Original Research Paper

Open Access

Assessment of Multiresidue Pesticides in Agricultural Soils from Ledang, Malaysia and Related Potential Health Risks

Khitam Jaber Nabhan*(**), Wan Mohd Afiq Wan Mohd Khalik*(***), Md Pauzi Abdullah*†, Mohamed Rozali Othman*, Anizan Isahak** and Siti Aminah Zulkepli***

*School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia
**Department of Chemistry, College of Science, Al-Mustansiriya University, 10052 Baghdad, Iraq
***School of Marine and Environmental Sciences, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Malaysia
****School of Environmental Science and Natural Resources, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia
†Corresponding author: Md Pauzi Abdullah

ABSTRACT

The concentration levels of organochlorine and organophosphorus pesticide residues in agriculture soils from paddy field were successfully investigated. Residues were isolated using the Soxhlet extraction method, following a clean-up process (SPE Florosil) and a final determination of targeted compounds performed by using a gas chromatography electron capture detector. The concentration levels ranged from 0.98 to 3.60 µg/kg of dry weight during the period of study. Only five compounds were found less frequent <50% out of 56 soil samples. The physical properties of soil samples were identified as acidic (pH 4.8 to 5.4), organic content (6.4 to 7.8%) and the particle size was dominated by the sandy fraction type. Hierarchical agglomerative cluster analysis was used to discriminate eight stations into two groups (C1: 1-4 and C2: 5-8) at $D_{link}/D_{max} \times 100 < 83$. Three components (PC1- PC3) explained about 89.30% of the total variance in the data sets from an eigen value of >1. The occurrences of HCH isomers, DDE, heptachlor epoxide and endosulfan compounds were recognized as the main contributors of pollutant in this area. Hazard quotient for adults and children health risks were calculated in the range of 8.57×10^{-9} - 5.23×10^{-5} and 4.44×10^{-8} - 2.71×10^{-4}, respectively. It was reflected that the present status is below than the acceptable risk level, HQ ≤ 1. Incremental lifetime cancer risk (ILCR) was recorded slightly higher for children ranging from 1.73×10^{-8} to 4.22×10^{-11} compared to the risk toward adults from 3.34×10^{-9} to 8.15×10^{-12}. It would be interesting to observe the details of the depth profile analysis to understand the mobility of pesticide residues for future study.

INTRODUCTION

The adoption of pesticides in the Malaysian agricultural environment is not a new subject and their usage has been well documented in the past decade. In fact, the Malaysian government has taken a proactive stance through banning several organochlorine pesticides including DDT, HCH isomer, or endosulfan which are known to cause harmful effects to human health. Nonetheless, the persistent characteristic of these pollutants has led to another environmental health concern, especially related to the fate of pollutant, and thus monitoring activities in many places have kept on going. After organochlorine usage was banned in most crop production, the alternative use of pesticide has led to a high demand of organophosphorus types (Kin et al. 2006, Kuet et al. 2008). Despite it being known as having less persistence compared to organochlorine, the threat-

ening effects on environmental risk and human health are still prevalent (Hui et al. 2010, Tahir et al. 2010, Shukor et al. 2015).

Chemical characteristics include hydrophobicity, retention capabilities and slow degradation process, making pesticides to have the tendency to accumulate in soils higher than other environmental compartments like water bodies, biota or food chains (Bhupander et al. 2011, Kumar et al. 2011, Pokethitiyook & Poolpak 2012). The health hazard varies depending on the magnitude, severity of exposure or inherent toxicity of chemicals (Hazarika 2011). The emergence of pesticide residues in agricultural soils has been extensively reported in literature. Despite the issue of pesticides being banned that is raised in many countries, they are continuously applied in agricultural activities due to their relatively low price and high effectiveness in control-

ling pests, weeds, and diseases in a short period (Moododi & Belagali 2008, Sanagi et al. 2011, Mohd Fuad et al. 2012).

For instance, agricultural soils taken from the vegetable planting area in Cameroon Highlands revealed that they had been affected by the presence of the DDT family, HCH isomers and endosulfan, varying at low levels of concentrations (Abdullah et al. 2015, Farina et al. 2016). For rice cultivation, the usage of pesticides to control pests which indirectly enhanced yield production is also not avoided. A study reported by Zakaria et al. (2003) indicated that aldrin, endrin, endosulfan and HCH isomers were insecticides found in the samples taken from paddy cultivation soils in Kedah. Meanwhile, a recent study reported by Kok (2014) revealed that γ-HCH, dieldrin and parathion were the most frequent pesticides detected in soil samples taken from Kuala Kedah, Kedah. Soils collected from the Manir paddy area, Terengganu also indicated the presence of DDT and HCH which have reached the maximum concentrations at 11.99 ng/g and 1.43 ng/g, respectively (Saad 2008).

The aims of this study are to assess the concentration level of multiresidue pesticides in agricultural soils from Ledang paddy fields, to identify the main contributor of pollutants and to evaluate the potential non-dietary health risks based on the present status.

