from the certified mass fraction values in Table 1 through multiplication by the density of the SRM 1640a solution. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the certified mass fraction value and the solution density. The coverage factor (k) for each analyte is determined from the Student's t-distribution corresponding to the degrees of freedom (df) and a 95 % level of confidence.

[2] The certified mass concentration values and expanded uncertainties are valid when the SRM solution is used within the temperature range (22 °C ± 5 °C).

Appendix III

Table 3. Reference Values for Elements in SRM 1640a Expressed in Mass Fraction Units[a]

Element	Mass Fraction (mg kg)			k	df
Calcium	5.570	±	0.016	2.120	16
Magnesium	1.0502	±	0.0034	2.262	9
Potassium	0.5753	±	0.0020	2.179	12
Silicon	5.169	±	0.017	2.074	22
Sodium	3.112	±	0.031	2.776	4
	(µg kg)				
Lithium	0.4034	±	0.0092	2.776	4
Rubidium	1.188	±	0.011	1.961	3204

[a] Reference mass fraction values are the ICP-OES or ICP-MS values, adjusted upward for transpiration that may occur over the certification period while the SRM bottle remains sealed inside the aluminized Mylar pouch. (NOTE: *No correction has been applied for transpiration that will occur after the pouch seal has been broken.* See "Instructions for Use" for more information.) The magnitude of the transpiration adjustment (0.11 %) was selected so that the actual mass fractions are expected to be equal to the corresponding reference values approximately halfway through the certification period. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the ICP-OES or ICP-MS analysis and the transpiration adjustment. The coverage factor (k) for each analyte is determined from the Student's t-distribution corresponding to the degrees of freedom (df) and a 95 % level of confidence.

Table 4. Reference Values for Elements in SRM 1640a Expressed in Mass Concentration Units[a]

Element	Mass Concentration [b] (mg L)			k	df
Calcium	5.615	±	0.021	2.005	54
Magnesium	1.0586	±	0.0041	2.045	29
Potassium	0.5799	±	0.0023	2.040	31
Silicon	5.210	±	0.021	2.005	54
Sodium	3.137	±	0.031	2.571	5
	(µg L)				
Lithium	0.4066	±	0.0094	2.776	4
Rubidium	1.198	±	0.011	1.961	3657

[a] Reference mass concentration values are calculated from the reference mass fraction values in Table 3 through multiplication by the density of the SRM 1640a solution. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated following the ISO Guide [2] as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the reference mass fraction value and the solution density. The coverage factor (k) for each analyte is determined from the Student's t-distribution corresponding to the degrees of freedom (df) and a 95 % level of confidence.

[b] The reference mass concentration values and expanded uncertainties are valid when the SRM solution is used within the temperature range (22 °C ± 5 °C).

Appendix III

REFERENCES

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Certificate Revision History: 08 June 2010 (This revision includes corrected lithium values in Tables 3 and 4 and minor editorial changes); 03 December 2009 (Original certificate date)

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

Appendix III

Quantitative Analysis - Summary Report
Sample ID: **SRM 1640a NIST NATURAL WATER**
Sample Date/Time: **Wednesday, January 27, 2016 12:37:17**
Dual Detector Mode: **Dual**
Sample File:
Method File: **C:\Elandata\Method\Quantitative Analysis.mth**
Dataset File: **C:\Elandata\DataSet\JAN 2016\SRM 1640a NIST NATURAL WATER.1699**

Summary

Table 2: Concentration of SRM 1640a NIST NATURAL WATER (ppb)

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD
Cu	63	1045204.405	**86.123**	0.36	0.4
Cd	111	17163.26	**3.827**	0.04	1.1
Cr	52	839859.099	**42.179**	0.53	1.3
Zn	66	158635.809	**45.007**	0.53	1.2
Ni	60	144225.452	**25.738**	0.4	1.6
Pb	208	306611.687	**12.938**	0.09	0.7
As	75	22285.763	**7.514**	0.12	1.5

Table 3: Percentage of ICP-MS Performance

Analyte	Conc. Mean of Elements in NIST Natural Water (µg/L)	Certified Value for Elements in SRM 1640a (µg/L)	Performance (%)
Cu	86.123	84.97	98.66
Cd	3.827	3.961	96.61
Cr	38.179	40.22	94.92
Zn	45.007	55.20	81.53
Ni	24.738	25.12	98.47
Pb	11.938	12.00	99.44
As	7.514	8.01	93.80

Appendix IV

Table 4: ICP-MS detection limit (mg/L)

