Heavy Metal Content of Paddy Plants in Langkawi, Kedah, Malaysia

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Abstract: The accumulation of heavy metals in paddy plants due to the utilization of rock phosphate, urea and N:P:K fertilizers for paddy cultivation over decades in Malaysia, has become a rising concern. Thus, the present study was aimed at determining the heavy metal concentration in two paddy varieties (MRQ 74 and MR 219) cultivated in Langkawi Island, situated in the state of Kedah, Malaysia. Extraction of the heavy metals (Fe, Zn, Cu, Pb and Cd) from the rice grain, leaf, stem and root were carried out using the acid digestion method with NHO\textsubscript{3}:HClO\textsubscript{4} (25:10 ml). The bioavailable heavy metals in the paddy soils were extracted using NH\textsubscript{4}CH\textsubscript{3}OO (pH 7) before their content was determined by atomic absorption spectrometry (AAS). The results showed that the accumulation of heavy metals in both varieties (MRQ 74 and MR 219) were similar. Among the metals studied, Fe and Mn concentrations were the highest in the paddy plants especially in the root and leaf respectively. The bioavailable Mn was also high in the paddy soils, and this amount corresponded to that of the plant uptake. On the other hand, although the bioavailable Fe was low in the soils, its accumulation in paddy plant parts was high. This might be attributed to the ability of the roots of the paddy plant to reduce Fe\textsuperscript{3+} ions from iron oxide and oxyhydroxide in soils to Fe\textsuperscript{2+} ions, that were absorbed by the plants. The low concentration of bioavailable Zn, Cu, Pb and Cd in the paddy soils were reflected in the low accumulation of those metals in the paddy plant parts.

Key words: Paddy plants, soils, heavy metals

INTRODUCTION

Paddy is one of the most important crops in Malaysia after oil palm. Previously paddy was planted once a year under rainfed conditions along the flood plains of rivers. After the use of irrigation was introduced by Prof. van de Goor and Mr. G. Zijlstra (F.A.O. Report 1617) (Anon, 2007), the ‘double cropping system’ was introduced to Malaysia, hence new areas for rice planting were opened to meet the local demand. In the year 2011 paddy planting areas in Malaysia totalled 683,677 ha of which 515,555 ha were in Peninsular Malaysia with 42,526 ha and 123,596 ha in Sabah and Sarawak, respectively (Anon, 2011). In 2011, Malaysia produced approximately 2,665,098 tonnes comprising 2,311,978, 145,194 and 207,925 tonnes from peninsular Malaysia, Sabah and Sarawak respectively (Anon, 2011).

The production of rice in Malaysia is still insufficient to meet local demand and various steps are being taken by the Malaysian government to increase productivity besides exploring new areas for paddy cultivation. MARDI (Malaysian Agricultural Research and Development Institute) a government agency, is mainly involved in crop development and through their research and trials have managed to produce over the years, several new paddy varieties including MR 73, MR 74, MR 219 and MR 220 (MARDI, 2001). However, the most popular varieties currently grown throughout Malaysia are MR 219 and MR220 (Anon, 2011). Many types of fertilizers and pesticides have been used in order to increase yields and reduce crop loss to pests and diseases.

A few years ago, rock phosphate was widely used in Malaysian paddy fields but recently it has been replaced with urea and compound fertilizers (N:P:K) of various formulations (Habibah et al., 2011). According to Ramachandran et al. (1998), rock phosphate is one of the materials used for manufacturing phosphatic fertilizers that contain trace amounts of Zn, Cd and other elements that originate in the phosphate rock (Adriano, 1986). Past research has indicated that the fertilizers and pesticides applied on crops were potential sources of heavy metal contamination to the plant. Heavy metal pollution not only results in adverse effects on various parameters relating to plant growth and yield, but also causes changes in the size, composition and activity of the microbial community within the particular area (Giller et al., 1998).

