Assessment of endocrine disruptors – DDTs and DEHP (plasticizer) in source water: a case study from Selangor, Malaysia

Santhi Armugam Veerasingam and Mustafa Ali Mohd

ABSTRACT

The presence of endocrine disruptors in source water is of great concern because of their suspected adverse effects on humans, even when present at very low levels. As the main source of potable water supply, rivers in Malaysia are highly susceptible to contamination by various endocrine disruptors originating from anthropogenic activities. In this study, the contamination levels of 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane (DDT) and its metabolites and di-(2-ethylhexyl) phthalate (DEHP) in rivers of Selangor were examined using gas chromatography–mass spectrometry. Samples were collected from sites representing source water for 18 drinking water treatment plants in Selangor between July 2008 and July 2009. DDT and its metabolites were detected in only 14% of the 192 samples analysed at levels ranging from 0.6 to 14.6 ng/L. Meanwhile DEHP was detected in 96.8% of the samples at levels ranging from below quantitation level (18 ng/L) to 970 ng/L. The detected levels of DDTs and DEHP were lower than the WHO and Malaysian Guidelines for Drinking Water Quality. Data obtained from this study should also serve as a reference point for future surveillance on these endocrine disruptors.

Key words | DDT, DEHP, endocrine disruptor, gas chromatography/mass spectrometry, river water, water and health

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INTRODUCTION

Interest in the public health effects of endocrine disrupting chemicals with regard to the effects of long-term low-dose exposures is increasing. The United States Environmental Protection Agency defines these chemicals as agents that interfere with the synthesis, secretion, transport, binding, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behaviour (Kavlock *et al.* 1996). A number of pesticides, plasticisers, alkylphenols and flame retardants used in agriculture, industrial and household applications have been identified as endocrine disruptors. Many of these end up in the aquatic environment, including source water, as a result of incomplete removal during sewage treatment processes, soil run-off or indiscriminate discharges into waterways. Additionally, conventional drinking water treatment processes that include coagulation and flocculation, sedimentation, filtration and chlorination are not able to eliminate many of these contaminants present in source water (Westerhoff *et al.* 2005; Gibs *et al.* 2007; Kim *et al.* 2007; Schenck *et al.* 2012). Recent studies have also shown the presence of many endocrine disruptors in drinking water (Kuch & Ballschmiter 2001; Boyd *et al.* 2003; Sodre *et al.* 2010). For example, a survey on drinking water from Kuwait found 28.5% of the 568 samples contained the endocrine disruptor di-(2-ethylhexyl) phthalate (DEHP) at an average level of 270 ng/L (Al-Mudhaf *et al.* 2009).

Malaysia is situated in Southeast Asia and covers an area of 329,758 km^2. Over the last century, Malaysia has seen great changes in its natural landscapes as land has been deforested to make way for rubber and oil palm plantations. This, in turn, saw the use of vast amounts of pesticides,

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including the banned organochlorine pesticides. Technical DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane), which consists mainly of *p,p′*-DDT (65–80%) and *o,p′*-DDT (15–21%), was one of the most widely used pesticides in Malaysia before being discontinued in 1998. Furthermore in 2002, Malaysia, as a signatory to the Stockholm Convention under the United Nations Environment Programme, implemented measures to reduce and eliminate the release of persistent organic pollutants into the environment. This included the import, export and use of DDT. However, because of its persistence, it is still detected in various compartments of the environment such as water, sediment and biota (Zakaria *et al.* 2003; Leong *et al.* 2007; Santhi *et al.* 2012; Santhi & Mustafa 2013).

Subsequently, in the last few decades, great tracts of agriculture land were developed to accommodate the development policy involved in becoming a middle-income country. Based on this policy, manufacturing activity became highly ranked in relation to national income. However, industrial and urban activities released vast amounts of organic contaminants into the receiving rivers. DEHP is an industrial chemical widely used in the manufacture of polyvinyl chloride (PVC) products to impart flexibility and durability. It is also found in medical devices, household items and toys. The total turnover of the plastics industry in Malaysia was around US$ 3.8 billion in 2005 (MPA 2005). Since DEHP is not chemically bonded to the matrix, it is easily released into the environment during production or manufacturing (Staples *et al.* 1997). Domestic and industrial wastewaters are important sources of DEHP in the environment including the receiving surface waters (Lin *et al.* 2009; Deblonde *et al.* 2011).

Both DDT and DEHP are known endocrine disruptors and have been identified as priority pollutants by the European Water Framework Directive and US Environment Protection Agency. DEHP has been shown to adversely affect the reproductive and developmental systems (Howdeshell *et al.* 2008; Lyche *et al.* 2009; Uren-Webster *et al.* 2010; Abdul-Ghani *et al.* 2012) with biological effects occurring at the low ng/L to μg/L levels in sensitive molluscs, amphibians and crustaceans (Oehlmann *et al.* 2009). Shi *et al.* (2012) suggested that observed thyroid hormone antagonist activities in water from the Yangtze River were due to the high concentrations of DEHP and di-butyl phthalate. DEHP is also suspected of having teratogenic effects as it induces gross malformations, damage to vital organs and imprinting deficits in chick models (Abdul-Ghani *et al.* 2012). DEHP was classified as a Group 2B substance, a possible human carcinogen by the International Agency for Research on Cancer (Rusyn & Corton 2012). In addition, a study conducted by Pant *et al.* (2008) suggests DEHP might contribute to deteriorating semen quality in men.

