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Profiles and removal efficiency of organochlorine pesticides with emphasis on DDTs and HCHs by two different sewage treatment works

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HIGHLIGHTS

- Wastewater treatment processes (WTP) were effective in removing OCPs.
- Secondary WTP were more effective in removing OCPs than primary one.
- Removal of OCPs may not entirely depend on sorption by particulate matter in WTP.

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ABSTRACT

The removal efficiencies of nine organochlorine pesticides (OCPs) were investigated in two sewage treatment works (STWs; Stonecutter Island [SCI] and Shatin [ST]). The levels of OCPs in sewage samples collected from SCI (chemically enhanced primary treatment) and ST (secondary treatment) were determined with gas chromatography–mass spectrometry. The crude sewage in the two STWs generally had low levels of total hexachlorocyclohexane (HCHs; total of alpha-, beta- and gamma-HCH; SCI, 19.4 ± 4.62 ng/L; ST, 12.1 ± 4.27 ng/L) and total dichloro-diphenyl-trichloroethane (DDTs; total of p,p' and o,p'-DDE, -DDD and -DDT; SCI, 6.31 ± 2.83 ng/L; ST, 6.09 ± 1.67 ng/L). High total removal efficiencies for total HCHs (SCI, $79.9 \pm 7.03\%$; ST, $82.5 \pm 2.51\%$) and total DDTs (SCI, $96.1\% \pm 3.37\%$; ST, $99 \pm 0.501\%$) were observed. In particular, ST achieved outstanding performance in the removal of heptachlor ($100\% \pm 0.00\%$), heptachlor epoxide ($94.8 \pm 3.96\%$), hexachloroben-zene ($99.7 \pm 0.387\%$), gamma-HCH ($100 \pm 0.00\%$) and total DDTs ($99.2 \pm 0.644\%$). There was no observable correlation between the removal efficiencies and the log K_{ow} values of individual OCPs, which suggests that the removal mechanisms may not be related to sorption by particulate matter. Removal of OCPs seems to rely more on other mechanisms such as volatilisation, advection and biotransformation. This study is the first to investigate the fate and distribution of OCPs throughout the entire sewage treatment process. The results

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provide valuable reference for potential modification of sewage treatment processes with regard to OCPs.

1. Introduction

Organochlorine pesticides (OCPs) are organic molecules that contain linked chlorine atoms and have high lipophilicity and neurotoxicity (El-Shahawi et al., 2010). They were produced as the second generation of pesticides to replace the first generation of pesticides made in the 1940s from inorganic compounds (sulphur, copper, lead and arsenic) (Chenier, 2002). OCPs like hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), dichloro-diphenyl-trichloroethane (DDT), chlordane, dieldrin, endrin, mirex, heptachlor and adrin have been used globally since the 1950s and have been regarded as effective and low-cost tools to deal with insect-associated problems. For example, DDT was a promising pesticide in agriculture development and disease control to eradicate disease-carrying insects (El-Shahawi et al., 2010). However, OCPs were discovered to be harmful to the environment and to human health due to their chronic toxicity, persistence in the environment, bioaccumulation and biomagnification along the food chain (Colborn et al., 1996; Yu et al., 2008). Like other persistent organic pollutants (POPs), OCPs are toxic and recalcitrant to degradation; they have low water solubility, high fat solubility and low vapour pressure; which results in their bioaccumulation and biomagnification in the ecosystem. OCPs such as DDTs and HCHs were listed amongst the 12 POPs banned by the Stockholm Convention (Stockholm Convention on POPs, 2010). Most industrialised countries have banned or restricted the use of POPs.

China and Hong Kong banned the use of DDTs in 1983 and 1988, respectively, and HCH in 1983 and 1991, respectively (HKWQRC, 2015; Wong et al., 2002). In Hong Kong, most OCPs are used for non-agricultural purposes such as domestic and outdoor pest control (Wong and Poon, 2003). However, OCPs have been detected in air samples collected in residential areas of Yuen Long (186 ± 183 fg m^{-3}) and Tsuen Wan (190 ± 239 fg m^{-3}) in the New Territories (Choi et al., 2009), and inland water sediments and fish (Nile tilapia [*Oreochromis niloticus*]) collected in the Shing Mun River in the New Territories contained DDTs (total of *p,p'*-DDE, -DDD and -DDT; ranging from 2.82 to 8.63 ng/g d.w. for sediments and 28.2 to 40.1 ng/g d.w. for fish) and HCHs (total of alpha-, beta- and gamma-HCH; ranging from 0.05 to 2.07 ng/g d.w. for sediments and 2.04 to 3.76 ng/g d.w. for fish (Zhou et al., 1999). Our recent study detected DDTs (13.8 ± 50.8 ng/g d.w.) and HCHs (6.01 ± 5.42 ng/g d.w.) in existing agricultural soil in Hong Kong, which may be due to atmospheric deposition from the Pearl River Delta (PRD) (Man et al., 2011). It was suggested that anti-fouling paints containing DDT were still used in fishing boats (to prevent attachment of barnacles on boats) in the PRD region. Other potential sources of OCPs include the local use of chlordane as a termiticide for wood, lindane (gamma-HCH) as an insecticide and discofol as a DDT-type pesticide (Li et al., 2007). In addition, sediments under aquaculture zones contained high levels of DDTs (ranging from 9.95 to 44.4 ng/g d.w.) and HCHs (ranging from 5.62 to 20.4 ng/g d.w.) in Hong Kong and South China due to the application of contaminated fish feed (trash fish or feed pellets containing high proportions of fish meal made of trash fish), in addition to the use of DDT-based antifouling paint (Wang et al., 2014). These OCPs in contaminated sediments can be transferred to local seafood and eventually enter human bodies via consumption. Our early study showed that OCPs such as DDTs ($r = 0.89, p < 0.001$) and HCHs ($r = 0.98, p < 0.001$) in human milk collected from both Hong Kong and Guangzhou were significantly correlated with the frequency of fish intake (Wong et al., 2002). Our recent study also demonstrated that levels of OCPs in the blood plasma of local people were significantly correlated with the bio-accessible OCP concentration in fish muscle purchased from local markets ($r^2 = 0.784, p < 0.001$) (Wang et al., 2013). These studies showed that OCPs such as DDTs and HCHs can accumulate and transfer via the food web and eventually end up in our bodies.

