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Physicochemical Properties and Water Quality Parameter of Paddy Soil and Water and Their Relationship With Pesticides Concentration

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ABSTRACT

Introduction: Pesticides may influence the physicochemical properties of soil and the water quality parameters, which is vital in maintaining soil fertility and producing high quality crops. Objective: This study aims to determine the relationship between the concentration of pesticides, the physicochemical properties of the paddy soil samples and the water quality parameters of paddy water samples. **Methods:** A total of 72 soil and 72 water samples were collected in Tanjung Karang, Malaysia. The paddy soil and water were extracted using Quick, Easy, Cheap, Efficient, Rugged and Safe (QuEChERS) and solid phase extraction (SPE) techniques respectively. The concentrations of pesticides were analysed in ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). The relationship of the concentration of target pesticides and the paddy soil and water physicochemical properties were studied using Spearman correlation. **Results:** In paddy soil, the concentration of propiconazole shows moderate positive correlation with manganese (Mn) ($r = 0.587$) ($p \leq 0.01$). Meanwhile buprofezin-total organic carbon (TOC) ($r = -0.55$) ($p \leq 0.01$), imidacloprid-cation exchange capacity (CEC) ($r = -0.519$) ($p \leq 0.01$), pymetrozine-sodium (Na) ($r = -0.588$) ($p \leq 0.01$), and trifloxystrobin-calcium (Ca) ($r = 0.566$) ($p \leq 0.01$) showed moderate negative correlation. Whereas in water, trifloxystrobin showed significant positive correlation with turbidity ($r = 0.718$) ($p \leq 0.01$) and tebuconazole showed negative correlation to dissolved oxygen (DO) ($r = 0.634$) ($p \leq 0.01$). **Conclusion:** The presence of pesticides in paddy field may influence the soil and water quality, thus regular monitoring of pesticides usage and nutrient management in soil is deemed important.

Keywords: Pesticides, Soil, Physicochemical, Water quality, Malaysia

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INTRODUCTION

Agriculture sector is one of the most essential sector in Malaysia. It contributed 7.3% of the total Gross Domestic Products for the country in 2018. One of the most essential crops is paddy which is highly sowed in Peninsular and East Malaysia. According to the Ministry of Agriculture Malaysia, Its production has increased from 2.51×10^6 metric ton in 2010 to 2.64×10^6 metric ton in 2014 (1). It provides the staple food not only for Malaysia but also for the neighbouring countries including Thailand, Philippines, Cambodia, and Vietnam (2). The downside of the increasing crop production is the greater demand in agricultural productivity which is achieved through the use of pesticides. The demand of this agrochemicals makes up to approximately 9% of the global market share, it is the third most consumed agrochemicals globally (3).

Pesticides is a chemical or biological substance that are able to deactivate pests through series of chemical reactions. Their movement to water via some major route such as leaching through soil, surface runoff (4,5), aerial drift, dust, and transport of vapour (5). Pesticides persistence in water bodies is affected by its solubility in water. Pesticides with high water solubility are more potent to move from agricultural to surface water via runoff or irrigation. Nevertheless, in heavy rainfall seasons, pesticides that are strongly bound to soil particles can also escape into the surface water (6). In irrigated crop such as paddy, water quality-related problems are one of the major concerns. For examples, high level of salinity in the irrigated water can prevent the uptake of water by crops and consequently reducing the yield or yield quality (7). Some major chemical and organic processes in soil are influenced by the soil physicochemical properties. For instance, the structure of soil is associated with its soil aeration, perforation of soil and absorption of water (8). Subsequently affecting other chemical and biotic processes such as repository of organic matter and degradation of contaminants (9,10). Extensive use of pesticides especially when they are applied together, along with their persistency in the environment may exhibit potential risk to human and also the environment (11). Thus, it is very important to monitor the trace levels of pesticides in environmental samples mainly due to their extensive use in agriculture sector.

The aim of this study is to determine the physico-chemical of paddy soil samples and water quality parameters of paddy water samples and to determine the relationship of concentration of pesticides in paddy soil with the physico-chemical properties parameters of the paddy soil samples, and the relationship of concentration of pesticides in paddy water with the water quality parameters of paddy water samples.

