

Occurrence of organochlorine pesticides in a tropical lake basin

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Abstract This study investigates the presence and distribution of organochlorine pesticides in streams and the lake in the Sembrong Lake Basin in Malaysia. The catchment of Sembrong Lake has been converted to agricultural areas over the past 30 years, with oil palm plantations and modern agricultural farming being the main land use. Surface water samples were collected from eight sites comprising the stream and lake and analysed for 19 organochlorine pesticides (OCPs). In situ measurement of temperature, dissolved oxygen, pH and conductivity were also undertaken at each site. Aldrin, endrin, δ -BHC, 4,4-DDT, methoxychlor and endosulfan were the main OCPs detected in the lake basin. The total OCP concentration ranged between 5.42 and 349.2 ng/L. The most frequently detected OCPs were δ -BHC, heptachlor and aldrin. The maximum values detected were 23.0, 43.2 and 50.4 ng/L respectively. The highest concentration of OCPs was attributed to 4,4-DDT, but such high residue was rare and only

detected once. Other OCP residues were low. Significant differences in the mean values were observed between lake and stream for dichlorodiphenyldichloroethylene (DDE) and α -endosulfan concentration ($p < 0.05$). The highest endosulfan, endrin and methoxychlor residues were found in lake sites, while the highest 4,4-DDT residues were observed for the river sites. Temporal variation of OCP residues was observed for heptachlor and β -endosulfan. The highest concentrations of pesticide residues were found in October. DDX and α/γ ratios indicate possible fresh inputs of the OCP pesticide in the basin.

Keywords Endocrine disrupting chemicals · Freshwater · Organochlorine · Pesticides · Sembrong reservoir

Introduction

Pesticides have been used as control agents for pests that are damaging agricultural crops and spreading diseases. In the agricultural sector, various types of pesticides have been manufactured to control weeds, fungi, insects, molluscs and rodents that attack crop harvests, seeds and plants (Larson et al. 1998). The synthetic organochlorine pesticides (OCPs) were first discovered in the late 1930s (Dikshith and Diwan 2003). The negative impacts of OCPs, which include their persistent presence in the environment and bioaccumulation hazards, have resulted in banning of the substances from worldwide application in the 1970s (Dikshith and

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Diwan 2003). Growing concerns about OCP persistence in the ecosystem has resulted in many studies detecting their residue in water, sediment and biota (Barlas et al. 2006; Caldas et al. 1999). Such studies have been undertaken extensively in rivers (Konstantinou et al. 2006; Leong et al. 2007; Cai et al. 2014), lakes (Barlas et al. 2006; Dai et al. 2011), irrigation canals and paddy fields (Meier et al. 1983; Ismail et al. 2012). Since the adoption of the Stockholm Convention on Persistent Organic Pollutants (POPs), Malaysia has banned OCPs in stages since the 1990s, starting with aldrin and dieldrin; the most recently such banned pesticide, alachlor, was banned in 2015 (DOA 2014).

Pesticide residues were reported to have been detected in streams and canals in Malaysia in the past, and their concentration was noted to have reduced over time, following the ban on applying these chemicals in the country (Abdullah 1995; Abdullah 2002). The detection of OCPs in streams was attributed to agriculture run-off. Sediment leaching and atmospheric deposition were other possible mechanisms for OCP spread in the environment (Wauchope 1978). Since most OCPs are persistent in the environment, their residues can be retained in the ecosystem over a long period of time. In Malaysia, commodity crops such as rubber and oil palm have had large-scale development throughout the country since the 1970s to support economic growth (Abdullah and Hezri 2008). Paddy fields and vegetable farms were developed in suitably localised areas in northern states such as Perak, Kedah and southern Pahang for paddy fields and highland areas in the Cameron Highlands, Pahang, and Kundasang, Sabah, for vegetable farms. Additionally, large-scale mixed farming comprising fruits, vegetable and livestock, known as modern agricultural scheme, was introduced in 2004 and involves areas in Southern Johor, with the aim of promoting extensive agricultural development in the country. Similar to other countries, various pesticides have been applied in all these plantations and farms to control pests and crop diseases and enhance production. Hence, pesticide residues have been found in canals and streams where paddy fields and vegetable farms had been established in Muda, Kedah, and Cameron Highlands, Pahang (Zakaria et al. 2003). The monitoring of OCP in water bodies such as lakes has not been undertaken extensively in Malaysia. Since most streams within any catchment in agricultural areas flow into water bodies, OCP residues in surface water may accumulate in these water bodies. Hence this study fills a gap in the

current literature on pesticide residues in water bodies in Malaysia.