Studies on OCPs in China have focused mainly on the documentation of these chemicals in the soils, atmosphere, rivers and bodies of water by analysing the sources and transportation pathways (Cai et al., 2007; Fu et al., 2003; Li et al., 2007; Tao et al., 2004; Xing et al., 2005). It is known that OCPs can be transported long distances and enter the environment through non-point sources such as runoff and vaporisation into the atmosphere after field application (Wang et al., 2007). In theory, sewage treatment systems filter urban and agricultural runoff before contaminants can enter aquatic environments. However, studies have recognised that the effluents of sewage treatment works (STWs) could be a significant source of toxic contaminants (Katsoyiannis and Samara, 2004; Pardos et al., 2004; Pham and Proulx, 1997). The ability of STWs to remove these OCPs was studied by Katsoyiannis and Samara (2004) in Greece, but similar studies from other countries, including China, are limited, although attempts have been made to investigate OCPs in sewage sludge for potential use in soil amendment (Liu et al., 2013; Wang et al., 2007).

The estimated annual use of OCPs in the PRD region, one of China's agricultural hotspots, between 1972 and 1982 was 76,000 to 10,000 t (Hua and Shan, 1996). The OCP load in the Pearl River was the highest in China, up to 863 t per year (Zhou, 1997). It is believed that OCPs are transferred from the PRD to Hong Kong via atmospheric deposition, as indicated above, and via water discharge into the coastal areas. The removal efficiencies of OCPs in STWs in Hong Kong should be quantified. It is hypothesised that different STWs possess different abilities to reduce OCP concentrations in wastewater. This study's objectives were: (1) to determine the removal efficiency of OCPs in two types of STWs; (2) to compare the capabilities of the two STWs in the removal of OCPs based on total, primary, and secondary treatment removal efficiency and the partition of OCPs in the final effluent/dewatered sludge; and (3) to characterise the profiles of DDT and HCH by evaluating their percentage to total DDTs and total HCHs in the two STWs.

2. Materials and methods

2.1. Study design

This study was designed to study the profile and removal efficiency of OCPs in two different types of STWs. Various stages of sewage products (influent [crude sewage; CS]), primary effluent [PE], final effluent [FE], mixed liquor [ML] activated sludge and dewatered sludge [cake]) were sampled for chemical and physical analyses. Stonecutter Island STW (SCI) was chosen to represent chemically enhanced primary treatment (CEPT) by adding ferric chloride and polymer to the sewage to help particulate matter (PM) form flocs and settle down. SCI is located in the south-western part of Kowloon and treats a large fraction of the urban sewage discharge around Victoria Harbour in Hong Kong (1.4 million m^3 of sewage per day). Shatin STW (ST) uses primary and secondary biologically activated sludge treatment. It is the largest secondary STW in Hong Kong and currently treats 0.25 million m^3 of sewage per day (DSD, 2009a, b).

2.2. Sampling

Samples from the two STWs were collected on five sunny days between November 2011 and February 2012 to avoid dilution of the samples by rain. All sewage samples were collected in precleaned, solvent-rinsed amber glass bottles with Teflon caps, whilst dewatered sludge (Cake) samples were wrapped with pre-baked aluminium foil at 450 °C and put into polypropylene plastic bags. All samples were kept in ice bricks during transportation to the laboratory. Three sampling points were used at SCI: (1) influent (CS) was taken as a mixture of multiple samples before ferric chloride and polymer treatment; (2) FE samples were taken as a mixture of multiple samples before chlorination; (3) dewatered sludge (Cake) samples were taken as a mixture of multiple samples from three centrifuges after the dehydration process. In contrast, five sampling points were used at ST: (1) influent (CS) was taken as a mixture of multiple samples before primary treatment; (2) PE was taken at the outlet of the primary sedimentation tank as a mixture of multiple samples; (3) FE was taken as a mixture of multiple samples at the effluent pump before ultraviolet disinfection; (4) ML was collected as mixture of multiple samples from bioreactors as activated sludge; and (5) dewatered sludge (Cake) was taken as a mixture of multiple samples from three skips in the facility after centrifuge dehydration.

2.3. Determination of total suspended solids and volatile suspended solids of liquid samples

Liquid samples including CS, PE and FE were separated into liquid portion (LP) and PM through filtration with 0.45 μm glass fibre filters (Whatman, Maidstone, UK). The PM and Cake samples were placed in an oven at 105 °C and dried until a stable constant weight was reached to determine the total suspended solids (g/L). The volatile suspended solids (g/L) content was then determined by 550 °C combustion in a furnace, based on the Standard Methods for the Examination of Water and Wastewater (APHA, 2012).

2.4. Extraction and determination of OCP extraction

Sewage samples (CS, PE and FE) were divided into LP and PM following the filtration method given in Section 2.3. All LP samples were stored within 5 days before laboratory analyses, whilst all PM samples from CS, PE, FE, ML and Cake were freeze-dried to eliminate the remaining moisture. Freeze-dried filter papers were weighed to calculate the PM weight and ground into fine powder. Cake samples were passed through a 0.154 mm sieve and stored at −21 °C before laboratory analyses. Because the PM in ST's FE was too limited to obtain a sufficient amount for laboratory analysis, the PM in samples of ML were used to replace the PM in FE. ML is a semi-liquid that was centrifuged at 300 rpm at 4 °C for 15 min, and the settled precipitate was freeze-dried and stored at −21 °C before laboratory analyses.