MATERIALS AND METHODS

Reagents and chemicals

Reference standards of pretilachlor (98.7%), tebuconazole (99.3%) and internal standard imidacloprid-d4 (99.0%) were purchased from Sigma-Aldrich (MO, USA). Whilst imidacloprid (99.0%), fipronil (99%), tricyclazole (99.0%), pymetrozine (99.0%), buprofezin (99.0%), propiconazole (99%), chlorantraniliprole (99.0%), trifloxystrobin (99.0%) difenoconazole (98.7%), azoxystrobin (98.5%) isoprothiolane (97.8%) and ammonium formate 10M in H2O were purchased from Dr. Ehrenstorfer (Germany). Reagent grade acetone and dichloromethane (DCM), HPLC grade acetonitrile (MeCN), HPLC grade acetone, HPLC grade DCM, HPLC grade methanol (MeOH), HPLC grade toluene and HPLC grade hexane were supplied by Fisher Scientific (New Hampshire, USA). Whilst reagent grade dichlorodimethylsilane (DMDCS) (98%), MeOH and hydrochloric acid (HCl) 37% were bought from Merck (Darmstadt, Germany). Sodium acetate (NaAc) (99.0%), sodium thiosulphate (Na2S2O3) (99.0%), magnesium sulphate (MgSO4) (99.0%), acetic acid (HAc) (50.0%), and formic acid (98.0%), and were sourced by R&M Chemicals (Malaysia). QuEChERS Dispersive kit 15 mL with Association of Analytical Communities (AOAC) method was sourced by Agilent Technologies (CA, USA). Nylon membrane (0.22 µm and 0.45 µm) were obtained from Membrane Solutions (USA) and Glass fibre filter (GFF) was purchased from Sartorius (Germany). Oasis® (hydrophilic-lipophilic balance) HLB SPE cartridge 3 mL 60 mg and Oasis® HLB SPE cartridge 6 mL 200 mg were purchased from Waters (MA, USA). Solid phase extraction (SPE) 12-Position Vacuum, Manifold Set was obtained from Phenomenex (CA, USA). Ultrapure water was sourced by Milli-Q Advantage A10 (France).

Concentration of pesticides in paddy soil and water

Field sampling

A descriptive laboratory study was conducted by collecting 72 paddy soil and 72 paddy water samples using purposive and composite sampling technique in Kampung Sawah Sempadan, Selangor, Malaysia. According to Toriman et al. (2014), Kampung Sawah Sempadan covers more than 1400 lots which consists of 24 blocks (A-X). The samples were individually collected at five points on each paddy plot, and homogenized before they were divided into 3 replicates for each block. The samples were collected according to USEPA Method 1699 (12) in which paddy soil samples were retrieved between 15 cm to 20 cm depth using a stainless steel spade and stored in zip-lock plastic bags. Meanwhile, paddy water samples were obtained using plastic bucket and kept in amber glass Scott bottles (1 L) before adding 80 mg of sodium thiosulphate. The soil and water samples were kept in ice box upon transfer to Environmental Health Laboratory, Faculty of Medicine and Health Sciences, UPM. Fig. 1 presents the study location map and sampling sites.

Extraction of paddy soil and water samples

Once reaching the laboratory, the paddy soil samples were kept at -20°C whereas the paddy water samples were kept at 4°C. The paddy soil and water samples were extracted according to (13). Ten gram of paddy soil samples were sieved and extracted using the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method with 6.0 g MgSO4 , 1.5 g NaAc and 100 µL Hac and cleaned with dispersive solid phase extraction (dSPE) technique. Whereas the 250 mL of paddy water

