



## Persistence, temporal and spatial profiles of ultraviolet absorbents and phenolic personal care products in riverine and estuarine sediment of the Pearl River catchment, China



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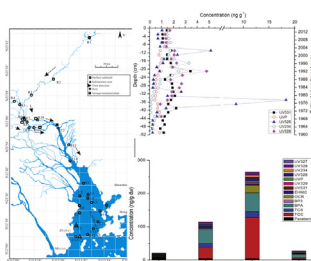
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### HIGHLIGHTS

- The PCPs were widely present in the sediment.
- UV stabilizers and TCC were fairly persistent in sediment.
- PCPs' temporal trend mirrored industrial developments and waste treatment.
- No significant in-situ TCC dechlorination in the sediment.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A variety of personal care products have been classified as emerging contaminants (ECs). Occurrence, fate, spatial and vertical profiles of 13 ultraviolet absorbents, triclocarban (TCC) and its dechlorinated products, triclosan (TCS), 2-phenylphenol and parabens were investigated in riverine and estuarine sediment of the Pearl River catchment, China. Bisphenol A (BPA), a widely applied plasticizer, was also investigated. The ECs were widely present in the bed sediment. TCC was the most abundant with a maximum concentration of 332 ng g<sup>-1</sup> dry weight. The other prominent ECs included BPA, TCS, octocrylene, and benzotriazole UV stabilizers UV326 and UV328. Treated wastewater effluent was the major source of the ECs in the riverine sediment. TCC, BPA, TCS, methyparaben, UV531, UV326, and UV328 were also detected throughout the estuarine sediment cores, indicating their persistence in the sediment. Temporal trends of the ECs in the sediment cores reflected a combined effect of industrial development, population growth, human life quality improvement, and waste treatment capacity in the Pearl River Delta over the last decades. TCC dechlorination products were frequently detected in the bed sediment with higher levels near treated effluent outlets but only occasionally observed in the sediment cores, suggesting insignificant in-situ TCC dechlorination in the sediment.

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**Table 1**  
The investigated emerging contaminants.

Class	Compound/abbreviation	CAS No	LogK <sub>ow</sub>
preservative	methylparaben/MP	99–76-3	1.96
preservative	ethylparaben/EP	120–47-8	2.47
preservative	propylparaben/PP	94–13-3	3.04
preservative	butylparaben/BP	94–26-8	3.57
disinfectant	2-phenylphenol/PHP	90–43-7	3.09
disinfectant	triclosan/TCS	3380–34-5	4.76
disinfectant	triclocarban/TCC	101–20-2	4.9
plasticizer	bisphenol A/BPA	80–05-7	3.32
metabolite	nonchlorinated carbanilide/NCC	102–07-8	— <sup>a</sup>
metabolite	dichlorocarbanilide/DCC	1219–99-4	— <sup>a</sup>
UV filter	2-hydroxy- 4-methoxybenzophenone/BP3	131–57-7	3.52
UV filter	3-(4-methylbenzylidene)camphor/4MBC	36861–47-9	5.47
UV filter	octocrylene/OCR	6197–30-4	6.88
UV filter	octyldimethylparaaminobenzoate/ODPABA	21245–02-3	5.77
UV filter	avobenzone/AVO	70356–09-1	2.41
UV filter	2-ethylhexyl 4-methoxycinnamate/EHMC	5466–77-3	5.80
UV stabilizer/plasticizer	UV531	1843–05-6	6.42
UV stabilizer	UVP	2440–22-4	3.00
UV stabilizer	UV329	3147–75-9	6.21
UV stabilizer	UV326	3896–11-5	5.52
UV stabilizer	UV234	70321–86-7	7.67
UV stabilizer	UV328	25973–55-1	7.22
UV stabilizer	UV327	3864–99-1	6.75

<sup>a</sup> no report.

## 1. Introduction

Personal care products (PCPs), such as sunscreens and lotions, are produced to improve quality of human lives. Production and consumption of PCPs keep increasing due to growing population and people's pursuit for better quality of life. Bisphenol A (BPA) is widely applied as a stabilizing agent in plastics and as an additive in thermal paper and paper coatings. A variety of PCPs as well as BPA may find their way to the environment after consumption and have been listed as emerging contaminants [1]. Among the big family of emerging contaminants, chemicals such as BPA, preservatives (e.g. parabens), antimicrobials (e.g. triclosan and triclocarban), and various organic ultraviolet absorbents (UVAs) have caused particular concerns due to their confirmed or suspected endocrine disrupting impacts on organisms, posing threats to the health of ecological systems [2–7]. In addition, their general toxic effects on non-target organisms were also reported [4].

