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Occurrence of quaternary ammonium compounds (QACs) and their application as a tracer for sewage derived pollution in urban estuarine sediments

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ABSTRACT

Particle reactive organic contaminants in estuarine sediments can lead to various environmental problems affecting ecosystem and public health. In this study, the occurrence and homologous distribution pattern of quaternary ammonium compounds (QACs) in the surficial sediments collected from the Pearl River Estuary (PRE), China were examined along with polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs). The composition pattern of the QACs was found to be uniform in most of the sediments analyzed throughout the PRE, and the average composition pattern was identical to that determined in the sewage sludge from Guangzhou, the biggest city in the PRE. Dialkyldimethylammonium compounds, the most abundant type of QACs, positively correlated to the total concentrations of PCBs and PBDEs in most of the sediments with similar composition patterns. Therefore, the QACs are proposed as potential tracers to evaluate the transport of sewage-derived pollution in estuarine environments.

1. Introduction

Currently, quaternary ammonium compounds (QACs) are one of the major classes of cationic surfactants used as the ingredients in fabric softeners, disinfectants, detergents, and numerous personal care products (Cross and Singer, 1994; Levinson, 1999). Because of hydrophobic cation-exchange characteristics, QACs tend to adsorb strongly on sludge and sediment, and the sorption energies are controlled by both the hydrophobic effect of their long alkyl chains and favorable electrostatic interactions between the cationic ammonium head group of QACs and cation-exchange sites on the surface of natural particles. Extremely high levels of QACs have been reported in the municipal sewage sludge (up to 9200 μg/g) prior to a voluntary phase-out of dialkyldimethylammonium compounds (DADMACs) as the fabric softener ingredient in Europe during the early 1990s (Fernandez et al., 1991; Gerike et al., 1994; Martinez-Carballo et al., 2007). However, the occurrence and fate of QACs in the environment are rarely studied (Chiaia-Hernandez et al., 2013; Lara-Martin et al., 2010; Li and Brownawell, 2010). Recently, studies have shown that the sediment-sorbed QACs are ubiquitous and persistent in the urban estuarine sediments of the Hudson River Estuary (HRE) in the USA with higher concentrations than the other conventional organic contaminants, e.g., polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Li and Brownawell, 2010).

The congeners of the QACs detected in natural environments consist of three major structural classes: (i) DADMACs, with double *n*-alkyl chains of even carbon alkyl lengths varying between C8 and C18 (Li and Brownawell, 2009); (ii) alkyltrimethylammonium compounds (ATMACs), with a single *n*-alkyl chain between C12 and C22 (Lara-Martin et al., 2010); and (iii) benzylalkyldimethylammonium compounds (BACs), with alkyl chain lengths between C12 and C18 (Li and Brownawell, 2010). The disinfectants containing BACs and DADMACs have been used for more than 60 years, and bacteria QAC resistance gene has been isolated from the contaminated environments and showed potential for co-selecting antibiotic resistance gene (Gaze et al., 2005). Recently, studies have shown that QACs can serve as the precursors of *n*-nitrosodimethylamine (NDMA) synthesis during the disinfection of wastewater (Kemper et al., 2010).

The Pearl River Estuary (the PRE) located in southern China (Fig. 1) is one of the most urbanized estuaries heavily affected by the rapid economic and population growth, and persistent organic

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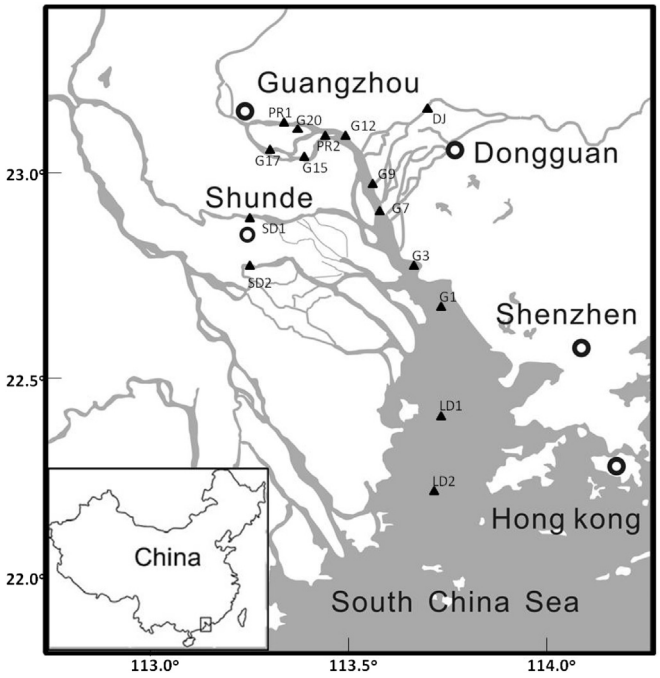

