Comparison of the Level of Organochlorine Residues in Paddy Crops from Two Different Cultivation Practices
(Perbandingan Aras Sisa Organoklorin dalam Tanaman Padi daripada Dua Penanaman Berbeza)

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ABSTRACT
This study was conducted to investigate pesticide residues in paddy crops derived from two different types of cultivation, namely the cultural plot managed by the Malaysian Agriculture Research and Development Institute (MARDI) and the second from the farmers’ rice fields which did not follow schedules suggested by MARDI. Sample collection was carried out at post harvest. To determine the concentration of organochlorine pesticides, a gas chromatograph equipped with an electron capture detector (GC-ECD) was used. The range of pesticide residues in the leaf samples was from N/D to 579.60 ppb, in stem samples from N/D to 368.93 ppb and in the rice grain from N/D to 22.37 ppb. Some of the rice samples had levels that exceeded the standard MRL (as stipulated by WHO).

Keywords: Paddy crop; pesticide residue; organochlorine

INTRODUCTION
Rice or *Oryza sativa* L. is the most important staple food for a large part of the world’s human population. To protect the paddy plants from algae, weeds, insects and diseases, pesticides such as herbicides, insecticides and fungicides are used. Even when pesticides are used correctly, the residues tend to remain in the paddy plants (Stepan et al. 2005).

Today, there are more than 500 compounds that have been registered as pesticides or their metabolites worldwide (Rene & Piet 1999). Pesticides are mainly used to eliminate or control pests (Margni et al. 2002; Waxman 1998). They are classified according to the functional group in their molecular structures (i.e. inorganic, organonitrogen, organohalogen or organosulphur) or their biological activity towards target species (i.e. insecticide, herbicide and fungicide) (Ahmed 2001). Pesticide products normally contain one or more active compounds formulated with other compounds (Margni et al. 2002). The three main groups of pesticides are insecticides, herbicides and fungicides. There are also rodenticides, nematicides and molluscides (Waxman 1998). Herbicides are the most commonly used pesticide, followed by insecticides and fungicides (Ahmed 2001).

Pesticide usage in agriculture increased dramatically after the Second World War (WWII) contributing to increased food production (Ahmed 2001). The use of pesticides is crucial to fulfilling the world’s food demand since there are no better alternatives (Goncalves & Alpendurada 2005). According to Pimentel and Livitan (1986), 455×10^6 kg of pesticides are used annually in the USA which made up of 60% herbicides, 24% insecticides and 16% fungicides. More than 90% of the pesticides used in cotton, coffee, corn and paddy crops are insecticides, herbicides and fungicides (Kishimba et al. 2004). The total pesticide usage in the world was more than 5.0 billion metric tons in 1999 and 2000 (USEPA 2007). Malaysia uses more than 200000 tons of pesticide products annually, comprising more than 50000 tons of active compounds (FAO 2005).

According to Rahman et al. (1995), chemical residues can be traced in agricultural products due to pesticides usage in cultivation process. Studies carried out by Ahmad et al. (2008) on husk and unhusk rice found that the level of pesticides residue in both rice exceeded the maximum level permitted by WHO but no poisoning cases from the pesticides were reported.
The objective of the current study was to compare the levels of organochlorine pesticides (OCPs) in the leaves, stems and rice grains of the paddy plants that were produced by two different cultivation practices; the first plot managed by the Malaysian Agriculture Research and Development Institute (MARDI) and the second managed by farmers who did not follow the schedule practiced by MARDI. Solvent extraction (SE) method was chosen to extract the pesticides from the samples. The results will also depict whether organochlorine pesticides which have been applied in the paddy fields for decades, are still persistent in the environment.

MATERIALS AND METHODS

SAMPLES

Paddy plants cultivated by MARDI and farmers (who did not follow schedule practiced by MARDI) were harvested from paddy fields in Tanjung Karang, Selangor, Malaysia. The rice fields managed by farmers did not follow the scheduled dates for flooding, planting and harvesting as prepared by the authority. For samples depicting the outcome of research cultivation, the plants were collected from fields managed by the Malaysian Agriculture Research and Development Institute (MARDI) whilst for samples from the farmers’ own cultivation practices, the plants were collected from the village farmers’ paddy fields. All the samples were collected from three different sites; water inlet, mid-field and water outlet areas of the paddy fields. The plants were then separated into three categories; leaves, stems and rice grains.

STANDARDS AND REAGENTS

The standard stock solutions of OCPs were purchased from the Laboratories of Dr. Ehrenstorfer-Schafers in Germany. The Ethyl acetate, toluene and hexane used were of GC grade and were purchased from Merck. The standard solutions were prepared from dilutions of the respective standard stock solutions to concentrations of 1.0, 0.5, 0.1 and 0.05 μg/mL with toluene/hexane (1:1).

APPARATUS

A gas chromatograph (Agilent 4890) equipped with an electron capture detector (ECD) was used. The chromatographic column employed for the analysis was DB-5 (Crosslinked 5% Phenyl Methyl Siloxane), 30.0 m × 0.25 mm with 0.25 μm film thickness. The Envi-Florisil cartridges (1 g) for SPE were purchased from Supelco, USA. An ultrasonic water bath (with a generator output capacity of 500 W and frequency 59 kHz) was used.

