



## Sequential ASE extraction of alkylphenols from sediments: Occurrence and environmental implications

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### ARTICLE INFO

#### Article history:

Received 24 January 2011

Received in revised form 20 May 2011

Accepted 21 May 2011

Available online 12 June 2011

#### Keywords:

Alkylphenols

Sediments

Soxhlet

Sequential ASE extraction

### ABSTRACT

The occurrence of alkylphenols (APs) including nonylphenol (NP) and octylphenol (OP) in the riverine sediments from the Pearl River Delta (PRD), South China was investigated and compared by Soxhlet extraction (S-APs) with dichloromethane and by sequential accelerated solvent extraction (ASE) (A-APs) with 1:6 toluene/methanol, respectively. Concentrations of OP and NP range from <1 to 463 ng/g dw and 31–21,885 ng/g dw, respectively, demonstrating that the contamination level of APs in the PRD is one of the highest in the world. Moreover, the A-APs contents are highly significantly related to and on average 1.5 times the S-APs contents. For sequential two ASE extractions, APs in the first extract accounts for 82.2–99.2% of their total contents in the sequential two extractions. The correlation analysis shows that S-APs and A-APs are both significantly associated with the contents of total organic carbon (TOC), suggesting that the variable extraction efficiency of these two methods is related to the presence of condensed organic matter in the sediments.

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### 1. Introduction

Alkylphenols (APs) are degradation products of alkylphenol ethoxylates (APEOs), which are widely used as non-ionic surfactants in domestic and industrial detergents, emulsifiers, dispersants, solubilizing agents and other applications [1,2]. Octylphenol ethoxylates (OPEOs) and nonylphenol ethoxylates (NPEOs) are two of the most common surfactants in the marketplaces. NPEOs and OPEOs respectively account for about 80% and 20% of total APEOs with annual global production of 500,000 tons, considerable amounts of which ends up in the aquatic environment [1,3]. Biological transformations by progressive shortening of the APEO ethoxylate chain under aerobic and anaerobic conditions results in the formation of alkylphenol mono- and diethoxylates [4–6]. However, it has been suggested that the final transformation to alkylphenols (APs) occurs primarily under anaerobic conditions [5,6]. 4-Nonylphenol (NP) and 4-*tert*-octylphenol (OP) are more toxic and persistent than their ethoxylated precursors [7]. The concern over ubiquitous APs in the environment has been increasing due to their toxicity [8–10], estrogenic activity [11–13], and massive use. It was reported that the annual production of NP approximately reached 45,000 tons in the EU [14] and 16,000 tons in China [15].

In recent decades, the thriving economy and rapidly growing industrial and municipal development in the Pearl River Delta (PRD), which is the second largest river systems in China in terms of annual discharge ( $3.49 \times 10^{11} \text{ m}^3$ ), leads to substantial accumulation of toxic organic compounds. The aquatic environment pollution is increasingly serious in this region. Although recent investigations found high levels of persistent organic pollutants in the PRD riverine and estuarine environments [16], the information about emerging endocrine disrupting chemicals such as APs is quite limited in this region to date [17–19].

Since sediments are the ultimate sink and reservoir of environmentally persistent, hydrophobic contaminants, research on the sediment contamination of APs has been widely carried out [7,20–26], which is essential in assessing the pollution of water bodies and risk posed to aquatic organisms. Moreover, soil/sediment organic matter (SOM) differs in polarity, elemental composition, aromaticity, condensation, and degree of diagenetic evolution from a loose polymer to condensed structures. So heterogeneity of SOM is relevant to sorption, sequestration, extraction, distribution, and fate of hydrophobic organic compounds (HOCs), etc. [27,28]. In recent investigations on the soil/sediment samples in PRD [29–31], it was found that condensed organic matter such as nonhydrolyzable organic carbon (NHC), diagenetically altered organic matter, and black carbon (BC) is relevant to the extraction and distribution of native PAHs. In PRD, the NHC composed about 67% of a organic carbon (OC). The PAH contents extracted by the three-time ASE is 2.11 times than those by the Soxhlet

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extraction method. However, it is uncertain how condensed organic matter affects extraction, distribution, and fate of APs. Recent investigations have also shown that organic chemicals form freely extractable, lipid-bounded, and mineral-bound residues in soil and sediment environments [32–34]. But the understanding of the processes responsible for bound residue formation and the subsequent environmental fate of bound residues is limited. In this study, 28 riverine sediments were collected from the PRD to investigate the occurrence and distribution of APs. We also analyzed 10 of the sediments with Soxhlet and sequential ASE extraction methods, respectively, and compared the APs contents extracted by these two methods and correlated them with total organic carbon (TOC), in order to explore variable extraction efficiency of APs.

