

PATTERN RECOGNITION OF THE PRESENCE AND DISTRIBUTION OF ORGANOCHLORINE PESTICIDES IN SEDIMENT OF CAMERON HIGHLANDS, MALAYSIA

(Pengenalan Corak Kehadiran dan Taburan Racun Perosak Organoklorin di dalam Sedimen
Cameron Highlands, Malaysia)

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Abstract

This study aimed to assess the environmental situation of 18 organochlorine pesticides (OCPs), of which some are members of Persistent Organic Pollutants (POPs) in the sediment of an intensive agriculture area as well as popular tourism destination of Cameron Highlands, Malaysia. A total of 56 surface sediment samples were collected at eight selected sampling points along the two main rivers in the area namely Telom and Bertam Rivers during the dry and wet seasons in 2011. The OCPs levels detected were between 0.41 – 82.16 (mean of 21.33 ± 18.54) ng/g of dry weight. A total of 15 OCPs namely 4,4' DDT, 4,4' DDD, 4,4' DDE, γ -HCH, β -HCH, aldrin, dieldrin, endrin, endosulfan I, endosulfan II endosulfan sulfate, heptachlor and heptachlor epoxide were detected in all sediment samples. Multivariate analysis of the 15 detected OCPs with respect to the type of land-use shows that endosulfan I was found around the tea plantation areas; γ -HCH was found near vegetable plantation areas; 4,4' DDE and aldrin were found near Blue Valley station; and endrin, heptachlor, 4,4' DDD, 4,4' DDT, and heptachlor epoxide were found in the nearby villages. Four clusters (C1; 1, C2; 1, C3; 2 and C4; 4 stations) were generated using a cluster analysis method. Four latent factors (74.36 % of total variance) were identified by principle component and factor analysis method. Three classifications namely tea plantations, vegetable plantations, and villages provide 83.90 % of the composition pattern of 15 OCPs, whereas 3 OCPs are significant components in discriminating organochlorine pesticides contamination detected in sediment samples. Pollutants seemed to enter the river through the run-off from agricultural areas and villages. HCH isomer (β -HCH) was mostly found in the downstream stations of the rivers.

Keywords: chemometric, environmental quality, multivariate analysis, persistent organic pollutants (POPs), sediment

Abstrak

Kajian ini dilakukan bertujuan menilai persekitaran 18 racun perosak organoklorin (OCPs), di mana sebahagiannya adalah pencemar organik kekal (POPs) wujud di dalam sedimen dari kawasan pertanian intensif serta destinasi pelancongan popular iaitu Cameron Highlands, Malaysia. Sejumlah 56 sampel sedimen permukaan dikumpul dari lapan titik persampelan terpilih di sepanjang dua sungai utama iaitu Sungai Telom dan Sungai Bertam semasa musim kering dan basah pada tahun 2011. Aras kandungan OCPs dikesan antara julat 0.41 – 82.16 (min 21.33 ± 18.54) ng/g berat kering. Sejumlah 15 OCPs iaitu 4,4' DDT, 4,4' DDD, 4,4' DDE, γ -HCH, β -HCH, aldrin, dieldrin, endrin, endosulfan I, endosulfan II endosulfan sulfat, heptaklor dan heptaklor epoksida dikesan dalam semua sampel sedimen. Analisis multivariat terhadap 15 OCPs yang dikesan menunjukkan bahawa endosulfan I ditemui di sekitar kawasan ladang teh; γ -HCH ditemui berhampiran kawasan ladang sayur-sayuran; 4,4' DDE dan

aldrin ditemui berhampiran stesen Blue Valley; dan endrin, heptaklor, 4,4' DDD, 4,4' DDT, dan heptaklor epoksida ditemui di kampung – kampung yang berhampiran. Empat kluster (C1; 1, C2; 1, C3; 2 dan C4; 4 stesen) telah dibentuk dengan menggunakan kaedah analisis kelompok. Empat faktor utama (74.36 % daripada jumlah varians) telah dikenal pasti melalui kaedah analisis komponen utama dan analisis faktor. Tiga klasifikasi pengaruh iaitu ladang teh, ladang sayur-sayuran dan kampung-kampung telah menjelaskan 83.90 % corak komposisi 15 OCPs, manakala 3 jenis OCPs merupakan komponen penting dalam membezakan pencemaran racun perosak organoklorin yang dikesan di dalam sampel sedimen. Bahan pencemar cenderung masuk ke dalam sungai melalui air larian dari kawasan pertanian dan kampung-kampung. Isomer HCH (β -HCH) paling kerap ditemui di stesen – stesen hiliran sungai.

Kata kunci: kimometrik, kualiti alam sekitar, analisis multivariat, pencemar organik kekal (POPs), sedimen

Introduction

Since their introduction in the 1940s, organochlorine pesticides (OCPs) have improved crop yields and drastically reduced recorded cases of malaria [1, 2]. In agriculture, the estimated consumption value of lindane has been reported (in thousands of tons) to be 287.16 (Europe), 73.20 (Asia), 63.57 (America), 28.54 (Africa), and 1.03 (Oceania) [3, 4]. As a result, human health and the environment have experienced a number of serious changes owing to the growing use of OCPs [5]. In potential risk terms, these components possess toxic properties, resist degradation, as well as bio-accumulate and persist in terrestrial and aquatic ecosystems. The formulations of Pesticide Act and the Stockholm Convention on Persistent Organic Pollutants in 1974 are the two most significant reasons for the reduction in the use of POP pesticides worldwide. However, the distribution and utilization of some OCPs have not ceased completely. Therefore, massive usage of POPs continually results in contamination around the world.