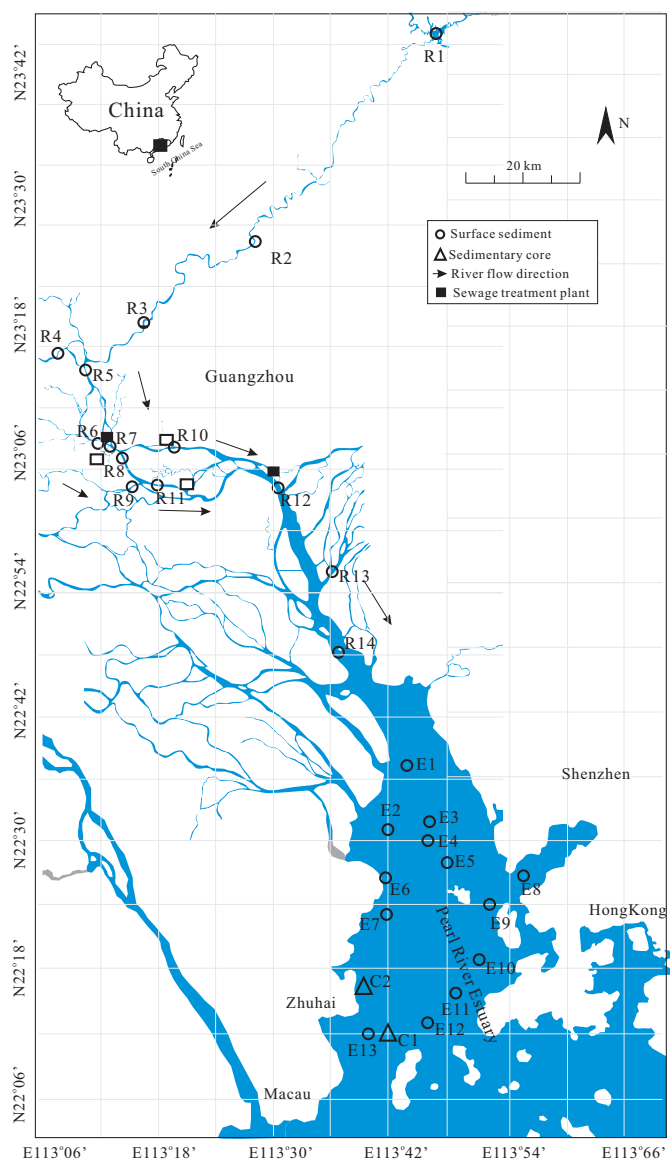
Many of these emerging contaminants are high-production chemicals. For example, BPA has an annual production of over 4.6 million tons globally [8,9]. Triclosan (TCS) and triclocarban (TCC) are widely used as disinfectants in such products as soaps, shampoos, body lotions, toothpastes, paints, and plastics at levels of up to 2% and 0.3% (w/w), respectively [10]. Parabens are preservatives added in cosmetics, pharmaceuticals, and foodstuffs [11,12]. UVAs are widely applied in sunscreens, cosmetics, etc., comprising up to 20% of mass weight for protecting humans from harmful UV radiation. They are also added in a variety of industrial products, such as textiles and paints, to protect the products from yellowing [13]. Significant amounts of these emerging contaminants are being discharged into the environment via treated and untreated wastewater, recreational activities, and other human activities. As a result, they have been widely detected in rivers, lakes, seas, groundwater, and organism tissues [9,14–27].

Sediment can be a significant sink for these emerging contaminants in the environment considering their moderate to high lipophilicity indicated by octanol-water partition coefficients (log K<sub>ow</sub>) between 1.96–7.67 (Table 1). Available research revealed the presence of TCC, TCS, BPA, parabens, and several UVAs in sediment [9,15,23,28–31]. Some of these compounds (e.g. TCC) were found to be fairly persistent [7,24,32]. Accumulation of these emerging contaminants in sediment may pose risks to wildlife,

especially benthic and sediment-dwelling organisms because these chemicals can be bio-accumulative in organisms and even be bio-transferable in food chains [4,17,33,34].

Pearl River Delta (PRD) is one of the most industrialized areas in China with a population of more than 50 million. The annual wastewater production has been about 9 billion m<sup>3</sup>, of which about 7 and 2 billion m<sup>3</sup> are domestic wastewater and industrial wastewater, respectively, in recent years. All the industrial wastewater and about 90% of the domestic wastewater are treated before discharge. The treated and untreated wastewater is finally discharged into the Pearl River and its tributaries. Furthermore, located in the south end of the subtropical zone, the PRD has warm and humid weather with annual sunshine of 1600–2000 h [35]. Products containing disinfectants, preservatives, and UVAs are therefore expected to be consumed in large quantities. Previous research has revealed high concentrations of TCS, TCC, parabens, and BPA in wastewater and river water of the PRD [36–38]. However, only few work studied some phenolic endocrine disrupting emerging contaminants (e.g., TCC, TCS, and BPA) in sediment in the Pearl River catchment [36,38]. Furthermore, occurrence and fate of the UV absorbents in the sediment in this area have not been revealed yet.

In this context, the objectives of this study are to (1) illustrate occurrence and spatial distribution of the emerging contaminants and their dechlorination products in bed sediment of the Pearl River and Pearl River Estuary (PRE), (2) delineate sedimentary profiles of the emerging contaminants in the PRE, and (3) investigate mechanisms of accumulation of these emerging contaminants and their fate in the sediment of the Pearl River and the PRE. The 21 emerging contaminants in this work belonged to commonly used disinfectants, preservatives, ultraviolet filters, ultraviolet stabilizers, and plasticizer as detailed in Table 1. Two dechlorination products of TCC were also included to demonstrate fate of TCC in the sediment. To the best of our knowledge, the benzophenone UV stabilizer UV531 in the environment was not reported so far. This is also the first work to reveal dechlorination products of TCC in the environment of China. Fate of TCC was consequently discussed, such as when and where the dechlorination happened. Furthermore, records of the UV absorbents in sedimentary cores were delineated to reveal environmental persistence of these compounds, which has been rarely reported. This work provided insight into distribution, temporal trends, and fate of the emerging contaminants in the



**Fig. 1.** Sketch map of the study area with locations of the sampling sites for bed sediment and cores.

riverine and estuarine environment of well industrialized areas of China.