This paper focuses on the assessment of pesticide residues present in surface water situated close to modern agricultural development areas and large oil palm plantations. The rapid growth of modern agriculture in Kluang over the past 20 years has resulted in significant deterioration of lake water quality in the Sembrong reservoir. Eutrophication in this waterbody has caused frequent algal blooms and disruption to the district's water supply (Singh et al. 2013; Sharip et al. 2014; Wellson et al. 2016; Sharip et al. 2017). Heavy metals that disrupt the endocrine system, such as arsenic and lead, have also been detected in the waterbody (Baharim et al. 2016). The water quality of the Sembrong and Merpo rivers, the two main tributaries flowing into the lake, were reported as slightly polluted and clean respectively (Awang et al. 2015). To our knowledge, no measurements have been undertaken to detect pesticide residues in this Sembrong Lake Basin. This study aims at evaluating (i) the occurrence of OCPs in the streams and lake of mixed agricultural areas, (ii) the spatial and temporal variation of OCPs in the lake basin, (iii) the variation of OCP residues based on different agricultural activities and (iv) the level of OCP residues at different lake depth. The findings of this study will provide significant information on OCP occurrence in a tropical lake in general and, more specifically, a basis for future monitoring OCPs in the respective water body.

Materials and methods

Study area

Sembrong Lake (1.96°–2.08° N, 103.12°–103.3° E) is a large (~ 8.5 km²) and shallow (mean depth ~ 3 m) reservoir located roughly 20 km from the Kluang town. The lake was created in 1984 by inundating the Merpo and Sembrong rivers for 100-year return period flood mitigation of the downstream areas (JPS and UTHM 2012). The lake has been a major source of water supply source for the Kluang district since the 1990s. About two million litre/day (MLD) of water was tapped directly from the Sembrong reservoir to a nearby water treatment plant. However, under the Malaysian Development project, modern agricultural farming was also initiated in the area in 2004. The catchment of the lake (catchment area ~ 130 km²) was converted in phases

from forest to agricultural areas since the construction of the dam (Fig. 1). Rubber, which is the main agricultural activity during the 1960s, was replaced by oil palm in the 1980s. The current land use as surveyed in 2014 indicates that more than 95% of the land use within the lake catchment is employed for agriculture, including livestock farms.

Data collection

Eight sampling sites were selected within the lake basin, covering upstream to most downstream—near the dam, as shown in Fig. 2. Sites were selected randomly comprising different activities in the sub-catchments (Table 1). Sampling points S1–S4 represent river site while sampling points S5–S8 represent lake site. Data collection included in situ measurement using a multi-parameter probe to measure pH, temperature, dissolved oxygen (DO) and conductivity. Water samples were collected for analysis of OCPs, iron, manganese, total suspended solids (TSS), dissolved organic carbon (DOC) and total phosphorus (TP). Samples were collected at near surface monthly from May 2016 to October 2016. In the lake site, samples were taken at two depths (near surface and near bottom) at sites having

depth of > 2 m. Water samples for OCP analysis were collected using a 1-l glass bottle while water samples for chemical analysis were collected using 1-l and 250-ml bottle. OCP samples were grabbed in duplicates from each site and were acidified to pH 2 using 10% nitric acid in the field to control biological productivity. Additional OCP samples were collected once from the tap water near a building located beside the lake that received water from nearby water treatment system. All the water samples were stored in the cooler box at 4 °C and immediately transported to the laboratory. Samples were preserved in a cold room until analysis.

Laboratory analysis

Analyses were carried out in an accredited laboratory using established and validated method. All samples for chemical analysis were performed in accordance to standard methods (APHA 2012). Water samples for OCP analysis were filtered using 0.45 µm GF/C membrane filters prior to extraction using solid phase extraction system (SPE). Extraction of samples and OCP analyses were carried out in accordance with the US EPA (2007). The samples were extracted using hexane, acetone and water reagents. OCP analytes were

