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Aquaculture-derived enrichment of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in coastal sediments of Hong Kong and adjacent mainland China

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HIGHLIGHTS

- Aquaculture could derive significant enrichment of OCPs in coastal sediments.
- The enriched OCPs were mainly derived from fish feeds and DDT-based antifouling paints.
- This is the first study for aquaculture-derived OCP contaminations in coastal sediments.

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ABSTRACT

To evaluate contamination of sediments along the coast of Hong Kong and adjacent mainland China, concentrations of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in surface and core sediments were measured in six mariculture zones. In surface sediments (0 to 5 cm), concentrations of $\sum$HCHs and $\sum$DDTs in mariculture sediments were approximately 1.3- and 7.7-fold greater, respectively, than those detected in sediments at corresponding reference sites, which were 1 to 2 km away in areas where there was no mariculture. Similarly, in cores of sediments, concentrations of $\sum$HCHs and $\sum$DDTs were 1.2- and 14-fold greater in mariculture zones, respectively. Enrichment relative to regional background concentrations, expressed as percentages was as large as 8.67×10^3% for *o,p'-DDD*. The major sources of the enriched organochlorine pesticides (OCPs) were hypothesized to be derived from the use of contaminated fish feeds and anti-fouling paints for maintaining fish cages. Results of ecological risk assessments revealed that enriched OCPs had a large potential to contaminate the surrounding marine environment and lead to adverse effects on the associated biota. To our knowledge, this is the first study to evaluate the differences of OCP contaminations between mariculture and natural coastal sediments.

1. Introduction

Rapid development of aquaculture has raised concerns about the potential for these operations to cause adverse effects on the local coastal marine environment (Cao et al., 2007). One of the most negative effects of cage aquaculture is uncontrolled release of extra-loads of nutrients, suspended solids and organic matters to the water and sediments (Yokoyama et al., 2006). Nutrient enrichment in sediments in the vicinity of mariculture is common all over the world, such as Japan (Yokoyama et al., 2006), Turkey (Alpaslan and Pulatsü, 2008) and Spain (Mendiguchia et al., 2006). In Hong Kong, the average annual total phosphorus (TP) loads to sediments beneath mariculture cages increased by 13.2-fold relative to those at reference locations (Gao et al., 2005).

Enrichment of nutrients could change the physical–chemical characteristics of sediments, which act as a sink for heavy metals and persistent organic pollutants (POPs). Results of previous studies indicated that heavy metals such as copper (Cu), zinc (Zn), lead (Pb) and

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cadmium (Cd) were enriched in sediments near mariculture facilities due to the presence of unconsumed fish feeds and antifouling paints (Dean et al., 2007; Mendiguchia et al., 2006). Concentrations of trace organic pollutants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) were great in fish feeds manufactured in the Pearl River Delta (PRD) (Guo et al., 2009b), Canada (Kelly et al., 2008), Spain (Serrano et al., 2003) and Hong Kong (Leung et al., 2010). However, data about enrichment of persistent organic pollutants (POPs) in sediments in the vicinity of mariculture facilities are limited worldwide including the PRD. Concentrations of PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), PBDEs, OCPs, and polycyclic aromatic hydrocarbons (PAHs) in anoxic sediments under fish farm net pens in New Brunswick were greater than those at other sites (Sather et al., 2006). Concentrations of PAH in sediments under mariculture facilities were significantly greater than those in coastal sediments where there was no mariculture facility (Wang et al., 2010). Those authors suggested that fish feeds might be the main source of the enriched PAHs in the mariculture sediments.

We hypothesized that OCPs could be greater in sediments near mariculture facilities in Hong Kong and adjacent mainland China. The specific objectives were to: (1) characterize concentrations of OCPs in mariculture surface and core sediments of Hong Kong and adjacent mainland China; (2) compare the concentrations of OCPs in marine culture sediments and their corresponding reference sediments; and (3) evaluate the sources, burden and ecological risks of OCPs in sediments under mariculture facilities. To our knowledge, this is the first study to evaluate the differences of OCP contaminations in coastal sediments between areas with and without mariculture.

2. Materials and methods

2.1. Study area and sampling

Six cage mariculture farms located at Xixiang (XX), Tsing Yi (TY), Sam Mun Tsai (SMT), Mirs Bay (MB), Sai Kung (SK) and Tung Lung Chau (TLC) were chosen for the present study (Fig. S1). Six sampling sites were chosen for each direction to represent the typical, subtropical fish farming regions in Hong Kong and adjacent mainland China. Detailed information for these sampling sites is shown in Table S1. Total organic carbon (TOC) concentrations in surface sediments and cores for each sampling site are listed in Tables S2 and S3. Detailed information on the physical properties of sediments has been reported previously (Liang et al., 2012). Species cultured in these mariculture "farms" included Red snapper (*Lutjanus campechanus*), Orange-spotted grouper (*Epinephelus coioides*) and Snubnose pompano (*Trachinotus blochii*). In the period of July to September 2008, at least three surface (0–5 cm, using a stainless steel grab sampler) and core (using a KC Kajak sediment core sampler, ø60/52 mm, length 100 cm, Denmark) samples of sediments were collected from each site. Sediments at mariculture facilities were collected beneath cages, while reference sediments were collected about 1–2 km away from the cage, but in the general vicinity. The total number of samples of surface sediments was 36 (18 mariculture surface samples and 18 reference surface samples), and the total number of cores was 36 (18 mariculture core samples and 18 reference core sediments). Cores of sediments were sectioned into 2.5 cm intervals for the first 10 cm, then 5 cm intervals to 40 cm, and then 10 cm intervals to the end. Fish feeds including waste fish ($n = 6$) and dry pellet feeds ($n = 9$) were collected from TLC fish farms. All samples were packed in aluminium foil, transported to the laboratory and kept at −20 °C until further analyses.