Meanwhile, DDT and its metabolites, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), were found to affect the adult ovary and uterine functions through either independent or dependent oestrogen-receptor-mediated pathways (Tiemann 2008). Vitellogenesis, a process whereby yolky eggs are normally produced in females in response to oestrogens, was induced by *o,p′*-DDT in mature male tilapia (Leanos-Castaneda *et al.* 2007). Similarly *p,p′*-DDE elevated the gene expressions of vitellogenins and an oestrogen receptor in Japanese medaka (Zhang & Hu 2008). In recent years, DDT has been associated with pancreatic cancer, adverse birth outcomes and neuropsychological disorders in humans (Beard 2006).

Rivers account for almost all the potable water supply for the 29 million inhabitants in Malaysia. Most Malaysians have access to drinking water that is bacteriologically safe and free from inorganic contaminants. However, there have been few or no data available on endocrine disruptors in source or drinking water. Although a guideline value is set for DEHP in the Malaysian Drinking Water Quality Guidelines, it is currently not monitored while data on DDT are not widely available. As an integral part of preventive management of drinking water is to identify the contaminants found in source water, this study aims to assess the levels of DDTs (DDT and metabolites) and DEHP in source water abstracted by the conventional drinking water treatment plants (DWTPs) in Selangor. Moreover, we investigated the sources of DEHP pollution in an urban catchment area.

METHODS

Study area and sample collection

Selangor is the most urbanised and populated state in Malaysia with a population of 5.2 million in 2010. It

contributed the highest percentage share (22.1%) of the national GDP in 2008, mostly from agriculture and manufacturing activities. Water for the state is provided from surface water by direct abstraction from rivers or from impounding reservoirs. The major riverine systems in the state are the Langat, Bernam, Selangor, Buloh, Kelang and Tengi, providing water for the needs of the state, the administrative capital Putrajaya and the federal capital Kuala Lumpur.

In this study, 18 sites representing intakes of DWTPs from five river basins were selected (Figure 1(a) and Table 1). The samples from each site represent the quality of source water abstracted by the DWTPs. All the samples were collected with the assistance of various district health staff as they have access to the restricted area where the sampling sites are located. These staff are involved in their departmental water quality surveillance programme and have sufficient training in sample collection and in using *in situ* measuring equipment. Sample collection for the pesticide analysis took place from July 2008 to July 2009, mostly on a monthly basis while sampling for DEHP analysis took place from September 2008 until July 2009. No sampling was carried out in October 2008 and samples were not collected from sites 8, 12, 13 and 15 to 18 in March 2009 due to unavailability of district health staff. In addition, sampling at site 4 was stopped in early 2009 due to difficulty in sample collection. Also sampling at site 7 and site 14 was stopped from January 2009 to April 2009 and from November 2008 to May 2009, respectively, due to shut down of the respective DWTPs, thus cutting off access to the sampling sites. Overall, a total of 192 and 148 samples were collected for DDT and DEHP analysis, respectively.

Grab samples were collected in solvent-cleaned 1 L amber glass bottles. The bottles were rinsed with sample water prior to filling and closed with aluminium-foil-lined caps. They were preserved from microbial activity by acidification with nitric acid. *In situ* measurements of pH, temperature and turbidity were also recorded.

Point source pollution sampling

Sampling to identify DEHP pollution point sources was carried out at eight sites in the urban catchment area of Salak Tinggi DWTP (Figure 1(b)). This DWTP has experienced frequent shut-downs due to poor quality of source water (PNSB 2010). While the surrounding area is mostly given over to agriculture, there are many industries, townships and housing estates upstream of this DWTP. Samples were collected downstream of Nilai Industrial Estate (sample 1), at outlets of sewage treatment plants (sample 2, 3 and 4), downstream from a wet market (sample 5), from an irrigation drain (sample 6), downstream of the Batang Labu River (sample 7) and near to Salak Tinggi DWTP intake (sample 8). In addition to the *in situ* measurements of pH, turbidity, temperature, measurements of dissolved oxygen were recorded using a Hach Oximeter. All the samples were transported to the laboratory in a cool box at 4 °C and filtered with Whatman GF/B (1.0 μm) and GF/F (0.7 μm) glass fibre filters to remove suspended particulate matter. They were then stored in the dark at 4 °C and analysed within 48 hours of collection.

Reagents and standards

Pure standards of *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDT and *o,p′*-DDT were purchased from Supelco (Bellefonte, USA) and standards of *p,p′*-DDD and *o,p′*-DDD were obtained from Sigma-Aldrich (Germany). Internal standards benzyl benzoateandchrysene-d_{12} were from Supelco and surrogate ^{13}C-*p,p′*-DDT was from Dr Ehrenstorfer (Germany). Stock solutions of 100 mg/L standards were prepared in methanol and stored at –20 °C. Working standards at different concentrations were prepared daily.