## 2. Experimental

### 2.1. Study area description and sample collection

Four major tributaries of the Pearl River system were selected for sampling (Fig. 1). The Zhujiang River (ZR) and Dongjiang River (DR) are located in the northeast of PRD. ZR flows through the city of Guangzhou, the biggest city in the south of China, which is highly urbanized with a population of 12 million and various industries. DR serves as the drinking water source of Dongguan, Shenzhen, and Hong Kong. It runs across the city of Dongguan, where manufacturing and processing industries are well developed. The two rivers join at the Shizhiyang Waterway and flow into the Pearl River Estuary through the Humen outlet. The Xijiang River (XR) and Beijiang River (BR) lying in the southwest of PRD run across less developed areas. XR drains into the estuary through the Modaomen, Jitimen, and Hutiaomen outlets, and BR flows into the estuary via the Jiaomen, Hongqimen and Hengmen outlets. 28 surface sediments (0–20 cm) were collected from ZR, DR, XR, and BR (Fig. 1) in July 2006 and February 2007, respectively, using a stainless steel grab sampler. The sediment samples were kept at  $-20^{\circ}\text{C}$  until further analysis.

### 2.2. Chemicals

4-Nonylphenol (mixture of 11 compounds with branched side chain), 4-*tert*-octylphenol (93%), 4-*tert*-butylphenol (98%) and 4- $\alpha$ -cumylphenol (98%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Organic solvents were analytical grade and redistilled using a glass system. Neutral silica gel (80–100 mesh) was Soxhlet extracted with dichloromethane for 72 h, activated at  $180^{\circ}\text{C}$  for 12 h and then deactivated by adding 5% distilled water.

### 2.3. Soxhlet extraction

The descriptions of materials and analytical procedure, namely, extraction, separation and analysis of APs for the samples were detailed elsewhere [7,17,18]. Briefly, the samples were freeze-dried under  $-47^{\circ}\text{C}$  for 24 h, pulverized, and passed through an 80 mesh stainless steel sieve. 4-*Tert*-butylphenol was added to each sample as a surrogate standard and activated copper was added for desulfurization. About 10 g of each sample was Soxhlet-extracted for 48 h with dichloromethane. The extracts were concentrated and solvent-exchanged to hexane using a rotary evaporator and then purified using silica column chromatography (1 cm i.d.  $\times$  9 cm). After washing with 20 mL dichloromethane/hexane (30:70), the column was eluted with 40 mL dichloromethane/hexane (80:20). The eluate was collected and concentrated to 0.2 mL under a gentle nitrogen stream for further instrument analysis.

### 2.4. ASE extraction

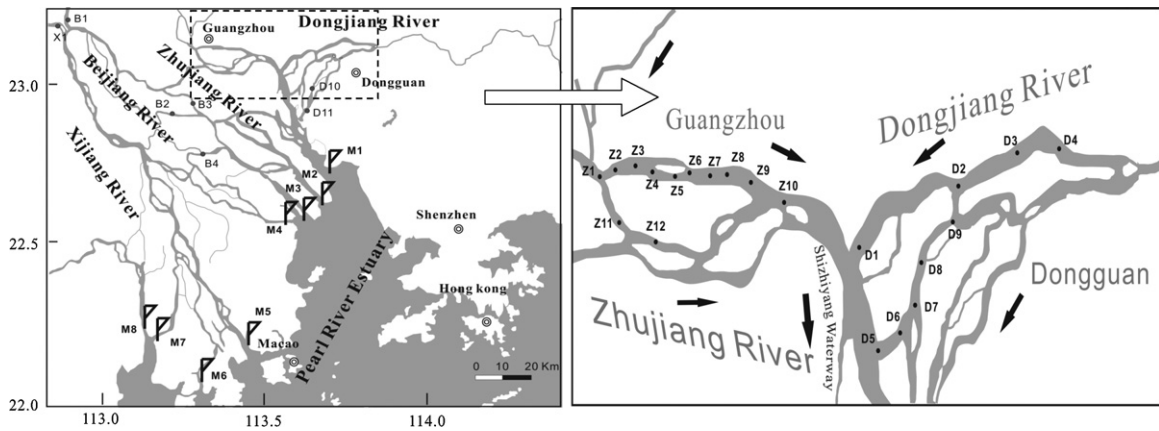
ASE has been used to extract various hydrophobic organic compounds from different environmental samples. Some studies have made a comparison between ASE and Soxhlet extraction and found that the performance of ASE was consistently equivalent to or better than Soxhlet extraction [35,36]. The ASE (Dionex 300, USA) is an automated system for extracting organic compounds from a variety of solid samples. ASE accelerates the traditional extraction process by using solvents at elevated temperatures and pressure. According to the previous investigations on PAHs [28,37], it was found that a mixture of toluene/methanol (1:6) was more effective than dichloromethane for the extraction of PAHs. Hence, we selected a mixture of toluene/methanol (1:6) as the ASE extracts for APs in the selected sediments. About 10 g freeze-dried sediment samples and 10 g quartz sands were mixed and packed into the extraction cell with glass-fiber filters (1  $\mu\text{m}$  pore diameter) at each end in order to prevent fine particles eluting into the collection bottles. The quartz sands and cells were ultrasonically washed with methanol prior to use. Each sample was sequentially extracted with a mixture of toluene/methanol (1:6) for two times and each extraction was consisted of two cycles. During the extraction, each extraction cycle lasted for 5 min at  $100^{\circ}\text{C}$  and under a pressure of 14 Mpa. After two cycles of extraction, the extracts were flushed into a collection bottle and the packed cell was rinsed again with 60% volume of the same solvent and flushed into the same collection bottle, and finally purged with gaseous nitrogen for 1.5 min. The extracts were concentrated, solvent-exchanged to hexane, and purified using the same procedure as the Soxhlet extraction.