MATERIALS AND METHODS

Study area: Ledang is situated in Tangkak, one of the districts in Johor state, Peninsular Malaysia. One of the tourist attractions in this area is the Gunung Ledang National Park. The paddy field cultivation area was chosen as the subject of the study and it is located in the Kesang area (Fig. 1). The main river flows in this area is the Kesang River. Eight stations selected in this study were marked using the GPS Explorist 300. The stations were labelled as follows: S1 (2°8'39.101" N, 102°32'31.145" E), S2 (2°8'43.544" N, 102°32'29.878" E), S3 (2°8'39.479" N, 102°32'37.338" E), S4 (2°8'42.111" N, 102°32'42.810" E), S5 (2°8'40.023" N, 102°32'29.277" E), S6 (2°8'46.978" N, 102°32'27.063" E), S7 (2°8'34.857" N, 102°32'23.5638" E), and S8 (2°8'44.631" N, 102°32' 20.439" E).

Sample collection: Soil samples (in total fifty-six) were collected from 0-20 cm of the top surface of paddy fields at eight different locations. Sampling activities were performed monthly from October 2015 to March 2016. About 500 g of soil samples were taken using a pre-cleaned plastic shovel from each sampling site. The samples were then placed on wrapped baked aluminium foil, transferred into zip-lock polyethylene bag, and placed into an ice-filled cool box before being transferred to the laboratory for further analysis.

Chemical and Reagent: Seventeen reference pesticide standards, namely hexachlorocyclohexane isomers (α, β, γ, δ), aldrin, diazinon, malathion, chlorpyrifos, heptachlor, endosulfan, dichlorodiphenyl trichloroethane family (4,4'-DDT, 4,4'-DDE,4-4'-DDD), dieldrin, endrine and endosulfan sulphate were purchased from Sigma-Aldrich (St. Louise USA) while heptachlor epoxide was purchased from Supelco (Bellefonte, USA). All organic solvents used for sample extraction and analysis (methanol, n-hexane, acetone and ethyl acetate) were HPLC grade purchased from Merck, (New Jersey, USA). Resprep Florisil cartridge (3 mL, 500 mg) was purchased from Restek (Bellefonte, USA). Deionized water (18 Ω) was obtained by using a Milli-Q EasyRodi system (Barnstead, USA).

Method of extraction and analysis: The soil samples were firstly divided into two portions. One portion was used to measure the pH, organic carbon, moisture content and particle size. Meanwhile, the remaining portion was used to determine pesticide concentrations. For the particle size analysis, a series of laboratory mesh sieves ranging from 200-2 μm were applied on 100 g of soil samples. The particle fraction was scaled based on guidelines set by the International Soil Science Scheme as follows: sand (< 200 μm) silt (< 20 μm) and clay (<2 μm), respectively (Khalik et al. 2013). Organic carbon in the soil samples was determined based on the Loss on Ignition (LOI) method. The sample was introduced to heat at a high temperature (600°C) until the weight constant was observed. The pH of soil samples was prepared using a 1:5 soil-water slurry before being measured using a pH meter.

For pesticide determination, the soil samples (25 g) were dried for 12 hours at 105°C. Then, the samples were sieved < 250 μm to discard large particles. Next, 15 g of air-dried ground homogenized soil sample was transferred to a round bottomed flask, mixed with 7 g of anhydrous sodium sulfate and followed by an additional 150 mL of n-hexane-acetone (ratio 1:1). After the extraction process was completed (within 3 hours), the extracted samples were concentrated to a final volume of 1 mL using an evaporator, Model BUCHI Rotavapor R-124. Later, the solution was loaded onto the Florisil column for the clean-up process. The sorbent was eluted with 10 mL of 1:1 (n-hexane-ethyl acetate). After that, the final solution was concentrated to 1 mL under a gentle stream of nitrogen gas. The extracted samples were transferred to 3 mL pre-cleaned vials and kept in a freezer until ready for analysis.

