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Distribution, mass inventories, and ecological risk assessment of legacy and emerging contaminants in sediments from the Pearl River Estuary in China

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HIGHLIGHTS

- Surfactants are the most predominant contaminants in PRE sediments followed by PAHs.
- Highest concentrations were found near Guangzhou city and Macao.
- Wastewater discharges are a major source of contamination, except for UV filters.
- Triisobutylphosphate and 2-ethylxheyldiphenylphospate are detected for the first time.
- Legacy contaminants still pose a significant risk for the benthic communities at PRE.

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ABSTRACT

This study focused on comparing the occurrences and environmental toxic risks for diverse priority and emerging contaminants (>100 chemicals) in the sediments from the Pearl River Estuary (PRE, China). The most predominant compounds were cationic surfactants, organophosphate flame retardants (e.g., triisobutylphosphate), and polycyclic aromatic hydrocarbons (PAHs), accounting for >75% of the total mass inventory (~330 metric tons). Wastewater discharges seem to be one of the main sources of pollution in the area, as the highest concentrations (>1000 ng g^{-1} for some chemicals) were reported in the upper part of the PRE (near Guangzhou city) and Macau. Highest levels of ultraviolet (UV) filters, however, were observed in recreational areas, revealing the importance of direct sources (e.g., outdoor activities). An environmental risk assessment showed that PAHs and dichlorodiphenyl dichloroethylene had the highest hazard quotient (HQ) values (up to 233). Nonylphenol, a metabolite from nonionic surfactant, and two UV filters (2-ethyl-hexyl-4-trimethoxycinnamate and 4-methylbenzylidene camphor) also posed a significant threat to benthic species (HQ > 1). Further research through the realization of monitoring campaigns and toxicity tests is encouraged, as the exposure of the resident aquatic organisms and human population to these and other emerging chemicals is expected to increase over the years.

1. Introduction

Since the second half of the 20th Century, the synthesis of new chemicals has experienced an exponential growth. Negative effects of some synthetic chemicals on the environment and human health became apparent soon after their widespread release into the environment during the 1960–70s. This resulted in contaminant phase-outs or restrictive legal actions in the case of some compounds such as polychlorinated biphenyls (PCBs) or many organochlorinated pesticides (e.g., DDT), now known as legacy contaminants that are still detected in the environment because of their high persistence. Some of these anthropogenic chemicals may adversely affect the biota even at very low concentrations, e. g, endocrine disrupting compounds (EDCs) such as nonylphenol (NP) and polybrominated diphenyl ethers (PBDEs) that can act through the receptor mediated responses. In recent years, there

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has been a significant concern focused on new contaminants called emerging pollutants [1]; however, unfortunately, the same analytical advances that have allowed for their low-level detection, neither offer knowledge about whether a newly detected contaminant is of eco/toxicological interest nor their environmental behavior and fate. Therefore, assessing the occurrence, distribution, reactivity, and effects of these chemicals in the environment remains major time- and resource-intensive challenges.

Ecosystems of urbanized estuaries are directly threatened by organic contaminants due to direct and in-direct inputs derived from enhanced human activity. More specifically, Pearl River Estuary (PRE) located in southern China (Fig. 1), one of the most urbanized estuaries heavily affected by the rapid economic (GDP > 400 million USD) and population growth (>80 million inhabitants). The concentrations of organic contaminants in this aquatic system have been extensively monitored over the last decades through a series of sampling campaigns, and most of them aimed to the screening of persistent organic pollutants (POPs). Thus, the presence of PCBs and PBDEs has been confirmed in the air [2], sediment [3,4], soils [5], and biota [6]. The annual release of PBDEs in wastewater was estimated at 2280 kg/year by measuring their concentrations in the sewage effluents discharged to the PRE [7]. Previous results showed that the levels of PAHs, organochlorine pesticides (OCPs), and halogenated flame retardants and their composition patterns were well preserved in the sediments, and their chronological records could reflect the evolution of the pollution inputs, because of the rapid growth of population and the development of manufacturing industries in the PRE [4,8–10]. Additionally, the use of geochemical markers such as linear alkylbenzenes (LABs) [11] and quaternary ammonium compounds (QACs) [12] has confirmed the effect of municipal sewage pollution in the sediments of the PRE and South China Sea (SCS). High correlation coefficients were found among these markers and the POPs in the Pearl River, indicating that they had similar sources, and both were associated with sewage-derived particles. The decrease in the concentrations of contaminants with increasing distance from the PRE towards the ocean also suggests advective transport. Chen and coworkers [13] estimated that the riverine input influence reached approximately between 124 and 276 km from the end of the estuary. To better evaluate the role of sediments as a sink for a significant fraction of organic contaminants and their potential risk as secondary sources, mass inventories in the PRE have been also calculated for PAHs (126 tons) and OCPs (0.4 tons) in the PRE sediments [14], as well as PBDEs in the PRE sediments [9] and soils [5].

Regarding emerging contaminants, most of the research in China has been focused on pharmaceuticals and related compounds (PhACs). Recently, Bu et al. [15] reviewed PhACs and identified six compounds (three antibiotics and three anti-inflammatories) as priority contaminants in waters [15]. However, there remains a paucity of information on the relative importance of these and other emerging sewage-derived organic contaminants (e.g., personal care products, PCPs) in sewage-affected sediments. There are only a few studies on the distribution of polycyclic fragrances [16], triclosan [17], and other EDCs [18,19], and most of them focused in the upper part of the PRE (and adjacent rivers) and their removal efficiencies in local wastewater treatment plants (WWTPs). Two notable exceptions are very recent data on perfluorinated surfactants [20] and endocrine disrupting compounds (EDCs) [21] from the two surveys in marine areas. The rapid evolution of production and usage for newly introduced organic chemicals and the lack of data on their occurrence in the PRE contrast with the extensively studied distribution of legacy contaminants in this area. Monitoring both classes together has not been performed until now and it would allow for a direct comparison between their levels and their relative risk to aquatic biota trough environmental risk assessments for those chemicals for which ecotoxicological data is available

Therefore, the main goal of the study was to establish the first comprehensive and comparative study on the current status of legacy and emerging chemicals in the PRE region. More specifically, we aimed to: a) evaluate the occurrence and distribution of diverse particle-reactive organic contaminants in surface sediments, b) calculate and compare their mass inventories to establish their relative abundance, and c) perform a preliminary environmental risk assessment for selected chemicals with preexisting ecotoxicological information in PRE sediments. To achieve these objectives, we have covered a large area (3295 km^2, 31 sampling stations) and screened over one hundred relatively highly hydrophobic compounds ($\log K_{ow} > 4$) including hydrocarbons (16 PAHs), flame retardants (five PCB congeners and nine recently introduced organophosphate compounds), pesticides (18 organochlorines, five organophosphorus, eight triazines, and seven pyrethroids), surfactants (NP and the homologous series of two major QAC groups), and PCPs (13 fragrances, 10 UV filters, and two antimicrobials).