Since 2002, Malaysia was a signatory to the Stockholm Convention on POPs and committed to carrying out a GEF/UNEP-funded project for the gradual growth of a National Implementation Plan (NIP) for POPs management [6]. Historically, the use of pesticides in Malaysia was not subjected to regulatory control until the Agricultural Chemicals Board was established under the Agricultural Chemicals Act 1974. The use of persistent OCPs was then gradually controlled by a series of governmental rules. This policy led to their controlled use in the mid-1970s. Pesticides have been used to enhance the crop yields in Malaysia since the Second World War [7]. The country became a model for the World Health Organization (WHO), following the successful control of malaria mosquito vectors by DDT during the 1950s [8]. Most of the regulated pesticides under the Pesticide Act 1974 were used in the agriculture sector until they were banned in the late 1990s [9]. Despite that residues of these pesticides have been frequently found in various media of the environment such as water, sediment and biota [6, 10, 11].

Several monitoring projects have been conducted in Asian countries especially investigate ubiquitous impact of banned pesticides residues on water or sediment quality of rivers namely Han River, South Korea [5], Gomti River, India [3], Daliao River and Qiantang River, China [12, 13] and ASEAN countries in Red and Duong River (Vietnam), Mae Klong River (Thailand) and Mekong River in Laos-Thailand border [14 – 16]. Malaysia, a part of global crop production countries also having similar problems. One of hot spot point source of OCPs pollution in Malaysia is Cameron Highlands, a highly intensive agriculture area. Cameron Highlands is drained by three main rivers namely Telom, Bertam and Lemoi Rivers, formed an important source of water supply for its community, irrigation for highland farming, recreational activities and hydroelectric power.

Over the last decade, the rivers of the Cameron Highlands were polluted, and environmental problems became widespread. The water quality of rivers, particularly Telom and Bertam, have deteriorated significantly as a result of land clearing for agriculture, excessive use of pesticides and fertilizers, as well as domestic sewage from urban areas [17]. Therefore, improving the quality of water in rivers of Cameron Highlands is necessary to prevent further deterioration, thus enabling this area to continue as the main source of vegetable or flower production for Malaysia. This is very crucial since the most developed area in Cameron Highlands was in the upstream area of the river.

In multivariate statistical analysis, there is an assumption that the measured chemical concentrations in a specific sample are influenced collectively by several contributions from independent sources in environment. These independent sources include industry, agriculture, urbanization or nature [18, 19]. The definition of the mentioned

sources is through individual chemical composition, geographical and temporal or compartmental distribution. Multivariate statistical analysis is used to transform group of data sets into a new set of relevant and clear data. Hence, the retrieved environmental data is disintegrated in different components to describe the principal sources of variance in data. The mentioned methods serve a clearer comprehension of the collected data for long observation periods in monitoring phases. Previous research studies have been demonstrated that multivariate statistical analysis was useful tools to evaluate the quality of sediment and surface waters [20 – 24].

Pattern recognition is a prominent method within multivariate statistical analysis that classifies the unknown matters into a class based on pre-identified classes. There has been several research studies focused on a great number of different samples in food, biological, medical and environmental matrices. One of the main objectives of data analysis is acquiring information regarding the source and quality of the samples. The most important issue in the analysis is finding out about the characteristics of the samples through performing measurement of objects which are relevant to the study [20]. The most widely used application among multivariate methods is multivariate calibration (mainly based on principal component analysis, partial least squares regression and artificial neural networks) especially in quantitative analysis of complex mixtures. Miah and Moore [25] has published a study on parameter design as a quality control method based on multivariate statistical analysis, while Saidenberg et al. [26] was able to predict the biological activities of peptides. However, Sârbu and Pop [27] discussed about the disadvantages of the PCA in his study mentioning that multivariate statistical analysis is sensitive to outliers, missing data, and also sensitive to the poor linear correlation between variables occurred due to weak distribution of variables.

The objectives of this research work are 1) to investigate the levels and distribution of organochlorine pesticides in sediments of Cameron Highlands river system, 2) to assess the possible point sources of OCPs contaminant and 3) to discriminate latent factors exhibit in spatial variation using multivariate statistical analysis.

Materials and Methods

Study Area

Cameron Highlands is a district located at 4°28' N, 101°23' E, in the north-west of the state of Pahang, east coast of Peninsular Malaysia. Figure 1 shows the study area and the geographical position of sampling points are listed in Table 1. The area is mountainous with 10 – 35° slopes. It has a moderate temperature of 14 – 24 °C throughout the year with an average rainfall of 2800 mm [28] and no month without rainfall. Most vegetables here are grown at between 900 and 1400 m altitude. Eight sampling sites along the Bertam and Telom Rivers were selected and a total of 56 sediment samples were collected during wet and dry seasons. February, June and July were considered as the dry season and April, May, August and November as the wet season in 2011 based on the meteorological report.

Table 1. Station, coordinate location and range of particle size of sediment samples.