Different plant varieties normally behave differently with regard to their characteristics and responses to environmental factors. As several paddy varieties are grown in Malaysia, it is useful to study the effects of heavy metals on the different varieties in order to determine the most suitable variety for specific locations throughout the country. The aim of the present study was to determine the heavy metal content in the plant parts of two paddy varieties (MRQ 74 and MR 219) grown at selected areas in Langkawi, Kedah.
MATERIALS AND METHODS

Sampling site:
The study was carried out at Kampung Sungai Kedak, Mukim Mat Sirat, Langkawi Island, Kedah. Four paddy planting areas where the two paddy varieties namely MRQ 74 and MR 219, were grown, were selected randomly. At each area, four plots (1,000 m² each) were randomly selected for sampling activities. Soil samples were taken from 0 to 30 cm depth with a soil hand auger. Several paddy plants were uprooted with the soil from each plot and stored in clean plastic bags. In the laboratory, the soil samples were dried at room temperature before being ground and passed through a 250 µm sieve, prior to analysis. The paddy plants were washed with running tap water followed by two rinses with distilled water and one rinse with deionized distilled water. Subsequently the samples were dried with clean tissue, cut and separated into leaf, stem, root and grain, and oven-dried until constant weight was achieved (AOAC, 1984). The heavy metals in the paddy plant parts were extracted using the acid digestion method (AOAC, 1984) with NHO₃: HClO₄ (25: 10 ml).
The heavy metals in the soil were extracted using ammonium acetate (pH 7) (Badri, 1984). Ten grams of soil were weighed into a Kartell bottle, then 50 ml of 1.0 m NH₄CH₃OO (pH 7) were added and the mixture, shaken for 1½ hr, followed by centrifuging at 3000 rpm for 30 minutes. The samples were then filtered using 0.45 µm milipore filter paper. The heavy metals (Pb, Cd, Cu, Zn, Fe and Mn) studied were determined by atomic absorption spectrophotometry, (AAS) (Perkin Elmer Model 3300). Other parameters studied were percentage organic carbon (Walkey and Black, 1934), soil pH (Dudridge and Wainright, 1981) and grain size of <0.63 µm (Badri, 1984).

RESULTS AND DISCUSSION

Heavy Metals In The Paddy Plant:
The concentration and type of heavy metals found in the various parts of the paddy plants are listed in Table 1. The results showed that Fe and Mn were detected in the highest concentrations for both the varieties of paddy studied except at stations 1 and 4, where Fe was not detected in the root whilst Mn was mostly found in the leaf.
The Duncan analysis indicated that the Cu concentration was highest in the leaf but Zn was highest in the roots of the studied paddy plants. The concentration of Pb in the whole paddy plant for both varieties was quite low in the samples from all the stations except for station 2, where a higher level was found in the roots (Table 1).
The Cd content was significantly the highest in the rice grains for both the studied varieties but its concentration in the rice grain and other parts of the paddy plant was much lower than that reported for the paddy plants, from Kota Marudu, Sabah (Yap et al., 2009). However the paddy plants from Kota Marudu, showed no significant difference (p<0.05) for Cd content in the various parts of the paddy plant. This could suggest that the fertilizers and pesticides applied in Langkawi did not cause an increase in the Cd content of the paddy plant. The maximum level of Cd detected in the rice grain (in the above study) was also below the permissible level as stipulated in Cordex Allimatarious (which is 0.4 mg/kg) and the Malaysian Food Act 1983 and Food regulations 1985 (which is 1 mg/kg).
In general Fe, Pb and Zn were found to be in the highest concentration in the root of the paddy plant but Cu and Mn were highest in the leaf and stem. Accumulation of Fe was found to be the highest in the root at the stations where the soil pH>5.0 (such as at the station two and three which had soil pH of 5.0 and 5.45 respectively), (Table 3). According to Kilcoyne et al. (2000) Fe will precipitate at the root surface of the paddy plant when soil pH >5.5 but in the present study, accumulation started to take place for soil of pH >5.0. This could be due to the clayey soil type at Langkawi.
According to Hopkins (1999) metals such as Fe, Mn, Cu and Zn are found in plants because they are nutrients which are required for photosynthesis and various metabolic processes in the plant (Hopkins, 1999). Pb and Cd are toxic metals that can accumulate in various parts of the plant without any particular function (Kabat-Pendas and Pendas, 1984). In the present study, the Pb content was found to be quite high in the paddy plants and the source of the Pb could have arisen from the emission from motor vehicles as Langkawi Island is a small but popular tourist destination.

