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RESEARCH ARTICLE

The interactive effect of the season and estuary position on the concentration of persistent organic pollutants in water and sediment from the Cua Dai estuary in Vietnam

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Abstract

The current study was conducted in the Cua Dai estuary, Vietnam, (1) to assess the status of persistent organic pollutants (POPs) and (2) to examine the interactive effect of season and estuary position on the concentration of the pollutants in surface water and sediment. Fifty-two water and sediment samples were taken in the dry and rainy seasons from inner- and outer-estuary positions to analyze for six POPs, including hexachlorocyclohexane isomers (HCHs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), heptachlor, aldrin, dieldrin, and polychlorinated biphenyl (PCBs). The averaged concentrations of the respective POPs in water samples were 0.07, 0.1, 0.01, 0.03, 0.001, and 0.2 μg L^{-1} and in sediment samples were 2.6, 3.1, 0.9, 0.2, 0.2, and 121 μg kg^{-1}. Of the six POPs examined, the concentration of DDTs in sediment samples and PCBs in water samples was significantly affected by the interactive effect of the two examined factors. The concentrations of HCHs, DDTs, heptachlor, and aldrin in water samples and of HCHs in sediment samples were significantly higher in the rainy season than in the dry season. Sediment samples collected from the inner position had a significantly higher concentration of HCHs and PCBs than in the outer position. Some mechanisms possibly influenced the varying POP concentration could include (1) greater riverine discharge in the rainy season and (2) the sea dilution effect in the outer position. Therefore, the concentration of the individual examined POPs in water and sediment in the Cua Dai estuary significantly depended on either the season, estuary position, or their combination.

Keywords Organochlorine pesticides · HCHs · DDTs · PCBs · Estuary · Water · Sediment

Introduction

Persistent organic pollutants (POPs) are organic compounds, which are environmentally persistent, long-distance transported, bio-accumulative, and potentially toxic (UN 2017). POPs, existing in different forms, could be grouped into three categories, including (1) agricultural pesticides, (2) industrial chemical products or byproducts, and (3) intentional

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products (Hayat et al. 2010). The first may include the first generation of organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCHs), dichlorodiphenyltrichloroethane (DDTs), heptachlor, dieldrin, and aldrin and the second may include polychlorinated biphenyls (PCBs). Chemically, a common feature of these compounds is chlorine containing that partially determines their environmental persistence and toxicology. Although POPs were banned or restricted for use globally a few decades ago (UNEP 2003), because of environmental persistence and long-range transport, they were detected in different environments, such as the oceans (Ma et al. 2015), the seas (Fuoco et al. 2009), the water and sediment (Wang et al. 2003), the air (Nost et al. 2018), and the polar regions (Mangano et al. 2017).

Originally, POPs could be applied to agricultural fields, residential, and industrial areas for different purposes. POP residues in the applied areas could be transported to an estuary of a river. As a result, POP status in the estuary could be affected by seasonal variation, which has higher rainfall in the rainy season than in the dry season. Seasonal variation of the concentration of some OCPs in river water was reported by Ramesh et al. (1990) and the authors attributed to agricultural production, such as flowering season of the paddy rice in the upper river catchment. Similarly, Sujatha et al. (1999) found varying concentrations of some OCPs in water samples taken before and after the monsoon season in an estuary in India. The authors linked the concentration variation to the agricultural runoff, which was affected by the monsoon and agricultural practices, such as tilling. A study by Li et al. (2014) reported that there were differences in POP concentration between the inner and outer positions of the Yangtze estuary, China. The differences also depended on the seasonal variation determining the seasonal discharge of the river that transported POPs from the upper river catchment to the estuary. These may indicate that there could be the interactive effect of the season and estuary position on the POP concentration in water and sediment in an estuary. Nevertheless, such the information is limited from literature.

In Vietnam, POPs were used for various purposes, such as agricultural production improvement, public health protection, and industrial production. It was estimated that an approximate amount of 6500–9000 tons year^{-1} of some organochlorine pesticides such as DDT and hexachlorobenzene (HCB) were imported to Vietnam for use during the 1980s (Sinh et al. 1999). Although being banned of using, by November 1992, there was 3640 kg of POPs, mainly DDTs and HCB, still remaining in some provinces in Vietnam awaiting for disposal (Sinh et al. 1999). This means that illegal application of DDTs and HCB could happen after the year 1992. There were a number of studies conducted to examine the presence of POPs in different local environments throughout Vietnam. For example, Dang et al. (1999) reported that HCHs in sediment samples collected from coastal regions in northern Vietnam varied from 1.2 to 33.7 ng g^{-1}, DDTs from 6.2 to 10.4 ng g^{-1}, and PCBs from 0.47 to 28.1 ng g^{-1}. Minh et al. (2007a) found that sediment collected in canals located in Ho Chi Minh City had a significantly higher OCP concentration than that in the Sai Gon-Dong Nai river and its estuary. In a comprehensive review, Minh et al. (2008) documented that many POPs have been detected and reported from different locations throughout Vietnam territory, such as Ho Chi Minh City, Hanoi, Binh Tri Thien province, Mekong river delta, and Hai Phong province. These studies assessed the levels of the POPs in different environments from agricultural fields to industrial and urban areas in Vietnam. However, information on the seasonal variation of POPs and the effect of estuary position on the POP concentration in sediment and water in an estuary in the middle of Vietnam is limited.