## 2. Experimental

### 2.1. Study area and sampling

As the third largest river in China, the Pearl River runs through Guangdong Province from northwest to southeast and finally merges into the South China Sea via the PRE.

Fourteen riverine sediment samples were collected along the Pearl River, covering rural, suburban, and urban sections. Thirteen estuarine bed sediments were collected in the PRE, which is considered an important reservoir of pollutants from the Pearl River. Two sedimentary cores named C1 (22°12', 113°42') and C2 (22°17', 113°38') were collected in 2005 and 2014, respectively, in the PRE in order to delineate vertical profiles of the emerging contaminants. Locations of the sampling sites including the bed sediments and sediment cores were illustrated in Fig. 1. A sedimentation rate of 0.97 cm/y was determined previously in the area nearby the loca-

tions of the cores [36] and therefore was used to estimate of the year of deposition.

Bed sediment samples ( $\leq 5$  cm in depth) were collected with a clean stainless steel scoop, wrapped in clean aluminum foil, and sealed in ziplock polyethylene bags. The sedimentary core was collected using a gravity corer with a depth of 42 cm and was sliced at the site in intervals of 3 cm. All the sediment samples were stored at  $-20^{\circ}\text{C}$  in dark before treatment.

### 2.2. Analytes

All the chemical standards, nonchlorinated carbanilide (NCC), and deuterated BPA (BPA- $d_{16}$ ) and benzophenone (BP- $d_{10}$ ) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dichlorocarbanilide (DCC) was a product of ABCR GmbH & Co. KG (Karlsruhe, Germany). Deuterated triclosan (TCS- $d_5$ ), triclocarban (TCC- $d_4$ ), and ( $\pm$ )-3-(4-methylbenzylidene- $d_4$ )camphor (4-MBC- $d_4$ ) were bought from C/D/N isotopes (Pointe-Claire, Quebec, Canada).

### 2.3. Sample treatment and analysis

Sample treatment and analysis have been reported previously [39,40]. Briefly, an aliquot of lyophilized and homogenized sediment was treated by ultrasonic assisted extraction (USE). For analysis of the phenolic compounds except TCC and its two dechlorination products (NCC and DCC), the USE extract was cleaned up by solid phase extraction (SPE) on an Oasis HLB cartridge, followed by derivatization with dansyl chloride. For analysis of the UVAs, TCC, DCC, and NCC, the USE extract was cleaned up on a silica gel chromatograph column. The chemicals were determined by ultra-high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). Detailed information about treatment of the samples and determination of the chemicals was also provided in the Supporting Material.

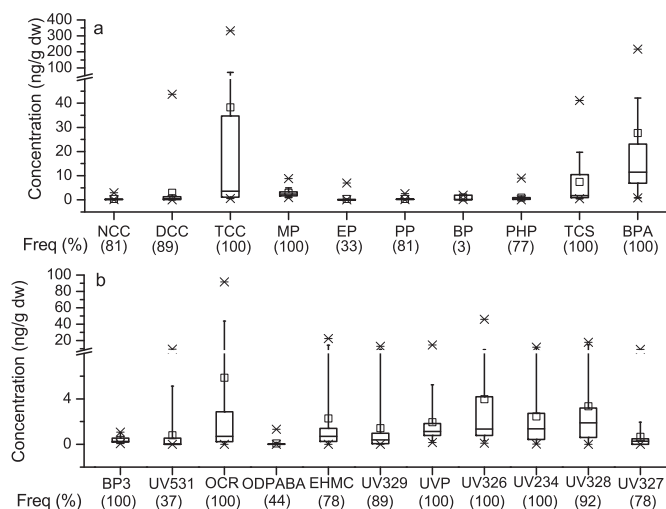
### 2.4. Quality assurance

Great precautions were taken to minimize procedural contamination, considering the wide application of the investigated compounds. Glass and polytetrafluoroethylene wares were used in sample treatment. Nitrile gloves were always used and personnel who collected the samples and conducted sample treatment and analysis did not wear any cosmetics and personal care products that potentially contained the target compounds in this work.