### 2.5. Instrumental analysis

Known quantity (1000 ng) of 4- $\alpha$ -cumylphenol was added to the sample concentrates prior to the instrumental analysis as internal standard in order to quantify APs. APs were analyzed using a Thermo-Scientific system consisting of a TRACE GC ULTRA gas chromatograph, an AS 3000 autosampler, and a DSQ quadrupole mass spectrometer equipped with EI source. A DB-5 (J&W Scientific) fused silica capillary column (30 m  $\times$  0.25  $\mu\text{m}$   $\times$  0.25 mm i.d.) was used with helium as the carrier gas at a constant flow of 1 mL/min. The injection port, transfer line, and ion source temperatures were set at  $280^{\circ}\text{C}$ ,  $280^{\circ}\text{C}$ , and  $250^{\circ}\text{C}$ , respectively. The oven temperature was held at  $70^{\circ}\text{C}$  for 2 min, then programmed at  $30^{\circ}\text{C}/\text{min}$  to  $180^{\circ}\text{C}$ , at  $2^{\circ}\text{C}/\text{min}$  to  $200^{\circ}\text{C}$ , at  $30^{\circ}\text{C}/\text{min}$  to  $300^{\circ}\text{C}$ , and held for 10 min. 1  $\mu\text{L}$  sample was injected in splitless mode and a selected ion monitoring mode (SIM) was employed after the solvent delay for 5 min. 107, 121, 135, 149, 177, 220 were selected as the characteristic ions ( $m/z$ ). Limits of detection (LOD) was estimated with the ratio of signal to noise ( $S/N=10$ ).

An ultrasonic extraction method was applied to the 10 selected sediment samples to be compared with both of the Soxhlet and the ASE extractions in this study. Briefly, 5 g of each freeze-dried sample was ultrasonically extracted with 10 mL of methanol twice and subsequently 10 mL of acetone for two times, and the ultrasonication extraction was kept for 5 min during each extraction. The sediment extracts were concentrated and purified by a silica gel column and then back-extracted through a C-18 SPE cartridge. The eluate was dehydrated with anhydrous sodium sulfate, concentrated by rotary evaporation and by gentle nitrogen gas stream sequentially, and finally derivatized with *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA). In this method, the average recoveries of OP and NP in the spiking blanks were  $85.6 \pm 10.7\%$  and  $109.9 \pm 5.6\%$ , respectively ( $n=3$ ), and the recovery of surrogate standard BPA- $d_{16}$  in the sediment samples was  $101.5 \pm 9.1\%$  ( $n=4$ ).

OP and NP of the 10 selected samples ranged from 2.7 to 142 ng/g dw and from 205 to 16,198 ng/g dw, respectively, which



**Fig. 1.** Map of the study area and the sample sites. Flags represent eight main outlets of PRD, i.e., M1-Humen, M2-Jiaomen, M3-Hongqimen, M4-Hengmen, M5-Modaomen, M6-Jitimen, M7-Hutiaomen, M8-Yamen. The arrows in the right graph indicate the water flow direction.

were at the same order of magnitude as those found by the Soxhlet or ASE extractions. Moreover, linear regression analyses yielded significant correlations between APs concentrations by the ultrasonic extraction (U-OP/NP) and those by the Soxhlet extraction (S-OP/NP) or by the sequential ASE extraction (A-OP/NP), as shown in Fig. 2. However, ultrasonic clearly has lower extraction efficiency than Soxhlet or ASE, suggesting that they might extract different fractions of APs in the investigated sediments, and/or it might be related to different solvents used in the extraction.

