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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 ± 7.03%; ST, 82.5 ± 2.51%) and total DDTs (SCI, 96.1% ± 3.37%; ST, 99 ± 0.501%) were observed. In particular, ST achieved outstanding performance in the removal of heptachlor (100% ± 0.00%), heptachlor epoxide (94.8 ± 3.96%), hexachlorobenzene (99.7 ± 0.387%), gamma-HCH (100 ± 0.00%) and total DDTs (99.2 ± 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 $\pm$ 183 fg m^{-3}) and Tsuen Wan (190 $\pm$ 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 $\pm$ 50.8 ng/g d.w.) and HCHs (6.01 $\pm$ 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.