ASSESSMENT OF COPPER AND CADMIUM IN SOILS FROM PADDY FIELDS

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ABSTRACT

Some heavy metals are regarded as toxic trace elements in the environment. Heavy metal pollution in soil or rice grains is of increasing concern. The present study investigated the concentration of Cd and Cu in the paddy field soils where it was collected from Juasseh, Negeri Sembilan and Sekinchan, Selangor. Soil samples were treated with aqua-regia method to determine total metal concentrations as well as sequential extraction technique (SET) to determine the metals bioavailability to plants. The heavy metals concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS) in Universiti Putra Malaysia. Overall, both of the sites were highly contaminated because Cu has exceeded the permissible limit with the highest value of 1682.99 µg/g dw when compared to China. Resistant fraction was detected as the highest accumulation of Cu, indicating that metal was mostly associated with naturally origins and not available to plants, whereas Cd was found to be accumulated highest in acid reducible fraction. Some of the factors influencing the bioavailability of metals and their occurrences in crops studied were soil pH and organic matter content.

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LIST OF ABBREVIATIONS

°C	Degree Celsius
µg/g dw	Microgram per Gram Dry Weight
Cd	Cadmium
cm	Centimetre
Cr	Chromium
Cu	Copper
EFLE	Easily or Freely Leachable and Exchangeable
Fe	Iron
g	Gram
H_20_2	Hydrogen Peroxide
Hg	Mercury
M	Molar
mg	Milligrams
mL	Milliliter
Mn	Manganese
Pb	Lead
rpm	Revolutions per Minute
SET	Sequential Extraction Technique

1.0 CHAPTER 1:

INTRODUCTION

In most of the countries, including Malaysia, rice has been the most important staple food and people rely on it for growth and survival (Sow et al., 2013). Paddy industry has contributed an economic importance to our country which is the reason why government focus much on this industry (Nurul Nadia, Mad Nasir, Zainalabidin, & Alias, 2012). In fact, rice is also an important commodity in food security agenda for most of the countries worldwide (Mohd Rashid & Mohd Dainuri, 2013). Hence, many activities has been done in order to produce a better quality of paddy and to increase its yield. Consequently, some of the paddy soils are contaminated with heavy metals due to the transformations made to improve the paddy production (Sow et al., 2013).

Heavy metals contamination has been a controversial issue in agricultural environmental studies for a long time. Environmental pollution problem not only caused by the heavy metals that happen naturally in environment, in fact, the increasing concentration of heavy metals also originates from the anthropogenic sources (Md. Faruk, Sinin, & Md. Rezaur, 2015; Satpathy, Reddy & Dhal, 2014) such as the pesticides and fertilizers (Jiao, Teng, Zhan, Wu & Lin, 2015). These heavy metals accumulate in soil which resulted to health issues, food quality issues as well as food safety issues. Hence, when these soils are employed as crop production, there is possibility that the heavy metals would give harm to human, plants and animals (Satpathy et al., 2014; Wong, Li, Zhang, Qi & Min, 2002).

Since metals from anthropogenic inputs are normally deposited in the top soils, thus soils are thought to be an incredible form of media to screen and detect heavy metal contamination (Satpathy et al., 2014). Soil with heavy metals unfavorably influences the entire biological community when these dangerous heavy metals resettle into groundwater, which may bring about a huge risk to environments because of bioaccumulation and translocation (Bhagure & Mirgane, 2011). Heavy metals affects human health via ingestion, inhalation and dermal contact absorption (Jiao et al., 2015). Shimbo et al. (2001) found that rice is one of the major sources of Cd to people in Asia. There is a clear proof that Cd

contaminated rice farm in Asia is interconnected with the renal tubular dysfunction of human (Chaney et al., 2005).

There were also reports stated that crop plants have distinctive capacities to ingest and accumulate heavy metals in their body parts. The occurrence of absorption and accumulation of heavy metals in the 25 cm soil zone surface is presumably because of relatively high organic substances and there is possibility that the plants absorb heavy metals from this layer of soil, where it is mostly influenced by pollutants due to anthropogenic activities (Satpathy et al., 2014). According to Alloway (2009), consumable parts such as rice grain are one of the parts of the plant to directly transport heavy metals to human body and as a result would cause a risk on human health. These metals existing in environment is quite a concern for us due to their bioaccumulation, biomagnification characters and persistence nature which makes them toxic to human, animals as well as plants (Satpathy et al., 2014).

Therefore, the objective of this study is:

i. To determine the total Cd and Cu concentration in Juasseh, Negeri Sembilan and Sekinchan, Selangor through total aqua-regia method

ii. To determine the Cd and Cu concentration in each geochemical fraction through the sequential extraction method

iii. To study the effect of pH and soil organic content to the mobility and bioavailibilty of Cd and Cu in the soil.

2.0 CHAPTER 2

LITERATURE REVIEW

2.1 PADDY INDUSTRY

Rice is the national staple food of many countries including Malaysia. Other than being the major source of food, it also provides source of income to 172,000 paddy farmers in Malaysia in 2009 (Nurul Nadia et al., 2012). Since the paddy industry holds an important role in economically, politically and socially, hence it has always been closely monitored by the government. Lately, the incident of staple food crisis impacting many countries turned serious when China, Vietnam and India had restricted the exporting of rice to other countries which shows how important the industry is (Shahrina, Shuhaida & Moho Stamburi, 2014). Paddy has became a precious commodity as the consumption of rice has rised rapidly in the past few decades. In 2012, the production of rice was approximately to be 724.5 million tons as claimed by Food and Agriculture Organization (FAO). Rice is the staple food that is consumed by most of the people especially in Asia where 92 % of the total rice is produced (Arunakumara, Walpola & Yoon, 2013).