The solvents (methanol, acetone, hexane) used were Merck gas chromatography (GC) grade (Darmstadt, Germany) and were further distilled in all-glass apparatus prior to use. Ethyl acetate and dichloromethane were pesticide grade from Fisher Scientific (UK) and were used as supplied. Sodium sulphate, sodium chloride and nitric acid were from Merck (Darmstadt, Germany).

The glassware for DEHP analysis was initially rinsed with Milli-Q water and baked at 400 °C for 5 hours. Before use, it was further rinsed with 2 mL of hexane:acetone (1:1). The glass fibre filters were also rinsed in acetone and baked at 400 °C for 4 hours. Silica-based bonded C18 (EC) 1 g/6 mL cartridges were obtained from Biotage (EU). 'Sole' brand mineral water from Italy was used for DEHP method validation and preparation of the calibration curve.

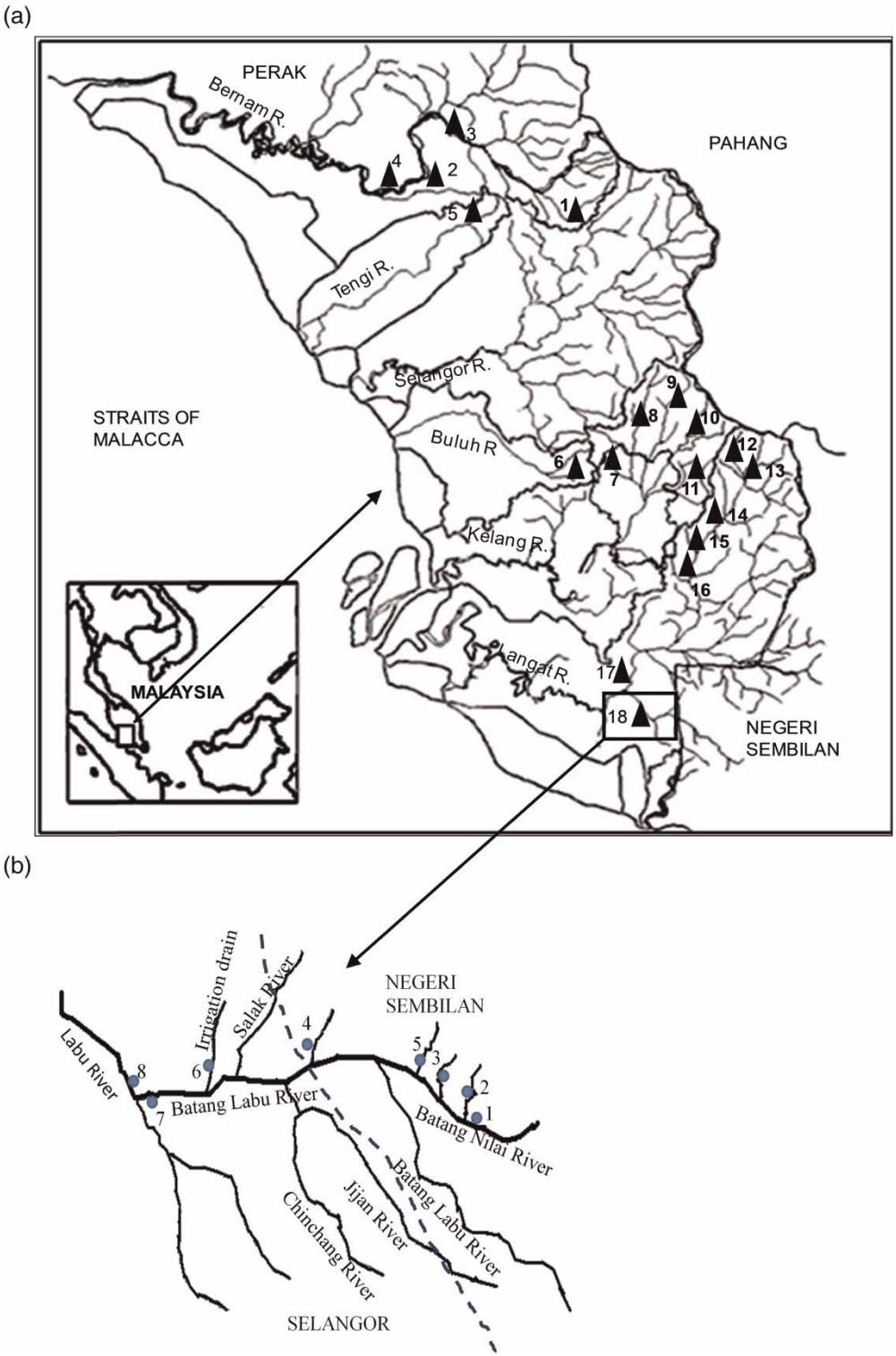

Figure 1 | (a) Location of the sampling sites. Samples 1–4 were from Bernam River and its tributaries (Bernam River basin); samples 5 and 6 from Tengi River and Buloh River, respectively; samples 7–11 from Kelang River and its tributaries (Kelang River basin); samples 12–18 from Langat River and its tributaries (Langat River basin). (b) Location of sampling sites for point source pollution sources.