Quantitative and qualitative analyses for pesticide determination were carried out using a gas chromatography-electron capture detector (GC-ECD, Model Varian CP3800). The DB-5 capillary column dimension (30 m × 0.32 μm × 1.0 μm thickness) was used for chromatographic
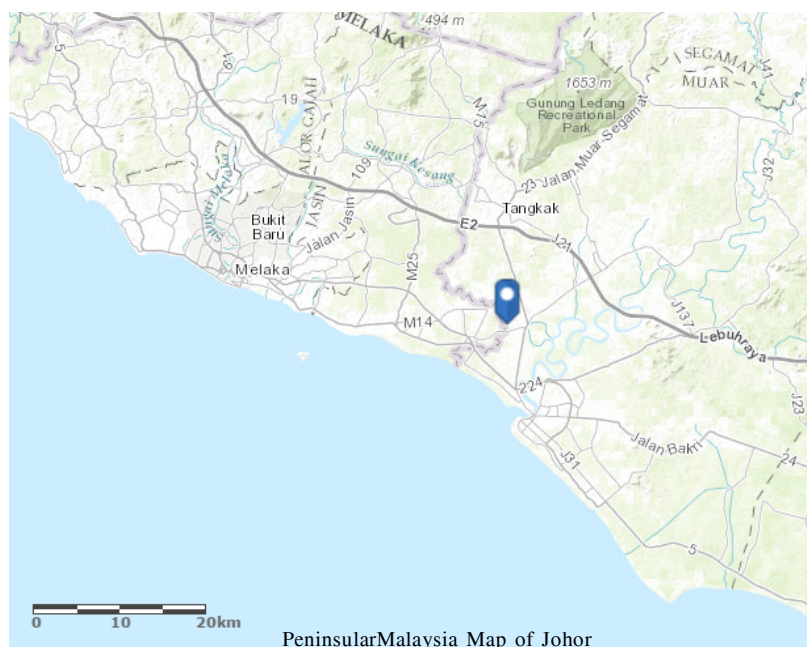
Fig. 1: Map of location study in Johor, Malaysia.

separation of the targeted pesticides. The oven program was setup as follows: Initial 90°C to 170°C (ramped with 3.5°C min⁻¹), then up to 280°C (ramped with 5°C min⁻¹). The volume of extract injected was 1 μL with a total runtime of 45.86 minutes. Injector and detector temperatures were maintained at 250°C and 300°C, respectively. Purified nitrogen gas was controlled at a flow rate of 1.5 mL min⁻¹. Identification of each compound was made by the standard solution retention time (t_R). Pesticide concentrations were expressed as mean values and on an air-dried weight basis.

Validation of extraction method: Method validation including linearity, recovery and detection limits were carried out in this study. It was a necessity to ensure that the method was working well and reliable. Validation work was performed prior to the analysis for every batch trip of the samples. Calibration plot was constructed in the range of 0.05-50 μg/L based on concentration of spiked standard solution. Recovery tests were studied by spiking two concentration levels of standard solutions. Detection limits were calculated based on the slope of the calibration curves method (Saadati et al. 2013).

Calibration plots were constructed for all compounds and the resulting correlation coefficients (r^2) for the calibration curves were > 0.992. The recoveries of pesticides from the spiked sample based on a triplicate analysis were calculated in the range of 75±3.38 - 116±2.85%. Detection limits were

accounted from 0.012 ng/kg (DDT-lowest) to 0.15 ng/kg (endosulfan-highest).

Data analysis: A Pearson correlation analysis was carried out to evaluate the correlation between the physico-chemical parameters of the soil or the concentration levels of multiresidue pesticides detected. Statistical significance tests were carried out at $p < 0.05$. Multivariate statistical analysis was applied for clustering, namely the hierarchical agglomerative cluster analysis (HACA), while principal components analysis (PCA) with factor analysis (FA) were used to identify the source of appointment. Factor loadings were scaled as follow: strong (VF>0.75), moderate (0.75<VF> 0.5) and weak (<0.50), corresponding to absolute varifactors (VF) value, respectively (Yerel & Ankara 2001, Khalik et al. 2015). All data interpretations were run using Minitab Version 17.

Health risk assessment: In this study, human health risk on non-dietary exposure was calculated in terms of the lifetime average daily dose (LADD), incremental lifetime cancer risk (ILCR) and non-cancer hazard quotients (HQs) for adults and children, respectively. The estimation of health risk was performed using the following equation 1-3:

$$\text{LADD (mgkg}^{-1}\text{day}^{-1}) = \frac{(Cs \times IR \times CF \times EF \times ED)}{(BW \times AT)} \quad ...(1)$$

$$ILCR = \frac{LADD}{CSF} \quad ...(2)$$

$$HQ = \frac{LADI}{RfD} \qquad ...(3)$$

Where Cs is the pollutant concentration in sample (mg kg^{-1}), IR refers to the ingestion rate (100 mg/day for adults and 200 mg/day for children), CF denotes the unit conversion factor, EF is exposure frequency (365 days/year), and ED is the lifetime exposure duration. In this case, adults (70 years) and children (12 years) were chosen. BW is the bodyweight (adults, 70 kg; children, 27 kg) and AT is the average time for carcinogens (EF × ED days). CSF and RfD are the oral cancer slope factor and reference dose for each compound, expressed in mg kg^{-1} day^{-1}. The slope factor and reference dose were used following the proposed guideline by USEPA (Kumar et al. 2014, Sruthi et al. 2017).