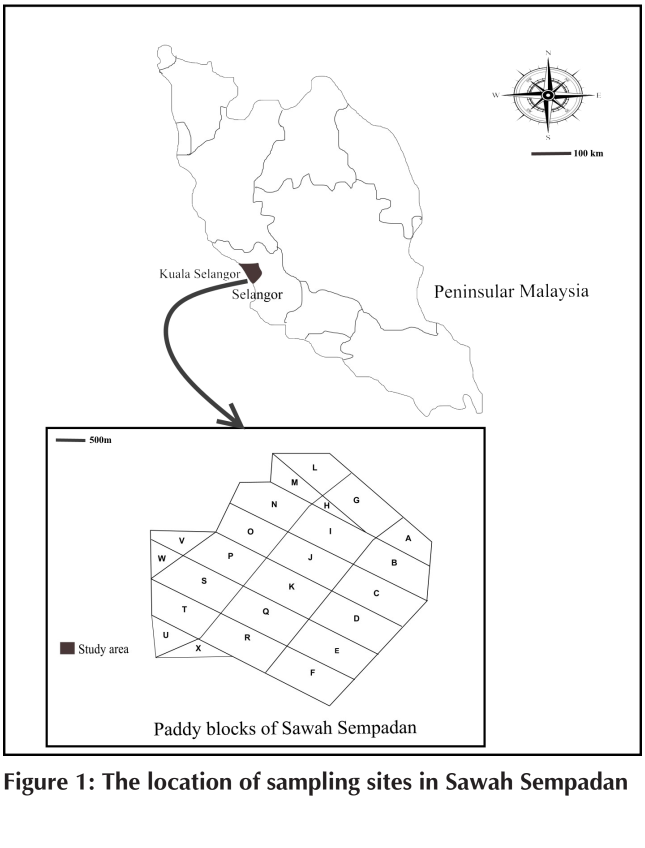

Figure 1: The location of sampling sites in Sawah Sempadan

samples were filtered with 1.0 µm glass filter fibre (GFF) (Sartorius (Germany)) and 0.45µm nylon membrane (Membrane Solutions (USA)) before extracted using solid phase extraction (SPE) method. The details of soil and water extraction method can be referred from (13). The extracts were analysed using UHPLC-MS/MS.

UHPLC-MS/MS analysis

The concentration of pesticides in paddy soil and water samples were analysed using method as reported in (13). Agilent 1290 Infinity UHPLC (Agilent, USA) system coupled to 6490 triple quadrupole mass spectrometer in ESI mode (Agilent, USA) were used to analyse the target analytes. The instrument was equipped with Zorbax Eclipse Plus C18 column (2.1 mm I.D. Ч 50 mm length, 1.8 µm particle size) (Agilent, USA). The optimised mobile phase was ultrapure water with 5 mM ammonium formate 0.1% formic acid and (mobile phase A) and HPLC grade MeOH with 5 mM ammonium formate 0.1% formic acid (mobile phase B). The column temperature, volume of injection and flow rate were set at 40 °C, 2 µL and 0.5 mL min^{-1} respectively with 20 minutes run time. The detailed procedure of UHPLC-MS/MS analysis can be obtained in (13).

Determination of physicochemical properties of paddy soil and water samples

Upon reaching the laboratory, five hundred grams of soil samples were collected in a zip-lock plastic bag and transported to Espek Research and Advisory Services (ERAS), Rubber Industry Smallholders Development Authority (RISDA) for the analysis of the sample physicochemical properties. The analysis was carried out to determine a relationship of pesticides concentration in soil sample and the sample physicochemical properties. For soil samples, physicochemical properties such as pH, soil moisture, cation exchange capacity (CEC), total organic carbon (TOC), concentration of macro elements (total phosphorus (TP), total nitrogen (TN), available phosphorus (AP), sodium (Na), magnesium (Mg), potassium (K), and calcium (Ca)), carbon-to-nitrogen ratio (C/N), and heavy metal content (iron (Fe), boron (B), manganese (Mn), zinc (Zn) and copper (Cu)) were analysed. The TOC and TN were analysed in vario MACRO cube elemental analyser (Elementar, Germany). The heavy metal contents, CEC, TP, AP, K, and Na were determined using ICP-Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer, MA, USA). While Mg and Ca were determined using atomic absorption spectrophotometer (AAS) (Shimadzu, Japan). Methods for analysis of all the parameters were provided by Espek Research & Advisory Services (ERAS), RISDA Estates Sdn. Bhd. Based on the method M.S 678 outlined by the Standard and Industrial Research Institute of Malaysia (SIRIM).

For water samples, in-situ water quality parameters such as pH, temperature, electrical conductivity (EC), salinity, turbidity, dissolved oxygen (DO), total dissolved solids (TDS) and resistivity were measured on field using the respective instruments. The pH was measured using EUTECH pH450 (Thermo Fisher Scientific, USA). The temperature and DO were measured using Eutech DO 450 Waterproof Portable Meter (Thermo Fisher Scientific, USA). Electrical conductivity, salinity, resistivity, and TDS were measured using Eutech Cyberscan COND610 (Thermo Fisher Scientific, USA). Turbidity was measured using 2100Q Portable Turbidimeter (HACH, USA). All parameters were measured and recorded three times on site to ensure that the readings taken were accurate.