Code	Station Name	Location (Coordinate)	Particle size (mm)
Station 1	Blue Valley	04° 32.998 N, 101° 24.666 E	0.5-2
station 2	Terla	04° 35.329 N, 101° 25.022 E	0.355-1
Station 3	Golf course	04° 29.225 N, 101° 23.065 E	0.5-1
Station 4	Taman Sedia	04° 28.900 N, 101° 22.230 E	0.5-1
Station 5	Fama Office	04° 28.580 N, 101° 22.885 E	1-2
Station 6	Parit Fall	04° 28.467 N, 101° 23.045 E	0.7-2
Station 7	BOH (tea plantation)	04° 25.871 N, 101° 23.275 E	1-4
Station 8	Habu	04° 26.565 N, 101° 23.280 E	0.25-2

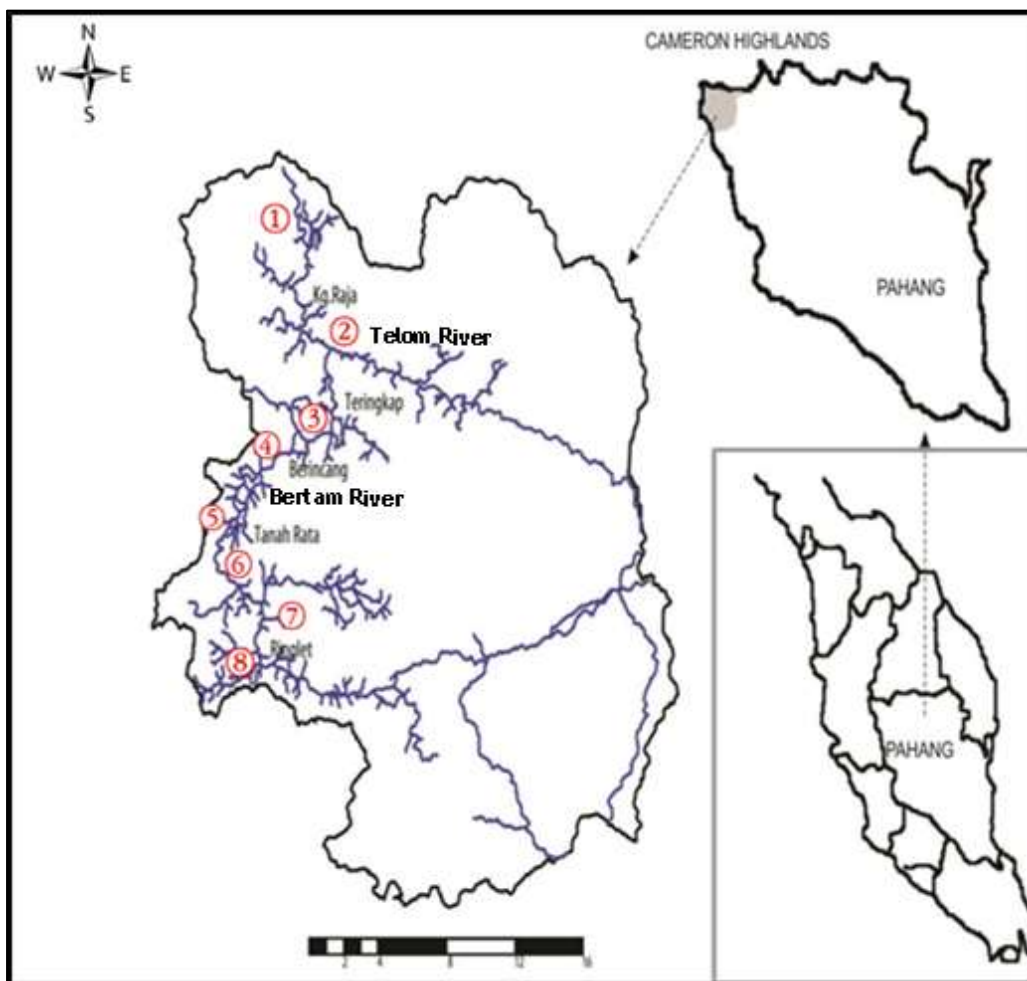


Figure 1. Location of stations in Cameron Highlands (inside; map of Peninsular Malaysia)

Chemical and Reagents

The ampoule of mixed organochlorine pesticide standards consisted of α -HCH, β -HCH, γ -HCH, δ -HCH, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldehyde, methoxychlor and endrin ketone was obtained from Supelco (Belle-Fonte, USA). The stock solution (200 ppm) of mixed OCPs was prepared in 10 mL of n-hexane pesticide grade. Fresh working standard solutions containing a mixture of the mixed OCP, surrogates (2, 4, 5, 6-tetrachloro-m-xylene & decachlorobiphenyl) and the internal standard component (pentachloronitrobenzene) were prepared by stepwise dilution of the stock solution with the range 1.95, 3.91, 7.81, 15.63, 31.25 and 62.5 $\mu\text{g/L}$. Deionized water was obtained by using a Milli-Q Easypure Rodi system (Barnstead, USA). All glassware was rinsed with analytical n-hexane before use. All the solvents which were used for extraction, cleanup and enhancement were pesticide grades. The anhydrous sodium sulfate was purified by heating it to 400 $^{\circ}\text{C}$ for 4 hours. Florisil (PR Grade) was used for cleanup in an activated form [29, 30].

Sampling and Laboratory Analysis

The sediment samples were collected with a Peterson grab sampler to a depth of about 5cm. The sediment samples were wrapped in aluminum foil and stored at 4 °C until analysis. Approximately 250 g of the sediment from each station was used to determine the particle size. The samples were transferred to laboratory prior to the extraction process.

