

Nonylphenol and octylphenol in riverine waters and surface sediments of the Pearl River Estuaries, South China: occurrence, ecological and human health risks

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ABSTRACT

The temporal–spatial distribution and risks of nonylphenol (NP) and octylphenol (OP) in the surface waters and sediments from the six major riverine runoff outlets of the Pearl River Estuaries (PRE) were investigated. NP and OP were detected in all samples. It is worth mentioning that the levels of NP and OP in July in waters ranged from 1,740 to 16,200 ng L⁻¹, and from 1,265 to 15,700 ng L⁻¹, respectively; in sediments, they ranged from 28 to 92 ng g⁻¹ dw and from 2.7 to 42 ng g⁻¹ dw, respectively. According to aquatic risk assessment based on hazard quotient (HQ), NP and OP posed a high potential ecological risk (HQ > 1) to relevant aquatic organisms (excluding the alga, *Selenastrum capricornutum*), indicating that aquatic organisms, in particular crustaceans, have been significantly affected by NP and OP. Although the risk of NP for humans in water was regarded as endurable according to tolerable daily intake, it was higher than the drinking water safety limit (0.5 µg L⁻¹). The results indicated that the heavy contamination caused by NP and OP and their adverse effect on local aquatic organisms in the PRE deserved to arouse wide concern.

Key words | nonylphenol, octylphenol, Pearl River Estuaries, risk assessment, riverine water, surface sediment

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INTRODUCTION

Alkylphenols (APs), especially 4-nonylphenol (NP) and octylphenol (OP), in aquatic ecosystems have aroused worldwide concern for their moderately estrogenic potency and massive usage (Yang *et al.* 2014). NP and OP are the main biodegradation products of alkylphenol ethoxylates (APEOs), which have been widely used as non-ionic surfactants in domestic detergents, pesticide formulations and industrial products (Chen *et al.* 2006). NP and OP are more persistently toxic than their ethoxylated precursors. And it is estimated that the main route of their introduction into the environment is the discharge of effluents from industrial discharges, sewage treatment works, and municipal wastewaters (Mortazavi *et al.* 2012).

As a group of xenoestrogens, NP and OP show multiple modes of endocrine disruption activity. Due to their endocrine disrupting effects, NP and OP were included in the

list of priority hazardous substances in the field of water policy by the European Union Water Framework Directive 2000/60/EC (Commission Directive 2000/60/EC 2000). Since January 2005, the EU Directive has come into force and restricted the sale and use of products containing more than 0.1% NPE or NP. However, many other countries, including China, India and several South American countries continue to use APEOs in large amounts without rigorous water quality control (Soares *et al.* 2008).

NP and OP are widespread organic pollutants that can be detected in various environmental matrices, such as wastewaters, rivers, sediment and biota (Yu *et al.* 2013; Salgueiro-González *et al.* 2015). The Pearl River Delta (PRD), a special economic zone located in southeastern China, has become one of the most urbanized and developed areas in China connecting the Pearl River Estuaries

(PRE) via eight major estuaries. However, with the rapid development of industrialization and urbanization, the environment of the PRD has been severely deteriorated by the uncontrolled release of wastewaters (Chen *et al.* 2006). It has been reported that the levels of NP and OP in the PRD were in the range of 117–865 and 1–14 ng L⁻¹ in water, those in algae were in the range of 53–282 and 2–13 ng g⁻¹ dw and those in carp bile were in the range of 950–4,648 and 14–39 ng g⁻¹ dw, respectively (Yang *et al.* 2014). Xu *et al.* (1993) reported that annually the freshwater with suspended solids flowing into the PRE through eight major outlets totalled 3.3×10^{11} m³. Due to their hydrophobic nature, APs in waters tend to be associated with particulate matter that can settle onto bottom sediments and accumulate continuously, eventually posing a potential environmental threat to aquatic organisms (Gong *et al.* 2011a). Therefore, it was crucial to investigate the levels of NP and OP in the PRE, and further research was needed to evaluate the ecological risks. The objectives of the present study were to comprehensively investigate the temporal-spatial variation of NP and OP in the surface waters and sediments from the main riverine runoff outlets of the PRE, and to preliminarily assess the potential risks to resident organisms and humans.