Whereas, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were determined in the laboratory. Chemical oxygen demand was conducted based on HACH Chemical-Reactor Digestion Method 8000 (14) by preheating the DRB 200 Single Block Reactor (HACH, USA) to 150°C, then 2 mL of water samples were added into COD digestion vials (HACH, USA) and the vials were inverted slowly for a few times before they were heated in the pre-heat reactor for 2 hours. After that, the vials were allowed to cool to room temperature. Next, the colorimetric procedure was conducted in 431 COD ULR program in DR 1900 Spectrophotometer (HACH, USA). The BOD were conducted based on the BOD_5 method in which the incubation period is 5 days at 20°C. If the predicted BOD_5 value of a sample is less than 7 mg L^{-1}, no sample dilution is needed (15). Previous studies reported BOD_5 value lower than 7 mg L^{-1} in paddy field irrigation (16,17). Thus no dilution required in this study. The samples pH was adjusted between 6.5 and 7.5. Then, 300 mL of paddy water samples were poured into the BOD bottles and the bottles were incubated at 20°C ± 1°C. After 15 minutes, the initial DO (DO0) of each sample was recorded. The samples were kept in the incubator for 5 days. On the 5th day, the final DO (DO_1) of each sample was recorded. The BOD_5 was determined based on the Eq. (1).

$$BOD_5 = DO_1 - DO_0 \qquad \text{Eq. (1)}$$

Where,

DO_1= final DO of paddy water sample after 5-day incubation

DO_0= initial DO pf paddy water sample on the first day of incubation

Relationship of the concentration of target pesticides and paddy soil physicochemical properties and paddy water quality parameters

The statistical analysis was conducted in International Business Machines Corporation (IBM) Statistical Package for the Social Sciences version 24 (IBM SPSS 24). Normality and outliers of data set was identified using Shapiro-Wilk test (significance level 0.05) and box-plots respectively. Spearman's Rank Order correlation ($p < 0.01$) was carried out to determine the correlation of concentration of pesticides in paddy soil and the concentration of pesticides in paddy water. Non-parametric Spearman correlation was performed to determine the relationship of the concentration of target analytes and the physicochemical properties of paddy soil, and the relationship of the concentration of target analytes and paddy water quality parameters. In addition, the Spearman correlation was also carried out to determine the intra-correlation among the physicochemical properties and water quality parameters. Differences were considered significant only when p values were less than 0.01.

RESULTS

Concentration of target pesticides in paddy soil samples

All of the target pesticides in this study were present in paddy soil and water samples collected from 24 paddy blocks (Block A to Block X). The mean, standard deviation (SD), minimum, maximum concentration and frequency of detection of each pesticide were presented in Table I.

Table I shows that chlorantraniliprole had the highest mean concentration (15.82 ng g^{-1}) among the target analytes. Meanwhile tricyclazole had the lowest mean concentration (0.58 ng g^{-1}) among all target analytes. The maximum reported concentration among the target analytes were ranged from 3.85 ng g^{-1} (tricyclazole) to 153.44 ng g^{-1} (azoxystrobin). Chlorantraniliprole, isoprothiolane and trifloxystrobin showed the highest frequency of detection (100%) while fipronil showed the lowest frequency of detection (54%) in paddy soil samples.

Concentration of target pesticides in paddy water samples

The mean, standard deviation (SD), minimum, maximum concentration and frequency of detection of each pesticide in paddy water samples were presented in Table I.

Chlorantraniliprole had the highest mean concentration (6.56 ng mL^{-1}), meanwhile pretilachlor and trifloxystrobin had the lowest mean concentration in water (0.03 ng mL^{-1}) among the target analytes. The maximum reported concentrations were ranged between 0.11 ng mL^{-1} (pretilachlor and trifloxystrobin) and 70.92 ng mL^{-1} (azoxystrobin). Azoxystrobin, chlorantraniliprole and trifloxystrobin showed the highest frequency of detection (100%) while tebuconazole showed the lowest frequency of detection (17%) in paddy water samples.

Physicochemical properties of paddy soil samples

Table II summarises the descriptive statistics of the physicochemical properties of paddy soil samples. Table II shows that the soil samples in this study were moderately acidic, ranging between 5.7 and 6.8. The TOC, soil moisture and TN in this study ranged from 0.95 to 6.3%, 22 to 120.4% and 0.04 to 0.26% respectively. The C/N range in each soil samples are between 6 and 26. The CEC are ranged from 5.28 to 21.51 meq 100g^{-1}.