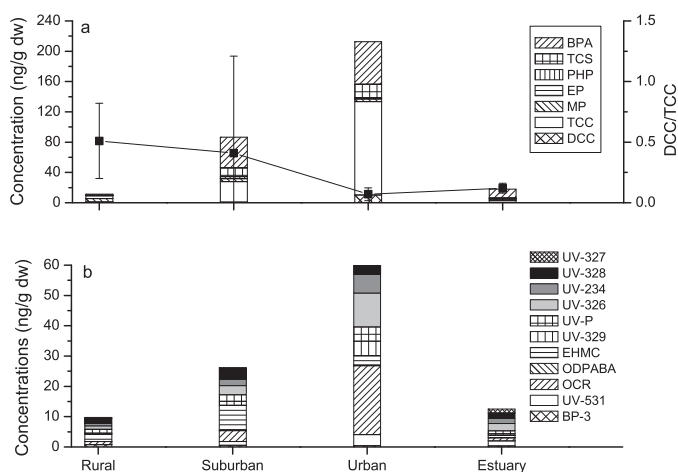
Recoveries were 45–90% for the phenolic compounds and 55–118% for the UV absorbents. The limits of quantification (LOQs) ranged from 0.003 to  $0.5\text{ ng g}^{-1}$  dry weight (dw). Procedural blanks and instrumental blanks were set to monitor procedural contamination and instrumental performance. Trace amounts of BPA, UV531, UV234, and UV328 were detected in the procedural blanks and were appropriately subtracted from the reported results. Repeatability obtained by duplicated analysis of randomly selected samples was mostly within 20%. Detailed information about the QA/QC procedure was described previously [39,40] and was also provided in the Supplementary Material.

### 2.5. Data processing

The data were processed by Origin 8.0 (OriginLab, Northampton, MA, USA) and SPSS 11.5 (SPSS, Chicago, IL, USA). Principal component analysis (PCA), factor analysis, correlation analysis, and one-way ANOVA were performed. During the statistical analyses, when an analyte was not detected, the concentration was set at 0 and when an analyte was detected below its LOQ, the concentra-



**Fig. 2.** Boxplot of the emerging contaminants in bed sediment of the Pearl River catchment. (a) phenolic compounds, and (b) UV absorbents. Abbreviations of the compounds see in Table 1. Numbers in parentheses are detected frequencies with concentrations above LOQs.



**Fig. 3.** Spatial profiles of the emerging contaminants in riverine and estuarine sediment of the Pearl River catchment. (a) phenolic compounds, and (b) UV absorbents.

tion was set at half of the LOQ. Statistical significance was set at  $p \leq 0.05$ .

### 3. Results and discussion

#### 3.1. Occurrence of the emerging contaminants in riverine and estuarine sediment

Most of the emerging contaminants were detected at least once in the sediment. The UV filter 3-(4-methylbenzylidene)camphor (4MBC) was not detected in any sediment sample. Previous research reported undetectable 4MBC in sediment from Japan and Hong Kong, which was ascribed to its banned use in cosmetics in Japan and the United States [23,29]. However, 4MBC was detected in water and sediment of Europe [4,41]. The absence of 4MBC in the sediment of the Pearl River and PRE may be associated with its infrequent usage in cosmetics and personal care products that are currently marketed in China (unpublished data). Besides, benzophenone 3 (BP3) was constantly at low levels ( $0.16\text{--}1.07\text{ ng g}^{-1}\text{ dw}$ ) and octyl-dimethyl-*p*-aminobenzoic acid (ODPABA) was detected mostly close to its limit of detection (Fig. 3b). Previous research reported no or less frequent detection of

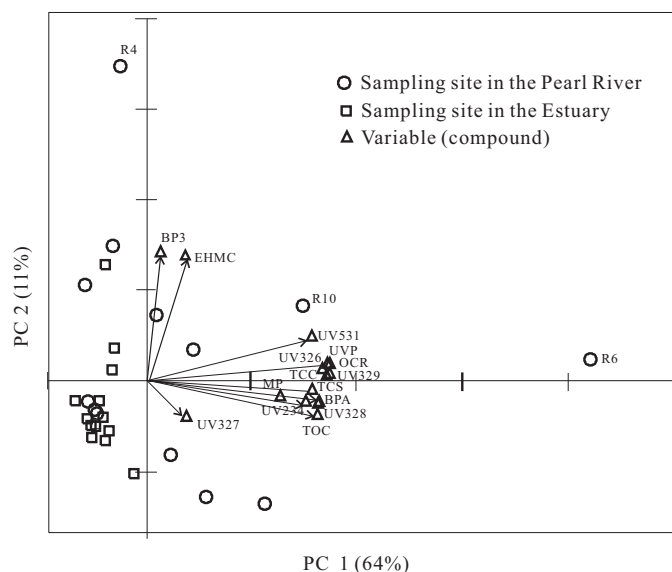
BP3 and ODPABA in sediments [15,29], although BP3 was frequently detected in waters [25]. The low concentration of BP3 in the sediment in this work was probably associated with its relative higher water solubility as well as less addition in products of China, which is  $20.1\text{ ng g}^{-1}$  compared with  $1200\text{ ng g}^{-1}$  in products of USA [21]. Avobenzone, also a UV filter, could not be accurately determined due to severe matrix interference. Therefore, BP3, ODPABA, AVO, and 4-MBC will not be included in the following detailed discussion.