2.2 HEAVY METALS

Any toxic metal can be regarded as heavy metal, in spite of their density or atomic mass (Singh, Gautam, Mishra & Gupta, 2011). Heavy metals such as Pb, Cr, Hg and Cd are classified as key monitoring pollutants in paddy soil as they have an irreversible accumulation, persistent and possible toxicity feature (Liu, 2016). Because of their high degree of toxicity, they were ranked among the prime concern metals that are of public health significance. According to the International Agency for Research on Cancer and the U.S. Environmental Protection Agency, they were also classified as human carcinogens (Tchounwou, Yedjou, Patlolla & Sutton, 2012). Any metal (or metalloid) species might be viewed as a contaminant if it happens where it is undesirable, or in a form or amount that lead to harmful environmental or human impact (Singh et al., 2011). According to Tchounwou et al., (2012), their toxicity depends on several factors including the chemical species, route of exposure and dose.

2.2.1 Sources of Heavy Metals

Heavy metals contaminations can be either from natural or anthropogenic sources. Natural phenomenon such as weathering, soil erosion, organic matter decay and rainfall are some of the factors that lead to heavy metal contamination in the soil (Baruah, Das, Haque, Medhi, & Misra, 2011). Other than that, there are also some natural origins include components exist in parent rocks, biogenic releases, forest fires and volcanic activity which might cause heavy metal contaminations (Ungureanu, Iancu, Pintilei, & Chicoș, 2017). If weathering occurs, the primary crystalline structures of some rock minerals are completely cleaved, allowing chemical elements to be carried towards groundwater or surface water target, or probably adsorbed in the topsoil (Arunakumara et al., 2013).

Natural soils have large differences to urban soils as the urban ones are strongly affected by human and usually there is a larger amount of contaminants present than those in the countryside ones due to the higher density of anthropogenic activity (Ungureanu et al., 2017). Some of the examples of anthropogenic inputs includes industrial wastes, sewage, traffic emissions, pesticides and fertilizers (Jiao, Teng, Zhan, Wu & Lin, 2015; Maryam, Sobhanardakani, Karimi & Sorooshnia, 2015). Frequent use of fertilizers and pesticides are one of the major source of heavy metal contaminations in soil as the pollutants might be accumulated by the soil, this is due to the heavy metals are attached to different phases or soil component such as biological or organic substances, carbonates, sulfides, Fe–Mn oxyhydrates and clay minerals (Sow et al., 2013).

2.2.2 Bioavailability of Heavy Metals

The heavy metals uptake by plants is predominantly affected by the metal availability and mobility in soils. To be more specific, the availability and mobility of heavy metals are determined through adsorption and desorption properties of soils (Zeng et al., 2011). The chemical properties of metals in soil has been linked to factors such as soil mineralogy, organic matter, pH and cation-exchange capacity which might cause alteration of metals bioavailability to plants (Takáč, Szabová, Kozáková & Benková, 2009). However, out of all the factors, pH was discovered to be the major key in affecting the metals bioavailability in soil as it has the most influence on the metals solubility (Zeng et al., 2011). Besides that, organic matter content in soil is also an important factor in metal bioavailability. It plays an

important role in metal binding although the portion of it in the soil is much lower than the clay (Rieuwerts, Thornton, Farago & Ashmore, 1998). Apart from acting as chelates, organic matter shows the potential for the soil to retain heavy metals in an exchangeable appearance (Zeng et al., 2011). Soil with high organic matter content contributed to the acidification of soil, hence more bioavailable to plants. There were various reports on significant negative correlations between soil pH and heavy metals bioavailability but positive correlations between organic matter and metals bioavailability (Chibuike & Obiora, 2014; Zeng et al., 2011).

2.3 CADMIUM

2.3.1 Accumulation of Cd in Soil

Cadmium is regarded as one of the most non-nutritive toxic trace elements in the environment and it is harmful to humans. Its accumulation and fast incorporation into food chain as well as its persistence in the environment and increased emissions resulting from its use, production and disposal has lead to its possible environmental threat (Ji, Chen, Li & Ni, 2012). Cadmium sources to paddy soils can be natural or by contamination from industrial discharge, sewage sludge, base-metal mining or fertilizers derived from the phosphate rock (Meharg, 2013; Roberts, 2014). In China and Japan, there was a report on Cd intake by the locals due to the rice in which the local paddy soil was contaminated (Rodda, Li, & Reid, 2011).

Cadmium would eventually accumulate into grains after the being taken up from the soil by through some transporting approaches. According to Rodda et al. (2011), Cd is recognized as both xylem and phloem mobile although the translocation of Cd mechanisms in plants are not entirely confirmed. Cadmium is rapidly transported from roots to shoots by the xylem after absorption (Uraguchi & Fujiwara, 2012). The total Cd present in the soil does not really contribute to the danger of Cd accumulation by crops, instead it is more likely linked to its availability due to crop, soil, environment and management. Soil pH is normally considered as one of the major factor affecting Cd absorption from the soil (Roberts. 2014).