Heavy metals	ICP-MS detection limit (mg/L)*
Cu	2.0×10^{-7}
Cr	2.0×10^{-7}
Zn	3.0×10^{-7}
Ni	4.0×10^{-7}
Pb	4.0×10^{-8}
As	9.0×10^{-7}
Cd	9.0×10^{-8}

*ICP-MS detection limit from Perkin Elmer

Appendix V

Table 5: Concentrations of heavy metals in paddy water (mg/L)

Sampling point	Cu	Cr	Zn	Ni	Pb	As	Cd
A1	0.0022	0.0053	0.0121	0.0037	0.0015	0.0194	0.000039
A2	0.0028	0.0063	0.0126	0.0027	0.002	0.0246	0.000031
A3	0.0025	0.0067	0.0112	0.0026	0.002	0.0227	0.000022
B1	0.0017	0.0011	0.0036	0.0018	0.0009	0.016	0.000011
B2	0.0014	0.0011	0.0025	0.0019	0.001	0.016	0.000012
B3	0.0012	0.0095	0.0031	0.0013	0.0008	0.0013	0.000011
C1	0.0012	0.0034	0.0049	0.0013	0.0015	0.0047	0.000017
C2	0.0012	0.0035	0.0053	0.0011	0.002	0.0031	0.000017
C3	0.0032	0.0029	0.0057	0.0075	0.0011	0.0033	0.000014
D1	0.0021	0.0042	0.0016	0.0031	0.0014	0.0035	0.000031
D2	0.0015	0.0041	0.0012	0.0039	0.0014	0.0033	0.000025
D3	0.0016	0.0037	0.0011	0.0015	0.0015	0.0028	0.000019
E1	0.0015	0.0053	0.0084	0.005	0.0014	0.0043	0.000034
E2	0.0013	0.0048	0.0059	0.0012	0.0013	0.0041	0.000017
E3	0.0013	0.0044	0.005	0.0009	0.0014	0.0039	0.000018
F1	0.0033	0.0072	0.0073	0.003	0.0012	0.0063	0.000022
F2	0.0056	0.0041	0.0066	0.0015	0.0027	0.0052	0.000016
F3	0.0014	0.0023	0.0088	0.001	0.0018	0.0035	0.000013
G1	0.0059	0.0028	0.0096	0.0022	0.0011	0.0034	0.000011
G2	0.0036	0.0062	0.0062	0.0026	0.0008	0.0065	0.00001
G3	0.0023	0.0035	0.0031	0.0016	0.0007	0.0049	0.000009
H1	0.005	0.0063	0.0149	0.0025	0.0009	0.0168	0.000026
H2	0.0021	0.0052	0.013	0.002	0.001	0.0093	0.000016
H3	0.0021	0.0067	0.009	0.0022	0.0009	0.0084	0.000012
I1	0.0062	0.0054	0.0086	0.0033	0.0064	0.0146	0.000029
I2	0.002	0.0049	0.0016	0.0017	0.0015	0.0095	0.000016
I3	0.0052	0.0064	0.0012	0.0022	0.0008	0.0112	0.000032
J1	0.0013	0.0025	0.0092	0.0028	0.0011	0.0029	0.000012
J2	0.0011	0.0021	0.0081	0.0014	0.001	0.0025	0.000008
J3	0.0022	0.002	0.0098	0.0017	0.001	0.0023	0.00001
K1	0.0025	0.0055	0.0013	0.0027	0.0016	0.0184	0.000036
K2	0.0029	0.0062	0.0073	0.0031	0.0014	0.0178	0.000028
K3	0.0021	0.0063	0.0082	0.0019	0.0014	0.015	0.000025
L1	0.0021	0.0037	0.0036	0.0025	0.0007	0.003	0.00001
L2	0.0023	0.0025	0.0062	0.0029	0.0007	0.0027	0.000017
L3	0.0021	0.0022	0.0111	0.0023	0.0009	0.0029	0.000026
M1	0.0035	0.008	0.0109	0.0042	0.0015	0.0048	0.000018
M2	0.003	0.0081	0.0073	0.0027	0.0015	0.0045	0.000014
M3	0.0036	0.0069	0.007	0.0026	0.0018	0.0036	0.00002