To extract OCPs from PM and Cake, samples were placed into pre-baked glass-fibre filters (450 °C for 8 h), mixed with known amounts of m-terphenyl (Sigma-Aldrich Co; as an internal standard) and anhydrous sodium sulphate (to eliminate water content) and transferred into pre-cleaned stainless-steel cells for the accelerated solvent extraction (ASE 200, DIONEX Inc) process (dichloromethane [DCM] and hexane [1:3 v/v] at 1500 psi and 110 °C for 6 min for two cycles based on the US EPA Method 3540C (USEPA, 1996a). The extracts were concentrated using a rotary evaporator for subsequent clean-up procedures. According to US EPA Method 3620B (USEPA, 1996b), florisil column clean-up was applied to purify the concentrated extracts; the eluted solvents used were n-hexane and DCM (1:1 v/v). The cleaned extracts were reduced to less than 3 mL using a rotary evaporator and further reduced to less than 0.2 mL under a gentle nitrogen stream. Tetrachloro-m-xylene was then added to the sample extracts as an internal standard for quantitation. Finally, the sample extracts were topped up to 0.2 mL with n-hexane for gas chromatography/mass spectrometry.

To extract OCPs from filtered liquid samples, the solid-phase extraction method was adopted. The C18 solid-phase extraction cartridges were first conditioned by washing with methanol, ethyl acetate:DCM (50:50), methanol and MilliQ. After loading samples, solid-phase extraction cartridges were air dried for 15 min in a vacuum to remove as much residual water as possible. The retained analytes were eluted with ethyl acetate: DCM (50:50). The collected elutes were evaporated under nitrogen, and tetrachloro-m-xylene was added to the sample extracts as an internal standard. The final extract was reconstituted to 0.2 mL with n-hexane for gas chromatography/mass spectrometry.

US EPA Standard Method 8270C (USEPA, 1996c) was used for identification and quantification of nine OCPs (aldrin; chlordane [*cis-* and *trans-* chlordane, *cis-* and *trans-* nonachlor, oxychlordane]; DDTs [*p,p'*-DDE, -DDD, -DDT and *o,p'*-DDE, -DDD, DDT]; dieldrin; endrin; heptachlor [heptachlor, heptachlor epoxide]; HCB; alpha-, beta- and gamma-HCH; and mirex) using a gas chromatograph (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c), in negative chemical ionisation mode, with methane used as a reactant gas. The gas chromatography column used for quantification was a DB-XLB fused silica capillary column (J & W Scientific Inc., Folsom, CA) with 0.25 mm i.d.×60 m × 0.25 μm film. The most abundant ions were selected for quantification, and two reference ions were used for confirmation of each analyte in SIM mode.

2.5. Quality control

A procedural blank (Solvent) was processed in each set of samples, and the proposed variation between the concentrations of analytes in duplicate samples was less than 20%. Known amounts of standard were added to sewage liquid and solid samples before the extractions and analysis using methods described above for testing recovery. The recovery efficiencies for OCPs were 82.2 ± 5.73% for liquid samples (CS, PM and FE) and 77.7 ± 3.09% for solid samples (cake and PM). Blank samples without spiking were analysed to determine whether any contamination occurred during the analyses.

2.6. Calculation of the removal efficiency of OCPs by STWs, distribution coefficient of OCPs and partition of OCPs in PM in STWs

The removal efficiencies and distribution profiles of OCPs in the sewage treatment process were calculated with the reported analytical data of liquid samples (CS-LP, PE-LP and FE-LP in ng/L) and solid samples (CS-PM, PE-PM, FE-PM and Cake in ng/g d.w.) based on flow analysis. The profile for the distribution of each OCP was calculated based on per litre of raw sewage flow calculated using the operational data, including average daily sewage flow in m^3 per day, average daily Cake produced in kg/day, TS g/L in Cake, total suspended solids g/L in CS, and PE and FE of STWs provided by the Drainage Service Department, HKSAR (Table S1 in Supplementary Information).

The abbreviations and descriptions of the equations are listed in Table S2 and Equations (Supplementary Information). The equations used to calculate total, primary and secondary removal efficiency by STWs and distribution coefficient of OCPs in liquids (FE-T) and in solids (Cake) are listed in Equations (Supplementary Information).

2.7. Data analysis

Quantitative data analysis was carried out with SPSS for Windows (v16.0; SPSS, Chicago, IL). The Shapiro–Wilk test was used to check the normality of the data. Student's *t*-test was used to assess the differences between the two STWs for normally distributed data, whilst the Mann–Whitney U test was used for abnormally distributed data. Spearman correlation coefficients were used to determine the relationship between the total removal efficiency of individual OCPs against their log octanol–water partition coefficient (log K_{ow}). The significance level was set at a p level of less than 0.05 (two-tailed), and the data were presented as means ± standard deviation.

3. Results and discussion

3.1. Concentrations of OCPs

Nine OCPs — aldrin, chlordane (cis- and trans-chlordane, cis- and trans-nonachlor, oxychlordane), DDT (*p,p'*-DDE, -DDD, -DDT and *o,p'*-DDE, -DDD, DDT), dieldrin, endrin, heptachlor (heptachlor, heptachlor epoxide), HCB, HCH (alpha-, beta- and gamma-), and mirex were detected in the wastewater samples from SCI and ST. The OCPs concentrations in the two studied STWs showed similar patterns (Table 1). Some OCPs (trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, *p,p'*-DDD) were not detected (i.e., below the detection limit). These chemicals are not shown in Table 1, except for *p,p'*-DDD, which is one of the DDT metabolite isomers and hence taken into account in the total DDTs (USEPA, 1996c). The most abundant OCPs in the influent (CS) were HCHs, with mean concentrations of 19.4 ± 4.62 ng/L in SCI and 12.1 ± 4.27 ng/L in ST, followed by total DDTs, with mean concentrations of 6.31 ± 2.83 ng/L in SCI and 6.09 ± 1.67 ng/L in ST, whilst *p,p'*-DDE was the most dominantly detected metabolite. The mean concentrations for total OCPs in the influent CS in SCI and ST were 39.0 ± 9.58 ng/L and 31.5 ± 6.32 ng/L, respectively.

Although Hong Kong is located at the estuary of the PRD, the two studied STWs had much lower levels of OCPs than those reported in Guangzhou and Greece, which had OCP (alpha-, beta-, gamma-HCHs, DDE, DDT) concentrations as high as 1200 ng/L (Yang et al., 1997) and 653 ng/L (Katsoyiannis and Samara, 2004), respectively. In particular, the HCH and DDT levels detected in CS in this study were much lower than those reported in Daya Bay (far from the PRD), which were as high as 500 ng/L of HCHs (alpha-, beta-, gamma-, delta-HCH) and 100 ng/L of DDTs (*p,p'*- DDE, *p,p'*-DDD and *p,p'*-DDT) (Zhou et al., 2001). This suggests that the two studied Hong Kong STWs were receiving wastewater with less OCP contamination than other regions in the PRD. The HCH and DDT levels in this study were also much lower than those reported in Greece (66.4 ng/L of HCHs [alpha-, beta- and gamma-HCH] and 40.9 ng/L of DDTs [*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT]) (Katsoyiannis and Samara, 2004).