Globally and nationally, there is still a knowledge gap about the relationship between the combination of season and estuary position with the concentration of some POPs needed to be addressed. Therefore, the current study was conducted on the Cua Dai estuary, Hoi An City, Quang Nam province, Vietnam in 2013 and 2014. The aims of the current study were to (1) to assess the status of POPs and (2) to examine the interactive effect of season and estuary position on the concentration of the pollutants in surface water and sediment.

Materials and methods

Study area

The current study was conducted in the Cua Dai estuary, located in Hoi An City, Quang Nam province, Vietnam (108°2′–108°25′E and 15°51′–15°54′N) (Fig. 1). The estuary is the boundary of the Thu Bon River system with the East Sea of Vietnam. The Cua Dai estuary had a total catchment area of 10,350 km^2, which is flat along the coast and elevated toward the west. There are two other main rivers (Vu Gia and Truong Giang river) collectively adding water to the Thu Bon River, before coming to the Cua Dai estuary. The total length of the Thu Bon river system is around 189 km, and the total annual discharge is approximately 21.1 billion m^3. The area of paddy field in the catchment of the Thu Bon river system is around 798,790 ha. The river catchment has two distinct seasons: the rainy season is from September to December, and the dry season is from January to August with a total annual rainfall from 2000 to 2500 mm.

Sampling design

Thirteen sites surrounding the boundary of the Cua Dai estuary with the sea were selected for the current study (Fig. 1). The Cua Dai estuary was geographically divided into two

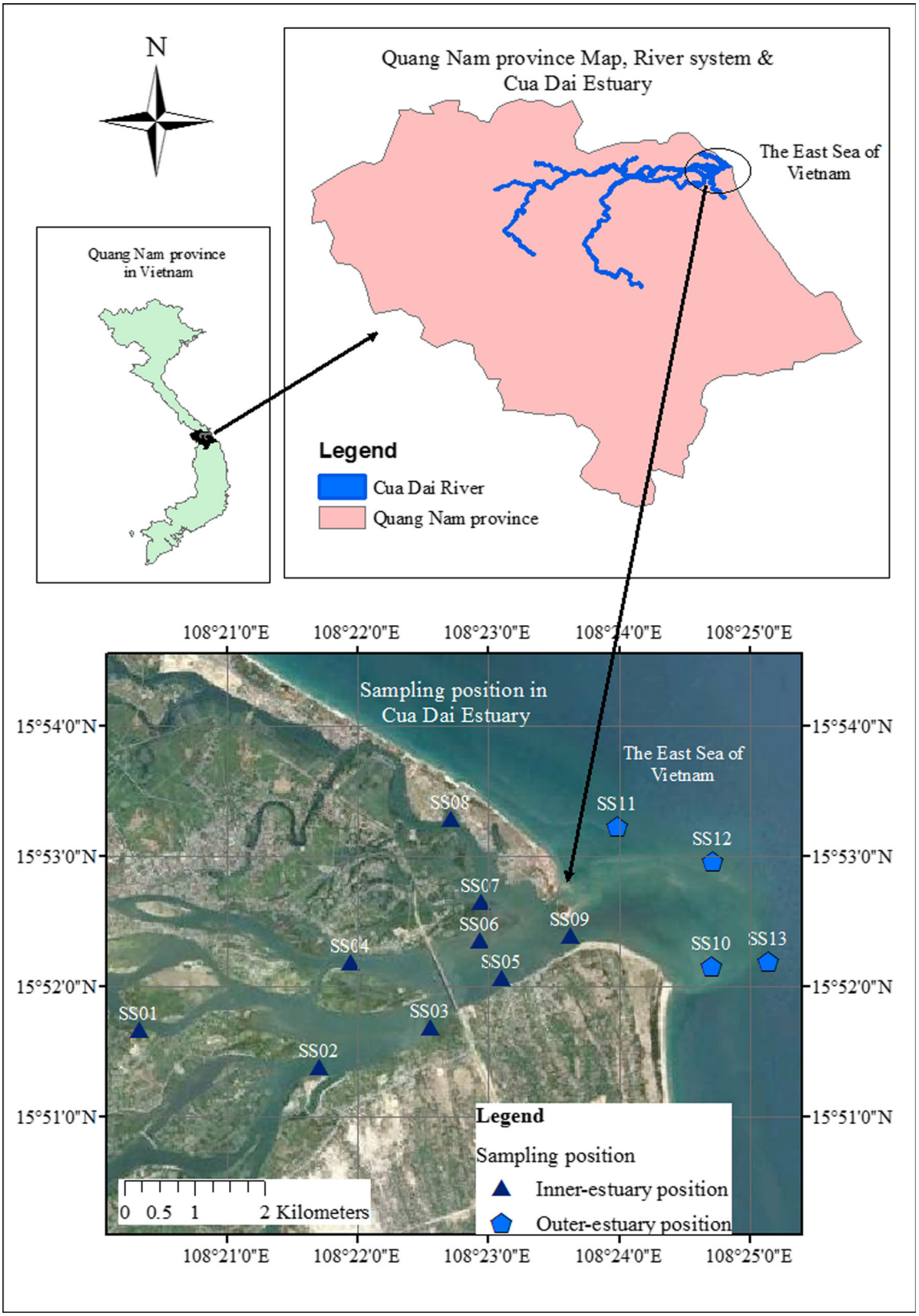

Fig. 1 The Cua Dai estuary and sampling positions

parts, inner-estuary position (hereafter referring to inner position) and outer-estuary position (hereafter referring to outer position). Nine sampling sites were randomly selected within the inner position and four sampling sites were randomly