Appendix V

Sampling point	Cu	Cr	Zn	Ni	Pb	As	Cd
N1	0.0034	0.0035	0.0101	0.002	0.0017	0.0064	0.000017
N2	0.0018	0.0024	0.0077	0.0015	0.0012	0.0045	0.00001
N3	0.0019	0.0022	0.0061	0.0021	0.0009	0.0059	0.00001
O1	0.0014	0.0061	0.0035	0.0019	0.0016	0.0047	0.000012
O2	0.0013	0.0033	0.006	0.0012	0.0011	0.0042	0.00002
O3	0.0015	0.0028	0.0105	0.0015	0.0014	0.0031	0.000017
P1	0.0016	0.0021	0.0122	0.0023	0.0016	0.0099	0.000022
P2	0.0017	0.003	0.0116	0.0044	0.002	0.0113	0.000025
P3	0.0015	0.0023	0.0137	0.0034	0.0016	0.0096	0.000028
Q1	0.0018	0.0048	0.0069	0.0067	0.0009	0.0219	0.000025
Q2	0.0017	0.0051	0.0062	0.0011	0.0013	0.0218	0.00003
Q3	0.0018	0.0062	0.0058	0.0024	0.0014	0.0229	0.000034
R1	0.0045	0.0042	0.0197	0.0013	0.0039	0.0104	0.000103
R2	0.0033	0.0035	0.0124	0.0033	0.0019	0.0088	0.000045
R3	0.0024	0.003	0.0131	0.0059	0.0015	0.0076	0.000038
S1	0.0023	0.0049	0.0213	0.0036	0.0016	0.0073	0.000035
S2	0.0021	0.0056	0.0102	0.0032	0.0016	0.0075	0.000021
S3	0.0022	0.0057	0.0067	0.003	0.0016	0.0087	0.000012
T1	0.0018	0.0049	0.0122	0.0026	0.0029	0.0204	0.000026
T2	0.0021	0.004	0.0101	0.0023	0.0025	0.0173	0.000019
T3	0.0027	0.0063	0.0099	0.003	0.004	0.0334	0.000044
U1	0.0033	0.0042	0.0221	0.0032	0.0033	0.0098	0.00005
U2	0.0022	0.0058	0.0078	0.0022	0.0019	0.0204	0.000025
U3	0.0017	0.0054	0.0064	0.0022	0.0014	0.0268	0.000019
V1	0.0015	0.0025	0.0064	0.0028	0.0024	0.0141	0.000008
V2	0.0023	0.0024	0.0091	0.0028	0.0023	0.0126	0.000007
V3	0.0017	0.0021	0.0123	0.0022	0.0021	0.0126	0.000007
W1	0.0036	0.0046	0.0119	0.0041	0.0011	0.0142	0.000024
W2	0.0023	0.0036	0.0066	0.0024	0.0014	0.0092	0.000018
W3	0.0019	0.0025	0.0088	0.0024	0.0015	0.0055	0.00002
X1	0.0037	0.0067	0.0103	0.0051	0.0023	0.0213	0.000034
X2	0.0045	0.0076	0.0105	0.0027	0.0028	0.0239	0.000042
X3	0.0063	0.0076	0.0154	0.003	0.0031	0.0219	0.000044

Appendix VI

Table 6: In-Situ Water Quality Parameters

Sampling points	Temperature (°C)	pH	EC (µs/cm)	DO (mg/L)	Turbidity (NTU)
A1	33.7	7.2	211.3	6.7	41.8
A2	33.8	7.4	225.0	6.4	43.3
A3	33.1	7.6	233.6	6.7	51.5
B1	32.3	8.1	400.0	7.6	51.0
B2	32.4	8.1	435.3	7.6	57.7
B3	32.2	7.9	381.7	7.4	51.6
C1	32.9	7.1	391.3	6.7	54.3
C2	33.9	7.1	380.6	6.4	56.0
C3	33.6	7.3	277.9	7.8	55.8
D1	33.6	7.0	124.2	6.9	65.8
D2	32.8	7.1	125.2	6.3	66.9
D3	33.1	7.1	132.2	7.1	73.5
E1	35.4	7.7	161.9	6.8	71.0
E2	36.0	7.6	155.4	6.7	75.1
E3	35.9	7.8	147.3	6.9	76.9
F1	36.5	7.1	281.2	6.3	64.8
F2	35.2	6.9	261.0	7.3	69.2
F3	37.5	7.1	282.4	6.2	60.8
G1	34.4	7.3	194.4	7.7	97.3
G2	32.6	7.6	190.0	7.6	95.2
G3	33.4	7.1	192.2	7.1	88.0
H1	35.8	8.0	198.4	8.0	52.7
H2	34.2	7.8	179.5	8.1	55.6
H3	33.9	8.2	193.4	8.1	58.2
I1	33.4	8.3	192.3	6.8	52.5
I2	33.3	8.3	197.3	6.6	52.7
I3	32.4	8.2	189.3	6.6	41.7
J1	31.6	7.1	261.4	7.8	73.9
J2	30.4	7.1	253.7	7.9	69.9
J3	31.0	7.3	250.8	7.2	82.1
K1	34.5	8.5	212.7	8.4	44.0
K2	33.7	8.8	211.9	7.3	49.6
K3	33.9	8.4	190.6	7.6	40.4
L1	30.7	6.6	381.8	7.0	55.0
L2	32.7	6.6	445.4	7.2	57.3
L3	32.1	6.5	385.0	7.2	52.1
M1	39.3	8.0	368.7	6.5	175.0
M2	35.5	8.0	397.4	6.9	177.0