2. Experimental

2.1. Study area and sampling

The PRE is one of the most urbanized areas in China, because of the rapid economic and population growth in the region. It receives 14,000 kilotons of wastewater per day from the major cities such as Guangzhou, Foshan, and Dongguan (Environmental Status Bulletins of Guangdong Province, China; http://www.gdepb.gov.cn/). The organic contaminants are generated by the industries, agriculture, and electronic waste (E-waste) recycling areas [22]. In this study, 31 surface sediment samples were collected from the PRE region and the adjacent northern SCS during two cruises in July and December 2012 (Fig. 1). Top 5 cm sediment samples were collected using a Van Veen stainless steel grab sampler. Each sediment sample was stored in a glass bottle pre-baked at 450 °C for 8 h and stored at −20 °C until further treatment. All the samples were then freeze-dried in the lab and homogenized prior to the analysis of different organic contaminants. Specific details on each sampling station (location, total organic carbon content, and concentration of target compounds) are listed in Table 1S in the Supporting Information.

2.2. Chemicals, sample extraction, purification, and analysis

The extraction and determination of QACs were carried out using a previous methodology [12] based on ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC–MS/MS). The rest of target compounds are susceptible for gas chromatography–tandem mass spectrometry (GC–MS/MS) analysis and were determined following another methodology developed by our group [23]. More information on this can be found in these references and in the Supporting Information.

2.3. Data analysis

Ordinary Kriging interpolation analysis based on the spherical model was used to predict and visualize the spatial distribution of the data in the PRE region by using ArcGIS 10 software. Further information on this approach has been reported by Chen et al. [24], where they plotted the distribution maps of PBDEs in the sediments from the same sampling area. We also used this interpolation analysis to calculate the mass inventories of all the contaminants detected in the sampling area using a modification of the approach followed by Chen et al. [14]. Briefly, for the Kriging analysis, the PRE region area plotted in Fig. 1S (Supporting Information) was

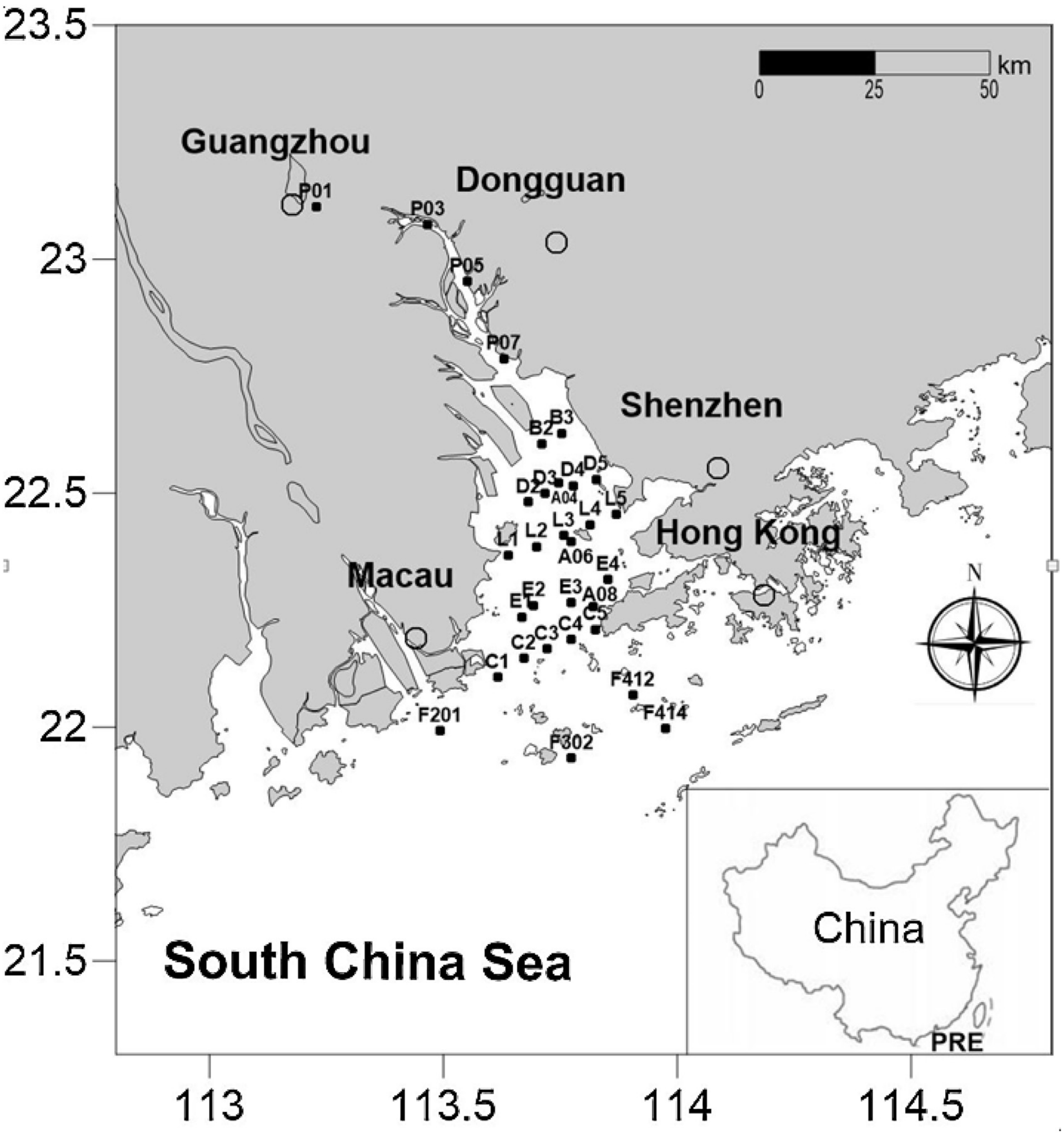

Fig. 1. Map showing the location of Pearl River Estuary (PRE) and the sampling stations.

divided into ~100,000 grid cells of 0.1 km^2 each, and the concentrations of target compounds were interpolated. The inventory (I, in kilograms) for every contaminant was calculated by the following Equation (1):.

$$I = \sum k C_i A d \rho \quad (1)$$

where C_i is the sediment concentration in ith cell (ng/g), A is the area of the cell (0.1 km^2), d is the thickness of sediment sampled (cm), ρ is the average density of the dry sediment particles (g/cm^3), and k is a conversion factor. We assumed sediment density of 1.5 g/cm^3 and a sediment thickness of 5 cm, the same values used by previous authors [3,14] for the estimation of mass inventories of halogenated flame retardants in the PRE.