selected in the outer position for the current study. Samplings were conducted in two seasons (rainy season: September 2013 and November 2014, dry season: April 2014 and July 2014) from the thirteen sites selected. For water samples, the samples were collected from the 0–50-cm surface water layer using a Van Dorn water sampler. Five samplings for one site were taken and the collected water was mixed and around 4 l of water per site were taken into a glass bottle. For sediment samples, the samples were taken using a Petersen grab and the sediment for the top 0–10-cm layer was carefully taken with a stainless steel knife. Five grabs were taken and the 0–10-cm sediment from these grabs was mixed and around 2 kg of the sediment was taken into a glass bottle. All the sample bottles were immediately stored in an ice-chest at 4 °C and transported to the laboratory for analysis. A global positioning system (GPS) device was used to locate the 13 selected sites to take both sediment and water samples four times during 2013 and 2014.

Chemical analyses

For water samples: 52 water samples (13 sites × 4 times) were analyzed for concentrations of the six POPs and some selected quality parameters (pH, turbidity, salinity, electrical conductivity (EC), and dissolved oxygen (DO)). Hexachlorocyclohexane isomers (HCHs, α-HCH, β-HCH, γ-HCH, and δ-HCH), dichlorodiphenyltrichloroethane and its metabolites (DDTs, o,p′-DDT, p,p′-DDT, p,p′-DDE, p,p′-DDD), heptachlor, aldrin, dieldrin, and polychlorinated biphenyl (PCBs, PCB congeners 28, 52, 101, 118, 138, 152, and 180) were quantified, following the procedure by Nhan et al. (1998) and Zheng et al. (2016). In brief, a total amount of 1000 ml of the collected water sample was filtered with a Whatman filter paper (i.d. 70 mm) to remove debris and suspended materials and then poured into a 2-l separatory funnel. For the first liquid-liquid extraction (LLE), 60 ml dichloromethane (DCM) was added and shaken vigorously for 10 min before two-phase separation. The water phase was drained from the separatory funnel into a 1000-ml beaker. The organic-phase was carefully poured into a flask containing 20 g of anhydrous sodium sulfate. The extract was concentrated to the volume of 2 ml using a vacuum rotary evaporator. The clean-up was performed using Florisil cartridges. The cartridges were eluted with 7 ml of hexane for PCB congeners. Then, the column was eluted with 12 ml of the mixture containing 80% of hexane and 20% of dichloromethane for the pesticide fraction. Finally, the eluted solution was concentrated under a gentle stream of nitrogen flow and then analyzed for the examined POPs using gas chromatography equipped with an electron capture detector (GC-ECD) (Varian Co., USA). The selected water quality parameters were determined in situ using pH meter for pH, Hach DR/2010 spectrophotometer for turbidity, Hanna HI931100 salinity meter for salinity, oxi 3210 portable dissolved oxygen meter for DO, and electrical conductivity meter for EC.

For sediment samples, the samples were analyzed for the same POPs as in the water samples, following the procedure by Nhan et al. (1998) and Zheng et al. (2016). The collected sediments were air-dried and a10-g dried sediment sample was mixed with anhydrous sodium sulfate, transferred to an extraction thimble, and placed in a Soxhlet extractor. The mixture was extracted with 300 ml of acetone: *n*-hexane (1:1, *v*/*v*) for 16 h. The extracts were then combined and desulfurized through activated copper powder and then concentrated to a few milliliters in a rotary evaporator at a temperature of 35 °C. The remaining extract was transferred to the top of a glass column packed with 8 g Florisil followed by elution with 40 ml of hexane for PCB congeners and 120 ml of mixture *n*-hexane: DCM (4:1, *v*/*v*) for the pesticide fraction. Each fraction was concentrated under a flow of nitrogen and stored at 4 °C before analyzing using the GC-ECD system. In addition, total organic carbon was determined using a Shimadzu TOC Analyzers.

Statistical analyses

The current study was set up as a two-factor completely randomized design with varying replicates (Ott and Longnecker 2011). The POP concentrations in water and sediment samples were examined under two seasons (dry and rainy season) and two estuary positions (inner and outer position) (two factors). An analysis of variance (ANOVA) following a two-factor experimental design was conducted, using JMP 10 (SAS Institute Inc, NC, USA). The overall ANOVA model was $\gamma_{ijk} = \mu + \beta_i + \alpha_j + \beta\alpha_{ij} + \in_{ijk}$, where γ_{ijk} is the response of individual combination; μ is overall mean; β_i is a fixed effect of the *i*th level of the season factor; α_j is the fixed effect of the *j*th level of the position factor; $\beta\alpha_{ij}$ is the interactive effect of the season and position; and $\in_{ijk}$ is the random error with mean zero and having normal distribution (Ott and Longnecker 2011). Firstly, the interactive effect was examined and if significant with $P \leq 0.05$, the Tukey honestly significant difference test was applied to classify the four combinations (two seasons by two positions). If not, the main effects of season and position were examined. If any of the two main effects was significant ($P \leq 0.05$), Student's *t* test was applied to classify individual factors. If there was no significant effect shown, no Student's *t* test was applied and the concentrations of the POP were summarized for mean, standard error, maximal and minimal values. All figures were made using Sigmaplot 12 (Systat Software Inc.).