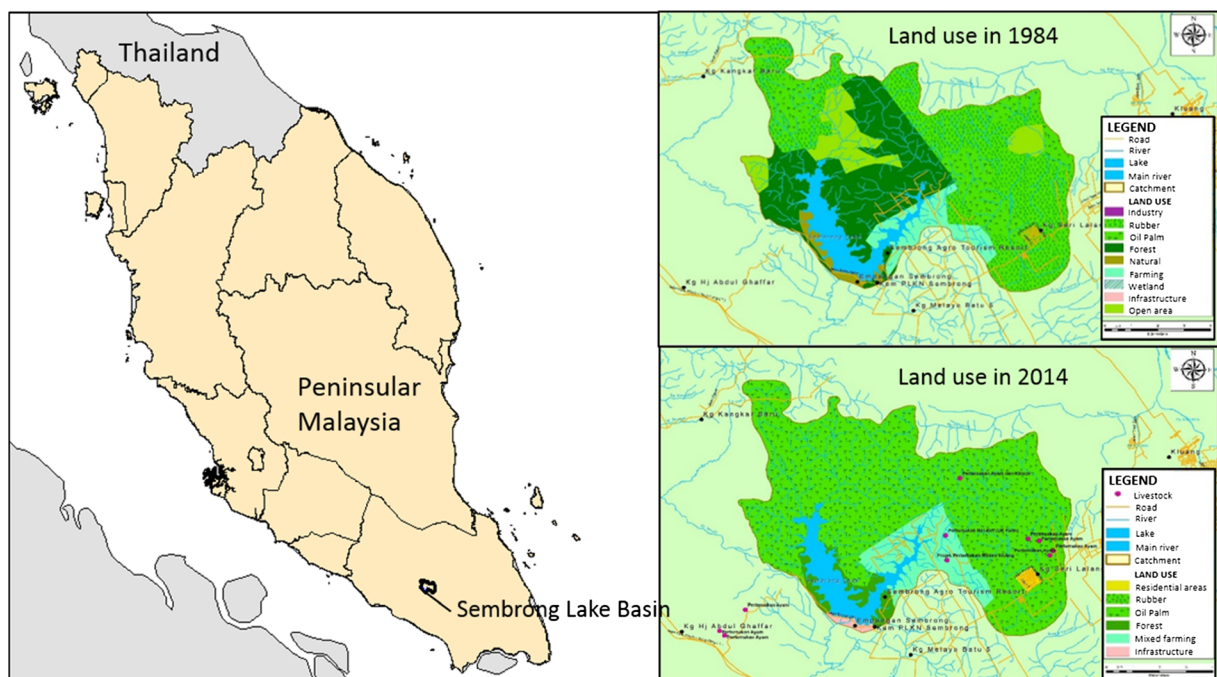
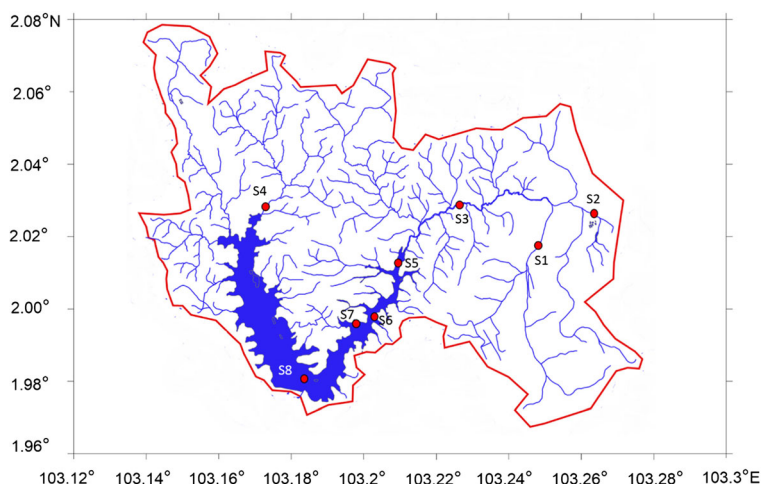


Fig. 1 Catchment changes within the Sembrong Lake Basin

Fig. 2 Map of sampling points within the Sembrong Lake basin in coordinates (longitude, latitude)



analysed using gas chromatography with ^{63}Ni electron capture detector (GC-ECD, Agilent 6890, USA) and DB-35MS capillary column (30 m $\times$ 0.32 mm i.d. $\times$ 0.25 μm film thickness). The injector and detector temperature in this study were fixed at 260 and 300 $^{\circ}\text{C}$ respectively. For the analysis of OCP compounds, nitrogen was used as carrier gas. The oven temperature was set at initial temperature of 110 $^{\circ}\text{C}$ for about 30 s, then increases at 30 $^{\circ}\text{C}/\text{min}$ to final temperature of 300 $^{\circ}\text{C}$ and held for 2 min. In general, OCP concentration was determined by identifying and evaluating the peak height of the samples from the result of the chromatograph with the calibration curves of the standard and their retention times. Quality control was also performed to check for interference, cross-contamination, and to ensure the reproducibility of the methods. For

every set of 10 samples, procedural blanks and spiked blanks were performed. Residues of the studied compounds were not detected in all the blanks analysed. In this study, recoveries varied from 70 to 130%. The limit of detection for the OCP residues in the water samples ranged between 0.01 and 8 ng/L.

Data analysis

For statistical analysis, this study considered EDC data detected by the instruments. All data were $\log_{10}$ transformed to improve normality. Sites were categorised into stream and lake. In addition, means of OCP residues from different land use were also categorised into three activities, namely (i) oil palm, (ii) mixed farming and (iii) mixed agriculture and other land use. Lake depth was categorised as (i) near surface level and (ii) near bottom level. Univariate and multivariate analyses, such as repeated measures and a two-way between-groups ANOVAs, were used to analyse significant differences in means between sites, month and their interactions. If sites and month had significant interactive effects, post hoc tests were carried out using Bonferroni method. Separate independent non-parametric Mann-Whitney test and Kruskal-Wallis one-way ANOVA were used to evaluate effect of lake depth and land use activities on the pesticide variation respectively. Correlation tests were used to determine statistical relationship between studied residues and physico-chemical parameters. Statistical analyses were performed using SPSS 22.0 (SPSS Inc., Chicago, USA). Significance was set at $p < 0.05$.