The ecological risk assessment was based on the United States Environmental Protection Agency ecological risk assessment framework and has been previously used in other studies in the PRE [25]. Thus, hazard quotients (HQs) were used to evaluate the ecological risk of the chemicals predicted with no effect concentration (PNEC) values available by comparing them with the measured environmental concentrations (MEC) by the following Equation (2).

$$HQ = MEC/PNEC \quad (2)$$

The confirmation of potential risk was based on the HQ value of >1, indicating a higher ecological risk. The average and maximum concentrations in the surface sediments were used as the MEC, whereas the PNEC values were derived from the chronic toxicity and acute toxicity data from the literature. More in detail, the PNEC values were calculated using no observed effect concentrations (NOEC) from chronic toxicity studies, but for PAHs and PCBs (Table 2S, Supporting information), where acute toxic endpoints (half maximal effective concentration, or EC50) were used instead. Depending on the approach used, PNEC values were calculated either dividing acute toxicity values by a factor of 1000 or chronic toxicity values by a factor of 100.

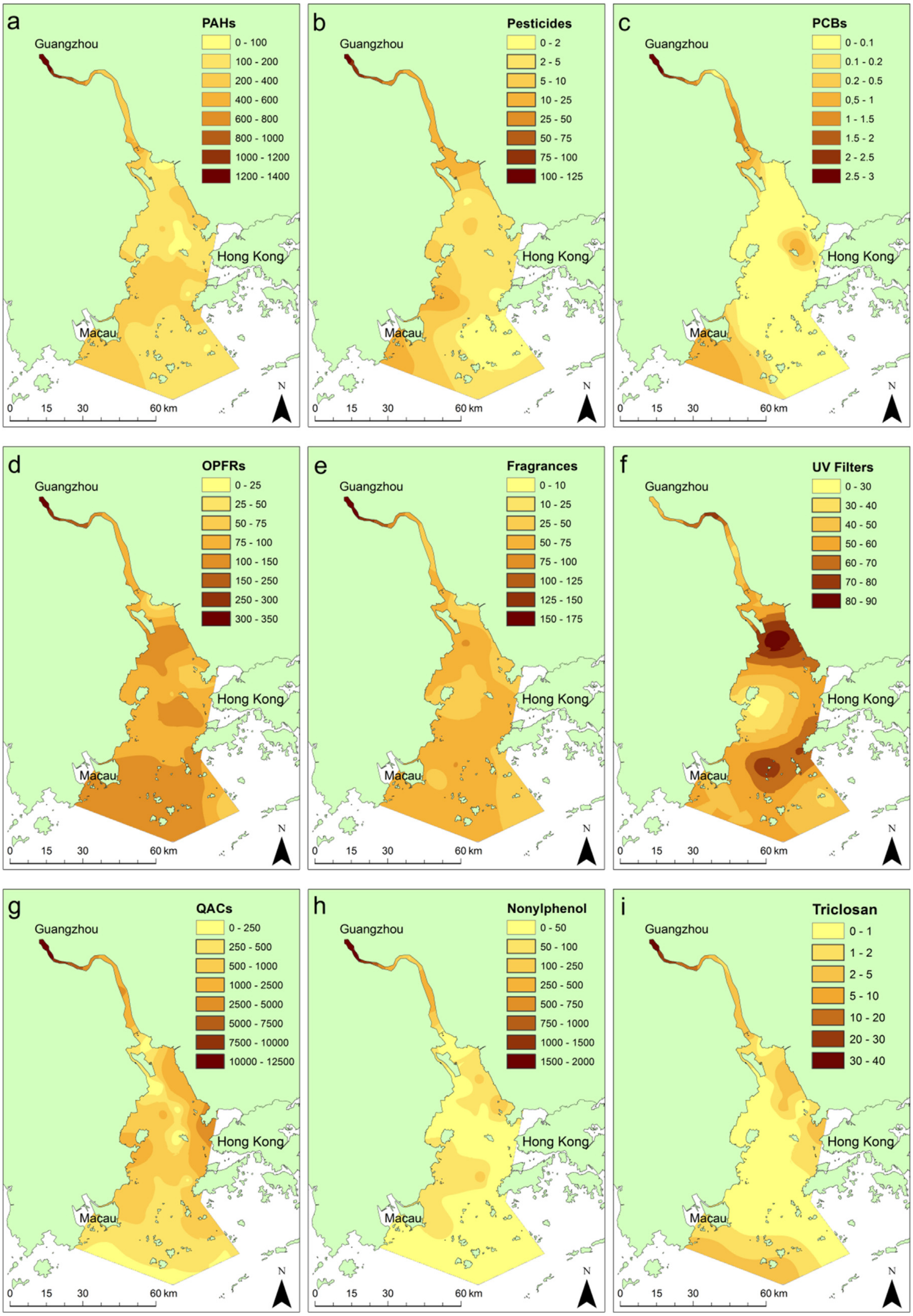

Fig. 2. Maps showing the concentrations (ng g^{-1}) and distribution of different classes of organic contaminants in surface sediments (0–5 cm) from PRE: a) PAHs, b) pesticides, c) PCBs, d) organophosphate flame retardants, e) fragrances, f) UV filters, g) quaternary ammonium compounds, h) nonylphenol, and i) triclosan.

3. Results and discussion

3.1. Distribution of legacy contaminants in PRE

Fig. 2a–c shows the distribution of priority contaminants (PAHs, pesticides, and PCBs) in the PRE surface sediments. Legacy contaminants such as organochlorinated pesticides (e.g., DDT, chlordane, and aldrin) are included here. Among these compounds, PAHs are clearly predominant and have been one of the most extensively studied contaminants in this area [10,14,22,26,27] over the last decade. In this study, PAHs were detected in all the samples, and their total concentrations ranged from 53 to 1369 ng g^{-1}, and the highest values reached in the north part of the PRE (stations P01 to P07), near Guangzhou city (Fig. 2a). These values are within the same order of magnitude with those previously reported (e.g., 138–1100 ng g^{-1} by Chen and coworkers, 2006 [14]). The most predominant PAHs in the study area were phenanthrene (PHE), pyrene (PYR), and fluoranthene (FLT), accounting for >50% of the total amount (Table 1). In general, the concentrations of PAHs (as well as most of the rest of target compounds considered in this study) decreased along the estuary from north to south, because of the reactivity of these compounds and dilution processes. The concentration of these chemicals in the area located between Macau and Hong Kong increased again and reached to >200 ng g^{-1} because of the effect of so-called “marginal filter”. Briefly, this filter is at the river-sea boundary zone where organic-rich, fine-grain suspended particles tend to deposit [14] (Fig. 1S) due to the mixing of fresh fluvial water and saline water with very different compositions (in terms of dissolved and suspended matter, as well as biota). Processes that eliminate particles from the water column are formation of natural sorbents made of clay, organic matter and iron, and the presence of phytoplankton and filtering organisms. The extension of this area was significantly larger towards the western part of the PRE, as apparently most of the water from the estuary, affected by the Coriolis Force and the prevailing wind, (monsoon), flows toward the west carrying large amounts of pollutants [8].