Sediment sample was divided into two portions. First part, the water content of sediment was determined by oven drying about 10 g of wet sediment for 12 hours at 105 °C. Then, a series of mesh sieves ranging from 0.0125 mm to 64 mm were applied to determine the particle size of the sediment samples. Meanwhile in second portion, an approximately 10 g of an air-dried grounded homogenized sediment sample was mixed with 10 g of anhydrous sodium sulfate, which was spiked with 1mL of 0.160 ppm surrogate solutions and then extracted with 300 mL of n-hexane/acetone 50:50 for six hours in a Soxhlet extractor. The extracted volume was reduced using a Rotovap evaporator to about 5 mL. Then, the solution was loaded onto the Florisil column cleanup packed with 20 g of activated Florisil. The Florisil column was eluted three times consecutively with 65 mL of n-hexane, 45 mL of 70:30 n-hexane/dichloromethane and 55 mL of dichloromethane. The cleaned solution was concentrated by evaporating the solvent using a Rotovapor-R-3000 evaporator. This solution was further concentrated to 2 mL with a stream of high purity nitrogen. 1 µL of the concentrated solution was spiked with exactly 1 µL at 100 ppm of internal standard before injection into the GC-ECD.

Instrumentation

A temperature programming system was implemented to separate all 18 OCPs by the Varian chromopack CP-3800 Gas Chromatograph. The instrument was equipped with a ⁶³Ni electron capture detector and a 30 m x 0.32 mm i.d. (0.25 µm film thickness) HP-5ms fused silica capillary column. Purified nitrogen gas was supplied as the carrier gas at 1.5 mL/min. The oven temperature was maintained at initial 90 °C for 1 min and increased to 170 °C at a rate of 3.5 °C/min. The temperature was then increased further to 280 °C at a rate of 5 °C/min. The injector and detector temperatures were held constant at 250 and 300 °C, respectively. A standard mixture of 18 pesticide solution mixed with the surrogate and internal standard at concentration of 31.25 ng/mL was used to optimize the performance of the GC-ECD.

Gas chromatograph mass spectrometer (GC/MS) analyses were performed with an Agilent 7890A gas chromatograph (GC) directly coupled to the mass spectrometer system (MS) of an Agilent 5975C inert MSD with a triple-axis detector to confirm the order of components and the identity of each peak in real samples. A mixed standard of 2 ppm of target OCPs and surrogates was employed in GC/MS. The internal standard concentration was kept constant in all solutions at 100 µg/L. Relative response factors were applied to quantify data. Percentage recoveries were verified by the surrogate component. Surrogate standards were added to each sample to monitor extraction performance and matrix effects. A recovery value of between 75 - 125% was considered for quantification and 65 - 135% for qualification. The concentrations of the OCPs were not modified by the recovery ratios of the surrogates. Every sample was analyzed in triplicate, and the average amount was applied in the data analysis. Method Detection Limit (MDL) was found by analyzing a laboratory fortified blank as a real sample as described in Saadati et al. [31]. The value of Method Quantification Level (MQL) was found to be in the range of 0.002 to 0.004 ng/g.

Statistical Analysis

Factor analysis can be used to reduce a large number of related variables to a more manageable number. Exploratory data analysis was performed in the early stages of the result and discussion portion to gather information on the total amount of OCPs and the composition based on temporal and spatial distributions. Confirmatory factor analysis, which is a more complex and sophisticated set of techniques was used to confirm the theory concerning the source of OCPs underlying a set of OCP groups, stations or land use. Sample size and strength of relationships among OCPs are the factors that should be considered before data analysis. A total of 56 samples are sufficient for factor analysis.

All statistical analyses were performed using Statistical Package for the Social Science (SPSS) for Windows Version 18.0 (2010). All data were tested for the basic assumption of normality and homogeneity of variance

inherent in linear model statistics by normal probability plots generated by the univariate procedures in the SPSS package. All statistical significances were considered when $P < 0.05$. The concentration of contaminants reported as “not detected” were assigned half of the detection limit value for statistical analysis purposes. For large samples (n_1 and $n_2 > 30$) taken from any distribution of x (i.e., even a distribution that is not normal), the mean \bar{x} is normally distributed with a variance σ^2/n [19]. Consequently, as 56 samples of sediment were analyzed, the data were considered as normally distributed.

Results and Discussion

Seasonal Influence

In the present study, samples were collected seven times from the eight stations at Bertam and Telom Rivers during the wet and dry seasons. Figure 2 shows a box plot of the distribution of OCPs during the wet and dry seasons in 2011. February, June, and July were considered as dry season, with a monthly average rainfall of 50 mm to 150 mm, meanwhile April, May, August, and November were considered as wet season, with a monthly average rainfall of 300 mm to 400 mm. Results indicate that the mean of the target OCPs in the Cameron Highlands sediments were higher in the wet season than that in the dry season in line with those reported by Zhou et al. [13]. It also stated that OCPs in Zhejiang Province (East China) were released from wet deposits or from soil being eroded into water because of heavy rains. The α/γ ratio is basically considered to be helpful in determining the contamination source based on the difference in ratio from the technical or pesticide origins. The isomeric composition of HCH is generally 60% to 70% α , 5% to 12% β , 10% to 12% γ , and 6% to 10% δ , with a 3–7 α/γ ratio [1, 12, 32]. In this study, α -HCH was found to be below the detection limit in nearly 50% of the samples sediments. For the rest of the samples, the α/γ ratio for the sediment samples was 0.11.