Fig. 1. Locations of the sampling sites in the Pearl River Estuary.

pollutants (POPs) including PCBs and polybrominated diphenylethers (PBDEs) have been widely detected in the air (Chen et al., 2009; Zhang et al., 2009), sediment (Chen et al., 2013; Mai et al., 2005a, 2005b), and biota (Luo et al., 2009). Previous results showed that the levels of PCBs and PBDEs and their composition patterns were well preserved in the sediments, and the 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 (Chen et al., 2013; Mai et al., 2005a, 2005b). The municipal sewage pollution was proved to have significant effects in the sediments of the PRE and South China Sea (SCS) using geochemical markers, e.g., linear alkylbenzenes (LABs) (Liu et al., 2013; Luo et al., 2008). High correlation coefficients were found between the LABs and PBDEs in the Pearl River, indicating that they had similar sources and both associated with sewage-derived particles (Luo et al., 2008). 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 (Peng et al., 2009). However, there remains a paucity of information on the relative importance of the sewage-derived organic contaminants in the urban sediments, and how the homologous distribution patterns of these compounds are related to their sources.

In this study, a robust method using ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS-MS) was developed for the analysis of the QACs in the sediments. The concentrations and composition patterns of these QACs in the PRE sediments and the sludge from a local sewage treatment plant were determined to evaluate their origin of occurrence and provide insights into the use of QACs as sensitive and persistent tracers for sewage pollution input. The correlation of DADMACs with PCBs and PBDEs analyzed in the same set of sediments along with their composition patterns provided a better understanding of their sources and spatial distribution patterns in the PRE.

2. Experimental section

2.1. Study area and sediment samples

The Pearl River or Zhujiang River in Chinese ranks as the third longest river in China and flows into the SCS mainly through the PRE (Fig. 1). The PRE is one of the most urbanized estuaries 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 (see the Environmental Status Bulletins of Guangdong Province, China; http://www.gdepb.gov.cn/). The organic contaminants are generated by the industrial activities, agriculture, and electronic waste (E-waste) recycling areas (Chen et al., 2013).

The detailed information on the sample collection has been described in a previous study (Feng et al., 2012). Briefly, the surface sediment (0–5 cm) was collected using a Van Veen stainless steel grab sampler in October 2010 from the PRE region and tributaries of the Pearl River (Fig. 1). The samples to be analyzed for QACs in this work was selected based on the availability of other data on the sediment properties such as the total organic carbon (TOC) and organic contaminants (e.g., PBDEs) determined on splits of the same sediments (Chen et al., 2013; Feng et al., 2012). The sewage sludge samples analyzed in this study were obtained from a wastewater treatment plant in Guangzhou, which serves 2.1 million people and treats 200 kilotons of municipal wastewater per day.

2.2. Sample analysis

The analytical method for the analysis of QACs was modified and improved from our previous study (Li and Brownawell, 2009, 2010). Briefly, a stable isotope standard (D25 DADMAC12:12; 50 ng) was spiked as the surrogate standard in a 0.1 g of the freeze-dried sediment before the extraction. The sediment samples were extracted at 60 °C using an ultrasonic bath for three times (1 h × 3) with 5 mL of acidic (1M HCl) methanol. After the centrifugation, the combined extracts were collected in 20 mL test tubes and evaporated to dryness under a flow of nitrogen. The samples were then washed with 4 × 5 mL of water, and a total of 20 mL water was transferred to a 50 mL separatory funnel for liquid–liquid extraction. The water was extracted with 3 × 5 mL of chloroform, and the combined chloroform extracts was transferred into the original test tube and evaporated to dryness under a gentle flow of nitrogen. The sample extracts were spiked with 5 ng of tridodecylamine as the internal standard and reconstituted with a 1 mL 1:1 acetonitrile: water solution in an injection vial. The QACs were separated and analyzed by UPLC-MS-MS using an Agilent 1290 UPLC coupled with 6490 triple quadrupole mass spectrometer. All the QAC congeners investigated in this study were separated using a Thermo Scientific C18 column (50 × 2.1 mm, 1.9 μm,Thermo Scientific, USA) with a mobile phase flow rate of 0.2 mL/min. The mobile phases and elution gradients are described in the Supporting Information Table S1. The electrospray ionization in a positive ionization mode was conducted using a capillary and nozzle voltage of 3000 and 1500 V, respectively. A multiple reaction monitoring experiment was applied for the detection. The optimized collision energies, mass of the precursor and product ions, retention times, and method detection limits for each of the compounds are listed in Table S2 of the Supporting Information. A six-point quantitative calibration series (typically 0.1–20 ng/mL) was analyzed daily. The analysis responses were normalized to the surrogate standard for the quantification. The recovery of each of the sample was calculated using the response of the surrogate standard normalized to the internal standard. The average recovery of all the analyzed samples was 87 ± 10% ($n = 32$).