Table 1 | Drinking water treatment plants (DWTPs) and description of sampling sites

Site	DWTP	Description	Site	DWTP	Description
1	Kalumpang	Agricultural activity in surrounding area	10	Gombak	Located in a valley, recreation activities, vegetable farming further upstream, nearby Kuala Lumpur-Karak highway
2	Selisek	Agricultural activity in surrounding area	11	Ampang intake	Forest reserve, recreational activity
3	Dusun	Agricultural and sand mining activities in surrounding area	12	Lolo	No agriculture, industrial or human settlements nearby
4	Bernam River Head	Agricultural and sand mining activities in surrounding area	13	Pangsoon	No agriculture, industrial or human settlements nearby
5	Tengi	Pristine location	14	Serai	Land clearing activity upstream
6	Kepong	Pristine location, indigenous people foraging and hunting nearby	15	Langat	Agricultural, industrial and land clearing activities in surrounding area, human settlements and domestic waste dumping site upstream
7	Keroh	Forest reserve	16	Cheras	Townships, industrial, sand mining and agricultural activities in surrounding area
8	Sg.Batu	Water recreation activities upstream	17	Bukit Tampoi	Townships, industrial, sand mining and agricultural activities in surrounding area
9	Rumput	Pristine location	18	Salak Tinggi	Surrounded by oil palm plantations, industrial activities and township further upstream

Sample extraction

Sample extraction for DDT and DEHP was as previously described in Santhi & Mustafa (2013). Briefly, for the extraction of DDTs and its metabolites, 500 mL of sample was extracted twice with 50 mL ethyl acetate:dichloromethane mixture (1:1). The combined organic phase was then dried by passing through anhydrous sodium sulphate and concentrated to 3–5 mL in a rotary evaporator. It was further dried under a gentle stream of nitrogen. The sample was reconstituted in 150 μL of hexane and 10 μL of 1 μg/mL internal standard chrysene-d_{12}. Two microlitres of sample was injected into the gas chromatograph–mass spectrometer (GC–MS) for analysis.

For the extraction of DEHP, 1 L of sample was spiked with 50 ng internal standard benzyl benzoate before passing through the conditioned C18 cartridge. The cartridge was conditioned by passing 6 mL of acetone: hexane (1:1), followed by 10 mL of methanol and 10 mL of water. Elution was performed with 4×2.5 mL of acetone:hexane (1:1). The eluants were dried under a gentle stream of nitrogen and prior to analysis, reconstituted with 100 μL of acetone: hexane (1:1). Since DEHP was extracted and analysed together with alkylphenols and bisphenol A, the samples were derivatised before injection. For derivatisation, 20 μL of BSTFA + 1% TMS was added to the solution before being derivatised at 75 °C for 40 minutes. One microlitre was injected into the GC–MS for analysis.

Gas chromatography–mass spectrometry conditions

Determination of the studied compounds was achieved using a Shimadzu QP-2010 GC–MS coupled with an auto sampler (AOC-20S Shimadzu) and equipped with a SGE BP-1(Australia) capillary column (length: 30 m; i.d: 0.25 mm; film thickness: 0.25 μm). Identification was based on retention time and relative intensities of quantification and confirmation ions. Quantitative analysis was carried out in selected ion monitoring mode using internal standard calibration. Analytical conditions are shown in Table 2.

Quality assurance and quality control

Since DEHP is a ubiquitous contaminant in the environment, rigorous contamination control measures were taken during sample collection, extraction and analysis. For each batch of samples, a blank using mineral water (procedural blank), spiked blank and duplicate samples were included.

Table 2 | Analytical conditions for GC–MS analysis of the target compounds

Compound	DDTs and metabolites	DEHP
Column	ZB-1 (30 m × 0.25 mm × 0.25 μm)	ZB-1 (30 m × 0.25 mm × 0.25 μm)
Temperature programme	70 °C (hold 1 min), 20 °C/min to 160 °C, 2 °C/min to 190 °C, 15 °C/min to 320 °C (hold 5 min)	80 °C (hold 1 min), 15 °C/min to 250 °C, 30 °C/min to 300 °C (hold 7 min)
Injection port	250 °C	280 °C
Detector	270 °C	300 °C
Carrier gas	Nitrogen	Nitrogen
Flow rate	2.25 mL/min	1.45 mL/min

The limit of detection for DDT and its metabolites was from 0.2 to 0.9 ng/L and for DEHP was set at 6 ng/L. Linearity, recoveries, detection and limits of quantification (LOQs) are shown in Table 3.