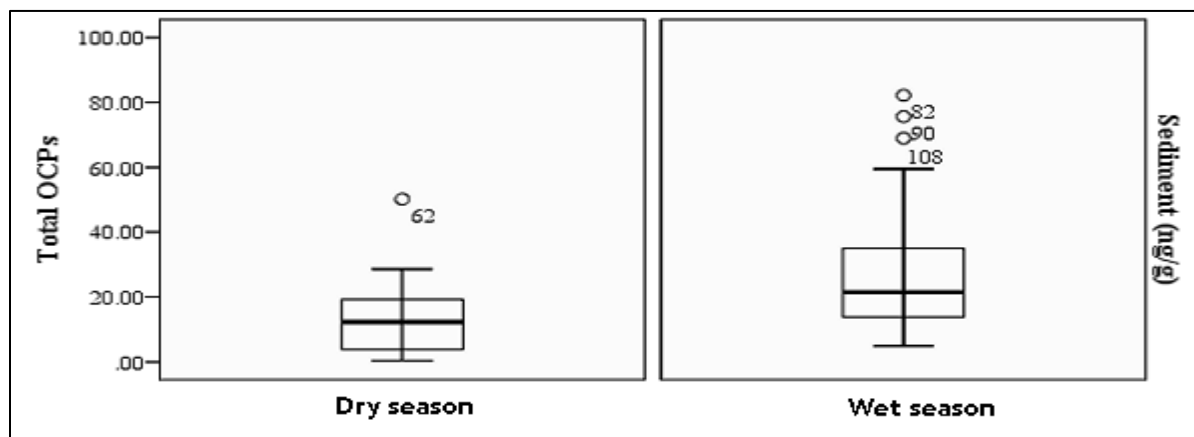


Figure 2. A box plot of the distribution of Σ OCPs during wet and dry seasons (inner circle numbered is outlier data)

The release of OCPs can be associated with surface runoff from tea and vegetable plantations and with the exposure of soil to pesticides. Pesticide usage was increased during the wet season because pesticides were washed off more quickly. Mazlan and Mumford [33] also pointed out that an increase in pest infestation during the wet season resulted in higher consumption of pesticides. The relationships among rainfall, soil erosion and released OCPs can be determined by comparing OCP grouped values (Figure 3). The highest amounts of HCHs, DDTs, endosulfans, endrin, and heptachlors were detected during the wet season. These components appear originate from vegetable farms and rural pollution sources near the sampling stations. The slope of an area can enhance the transportation of pesticides during wet season. Toriman et al. [34] has indicated higher soil loss in Telom catchment than Bertam catchment occurred in their study. Seasonal distributions also exhibit several differences. A higher amount of rainfall causes contamination from the soil and other point or nonpoint sources. The study area did not experience any month without rainfall; thus, the effect of rainfall could not be neglected completely even during the dry season. Furthermore, wet and dry seasons were not completely separated from each other; the monthly sequence in this study was dry–wet–wet–dry–dry–wet–wet.

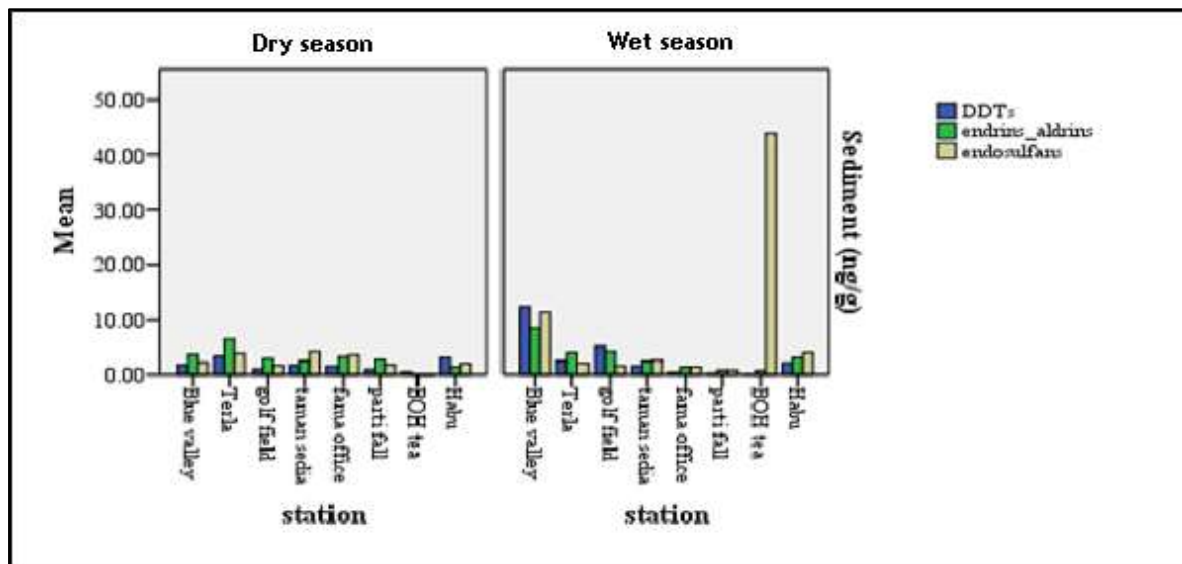


Figure 3. Spatial and temporal variation of grouped OCPs in sediment samples

The Σ OCPs in sediment samples showed no difference during the wet and dry seasons except individually for γ -HCH ($p = 0.015$), endosulfan I ($p = 0.045$), and endosulfan II ($p = 0.014$). Differences found for γ -HCH and endosulfans indicate possible new inputs to sediments during the wet season. The results of this data analysis support the findings that the HCH isomer ratio indicates possible new inputs of lindane [35].

Site Similarities

Data sets were grouped based on sample similarities. An unsupervised classification was applied to OCP values of sediment samples from different stations. The squared Euclidean distance was used as the interval measure for clustering through distinct linkage methods according to Ward's method. Raw data was computed after standardization based on Z-scores of the variable. Cluster analysis resulted in data set groups based on similarities within a class and dissimilarities among different classes. In previous studies, cluster analysis was used to interpret data representing patterns and compositions for the evaluation of spatial and temporal variations in water quality of Gomti River, India [36] and for identifying sources of organic contaminants in Langat River, Malaysia [37]. Figure 4 presents the dendrogram of the locations of different sites along Bertam and Telom Rivers.