Relationship between the concentration of target pesticides and physicochemical parameters in paddy soil samples

Spearman's Rank Order correlation coefficients were calculated to investigate the relationship ($p \leq 0.01$) of the concentrations of the thirteen target analytes with the soil physico-chemical properties. The findings are tabulated in Table III.

Based on Table III, TOC-C/N showed strong positive correlation with r = 0.919 and $p \leq 0.01$. Carbon-to nitrogen ratio is a ratio of organic carbon content to total nitrogen content in the soil, this explains the correlation between the two variables. However, there was no significant correlation showed between C/N and TN. The table also shows strong positive correlation between

Table I: Concentration of pesticides in paddy soil (n = 72) and water samples (n = 72)

Analyte	Soil				Water			
	Mean ± SD (ng g^{-1})	Maximum (ng g^{-1})	Minimum (ng g^{-1})	Frequency of detection (%)	Mean ± SD (ng mL^{-1})	Maximum (ng mL^{-1})	Minimum (ng mL^{-1})	Frequency of detection (%)
Azoxystobin	11.62 ± 31	153.44	<MQL	79	5.83 ± 15	70.92	0.03	100
Buprofezin	1.85 ± 21	8.66	<MQL	92	0.04 ± 0.1	0.23	<MQL	96
Chlorantraniliprole	15.82 ±14	61.27	3.79	100	6.56 ± 8	33.41	0.06	100
Difenoconazole	2.24 ± 2	7.79	<MQL	88	0.48 ± 1	4.16	<MQL	83
Fipronil	2.39 ± 4	13.22	<MQL	54	1.03 ± 3	11.94	<MQL	50
Imidacloprid	1.31 ± 2	8.27	<MQL	58	0.70 ± 3	15.49	<MQL	42
Isoprothiolane	9.67 ± 12	42.92	0.55	100	6.29 ± 12	51.54	<MQL	96
Pretilachlor	1.30 ± 2	9.94	<MQL	63	0.03 ± 0.1	0.11	<MQL	96
Propiconazole	4.30 ± 6	25.50	<MQL	75	0.58 ± 2	12.43	<MQL	71
Pymetrozine	1.70 ± 3	15.05	<MQL	71	0.49 ± 2	10.85	<MQL	67
Tebuconazole	1.53 ± 2	9.56	<MQL	63	0.05 ± 0.2	0.97	<MQL	17
Tricyclazole	0.58 ± 1	3.85	<MQL	96	0.07 ± 0.2	1.25	<MQL	92
Trifloxystrobin	1.77 ± 1	4.12	0.53	100	0.03 ± 0.1	0.11	0.01	100

Table II: Descriptive statistics of soil physico-chemical properties

Variable	Mean	SD	Standard error	Mini-mum	Maxi-mum	Coefficient of variance (%)
pH	6.3	0.3	0.1	5.70	6.8	4.71
TOC (%)	3.3	1.4	0.3	0.95	6.3	43.51
Moisture (%)	42.5	18.6	3.8	22.00	120.4	43.87
TN (%)	0.21	0.04	0.01	0.04	0.26	21.10
CN	17.6	5.8	1.2	6.00	26.0	32.75
TP (mg L^{-1})	547.9	256.7	52.4	59.00	1210.0	46.85
AP (mg L^{-1})	41.5	27.5	5.6	2.00	98.0	66.23
B (mg L^{-1})	331.8	219.1	44.7	0.25	874.2	66.03
Mn (mg L^{-1})	1.2	0.7	0.1	0.07	2.9	62.57
Cu (mg L^{-1})	6.3	4.0	0.8	0.12	19.2	63.95
Fe (mg L^{-1})	22.6	14.4	2.9	1.45	49.5	63.71
Zn (mg L^{-1})	0.2	0.2	0.0	0.05	0.6	68.19
K (meq $100g^{-1}$)	0.4	0.1	0.0	0.14	0.7	39.34
Ca (meq $100g^{-1}$)	10.8	4.6	0.9	3.82	20.6	42.20
Mg (meq $100g^{-1}$)	3.24	1.55	1.04	1.28	7.76	47.87
Na (meq $100g^{-1}$)	0.34	0.14	0.88	0.13	0.69	42.61
CEC (meq $100g^{-1}$)	15.00	4.68	-0.50	5.28	21.51	31.22

K and Mg (r = 0.726) (p≤ 0.01). Besides that, B shows moderate positive correlation (p≤ 0.01) with Mn (r = 0.543), and Cu (r = 0.550). In return there is a moderate positive correlation between Mn and Cu, (p≤ 0.01), (r = 0.565) and Cu shows positive correlation with Fe and K with r 0.630 and 0.545 respectively.