Statistical analysis

All analysis was carried out using Statistical Package for Social Sciences (SPSS) for Windows, Version 15.0 (SPSS Inc., Chicago, IL, USA). Descriptive statistics provided the mean, median, standard deviation and range. Samples with levels below detection limits were set to zero. Samples with levels below the LOQ were not quantified when calculating DDTs (DDTs, including *o,p′*-, *p,p′*-DDT, DDD and DDE). Prior to analysis, data were checked for homogeneity. The concentrations in different classes of water were compared using analysis of variance (ANOVA) where statistical significance was accepted at $p < 0.05$. In order to understand seasonal variations of the contaminant levels, the collected samples were grouped into rainy season (September, November and December 2008, and April and May 2009) and dry season (July and August 2008 and January, February, March, June and July 2009).

RESULTS AND DISCUSSION

DDT level in source water

There were limited data on the contamination level of DDT and its metabolites in Malaysian rivers and practically no data for its contamination levels in source water. The numbers of samples with detectable levels of DDTs were as follows: *o,p*-DDD (10), *p,p*-DDD (9), *o,p*-DDE (1), *p,p*-DDE

Table 3 | Extraction parameters correlation coefficient, percentage mean recovery ($n = 3$) and relative standard deviation (RSD; in parentheses), detection limit (LOD) and quantification limit (LOQ) for the target compounds

		Mean recovery (RSD)				
Compound	Correlation coefficient, R^2	QC 1[a]	QC 2[b]	QC 3[c]	LOD (ng/L)	LOQ (ng/L)
o,p′- DDD	0.9996	104 (3.9)	91 (3.4)	111 (6.1)	0.2	0.6
p,p′- DDD	0.9999	99 (6.1)	102 (13.6)	102 (6.7)	0.3	0.9
o,p′- DDE	0.9960	95 (4.9)	99 (6.0)	98 (6.6)	0.3	0.9
p,p′- DDE	0.9969	102 (7.8)	107 (6.8)	111 (5.1)	0.9	2.7
o,p′- DDT	0.9976	95 (4.4)	103 (14.3)	102 (6.7)	0.3	0.9
p,p′- DDT	0.9928	88 (10.4)	100 (10.0)	101 (8.5)	0.3	0.9
DEHP	0.9963	86 (4.2)	86 (3.7)	88 (12.3)	6.0	18

QC: quality control.
[a]QC 1 = 20 ng/L for DEHP and 20 ng/L for DDT and metabolites.
[b]QC 2 = 200 ng/L for DEHP and 50 ng/L for DDT and metabolites.
[c]QC 3 = 1,000 ng/L for DEHP and 75 ng/L for DDT and metabolites.

(11), *o,p*-DDT (5) and *p,p*-DDT (12). Although 11 samples had detectable level of *p,p′*-DDE, 10 samples were not quantifiable (<LOQ). DDTs (DDTs, including *o,p′*-, *p,p′*-DDT, DDD and DDE) were detected in 27 out of 192 samples (14%) at levels ranging from 0.6 to 14.6 ng/L (Table 4). Twelve percent of source water samples from the Bernam River basin (sites 1–4) had detectable levels of DDTs. The highest levels were also detected in this basin at sites 2 and 4 representing Selisek and Bernam River Head DWTP, respectively. Previously, Tan & Vijayaletchumy (1994) reported the level of *p,p′*-DDE and *p,p′*-DDT to be 190 ng/L in the Bernam River. Meanwhile, 18% of source water for the DWTPs located in the Kelang River basin (sites 7–11) had DDTs ranging from 0.6 to 12.2 ng/L. These sites are located upstream, mostly at pristine locations or in forest reserves with limited agriculture activities except for site 10. The detected levels were similar to the 9.5 ng/L detected previously in the Klang River (Tan & Vijayaletchumy 1994). In addition, only 10% of samples collected from the seven sampling sites (site 12–18) in the Langat River basin had DDTs at levels ranging from 2.8 to 9.2 ng/L. Site 18 (Salak Tinggi DWTP), which is surrounded by palm oil plantations, had the highest frequency of detection while no DDT residues were detected at sites 13 and 14.

Results from this study shows that DDTs are still detected in some source water albeit at decreased levels. However, no cumulative effect is seen in the levels detected along the main rivers of Bernam, Kelang and Langat. In addition, while all three sites with no detectable level of DDTs are located in a pristine area or forest reserve, not all sites located at pristine locations were free of DDTs. Similarly, in a study by Leong *et al.* (2007), DDTs were detected at sites far from agricultural or industrial activities in the Selangor River basin, most likely due to past fumigation activities for vector control.

DEHP level in source water

Detection frequency and a summary of the measured levels of DEHP at each sampling sites are shown in Table 5.