Apart from natural sources (e.g., diagenesis), PAHs can be derived from human activities such as combustion of fossil fuels, various industrial processes, biomass burning, waste incineration, and oil spills. They can enter aquatic systems through irrigation, wastewater discharges, and atmospheric deposition. Specific PAH sources can be identified by using different ratios [27]. Thus, different components such as anthracene and PHE (ANT/ANT + PHE), FLT and PYR (FLT/FLT + PYR), indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (IP/IP + BPER), and benzo[a]anthracene and chrysene (BA/BA + CHR) from all the sediment samples can be integrated (Fig. 3). The analysis of these ratios reveals that most of the samples were within the regions of petroleum and biomass combustion, indicating pyrolytic sources. This is in agreement with more detailed studies within the same area that claim vehicular emissions and coal combustion to be the two main sources for PAHs in Hong Kong [27] and Macau [26]. More specifically, Chen and coworkers (2013) observed that for marine sediments, traffic tunnel was the largest PAH source (57.61%) in the region, followed by power plant (22.86%), gasoline engine (17.71%), and coal residential source (1.82%) [22]. Another fraction of the contamination can be also derived from diesel spillage from ships and boats [26], mainly in those sample stations located at nearby ports. The results from this type of diagnostics, however, must be taken carefully as these ratios, especially those calculated from low molecular weight PAHs (e.g., ANT/ANT + PHE), are susceptible to changes by chemical and photochemical reactions during transport from sources to receptor sites. Liu et al. [10] reported different composition of PAHs in the marine sediments from the adjacent SCS (dominated by PHE, IP, and BPER among others) and analyzed the FLT/FLT + PYR and IP/IP + BPER ratios (>0.5); they concluded that

Table 1
Minimum, maximum, and mean concentrations (ng g^{-1}) of target compounds detected in the sediment samples (n = 31) from the PRE. Detection frequency (%) and relative percentages of target compounds within their class are also shown, as well as the total mass (kg) of every class of compounds. Limits of detection (LOD) are usually from < 0.1 to 1 ng g^{-1}, depending on the analyte [12,23].

Compound	Minimum	Maximum	Mean	% detection	% or mass
Naphthalene	1.3	156	12	100	5
Acenaphthene	0.4	15	2	100	1
Acenaphtylene	<LOD	12	2	100	1
Anthracene	<LOD	35	5	97	2
Fluorene	0.7	41	6	100	3
Phenanthrene	14.1	208	53	100	23
Pyrene	5.1	252	41	100	18
Chrysene	3.2	120	18	100	8
Benz[a]anthracene	1.4	65	9	100	4
Fluoranthene	5.1	209	30	100	13
Benzo[b,k]fluoranthene	2.1	78	14	100	6
Benzo[a]pyrene	0.8	55	10	100	4
Dibenz[a,h]anthracene	0.2	11	2	100	1
Benzo[g,h,i]perylene	1.4	66	15	100	6
Indeno[1,2,3-cd]pyrene	1.5	47	11	100	5
PAHs	*53*	*1369*	*231*		*50299 kg*
PCB101	<LOD	1.2	0.1	16	32
PCB138	<LOD	1.2	0.1	29	52
PCB180	<LOD	0.7	0.0	10	17
PCBs	0.0	3.0	0.3		42 kg
Aldrin	<LOD	2.0	0.1	3	1
DDT	<LOD	8.4	0.8	19	13
DDE	<LOD	6.3	0.8	84	13
DDD	<LOD	7.4	1.5	87	24
HCH	<LOD	10.8	0.9	68	14
Cis-chlordane	<LOD	0.3	0.0	3	0
Trans-chlordane	<LOD	0.2	0.0	3	0
Chlorpyrifos	<LOD	4.5	0.2	6	3
Terbuthylazine	<LOD	1.4	0.2	16	3
Phenothrin	<LOD	16.8	0.5	3	8
Bifenthrin	<LOD	4.9	1.3	97	21
Pesticides	0	57	6		1229 kg
TPP	<LOD	39	2	81	2
TIBP	50	124	78	100	75
TNBP	0.1	21	6	100	6
TEHP	<LOD	136	4	3	4
EHDPP	0.3	72	13	100	13
Organophosphates	58	322	104		25294 kg
3-OHBP	<LOD	0.7	0.1	16	0
BP-3	<LOD	4.0	1.0	87	2
OC	<LOD	105.2	37.8	97	64
HMS	<LOD	10.7	4.5	97	8
EHS	<LOD	13.7	4.9	97	8
EHMC	<LOD	30.1	3.1	68	5
4-MBC	<LOD	25.4	7.9	84	13
UV filters	5	139	59		13218 kg
Musk xylene	<LOD	56	2	6	3
Galaxolide	<LOD	56	4	100	7
Tonalide	<LOD	24	3	97	5
OTNE	18	86	47	100	79
Cashmeran	<LOD	28	4	74	6
Fragrances	25	175	60		13626 kg
Triclosan	<LOD	32.6	2.0	96	337 kg
Methyl-triclosan	<LOD	0.8	0.0	6	
Nonylphenol	<LOD	1907	114	97	15094 kg
BAC12	5	691	98	100	53
BAC14	4	510	64	100	34
BAC16	0	73	12	97	6
BAC18	0	148	12	97	6
BACs	10	1345	186		16
DADMAC10:10	<LOD	189	22	97	2
DADMAC12:12	<LOD	47	5	94	1
DADMAC12:14	<LOD	15	1	94	0
DADMAC14:14	<LOD	2	1	90	0
DADMAC14:16	<LOD	49	4	100	0
DADMAC16:16	3	960	73	100	8
DADMAC16:18	8	2127	183	100	19
DADMAC18:18	23	7667	664	100	70
DADMACs	40	10917	953		84
QACs	50	12262	1139		198655 kg