Four major clusters are shown in Figure 4, indicating four groups of stations. The first two clusters are Blue Valley and BOH Tea Plantation stations, corresponding to sites with a land use of mostly tea plantations. Blue Valley is located along Telom River, whereas BOH Tea Plantation is located downstream of Bertam River. These two points form two clusters because of the distance in their geographic positions [24], whereas the other points are localized nearby. Variations in distance may be used to infer several environmental conditions of OCP values caused by nonpoint source pollutions or seasonal variations in OCP levels [35]. Pollution in these two stations was assumed to come from tea plantations; however, most OCPs present in these areas were from past heavy usage of these pesticides.

Cluster 3 consists of Taman Sedia, a housing area, (station 4) and Parit Fall (a popular waterfall) (station 6). These stations were located in the village area, and the pollution source was considered to be mostly drainages from municipal and tourist centers. Station 4 is near Brinchang town. The past study from Malakahmad et al. [38] explicated that these two areas were point sources of municipal pollution in the study area. It also revealed that Brinchang and Tanah Rata hold approximately 71% of total commercial point sources of pollution. The last cluster

includes Terla, FAMA Office, Golf course and Habu stations. These stations were located in areas covered mostly by vegetable plantations.

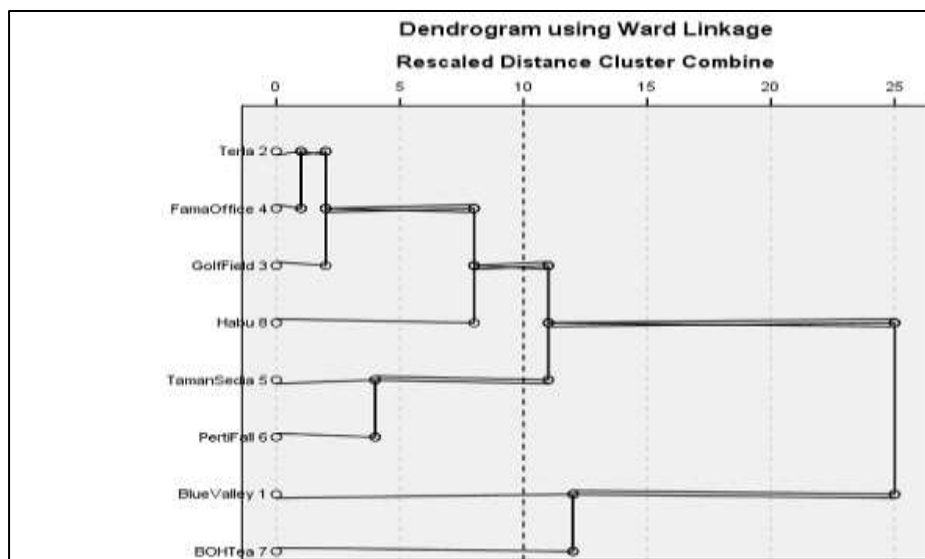


Figure 4. The dendrogram of the group of stations using Ward's method

Spatial Variation

Spatial discriminant analysis was performed using standardized data of sediment samples. The plot of the discriminant functions is presented in Figure 5. The three sources assigned to agricultural areas (tea and vegetables) and the villages are clearly shown in the plot. The classification matrix of the sediment data set obtained from the standard mode of discriminant analysis is shown in Table 2. The standard mode led the corresponding correlation matrix to assign 83.9% while correctly using the 15 OCPs. Notably, three OCPs were not detected in sediment samples, namely, methoxychlor, endrin aldehyde, and endrin ketone.

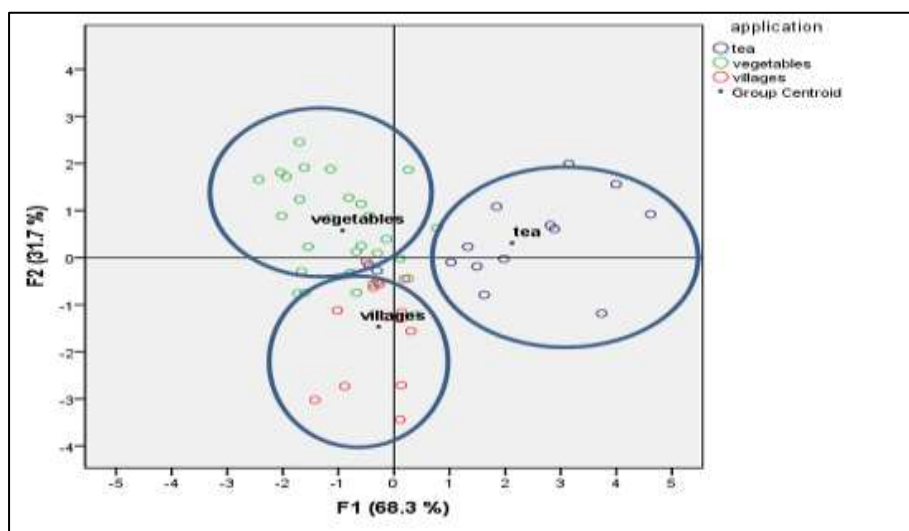


Figure 5. Loading plot of discriminant function for pollution sources based on sediment data sets

Figure 5 indicates the overlapping areas between the vegetable plantation and village data set. Therefore, the result confirms that no specific source is assigned to vegetable plantations or village areas in several cases. Background usage of OCPs results from having these chemicals in the runoff that washes soil everywhere in the area. Villages and agricultural areas near each other were assumed to have the same sources of background OCP contamination in the study area.