RESULTS AND DISCUSSION

Characterization of soil samples: Analysis of the soil samples indicated that the paddy fields in Ledang have acidic properties in the mean range from pH 4.8 to 5.4. Organic carbon content in soil varied from 6.4 to 7.8% for every 10 g weight of samples. The increase of organic matter content in soil can supply more carbon source to facilitate microbial degradation of organochlorine pesticides, thus the content of organic carbon could reflect the impact of pesticide retaining in soil environments (Devi et al. 2013). In this study, strong correlation was exhibited between organic content and DDT (r = 0.91), DDD (r = 0.85), dieldrin (r = 0.88), heptachlor epoxide (r = 0.85), chlorphyrifos (r = 0.87), and γ-HCH (r = 0.86). The particle size of soil samples recorded varied between 7.65-18.46% (sand), 0.20-1.40% (silt) and 1.20-10.45% (clay), respectively. Particle size distribution followed the trend: sand > clay > silt in all sampling stations and did not show any significant difference, p > 0.05. The moisture content was calculated within the range of 0.87-2.58%, and showed no significant difference for spatial variation. The clay fraction size correlated well with moisture content (r = 0.88), as it is known to have high water retention capacity compared to the sandy type.

Pesticide levels in soil samples: Table 1 presents the concentration levels of organochlorine and organophosphorus pesticides measured in the soil samples. The total concentration of pesticide residues only showed small variations in different locations of the sampling sites. It was recorded in the range of concentration from 0.98 to 3.60 µg/kg. Aldrin, endosulfan, endosulfan sulfate, dieldrin, DDD, DDE, HCH isomers, heptachlor and heptachlor epoxide were major pesticide residues detected in which the frequency detection was higher than 50% of the total samples. Among HCH isomers, α HCH and γ HCH were the most frequent in measuring soil samples with the mean concentrations during the

Table 1: The concentration levels of pesticide residues in soil samples.

	Range (µg/kg)	Mean ± SD (µg/kg)	FD (%)
α HCH	0.175-0.191	0.182±0.003	90
β HCH	0.038-0.209	0.167±0.005	70
γ HCH	0.169-0.203	0.183±0.008	90
δ HCH	0.050-0.207	0.177±0.002	30
Aldrin	0.009-0.169	0.119±0.001	50
Chlorphyrifos	0.020-0.101	0.069±0.003	40
DDT	0.006-0.119	0.058±0.001	40
DDD	0.017-0.509	0.212±0.015	50
DDE	0.037-0.291	0.240±0.003	90
Diazinon	0.054-0.095	0.069±0.002	30
Dieldrin	0.046-0.214	0.126±0.008	65
Endosulfan	0.070-0.352	0.178±0.007	60
Endosulfan Sulfate	0.005-0.139	0.106±0.006	60
Endrine	0.048-0.319	0.115±0.002	30
Heptachlor	0.051-0.231	0.182±0.005	55
Heptachlor Epoxide	0.060-0.293	0.199±0.070	75
Malathion	0.059-0.078	0.068±0.003	15

*FD = frequency of detection; SD = standard deviation

monitoring period of 0.182 ± 0.003 µg/kg and 0.183 ± 0.008 µg/kg, respectively. The levels of SHCH in the paddy soil were found to be in the range of 0.43-0.80 µg/kg. The isomeric ratio of HCH compounds calculated were higher than the parent compound, β-HCH >1 (2.7- 10.4) which reflected the fact that the occurrence of HCH isomer is linked to aged application. Concentrations of HCH isomer were found to be in the order of γ-HCH > α-HCH > δ-HCH > β-HCH.

The composition of HCH isomer is available in technical grade α-HCH (60-70%), β-HCH (5-12%), γ-HCH (10-15%) and δ-HCH (6-10%) (Fang et al. 2007, Jeyakumar et al. 2014) or lindane, 90% of γ-HCH. In fact, the ratio α to γ isomer range in this study was from 0.91 to 1.05, which was below the technical mixture. Devi et al. (2013) stated that if the ratio of α to γ exhibited to be larger than 1, this indicated the use of technical HCH. Contrarily, Willet et al. (1998) has proposed the lindane as the major source when the ratio is reducing close to 1 or even less. Thus, the main source of HCH in this area was reflected to the usage of lindane. The dominance in the usage of γ-HCH in Malaysian paddy cultivation had also been documented by Zakaria et al. (2003) in a previous study.

The concentration of the ΣDDT family ranged from 0.06 to 0.92 µg/kg. Among the DDT family, DDE was observed to be predominantly higher than other compounds. The distribution of DDT family is predominant in the following order: DDE > DDD > DDT. Maximum concentration of DDE was observed at station S1 with the value of 0.29 µg/kg. The ratio of (DDE+DDD)/ΣDDTs can be used as an indicative index to assess possible pollution sources. In this study, the

metabolite ratio analysis revealed that the total metabolite form (DDD + DDE) was higher than the parent compounds, DDT > 1 (7.85). Thus, the results can substantiate the claim that the cause of DDT is aged application. Furthermore, the ratio of DDT and DDE can be used to estimate whether recent inputs of technical DDT exist or vice versa. A ratio value of 0.33 or less is considered as aged mixture, while a relatively high DDT/DDE ratio implies a recent input (Bhupander et al. 2011). In this study, the ratio between DDT/DDE was recorded low at 0.02-0.16 for S5 till S8, while stations S1-S4 recorded higher in the range of 0.36 to 0.40. Thus, it may indicate that technical grade DDT is still being used in the conventional cultivation area, but not in the organic scheme.