The analytical method used for the analysis of PCBs in the sediment samples has been reported in a previous study (Mai et al., 2002, 2005b). Briefly, the freeze-dried sediment samples were spiked with the surrogate standards (2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl) and Soxhlet extracted with a 1:1 acetone and hexane mixture for 72 h. Activated copper granules were added during the extraction to remove the elemental sulfur present in the samples. The extract was concentrated and purified using a 10 mm i.d. silica column packed, from the bottom to the top, with 10% silver nitrate silica gel (6 cm), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica (12 cm), and anhydrous sodium sulfate. The fraction containing the PCBs was eluted with 50 mL of hexane and collected for further analysis. The volume of the PCB fraction was reduced to 50 μL under a gentle stream of nitrogen. A known amount of internal standard (pentachloronitrobenzene) was added to the extract prior to the instrumental analysis. The sample extracts were analyzed using a Hewlett–Packard 6890 gas chromatograph equipped with an electron capture detector and a DB-5 fused silica capillary column (60 m × 0.25 mm i.d. with 0.25 μm film thickness). A total of 70 chromatographic peaks representing 112 individual or co-eluting congeners were quantified using a secondary Aroclors 1242/1248/1254/1260 mixture (1:1:1:1) standard characterized with 120 individual PCB congeners. The detailed operating conditions, quantification, and peak confirmation have been described in a previous report (Mai et al., 2002).

3. Results and discussion

3.1. Occurrence of QACs, PCBs, and PBDEs in the PRE sediments

The analysis results of QAC congeners in the sediments from the PRE are listed in Table 1 and S3. All the sediment samples had detectable levels of BACs, ATMACs, and DADMACs because of the high sensitivity of the analytical method applied in this study. The ranges of total BACs, ATMACs, and DADMACs were 49.3–1050,

Table 1
List of % TOC content, total concentrations of QAC sub groups, total PCBs, and PBDEs in the PRE sediments.

Sample ID	TOC %	BACs ng/g	ATMACs ng/g	DADMACs ng/g	PCBs ng/g	PBDEs[a] ng/g
PR1	2.4	596	2010	7700	31.7	150
PR2	0.6	157	127	1060	17.1	16.0
LD1	1.2	205	42.4	784	8.60	17.7
LD2	1.1	137	54.7	932	10.1	15.3
SD1	0.4	261	144	1090	10.9	44.8
SD2	0.8	49.3	16.5	548	7.69	5.80
DJ	0.9	77.9	43.5	1050	16.1	437
G1	0.7	58.7	20.6	159	8.76	10.7
G3	1.1	1530	168	810	9.82	53.3
G7	1.2	623	184	1160	12.9	73.4
G9	1.1	639	374	2650	16.3	170
G12	1.1	727	1010	4140	26.2	141
G15	2.5	1050	1620	6490	9.73	374
G17	1.0	480	428	2110	32.3	261
G20	1.9	424	474	1950	20.4	121

[a] data from Chen et al., (2013).