The concentration of propiconazole shows moderate positive correlation with Mn (r = 0.587) (p≤ 0.01). Meanwhile buprofezin-TOC (r = -0.55), imidacloprid-CEC (r = -0.519), pymetrozine-Na (r = -0.588) and trifloxystrobin-Ca (r = 0.566) showed moderate negative correlation.

Determination of water quality parameters of paddy water

The descriptive statistics of water quality parameters such as pH, temperature, EC, DO, turbidity, salinity, resistivity, TDS, COD and BOD are summarised in Table IV.

The temperature of the paddy water samples were around room temperature (25 to 31°C). All samples varied from acidic to neutral with few samples showed slight basic pH (5.4 to 7.5). The mean of EC and TDS were ranged from 120.1 µS/cm, and 164.4 mg L^{-1} respectively. While the mean of turbidity, salinity and resistivity were 142.2 NTU, 163.0 mg L^{-1} and 4.4 Ω respectively. The DO, COD and BOD were ranged between 2.3 to 7.6 mg L^{-1}, 0.1 mg L^{-1} and 0.9 mg L^{-1}, and 0.3 mg L^{-1} and 5.9 mg L^{-1} respectively. Besides temperature and pH, the coefficient of variance shows there was a great variation in the water quality parameters in all blocks.

Relationship between the concentration of target pesticides and the water quality parameters in paddy water samples

Table V summarises the correlation coefficient of pesticide concentrations in paddy water and the water quality parameters. Trifloxystrobin concentration showed significant positive correlation with turbidity (r = 0.718) (p≤ 0.01) and tebuconazole showed negative correlation to DO (r = 0.634) (p≤ 0.01), while the rest of pesticide concentrations showed no significant correlation with the water quality parameters. Table V shows strong positive correlation between salinity and EC, salinity and TDS and TDS and EC. However, there are negative correlations between the three parameters with resistivity.

DISCUSSION

A similar study in Sawah Sempadan reported lower pH (4.7) and comparable TOC, TN and AP (4.1%, 0.4% and 43.2 mg kg^{-1} respectively) with the paddy soil samples in this study (18). The optimum range of soil pH to be sufficiently available for nutrients is between 6.0 to 7.5 (19). Based on the optimum limit of TN percentage which was set in four categories; low, medium, high and very high (< 0.180%, 0.180-0.360%, 0.361-0.450% and > 0.45% respectively) (20). In this study, TN falls on low and medium category ranging from 0.04 to 0.26%. The mean AP in Table II is within the optimum range for paddy requirements as outlined by Malaysian Agriculture Research and Development Institute (MARDI) (21). Except pH, the coefficients of variance of the physico-chemical properties are high ranging from 21.1% to 68.2%. This suggests that the physico-chemical properties had large variation in the soils. This might be caused by a number of factors such as random or systematic errors in measurements, characteristic of soil, paddy types, tillage and covering practices, nutrient mineralization in soil and pesticide applications (18).Whereas, the pH, DO, BOD and COD of the paddy water samples in this study are outside the range outlined in the National Water Quality Standards in Malaysia (Table VI) by Department of Environment Malaysia (DOE) (22). Similarly, Haroun et al. (2015) (17) has reported the same findings in paddy plot.

Similar to this study, previous study has reported the strong positive correlation between K and Mg with comparable r (0.72) (p≤ 0.01) (23). In addition, the study also reported no significant correlation between pH and TOC. There is also moderate positive correlation between TOC and TN (r= 0.597, p≤ 0.01) which is in conformity to a study by Za et al. (25), the positive correlation may be caused by the soil microbial release of mineralizable nitrogen in consistent amounts.