**2.6. Analysis of organic carbon**

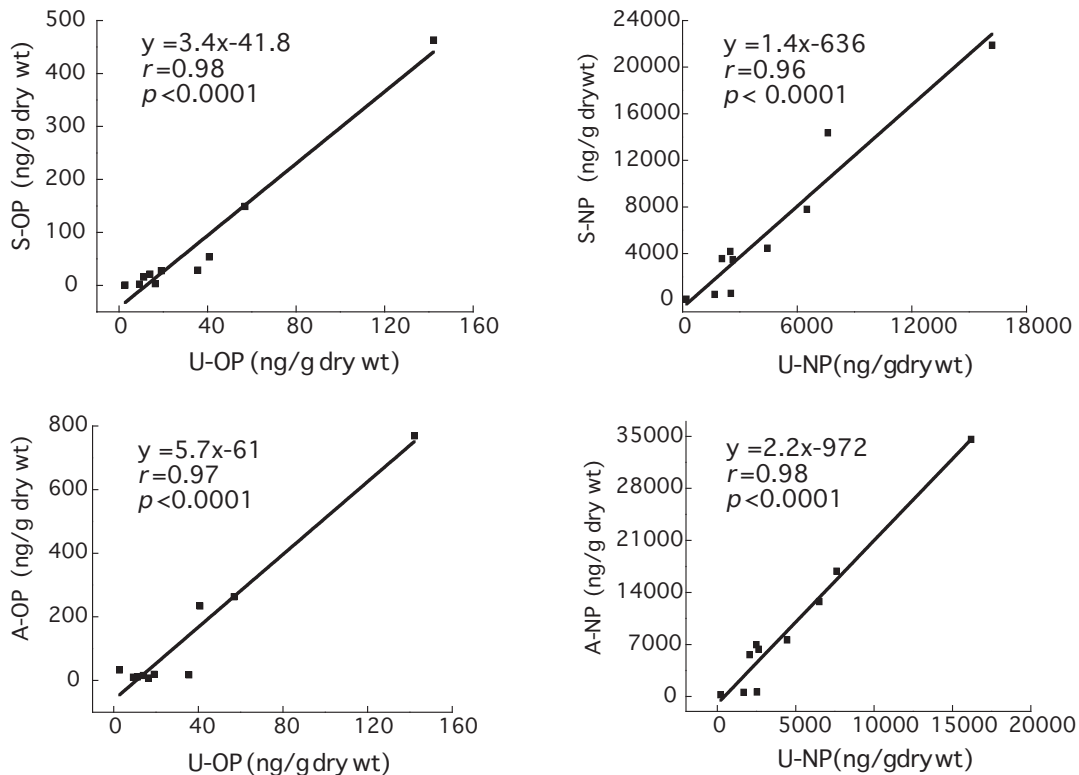
The analytical methods for organic carbon in the sediment samples were reported elsewhere [30]. In brief, about 5 g of the freeze-dried sediment sample was treated with 10% HCl for 24 h to

remove inorganic carbon, and then dried overnight at 105 °C. The organic carbon was quantified on an elemental analyzer (Vario EL III Elementar, Germany) with acetanilide used as external standard.

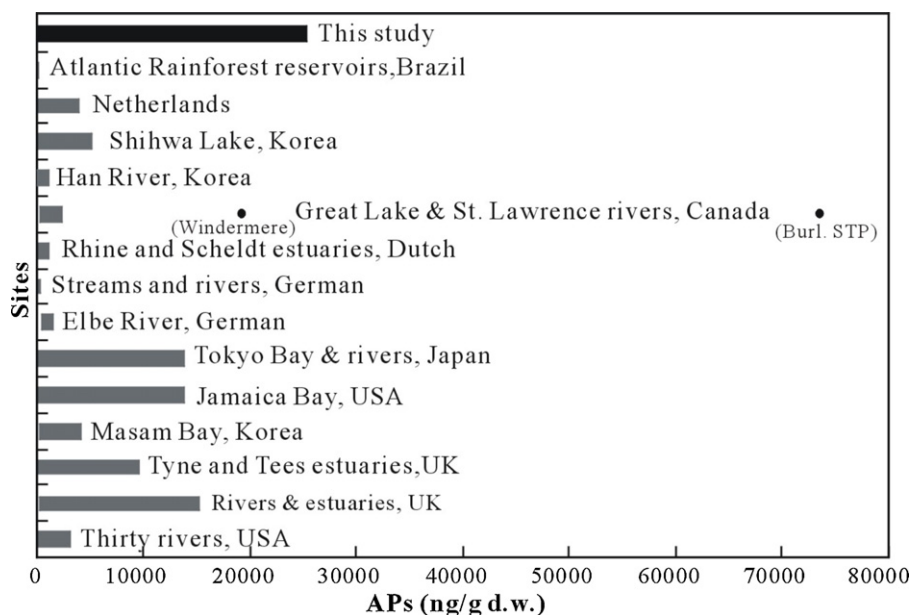
**3. Results and discussion**

**3.1. AP contents by Soxhlet extraction and distribution**

All the sediment samples were analyzed by the Soxhlet extraction, and the concentrations of OP and NP ranged from <0.50 to 463 ng/g dw and 31.0–21,885 ng/g dw, with an average of 40.3 and 3,686 ng/g dw, respectively (Table 1). OP was 1–2 order magnitude lower than NP, which is consistent with other previous investigations [7,38]. Compared with the other aquatic surface sediments (Fig. 3), the concentrations of total APs in this study are generally



**Fig. 2.** Relationship of U-OP/NP concentrations by ultrasonic extraction with S-OP/NP concentrations by Soxhlet extraction and A-OP/NP concentrations by sequential ASE extraction in the selected 10 sediments.



**Fig. 3.** Comparison of the APs concentrations in the sediments of the PRD with those of other overseas aquatic surface sediments. References cited sequentially are [41,42,25,26,38,23,40,43,7,22,44,45,39,21].

higher than most of those reported for other areas of the world, and lower than those of the two samples in the Hamilton Harbor site, Canada [20–26,38–45]. High concentrations of APs were reported for other highly industrialized and urbanized areas, such as Hamilton Harbor of the Great Lakes (up to 72,000 ng/g dw of NP and 1800 ng/g dw of OP) [38], Virginia (USA) sediments adjacent to STPs and outfall (up to 14,100 ng/g dw) [23], and Jamaica Bay (NY, USA)(up to 13,700 ng/g dw of NP and 45 ng/g dw of OP) [25]. How-

**Table 1**  
Concentrations of APs measured by Soxhlet extraction and total organic carbon (TOC) in the surface sediments from the PRD system.