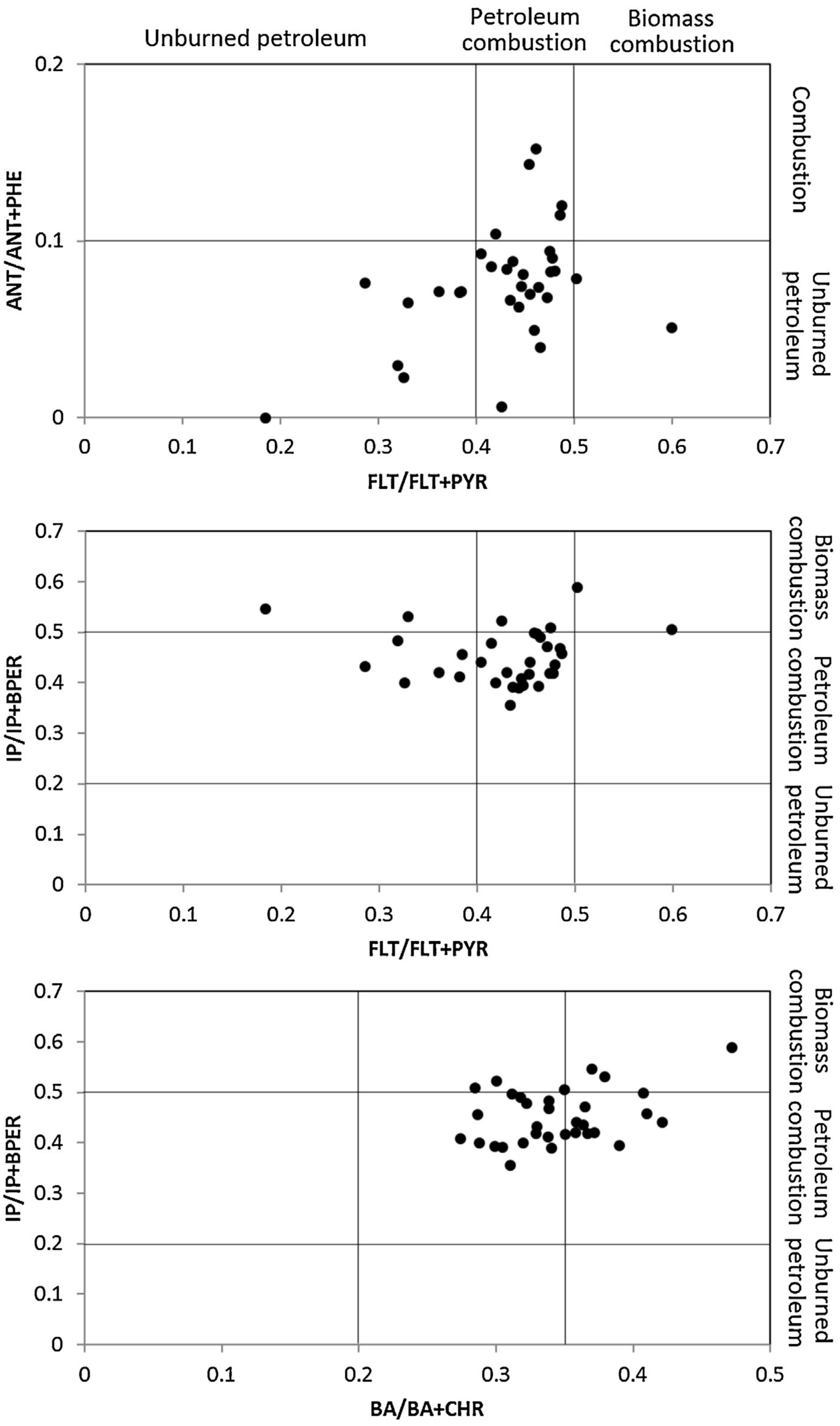

Fig. 3. Different PAH ratio plots for the surface sediments samples from the PRE. Several PAHs have been considered: anthracene (ANT), phenanthrene (PHE), fluoranthene (FLT), pyrene (PYR), benzo[g,h,i]perylene (BPER), indeno[1,2,3-cd]pyerene (IP), benzo[a]anthracene (BA), and chrysene (CHR).

biomass burning and domestic coal combustion were the top two emission sources affecting these offshore sediments rather than traffic sources [10].

Several classes of pesticides were detected in the PRE surface sediments. Their spatial distribution is in agreement to that described for PAHs, suggesting similar transport mechanisms, as previously pointed out in a previous comparative study on PAHs and OCPs [14]. Table 1 shows that this class of pesticides (which not only includes DDT and its metabolites, but also hexachlorocyclohexane or HCH) accounts for >60% of the total amount and has the highest frequency of detection. The concentrations of DDX (DDT + DDE + DDD) in the northern part of the estuary (five northernmost sampling stations) were >20 ng g^{-1}, decreasing to average values of <2 ng g^{-1} in the rest of the PRE, within the same range (from 0.04 to 2.48 ng g^{-1}) as reported in a previous study [14]. The northern part of the PRE is therefore most important in terms of pesticide contamination, especially because the ratio of DDT/(DDE + DDD) was between 0.8 and 2.3, indicating recent organochlorine inputs, whereas the ratio dropped to 0 in the rest of the sampling stations as DDT was not detected. The use of DDT and HCH was restricted in China in 1983 [8], but several rebounds in their concentrations have been registered in sediment cores since then, indicating that the amounts deposited after the production ban may be derived from soil residues because of the increase in soil runoff enhanced by the large-scale land transform and regional flooding in the PRE region. In addition, DDT had been banned in China, but recently (2009), its use in anti-fouling paints can be also considered as another source, because DDX concentrations ranging from 9 to 7350 ng g^{-1}, which is generally 1–2 orders of magnitude higher than those of the adjacent estuarine/marine sediments, have been measured in fishing harbors at the PRE [28].

The presence of most modern pesticides, currently used in the area, was also noticeable, with two pyrethroids, phenonthrin and biphentrin, being the most abundant, up to 17 and 5 ng g^{-1}, respectively, and these values were recorded in the northernmost sampling station, located at Guangzhou (Fig. 2b). A recent study [29] on the urban waterways of this city and Dongguan and Shenzhen (two other settlements located in the eastern shore of PRE, north of Hong Kong) shows that pyrethroids are nowadays the most widely used pesticides, and that they concentrate in the sediments from most urbanized areas rather than from less populated agricultural areas. Chlorpyrifos was the only organophosphorus pesticide detected in that study, same as here, but at lower concentrations than pyrethroids. Traces of terbuthylazine (<2 ng g^{-1}, <20%), a triazine, were also detected in the samples.

PCBs, the last group of priority contaminants considered in this study, have also been researched in the PRE region. Mai and coworkers (2005) have observed that in spite of their ban in China in the early 1980s, an increase in the PCB fluxes from 1989 to 1997 correlated to the growth of gross domestic product per capita in the region and the decline of agricultural land use [4]. Apparently, the emissions from the PCB-containing electrical equipment were responsible for the fluxes during that period of time. In this case, PCBs were detected only in the samples in the northern part of the estuary and Macao and Hong Kong shores (Fig. 2c), and their concentration was very low (<3 ng g^{-1}). This is not surprising considering that they were substituted decades ago by other halogenated flame retardants such as PBDEs, whose concentrations have been rapidly increasing over the last decades according to their records in dated sediment cores [9]. Their spatial distribution in surface sediments, nevertheless, matches to that observed for PBDEs [3], suggesting similar sources (riverine run-off from electronic manufacturing plants in the area according to Guan et al. [30]), transport and persistent behavior in sediments.