Table 1 Site and main activities within the sub-catchment

Site	Main activities within sub-catchment
S1	River; oil palm plantation, residential areas, workshop and small factories
S2	River; oil palm plantation, palm oil mill, nursery
S3	River; oil palm plantation
S4	River; oil palm plantation
S5	Lake; oil palm plantation, agro-resort, fruit orchard
S6	Lake; vegetable farm, fruit orchard
S7	Lake; vegetable farm
S8	Lake and near water intake, most downstream; oil palm plantation, modern farming

Results and discussion

Levels of pesticide residues and their spatial variation

This study was carried out to investigate the detection and distribution of pesticide residues, specifically OCPs in the selected agricultural basin. In total, 16 OCPs out of 19 OCPs studied were detected. Table 2 shows the mean and range of OCP concentrations detected in the Sembrong Lake Basin. The most frequently detected OCPs (> 10% detection), in decreasing order, were δ -BHC, heptachlor > aldrin, methoxychlor > endrin > α -BHC > 4,4-DDT, and γ -BHC > endosulfan sulphate. Only endrin aldehyde, heptachlor epoxide and gamma chlordane were not detected in all samples, while other parameters were detected at low frequencies (< 10%). The OCP with the highest detected concentration was 4,4-DDT, followed by methoxychlor, β -endosulfan and aldrin. The maximum concentration of 4,4-DDT was 1873 ng/L. This value is still below the National Drinking Water Quality Standards (NDWQS) (2000 ng/L, MOH 2004). The mean concentration of 4,4-DDT found in this study was similar to the mean

concentration reported by Fosu-Mensah et al. (2016) in river water samples from cocoa producing areas in Ghana. The OCPs that exceeded National Drinking Water Quality Standards were aldrin and heptachlor with maximum concentrations of 50.4 and 43.2 ng/L respectively. The presence of a high concentration of aldrin in the surface water sample is a concern, due to the fact that aldrin is highly volatile and easily degradable to dieldrin. Such high residues of aldrin found in this study indicate fresh input and possibly the illegal use of products containing the substance.

In this study, α -BHC residue was detected more frequently compared to γ -BHC, contrasting with the findings in some publications, where γ -BHC was the most common isomer detected (Zakaria et al. 2003; Saadati et al. 2012). The ratio of α/γ , which is commonly used to identify pollutant sources, was 0.1 to 29. Roughly half of the samples had a high γ -BHC concentration compared to the technical BHC composition, suggesting fresh inputs, while the balance had a high α -BHC, indicating historical applications. These findings are consistent with earlier results by Saadati et al. (2012) in the Bertam River Basin, which found high γ -

Table 2 Mean and range ($n = 47$) of OCP concentrations in the Sembrong Lake Basin

Organochlorine pesticides	Concentrations (ng/L)				Frequency of detection %
	Range	Mean	SD	NDWQS	
δ -BHC	0–23.0	2.26	4.65	2000	29.8
α -BHC	0–14.70	0.93	2.75	2000	14.9
γ -BHC	0–7.80	0.50	1.70	2000	12.8
β -BHC	0–14.90	0.55	2.52	2000	6.4
γ -Chlordane	0	0	0	200	0
α -Chlordane	0–23.50	0.76	3.66	200	8.5
Aldrin	0–50.40	3.17	9.42	30	27.7
Dieldrin	0–9.30	0.38	1.56	30	8.5
4,4-DDT	0–1873.60	40.44	273.22	2000	12.8
4,4-DDD	0–14.40	0.31	2.10	2000	2.1
4,4-DDE	0–12.70	0.29	1.86	2000	4.2
Endrin	0–51.40	2.78	8.30	600	21.2
Heptachlor	0–43.20	3.73	8.80	30	29.8
Heptachlor epoxide	0	0	0	30	0
Methoxychlor	0–234.70	14.33	48.20	20,000	27.7
α -Endosulfan	0–5.30	0.14	0.80	30,000	4.3
β -Endosulfan	0–121.5	3.22	17.88	30,000	6.4
Endrin aldehyde	0	0	0	600	0
Endosulfan sulphate	0–14.70	1.01	3.44	30,000	10.6