16.5–2010, and 159–7700 ng/g respectively, with median values of 452, 176, and 1120 ng/g respectively. The levels of QAC congeners in the PRE sediments were relatively lower than those found in the highly urbanized HRE in the USA, with median values of 1500, 520, and 26,200 ng/g for the BACs, ATMACs, and DADMACs (Li and Brownawell, 2010), but higher than the riverine sediments affected by the sewage wastewater input in Austria with median values of 100, 6.8, and 161 ng/g (Martinez-Carballo et al., 2007). In terms of the spatial distribution pattern in the PRE, the concentrations of the QACs were higher in the upper part of the estuary, while lower values were found in the middle and lower parts of the estuary. The highest concentrations of ATMACs (2010 ng/g) and DADMACs (7700 ng/g) were detected in Sample PR1,which was located close to Guangzhou, the largest city of south China with more than 13 million inhabitants (Fig. 1). The municipal wastewater input was thought to be the major source of the QACs in the sediments as discussed in the following section. However, the highest concentration of BACs was detected in Sample G3 (1530 ng/g), and as discussed below, a different composition pattern was found in Sample G3 compared to the rest of the sediments analyzed in this study (Fig. 2). Lower levels of QAC congeners were found in Samples LD1 and LD2 located in the middle and lower parts of the PRE (Fig. 1), where freshwater mixed with seawater and biogenic sedimentation appeared to be dominant. The lowest level of QACs was found in Sample SD2 located in the Xijiang River, which flows through a less urbanized and industrialized region with a relatively lower effect of the sewage-derived pollution (Chen et al., 2013; Mai et al., 2005a). Extremely high concentrations of QACs were detected in the sludge from the sewage treatment plant at Guangzhou (Table S1). The total BACs, ATMACs, and DADMACs in the sludge were 3,610, 8300, and 156,000 ng/g, and the total concentration of QACs (167 μg/g) in this sludge was higher than that measured in the sludge samples from Austria (22–103 μg/g) (Martinez-Carballo et al., 2007).

Two groups of particle reactive organic contaminants, PCBs and PBDEs, were also analyzed in the same set of the sediment samples (Table 1), and the concentrations of the major PCB and PBDE congeners are listed in the Supporting Information (Tables S4 and S5). The total concentration of PCBs ranged between 7.69 and 32.3 ng/g with a median value of 13 ng/g (Table 1). Relatively higher concentrations of PCBs were found in two samples (G17 and PR1) from the upper estuary area close to Guangzhou (Fig. 1). Similar to a previous study (Chen et al., 2013), the highest total PBDE concentration was detected in the surface sediment from the Dongjiang River (Sample DJ, total PBDEs = 437 ng/g), which flows through a large electronics manufacturing center. The second highest level was detected in the sediment in the upper PRE region (G15, 374 ng/g), where the industrial and municipal waste input from Guangzhou dominated.