3.2. *Occurrence and distribution of emerging contaminants in the PRE sediments*

Fig. 2d–i shows the spatial distribution and concentrations (in ng g^{-1}) of different classes of new contaminants detected in the surface sediments from the PRE region in this study for the first time. The molecular structures for those detected (Table S1) are displayed in Fig. 2S (Supporting information). Continuing with the end of the previous section on flame retardants, we have focused our attention in new non-halogenated compounds based on phosphate (OPFRs), whereas most of the current research in the area is still centered on describing the distribution, transport, and temporal trends of PBDEs [24,31,32]. These studies reported a recent decrease in the concentrations of these chemicals as a consequence of the progressive phase-out of some of their components (starting with penta- and octa-PBDEs, deca-PBDEs coming next) and the appearance of some new halogenated substitutes (namely tetrabromobisphenol A and hexabromocyclododecane among others) supposed to be more environmentally friendly, but no information on the occurrence of non-halogenated flame retardants is available yet. To the best of our knowledge, there is only one report on the occurrence of OPFRs in the wastewater sludge from 19 local WWTPs [33], reporting the detection of all the analytes in the samples. This study reports the existence of three ubiquitous components, tri-isobutylphosphate (TIBP), tri-*n*-butylphosphate (TNBP), 2-ethylhexyl diphenylphosphate (EHDPP), in sludge, which are the same compounds that we have also observed in our sediment samples. Moreover, Fig. 2d shows the distribution of the total concentrations of OPFRs in the PRE, which is similar to that previously reported for PCBs, PAHs, and even PBDEs [24]. Thus, the highest concentrations occur in the upper part of the estuary and between Macau and Hong Kong (Fig. 2d). The concentration of these flame retardants ranged from 58 to 322 ng g^{-1}, with an average value of >100 ng g^{-1}, and are comparable to those previously measured for PBDEs in the same sampling sites [24,31,32].

The second group of emerging contaminants includes two types of ingredients frequently used in PCPs: synthetic and UV filters. The concentrations of the fragrances ranged between 25 and 175 ng g^{-1} and were very similar to that reported by Zeng et al. [16] (6–167 ng g^{-1}) in a study on the distribution of three polycyclic musks (galaxolide, tonalide, and celestolide) in the upper part of the PRE and Macau. In our case, we extended the range of compounds by also including nitro (e.g., musk xylene, detected in only two sampling stations) and macrocyclic musks (e.g., musk R1), but only four (galaxolide, tonalide, OTNE, and cashmeran) out of 13 target compounds were detected in most samples, all of them being polycyclic musks and showing a high detection frequency (>70%). The significant positive correlation between the galaxolide to tonalide ratios can be used as a tracer for source discrimination and for the degree of degradation in the environment considering that these ratios are between 3.4 and 7.6 (average of 5.3) in the sludge from local WWTPs [16]. In our surface sediments, these ratios ranged from 0.5 to 2.5, with an average of 1.2, indicating that the galaxolide degradation is enhanced in the environment. As expected, the sediments collected in the northernmost part of the estuary had the highest concentrations of polycyclic musks, because of the large amounts of municipal sewage and industrial wastewater discharged from the city of Guangzhou (Fig. 2e). The concentrations of polycyclic musks were also higher in the samples collected from the coast of Macau, which receives not only effluents from Macau but also fluvial suspended particles from the PRE water network [16]. The main novelty of this study is the identification of OTNE, also known as Iso-E-super, in all the sediment samples. The occurrence and environmental behavior of this chemical in aquatic systems is scarcely reported in spite of being one of the most popular fragrances recently measured in WWTPs from the European Union (mass flows are between 0.9 and 1.9 g per inhabitant and year according to [34]). The ubiquity of OTNE in the PRE region must be related to its high persistence, as this compound has been reported to have poor removal rates during the sewage treatment (56–64%, the main fraction accounting for sorption to sludge) and is not readily biodegradable in OECD tests.

Seven out of 10 UV filters were detected in the study area, with octocrylene (OC) accounting for the highest concentrations (>100 ng g^{-1}). OC was the most frequently detected analyte (97%) together with 2-ethylhexyl salicylate (EHS) and homosalate (HMS). This is in contrast with the only existing study of the presence and distribution of UV filters in the PRE, which is limited to some sediment samples collected in Hong Kong bay [35]. There, 11 different compounds were considered, and BMDM and ODPABA (two chemicals not included in this study), and EHMC were predominant over the rest of UV filters. The distribution of UV filters, nevertheless, is significantly different than that previously described for the rest of target compounds in this study. Thus, there is a net accumulation of UV filters in the east part of the estuary rather than in the west, especially in the surroundings of Hong Kong (Fig. 2f). Although that area was not covered during our sampling campaigns, Tsui and coworkers (2015) [35] have reported even higher concentrations (>1000 ng g^{-1}) in the stations adjacent to the city (e.g., Victoria Bay) [35]. Wastewater discharges are not the only main sources of UV filters, but the importance of direct inputs via recreational activities (e.g., swimming) has to be considered as all the detectable UV filters showed higher detection frequencies from direct sources rather than indirect sources [35]. This is confirmed in the current study, because of the predominance of these compounds in the surroundings of Lantau Island, the largest island of Hong Kong (located in the mouth of the PRE) for outdoor activities for most tourists and city residents.

The last three classes of compounds included in this study (Fig. 2g–i) were sewage-derived chemicals including cationic surfactants (quaternary ammonium compounds, or QACs), NP (one of the main metabolites of nonylphenol ethoxylates (NPEO), nonionic surfactants), and the sum of triclosan and its metabolite methyl-triclosan. NP (Fig. 2h), is one of the most widely studied EDCs, first measured in the PRE by Chen and coworkers (2006) [13] and monitored in several surveys alone [25] or together with other EDCs [18,21]. A comparative study pointed out NP as the main EDC in the area in terms of concentration (>10,000 ng g^{-1} occasionally) [18], because bisphenol A and steroid estrogens are usually one or two orders of magnitude lower, respectively. All the previous data on the longitudinal distribution of NP along the PRE showed the highest concentrations in the northern part of the estuary and lower concentrations in the sediments adjacent to Macau, in agreement with our data (Fig. 2h). Thus, levels up to 7808 ng g^{-1} were reported in the surroundings of Guangzhou city (Zhujiang river) [13], sharply decreasing to 100 ng g^{-1}, a few miles away towards the south [25]. A direct correlation was observed between the NP concentration and the organic carbon content in this study, indicating that this is one of the most important features in the sediments controlling the levels of this chemical [13] We have also observed statistically significant ($p < 0.05$) correlation between organic carbon content and concentrations of QACs, pesticides and PAHs, but not for other target compounds (e.g., UV filters, OPFRs, and fragrances). As described in the next section, NP is still an environmental concern in the PRE. The analysis of dated sediment cores reveals that the peak fluxes of NP have occurred in the mid-1980s, coincident with the rapid economic growth in the PRE region, but later decreased because of the implementation of sewage treatment in the late 1980s [36]. The fluxes increased again since the 1990s, because of the lack of adequate wastewater treatment facilities and the uninterrupted economic growth in the area.