TCC, BPA, TCS, and methylparaben (MP) were the predominant phenolic compounds, with maximum concentrations of 332, 217.7, 41.7, and  $8.8\text{ ng g}^{-1}\text{ dw}$ , respectively, falling within ranges reported worldwide [9,20,24]. However, the concentration of BPA was much lower than that detected in lake sediment of Korea [9]. MP represented  $87 \pm 13\%$  (mean  $\pm$  SD) of the total parabens, which was consistent with the result for sediments from the U.S., Japan, and Korea [20]. The two dechlorination products of TCC, DCC and NCC, were also frequently detected up to 3.0 and  $43.7\text{ ng g}^{-1}$ , respectively (Fig. 2a), especially in the urban section of the Pearl River, which was comparable to those reported for the freshwater sediment of Minnesota, USA [24]. The average concentration of the phenolic compounds followed the order TCC ( $39.7\text{ ng g}^{-1}\text{ dw}$ ) > BPA ( $27.7\text{ ng g}^{-1}\text{ dw}$ ) > TCS ( $7.4\text{ ng g}^{-1}\text{ dw}$ ) > MP, DCC ( $3.0\text{ ng g}^{-1}\text{ dw}$ ) > phenylphenol ( $1.0\text{ ng g}^{-1}\text{ dw}$ ) > propylparaben, ethylparaben, NCC ( $0.4\text{ ng g}^{-1}\text{ dw}$ ). Butylparaben was rarely detected (Fig. 2a).

UV filters octocrylene (OCR) and 2-ethylhexyl 4-methoxycinnamate (EHMC), and benzotriazole UV stabilizers including UV326, UV328, UV234, and UVP were the major UVAs in the sediment (Fig. 2b), which was generally in agreement with the results for sediments from Japan [23,29,34], Germany [41], France [15], USA [29], and Hong Kong [23]. Among the benzotriazole UV stabilizers, UV326 had the highest maximum and average concentrations in the sediment of the Pearl River and PRE, followed in order by UV328, UV234, UVP, UV329, and UV327, which was slightly different from the results reported for sediments from Japan and USA in which UV328 was the most abundant [29,30,34]. In addition, the total concentration of the benzotriazole UV stabilizers in the Pearl River sediment (mean of  $25.0\text{ ng g}^{-1}$ ) were obviously lower than those in the sediment of wastewater-impacted rivers (mean of  $84\text{--}197\text{ ng g}^{-1}$ ) and streams (mean of  $188\text{ ng g}^{-1}$ ) in Japan [29]. Maximum concentrations of the UV filters OCR and EHMC were  $91.7$  and  $22.4\text{ ng g}^{-1}\text{ dw}$ , respectively, similar to the results for sediments from eastern Mediterranean river transition and coastal zones [15], Germany [41], and Japan [29], but obviously lower than those in sediment from Hong Kong [23]. EHMC is used as a UV filter in >95% cosmetics and sunscreens currently marketed in China at up to 17.4% of product volume (unpublished data), which may explain well its wide presence and relatively high level. It's noteworthy to mention that UV531, a benzophenone UV stabilizer and a widely applied plasticizer, was detected frequently in the urban section of the Pearl River, with a maximum concentration of  $9.54\text{ ng g}^{-1}\text{ dw}$  (Fig. 2b), though it has rarely been reported in the environment.

Zhao et al. (2010) detected TCC and TCS at  $<\text{LOQ}\text{--}2633\text{ ng g}^{-1}$  and  $<\text{LOQ}\text{--}1329\text{ ng g}^{-1}$ , respectively, in the riverine sediment of the Pearl River system and suggested a high risks to organisms from sediment derived pore water [38]. Contaminants in the environment might exhibit mixture toxicity, even at levels at which individual substances showed no or slight effects [42]. Although there is no report so far regarding mixture toxicity of the investigated emerging contaminants, considering confirmed and suspected environmental toxicities (e.g., endocrine disrupting properties) of BPA, TCS, TCC, parabens, OCR, and some benzotriazole UV stabilizers, it's suggested from results of this work that the cocktail of the emerging contaminants in the sediment of the Pearl





**Fig. 4.** Principal Component analysis result of the emerging contaminants in riverine and estuarine sediment of the Pearl River catchment.

River and Pearl River Estuary might pose threats to the ecological system.

### 3.2. Spatial profiles of the emerging contaminants in the Pearl River catchment

Both concentration and composition of the emerging contaminants showed obvious spatial differences. The total concentration was the highest in the urban section of the Pearl River ( $278.8 \pm 291.9 \text{ ng g}^{-1}$ ), followed by suburban section ( $112.3 \pm 101.3 \text{ ng g}^{-1}$ ), the PRE ( $28.9 \pm 10.1 \text{ ng g}^{-1}$ ), and the rural section ( $21.4 \pm 6.3 \text{ ng g}^{-1}$ ). In the urban section of the Pearl River, TCC ( $123.4 \pm 131.7 \text{ ng g}^{-1}$ ) was the most abundant phenolic compound, followed in order by BPA ( $56.1 \pm 72.9 \text{ ng g}^{-1}$ ), TCS ( $17.8 \pm 12.4 \text{ ng g}^{-1}$ ), DCC ( $10.1 \pm 15.7 \text{ ng g}^{-1}$ ), and MP ( $3.5 \pm 2.6 \text{ ng g}^{-1}$ ), whereas in the suburban section and the PRE, BPA was the most abundant while DCC was detected at quite low levels (Fig. 3a). Like the phenolic compounds, concentrations of the UVAs in the Pearl River (especially in the urban section) were obviously higher than those in the PRE. In addition, although UV531 was frequently detected in the urban section of the Pearl River, it was observed only occasionally and at low levels in the rural and suburban sections as well as the PRE.