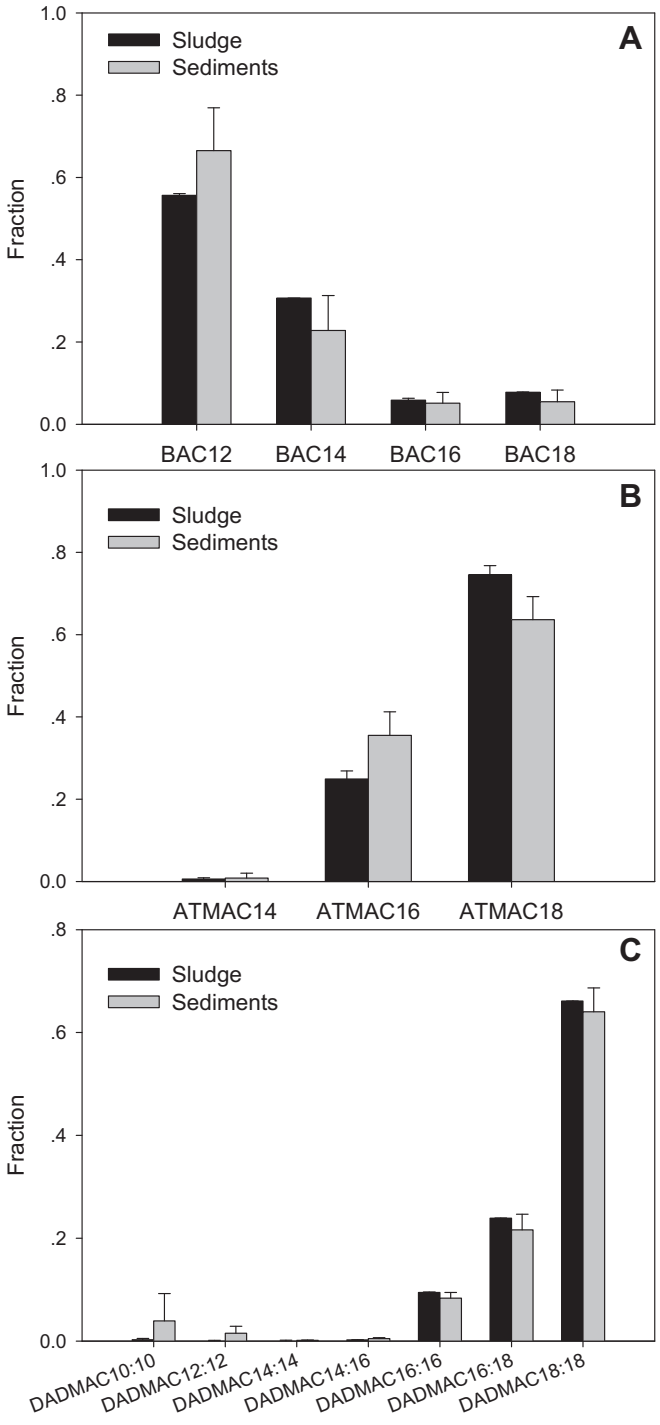

Fig. 2. Average compositions of the three sub-groups of QACs in the sediments of the PRE and the sewage sludge from treatment plant in Guangzhou: BACs (excluding sample G3) (A); ATMACs (B) and DADMACs (C).

The comparison of the QAC, PCB, and PBDE levels in the sediments of the PRE and HRE are shown in Table 2. The maximum, mean, and median levels of these three groups of reactive organic contaminants were significantly lower in the PRE compared to

Table 2
Comparison of TOC, total concentrations of PCBs, PBDEs, and QACs in surficial sediments in the Pearl River Estuary and Hudson River Estuary.

	TOC %		PCBs μg/g		PBDEs μg/g		QACs μg/g	
	HRE[a]	PRE	HRE[a]	PRE	HRE[a]	PRE	HRE[a]	PRE
Minimum	0.2	0.4	n.d.	0.008	n.d.	0.006	0.98	0.24
Maximum	10	2.5	2.5	0.032	0.49	0.43	110	10
Mean	3.5	1.2	0.15	0.016	0.23	0.13	34	3.1
Median	3.0	1.1	0.043	0.013	0.22	0.073	27	2.0

n.d. not detected.
[a] data from Li and Brownawell (2010).

those in the HRE. This is probably because that there could be less discharge of QACs in the PRE than the HRE, and the sediment samples collected from the HRE were more selective in representing the municipal wastewater input (Li and Brownawell, 2010). Further, the natural sedimentation in the PRE may have a relatively higher dilution factor. Another possible reason could be due to the less sorption of these organic contaminants on the sinking particles in the PRE because the TOC found in the PRE sediments was generally less than that in the HRE sediments (Table 2), even though, as discussed below, the TOC was not the only factor that controlled the redistribution of these organic contaminants in the PRE sediments.

3.2. Composition of QACs in PRE sediments

The average compositions of BACs, ATMACs, and DADMACs determined in all the sediment samples analyzed along with the sludge sample from Guangzhou are shown in Fig. 2. The BAC compositions are shown in Fig. 2A except for sample G3, which may be influenced by different sources as discussed below. The average percentage of BAC12, BAC14, BAC16, and BAC18 (the numbers refer to the length of the alkyl chain in QAC) in the sediments was 69%, 21%, 5%, and 6%, which were similar to those detected in the riverine sediments in Austria (Martinez-Carballo et al., 2007). The composition patterns detected in the sediments were similar to the industrial mixture of BACs (Acros/Fisher Scientific, Pittsburgh, PA, USA), also known as benzalkonium, containing 50%, 30%, 17%, and 3% of BAC12 to BAC18, respectively. ATMAC16 and ATMAC18 were two major congeners of ATMACs with an average percentage of 36% and 64%, respectively. For the DADMACs, the longer alkyl chain length congeners, e.g., 16:16, 16:18, and 18:18 represented 8%, 22%, and 64% of the total DADMACs detected in the sediments, and a similar pattern was also found in the sediments of the HRE (Li and Brownawell, 2010). In this study, DADMAC (10:10) contributed a minor fraction of the total DADMACs with an average percentage of 4%. However, it was a major DADMAC congener (up to 100%) in the riverine sediments from Austria (Martinez-Carballo et al., 2007). More water-soluble DADMACs have been applied as the active ingredients in the third and fourth generations of "QAC-disinfectants" instead of using only BACs, and there may be a major difference in the active ingredient in the commercial "QAC-disinfectant" between Austria and China that resulted in a different composition pattern of DADMACs in the sediments from the two regions. The average composition patterns of the QAC congeners were uniform in all the sediments analyzed from the PRE with limited standard variations (Fig. 2), indicating the persistence of QACs during the transport in the estuary. An identical congener fraction pattern was found in the sewage sludge sample from Guangzhou, indicating the major contribution from the municipal wastewater input of QACs to the sediments, and a slight transformation of QACs in the sediments was observed owing to their super strong hydrophobicity (Li and Brownawell, 2010).