Strong correlation was exhibited between DDT and DDD with $r^2 = 0.94$. It was a good indicator that DDD is a dechlorinated product of DDT compounds. Ratios of metabolite/parent compound were calculated to understand the degradation pathway of DDT in soils using the approach in a literature as suggested by Fang et al. (2007). In this study, the rank of degradation followed the order DDD+DDE/DDT > DDE/DDT > DDD/DDT, thus reflecting the main degradation pathway starting from DDT, DDD to DDE.

Endosulfan is one of the banned pesticides listed in Malaysia. The concentration level of this pollutant was recorded to be highest at 0.35 µg/kg in a soil sample taken from station S1. Despite the half-life of α-endosulfan (12- 39 days), it was known to be lesser than β-endosulfan and the isomeric ratio cannot be calculated since β-endosulfan was not measured during this study. Endosulfan sulphate is the metabolite of α-endosulfan and β-endosulfan. In this case, the frequency of detection for both endosulfan types was equivalent. The correlation status between both the compounds was weak with $r^2 = 0.36$, even though no significant difference was recorded between the sampling stations, p >0.05.
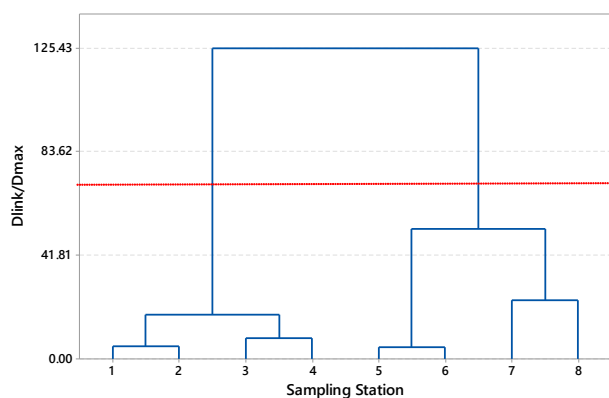
Heptachlor epoxide is a degradation product of heptachlor. It is adsorbed strongly in the soil and is very resistant to biodegradation process (Kim & Smith 2001). In this study, the frequency detection of heptachlor epoxide was higher than heptachlor with a pooled mean concentration of 0.19 µg/kg. Moderate correlation was exhibited between heptachlor and heptachlor epoxide with $r^2 = 0.72$, which is linked to the assumption that they came from same source and heptachlor epoxide as the major degradation product. Furthermore, the usage of heptachlor in rice cultivation activities was previously found in a study by Zakaria et al. (2003) with the mean concentration at 17.24 µg/kg from soil samples in Kedah, the northern side of Peninsular Malaysia.

The concentration levels of organophosphorus pesticides were found less compared to organochlorine pesticides. For instance, malathion was less frequent among pesticide residues found at only 15% in the soil samples. Maximum concentration was measured only at 0.078 µg/kg from station S7. Chlorpyrifos and diazinon were both detected in the soil samples with the mean concentration measured at 0.069 µg/kg. The concentration levels of ΣOPP were calculated, ranging from 0.14 µg/kg to 0.26 µg/kg during this study. The spatial pattern also showed no significant difference between organophosphorus pesticide residues, p > 0.05.

Multivariate statistical analysis: Cluster analysis was performed to elucidate the similarity of pesticide levels among the sampling stations. Cluster analysis is an unsupervised method used to classify variables or cases (observations/samples) based on homogeneity or heterogeneity levels (Zubir et al. 2016). The dendrogram of cluster analysis as rendered by the Ward's method is depicted in Fig. 2. In this study, eight stations were grouped into two clusters namely Cluster A and B at $D_{link}/D_{max} \times 100 < 83$. Cluster A consisted of stations 1, 2, 3 and 4, while the remaining stations were

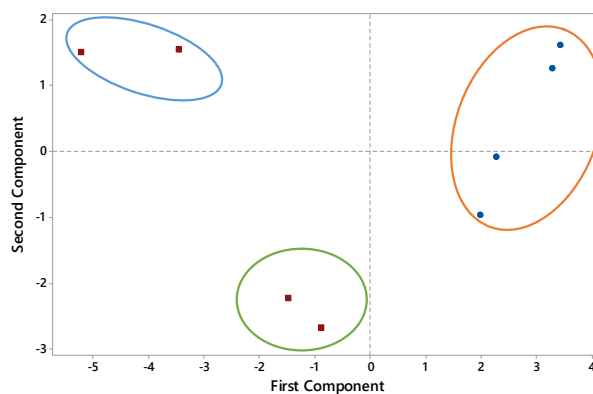Fig. 2: The dendrogram of cluster analysis.

Fig. 3: The loading plot of discriminant function for pollution sources (PC1×PC2).

Table 2: Risk assessment in soil for adults and children.