Site	Concentrations			TOC (%)
	NP (ng/g, dry wt.)	OP (ng/g, dry wt.)	$\sum$ APs <sup>a</sup> (ng/g, dry wt.)	
Z1	4459	28.6	4488	2.29
Z2	4291	26.5	4318	3.55
Z3	3918	28.3	3946	3.57
Z4	14,356	149	14,505	4.03
Z5	6411	53.4	6464	3.58
Z6	4182	27.5	4210	1.57
Z7	3569	15.8	3585	1.72
Z8	7793	53.7	7847	2.13
Z9	2687	10.4	2697	1.84
Z10	3718	17.2	3735	1.88
Z11	21,885	463	22,348	12.7
Z12	3474	21.1	3495	2.86
D1	1820	5.25	1825	2.33
D2	5292	129	5421	7.86
D3	2996	19.7	3016	2.75
D4	384	2.90	387	1.58
D5	803	3.77	807	1.87
D6	1771	8.98	1780	2.42
D7	2741	18.0	2759	3.28
D8	2013	6.46	2020	2.61
D9	3317	32.9	3350	3.77
D10	577	3.07	580	1.50
D11	486	2.24	488	1.34
B1	60.0	<0.50	60.0	0.439
B2	59.0	0.63	59.6	0.967
B3	36.0	<0.50	36.0	0.977
B4	82.0	0.50	82.5	1.28
X1	31.0	<0.50	31.0	1.43

<sup>a</sup>  $\sum$  APs refers to the total of OP and NP.

ever, the concentrations of NP and OP in surface sediments from the Pearl River estuary and nearby South China Sea ranged from 59 to 571 ng/g dw for NP and from 1 to 18 ng/g dw for OP [20], which were comparable to those found in Tokyo Bay (120–640 ng/g dw of NP and 6–10 ng/g dw of OP) [10]. The above result suggests that the Pearl River System has been significantly polluted by APs, and the contamination level in the PRD is one of the highest in the world.

Until now there have been limited reports on the APs pollution in the riverine sediments in China. The NP concentrations in this study (31–21,885 ng/g dw) are much higher than those of the Yellow River (Lanzhou Reach) (38.9–863 ng/g dw) [46], and are similar to those documented in adjacent rivers of the Jiaozhou Bay (23.8–39,700 ng/g dw) [47]. The OP levels in this study ranging from <0.50 to 463 ng/g dw are similar to those in adjacent rivers of the Jiaozhou Bay [47], where they varied from 1.6 to 146 ng/g dw.

The spatial distribution of the EDCs in the surface sediments of the rivers from the PRD is shown in Fig. 4. The concentrations of APs (total of OP and NP) was evidently higher in ZR (Z1–Z12) (Table 1) than in the other rivers. APs in ZR were in a range from 2687 to 21,885 ng/g dw, in which the highest was found at Z11 of the back channel (Z11–Z12), while the highest one in the front channel (Z2–Z10) was found at Z4. On a whole, APs varied indistinctively from the upstream Z1 to the downstream Z10, except for Z11 where the surface sediment could be polluted by point sources nearby. This is related to the fact that ZR passes through the densely populated and highly industrialized city Guangzhou, whereas DR wanders across the Dongguan city with a developed manufacturing industry but a smaller population. Therefore, ZR receives much more domestic and industrial wastewater compared with DR. XR and BR are the upper tributaries of the PRD system and mainly flow through the rural areas of the Pearl River Delta with low anthropogenic impacts, which could be responsible for the low pollution levels of APs in the B1–B4 and X1 samples.

It is noted that the APs concentrations at Z4 and Z11 were substantially higher than those of the other sites, possibly suggesting the presence of contamination sources near these two sites. During the investigation, it was found that a modern sewage treatment plant and several large-scale factories were situated near Z4 and Z11 respectively and drains out a large amount of effluents to the ZR.