3.3. DADMACs as a tracer for sewage-derived pollution

The hydrophobic organic contaminants from various sources tend to associate with suspended particles and eventually deposited in sediments, which can then act as a reservoir and long-term source for the ecosystem. The distribution of reactive organic contaminants such as QACs, PCBs, and PBDEs in the sediments of an urbanized estuary can mainly be controlled by three factors: (i) different sources and input pathways, (ii) redistribution during transport, and (iii) chemical and biological transformation in water column and sediment. The upper part of the PRE, from where most of the samples were collected in this study, was characterized by the presence of extremely high level of nutrients as well as low oxygen and high sedimentation rate (Guo et al., 2009). The biogeochemical characteristics of fast sedimentation and reducing environment facilitate the preservation of organic contaminants such as QACs, PCBs, and PBDEs. The redistribution of particle reactive organic contaminants (e.g., PCBs and PBDEs) is related to the characteristics of suspended particles in the water column such as particulate organic carbons, colloidal nature, and black carbon content (Chen et al., 2011). However, no clear correlations were observed between the TOC in the sediments vs. all the three groups of the organic contaminants analyzed in this study (Figure S1). Similarly, the poor correlations between the TOC, sediment grain size, and PBDEs were also found in the sediments of the coastal East China Sea (Li et al., 2012). This indicated that the distribution of reactive organic contaminants can relate more to specific land-based sources than to their sorption to natural particles. Therefore, source-specific tracers can be very helpful in the study of sediment contamination in the urban coastal areas.

Recently, the sewage tracers such as LAB, coprostanol (COP), and trialkylamine (TAM) have been utilized to interpret the sources, transport, and environmental fates of the domestic contaminants in the natural suspended particles and sediments (Eganhouse, 1997; Liu et al., 2013; Luo et al., 2008; Maldonado et al., 1999). Trialkylamine, which is a trace impurity of DADMAC in fabric softeners, is shown to be a more conservative tracer than LAB, mainly produced as the intermediate in the production of anion surfactants, for the urban sewage contamination in the coastal areas (Valls et al., 1989). Maldonado et al. (1999) compared the distribution of TAM and COP in open seawater and suspended particles from the western Mediterranean and the northwestern Black Sea, and showed the advantage of using TAM as the tracer to evaluate the long-range transport of domestic pollution into the open sea. Lamoureux and Brownawell (1999) provided the evidence that LAB was significantly degraded after reaching the sediments at the Deep Water Disposal (DWD) Site for the sewage sludge, 106 miles off the New Jersey coast in the USA. However, DADMACs were found to be more persistent in the same sediments at the DWD Site, indicating a good correlation with silver, another potential tracer for sewage-derived pollution (Li and Brownawell, 2010). As described above, QACs were source specific with relatively high levels and uniform composition throughout the estuary. Among all the QAC congeners, DADMACs are more hydrophobic and persistent than ATMACs and BACs because of the twin alkyl chain structure. Thus, the detection of DADMACs in the sediments can be applied as an indication of contaminants derived from the municipal sewage waste input.

The total BAC concentrations as a function of the DADMAC concentrations for all the sediments analyzed from the PRE are shown in Fig. 3A. Neglecting Sample G3, the total BAC concentration in the sediments was consistent with a primary sewage-derived source ($y = 0.1x + 155.9$, $r^2 = 0.61$, $p < 0.001$). However, the higher ratio of total BACs to DADMACs was found in Sample G3, with significantly ($p < 0.036$) different composition of the BAC congeners than the average for all the other sediments (Fig. 4A).