Table 1

Concentrations of OCPs in sewage treatment works (ng/L).

OCPs	Influent		Primary effluent	Final effluent	
	SCI	ST	ST	SCI	ST
cis-chlordane	0.172 ± 0.0360 e	N.D.	ND	0.00900 ± 0.0150 b	N.D.
heptachlor	3.86 ± 2.29 cde	3.05 ± 1.76 bcde	1.28 ± 0.923 b	N.D.	0.001 ± 0.00200 c
heptachlor epoxide	N.D.	4.80 ± 1.90 bcd	1.30 ± 1.76 b	N.D.	1.24 ± 1.45 abc
p, p'-DDT	2.98 ± 2.68 cde	N.D.	1.49 ± 2.10 b	N.D.	N.D.
p, p'-DDE	2.49 ± 0.812 cde	3.01 ± 0.812 bcde	7.92 ± 3.74 a	0.161 ± 0.152 b	0.028 ± 0.133 c
p, p'-DDD	N.D.	N.D.	N.D.	N.D.	N.D.
o, p'-DDT	N.D.	1.16 ± 0.00 de	N.D.	N.D.	0.0100 ± 000 c
o, p'- DDE	0.457 ± 0.647 e	0.426 ± 0.361 e	0.026 ± 0.037 b	0.0340 ± 0.0490 b	N.D.
o, p'-DDD	0.39 ± 0.0110 e	1.50 ± 0.361 cde	N.D.	N.D.	0.021 ± 0.00 c
Dieldrin	N.D.	1.52 ± 0.323 cde	N.D.	N.D.	0.0250 ± 0.00c
Endrin	N.D.	0.214 ± 0.087 e	N.D.	N.D.	N.D.
Aldrin	2.17 ± 1.65 cde	N.D.	N.D.	N.D.	0.0480 ± 0.0230 c
HCB	0.371 ± 0.106 e	0.291 ± 0.069 e	1.42 ± 0.184 b	0.00900 ± 0.0160 b	0.004 ± 0.005 c
Mirex	1.86 ± 1.25 de	1.95 ± 0.633 cde	0.030 ± 0.061 b	0.0230 ± 0.0220 b	0.196 ± 0.0580 c
alpha-HCH	5.37 ± 1.02 cd	3.11 ± 0.202 bcde	1.38 ± 0.141 b	3.55 ± 1.71 a	0.630 ± 0.891 bc
beta-HCH	3.34 ± 1.97 cde	5.19 ± 0.174 bc	5.03 ± 4.43 ab	0.168 ± 0.041 b	1.44 ± 0.446 ab
gamma-HCH	10.6 ± 3.68 b	3.81 ± 4.65 bcde	1.21 ± 1.51 b	0.241 ± 0.122 b	N.D.
Total DDTs	6.31 ± 2.83 c	6.09 ± 1.67 b	9.43 ± 5.80 a	0.196 ± 0.103b	0.0580 ± 0.0130 c
Total HCHs	19.4 ± 4.62 a	12.1 ± 4.27 a	7.63 ± 2.78 a	3.96 ± 1.77 a	2.07 ± 0.445 a
Total OCPs	39.0 ± 9.58	31.5 ± 6.32	23.0 ± 10.7	4.04 ± 2.35	7.28 ± 6.25 c

Note: N.D. = Not Detected; SCI = Stonecutters Island Sewage Treatment Work; ST = Shatin Sewage Treatment Work; PRE = Primary removal efficiency; SRE = Secondary removal efficiency; TRE = Total removal efficiency.

After the primary and secondary treatments in SCI and ST, all OCP concentrations generally decreased throughout the treatment processes. However, the levels of p,p'-DDT, p,p'-DDE and HCB in ST increased after the primary treatment, whilst the levels of o,p'-DDT, o,p'-DDD, dieldrin, aldrin and mirex increased after the secondary treatment (shown in bold type in Table 1). The presence of these chemicals after treatment might be due to the breakdown of the maternal compounds such as DDT and dieldrin and due to historical deposit in the treatment tanks (ATSR, 2002; Zitko, 2003). Nevertheless, the concentrations of these chemicals increased after treatment at ST, but not after treatment at SCI, possibly due to the different treatment methods used in these two STWs. SCI and ST adopt CEPT and biologically activated sludge treatment, respectively. Coliform bacteria, such as *Escherichia coli* and *Streptococcus faecalis*, were activated during biological treatment in ST, and thus dieldrin could be converted to aldrin under nitrogen (Zitko, 2003).

3.2. OCP concentration in sludge

Table 2 summarises the mean concentrations (ng/g, d.w.) of OCPs (HCB, DDTs and HCHs) in sludge (Cake) reported in this study and those in similar studies. Because studies concerning OCP levels in various sewage products are limited, the results of this study can only be compared with studies conducted in China and Greece (Table 2). The OCPs detected in sludge were trans-nonachlor, heptachlor, heptachlor epoxide, dieldrin, endrin, aldrin, mirex, HCB, HCHs (alpha-HCH and beta-HCH) and DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT and o,p'-DDD). The OCPs that did not reach the detection limits included trans-chlordane, cis-nonachlor, oxychlordane and p,p'-DDE. Some of the OCPs that were not detected in the wastewater samples were also found to be under the detection limits in the sludge samples (Tables 1 and 2). Heptachlor and its metabolite heptachlor epoxide registered the highest concentrations in sludge (0.390 ± 0.550 ng/g d.w. [1.14% of total OCPs] and 6.39 ± 0.25 ng/g d.w. [18.7% of total OCPs], respectively, in SCI; 20.3 ± 6.26 ng/g d.w. [42.6% of total OCPs] and 14.5 ± 0.67 ng/g d.w. [30.5% of total OCPs], respectively, in ST). Similar findings were reported by Katsoyiannis and Samara (2004), who showed that heptachlor epoxide (270 ± 180 ng/g d.w.) dominated in the sludge profile and contributed to more than 60% of total OCPs. The heptachlor and heptachlor epoxide concentrations were significantly higher in ST than in SCI ($p < 0.05$, possibly because they have different sources of raw sewage. SCI receives wastewater from the urban areas of Kowloon and Hong Kong Island, whilst ST receives wastewater from the Shatin and Ma On Shan Districts, which were major agricultural areas in recent decades. Thus, the higher concentrations of heptachlor and its metabolites detected in ST might be a result of historical deposits.