Compounds	Adult			Children		
	ILCR	LADD (mgkg^{-1}d^{-1})	HQ	ILCR	LADD (mgkg^{-1}d^{-1})	HQ
α HCH	3.56×10^{-11}	2.37×10^{-10}	7.90×10^{-7}	1.84×10^{-10}	1.23×10^{-09}	4.09×10^{-6}
β HCH	1.03×10^{-12}	2.07×10^{-10}	6.90×10^{-7}	5.39×10^{-10}	1.07×10^{-09}	3.58×10^{-6}
γ HCH	1.78×10^{-10}	2.65×10^{-10}	8.85×10^{-7}	9.23×10^{-10}	1.37×10^{-09}	4.59×10^{-6}
δ HCH	1.10×10^{-10}	1.80×10^{-10}	6.00×10^{-7}	5.72×10^{-10}	9.33×10^{-10}	3.11×10^{-6}
Aldrin	8.15×10^{-12}	9.00×10^{-11}	3.00×10^{-6}	4.22×10^{-11}	4.66×10^{-10}	1.55×10^{-5}
Chlorpyrifos	-	2.85×10^{-11}	9.52×10^{-8}	-	1.48×10^{-10}	4.93×10^{-7}
DDT	2.64×10^{-10}	6.85×10^{-11}	1.37×10^{-7}	1.37×10^{-09}	3.55×10^{-10}	7.11×10^{-7}
DDD	3.34×10^{-09}	6.74×10^{-10}	1.34×10^{-6}	1.73×10^{-08}	3.49×10^{-09}	6.99×10^{-6}
DDE	9.87×10^{-10}	2.75×10^{-10}	5.51×10^{-7}	5.11×10^{-09}	1.43×10^{-09}	2.85×10^{-6}
Diazinon	-	2.14×10^{-11}	8.57×10^{-9}	-	1.11×10^{-10}	4.44×10^{-8}
Dieldrin	1.34×10^{-11}	3.14×10^{-10}	6.28×10^{-6}	6.99×10^{-11}	1.63×10^{-09}	3.25×10^{-5}
Endosulfan	-	3.95×10^{-10}	6.59×10^{-8}	-	2.05×10^{-09}	3.42×10^{-7}
Endo. Sulfate	-	1.67×10^{-10}	2.78×10^{-8}	-	8.66×10^{-10}	1.44×10^{-7}
Endrine	-	4.42×10^{-10}	1.47×10^{-6}	-	2.29×10^{-09}	7.65×10^{-6}
Heptachlor	4.00×10^{-11}	2.25×10^{-10}	2.25×10^{-6}	2.07×10^{-10}	1.17×10^{-09}	1.17×10^{-5}
Hept. Epoxide	5.65×10^{-11}	6.80×10^{-10}	5.23×10^{-5}	2.93×10^{-10}	3.52×10^{-09}	2.71×10^{-4}
Malathion	-	4.14×10^{-11}	2.07×10^{-9}	-	2.14×10^{-10}	1.07×10^{-8}

Dash symbol means no cancer slope value was provided

categorized under Cluster B. The similarity or dissimilarity between the two clusters was linked to different agriculture practices. Stations in cluster B are in the locations where farmers used an organic scheme and no pesticide was introduced directly in the last five years. The concentration levels of pesticide residues detected in this area were also slightly lower, 0.005-0.29 µg/kg compared to Cluster A (0.048-0.50 µg/kg). It is worthy to mention here that the similarity of stations 5 and 6 was close or uniform to the distance linkage between stations 1-4, and this was probably associated to the facts that first, these stations were close to each other and second, these areas shared the same irrigation systems, thus leading to the mobilization of pesticide pollutants. Hence, it is not surprising to detect pesticides, even though the farmers try to implement the organic scheme of cultivation activities.

The scree plot was used to identify the number of principal components. In this study, it is shown that the pronounce changed after 3 eigenvalues (10.52, 3.10 and 1.54) and accounted for 89.30% of the total variance in data sets from the eigenvalue of > 1. Communalities were recorded, ranging from 0.79-0.98 which indicated that the data sets were reliable to perform the principal component analysis and factor analysis. The first component was represented by a positive loading of α-HCH (VF = 0.85) and endosulfan (VF = 0.93) with 32.40% of total variance. The second component was associated at 30.60% and linked to a strong loading by γ-HCH (VF = 0.86) and moderate contribution of heptachlor epoxide(VF = 0.75). The third component accounted for 29.80% of the total variance with

strong negative loading on β-HCH (VF = -0.90) and DDE (VF = -0.96) residues, respectively.

According to the PCA/FA loading results, it was presumed that pesticide pollution was mainly derived from agricultural activities that were dominated by the presence of HCH isomers, DDE, heptachlor epoxide and endosulfan compounds. It was directly conforming to the pattern of frequency detection in the data sets of the soil samples. The demand on pesticide usage was also clearly dominated by the organochlorine type. The distribution of main contributors of pesticides in the first two components (PC1 × PC2) had led to the formation of loading plot as illustrated in Fig. 3. It is clearly shown that the stations in cluster A (blue color) are located close to each other compared to the red color which represents the stations in cluster B. One-way ANOVA explicating the total concentration levels of pesticides was significantly different between the clusters, $p < 0.05$.