Table 2. Classification matrix of discriminant analysis for 18 OCPs in sediment samples (n=56)

Classification Matrix ^a						
Application		Predicted Group Membership				
		Tea	Vegetables	Villages	Total	
Original	Count	Tea	12	1	1	14
		Vegetables	1	22	5	28
		Villages	0	1	13	14
%		Tea	85.7	7.1	7.1	100.0
		Vegetables	3.6	78.6	17.9	100.0
		Villages	.0	7.1	92.9	100.0

^a 83.9% of original grouped cases correctly classified.

The stepwise mode yielded 73.2% correctly classified cases using only three OCPs (endosulfan II, α -HCH, and 4,4' DDE) (Table 3); whereas the percentage of correctly classified cases in the standard mode is 78.6 % using HCH isomers (α -HCH, β -HCH, γ -HCH, and δ -HCH), endosulfans (endosulfan I, endosulfan II, and endosulfan sulfate) and DDTs (4,4' DDE, 4,4' DDD, and 4,4' DDT). Thus, discriminant analysis suggests that in this study the three classifications namely tea plantations, vegetable plantations and villages provide 83.9% the composition pattern of 15 OCPs, whereas 3 OCPs are significant components in discriminating OCP contamination detected in sediment samples among the sampling stations in Bertam and Telom Rivers. The three components are from DDT metabolites, HCH isomers, and endosulfan families, indicating the age of the applied OCPs since they are not specified for any type of pest control these days.

Table 3. Classification matrix discriminant analysis for 18 OCPs in the sediment samples (n=56, stepwise, will's lambda)

Classification Matrix ^a						
Application			Predicted Group Membership			
			Tea	Vegetables	Villages	Total
Original	Count	Tea	8	2	4	14
		Vegetables	0	26	2	28
		Villages	1	6	7	14
	%	Tea	57.1	14.3	28.6	100.0
		Vegetables	.0	92.9	7.1	100.0
		Villages	7.1	42.9	50.0	100.0

^a73.2% of original grouped cases correctly classified

Source Identification

The redundancy of different information suggests that factor analysis should be conducted to reduce the dimensionality of the data set. Principal component analysis (PCA) is a powerful technique for clustering data analysis. A total of 15 OCPs were subjected to PCA to identify spatial sources of pollution background in sediment

samples. The suitability of data sets for factor analysis was assessed prior to conducting PCA. An inspection of the correlation matrix revealed the presence of numerous coefficients 0.3 and above. The Kaiser–Meyer–Olkin value was 0.793, which exceeded the recommended value of 0.6 [39, 40] and Bartlett's test of Sphericity [41] was achieved statistical significance, thus supporting the factorability of the correlation matrix. The assumption of sample size and the factorability of the correlation matrix and linearity, which are requirements for factor analysis were initially checked (Table 4).

Table 4. Verifying suitability of the set of data for factor analysis

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		0.793
Bartlett's Test of Sphericity	Approx. Chi-Square	611.736
	Df	105
	Sig.	0.000
KMO = 0.793 > 0.6, Bartlett's Test of Sphericity is significant (Sig. value = 0.000 < 0.05)		

The PCA result has revealed the scree plot pronounced change after four components with eigenvalues > 1, thus explaining 41.7%, 14.68%, 9.60%, and 8.11% of the variance, respectively (Table 5). The scree plot showed in Figure 6 represents the four suggested components. This plot becomes flat, thus indicating that additional components contribute less to overall data variance.

Table 5. The PCA of 15 OCPs in sediment samples of Bertam and Telom Rivers

Component	Initial Eigenvalues			Sums of Squared Loadings					
	Total	% of Variance	Cumulative %	Extraction			Rotation		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.295	41.969	41.969	6.295	41.969	41.969	4.645	30.966	30.966
2	2.202	14.682	56.651	2.202	14.682	56.651	2.740	18.265	49.231
3	1.440	9.597	66.248	1.440	9.597	66.248	1.913	12.756	61.987
4	1.216	8.109	74.357	1.216	8.109	74.357	1.856	12.370	74.357
5	0.991	6.608	80.965						
6	0.789	5.258	86.223						
7	0.553	3.689	89.912						
8	0.380	2.532	92.444						
9	0.348	2.318	94.762						
10	0.214	1.427	96.188						
11	0.183	1.220	97.409						
12	0.146	0.975	98.384						
13	0.097	0.645	99.029						
14	0.086	0.572	99.601						
15	0.060	0.399	100.000						