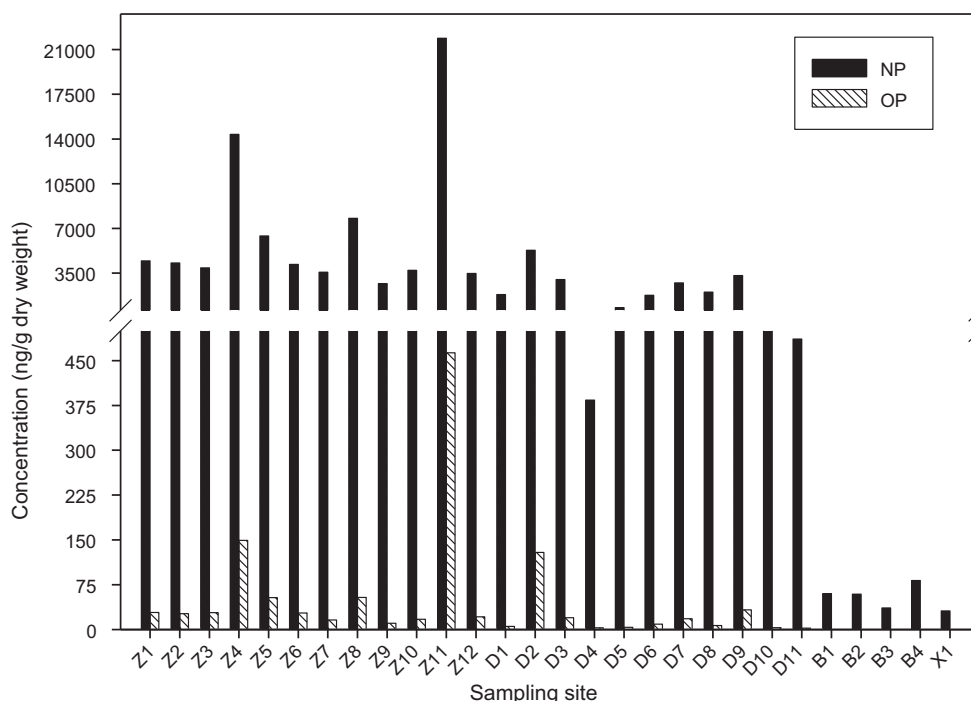


Fig. 4. Spatial distribution of the NP and OP concentrations in the 28 sediments from the PRD system.

Parallel fluctuations in the concentrations was observed for OP and NP (Fig. 4), which were probably attributed to their similar physicochemical properties and sources. There was also an obvious trend for the APs concentrations increasing from the upstream to the downstream in the ZJ and DJ rivers, which is similar to the decrease in the NP concentrations from the point-source site to the downstream of a river, as demonstrated by Hale et al. [20], Isobe et al. [7], and Blackburn et al. [39]. This observation can be attributed to the domestic and industrial sewage wastewater discharges in the urban areas of Guangzhou and Dongguan city, and the dilution of the discharged wastewater by the sea water.

3.2. APs contents by sequential ASE

The APs contents in the 10 selected samples were sequentially extracted by ASE twice. The concentrations of NP and OP in the first extraction (NP-1 and OP-1) were in the range from 247 to 34,578 ng/g dw and from 7.42 to 796 ng/g dw, with a mean value of 9212 and 138 ng/g dw, respectively; and in the second extraction, they ranged from 48.3 to 738 ng/g dw and from 0.54 to 40.9 ng/g dw, with a mean value of 180.3 and 6.6 ng/g dw, respectively (Table 2). The contents of APs in the first and second extractions accounted for 82.2–99.2% and 0.8–17.8% of the total contents extracted by the

two extractions, with an average of 95.1% and 4.9%, respectively. The result indicated that a small portion of APs was hard to be extracted by the routine one-time ASE, suggesting that the sequential two ASE extractions achieved a higher performance than the routine one ASE extraction.

The total APs contents extracted by the routine and the sequential ASE are respectively 1.1–3.4 and 1.2–4.1 times those of the traditional Soxhlet extraction. Statistical analysis shows that APs by the Soxhlet extraction and the ASE extraction display a highly significant correlation (Fig. 5). From the slope in Fig. 5, it is known that the APs contents of the sequential ASE are on average 1.5 times those of the Soxhlet extraction. The high extraction efficiency for ASE is partially due to its higher operation temperature under its high operation pressure. Under high temperature, the strong interaction between the solute molecule and the sample matrix greatly decreases. In our study, the operation temperature is 150 °C, which is 120 °C higher than the operation temperature of the Soxhlet extraction. According to the van't Hoff's law, the velocity of a

Table 2 Alkylphenol contents by two sequential accelerated solvents extraction.

Sample	OP-1/OP-2 (ng/g, dry wt.)	NP-1/NP-2 (ng/g, dry wt.)	$\sum$ APs-1/ $\sum$ APs-2 (ng/g, dry wt.)
Z1	17.6/1.14	7608/128	7625/129
Z4	263/4.86	16,847/738	17,109/742
Z6	19.0/0.72	6957/84.0	6976/84.7
Z7	10.8/1.31	5628/48.3	5638/49.3
Z8	234/0.54	12,761/108	12,994/109
Z11	769/40.9	34,579/407	35,347/448
Z12	15.4/0.72	6346/61.0	6361/61.7
D10	7.42/4.79	602/59.0	609/63.8
D11	10.1/4.66	546/64.0	556/68.7
B4	32.8/6.01	247/54.0	280/60.0

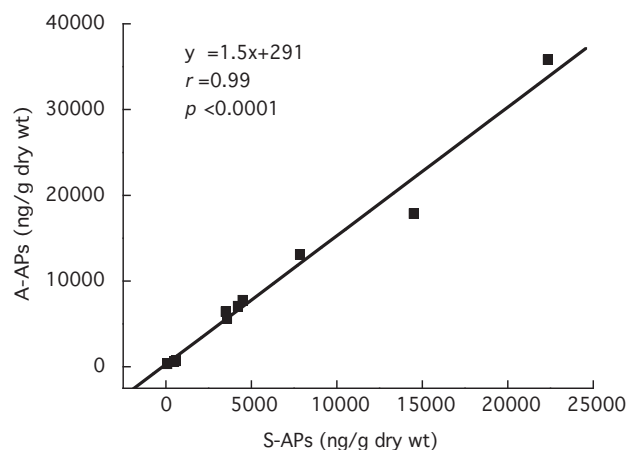


Fig. 5. Relationship of S-APs by Soxhlet extraction with A-APs by sequential ASE extraction in the 10 sediments.