On the other hand, little attention has been paid by the scientific community to QACs in spite that they are among the organic contaminants with the highest concentrations in sewage-impacted sediments (100% detection, up to 12,262 ng g^{-1} in this study, almost a ten-fold increase over other classes such as PAHs) (Fig. 2g). A continuous exponential increase of behentrimonium chloride (a class of QACs) over the last decades has been measured in dated sediment cores from Jamaica Bay (NY, United States) as a consequence of increasing production and use [37]. The only data available on QACs in the PRE comes from a recent study by our research group [12] where we reported similar levels and homologous patterns. A strong correlation was observed between them and priority contaminants (PCBs and PBDEs), indicating a high potential for QACs as tracers of the transport of sewage-derived pollution in aquatic environments. This potential is reinforced here as we plot the concentrations of dialkyldimethyl ammonium compounds (DADMACs), the main components of QACs (84%), versus other classes of contaminants (Fig. 3Sa–h). The correlation was heavily influenced by a single point (very high concentrations of most contaminants in sampling station P01), so we log transformed both the predictor and response variables. By doing so, we normalized the model residuals and used the standard F-test to determine the significance of the linear regression models. Statistically significant fits ($p < 0.1$) were obtained for most target compounds except for fragrances and UV filters. This suggests that sewage discharges are a common source for many of these chemicals, although other sources (e.g., atmospheric transport and combustion) have to be also considered as some of them are semi-volatile compounds (e.g., OPFRs and fragrances). Additionally, the lack of correlation for UV filters is in agreement with the previous assessment on the importance of UV filter direct sources by Tsui and coworkers (2015) [35] commented above.

Finally, triclosan was detected in 96% of the sediment samples at concentrations up to 32.6 ng g^{-1}. These values are significantly lower than those recently reported in a study in the upper part of the river (north of Guangzhou city) [17], where concentrations >1000 ng g^{-1} were detected in the Shijing River sediments. Methyl-triclosan, the main biotransformation product of triclosan, was only detected in 2 sampling stations at very low levels (<1 ng g^{-1}).

3.3. *Mass inventories of organic contaminants in PRE sediments and preliminary ecological risk assessment*

To assess the potential of sediments as a contamination source to the nearby oceanic environment (SCS), the mass inventories of all the contaminants detected in the present sampling region were estimated using a modification of the approach followed by Chen and coworkers [14]. Table 1 shows calculated mass inventories for different classes of contaminants. Additionally, an environmental risk assessment was performed using hazard quotients (HQs), which were calculated for those target compounds for which ecotoxicological data for sediments was available (Table 2S). In general, we estimated that all the analytes detected in the PRE sediments accounted for a total mass over 300 metric tons (Fig. 4). Assuming a sedimentary rate of 1 cm/yr, a reasonable estimate for the PRE from the results of the previous studies [4,8], the mass inventories reflected here would represent deposits in the last five years. The areas showing the highest potential risk for benthic organisms are the upper part of the estuary, and secondary area is the coast of Macau (Fig. 5) and is in agreement with the maximum values for most of the target compounds usually detected there.

Surfactants (e.g., QACs) and their metabolites (e.g., NP) accounted for the highest fraction of xenobiotics in the surface sediments (68%) (Fig. 4). Both QACs and NP are of environmental relevance. The first ones (200 metric tons) are the most toxic surfactants for aquatic species [38], and some of them are used as active ingredients in disinfectants (e.g., BACs). Data on their ecotoxicity for the sediment species is scarce (Table 2S), but their strong sorption capacity [12] may limit their bioavailability, and therefore their toxicity and bioconcentration potential [39]. In fact, HQ values (<0.1–0.7) were always <1 for all the sampling stations in spite of their concentrations in sediment exceeding 10 μg g^{-1} at some points. However, intensive exploitation of these and other disinfectants such as triclosan (0.3 tons in the PRE, HQ values similar to those for QACs) may result in bacterial resistance to these agents [40]. In fact, the European Union has recently banned the use of triclosan, as that of NPEO, a few years ago. NP, a NPEO degradation product, is a well-known EDC whose inventory in the PRE surface sediment was estimated to be 15 metric tons. A previous ecological risk assessment on NP in the PRE showed HQ values ranging

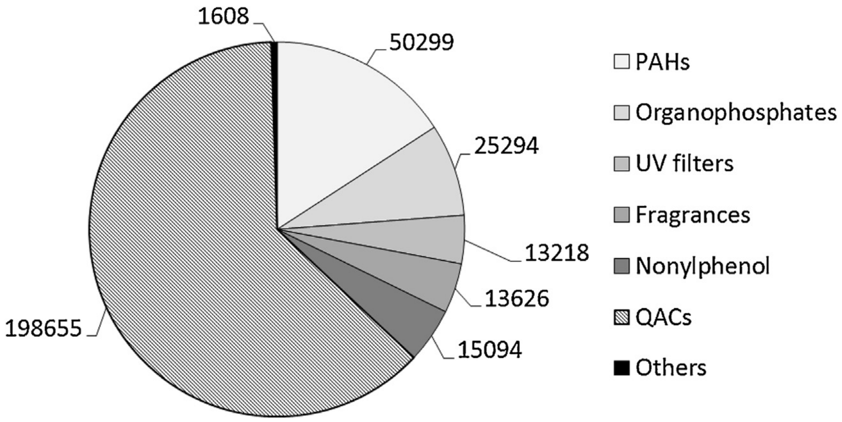

Fig. 4. Mass inventories (kg) for different classes of compounds in the surface sediments from the PRE, including polycyclic aromatic hydrocarbons (PAHs), quaternary ammonium compounds (QACs), and organophosphate flame retardants, among others.