Results

Organochlorine pesticides (HCHs and DDTs)

The concentrations of HCHs (including alpha, beta, gamma, delta-isomers) in 52 water samples collected from two estuary positions in two seasons varied from 0.01 to 0.37 μg L^{-1}, with a mean value of 0.07 μg L^{-1} (Supplementary Table 1). There was no interactive effect of the season and the estuary position on the HCH concentration in water samples. While the main effect of the estuary position (inner and outer position) was not significant, that of the season (the dry and rainy season) was significant on HCH concentration in water samples. The mean concentration of HCHs in water samples was significantly higher in the rainy season 0.11 μg L^{-1} than in the dry season 0.03 μg L^{-1} (Fig. 2a). In 52 sediment samples, HCH concentration varied from 0.49 to 8.64 μg kg^{-1} (Supplementary Table 2). There was no significant interactive effect of the season and the estuary position on HCH concentration of sediment samples, but the main effects of the two factors were significant (Fig. 2b, c). Sediment samples collected in the rainy season had a significantly higher concentration of HCHs (3.3 μg kg^{-1}) than those collected in the dry season (1.6 μg kg^{-1}). Sediment samples taken in the inner position had a significantly higher concentration of HCHs (2.9 μg kg^{-1}) than those taken in the outer position (2.0 μg kg^{-1}).

The concentration of DDTs (including *p*,*p*′-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD, and *o*,*p*′-DDT) in the 52 water samples varied from 0.02 to 0.42 μg L^{-1} and in 52 sediment samples from 1.14 to 8.12 μg kg^{-1}. The DDT concentration in water samples was not significantly influenced by the interactive effects of two examined factors but was significantly influenced by the season (Fig. 3a). The concentration of DDTs in water samples taken in the rainy season was 013 μg L^{-1}, significantly higher than that in the dry season (0.08 μg L^{-1}). In sediment samples, the concentration of DDTs was significantly affected by the interactive effect of the estuary position and the season (Fig. 3b). While in the rainy season, DDT concentrations in sediment samples taken from the inner and outer positions were similar, in the dry season, those taken from the inner position (4.4 μg kg^{-1}) were significantly higher than those from the outer position (1.7 μg kg^{-1}).

Organochlorine pesticides (heptachlor, aldrin, and dieldrin)

In sediment samples, the concentrations of heptachlor, aldrin, and dieldrin were not significantly influenced by either the

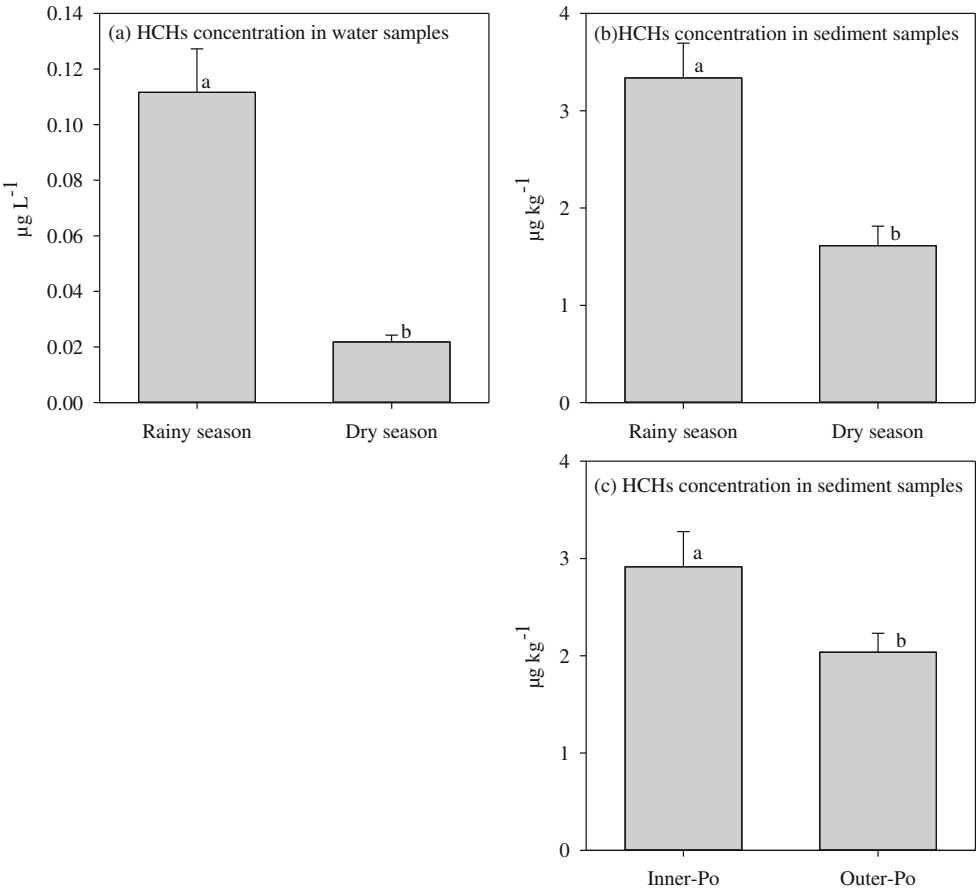

Fig. 2 **a**–**c** HCH concentrations in water and sediment samples. Error bars are the standard deviation of the mean. Within a panel, bars attached with the same letters are not significantly different from each other at $P \leq 0.05$. Inner-Po inner position, Outer-Po outer position