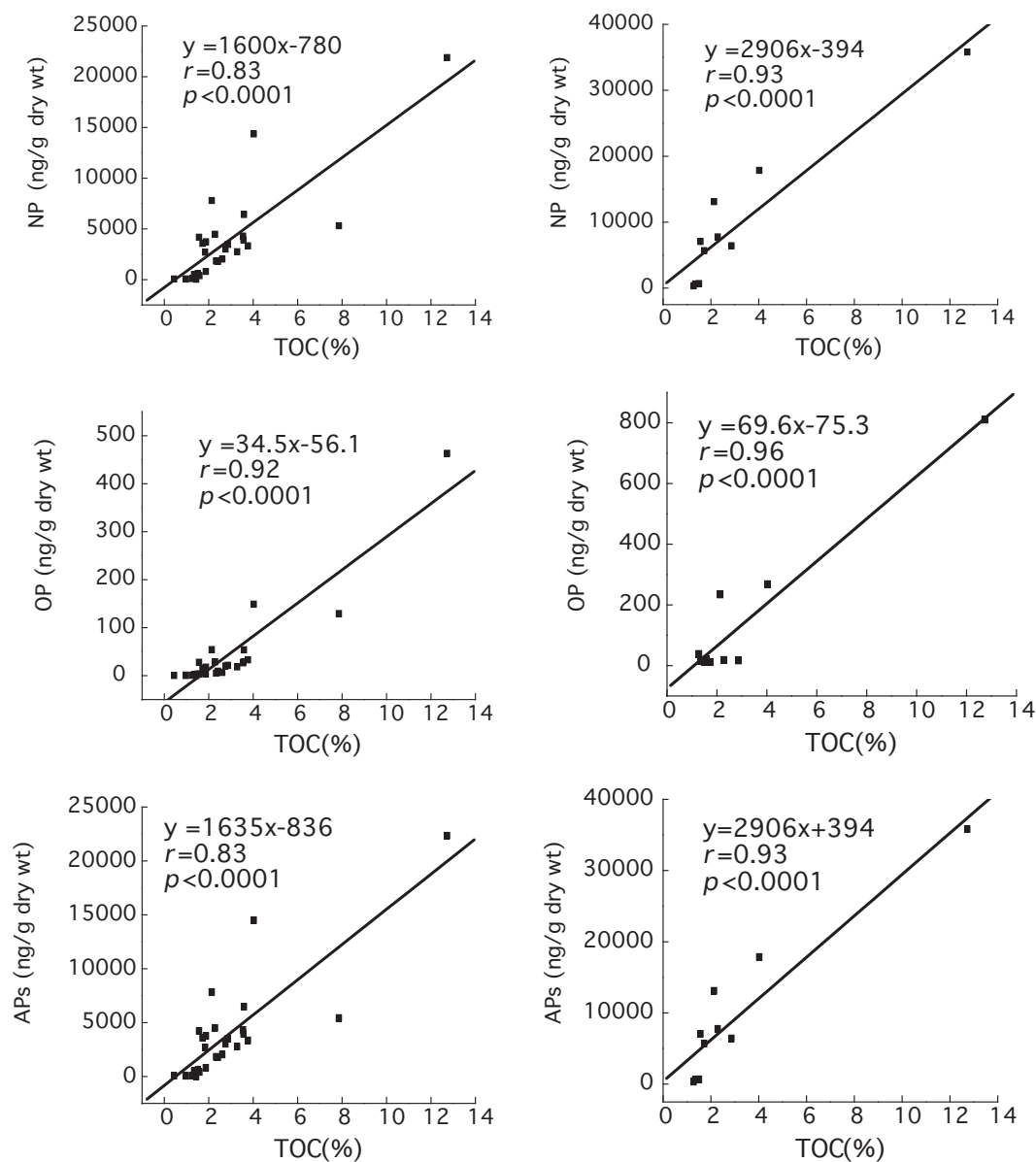


Fig. 6. Correlations between APs and TOC in the 28 sediments for the Soxhlet extraction, and in the 10 sediments for the twice sequential extraction, respectively.

reaction process is greatly enlarged at higher temperature. On the other hand, as the solvent has lower viscosity and surface tension under higher temperature, it easily penetrates through the sediment sample. So it is expected that ASE would achieve higher extraction efficiency than the Soxhlet extraction. The above result demonstrates that ASE is a very effective, quick extraction method for contaminated materials with high contents of condensed SOM. This result is also consistent with other observations that the ASE method is more effective for extraction of nonylphenolic estrogen compounds than the Soxhlet extraction method [36].

According to the previous investigations on PAHs [28,30,37], the extraction of APs from the condensed SOM may be analogously explained by a two-step mechanism involving swelling of the sorbent matrix and subsequent displacement of sorbates by the solvent molecules [37]. Small solvent molecules such as methanol can well penetrate into small pores or interlayer spaces of the condensed SOM, causing swelling within the physically restricted areas, and exposes less accessible sorption domains to the bulk solvent. The above result is also consistent with our investigation on PAHs, in which the PAH content extracted with the sequential three

solvent ASE (ASE Sum) is two times that using the Soxhlet extraction method. The ASE Sum extracted more PAH congeners than did the mixed solvent ASE or the Soxhlet extraction. In fact, the second and third extraction steps in the ASE Sum (toluene 1 and 2) still extracted considerable PAH amounts compared to the first acetone extraction step. The relationship of the PAH contents by ASE and Soxhlet with the NHC contents is highly significant, suggesting that condensed organic carbon is very important to the distribution of PAHs in the field soils and sediments [28,30].