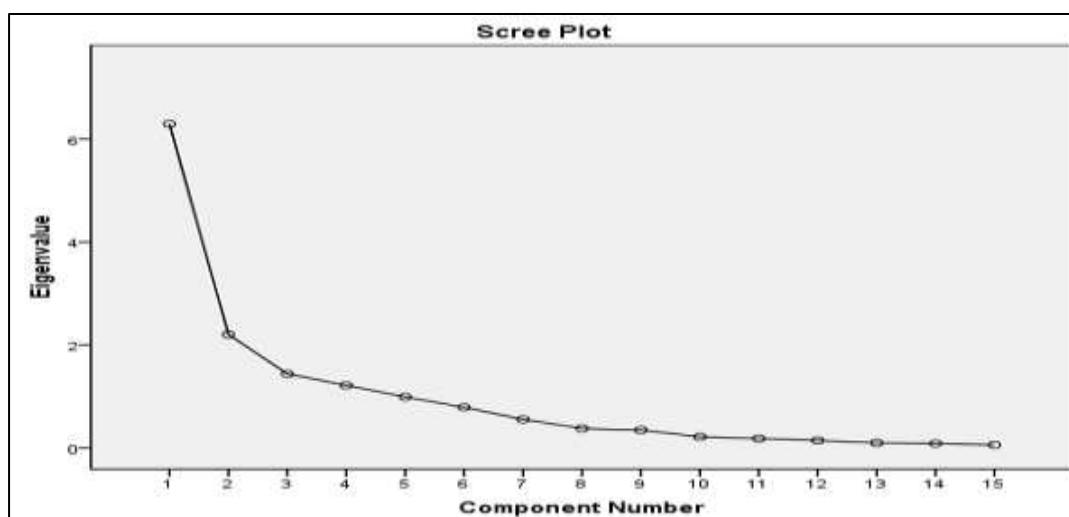


Figure 6. The scree plot presents the four components with eigenvalue >1

Varimax rotation was performed to aid in interpreting the four solution components. Osman et al. [37] in past study used loaded Varimax rotation to identify the source of organic contaminants in Langat River basin by extracting five components. The rotated solution revealed the presence of a component matrix [42], thus signifying a number of strong loadings. The interpretation of the four components was based on data tabulated in Table 6. Liu et al. [43] has considered the strength of the relationships in Varimax rotation, such as greater than 0.75, between 0.75 and 0.5, and between 0.5 and 0.3 as “strong,” “moderate,” and “weak” relationships, respectively. Therefore, five of the OCPs namely endrin, heptachlor, 4,4' DDD, 4,4' DDT and heptachlor epoxide loaded strongly on Component 1; aldrin and 4,4' DDE loaded on Component 2; γ -HCH and δ -HCH loaded on Component 3; and endosulfans I and II loaded on Component 4. These four principal components (PCs) agree with the cluster analysis results.

Component 1 has an accumulative variance of 30.97 % indicates the cluster of stations assigned to village areas, such as Parit Fall and Taman Sedia, by discriminant analysis. Detecting 4,4' DDD and heptachlor epoxide in this group reveals the source of past usage because 4,4' DDD is an anaerobic metabolite of 4,4' DDT whereas heptachlor epoxide is a degraded form of heptachlor. The ratio of DDT metabolites to the total DDT shows that most sources of DDTs come from past usage. The presence of 4,4' DDT in the sediments from this particular area leads to the possibility of sediments being a source of pollution for these particular OCPs. The values of 4,4' DDT exceeded the sediment quality guidelines in several cases. Sediment is one of the sources of pollution in the conceptual exposure model of pesticide pollutants.

Table 6. The factor loading (after Varimax rotation) for 15 OCPs detected in the sediment samples

Rotated Component Matrix ^a				
Compounds	Component			
	1	2	3	4
Endrin	0.873	0.390	0.079	0.107
Heptachlor	0.869	0.311	-0.036	0.091
4,4'-DDD	0.849	0.084	0.254	0.123
4,4'-DDT	0.815	0.349	0.024	0.140
Heptachlor epoxide	0.801	0.418	0.148	0.105
Dieldrin	0.701	-0.072	0.211	-0.100
Aldrin	-0.004	0.865	0.199	-0.058
4,4'-DDE	0.409	0.756	0.033	0.022

Endosulfan sulfate	0.268	0.681	0.009	-0.060
Alpha HCH	0.353	0.380	0.100	-0.086
Gamma HCH	0.060	-0.074	0.852	-0.139
Delta HCH	0.129	0.182	0.768	-0.003
Beta HCH	0.329	0.455	0.630	0.025
Endosulfan I	-0.087	-0.097	-0.055	0.959
Endosulfan II	0.331	-0.022	-0.084	0.908
Eigenvalue	4.64	2.74	1.91	1.86
Explained variance (%)	30.97	18.26	12.76	12.37
Cumulative (%)	30.97	49.23	61.99	74.36
Extraction Method: Principal Component Analysis, Rotation Method: Varimax with Kaiser Normalization, ^a Rotation converged in 6 iterations, strong loadings >0.75 are shown in bold				

Component 2 has a total variance of 18.26 % indicates the cluster assigned to tea plantation areas, including Blue Valley and BOH Tea Plantation stations, by discriminant analysis. The occurrence of 4,4' DDE in these stations reveals the possibility of a new input of 4,4' DDT since 4,4' DDE is an aerobic metabolite, thus the presence of these metabolites possibly come from water or degraded 4,4' DDT from soil surface in nearby locations. Component 3 has a total variance of 12.76 %, which include γ -HCH (lindane) and δ -HCH indicates the cluster assigned to vegetable plantation areas of four stations namely Fama Office, Terla, Golf Field and Habu. Apparently, γ -HCH (lindane) which has not been used for the last 10 years, had a high probability of been reintroduced recently in this particular area based on the ratio of HCH isomers. Component 4 has a total variance of 12.37%, which includes endosulfan I and II is assigned to the mostly tea plantation areas. Blue Valley and BOH Tea Plantation stations were found in a major cluster with assumed endosulfan usage. Endosulfan I and II degrade into endosulfan sulfate in the environment. The presence of endosulfan in the form of endosulfan I and II indicates their ongoing use.

Conclusion

Text

Acknowledgement

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References

1. Zakri, A.H. 2000. Title of article. *Name of the journal*, vol (no): pp.