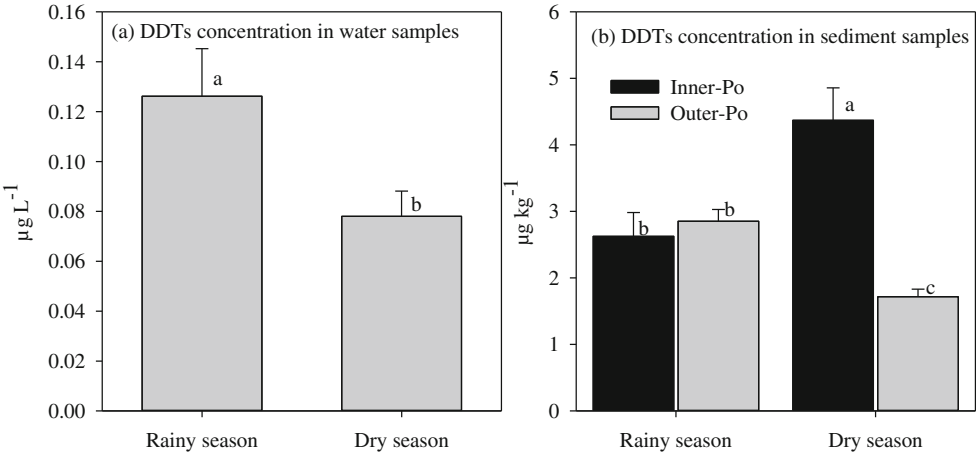

Fig. 3 **a**, **b** DDT concentration in water and sediment samples. Error bars are the standard deviation of the mean. Within a panel, bars attached with the same letters are not significantly different from each other at $P \leq 0.05$. Inner-Po inner position, Outer-Po outer position

interactive effect of the season with the estuary position or the main effect of the individual factors. The average concentrations of these OCPs were 0.91, 0.18, and 0.02 μg kg^{-1}, respectively (Table 1). Of the 52 samples analyzed, all sediment samples were detected to contain heptachlor; 35 sediment samples were detected to have aldrin, and 37 sediment samples were detected to have dieldrin.

In water samples, only dieldrin was not significantly affected by either the interactive effect of the two examined factors or the single effect of the individual factors. The average concentration of dieldrin in water samples was 0.0015 1.7 μg L^{-1} and 27 water samples, out of 52 samples analyzed, were detected to contain dieldrin. In contrast, the concentrations of heptachlor and aldrin, although not influenced by the interactive effect, were significantly affected by the season (Fig. 4a, b). The concentrations of heptachlor and aldrin in water samples were significantly higher in the rainy season (0.017, 0.054) than in the dry season (0.011, 0.002 μg L^{-1}, respectively).

Polychlorinated biphenyls

Overall PCB concentration in water samples varied from 0.03 to 1.05 μg L^{-1}, and in sediment samples from 24.7 to 329.7 μg kg^{-1}. There was a significant interactive effect of the estuary position with the season on the PCB concentration in water samples (Fig. 5a). For the inner position, water samples taken in the rainy season had a significantly higher concentration of PCBs (0.35 μg L^{-1}) than in the dry season (0.10 μg L^{-1}), whereas those taken from the outer position had a similar PCB concentration in both seasons. The concentration of PCBs in sediment samples was significantly higher in the inner position (138 μg kg^{-1}) than in the outer position (84 μg kg^{-1}) (Fig. 5b).

Table 1 Statistical values of the concentration of some POPs, of which their concentration was not significantly affected by the season or estuary position (Note: *sediment samples (μg kg^{-1}), **water samples (μg L^{-1}); *SE* standard error, $n = 52$)

Statistics	Heptachlor*	Aldrin*	Dieldrin*	Dieldrin**
Mean	0.91	0.18	0.02	0.0015
SE	0.06	0.03	0.01	0.0003
Max	2.90	0.91	0.23	0.0081
Min	0.35	0.00	0.00	0.0020

Selected quality parameters of water and sediment samples

There were significant differences in pH, turbidity, salinity, EC, and DO of water measured from the two estuary positions (inner and outer position) (Table 2 and Supplementary Table 3). The surface water measured from the outer position was significantly higher in salinity (2.2%), EC (3.6 mS^{-1}), and DO concentration (7.7 mg L^{-1}) than those from the inner position, 0.5 % for salinity, 0.8 mS^{-1} for EC, and 6.1 mgL^{-1} for DO. Nevertheless, the inner position had significantly higher pH (7.5), turbidity (67.2 FAU) in water, and total organic carbon in sediment (1.5 %) than the outer position (pH = 7.3, turbidity = 52.3 FAU, and total organic carbon = 0.9 %). Seasonal variation introduced a significant effect on the selected water quality parameters (Table 2). Water measured during the rainy season were significantly higher in turbidity, while lower in pH, salinity, EC, and DO than that measured during the dry season.