BHC, indicating the possible use of hexachlorocyclohexane (HCH) in Malaysia. HCH isomers (γ -, α - and β -BHC) and lindane were commonly used as seed treatment and fumigants in the agricultural sector, as well as in lice and scabies treatment in the public health sector (Gitahi et al. 2002; Vijgen et al. 2011; Fosu-Mensah et al. 2016). OCPs such as aldrin and dieldrin are utilised for controlling soil-inhabiting insects such as termites and also for grasshoppers (Gitahi et al. 2002). As aldrin binds strongly to soils and is resistant to soil leaching, it tends to bio-accumulate in the environment. The detected levels of aldrin in the present study are still low compared to those found in tea and vegetable farms in Bertam, Cameron Highlands (Zakaria et al. 2003; Saadati et al. 2012). In this study, dieldrin and endrin were occasionally detected but endrin was found more frequently. Endrin is an insecticide used for controlling pests such as rodents and was reported to be extremely toxic to aquatic organisms such as salmon and trout (Keilty et al. 1988). Other OCPs such as heptachlor and methoxychlor were widely used as insecticides on

agricultural crops and livestock. Both substances are persistent in nature and have a tendency to adsorb strongly to soil, remaining there for long periods. These OCPs were frequently detected in the samples of the current survey. However, heptachlor and methoxychlor residue levels in this study are higher than those reported in prior findings in Malaysia (Abdullah et al. 2015) and in other lakes in Greece (Golfopoulos et al. 2003).

OCP patterns within sites are shown in Table 3. The concentration of total OCPs ranged between 5.42 and 349.2 ng/L. The highest OCP concentration was detected at sites S2, S6, S7 and S8. High OCP concentration in site S2 was contributed to 4,4-DDT, while in site S7 and S8, this was attributed to methoxychlor. High OCP in S6 was attributed to endrin. Site S2 is located near a plant nursery, housing estate and palm oil mill. The presence of 4,4-DDT may indicate its use as a vector control or illegal insecticide application. The use of DDT, for example, for mosquito control in public health programmes in China, such as in the Songhua River, resulted in higher DDT concentrations being detected in

Table 3 Mean concentration of OCPs in different sites ($\pm$ SD) within the Sembrong Lake Basin

Organochlorine pesticides	S1 (n = 6)	S2 (n = 6)	S3 (n = 6)	S4 (n = 5)	S5 (n = 6)	S6 (n = 6)	S7 (n = 6)	S8 (n = 6)
δ -BHC	1.45 $\pm$ 3.6	2.41 $\pm$ 2.7	3.62 $\pm$ 6.4	2.4 $\pm$ 3.6	1.72 $\pm$ 3.2	5.13 $\pm$ 9.3	1.33 $\pm$ 3.2	0.00
α -BHC	0.00	2.45 $\pm$ 6.0	0.00	0.34 $\pm$ 0.8	2.3 $\pm$ 3.9	0.57 $\pm$ 1.4	1.63 $\pm$ 2.6	0.00
γ -BHC	0.8 $\pm$ 2.0	1.48 $\pm$ 3.1	0.55 $\pm$ 1.3	0.00	1.2 $\pm$ 2.9	0.00	0.00	0.00
β -BHC	0.00	1.5 $\pm$ 3.7	0.00	0.00	0.00	0.00	0.32 $\pm$ 0.8	2.48 $\pm$ 6.1
γ -Chlordane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
α -Chlordane	0.00	0.00	3.92 $\pm$ 9.6	0.00	0.00	1.57 $\pm$ 3.8	0.15 $\pm$ 0.4	0.30 $\pm$ 0.74
Aldrin	0.27 $\pm$ 0.6	9.77 $\pm$ 20.1	2.8 $\pm$ 5.5	0.00	0.5 $\pm$ 1.0	6.28 $\pm$ 15.4	4.0 $\pm$ 6.2	0.00
Dieldrin	0.00	2.17 $\pm$ 3.8	0.00	0.86 $\pm$ 1.9	0.07 $\pm$ 0.2	0.00	0.00	0.00
4,4-DDT	0.57 $\pm$ 1.4	312.2 $\pm$ 764.9	0.48 $\pm$ 1.2	3.2 $\pm$ 7.2	0.38 $\pm$ 0.9	0.00	0.43 $\pm$ 1.1	0.00
4,4-DDD	0.00	0.00	0.00	0.00	0.00	0.00	2.40 $\pm$ 5.9	0.00
4,4-DDE	0.00	0.00	0.00	0.00	0.00	0.18 $\pm$ 0.4	2.12 $\pm$ 5.2	0.00
Endrin	0.00	0.00	0.00	0.46 $\pm$ 1.0	0.83 $\pm$ 2.0	15.82 $\pm$ 18.9	4.80 $\pm$ 4.1	0.00
Heptachlor	0.48 $\pm$ 1.2	5.97 $\pm$ 12.9	0.5 $\pm$ 1.2	1.28 $\pm$ 2.9	2.92 $\pm$ 4.5	9.62 $\pm$ 17.4	6.08 $\pm$ 9.8	2.62 $\pm$ 5.4
Heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methoxychlor	1.85 $\pm$ 4.5	10.0 $\pm$ 17.4	0.32 $\pm$ 0.52	0.00	0.00	9.77 $\pm$ 23.9	51.4 $\pm$ 92.4	38.93 $\pm$ 92.9
α -Endosulfan	0.00	0.88 $\pm$ 2.2	0.00	0.00	0.00	0.00	0.23 $\pm$ 0.6	0.00
β -Endosulfan	0.00	0.00	0.00	0.00	0.00	2.0 $\pm$ 4.89	20.25 $\pm$ 49.6	2.82 $\pm$ 6.9
Endrin aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Endosulfan sulphate	0.00	0.25 $\pm$ 0.6	0.00	0.00	0.77 $\pm$ 1.9	2.42 $\pm$ 5.9	4.45 $\pm$ 6.9	0.00
Σ OCP	5.42 $\pm$ 7.7	349.15 $\pm$ 798.6	12.18 $\pm$ 21.5	7.11 $\pm$ 12.0	10.58 $\pm$ 11.0	53.35 $\pm$ 74.4	99.60 $\pm$ 176.0	47.15 $\pm$ 103.9