Health risk assessment: Health risk of pesticide residue in the human population was assessed mainly through the LADD, ILCR and HQ criteria. Risk assessment value was tabulated as given in Table 2. The estimated lifetime average daily dose of each pesticide was ranked as follows: endosulfan sulfate > δ-HCH > β-HCH > diazinon > heptachlor > α-HCH > γ-HCH > DDE > chlorphyrifos > dieldrin >endosulfan > malathion > endrine > DDD > heptachlor epoxide > DDT > aldrin. The permitted value of ILCR is between 10^{-6} and 10^{-4}, denoting less potential to cause cancer risks. The ILCR value of 10^{-6} or less is indicated as virtu-

ally safe and $>10^{-4}$ indicated a potential high health risk (Qu et al. 2005, Sruthi et al. 2017). The ILCR values for adults and children calculated during this study were ranked as follows: DDD > DDE > DDT > γ-HCH > δ-HCH > β-HCH > heptachlor epoxide > heptachlor > α-HCH > dieldrin > aldrin. The range was recorded to be slightly higher for exposure toward children from 1.73×10^{-8} to 4.22×10^{-11} compared to the risk toward adults from 3.34×10^{-9} to 8.15×10^{-12}.

The hazard quotients for adults and children exposure were calculated and the present status was in the range of 8.57×10^{-9}-5.23×10^{-5} to 4.44×10^{-8}-2.71×10^{-4}, respectively. Mean values were calculated at 3.34×10^{-6} and 1.74×10^{-5} for adults and children, respectively. The present data reflected that the contamination of soil quality is below than the acceptable risk level, HQ ≤ 1 (Kumar et al. 2014, Sruthi et al. 2017).

CONCLUSION

In the present study, the concentration levels, source apportionment in soil samples and the health risk towards human were successfully investigated. HCH isomers, DDE, heptachlor epoxide and endosulfan compounds were identified as the main contributors based on the outcome from the principal component and factor analysis. Cluster analysis was successfully applied to discriminate eight stations into two clusters based on the concentration levels of pesticides. The present data indicate that the studied soil quality will not generate the non-dietary health risk to human as HQ ≤ 1.

ACKNOWLEDGEMENT

REFERENCES

Abdullah, M.P., Saadati, N., Khalik, W.M.A.W.M. and Zakaria, Z. 2015. Pattern recognition of the presence and distribution of organochlorine pesticides in sediment of Cameron Highlands, Malaysia. Malaysian Journal of Analytical Sciences, 19(4): 692-706.

Bhupander, K., Richa, G., Gargi, G., Meenu, M., Kumar, S.S., Dev, P. Sanjer, K. and Sekhar, S.C. 2011. Residues of pesticides and herbicides in soils from agriculture areas of Delhi region, India. Journal of Environmental Earth Science, 1(2): 1-8.

Devi, N.L., Chakraborty, P., Shihua, Q. and Zhang, G. 2013. Selected organochlorine pesticides (OCPs) in surface soils from three major states from the northeastern part of India. Environmental Monitoring and Assessment, 185(8): 6667-6676.

Fang, W., Jiang, X., Bian, Y.R., Yao, F.X., Gao, H.J., Yu, G.F. and Schroll, R. 2007. Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China. Journal of Environmental Sciences, 19(5): 584-590.

Farina, Y., Abdullah, M.P., Bibi, N. and Khalik, W.M.A.W.M. 2016. Pesticides residues in agricultural soils and its health assessment for humans in Cameron Highlands, Malaysia. Malaysian Journal of Analytical Sciences, 20(6): 1346-1358.

Fuad, M.M., Junaidi, A.B., Habibah, A., Hamzah, J., Toriman, M.E., Lyndon, N. and Azima, A.M. 2012. The impact of pesticides on paddy farmers and ecosystem. Advances in Natural and Applied Sciences, 6(1): 65-70.

Hazarika, R. 2011. Effect of occupational exposure of pesticides on health of farmers of the agricultural fields of Sorbhug area of lower Assam. Nature Environment and Pollution Technology, 10(2): 237-241.

Hui, T.J., Ariffin, M.M. and Tahir, N.M. 2010. Adsorption of formulated chlorpyrifos on selected agricultural soils of Terengganu. Malaysian Journal of Analytical Sciences, 14(2): 76-81.

Jeyakumar, T., Kalaiarasi, I., Rajavel, A. and Anbu, M. 2014. Levels of organochlorine pesticide residues in water and sediment from selected agricultural sectors of Kanyakumari District, Tamil Nadu, India. International Journal of Environmental Research, 8(2): 493-500.

Khalik, W.W.M., Abdullah, M.P. and Al-Qaim, F.F. 2015. Chemometric application on surface river water quality: a case study of Linggi River, Malaysia. Iranica Journal of Energy & Environment, 6(3): 26-33.