### 3.3. Correlation of APs with TOC

As the sediment organic carbon plays an important role in the sorption of APs [22,24], the effect of TOC on the extraction and distribution of APs was investigated. Linear regression analysis demonstrates the significant relationships of NP, OP, and total APs with TOC and APs in the investigated samples (Fig. 6). The correlation coefficients are 0.82, 0.92, and 0.83, and 0.93, 0.96, and 0.93 in Fig. 6, respectively for the Soxhlet and the sequential ASE extraction. As NP and OP are moderately hydrophobic with a log  $K_{ow}$  value

of 4.48 and 4.12, respectively [48], they are mainly associated with organic-rich sediments [22]. On the other hand, APs are persistent in an anaerobic environment [49] and hard to be degraded when they are sorbed by the sediments.

### 3.4. Environmental implication

Historically contaminated (aged) sediment samples, where contact times may have been years and decades, can be enriched in the slow fraction owing to partial dissipation or degradation of more labile fractions before the collection [27]. When the total contaminant present must be determined by the extraction as in many field samples or in spiked samples where uncertain losses occurred during an experiment, the choice of extraction conditions is important to ensure complete recovery of the analytes. Extraction methods are commonly validated with freshly spiked solid samples. Unfortunately, validation is seldom performed on aged samples that are enriched in resistant fractions. As demonstrated in this study, APs by sequential two extractions with the mixed solvent are about 1.5 times those by traditional Soxhlet extraction (Fig. 5).

As the slow fraction is likely to have been underestimated due to incomplete recovery in some studies, this can lead to erroneous conclusions when some process of interest is being measured against the mass of contaminant believed to be present. For example, one may deem that biodegradation is successful when actually loss of only the labile fraction has been evaluated. Moreover, as the desorption kinetics in fate and effects models is very important in field samples, the initial mass of contaminants must be accurately known in order to better follow the fate of APs or other organic contaminants. Finally, the estrogenic effects of APs for benthic organisms are often estimated using the Soxhlet-extracted APs [7,40,46]. Although previous studies estimated the APs levels in the local areas were lower than their NOECs (no observed effect concentrations) or LOECs (lowest observed effect concentrations) [7,42], the exposure risk for benthic organisms might increase, considering the underestimation of total APs in the surface and suspended sediments by a factor of 1.2–4.1 with the Soxhlet extraction as demonstrated in this investigation. It is generally believed that the bound residue is not mobile because the contaminants are sequestered in the soil organic matrix. However, it was found that even the bound residue could become bioavailable under certain conditions. Therefore, the possible release and delayed environmental impact of the bound residues are also of a great concern [33,34]. It was reported that nonextracted atrazine, isoproturon, and dicamba residues in several soils could be absorbed to earthworm tissues [34]. It was also found that a considerable fraction of nonextractable PAH residues in a soil could be mineralized under different ecological stress conditions [35]. Although many investigators now pursue less aggressive extraction techniques to approximate or mimic bioavailability, how the different extraction methods are related to the bioavailability of APs in the sediments is our future research goal. Hence, the long-term risk and ecological effect of the unextractable fraction by the traditional Soxhlet extraction should be taken into account in the future investigation.

## 4. Conclusions

The alkylphenols (APs) including nonylphenol (NP) and octylphenol (OP) in the riverine sediments from the Pearl River Delta (PRD), South China was compared by Soxhlet extraction (S-APs) with dichloromethane and by sequential accelerated solvent extraction (ASE) (A-APs) with 1:6 toluene/methanol, respectively. Concentrations of OP and NP range from <1 to 463 ng/g dw and 31–21,885 ng/g dw, respectively, demonstrating that the contamination level of APs in the PRD is one of the highest in the world.

Moreover, the A-APs contents are highly significantly related to and on average 1.5 times the S-APs contents. The correlation analysis shows that S-APs and A-APs are both significantly associated with the contents of TOC, suggesting that the sorption mechanism for variable extraction efficiency of these two methods is related to the presence of condensed organic matter in the sediments. The above results indicate the underestimation of total APs by a factor 1.5 while assessing their exposure risk for aquatic organisms if the Soxhlet extraction is used, and the important effect of condensed organic matter on their extraction and distribution in the investigated field sediments.

## Acknowledgements

The authors would like to thank Professor Gan Zhang with the Guangzhou Institute of Geochemistry for their assistance. This study was supported by a “Team Project” and a general project of National Natural Science Foundation of China (nos. 40821003, 40972222), the Basic Research Program (973, 2009CB421604) and the Earmarked Foundation of the State Key Laboratory (SKLOG2008A05), the State Science and Technology Ministry of China. This is the contribution no. IS-1341 from GIG, CAS.

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