the river basin (Cai et al. 2014). In this study, the effects of sites were significantly different for endosulfan and 4,4,-DDE ($p < 0.01$) (Table 4). The highest endosulfan, endrin and methoxychlor residues were observed in lake sites, while the highest 4,4,-DDT residue was observed in the river site. Sites S6 and S7 are close to vegetable and fruit farms. Higher endosulfan and methoxychlor residues were present here, possibly due to the use of these insecticides in farming activities. Methoxychlor was reported to be commonly applied in fruit and vegetable farms. The mean concentrations of aldrin, endrin and endosulfan sulphate were significantly higher in surface water near vegetable farming areas compared to surface water near oil palm catchment areas indicating that the substances are possibly utilised for vegetable farming. Similar observation was reported in Zakaria et al. (2003); water samples near vegetable cultivation areas have high pesticide contamination compared to water samples near paddy fields (Zakaria et al. 2003). The mean values of the three detected OCPs were below the NDWQS (MOH 2004). In this study, accumulation

of OCPs does not increase from upstream areas to downstream areas.

From the perspective of the whole lake basin, the total OCP residues in this study are much lower compared to published findings for other lake basin such as Victoria Lake (Nyangababo et al. 2005) (Table 5) which could be related to its catchment size and agriculture practices. From the perspective of the lake, the maximum concentration of endrin, endosulfan, heptachlor and methoxychlor in Sembrong Lake are higher than the values reported in various lakes in Greece, India, Russia and Egypt (Iwata et al. 1995; Yamashita et al. 2000; Golfinopoulos et al. 2003; Mamta et al. 2015). For example, the maximum concentration of methoxychlor detected in Vistonida Lake, Greece, was 56 ng/L, which is four times smaller than the maximum concentration of 234.7 ng/L observed in this study. However, the maximum concentration of aldrin, dieldrin and 4,4-DDE in Sembrong Lake are lower than the values reported in published literature on other lakes. For example, the maximum concentration of aldrin recorded in Sembrong Lake was much lower than the maximum concentration of 95 and 200 ng/L recorded in Small Prespa Lake and Vistonida Lake, Greece (Golfinopoulos et al. 2003). Similarly, the maximum concentration of dieldrin recorded in this study was lower than the maximum concentration of 31 and 13.4 ng/L reported in Volvi Lake, Greece (Golfinopoulos et al. 2003), and Tighra reservoir, India (Mamta et al. 2015). The mean concentration of α -BHC found in this study is comparable with the mean values documented in Manzala Lake, Egypt (Yamashita et al. 2000), and Bosomtwi Lake, Ghana (Darko et al. 2008), while the mean value of γ -BHC found in this study is comparable with the mean values reported in other lakes such as Manzala Lake, Egypt (Yamashita et al. 2000), and Baiyangdian Lake, China (Dai et al. 2011). The list of lakes in Table 5 is not exhaustive. The values reported in this study may be comparable to OCP residues reported in other lakes in the USA and Europe.