Heavy Metals In The Paddy Soil:
The average concentration of bioavailable heavy metals in the paddy soils of the study area are shown in Table 2. Among the heavy metals studied, the concentration of easily leachable and exchangeable Mn was very high compared to that of Fe, Zn, Cu, Pb and Cd. However, its concentration was not significantly different among the soils of the different stations. Even though higher organic carbon content was detected in the MRQ 74 cultivated area, it did not affect the concentration of bioavailable heavy metals in those soils. Kampung Sg. Kedak at the Padang Masirat vicinity, was located on raised beach deposits and on part of the Sungai Melaka drainage basin. The area constituted loose and semi-consolidated alluvial mud, sand and gravel of marine and
fluviate origin as well as hill-wash deposits (Bosch, 1988; Director Geological Survey, 1966). The paddy soils in the study area were dominated by fine-grained sediments, in which the clay and silt percentages comprised more than 90% of the total content (Table 3). The soils were acidic (pH 4.84-5.45) and slightly high in organic matter content (5.91-11.26%).

In the study, the bioavailable manganese content was the highest among the heavy metals found in the paddy soils (30.94-40.95 mg/kg), followed by Fe, Zn, Cu, Pb and Cd. The concentration of bioavailable Mn was comparable to that of paddy soils in Kota Marudu (Yap et al., 2009). The high amount of this metal in paddy soils of the study area suggests extensive application of Mn-containing fertilizers and pesticides throughout the paddy cultivation activities. Habibah et al. (2011) reported that the N:P:K 13:13:17 and 12:12:17 contained certain amount of Mn. Continuous application of these fertilizers rendered the increase of Mn in the soils. Mn found in the bioavailable form in high concentration in the soils, corresponded to its high accumulation in the paddy plants in those soils.

The bioavailability of other heavy metals in the paddy soils was low. According to a previous report (Habibah et al., 2011), Fe in paddy soils tended to accumulate in the resistant forms. Mottles of iron oxide and oxyhydroxide were frequently found in paddy soils due to alternate flooding and merging throughout the paddy

### Table 1: Concentration of heavy metals (mg/kg) in paddy plants from Langkawi, Kedah

<table>
<thead>
<tr>
<th>Paddy plant parts/var</th>
<th>St. one / MRQ 74</th>
<th>St. two / MRQ 74</th>
<th>St. three / MR 219</th>
<th>St. four / MR 219</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Leaf</td>
<td>0.021±0.004a</td>
<td>0.024±0.006b</td>
<td>0.031±0.013a</td>
<td>0.039±0.014a</td>
</tr>
<tr>
<td>Rice Stem</td>
<td>0.010±0.005c</td>
<td>0.014±0.006b</td>
<td>0.016±0.004b</td>
<td>0.008±0.007b</td>
</tr>
<tr>
<td>Rice Root</td>
<td>0.0016±0.004b</td>
<td>0.0014±0.005b</td>
<td>0.0019±0.006b</td>
<td>0.0018±0.008b</td>
</tr>
</tbody>
</table>