Table III: Spearman rank correlation between concentrations of target analytes and soil physico-chemical parameters

Variable	Moisture	PH	TOC	TN	CN	TP	AP	B	Mn	Cu	Fe	Zn	K	Ca	Mg	Na	CEC
Moisture	1																
PH	ns	1															
TOC	0.456*	ns	1														
TN	0.415*	ns	0.597**	1													
CN	0.455*	ns	0.919**	ns	1												
TP	ns	ns	ns	0.423*	ns	1											
AP	ns	ns	ns	0.496*	ns	0.448*	1										
B	ns	ns	ns	ns	ns	ns	ns	1									
Mn	ns	ns	ns	ns	ns	ns	ns	0.543**	1								
Cu	ns	ns	ns	ns	ns	0.437*	ns	0.550**	0.565**	1							
Fe	ns	ns	ns	ns	ns	ns	ns	0.436*	0.407*	0.630**	1						
Zn	ns	ns	ns	ns	ns	ns	ns	-0.464*	ns	ns	ns	1					
K	ns	ns	ns	ns	ns	0.426*	0.450*	ns	ns	0.545**	ns	ns	1				
Ca	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	1			
Mg	ns	ns	ns	ns	ns	ns	ns	0.458*	ns	0.459*	0.461*	-0.419*	0.726**	ns	1		
Na	ns	-0.447*	ns	ns	ns	ns	ns	0.476*	ns	ns	ns	ns	ns	ns	0.483*	1	
CEC	ns	ns	ns	ns	ns	0.465*	ns	ns	ns	ns	ns	ns	0.576**	ns	0.668**	0.497*	1
Azo[a]	ns	ns	ns	ns	ns	ns	ns	0.443*	0.405*	ns	ns	ns	ns	ns	ns	ns	ns
Bup[b]	ns	-0.459*	-0.550**	ns	-0.503*	ns	ns	ns	0.508*	ns	ns	ns	ns	ns	ns	ns	ns
Chlo[c]	ns	0.426*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Dife[d]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Fip[e]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Imi[f]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-0.519**
Iso[g]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Pret[h]	ns	ns	-0.422*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Prop[i]	ns	ns	ns	ns	ns	ns	ns	ns	0.587**	ns	ns	ns	ns	ns	ns	ns	ns
Pym[j]	ns	ns	-0.416*	ns	-0.452*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-0.588**	ns
Teb[k]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Tric[l]	ns	ns	ns	-0.407*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Trif[m]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	-0.566**	ns	ns	ns

[a]azoxystrobin, [b]buprofezin, [c]chlorantraniliprole, [d]difenoconazole, [e]fipronil, [f]imidacloprid, [g]isoprothiolane, [h]pretilachlor, [i]propiconazole, [j]pymetrozine, [k]tebuconazole, [l]tricyclazole, [m]trifloxystrobin
ns = not significant *. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

Table IV: Descriptive statistics of water quality parameters in paddy water samples

Variable	Mean	SD	Standard error	Maximum	Minimum	Coefficient of variance (%)
Temperature (°C)	28.8	1.4	0.3	31.3	25.0	4.9
pH	6.4	0.5	0.1	7.5	5.4	8.0
EC (µS cm^{-1})	168.4	120.1	24.0	474.3	0.2	71.3
DO (mg L^{-1})	5.7	1.4	0.3	7.6	2.3	24.2
Turbidity (NTU)	142.2	120.0	24.0	574.0	51.0	84.4
Salinity (mg L^{-1})	163.0	115.6	23.1	461.6	1.2	70.9
Resistivity (Ω)	4.4	2.2	0.4	9.4	1.1	50.1
COD (mg L^{-1})	0.6	0.2	0.0	0.9	0.1	31.1
BOD (mg L^{-1})	3.3	1.6	0.3	5.9	0.3	49.2
TDS (mg L^{-1})	164.4	117.3	23.5	462.9	0.2	71.3

The positive correlation between propiconazole and Mn could be due to the mixture of these systemic fungicides such as Propico and Syngenta Propiconazole with protectant fungicides such as mancozeb or prochloraz manganese chloride. The efficacy of these fungicides when applied in combination may be higher than individually (26). Thus some of the farmers may opt to use these two types of fungicides together.