Discussion

POPs in the water samples

In addition to rainfall and atmospheric sources, in general, POPs present in the water of an estuary could be derived from two main sources, including (1) upstream transport from the river catchment, which could be from agricultural fields, industrial, and residential areas, and (2) onsite water-sediment

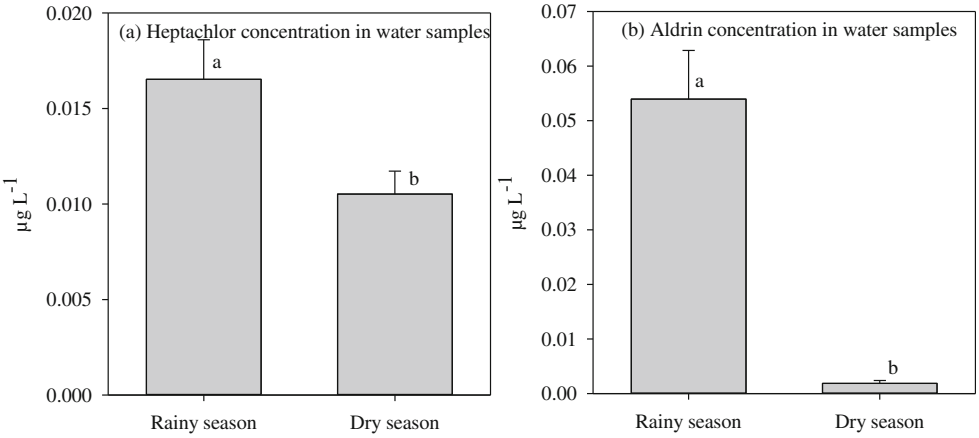

Fig. 4 **a**, **b** Heptachlor and aldrin concentrations in water samples. Error bars are the standard deviation of the mean. Within a panel, bars attached with the same letters are not significantly different from each other at $P \leq 0.05$

exchange. Another POP source could be added from the sea, but its contribution could be negligible due to the great dilution effect of the sea. The riverine transport of POPs was reported by a number of studies (Chau 2006). Williams (2011) found that the concentration of pesticide-originated POPs in Tarkwa Bay was higher in the summer season than in the winter season and the authors attributed to more agricultural and domestic activities in the summer season. Takeoka et al. (1991) reported that a small portion of HCHs applied to the catchment area was transported to the sea and that concentration of HCHs could be largely affected by the application of the pesticide during flowering season of paddy rice. Compared to previous results, the authors pointed out that the rate of riverine discharge could be the determinant of the HCHs amount drained to the sea. The onsite water-sediment exchange was used to explain the higher concentration of POPs in sediment samples than that in water samples (Zhang et al. 2003). Nevertheless, the effect of the onsite water-sediment exchange could exist for a relatively short period, as long as the river bottom is disturbed to re-suspend the sediment to the water phase. Due to hydrophobicity and low solubility (Da et al. 2014), POPs could hardly exist in the dissolved form in the aquatic environments but tend to be absorbed onto suspended sediment (O'Sullivan and Megson 2014), which eventually deposit to the bottom.

In brief, the concentration of POPs in the estuary water could be strongly related to (1) the POP application/discharge on the river catchment, including agricultural, industrial, and residential areas, and (2) rainfall or seasonal variation to transport the POP residues to the estuary. These may explain the findings from the current study that the concentrations of HCHs (Fig. 2a), DDTs (Fig. 3a), heptachlor (Fig. 4a), aldrin (Fig. 4b), and PCBs (Fig. 5b) in water samples were significantly higher in the rainy than in the dry season. In particular, the transport of these POPs from the Thu Bon River catchment to the Cua Dai estuary through a higher river discharge during rainy season could increase the POP concentration in water samples, compared to the dry season. These were in agreement with Barasa et al. (2007), who found that the concentration of Aldrin, dieldrin, and DDT residues was higher during the rainy season than the dry season. With a tendency of binding to organic matter in the soil (O'Sullivan and Megson 2014), POPs with the soil organic matter could be co-transported to the estuary position. The co-transport could be additionally evidenced by the observation in the current study that water turbidity in the rainy season was significantly

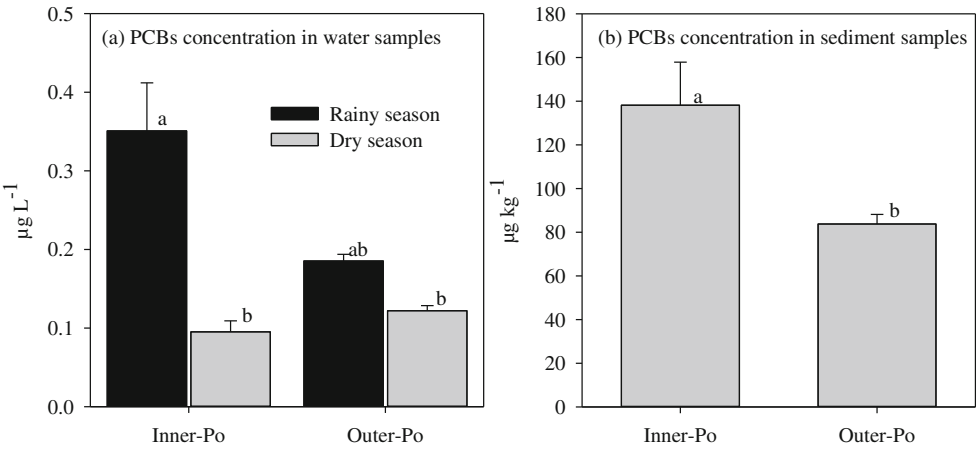

Fig. 5 **a**, **b** PCB concentration in water and sediment samples. Error bars are the standard deviation of the mean. Within a panel, bars attached with the same letters are not significantly different from each other at $P \leq 0.05$. Inner-Po inner position, Outer-Po outer position