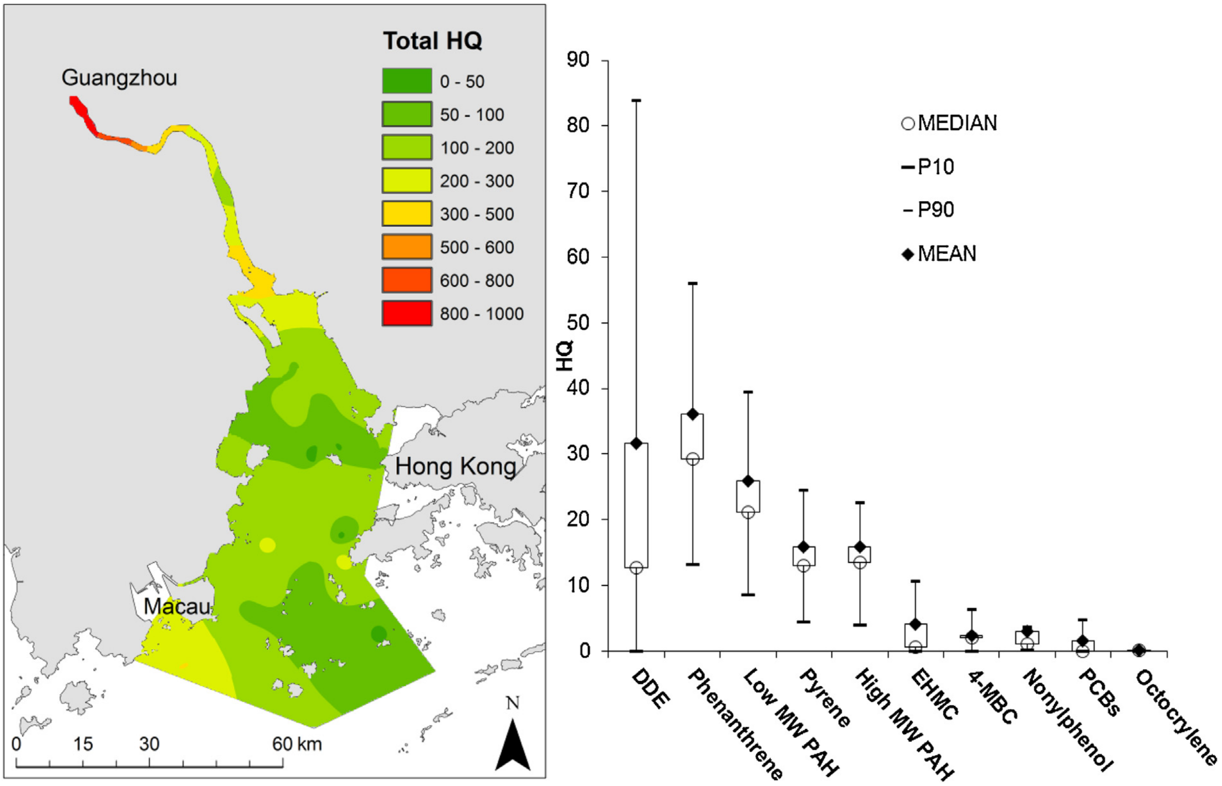

Fig. 5. Total risk assessment map for the surface sediments from PRE and top 10 most dangerous compounds in the area according to their hazard quotients (HQ).

from 3.6×10^{-5} to 35, with 64% of samples giving HQs > 1, indicating that the current levels pose a significant risk to relevant aquatic organisms in the region [25]. These values are in agreement with those reported here (up to 49) and imply that NP can be considered as one of the top 10 most dangerous compounds detected in the PRE region (Fig. 5). Two UV filters are also included in this ranking (EHMC and 4-MBC). A probabilistic ecological risk assessment recently performed by Tsui and coworkers (2015) [35] using Hong Kong sediments showed that the likelihood of EHMC causing toxic effects on reproduction in snails was over 84% and 32% based on the toxicity data of the two species (*Melanoides Tuberculata* and *Potamopyrgus antipodarum*), respectively, suggesting potential risks of UV filters to benthic organisms and possible adverse effects on the marine food web. More than 13 tons of these chemicals were calculated to be in the PRE sediments, roughly the same amount as of synthetic musks.

The importance of priority contaminants in terms of both the total mass and ecological risk cannot be neglected in spite that many of them are no longer produced (e.g., PCBs or DDT). Thus, PAHs are the second largest group of chemicals in the area in terms of mass (>50 metric tons) (Fig. 4). The results from a sampling campaign in 2002 [14] estimated that the PAH mass in the PRE was 126 tons, a value significantly higher than the one reported here. Differences can be attributed to different ways of calculation (the area was divided in 8 compartments only, and no interpolation was performed in that study) and/or the continuous decrease of the PAH concentrations in sediment that has been reported from the analysis of dated sediment cores [10]. Nevertheless, HQs were >1 in all the stations, showing the average values of 26 and 16 for low (2–3 rings) and high molecular (4–6 rings) weight PAHs, respectively. The PAH concentrations in the northern part of the PRE were higher than the Dutch target value of 1000 ng g^{-1} set by the Netherland Ministry of Housing (1994), with two individual components (phenanthrene and PYR) accounting for most of the toxicity (Fig. 5). In spite of the relatively low concentrations (<10 ng g^{-1}) and masses (1.3 tons) of pesticides and PCBs, these compounds still pose the greatest risk in the sediments from the region (Fig. 5). This is especially significant in the case of DDT and their metabolites, the most predominant pesticides in the region (0.4 tons according to Chen et al., 2006 [14]). The metabolite DDE has been identified as the chemical with the highest HQ value (up to 233 in sampling station P01, adjacent to Guangzhou city). The mass inventory of PCBs is very low (<50 kg), especially when compared to that for PBDEs (>8 tons according to Chen et al. [9]), although it would be significantly higher if the entire range of congeners had been considered. Their ecological risk cannot be ruled out in the upper part of the PRE (the HQ range is between 2 and 17 for stations P01 to P07). Notably, the new organophosphate flame retardants accounted for a higher total mass (>25 tons) than both PCBs and PBDEs. Further research would be necessary to discern whether the levels of these chemicals in the PRE sediments are increasing, as it was observed when PBDEs started substituting PCBs decades ago.

4. Conclusions

We have carried out the first comparative study on the occurrence and distribution of both priority and emerging contaminants in the surface sediments from the PRE. This is a step forward of previous studies in the area that were mainly focused on one or two classes of chemicals, mostly PAHs and halogenated compounds (i.e., PCBs, PBDEs, and, most recently perfluorinated substances). Our results show that surfactants are the most predominant contaminants in the PRE sediments (68% of the total mass), followed by PAHs (16%). The concentrations and mass inventories (up to 16% and >300 ng g^{-1}, respectively) of organophosphate flame retardants (PBDE substitutes) and some PCPs such as UV filters and fragrances are also noteworthy. Most of the chemicals follow similar distribution patterns, showing the highest concentrations in the northern part of the estuary, where Guangzhou city is located and in the sediments adjacent to Macao. Treated and untreated wastewater discharges seem to be a major source for these contaminants, as they are moderately to strongly correlated ($R^2 = 0.44–0.89$) to QACs, whose usefulness as sewage-derived contamination markers was demonstrated by a previous study [12]. Direct sources (e.g., outdoor activities) were also relevant for UV filters as maximum concentrations were measured near recreational areas. A preliminary risk assessment showed that PAHs and legacy contaminants such as DDT and PCBs still pose a significant risk for the benthic communities in the PRE region in spite of the reduction in their emissions over the last decades. Some new contaminants such as EHMC or 4-MBC may also pose negative effects. However, the risk assessment could not be carried out for all the target compounds detected in the area, because of the lack of toxicity data for sediment organisms. Thus, the discharge of alternative flame retardants (organophosphate compounds and others) into the environment still needs to be investigated in spite that they may be of concern as some of their components (i.e., TNBP and EHDPP) have been already detected in polar regions [41], indicating that they may also pose a risk to the environment in terms of persistence and bioaccumulation. In addition, because the concentrations of legacy pesticides are slowly decreasing in the PRE region [42], the exposure of the resident population to current-use pesticides (pyrethroids accounted for almost 30% of the total concentration of pesticides in our samples) is expected to increase over the years, and therefore further monitoring and human and environmental risk assessments are required.

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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.2016.02.046.

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