The concentrations of HCB in sludge (ST: 0.265 ± 0.374 ng/g d.w.; SCI: not detectable) in this study were prominently lower than those reported in China (145 ng/g d.w.) (Wang et al., 2007), Canada (42.0 ng/g d.w.) (Webber et al., 1996), the United Kingdom (33.0 ng/g d.w.) (Stevens et al., 2003), Greece (13.0 ng/g d.w.) (Katsoyiannis and Samara, 2004) and Switzerland (35.0 ng/g d.w.; (Frost et al., 1993). For the concentrations of 'drins', only a small amount of dieldrin (0.485 ± 0.686 ng/g d.w.) was found in the SCI sludge, and it was not detected in ST. Again, this level was much lower than that obtained from Greece (15 ng/g d.w.) (Katsoyiannis and Samara, 2004). However, whilst endrin and aldrin were not detected in Greece, they were found in the sludge of SCI at 6.56 ± 3.51 ng/g d.w. and 3.65 ± 2.24 ng/g d.w., respectively, and in that of ST at 1.00 ± 1.40 ng/g d.w. and 2.26 ± 0.0600 mg/g d.w., respectively. Similar to HCBs, the HCH concentrations

Table 2
Comparison of OCPs mean concentrations in sludge (ng/g d.w.) in this study with others.

OCPs\Region	Hong Kong SCI	Hong Kong ST	China	Canada	UK	Greece	Switzerland
trans-nonachlor	3.35 ab	N.D.	–	–	–	–	–
heptachlor	0.390 b	20.3 a	–	–	–	40.0	–
heptachlor epoxide	6.39 a	14.5 b	–	–	–	270	–
p, p'-DDT	N.D.	N.D.	10.0	–	–	N.D.	–
p, p'-DDE	N.D.	2.16 cd	143	13.0	13.0	24.0	–
p, p'-DDD	N.D.	3.34 cd	64.9	–	–	8.00	
o, p'-DDT	0.950 b	0.630 d	11.7	–	–	–	–
o, p'-DDE	N.D.	N.D.	–	–	–	–	–
o, p'-DDD	0.315 b	N.D.	–	–	–	–	–
Dieldrin	0.485 b	N.D.	–	–	–	15.0	–
Endrin	6.56 a	0.99 d	–	–	–	N.D.	–
Aldrin	3.65 ab	2.23 cd	–	–	–	N.D.	–
Mirex	4.50 ab	1.40 cd	–	–	–	7.00	–
HCB	N.D.	N.D.	145	42.0	33.0	13.0	35.0
alpha-HCH	4.33 ab	1.81	1.60	–	–	9.00	–
beta-HCH	3.27 ab	N.D.	16.8	–	–	21.0	–
gamma-HCH	N.D.	N.D.	0.600	–	–	2.00	39.0
delta-HCH	–	–	0.900	–	–	–	–
Total HCHs	7.60 a	1.81 cd	19.9	–	–	32.0	39.0
Total DDTs	1.27 b	6.13 c	230	13.0	13.0	32.0	
Total OCPs	34.1	47.6	395	55	39.0	–	74.0
References	Present study	Present study	Wang et al. (2007)	Webber et al. (1996)	Stevens et al. (2003)	Katsoyiannis and Samara (2004)	Frost et al. (1993)

Note: N.D. = Not Detected; SCI = Stonecutters Island Sewage Treatment Work; ST = Shatin Sewage Treatment Work.

found in this study were much lower than those in other studies; 21.0 ng/g d.w. and 23.0 ng/g d.w. were detected in China and Greece, respectively (Katsoyiannis and Samara, 2004; Wang et al., 2007). Significantly higher levels of total DDTs were found in the sludge samples collected from ST (6.13 ± 0.280 ng/g d.w.) than in those collected from SCI (1.27 ± 0.420 ng/g d.w.; $p < 0.05$), possibly for the same reason as the case of heptachlor mentioned previously.

3.3. Removal of OCPs

3.3.1. Total removal efficiency of OCPs in SCI and ST

The total removal efficiencies (TRE) of the nine OCPs in the sewage treatment process were calculated using Eq. (1) listed in Supplementary data. Fig. 1 shows the TRE (%) in SCI and ST. Chemicals that were not found in either plant are not included in Fig. 1. Heptachlor, HCB, mirex, gamma-HCH and total DDTs showed the highest TREs, ranging from 96.1 ± 3.37% to 100 ± 0%, whilst the mean TRE of total OCPs was 90.1 ± 3.60%. Total HCHs (TRE: 79.9 ± 7.03%) were removed less efficiently by sewage treatment; one of its metabolites, alpha-HCH, showed the lowest mean TRE (36.6 ± 23.0%) in SCI. The TRE of OCPs in ST had a pattern similar to that of SCI, which suggests that the two sewage treatment plants have similar abilities in the removal of these chemicals.

The outstanding performance of SCI was noted in the TRE of mirex, beta-HCH and total OCPs ($p < 0.05$) (Fig. 1), and suggests that the CEPT (with the addition of ferric chloride and polymer) applied in SCI performed better in removing these two compounds and total OCPs than the biological treatment in ST. The TREs for mirex, beta- HCH and total OCPs were 98.2 ± 1.86%, 93.5 ± 3.65% and 90.1 ± 3.6% in SCI and 88.9 ± 5.69%, 72.4 ± 7.67% and 74.5 ± 24.9% in ST, respectively. For others OCPs, the mean TREs of the two STWs were similar, with alpha-HCH and beta-HCH being the lowest both STWs and heptachlor being the highest (100%) for both STWs. The results of this study contradict those of another study that suggested that secondary wastewater treatment plants had a better performance in the removal of organic contaminants than those that adopted primary treatment (Rocha-Gutierrez and Lee, 2012) The TREs reported in both STWs were generally higher than those in Greece (Katsoyiannis and Samara, 2004), except for alpha-HCH in SCI and ST (36.3 and 78.8%, respectively) and beta-HCH in ST (72.3%).