Appendix VI

Sampling points	Temperature (°C)	pH	EC (µs/cm)	DO (mg/L)	Turbidity (NTU)
M3	36.1	7.7	397.2	6.8	141.0
N1	36.5	7.9	192.1	7.2	39.5
N2	37.3	8.2	223.7	8.2	38.6
N3	35.7	8.1	202.9	8.6	31.5
O1	35.8	7.9	119.5	6.8	75.2
O2	35.9	7.8	121.3	6.4	72.1
O3	36.2	8.2	113.5	6.8	75.7
P1	34.0	7.8	197.9	7.2	59.2
P2	35.1	7.6	195.4	6.9	51.7
P3	34.2	7.4	190.5	6.9	73.1
Q1	35.9	8.3	321.1	8.3	80.8
Q2	36.4	8.4	318.3	8.4	75.6
Q3	36.3	8.5	321.0	8.4	71.6
R1	35.5	8.7	202.0	6.7	34.2
R2	35.2	8.3	182.4	6.7	37.0
R3	36.9	8.5	192.3	6.0	35.6
S1	34.4	7.7	477.8	7.0	37.8
S2	34.7	7.7	433.8	7.1	30.2
S3	34.4	7.9	483.2	8.1	35.0
T1	35.0	7.6	172.8	6.9	42.3
T2	34.4	7.2	151.1	7.1	48.5
T3	34.0	7.8	170.9	6.7	48.3
U1	33.3	7.6	492.2	6.9	93.0
U2	34.2	8.0	500.4	7.2	92.1
U3	34.4	8.1	479.3	7.0	87.8
V1	37.0	6.7	238.8	6.7	105.0
V2	36.8	6.9	245.3	6.6	118.0
V3	37.2	6.7	257.4	7.3	109.0
W1	35.1	8.1	242.0	7.5	40.2
W2	34.3	8.2	246.2	7.7	48.9
W3	35.5	8.5	242.9	7.1	52.4
X1	37.5	7.9	234.2	6.9	116.0
X2	36.2	8.1	242.5	7.2	108.0
X3	37.2	8.1	239.3	7.7	106.0

Appendix VII

Figure 8: Perkin Elmer Sciex ICP-MS Elan 9000 used for the determination of heavy metals

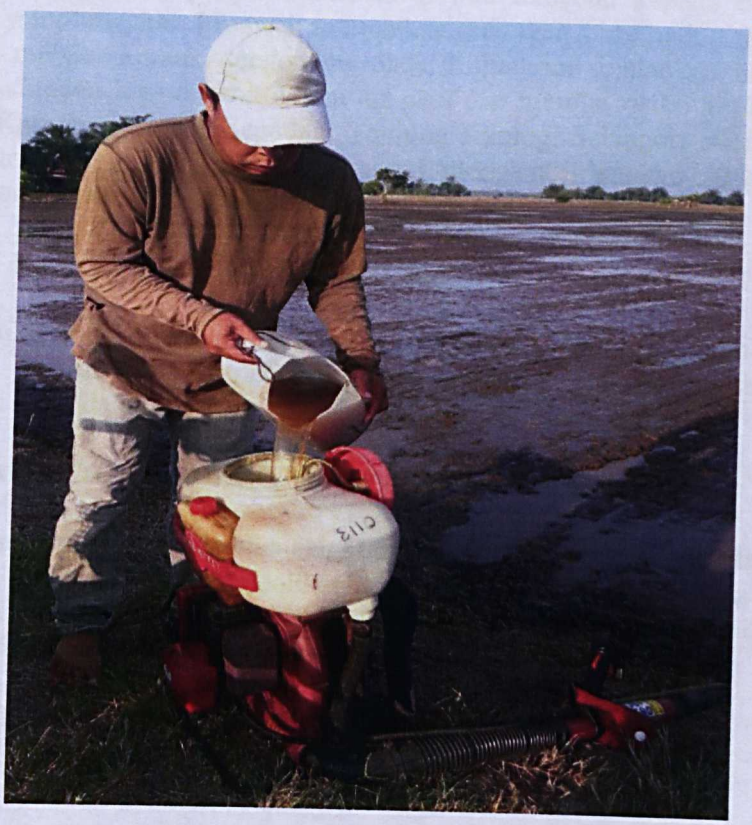

Figure 9: Example of farmer with no appropriate personal protective equipment (PPE)