Table 4 | Detection frequency and range of the detected DDTs at each sampling site

Sampling site	*o,p′*-DDD	*p,p′*-DDD	*o,p′*-DDE	*p,p′*-DDE	*o,p′*-DDT	*p,p′*-DDT	Samples detected (%)	Range of detected DDTs
1	ND	ND	ND	ND	1	ND	1/12(8)	1.4
2	2	1	ND	2	ND	1	3/12(25)	3.6–12.6
3	ND	1	ND	ND	1	1	1/12(8)	13.0
4	1	1	ND	1	1	1	1/6(17)	15.8
5	ND	2	ND	1	1	ND	3/12(25)	1.6–8.2
6	1	1	ND	2	ND	ND	3/12(25)	1.6–3.6
7	ND	ND	ND	ND	ND	ND	0/8(0)	ND
8	ND	1	ND	ND	ND	ND	1/11(9)	2.6
9	1	ND	1	ND	ND	1	3/12(25)	1.0–5.8
10	2	2	ND	1	ND	2	4/12(33)	0.6–12.2
11	1	ND	ND	1	1	ND	2/12(17)	2.2–3.2
12	ND	ND	ND	1	ND	1	1/11(9)	9.2
13	ND	ND	ND	ND	ND	ND	0/11(0)	ND
14	ND	ND	ND	ND	ND	ND	0/6(0)	ND
15	1	ND	ND	ND	ND	2	2/11(18)	5.8–8.2
16	ND	ND	ND	1	ND	ND	1/11(9)	2.8
17	ND	ND	ND	1	ND	ND	1/10(10)	<LOQ
18	1	ND	ND	ND	ND	3	4/11(36)	3.8–5.6

[a]DDTs = *o,p′*-DDD + *p,p′*-DDD + *o,p′*-DDE + *p,p′*-DDE + *o,p′*-DDT + *p,p′*-DDT.
<LOQ = below quantification level (LOQ for *p,p′*-DDE = 2.7 ng/L).
ND = not detected or less than detection limit (LOD); LOD for *o,p′*-DDD (0.2 ng/L), *p,p′*-DDD (0.3 ng/L), *o,p′*-DDE (0.3 ng/L), *p,p′*-DDE (0.9 ng/L), *o,p′*-DDT (0.3 ng/L), *p,p′*-DDT (0.3 ng/L).

Table 5 | Summary of water quality index (WQI), number of samples collected, frequency of detection, mean, median and range of DEHP level detected at each sampling site

Site	WQI[a]	Total samples	Detected (%)	Mean	Median	Range
1	I	9	8 (89)	64.2	<18.0	ND–296.6
2	II	7	7 (100)	118.3	20.0	<18.0–364.9
3	II	9	8 (89)	61.7	64.9	ND–207.7
4	III	4	4 (100)	251.5	273.8	125.9–332.3
5	II	7	6 (86)	19.5	<18.0	ND–48.6
6	I	10	9 (90)	97.7	84.9	ND–309.2
7	I	6	6 (100)	191.6	172.5	34.0–371.8
8	II	9	9 (100)	52.9	45.0	<18.0–130.5
9	II	10	10 (100)	155.3	134.9	<18.0–345.2
10	II	10	10 (100)	90.7	77.4	<18.0–164.2
11	I	10	10 (100)	82.7	99.5	<18.0–172.1
12	I	9	8 (89)	57.0	19.0	ND–172.0
13	I	9	9 (100)	66.4	45.5	<18.0–267.7
14	1	4	4 (100)	120.8	75.6	<18.0–319.8
15	II	9	9 (100)	217.5	146.9	43.9–537.9
16	III	9	9 (100)	224.8	179.5	52.5–552.5
17	III	8	8 (100)	286.7	271.5	81.8–595.5
18	III	9	9 (100)	389.6	363.0	<18.0–970.0

ND = not detected or less than detection limit (LOD = 6 ng/L).
Quantification limit (LOQ) = 18 ng/L.
[a]Data were obtained from PNSB (2009).

DEHP was detected in 96.8% of 142 samples including 18 samples with levels below quantification level (LOQ = 18 ng/L) indicating it is a ubiquitous contaminant in surface water. The detected levels ranged from <18.0 to 970 ng/L. Repeated sampling showed a clear difference in the levels detected between the sites with an increasing trend from rural sites (upstream) to urban sites located downstream. For example, samples collected downstream of the Langat River at sites 15, 16 and 17 had increasing levels of DEHP (Figure 2). This increasing trend is probably due to the influx of tributaries as well as to the increase in the number of pollution sources located downstream. Historically, the early settlements, such as the capital Kuala Lumpur, were located downstream of major rivers as waterways were an important route for transportation. The highest level of DEHP was detected at site 18 (970 ng/L), representing source water for the Salak Tinggi DWTP located at the Labu River, an important tributary of the Langat River. The Nilai Industrial Estate, which is located further upstream of site 18, in addition to the numerous housing estates and its sewage treatment plants, most likely contributed to the high levels of DEHP detected here.