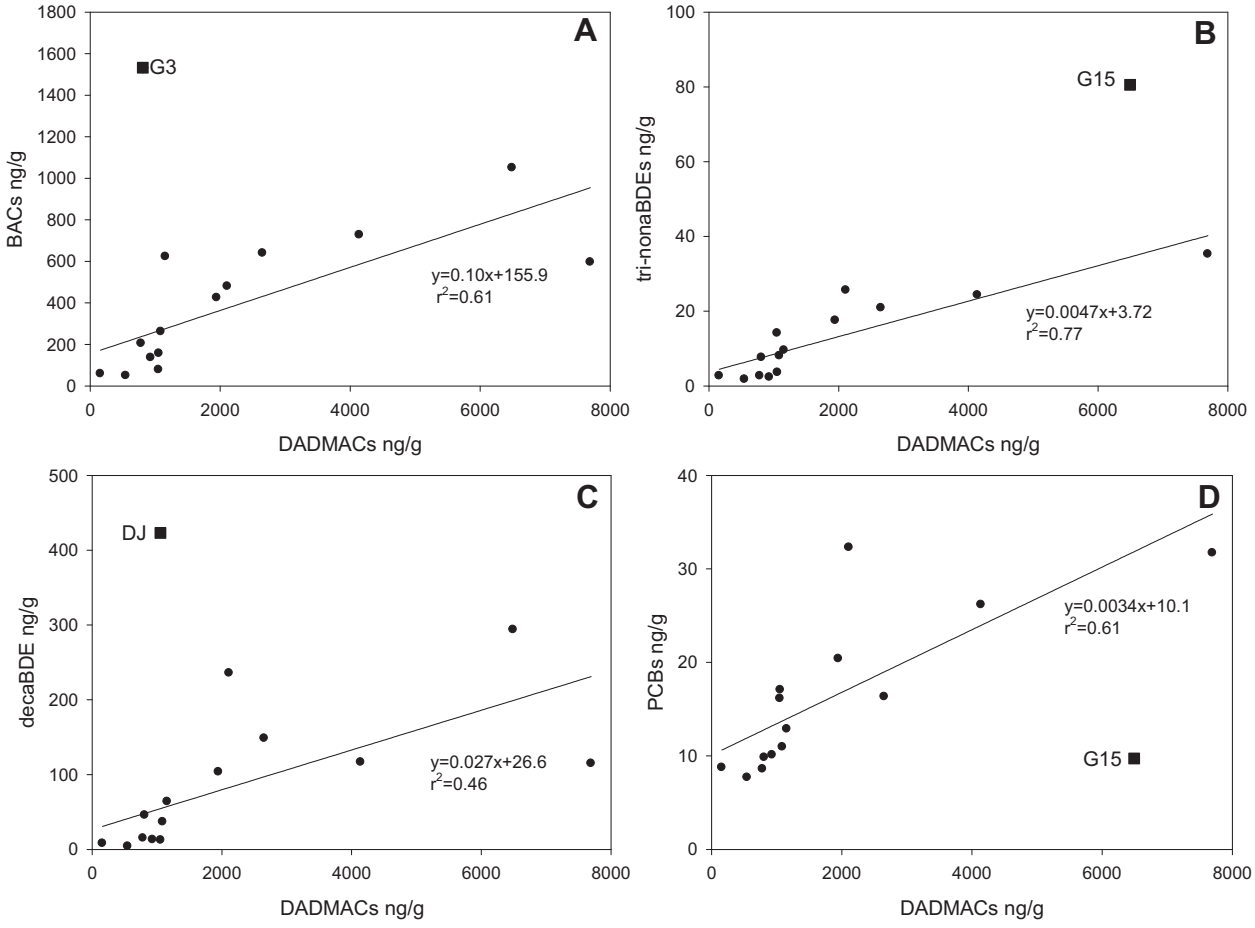

Fig. 3. Relationships between sediment concentrations of total DADMACs vs total BACs (A); tri-nonaBDEs (B); decaBDE (C) and total PCBs (D).

Thus, a relatively higher fraction of BAC14 and BAC16, and a lower fraction of BAC12 were found in Sample G3, thereby providing the support for a non-sewage source of the BACs.

The tri-nonaBDE and decaBDE also corresponded directly with the sewage-derived DADMACs in the sediments (Fig. 3B and C). Neglecting SamplesG15 and DJ, the linear regressions were $y = 0.0047x + 3.72$, $r^2 = 0.77$, $p < 0.0001$ and $y = 0.027x + 26.6$, $r^2 = 0.46$,$p < 0.0074$ respectively, indicating at the PBDE congeners were closely associated with sewage-derived particles in the sediments. This agreed with a previous study, where high correlation coefficients ($r^2 = 0.87$) were also found between the total concentrations of PBDEs and LAB in the sediments from the Pearl River (Luo et al., 2008). However, the concentration of tri-nonaBDEs in Sample G15 (80.6 μg/g) was approximately double the levels corresponding to the linear regression hypothesized to result from the sewage sources (Fig. 3B). In Sample G15, the fractions of hexaBDE, hept BDE, octaBDE, and nonaBDE were significantly higher ($p < 0.012$) than the average of the other sediments (Fig. 4B), indicating other possible sources with relatively more octaPBDE. The sediments from the Dongjiang River of the PRE have been heavily affected by the world's largest base for electronics/electrical production (Mai et al., 2005a, 2005b; Chen et al., 2013). The only sediment sample analyzed from the Dongjiang River (DJ) was detected with a higher ratio of decaBDE to DADMACs concentration (Fig. 3C). The characteristic of PBDE composition in sample DJ clearly showed a higher fraction of decaBDE derived from the local industrial sources (Fig. 4B).