Table 2 Selected quality parameters of water and sediment samples taken from two positions and two seasons. Within a column, data attached with the different letters are significantly different from each other at $P \leq 0.05$. Data in the parenthesis are the standard deviation of the mean (Note: *Inner-Po* inner position, *Outer-Po* outer position; *water samples, **sediment samples)

	pH*	Turbidity* (FAU)	Salinity* (%)	EC* (mS m^{-1})	DO* (mg L^{-1})	Total organic carbon** (%)
Estuary position						
Inner-Po	7.5^{a} (0.04)	67.2^{a} (5.38)	0.5^{b} (0.05)	0.8^{b} (0.08)	6.1^{b} (0.14)	1.5^{a} (0.16)
Outer-Po	7.3^{b} (0.03)	52.3^{b} (2.28)	2.2^{a} (0.12)	3.6^{a} (0.23)	7.7^{a} (0.06)	0.9^{b} (0.10)
Seasonal variation						
Rainy season	6.8^{b} (0.04)	87.2^{a} (6.95)	0.6^{b} (0.04)	1.1^{b} (0.09)	6.4^{b} (0.11)	1.2 (0.15)
Dry season	8.0^{a} (0.03)	32.3^{b} (0.71)	2.1^{a} (0.13)	3.3^{a} (0.23)	7.5^{a} (0.08)	1.2 (0.12)

higher than that in the dry season (Table 2). In contrast, Williams (2011) reported that POP concentration was higher in the dry season than in the rainy season. The author attributed to the stronger turbulence of the sediment often occurring during low tidal regime in the dry season. Nevertheless, the mechanism may not affect the water samples in the current study, because the samples were taken from the top water layer.

The single effect of the estuary position did not result in any different concentration of the examined POPs, but some selected quality parameters of water samples (Table 2). Compared to the outer position, the inner position had much lower salinity and EC, possibly because freshwater discharge from the upstream river could dilute or push some seawater out of the estuary mouth. However, the freshwater could contain a high concentration of suspended particular matters, which contaminated the inner-position water, indicated by a higher turbidity in the inner position than the outer position. The non-obvious difference in the concentration of the examined POPs in water samples between the two estuary positions in the current study could be explained that (1) during the rainy season, POPs binding to the suspended sediment in water tended to be transported to the sea part connected to the estuary mouth (the outer position) (Li et al. 2014), and subsequent dilution effect of the sea in the outer position could reduce their concentration. The dilution effect of the sea could be one important reason to explain that seasonal change in OCP concentration in the offshore sites was more stable and that in the inner estuary was more variable than the other (Li et al. 2014). (2) During the dry season, POPs binding to the suspended sediment could deposit fast in the inner position (Li et al. 2014) due to the natural purification of the aquatic environments.

POPs in sediment samples

The concentrations of the examined POPs in the sediment samples were much higher than those in the water samples, indicating that estuary sediment could be a significant sink of POPs and that the Thu Bon River catchment of the Cua Dai estuary was historically applied with the POPs. This was in agreement with the findings by Williams (2011). According to Zhang et al. (2003), POPs with hydrophobicity tended to bind to the sediment that could be re-suspended to the water phase upon disturbance, which may explain higher POP concentration in sediment than in water samples. Different from estuary water, which could be affected by upstream runoff at the sampling time, estuary sediment was more likely influenced by historical upstream transport and the deposition of the sampling-time transported sediment. Of the six POPs examined in the current study, two POPs in the sediment samples (HCHs and PCBs) had concentrations different between either two estuary positions (Figs. 2c and 5b) or two seasons (Fig. 4b). This indicated that the examined POP concentrations in the sediment samples were less affected by temporary seasonal variation or estuary position than those in the water samples. The concentrations of HCHs and PCBs of the sediment samples followed the general pattern of the water samples that were higher in the rainy season than in the dry season and higher in the inner position than in the outer position. This is in agreement with the finding by Sarkar et al. (1997) and Shi et al. (2016). The authors attributed to the surface runoff to distribute the historical pollutants to the estuary and sea tide to dilute the POP concentration. Upstream transport in the rainy season and dilution effect in the outer position due to the seawater may explain the differences. In addition, compared to the inner position, the sediment taken from the outer position may contain higher percentage of coarse materials, such as sand and small stones, which may adsorb POPs more weakly than the fine materials such as silt and clay, resulting in lower concentration of the POPs (Sarkar et al. 1997).