Levels of DEHP detected during the dry and rainy months were not significantly different, although lower levels were expected during the rainy months due to dilution effect. DEHP levels detected during the dry and rainy months ranged from not detected (ND) to 970 ng/L (155.6 ± 174.90 ng/L) and from ND to 595.5 ng/L (123.3 ± 143.65 ng/L), respectively. In Malaysia, storm water, similar to sullage water is normally drained by a series of drains, which eventually ends in the riverine system without any treatment. DEHP at levels up to 5,000 ng/L was previously detected in urban storm water from a high density traffic area in Sweden (Bjorklund *et al.* 2009). Detection of DEHP at pristine sites 5 and 9 although at lower levels, also suggests other sources of DEHP beside anthropogenic activities. In a study by Xie *et al.* (2005) on air-sea exchanges of phthalates in the North Sea, the average air-sea exchange flux for DEHP was +53 ng/m^2/day indicating net volatilisation of DEHP

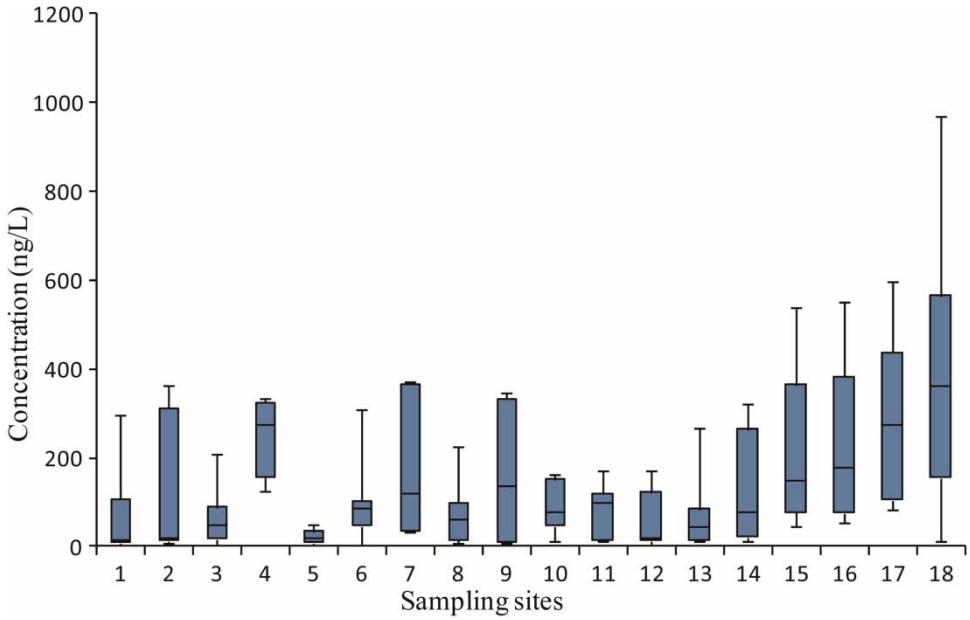

Figure 2 | Box plots for levels of DEHP detected at each sampling site during the study period. The line within the box is the median level while the upper and lower boundaries of each box represent 75th and 25th percentiles. The whiskers represent the maximum and minimum level.

from the sea. This suggests that the atmosphere is also a major contamination source of DEHP to the aquatic phase through dry deposition by descending particles and wet deposition by rainfall or snow.

The environmental fate and behaviour of DEHP is partly dependent on its water solubility and adsorption coefficient (log K_{oc}). Low water solubility with a high log K_{oc} will promote DEHP adsorption and transport together with suspended sediment (Zeng *et al.* 2009). The association between DEHP levels and suspended solid was investigated using turbidity measurements. Turbidity is strongly correlated to suspended solid: a high level of turbidity is indicative of a high level of suspended sediment (Cinque & Jayasuriya 2010; Huey & Meyer 2010). Although DEHP is suggested to be released from resuspended sediment during heavy rain, a clear correlation was ND between DEHP levels and water turbidity in this study.

Levels of DEHP based on DOE classification of river water quality

The Malaysian Department of Environment (DOE) classifies the quality of river water based on its usefulness using six parameters. These are total suspended solids, biochemical oxygen demand, chemical oxygen demand, dissolved oxygen, pH and ammoniacal nitrogen. Each of these parameters is given a weighting which is then used to derive the water quality index (WQI). Water with a WQI >92.7 is classified as Class I, 76.5–92.7 as Class II, 51.9–76.5 as Class III and 31.0–51.9 as Class IV. While Class I is pristine water and practically needs no treatment for potable use, Class IV is suitable for irrigation only. Both Class II and III water are suitable as potable water supply with conventional and extensive treatment, respectively. Level of DEHP in Class I, II and III water ranged from ND to 371.8 (mean: 55 ng/L), ND to 537.9 (mean: 71 ng/L) and <LOQ to 970.0 ng/L (mean: 253 ng/L) respectively. There was a statistically significant difference in DEHP level between Class I and Class II with Class III water suggesting some agreement in the degree of DEHP contamination with DOE classification.