3.3.2. Primary and secondary OCP removal efficiency in ST

Fig. 2 shows the primary (PRE) and secondary OCP removal efficiencies (SRE) in ST, calculated using Eqs. (2.1) and (2.2) (Supplementary data). For the PRE, three of nine comparable OCPs were negative, including HCB (-395 ± 55.4%), gamma-HCH (-117 ± 304%) and total DDTs (-47.4 ± 54.9%), but only HCB showed a significantly higher value ($p < 0.05$). The negative PRE could be attributed to the degradation and transformation of maternal compounds, such as HCH and DDTs, and to the release of the previously deposited HCB in the primary treatment tank.

Similar to the results for TRE, the mean SREs of the OCPs in ST showed no comparable and significant difference in all individual OCPs ($p > 0.05$) (Fig. 2). Compared with the data collected in Greece, SREs in ST performed better because most of
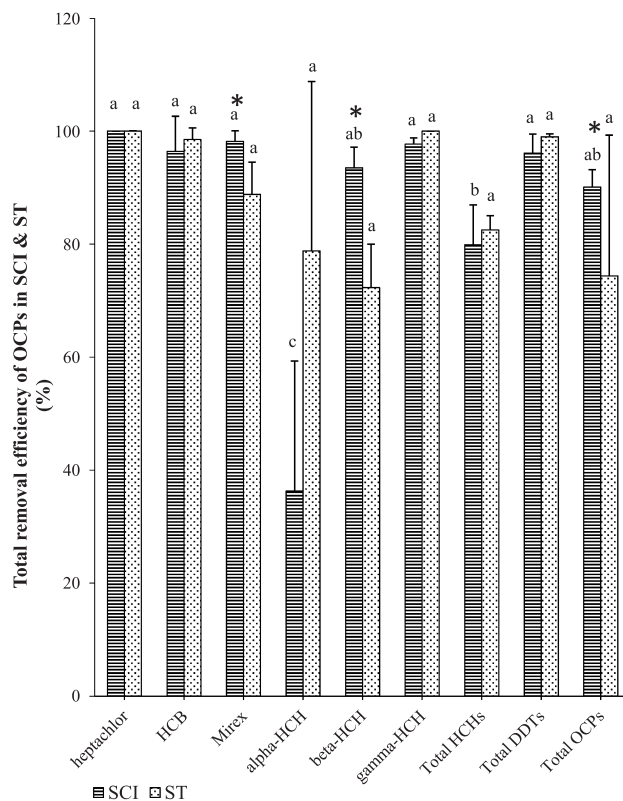
Fig. 1. Total removal efficiency of OCPs in SCI & ST (%). Note: SCI = Stonecutter Island Sewage Treatment Work; ST = Shatin Sewage Treatment Work; $* = p < 0.05$.

the SREs were at around 50%, ranging from 40 ± 20% for alpha-HCH and 80 ± 23% for heptachlor epoxide (Katsoyiannis and Samara, 2004). Significant differences were found between the PREs and SREs in HCB, total HCHs and total DDTs (Fig. 2). This implied that the biological process in secondary treatment was significantly more efficient than physical treatment (without the addition of ferric chloride and polymer).

3.4. Distribution coefficient in liquid and solid

According to Figs. 3(a) and (b), the distribution coefficient (%) of total OCPs in liquid (FE-T; 42.4% in SCI and 42.7% in ST) was only slightly lower than that in solid (Cake; 57.6% in SCI and 57.3% in ST). The log octanol–water partition coefficient (K_{ow}) of OCPs ranged from 3.72 to 6.91, meaning that they are hydrophobic and tend to bind to highly organic substances in the particulate forms of sewage, which are sludge and biosolid fraction (Fatone et al., 2011). Based on the log K_{ow} value, the OCPs in wastewater were expected to be removed mainly through sorption in PM and sedimentation of sludge, similar to other POPs (Pham and Proulx, 1997; Bedding et al., 1995; Peng et al., 2009; McIntyre et al., 1981). The relationships between solid–liquid partitioning of the hydrophobic contaminants and their log K_{ow} values are shown in Fig. 4. Similar to the findings of Katsoyiannis and Samara (2004), the TREs of the OCPs correlated poorly with their log K_{ow} ($r^2 = 0.24$ and 0.36 in SCI and ST, respectively), which suggests that although the log K_{ow} values of OCPs were similar to those of other POPs, the removal of OCPs seems to rely more on other mechanisms, such as volatilisation (including aldrin, chlordane [cis- and trans-chlordane, cis- and trans-nonachlor, oxychlordane], heptachlor [heptachlor, heptachlor epoxide] and HCB; except DDTs, endrin, dieldrin, alpha-, beta- and gamma-HCH and mirex), advection and biotransformation (Ouyang et al., 2013; Cincinelli et al., 2009; Katsoyiannis and Samara, 2004; Österreicher-Cunha et al., 2003; Waliszewski, 1993; Halfon, 1984; Nash, 1983; Isensee et al., 1976; Spencer et al., 1973). This also explained why the distribution coefficients (%) of OCPs in solids were similar to those in the water phase. Unlike polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons and other POPs, in which removal was achieved through sorption in sewage solids, the partition in solid and liquid of OCPs did not show a clear trend (Man et al., 2015, 2017). Only heptachlor, aldrin and mirex in SCI and heptachlor and total DDTs in ST were mainly attached to solids. HCHs, especially gamma-HCH, were mainly partitioned in liquid, as their log K_{ow} values (average 3.77) were the lowest amongst the OCPs.
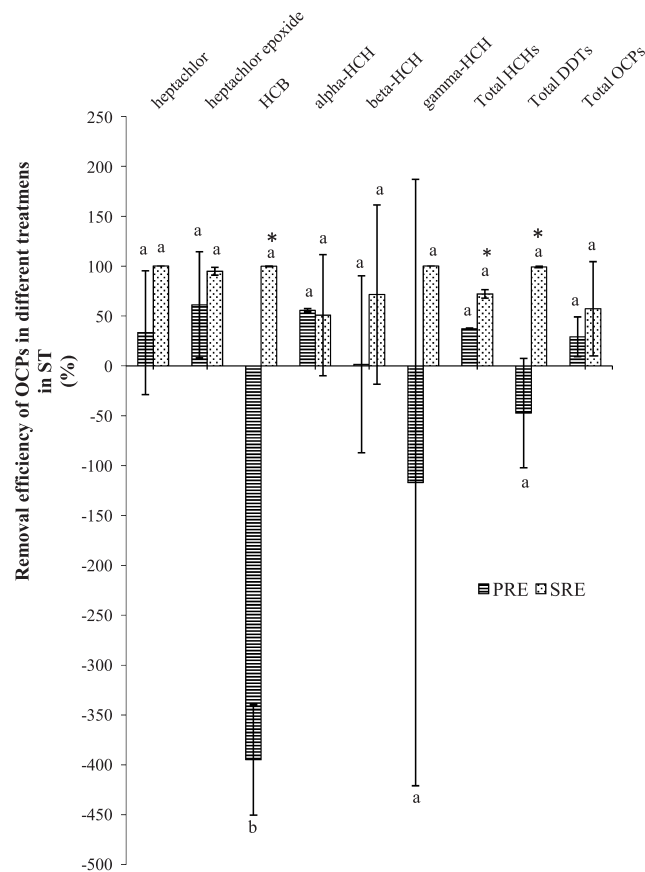
Fig. 2. Removal efficiency of OCPs in different treatments in ST (%). Note: ST = Shatin Sewage Treatment Work; PRE = Primary removal efficiency; SRE = Secondary removal efficiency; $* = p < 0.05$.