Khalik, W.W.M., Abdullah, M.P. and Sani, N.A.A. 2013. Preliminary studies on sediment characteristics and metals contaminants of Temenggor Lake, Malaysia. Journal of Sustainability Science and Management, 8(1): 80-86.

Kim, J. H. and Smith, A. 2001. Distribution of organochlorine pesticides in soils from South Korea. Chemosphere, 43(2): 137-140.

Kin, C.M., Huat, T.G. and Kumari, A. 2005. Determination of active ingredients in pesticide formulations by gas chromatography with an electron capture detector. Malaysian Journal of Analytical Sciences, 9(3): 552-556.

Kok, W.L. 2014. Identification status of pesticide residues and their effects on soil physiochemical properties at paddy field in Kuala Kedah, Kedah. Thesis Bachelor Degree, Faculty of Earth Sciences, Universiti Malaysia Kelantan.

Kuet, A.C.L. and Seng, L. 2008. Comparative study on cleanup procedures for the determination of organophosphorus pesticides in vegetables. Malaysian Journal of Analytical Sciences, 12(1): 105-110.

Kumar, B., Kumar, S., Gaur, R., Goel, G., Mishra, M., Singh, S.K. and Sharma, C.S. 2011. Persistent organochlorine pesticides and polychlorinated biphenyls in intensive agricultural soils from North India. Soil Water Research, 6(4): 190-197.

Kumar, B., Verma, V.K., Mishra, M., Gaur, R., Kumar, S. and Sharma, C.S. 2014. DDT and HCH (organochlorine pesticides) in residential soils and health assessment for human populations in Korba, India. Human and Ecological Risk Assessment: An International Journal, 20(6): 1538-1549.

Moododi, M.N. and Belagali, S.L. 2008. Determination of pesticide residues in some agricultural water samples by gas chromatography. Nature Environment and Pollution Technology, 7(4): 593-596.

Pokethitiyook, P. and Poolpak, T. 2012. Heptachlor and its Metabolites: Accumulation and Degradation in Sediment. INTECH Open Access Publisher.

Qu, C., Qi, S., Yang, D., Huang, H., Zhang, J., Chen, W., Yohannes, H.K. Sandy, E.H., Yang, J. and Xing, X. 2015. Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: A case study from Ningde,

southeast China. Journal of Geochemical Exploration, 149: 43- 51.

Saad, A.M. 2008. The distribution of organochlorine pesticides in the Manir paddy agricultural area. 4th International Conference on Environmental, Cultural, Econominc and Social Sustainability, Universiti Malaysia Terengganu.

Saadati, N., Abdullah, M.P., Zakaria, Z., Sany, S.B.T., Rezayi, M. and Hassonizadeh, H. 2013. Limit of detection and limit of quantification development procedures for organochlorine pesticides analysis in water and sediment matrices. Chemistry Central Journal, 7(1): 63-73.

Sanagi, M.M., Mokhtar, S.U., Miskam, M.A. and Ibrahim, W.A.W. 2011. Determination of organophosphorus pesticides by dispersive liquid-liquid microextraction coupled with gas chromatography-electron capture detection. Malaysian Journal of Analytical Sciences, 15(2): 232-239.

Shukor, N.S.A., Khazaai, S.N.M., Hussain, Z.M. and Jan, S.L.M. 2015. Degradation behavior of chlorpyrifos in spinach (*Spinacia oleracea*) and soil. Malaysian Journal of Analytical Sciences, 19(4): 722-729.

Sruthi, S.N., Shyleshchandran, M.S., Mathew, S.P. and Ramasamy, E.V. 2017. Contamination from organochlorine pesticides (OCPs) in agricultural soils of Kuttanad agroecosystem in India and related potential health risk. Environmental Science and Pollution Research, 24(1): 969-978.

Tahir, N.M., Soon, K.H., Ariffin, M.M. and Suratman, S. 2010. Chlorpyrifos and malathion residues in soils of a Terengganu golf course: A case Study. Malaysian Journal of Analytical Sciences, 14(2): 82-87.

Willet, K.L., Ulrich, E.M. and Hites, H.A. 1998. Differential toxicity and environmental fates of HCH isomers. Environmental Science and Technology, 32(15): 2197-2207.

Yerel, S. and Ankara, H. 2011. Application of multivariate statistical techniques in the assessment of water quality in Sakarya River, Turkey. Journal of the Geological Society of India, 78(6): 1-5.

Zakaria, Z., Heng, L.Y., Abdullah, P., Osman, R. and Din, L. 2003. The environmental contamination by organochlorine insecticides of some agricultural areas in Malaysia. Malaysian Journal of Chemistry, 5(1): 78-85.

Zubir, M.R.M., Osman, R. and Saim, N. 2016. Chemometric analysis of selected organic contaminants in surface water of Langat River basin. Malaysian Journal of Analytical Sciences, 20(2): 278-287.