Pollution sources of DEHP

As indicated in Figure 1(b), samples for point source pollution detection were collected from tributaries of the Labu River in the Langat River basin. The Langat River is one of the most important basins in Selangor providing

Table 6 | Basic water parameters and DEHP levels for point source pollution sources

Site	pH	Turbidity (NTU)	Dissolved oxygen (mg/L)	Temperature (°C)	DEHP (ng/L)
1	7.05	26	5.5	27.1	9,740
2	6.94	19	3.8	27.6	1,410
3	7.04	22	3.5	28.1	475
4	6.97	24	5.1	29.7	128
5	7.00	15	3.7	27.6	837
6	6 .86	14	6.3	29.5	404
7	6.98	85	3.5	29.7	179
8	6.95	94	3.0	29.7	58

NTU = nephelometric turbidity units.

raw water for potable use, agriculture, recreation, industries and fisheries. Agriculture occupies 53.1% of the land area in the basin while another 3.6% is used for commercial activities (Juahir *et al.* 2008). The sample collected at site 1, which is downstream of Nilai Industrial Estate had the highest DEHP level while samples collected downstream of sewage treatment plants had much lower levels (mean: 671 ± 663 ng/L) (Table 6). In addition, the DEHP level downstream of the wet market (sample 5) was lower than levels detected at site 1. Further down from the pollution sources, levels of DEHP decreased significantly (site 7) and the lowest level was detected near the intake point of Salak Tinggi DWTP (sample 8). The decreasing levels agrees with the findings of Vitali *et al.* (1997) that DEHP is adsorbed on particulate matter a few kilometres downstream of a point of emission with sediment being the final sink.

This preliminary study suggests industries contribute to high levels of DEHP to the river water. Previously it was reported that the sources of pollution in the Langat River were industrial discharges (58%), sewage treatment plants (28%), construction projects (12%) and pig farming (2%) (Khairuddin & Abd Malek 2002). The polluting industries reported in this basin producing plastic and PVC, textiles and electrical items (Osman *et al.* 2012) are highly likely to use the plasticiser DEHP. While effluents from sewage treatment plants also contributed to DEHP contamination in river water, the high *n*-octanol/water partition coefficients (log $K_{ow} = 7.5$) of DEHP suggests it is most likely adsorbed upon suspended matter and removed during the sewage treatment process. Previous studies conducted on waste water treatment process shows its removal efficiency ranging from 78 to 95% (Dargnat *et al.* 2009; Clara *et al.* 2010; Deblonde *et al.* 2011).

Guideline values for DDT and DEHP

Currently, there is no statutory maximum contaminant level for DEHP in source water in Malaysia. However, the acceptable value for DEHP in drinking water in the Malaysian Standard for Drinking Water Quality is set at 8 μg/L, similar to the guideline value established by the World Health Organization (WHO 2011). Meanwhile, the environmental quality standard for DEHP in surface waters under the European Directive 2008/105/EC is 1.3 μg/L. These guideline values were only exceeded in the sample collected near the industrial estate. However, the environmental risk limit derived for DEHP based on ecotoxicology and environmental chemistry data with survival, growth and reproduction endpoints was 190 ng/L (van Wezel *et al.* 2000). DEHP levels detected at many of the more polluted sites downstream were a few-fold higher than this limit. As for DDTs, the detected levels were two magnitudes lower than the maximum acceptable value of 2 μg/L prescribed for source water in the Malaysian Standard for Drinking Water Quality.

Comparison of DEHP level in source water with other water bodies

Levels of DEHP from this study were compared with other reported data from different water bodies (Table 7). DEHP levels detected in source water from this study is similar to the levels detected in urban lakes by Zeng *et al.* (2009) and the Yangtze River by Wang *et al.* (2008) in China, although they were two magnitudes lower than the levels detected in European countries (300–97,800 ng/L) (Fromme *et al.* 2002; Brossa *et al.* 2005; Vethaak *et al.* 2005; Gasperi *et al.* 2009). In addition, the levels detected in this study were much lower than the levels detected previously in the Klang River (Tan 1995). These differences may be attributed to the difference in sampling locations. Samples from the Klang River, for example, were collected

Table 7 | Levels of DEHP in surface water around the world

Location	Year	DEHP (ng/L)	Reference
Selangor	2008–2009	Class I: 55 Class II: 71 Class III: 253	This study
Klang River, Malaysia	1995	16,600	Tan (1995)
Ebre River, Spain	2005	1,940–11,830	Brossa *et al.* (2005)
The Netherlands	1999	<900–5,000	Vethaak *et al.* (2005)
Guangzhou, China	2005	87–630	Zeng *et al.* (2008)
Yangtze River	July 2005	34–456	Wang *et al.* (2008)
Seine River, France	2006–2007	1,000	Gasperi *et al.* (2009)
Rivers, lakes and channels, Germany	1997	330–97,800	Fromme *et al.* (2002)
Rivers, Taiwan	2000	ND–18,500	Yuan *et al.* (2002)

near pollution sources. Overall, the levels detected in this study are similar to the levels reported in weakly impacted surface water elsewhere.

CONCLUSION

This study provided the first detailed data on the levels of DDTs and DEHP in source water from Selangor. Although DDT has been banned since 1998, it is still detected at low levels in the source water. Meanwhile, DEHP was detected in more than 96% of the samples with an increasing trend at sites located further downstream due to the increase in the number of anthropogenic pollution sources. However, no seasonal variation was detected in DEHP levels. Study of point source pollution sources suggests industrial discharges are one of the main contributors of DEHP to the riverine system.

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