2.2. Identification and quantification of residues

Sediments were freeze-dried, homogenized and stored in desiccators prior to chemical analyses. Samples (2–3 g) were Soxhlet extracted according to US EPA Standard Method 3540 C (USEPA, 1996) using 100 ml of a mixture of acetone, dichloromethane (DCM) and n-hexane (1:1:1, v: v: v) for 16 to 18 h at 68 °C. Sufficient acid-washed copper powder was added to remove sulfur. The extract solution was concentrated to 2 ml with a rotary evaporator. About 10 ml n-hexane was added and then rotary evaporated to remove acetone and DCM. The concentrated extract was then cleaned-up by use of a multilayer silica gel column containing, from top to bottom, 1 g anhydrous sodium sulfate, 2 g of deactivated silica (3% organic-free reagent water, w/w), 8 g of acidic silica (44% concentrated sulfuric acid, w/w), 1 g of deactivated silica and 1 g of anhydrous sodium. OCPs were eluted with 90 ml n-hexane/dichloromethane (7:3, v/v). The eluate was then concentrated and passed through a florisil column with 160 ml n-hexane. Deuterated internal standard 2, 4, 5, 6-Tetrachloromxylene (TCmX) was added into all extracts to 100 ng g^{-1} prior to instrumental analysis for quantification. The final volume for all samples was 200 μl. OCPs were quantitatively analyzed by a Hewlett-Packard (HP) 6890 N gas chromatograph (GC) coupled with a HP-5973 mass selective detector (MSD) and a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column (J & W Scientific Co. Ltd., USA). The mass spectrometry mode is selected ion monitoring (SIM). An aliquot of the extract (1 μl) was injected with the aid of an auto sampler (Hewlett-Packard 7683 series). The oven temperature was programmed from 60 °C (initial time, 1 min) to 290 °C at a rate of 4 °C/min, held for 10 min. The 10 target OCP compounds included α-HCH, β-HCH, γ-HCH, δ-HCH, *o,p'-DDD*, *p,p'-DDD*, *o,p'-DDE*, *p,p'-DDE*, *o,p'-DDT* and *p,p'-DDT*. The standard curve was obtained by injecting standards of 1, 2, 5, 10, 20, and 50 ng OCP ml^{-1}. The limit of detection (LOD) for OCPs was 0.02 ng g^{-1} in the samples (dry weight, dw). If the concentration of a congener was less than the LOD, a value equal to half the LOD of the analytical method was attributed for statistical analysis, while it was set to zero for sum, mean and median calculations.

2.3. QA/QC

Surrogate standards (4 4′-dichlorbiphenyl) were added to all samples prior to extraction to quantify the procedural recoveries. For each batch of 20 field samples, a method blank (solvent), a spiked blank (standards spiked into solvent), a matrix spike (standards spiked into pre-extracted sediment), a sample duplicate, and a standard reference material (SRM 1941) sample from National Institute of Standards and Technology (NIST) were processed. The method blanks contained no detectable target analysts. Several quality control criteria were used to ensure the correct identification and quantization of the target compounds: first, retention times matched with those of the authentic reference compounds; second, the ratios of the two characteristic ions were within 15% of the theoretical values; third, the signal-to-noise (S/N) ratio was greater than three for the selected ions; fourth, the amount of the analytes in the sample had to be at least two times that in the blank sample if there were interferences. If any of these four criteria failed, the congener was excluded. Measured concentrations of target analytes in the NIST SRM 1941 were within 76.2–115% of the certified and reference values. The mean surrogate recovery was 93.7 ± 13.6%. The variance between the duplicate samples all less than 12%. The LOD using the present method was determined as the concentrations of analytes in a sample that gave rise to a peak with a signal-to-noise ratio (S/N) of 3. All the results were not corrected with the recovery ratios due to the acceptable recovery rates and reported in ng g^{-1}, dry weight (dw), at three significant figures.

2.4. Data analysis

The $\sum$HCHs was defined as the sum of α-HCH, β-HCH, γ-HCH and δ-HCH, $\sum$DDTs as the sum of *o,p'-DDT*, *p,p'-DDT*, *o,p'-DDE*, *p,p'-DDE*, *o, p'-DDD* and *p,p'-DDD*, and $\sum$OCPs as the sum of $\sum$HCHs and $\sum$DDTs. The enrichment percentage was calculated according to the