Salinity is a measure of salt amounts in water, while EC measures the water ability to transmit electrical current which depends on dissolved ions in the water (27). The ions are the product of salt breakdown in the water. Both EC and TDS are parameters used to measure salinity in which the higher EC and TDS, the higher water salinity (27,28), this explains the strong positive correlation between (a) salinity and EC, (b) salinity and TDS, and (c) EC and TDS with correlation coefficient ≥0.998. Table V shows negative correlation between the three parameters with resistivity. Resistivity is a reciprocal of conductivity (EC), it measures water ability to resist electrical current over a distance. This means EC and resistivity have negative linear relationship, and since

Table V: Spearman rank correlation of pesticides concentration in paddy water and water quality parameters

	Temperature	pH	EC	DO	Turbidity	Salinity	Resistivity	COD	BOD	TDS
				Correlation coefficient ®^{a}						
Temperature	1.000									
pH	ns	1.000								
EC	ns	ns	1.000	1.000						
DO	ns	ns	ns	ns						
Turbidity	ns	ns	ns	ns	1.000					
Salinity	ns	ns	0.998**	ns	ns	1.000				
Resistivity	ns	ns	-0.826**	ns	ns	-.0837**	1.000			
COD	-0.446*	ns	ns	0.643**	-0.575**	ns	ns	1.000		
BOD	0.477*	ns	ns	ns	ns	ns	ns	ns	1.000	
TDS	ns	ns	0.999**	ns	ns	0.998**	-0.825**	ns	ns	1.000
Azoxystrobin	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Buprofezin	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Chlorantranilirole	ns	ns	ns	ns	0.432*	ns	ns	ns	ns	ns
Difenoconazole	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Fipronil	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Imidacloprid	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Isoprothiolane	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Pretilachlor	ns	ns	ns	ns	0.494*	ns	ns	ns	ns	ns
Propiconazole	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Pymetrozine	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Tebuconazole	ns	ns	ns	-0.634**	ns	ns	ns	ns	ns	ns
Tricyclazole	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Trifloxystrobin	ns	ns	ns		0.718**	ns	ns	-.477*	ns	ns

ns = not significant; *. Correlation is significant at the 0.05 level (2-tailed); **. Correlation is significant at the 0.01 level (2-tailed).

Table VI: National Water Quality Index Classification

PARAMETER	UNIT	CLASS				
		I	II	III	IV	V
Ammoniacal Nitrogen	mg/l	< 0.1	0.1 - 0.3	0.3 - 0.9	0.9 - 2.7	> 2.7
Biochemical Oxygen Demand	mg/l	< 1	1 - 3	3 - 6	6 - 12	> 12
Chemical Oxygen Demand	mg/l	< 10	10 - 25	25 - 50	50 - 100	> 100
Dissolved Oxygen	mg/l	> 7	5 - 7	3 - 5	1 - 3	< 1
pH	-	> 7	6 - 7	5 - 6	< 5	> 5
Total Suspended Solid	mg/l	< 25	25 - 50	50 - 150	150 - 300	> 300
Water Quality Index (WQI)	-	< 92.7	76.5 - 92.7	51.9 - 76.5	31.0 - 51.9	> 31.0

Class I: Conservation of natural environment, Class II: good, conventional treatment is required, Class III: Extensive treatment required, Class IV: Irrigation, Class V: Bad which don't meet any of the above mentioned classes. [18]

EC has linear positive correlation with salinity and TDS, both parameters have the same correlation with resistivity as translated in Table V.

CONCLUSION

The occurrence of pesticide residues in agricultural soil and water may be influenced by the matrix physical and chemical properties, or vice versa. Alteration of soil and water physicochemical properties may alter their quality and fertility. The concentration of the thirteen target pesticides were quantified in paddy soil and water. Based on the results, all of the thirteen target analytes were present in soil and water samples. The most frequently detected analytes in soil were chlorantraniliprole, isoprothiolane and trifloxystrobin. Whereas, the most frequently detected analytes in water were and azoxystrobin, chlorantraniliprole and trifloxystrobin. Chlorantraniliprole had the highest mean concentration in both paddy soil (15.82 ng mL^{-1}) and water (6.56 ng mL^{-1}) samples. The concentration of propiconazole, buprofezin, imidacloprid, pymetrozine and trifloxystrobin in paddy soil were affected by Mn content, TOC, CEC, Na content and Ca content respectively. The concentration of trifloxystrobin in paddy water was significantly correlated to turbidity. The EC in paddy water had positive correlation with salinity and TDS, and negative correlation with resistivity. Pesticides have positive and negative effects on the soil and water physicochemical properties. Moderate application of pesticides should be employed to maintain the condition and the productivity of the matrix. Employers and agency such as Farmers' Organisation Authority (LPP) is recommended organising training programs or campaigns to raise awareness on suitable pesticides application. This will not only maintain the productivity of soil and water but also protect the farmers from unwarranted pesticide exposure.

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