The highest concentrations were observed for most of the emerging contaminants at sites R6 and R10, in the proximity of the effluent outfalls of two large scale sewage treatment plants (STPs) of Guangzhou, a metropolis of the PRD with a population of more than 15 million (Fig. 1). The PCA result illustrated point sources at sampling sites R6 and R10 (Fig. 4). Previous research reported elevated levels of TCS and TCC in the sediment of Greenwich Bay and Minnesota rivers in the vicinity of STP outfalls [24,31]. The targeted phenolic chemicals in municipal wastewater of Guangzhou have been found to be only partly removed during wastewater treatment and the treated effluent is discharged into the Pearl River system [37]. These results therefore demonstrated STP effluent as the major source of the emerging contaminants in the Pearl River catchment. However, relatively high concentrations of EHMC were found at sites R4 and R14 which were not near STP outfalls (Fig. 1) nor in the densely populated urban area, implying other sources of these emerging contaminants than STP effluents. There exist occasionally illegal discharges of untreated wastewater along streams and canals that are connected with the mainstream Pearl River and

tributaries. More investigation is needed to fully apportion sources of the emerging contaminants in the Pearl River catchment.

Previous studies reported a positive relationship between concentrations of the organic UV filters, TCC and DCC in sediments and population density [22,24]. Lower concentrations of the phenolic compounds and UV absorbents in the suburban and rural sections relative to the urban section of the Pearl River might be associated with less release due to smaller population. In the estuary, however, contribution from sources such as plastic and paint residues generated by fishing and shipping activities could also not be neglected, especially BPA and the UV stabilizers that are widely used as additives in plastics, paints, coatings, adhesives, and other industrial products. In addition, concentrations of these emerging contaminants in the estuary were quite constant, suggesting no significant point source input. The PCA result showed all the estuarine sediment samples clustering together, demonstrating non-point sources of the emerging contaminants in the PRE.

### 3.3. Vertical profiles of the emerging contaminants in the Pearl River Estuary

Sediment cores have been valuable tools to reconstruct historical inputs of contaminants [7,16,20,31]. All the emerging contaminants were analyzed in C1 whereas only UVAs were analyzed in C2. Composition of the phenolic compounds in C1 was similar to the bed sediment of the PRE, BPA, TCC, and TCS were detected throughout the core and showed a slightly upward increase in concentrations, reaching the highest levels in the top layer. Specifically, the concentration of TCS began to increase from the depth of 33 cm (corresponding approximately to 1973) and those of BPA and TCC increased from 24 cm (corresponding approximately to 1982), probably reflecting economic development and population expansion in the recent decades in the PRD due to the economic reform and openness of China. DCC and NCC were occasionally detected in some sections at trace levels, which was similar to that reported for a sediment core from Jamaica Bay, USA [7]. However, significant quantities of TCC dechlorination products were observed at lower layers in a core from the Chesapeake Bay, USA. Dechlorination of TCC was believed mainly to happen biologically under anoxic conditions. Differences in TCC dechlorination in Jamaica Bay and Chesapeake Bay was ascribed to distinct physico-chemical and associated biological characteristics of the two bays [7]. In addition, as the only quantifiable paraben, MP had an upward increasing concentration from the bottom to the highest at the depth of 27 cm (corresponding approximately to 1979), followed by an instant decline and a steady state at around  $3.0 \text{ ng g}^{-1}$  thereafter (Fig. 5a).

Vertical profiles of the UVAs varied to some extent in C1 and C2. UV326, EHMC, UV328, and UV531 were the predominant UVAs in C1 whereas UV326, UV328, UV531, and UV234 were predominant in C2 (Fig. 5b, c). The other UVAs were either not detected or constantly at low concentrations without pronounced trends in the cores and will therefore not be included in the following discussion.

EHMC was only detected in C1 with maximum concentration ( $8.7 \text{ ng g}^{-1} \text{ dw}$ ) in the top layer, followed by downward decrease to being unquantifiable at the depth of 27 cm (corresponding to approximately 1979) and there below. UV531 showed similar vertical profile in the two cores with concentrations fluctuating slightly at low levels in layers deposited before mid-1980s, reaching peak level in layers corresponding to early 1990s. However, the UV531 concentrations declined sharply from mid to late 1990s and then kept constant thereafter. The concentrations of benzotriazole stabilizers UV234 and UV 328 varied narrowly in C1. However, in C2, UV328 and UV234 showed similar vertical profiles to that of UV531 with maximum concentrations in layers corresponding early to mid-1990s. There were two peaks in the vertical profile of UV