### Table 2: Average concentration of available heavy metals in paddy soils of Langkawi (mg/kg)

<table>
<thead>
<tr>
<th>Station/Var</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST. ONE MRQ 74</td>
<td>0.009±0.020a</td>
<td>0.302±0.260a</td>
<td>0.199±0.133a</td>
<td>0.233±0.386a</td>
<td>0.387±0.110a</td>
<td>40.952±38.233a</td>
</tr>
<tr>
<td>ST. TWO MRQ 74</td>
<td>0.010±0.020a</td>
<td>0.281±0.323a</td>
<td>0.136±0.108a</td>
<td>0.469±0.419a</td>
<td>0.961±0.907a</td>
<td>28.915±20.251a</td>
</tr>
<tr>
<td>ST. THREE MR 219</td>
<td>0.025±0.035a</td>
<td>0.425±0.357a</td>
<td>0.183±0.143a</td>
<td>0.302±0.243</td>
<td>0.075±0.035a</td>
<td>30.943±24.020a</td>
</tr>
<tr>
<td>ST. FOUR MR 219</td>
<td>4.85±0.17b</td>
<td>7.08±1.49a</td>
<td>11.29±1.04a</td>
<td>9.20±8.08a</td>
<td>94.75±3.20a</td>
<td>94.20±3.85a</td>
</tr>
</tbody>
</table>

### Table 3: Average soil parameters at Langkawi

<table>
<thead>
<tr>
<th>Station/Var</th>
<th>pH</th>
<th>% organic matter</th>
<th>% grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST. ONE MRQ 74</td>
<td>4.84±0.41b</td>
<td>7.08±1.49a</td>
<td>94.20±3.85a</td>
</tr>
<tr>
<td>ST. TWO MRQ 74</td>
<td>5.00±0.34b</td>
<td>11.29±1.04a</td>
<td>92.20±8.08a</td>
</tr>
<tr>
<td>ST. THREE MR 219</td>
<td>5.45±0.77a</td>
<td>6.53±2.44a</td>
<td>92.75±4.70a</td>
</tr>
<tr>
<td>ST. FOUR MR 219</td>
<td>4.85±0.17b</td>
<td>5.91±1.40a</td>
<td>94.75±3.20a</td>
</tr>
</tbody>
</table>
cultivation activities. It was observed that such conditions prevailed in the study area. However, even though the bioavailable Fe was very low in the soils, this metal was found in relative high concentration in the paddy plants. According to Kabata-Pendias and Pendias (1984), Fe uptake by plants was metabolically controlled, and it could be absorbed as Fe$^{3+}$, Fe$^{2+}$, or as Fe chelates. The capability of plant roots to reduce Fe$^{3+}$ to Fe$^{2+}$ ions is believed to have contributed to the absorption of Fe in most plants. In the study, it was suggested that the paddy roots were capable of reducing the Fe$^{3+}$ ions from the iron precipitates and mottles in paddy soils to Fe$^{2+}$ ions which were subsequently absorbed. Apart from Fe, the low amount of bioavailable Zn, Cu, Pb and Cd indicated the naturally low amount of these metals in the Quaternary alluvial deposits from which the paddy soils were derived, and the low amount of anthropogenic inputs into the paddy soils of the study area. Possibly the low bioavailable Zn, Cu, Pb and Cd in the alluvial soils contributed to the low concentration of these metals in the paddy plant parts.

**Conclusion:**
Both the studied paddy varieties (MRQ 74 and MR 219) showed a similar pattern in the accumulation of heavy metals. Fe and Mn were detected in the highest concentration in the paddy plants especially in the root and leaf parts respectively. The rest of the metals were found to be generally low in concentration with Zn and Pb being present mainly in the root, Cu in the leaf and Cd in the rice grains. Nevertheless the Cd content in the rice grain was low and below the permissible level as stipulated in the Malaysian Food Act 1983, Food Regulations 1985 and Codex Alimentarius Commission. High concentration of Mn, mainly in the bioavailable form was found in the soils, and these levels were directly related to the high accumulation in the paddy plants. Even though the bioavailable Fe was very low in the soils, the concentration of this metal in the paddy plant was relatively high. It is suggested that biomagnification took place in the paddy plants with respect to iron. For the rest of the heavy metals studied, the low concentration of bioavailable Zn, Cu, Pb and Cd in the soils accounted for the low content of these metals in the paddy plant parts.

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