Appendix VIII

JAWATANKUASA ETIKA UNIVERSITI UNTUK
PENYELIDIKAN MELIBATKAN MANUSIA (JKEUPM)
UNIVERSITI PUTRA MALAYSIA,
43400 UPM SERDANG,
SELANGOR, MALAYSIA

BORANG B1: PENERANGAN DAN PERSETUJUAN RESPONDEN

Sila baca maklumat berikut dengan teliti. Sekiranya anda mempunyai sebarang pertanyaan, sila kemukakan kepada penyelidik.

1.TAJUK KAJIAN

Pencemaran logam berat dalam air padi dan penilaian risiko kesihatan dalam kalangan pesawah di Tanjung Karang, Selangor

2. PENGENALAN

Penilaian risiko kesihatan adalah satu proses dimana penyelidik akan menganggar keberangkalian terjadinya penyakit berbahaya jika terdedah kepada bahan kimia di persekitaran yang tercemar. Pesawah merupakan golongan yang paling terdedah kepada logam berat melalui kontak dengan air padi. Kajian ini dijalankan bertujuan untuk mengkaji kandungan logam berat dalam air padi dan menilai risiko kesihatan terhadap pesawah di Kampung Sawah Sepadan, Tanjung Karang, Selangor. Sekiranya terdapat risiko kesihatan, pesawah akan dinasihati untuk mengambil langkah berhati-hati semasa mengendalikan air padi.

3. APAKAH YANG PERLU ANDA LAKUKAN?

Responden dikehendaki menjawab borang soal selidik yang diberikan untuk tujuan mendapatkan informasi mengenai berat badan, tempoh dan kekerapan pendedahan kepada logam berat dalam air padi.

4. SIAPA YANG TIDAK BOLEH MENYERTAI KAJIAN INI?

Penduduk Kampung Sawah Sepadan yang tidak terlibat dalam aktiviti pertanian padi dan pesawah yang tidak mengendalikan air padi secara langsung serta terdedah kepada logam berat. Selain itu, kanak-kanak dan penduduk yang berusia 18 tahun ke bawah juga tidak dibenarkan terlibat dalam kajian ini.

5. APAKAH FAEDAH MENYERTAI KAJIAN INI?

a) KEPADA ANDA SEBAGAI PESERTA?

Kajian ini akan menilai jika terdapatnya risiko kesihatan kulit atau tidak apabila anda terdedah kepada logam berat. Selepas kajian selesai, anda akan

Appendix VIII

9. PERSETUJUAN

Saya.....No. Kad Pengenalan.....
beralamat.....
.....
.....dengan ini bersetuju untuk mengambil bahagian secara sukarela dalam penyelidikan yang tersebut di atas *(kajian klinikal/ percubaan ubat-ubatan/ rakaman video/ kumpulan sasaran/ temuduga/ soal selidik).

Saya telah diberi penjelasan secara menyeluruh mengenai penyelidikan ini dari segi metodologi, risiko dan komplikasi (seperti tertulis pada Helaian Penerangan Responden). Saya memahami bahawa saya berhak menarik diri dari penyelidikan ini pada bila-bila masa tanpa memberi sebarang alasan.Saya juga memahami bahawa sebarang maklumat yang berkaitan identiti saya akan dirahsiakan.

Saya* berminat / tidak berminat untuk mengetahui keputusan kajian yang melibatkan saya.

I setuju/tidak bersetuju untuk imei/gambar/rakaman video/ rakaman suara digunakan dalam apa jua bentuk penerbitan atau pembentangan. (sekiranya berkaitan).

*potong yang tidak berkenaan

Tandatangan .....
(*Responden*)

Tarikh :.....

Tandatangan .....
(*Saksi*)

Nama: .....

No. K/P: .....

Saya mengesahkan bahawa saya telah menerangkan kepada responden ini sifat dan tujuan penyelidikan yang tersebut di atas.

Tarikh .....

Tandatangan .....
(*Penyelidik*)