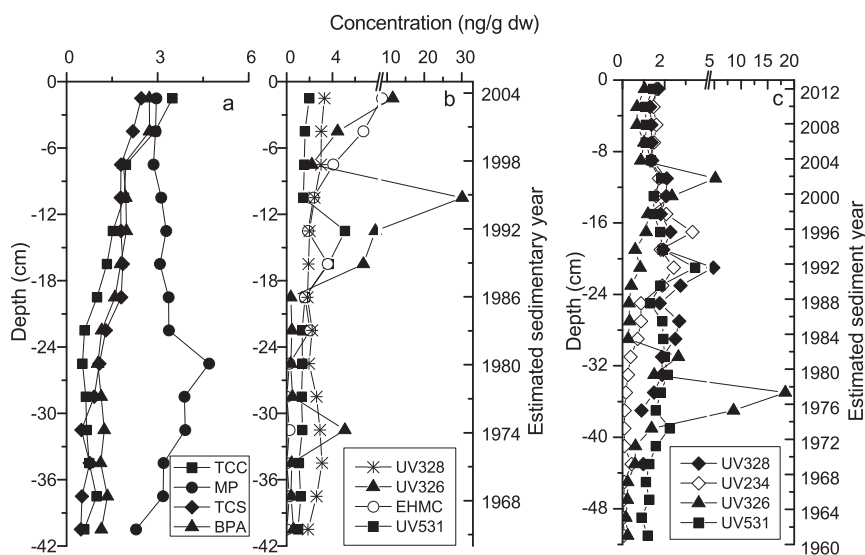


Fig. 5. Vertical profiles of the emerging contaminants in the Pearl River Estuary. (a) phenolic compounds in C1, (b) UV absorbents in C1, and (c) UV absorbents in C2.

326, though the concentration kept low below the depth corresponding to mid-1970s. Specifically, in C1, UV 326 concentration showed a small bump ( $5.1 \text{ ng g}^{-1} \text{ dw}$ ) at the layer corresponding to mid-1970s, started to increase significantly and reached maximum ( $30.2 \text{ ng g}^{-1} \text{ dw}$ ) at layers corresponding to late 1980s to mid-1990s, whereas in C2, the UV326 concentration increased obviously and peaked ( $18.3 \text{ ng g}^{-1} \text{ dw}$ ) at layers corresponding to late 1970s to early 1980s, followed by a sharp decline to a relatively low concentration with a smaller peak at the layer corresponding to early 2000s (Fig. 5b, c).

As mentioned above, wastewater has been recognized as the major source of the investigated emerging contaminants in the environment and vertical profiles of these chemicals in sediment cores might reflect their consumption and wastewater treatment efficiency in the studied areas [7,20,26]. The vertical profile of BPA in the sedimentary core was basically consistent with the result of the previous research [36], which was suggested to reflect economic development in the PRD in the last decades. TCC and TCS have been produced and consumed in large amounts worldwide since they were introduced into commerce in late 1950s and mid-1960s, respectively [10]. In lakes of Minnesota that were impacted by wastewater, accumulation rates and temporal trends of triclosan, its chlorinated derivatives and their dioxin photo-products were found to be a function of historical wastewater treatment operations and lake system scale [43]. Singer et al. (2002) found the concentration of TCS in the dated sediment cores from Lake Greifensee, Switzerland agreeing with its use [26]. Cantwell et al. (2010) suggested that the temporal trends of triclosan in four urbanized estuaries along the U.S. Atlantic Coast reflected increasing usage and improvements of the wastewater treatment over years [32]. The concentrations of TCS and TCC in the sediment cores of the U.S. East Coast were found to be associated with wastewater treatment development [7,31]. It's not clear when the two biocides were produced and used in China. However, it's reasonable that trace amounts of TCC and TCS were detected in the layers corresponding to late 1960s to late 1980s, considering both poor industrialization and smaller population during that period in the PRD, and consequently small discharge of these chemicals. As the bridgehead of Reform and Opening-up of China, the PRD has been experiencing economic growth and population expansion in the last 3 decades. Increasing concentrations in of TCC and TCS since 1980s might therefore reflect increasing input along with discharge of wastewater due to booming urbanization and enor-

mously growing population in the PRD. However, the situation of MP was a bit more complex. Liao et al. (2013) reported a gradual increase of the parabens concentrations in two lacustrine sediment cores from Michigan, USA, but a state of equilibrium in a sediment core from Tokyo Bay, Japan [20]. Steady state of MP concentration above the depth of 24 cm in the sediment core in the PRE might be mainly ascribed to implementation and continuing improvement of wastewater treatment since late 1980s in the PRD because parabens have been found to be readily eliminated from the wastewater by active sludge treatment in STPs [36].

Sedimentary records of the UVAs were rarely reported. Kameda et al. (2007) reported ubiquitous occurrence of EHMC over a 20-year period between 1977 and 1997 in a sediment core from Tokyo Bay, Japan [44]. There is no accurate information about the annual use and year UVAs were introduced into commerce in China. However, the presence of the UV stabilizers (e.g., UV326, UV328, and UV531) in deep layers of the sedimentary cores suggested persistence of these compounds in the environment once they were buried in sediment. Treatment of wastewater and solid waste in PRD was implemented since late 1980s and the capacity and technology have kept improving, which might be the cause of the obvious decrease in the concentration of the UV stabilizers as UV326 and UV326. Furthermore, increasing concentrations of the UVAs (e.g., UV326, UV531, and EHMC) in top layers in the sediment cores of the PRE might mirror rapid industrial development without efficient waste treatment in the PRD in the past years.