In the Cua Dai estuary from the current study, the concentrations of HCHs (0.5–8.6 μg kg^{-1}) in sediment were below the range of 1.2–33.7 μg kg^{-1} reported by Dang et al. (1999), and of DDTs (1.1–8.1 μg kg^{-1}) were also below the range of 6.25–10.42 μg kg^{-1} reported by the same authors in the sediment samples taken in northern coastline in Vietnam. The

DDT concentration in the current study was similar to those reported by Minh et al. (2007b) in the Mekong River delta in Vietnam. The similar concentrations of HCHs and DDTs in the current study may not reflect the rapidly volatile property of HCHs (Takeoka et al. 1991). After a certain time in contact with soil, the POPs could be completely adsorbed on soil components such as organic matter or soil particles, resulting in an almost-ceased POP loss (Alexander 2000). And in the completely adsorbed condition, the easily volatile property of the HCHs might not play any important role in determining their concentration in the soil and then estuary sediment.

Of the six POPs examined in the current study, PCBs had the highest concentration (73–183 μg kg^{-1}) in sediment samples. These numbers were much higher than these (0.039–9.2 μg kg^{-1}) reported by Minh et al. (2007b) in the sediment taken in the Mekong River delta in Vietnam. The PCB concentration in the current study was also higher than that reported by Chau (2006). The author attributed to the upstream transport of the POP to Hong Kong territories, resulting in POP accumulation in the investigated estuary. Pozo et al. (2014) found that PCB concentrations in sediment collected from the Lenga estuary, central Chile, varied from 20 to 10,000 μg kg^{-1}, which were much higher than those in the current study. The nature of the compounds such as low degradation and vaporization rate and low water solubility (Pozo et al. 2014) could explain the high values in the current study, although many reasons could contribute. More importantly, PCBs are those used in industrial production/equipment such as transformer, capacitors, heat transfer, paint, plastic, and flame retardant (European Commission 2018). Rapid urbanization and fast population growth in the river catchment of the Cua Dai estuary for the past years may discharge a considerable amount of PCBs to the residential areas and subsequent drainage of the PCB-containing effluent to estuary sediment may be one of the reasons for their highest concentration as shown in Fig. 5. Similarly, Minh et al. (2007b) pointed out that the main source of the PCBs was from metropolitan areas, which resulted in higher PCB concentration in the sediments taken close to the urban areas than the further sites.

The interactive effects

One interesting finding from the current study was the interactive effect of the season and estuary position on the DDT concentration of sediment samples (Fig. 3b) and PCB concentration of water samples (Fig. 5a). Compared to the dry season, the rainy season increased the concentration of some POPs in water and sediment in an estuary (Takeoka et al. 1991; Williams 2011) and the same effect was observed in the current study (Figs. 2a, b, 3a, 4a, b, and 5b). The estuary position effect on the POP concentrations was identified by Li et al. (2014). Li et al. (2014) concluded that in the dry season, POPs in the sediment tended to accumulate in the inner estuary rather than the outer estuary and vice versa. The reason given by the authors was that compared to the dry season, the rainy season had greater riverine discharge, which prevented the POP-containing suspended sediment from settling down in the inner estuary, and consequently, the suspended sediment tended to be transported to the sea part connected to the estuary mouth before deposition. However, these studies did not find the dilution effect of the sea that may reduce the rainy effect on the POP concentration in the outer-estuary position. The interesting finding of the interactive effect of the season and estuary position on the DDT concentration of the sediment samples and on PCB concentration of the water samples could support the combined effect of the two reported mechanisms. Assuming that a high riverine discharge during the rainy season tended to transport the suspended sediment to the outer position and vice versa (Li et al. 2014), the first mechanism of dilution effect of the sea could happen to diminish the transport effect of the rainy season, making DDT concentrations of the sediment samples similar between the outer and inner positions in the rainy season (Fig. 3b). The second mechanism of the seasonal effect could play a significant role in the dry season, which increased the DDT concentration of the sediment in the inner position, compared to the outer position. These interactive mechanisms could also explain the PCB concentrations of the water samples (Fig. 5b). In particular, for the inner position, higher riverine discharge in the rainy season could result in a higher PCB concentration of water samples than in the dry season, whereas for the outer position, the dilution effect of the sea could diminish the rainy effect and thus make the POP concentration of water samples similar between the two seasons.

Conclusions and implication

The interactive effects of the season and estuary positions on and the status of the concentration of some POPs in water and sediment were examined in the current study. Of the six POPs examined, the concentration of DDTs in sediment samples and PCBs in water samples was significantly affected by the interactive effect of the two examined factors. While in the dry season, the sediment concentration of DDTs was significantly higher in the inner position than the outer position, in the rainy season, a similar concentration was observed from both estuary positions. For the PCBs, the concentration of the POP of water samples taken from the inner position was significantly higher in the rainy season than in the dry season whereas similar concentrations in the two seasons were detected in the outer position. POP concentration in sediment samples was much higher than those in the water samples. The concentrations of HCHs, DDTs, heptachlor, aldrin of water samples, and HCHs of sediment samples were significantly higher in the rainy season than the dry season. Several mechanisms

involved in the variation of POP concentration could include larger riverine discharge in the rainy season to drain POPs to the Cua Dai estuary and dilution effect of the sea to reduce the POP concentration in the outer position. The presence of the six POPs in the estuary-water samples indicated that either recent application of the examined POPs or historical accumulation of the POPs in the river catchment could happen. In either case, the concentration of the individual examined POPs in water and sediment in the Cua Dai estuary significantly depended on either the season, estuary position, or their combination.

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