The detection of total PCB and DADMAC concentrations in the sediments was also well described by linear regression ($y = 0.0034x + 10.1$, $r^2 = 0.61$, $p < 0.0001$) except for Sample G15 (Fig. 3D),where a relatively lower total PCB to DADMAC ratio was found and the PCB congener composition showed relatively high penta PCBs and hexa PCBs than the average of all the other sediments (Fig. 4C). Notably, the positive interception of the linear regression was 10.1 ng/g, which was about one-third of the highest total PCB level found in this study (Sample PR1). This indicated that other than sewage-derived PCBs, there should be a uniform none-point source of PCBs, such as the input from aerosol, in this area which contributed a major fraction of the PCBs detected in the sediments.

4. Conclusions

High total QAC levels were observed in the PRE area with levels comparable to those found in the urbanized areas at Austria and the USA. The QAC homologous compositions were uniform throughout the study area, and the composition pattern was identical to that detected in the sewage sludge from Guangzhou. The PCBs and PBDEs in most of the PRE sediments analyzed in this research had a positive linear correlation with the total concentration of the DADMACs, and the latter proved to be a potential excellent tracer for the sewage-derived pollution in the urbanized estuarine environment.

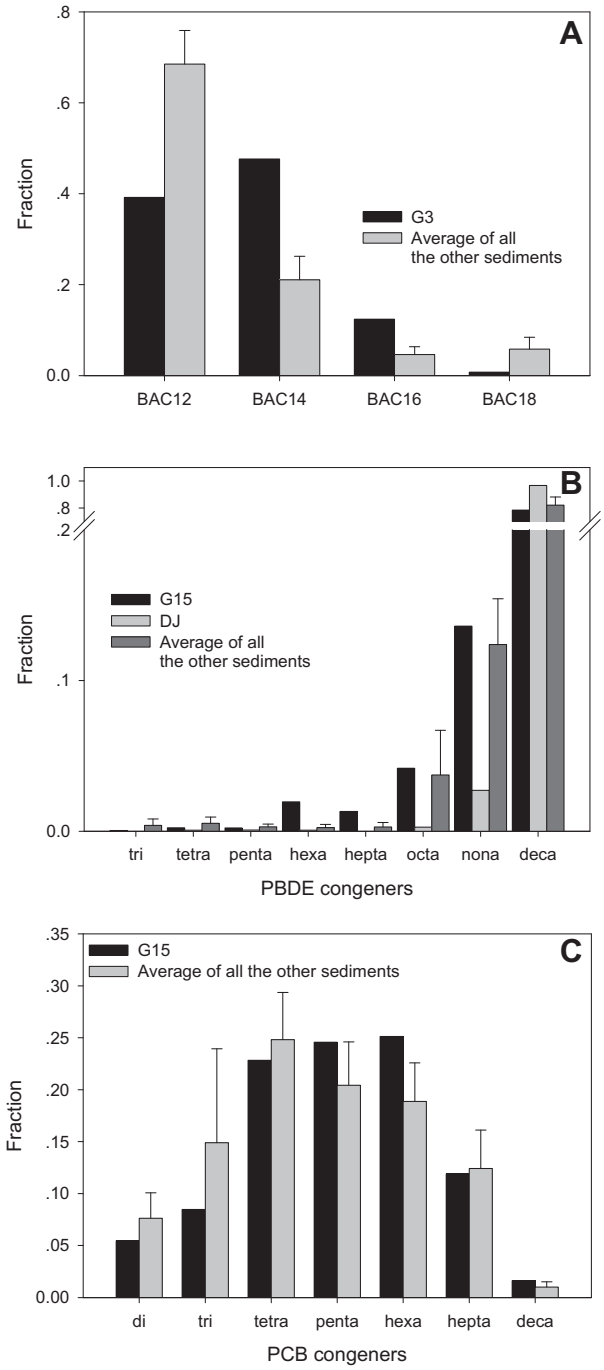

Fig. 4. Average compositions of BACs (A), PBDEs (B) and PCBs (C) in the sediments affected by potentially different pollution sources.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.10.028.

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