3.5. Percentage profiles of DDTs and HCHs

Fig. 5 shows the percentage of individual DDT (out of total DDTs) and individual HCH (out of total HCHs) in liquid and solid sewage samples obtained from SCI and ST. In the liquid sewage samples (Fig. 5(a)), only p,p'-DDT was found in the SCI raw wastewater, and no DDTs were detected in FE. Only o,p'-DDT was detected in the ST CS, whilst 83.7% p,p'-DDE and 12.3% p,p-DDT were detected in PE, which might be biotransformed from o,p'-DDT, and no DDT was detected in FE in ST. For HCHs in liquid samples, the dominant HCH in SCI CS was gamma-HCH (60%), followed by alpha-HCH (35.2%) and beta-HCH (4.86%). Only alpha-HCH was found in the FE of SCI. Compared with the samples collected from SCI, ST had more even distribution of HCHs in CS, with 33.5% alpha-HCH, 36.2% gamma-HCH and 30.3% beta-HCH. After primary treatment, beta-HCH (67.4%) became the dominant compound, whilst alpha-HCH occupied 20.3% and gamma-HCH 12.3% of the HCHs in PE. In FE, beta-HCH continued to dominate at 69.1%, followed by 30.9% of alpha HCH, whilst gamma-HCH was not detected in the liquid phase of sewage samples.

Fig. 5(b) shows the percentage profiles of the DDTs and HCHs in solid samples. For DDTs, p,p'-DDE dominated over 60% in both profiles of CS in the two STWs. Although o,p'-DDT was not detected in CS, it was also found in the Cake of both STWs and contributed to 75.1% in the SCI cake and 16.3% in the ST cake. p,p'-DDD was only found in the ST cake, and it comprised 54.4% of the total DDTs. In contrast, the percentage profiles of the HCHs in CS of both STWs were similar, with beta-HCH being the most dominant (more than 60%), followed by gamma-HCH and alpha-HCH. With biological treatment, only beta-HCH was found in the PM of ST-FE, whilst alpha-HCH had been removed in Cake. This finding suggests that biological treatment was effective in the removal of gamma-HCH in solids.

The profiles of DDTs and HCHs in both the water and solid phases of sewage are illustrated in Fig. 5(c). After primary and secondary treatments in the two studied STWs, the percentage of metabolites increased, such as p,p'- DDE and o,p'- DDE in SCI and o,p'- DDD in ST, whilst DDT decreased. After biological treatment, the FE in ST was dominated by p,p'- DDE (48.12%), followed by o,p'-DDD (35.5%), which may be derived via the biotransformation of o,p'-DDE in the PE. Although the o,p'-DDD disappeared in the ST PE, it was found again in the FE after biological treatment. As for HCHs, a decreasing trend was observed
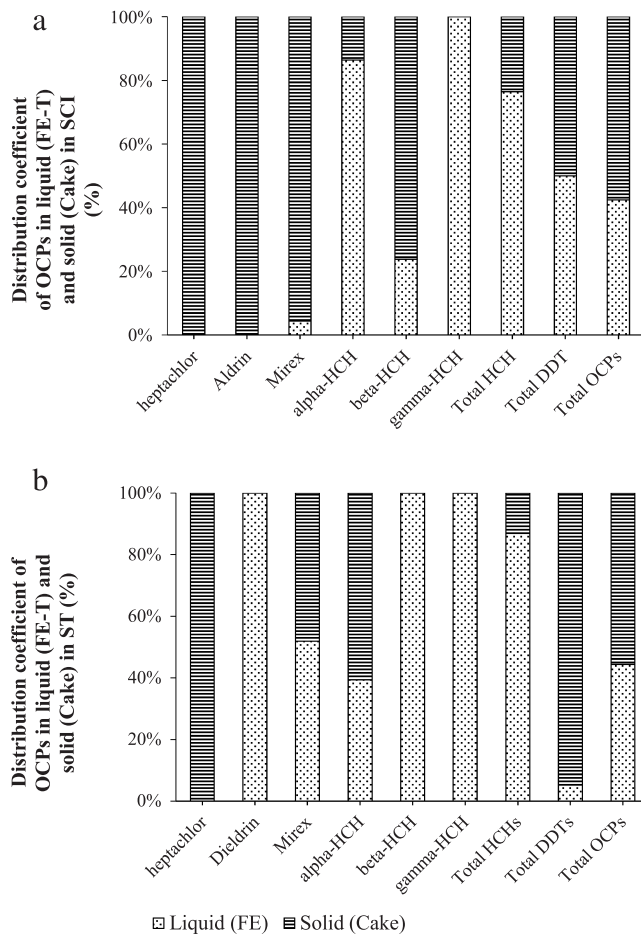
Fig. 3. Distribution coefficient (%) of OCPs in liquid (FE-T) and solid (Cake) in (a) SCI and (b) ST. Note: SCI = Stonecutter Sewage Treatment Work; ST = Shatin Sewage Treatment Work.
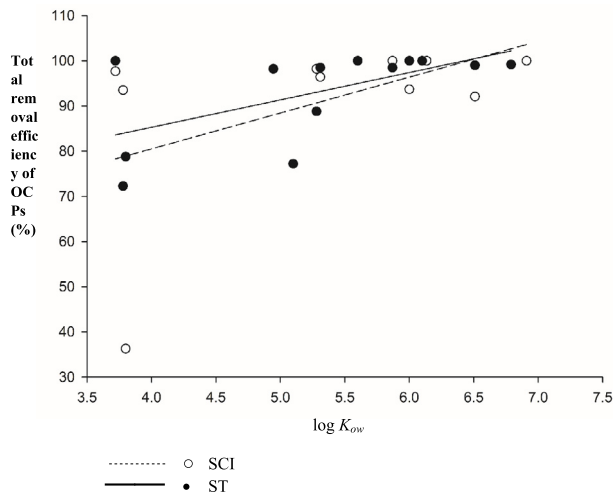