### 3.4. Behavior and fate of the emerging contaminants

The PCA result revealed close correlation among the endocrine disrupting emerging contaminants ( $p < 0.05$ ) with the exception of EHMC, BP3, and UV327 (Fig. 4), implying their similar sources and/or fate in the riverine and estuarine environment of the PRD. In addition, concentrations of the emerging contaminants showed close association with the contents of the organic carbon (TOC), indicating absorption of the emerging contaminants on organic carbon in the sediment, which is reasonable considering the moderate to high lipophilicity. This result was consistent with previous research about parabens [20], TCS, TCC [24,31], and benzotriazole UV stabilizers [29,34] in sediments.

In spite of poor correlation with the other emerging contaminants, EHMC and BP3 were closely correlated with each other ( $p < 0.05$ ). EHMC is readily degradable [41,45] whereas BP3 was

quite photostable in the aquatic environment [46,47]. Therefore, it's likely that EHMC and BP3 had similar sources rather than similar environmental fate in the sediment of the Pearl River and the PRE. Unlike the other emerging contaminants whose highest concentrations were observed at sites in the vicinity of STP outfalls, the maximal concentrations of EHMC and BP3 were detected at site R4, which was in the suburban section of the Pearl River and was not near STPs (Fig. 1), implying that the two chemicals were not mainly sourced from STPs effluent as the other emerging contaminants. Furthermore, the concentrations of EHMC and BP3 were very poorly correlated with TOC ( $p > 0.2$ ), suggesting non-governing impact of TOC on deposition of EHMC and BP3 in the sediment. Similar results were obtained for marine sediments from Hong Kong and Tokyo Bay, Japan, which was ascribed to partition of these chemicals to phases such as surface water in dynamic aquatic environments [23].

The two metabolites of TCC (i.e., DCC and NCC) were widely present in the bed sediment, with maximal levels in the vicinity of STP outfalls, implying STP effluent the major source of the metabolites. The ratio of DCC/TCC ranged from 0.012 to 0.730 (mean values of 0.134 and 0.118 in the Pearl River and the PRE, respectively), substantially higher than that of the technical-grade TCC which is about 0.002 [7], suggesting wide presence of TCC dechlorination. DCC concentration was in positive correlation with that of TCC ( $R = 0.85$ ,  $p < 0.001$ ), whereas NCC concentration showed no significant correlation with those of either DCC or TCC ( $R$  of  $-0.14$  and  $-0.17$ , respectively). This result agreed well with that for Minnesota freshwater sediment [24]. Previous research revealed in-situ TCC dechlorination in a sediment core from the Chesapeake Bay, Maryland, based on a significant negative correlation between TCC and its dechlorination products [7]. The absence of substantial detection of DCC and NCC in the sediment core of the PRE possibly suggested insignificant in-situ TCC dechlorination. From the above results and discussions, it is speculated that TCC dechlorination products (i.e., DCC and NCC) detected in the bed sediment of the Pearl River and the PRE were mainly stemmed from STP effluent rather than formed in-situ in the sediment.

TCC's concentration was around 6 and 2 times higher than that of TCS in the sediments of the Pearl River and the PRE, respectively. However, similar concentrations were observed for TCC and TCS in both treated and untreated wastewater of the study area [36], which meant that similar mass loads of TCC and TCS should have been discharged into the environment via wastewater. Even though TCS has a higher tendency to be partitioned to water than TCC considering its higher water solubility, obviously higher abundance of TCC might also imply its higher stability than TCS in the sediment. TCC was found to be more stable than TCS in aerobic soil with half-life of 108 and 18 days, respectively [48]. Similar discussions were provided for sediment in Chesapeake Bay, Jamaica Bay, and rivers, creeks, and lakes of Minnesota, USA [8,24].

#### 4. Conclusion

UV filters octocrylene, 2-ethylhexyl 4-methoxycinnamate, several benzotriazole UV stabilizers (e.g., UV326, UV234, UV328, UVP, and UV329), benzophenone UV stabilizer UV531, triclocarban, triclosan, bisphenol A, and methylparaben were widely present in riverine and estuarine sediment of the Pearl River catchment, with average concentrations from 1.0 to 39.7 ng g<sup>-1</sup> dw. Spatially, the concentrations of the investigated emerging contaminants were the highest in the urban section of the Pearl River. Maximum concentrations were usually observed near STP outfalls, indicating treated wastewater effluent the major source of the emerging contaminants in the sediment. In addition, UV326, UV328, UV531, TCC, TCS, BPA, and MP were widely detected throughout the sediment cores collected from the estuary, indi-

cating persistence of these compounds once accumulated in the sediment. Vertical trends of the emerging contaminants in the sediment cores corresponded generally with industrial development, population growth, and waste treatment capacity in the last decades in the Pearl River Delta. Two dechlorination products of TCC (i.e., nonchlorinated carbanilide and dichlorocarbanilide) were frequently detected in the bed sediment but only occasionally observed in the sediment cores at trace levels, suggesting insignificant in-situ dechlorination in the sediment. Further studies are required on bioaccumulation and biomagnification of these persistent emerging contaminants in aquatic organisms, especially in those benthic and detritus-feeding species in order to comprehensively reveal ecological risks of these contaminants.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.05.020>.

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