Temporal variation of OCP residue

The temporal variation of primary OCP residues is illustrated in Fig. 3. The highest concentrations of OCP were found in October. Analysis of variance indicated significant differences in mean values for heptachlor and β -endosulfan over month ($p < 0.01$). Seasonal distribution of OCP pesticides such as DDT

Table 4 Results of the multivariate analysis of OCP residues

Variable	Sites		Month		Site $\times$ month	
	<i>p</i> value	Effect size	<i>p</i> value	Effect size	<i>p</i> value	Effect size
δ -BHC	.060	.100	.031	.294	.143	.207
α -BHC	.216	.045	.307	.156	.029*	.296
γ -BHC	.563	.010	.258	.168	.793	.065
β -BHC	.750	.003	.048*	.271	.990	.016
γ -Chlordane	.249	.039	.199	.186	.161	.200
Aldrin	.049*	.109	.171	.196	.177	.194
Dieldrin	.191	.050	.110	.224	.197	.187
4,4-DDT	.190	.050	.668	.087	.605	.097
4,4-DDD	.190	.050	.173	.195	.173	.195
4,4-DDE	.005**	.209	.173	.195	.173	.195
Endrin	.028*	.134	.528	.110	.649	.090
Heptachlor	.101	.077	.000**	.632	.018*	.319
Methoxychlor	.216	.045	.080	.243	.051	.268
α -Endosulfan	.464	.016	.288	.160	.721	.078
β -Endosulfan	.020*	.149	.001**	.447	.001**	.447
Endrin aldehyde	.013*	.167	.031	.293	.022	.310
Σ Endosulfan	.002**	.002	.001**	.001	.000**	.000
Σ Xyclor	.248	.248	.461	.461	.508	.508
Σ OCP	.576	.009	.001**	.001	.011*	.011

* $p < 0.05$; ** $p < 0.01$

Table 5 (continued)

Lake	Concentrations (ng/L)					
	4,4-DDE	Endrin	Endosulfan	Endosulfan sulphate	Heptachlor	Methoxychlor
Vergoritida, Greece ^g	n.d.	n.d.	n.d.—12	n.d.—39	n.d.—20	n.d.
L. Prespa, Greece ^g	n.d.	n.d.	n.d.	n.d.—19	n.d.	n.d.
S. Prespa, Greece ^g	n.d.—12	n.d.—21	n.d.—37	n.d.—37	n.d.—10	n.d.
Victoria Basin ^h						
Uluabat, Turkey ⁱ						
Ramgarh, India ^j	n.d.—2,000,000				n.d.—60,000	
Tighara, India ^k		0–8.06			0–3.06	

Item in parentheses: Mean ± SD

n.d. = not detected

^aThis study^bYamashita et al. (2000)^cDarko et al. (2008)^dIwata et al. (1995)^eCaldas et al. (1999)^fDai et al. (2011)^gGolfinopoulos et al. (2003)^hNyangababo et al. (2005)ⁱBarlas et al. (2006)^jGupta et al. (2016)^kMamta et al. (2015)

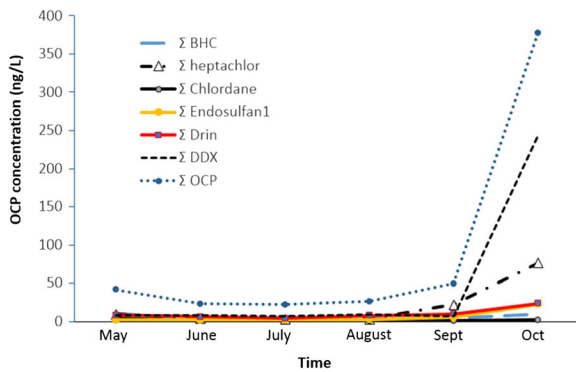


Fig. 3 Variation in total OCP residues over month ($n = 47$)

and HCH was observed in Cameron Highland with higher values detected during the wet season, associated with surface run-off from plantation areas (Abdullah et al. 2015). In this study, both 4,4-DDE and 4,4-DDD were only detected at two sites near the river in October while α -endosulfan residues were found in August 2016. Both 4,4-DDE and 4,4-DDD are metabolites of 4,4-DDT. The presence of 4,4-DDE and 4,4-DDD at site S7 indicates the breakdown or transformation of 4,4-DDT by microorganisms to more stable compounds, namely 4,4-DDE and 4,4-DDD. The DDE/DDT ratio may indicate fresh occurrence of DDT in the environment. The presence of 4,4-DDT was detected only twice in S2. In both cases, no concentration of 4,4-DDE or 4,4-DDD was detected in the same samples, suggesting the potential fresh input of 4,4-DDT into the stream. DDT has been widely used in the past as an insecticide for pest control in agricultural crops and an insecticide for malaria control. The presence of a high concentration of DDT in this study suggests that probably the compound is still in use within the lake basin. Similar temporal variation of OCP in water was reported in Ramgarh water reservoir in India with a maximum concentration of 4,4-DDT reported in October (Gupta et al. 2016). Temporal variation of OCP residues, such as endosulfan and endrin, was also observed in Tighra reservoir in India (Mamta et al. 2015). Endosulfan and 4,4-DDT residues were highest during the winter season while dieldrin residue was highest in summer and pre-monsoon seasons (Mamta et al. 2015). In this study, interactive effects of site and time showed significant differences for heptachlor, α -BHC and β -endosulfan ($p < 0.05$). This implies possible application of different pesticides at different sites in different months.