Fig. 4. Plot of total removal efficiency of individual OCPs against their log octanol–water partition coefficient (log K_{ow}). Note: SCI = Stonecutter Island Sewage Treatment Work; ST = Shatin Sewage Treatment Work.
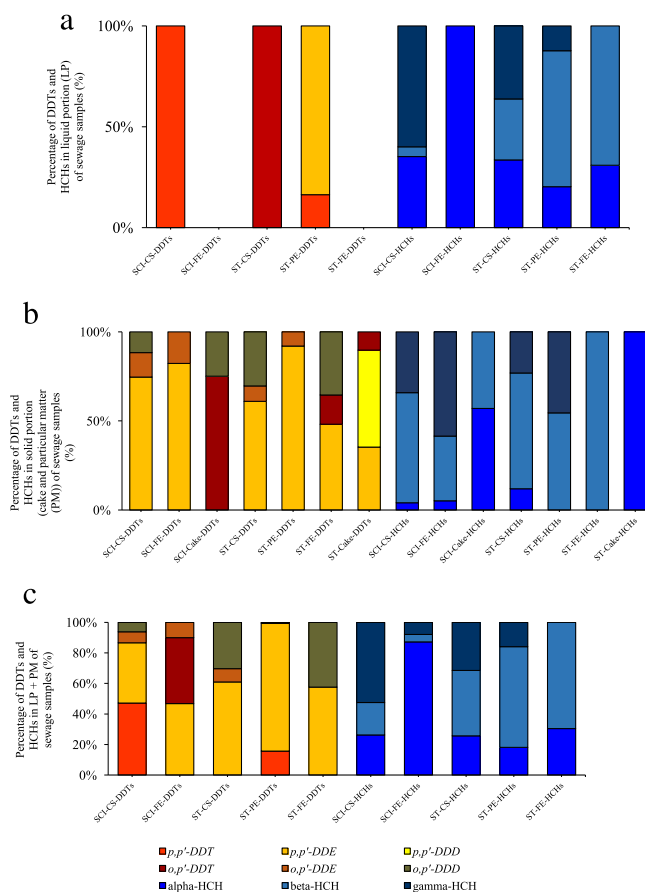
Fig. 5. Percentages profile of individual DDT and HCH in sewage samples to the total DDTs and total HCHs (%) (a) liquid of sewage; (b) solid (cake/ particular matter (PM) of sewage); and (c) total (liquid of sewage + PM of sewage). Note: SCI = Stonecutter Island Sewage Treatment Work; ST = Shatin Sewage Treatment Work.

in the percentage of gamma-HCH throughout the treatment process in both STWs. The percentage of alpha-HCH increased after treatment in SCI; however, beta-HCH became dominant throughout the treatment process in ST. This provides further evidence of the capability of secondary treatment to remove this chemical.

4. Conclusions

This study demonstrates the differences between CEPT (SCI) and secondary treatment with activated sludge (ST) in treating OCPs in municipal sewage. The two studied STWs received wastewater with lower concentrations of OCPs than those in other regions in the Pearl River Delta and those in other countries. In general, the concentrations of most of the OCPs showed a decreasing trend throughout the treatment processes. However, the increases in o,p'-DDT, o,p'-DDD, dieldrin, aldrin and mirex after the secondary treatment might be due to the breakdown of maternal compounds such as DDT and dieldrin and historical deposits in the treatment tanks. As in other studies, heptachlor and its metabolite, heptachlor epoxide, contributed most of the OCP profile in sludge. The two STWs showed similar performance in the removal of OCPs in terms of TRE. The significant differences between the PRE and SRE demonstrated that secondary treatment was more efficient than physical treatment (without the addition of ferric chloride and polymer) in the removal of total HCHs and DDTs. The distribution coefficients and TRE curve against the log K_{ow} values of individual OCPs suggest that although OCPs share some similar characteristics with other POPs in lipophilicity, the removal of OCPs seems to depend more upon other mechanisms, such as volatilisation, advection and biotransformation. The OCP profile provides further evidence of the transformation of OCP molecules (e.g., DDTs) and their corresponding metabolites (DDE and DDD). It also indicates the capability of biological treatment to remove gamma-HCH in both liquid and solid sewage samples. This study is one of the few to investigate the fate of OCPs in STWs, and its results will help to provide further information in the design and modification of municipal sewage treatment facilities.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2017.12.004.

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