SAMPLE PREPARATION

The methods used were adaptations of previous methods used (Lambropoulou & Albanis 2007; Mitsou et al. 2006). For the paddy plant and rice, the SE method was used. Samples include those that were spiked (2.0 g for leaves and stems, 1.0 g for rice) were each weighed and put into Erlenmayer flasks, followed by the addition of ethyl acetate solvent (50 mL for leaves and stems and 10 mL for rice). The mixtures were then shaken for 2 h before sonication for 20 min. Each sample extract was filtered into an Erlenmeyer flask containing sodium sulfate (Na₂SO₄) for absorption of water in the sample and then left for ½ hour. Then 5 mL of the extract was cleaned-up using the SPE Envi-Florisil cartridge and dried before 1 mL of hexane was added. At least three replicates were done for each sample. All the samples were then analysed by the GC-ECD.

GC ANALYSIS

Sample (1 μL) was injected in a splitless mode. The column used was DB-5. The oven temperature was increased from 100°C (held 3 min) to 190°C (held 3 min) at the rate of 30°C/min. The temperature was then increased to 270°C at the rate of 3°C/min and held for 3 min. Nitrogen of high purity was used as the carrier gas, at the flow rate of 1 mL/min and as the make-up gas at the flow rate of 50 mL/min.

RESULTS AND DISCUSSION

The results showed that there were different types of pesticides isolated from the samples collected from the MARDI managed rice fields and also that of the farmers’ own practice fields. For the farmers’ own practice plots, α-endosulfan, β-endosulfan and endosulfan-sulfate were isolated whilst for the MARDI plots, heptachlor and aldrin were isolated (due to the different situations in the paddy fields in terms of type of weeds and pests and types of pesticides used).

However, the residue level of pesticides in the farmers’ own practice areas was in the range of N/D – 579.60±8.92 ppb compared with that in the MARDI managed areas which had a range of N/D – 10.40±0.15 ppb. This showed that the village farmers use higher amounts of pesticides compared with MARDI, where following proper procedures was practiced.

| TABLE 1. Pesticide residues in paddy plants where MARDI cultivation is practised |
| LEAVES | STEMS | RICE |
| INLET | MID | OUTLET | INLET | MID | OUTLET | INLET | MID | OUTLET |
| Heptachlor | ND | ND | 5.28±0.30 | ND | ND | ND | ND | ND | ND |
| Aldrin | 9.65±0.20 | ND | 10.40±0.15 | ND | ND | 7.86±0.05 | ND | ND | ND |

ND = Not detected
The level of pesticides in the leaves (15.02±0.45 – 579.60±8.92 ppb for farmers’ own practice plots, compared with N/D – 10.40±0.15 ppb for MARDI plots) was higher than the level found in the stems (7.13±0.20 – 368.93±7.83 ppb for farmers’ own practice plots, N/D – 7.86±0.05 ppb for MARDI plots). The higher level in the leaves was because the pesticides were sprayed directly onto the paddy plants, whereby the leaves which have a greater surface contact area absorbed more compared with the stem surfaces which are covered by the leaves. Thus the leaves can directly absorb the sprayed pesticides, whilst the stems absorbed the remaining sprayed pesticides which entered the water and soil of the paddy fields. Furthermore, the stems contained more water than the other parts of the paddy plant, thereby diluting the absorbed pesticides.

With regard to the rice grains, only rice samples from the farmers’ own practice fields had endosulfan-sulfate residues whereas the samples from the MARDI plots, were pesticide free. The range of endosulfan-sulfate in the samples from the farmers’ own practice rice was N/D – 22.37±1.79 ppb. This level exceeds the permissible limit stipulated in the Malaysian Food Act 1983 & Food Regulations 1985 (2008) and the WHO (1990) standard (which stipulated not more than 0.01 mg/kg). However, no health problems have been reported on the consumption of the rice since the paddy grains during milling are mixed with grains from the entire paddy area and the concentration of the pesticide was reduced to below the permissible limit.

Water flow in the paddy field also affected the concentration of the pesticides. The concentration of pesticides in paddy plants at the water inlet area for both the MARDI and farmers’ own practice areas were the lowest compared to that in mid-field and outlet areas. This is because the clean water from the inlet areas diluted the pesticide residues in the paddy plants. Paddy plants at the water outlet area had the highest level of pesticides because all the pesticides in the water would have been carried from other areas in the paddy field into that area.

TABLE 2. Pesticide residues in paddy plants where farmer cultivation is practised

<table>
<thead>
<tr>
<th></th>
<th>LEAVES</th>
<th>STEMS</th>
<th>RICE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INLET</td>
<td>MID</td>
<td>OUTLET</td>
</tr>
<tr>
<td>α-Endosulfan</td>
<td>39.66±0.44</td>
<td>15.02±0.45</td>
<td>55.73±0.29</td>
</tr>
<tr>
<td>β-Endosulfan</td>
<td>272.07±28.35</td>
<td>181.53±8.27</td>
<td>404.68±24.72</td>
</tr>
<tr>
<td>Endosulfan-sulfate</td>
<td>344.33±9.65</td>
<td>579.60±8.92</td>
<td>547.67±7.43</td>
</tr>
</tbody>
</table>

CONCLUSION

From the study conducted, it can be concluded that by practicing MARDI’s techniques, less pesticides are used compared with the farmers’ own practice methods because of good management and correct usage of pesticides. The leaves of the paddy plants absorb more pesticides compared to the stems. Even though there were pesticide residues present in rice cultivated by the farmers’ own practice methods, the levels were still within the permissible limits, but they need to be monitored to ensure its safety to consumers. Paddy plants at the water inlet area had the lowest pesticide residue compared with plants at other areas of the paddy field.

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REFERENCES


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