Relationship of OCP residues with physico-chemical parameters

Temperature, pH, dissolved oxygen, DOC, TP and iron concentration vary between sites ($p < 0.05$). The lake site has higher temperature, DO, pH and DOC and lower TP and iron concentration compared to the river. In this study, strong correlation was found between total OCP and DOC consistent with other findings (Iwata et al. 1995; Cai et al. 2014). In terms of individual OCP, only endrin, heptachlor and methoxychlor were correlated to DOC. Both endrin and methoxychlor were correlated to temperature, pH and DO concentration. While γ -BHC and α -endosulfan were correlated to manganese, both 4,4-DDT and β -BHC residues were correlated to TP. No correlations were observed between all the OCP concentrations and iron. Only β -BHC was correlated to TSS. Strong correlations have been observed between OCP residues and DOC, TOC and TSS in other studies implying contribution of erosion and transport of soil attached pesticides (Iwata et al. 1995). This relationship was not clearly shown in this study. OCP residues showed a different trend with lake depth, with aldrin, endrin and heptachlor concentrations being high near lake bottom compared to near surface level, but the mean differences were not statistically significant ($p > 0.05$). Similarly, endosulfan sulphate residues were only detected near the lake bottom. Pesticides could accumulate and reside near sediment; however, hydrodynamic mixing and transport may influence their distribution in the water column.

Organochlorine pesticides were reported to have a shorter half-life in the tropics than in temperate areas, due to variation in soil types, ecology and climatological conditions (Wandiga 2001). Heavier rainfall amount and sandy soil condition in the tropics can promote soil erosion in open and agricultural areas and subsequently the transport of soil containing pesticide run-off from the areas to streams and water bodies. The bioaccumulation of OCP residues in water threatens the aquatic ecosystem and humans. OCP residues in the water may be consumed by aquatic life such as fishes, and other animals including livestock, thus posing risks to humans that depends on the aquatic food source and farm animals. Additionally, Sembrong Lake has served as a water supply reservoir for a population of more than 100,000 over the past 20 years. In this study, we found pesticide residues to be reasonably high near the water intake point. Trace concentrations of OCPs still pose

risks to human if accumulated. In our random sampling of the treated pipe water, we also found OCP residues such as aldrin, 4,4-DDT, heptachlor, methoxychlor and β -BHC in tap water. The values of β -BHC residues were highest in the tap water compared to any other samples (~ 67.4 ng/L). This indicates that pesticide residues remain in the water distribution system despite treatment and poses a risk to the human population. Similar OCP residues in the distribution system were detected in the tap water of Brinchang town in Malaysia, which utilises river water downstream of agriculture areas (Abdullah et al. 2015). A few studies have shown that removal of some endocrine disrupting contaminants such as pesticides by conventional treatment system were inadequate, and removal efficiencies for the pesticides varied with individual or combination of treatment methods (Petrovic et al. 2003; Donald et al. 2007; Ormad et al. 2008). Monitoring of OCP residues needs to be performed in all water bodies, in particular the water supply reservoirs, to enable informed decision-making in preventing and controlling any illegal uses of the substances within the lake basin and protecting the whole aquatic ecosystem and humans. For Sembrong Lake, in particular, an educational program on pesticides needs to be introduced to farmers within the lake catchment to create awareness of the threats and risks of pesticide application to consumers and the environment. Other measures that can be considered to minimise OCPs risks to the whole ecosystem include (i) adopting more environmental friendly agricultural activities such as organic farming, (ii) widening and enforcing the lake reserve and buffer zone and/or (iii) relocating mixed farming activities away from the lake shore.

Conclusion

This study documents the spatial and temporal distribution of OCP residues in the Sembrong Lake Basin in Malaysia. The findings of this study indicate the presence of OCP pesticides in the stream and lake. Total OCP concentration in the water ranged from 5.7 to 346.45 ng/L. The primary OCPs detected were 4,4-DDT, aldrin, endrin, endosulfan, methoxychlor and heptachlor. Spatial variation of OCP residues in different sites indicates a range of different agricultural practices within the area. Roughly half of the 25% detection of a low α/γ ratio and the entire 17% detection of low DDE/DDT suggest new inputs of pesticides in the areas.

Concentrations of 4,4-DDE varied between sites while β -endosulfan and heptachlor residues varied between months ($p < 0.01$). Significant interactive effect of sites and month was observed in β -endosulfan residues. Detection of OCP residues also varied temporally, indicating effects of different pesticide application timing or seasonal rainfall patterns and soil exposure. The presence of pesticide residues in tap water indicates contamination and persistence of residues that pose human health risks for the nearby population.

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