MATERIALS AND METHODS

Chemicals and reagents

High-performance liquid chromatography (HPLC)-grade methanol (Merck), redistilled analytical-grade solvents including dichloromethane, hexane and distilled water were used for analysis. Standards of NP (mixture of compounds with different isomers), and 4-t-octylphenol (97%) were purchased from Sigma Aldrich. Neutral silica gel (100–200 mesh) was activated at 500 °C for 8 h and then deactivated by adding 5% distilled water. All the glassware used for organic compound analyses was burned at 450 °C for 6 h prior to use.

Site description and sample collection

The Pearl River is the largest and most complex water system in Southern China with an annual discharge of 3.49×10^{11} m³

(Gong *et al.* 2011b). Amid the annual sediment discharge of 70.98 million tons, 20% of sediments were deposited in estuary, and others were input into the South China Sea (SCS) through eight estuaries. It consists of three main tributaries: East River, North River and West River, and merges into the PRE. North River and East River flow into the SCS mainly via the eastern estuaries, including Humen (HM), Jiaomen (JM), Hongqimen (HQ) and Hengmen (HE), while West River mostly discharges through the western estuaries, including Modaomen (MD), Jitimen (JT), Hutiaomen (HT) and Yamen (YM) (Figure 1). Moreover, East River supplies fresh water for many cities including Guangzhou, Dongguan, Shenzhen and Hong Kong.

Water samples and surface sediments from six riverine runoff outlets of the PRD (marked S1–S7 in Figure 1) were carried out in July 2013. The surface water and sediment samples were collected from seven locations (two adjacent sites collected for each location), which are described in Table S1 in the Supplementary Material (available with the online version of this paper). Water samples at 0.5 m below the surface were collected in pretreated 4 L amber glass bottles and acidified with 6 M HCl to pH < 2 to suppress microbial activities. Surface sediment samples (0–5 cm) were also taken at each site with a

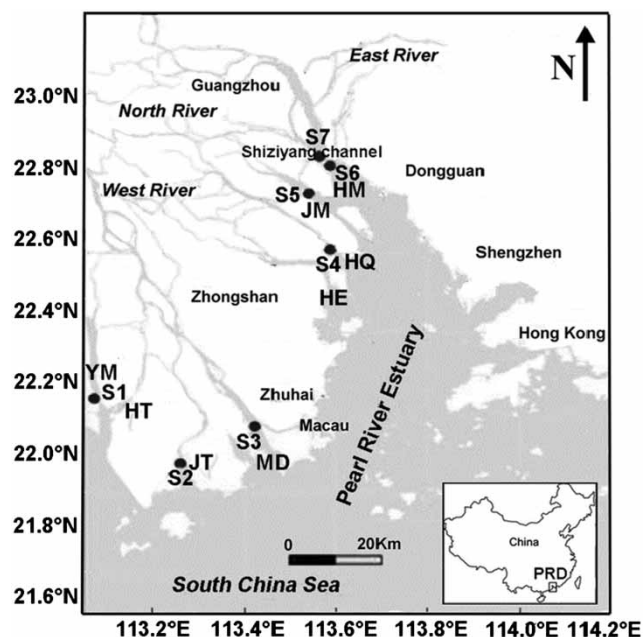


Figure 1 | Sketch map of the sampling sites in the PRE, South China. The eight major runoff outlets are represented by HM, JM, HQ, HE, MD, JT, HT and YM.

static gravity corer (three subsamples per site). The collected samples were immediately transferred to the laboratory in a cooler. Upon transport to the laboratory, the water samples were filtered through glass fiber filters (GF/F, Whatman 0.45 μm effective pore size), and stored at 4 °C and extracted within 48 h. The sediment samples were stored at -20 °C until further analysis.

Sample preparation

Water samples were extracted according to the work of Oh *et al.* (2009) with some modification. Liquid-liquid extraction was performed under acidic conditions (pH 2–3) using dichloromethane as solvent. Each filtered water sample (1 L each) was extracted using 30 mL dichloromethane three times, and the solutions were vigorously shaken for 5 min. The extraction phase was combined and dehydrated with anhydrous sodium sulfate. The extracts were evaporated to dryness under a rotary evaporator at 35 °C and re-dissolved in 1 mL methanol for analysis.

Sediment samples were freeze-dried and homogenized, and then sieved through an 80-meshed stainless steel mesh. The method of the extraction in sediments was modified from the previous study (Chen *et al.* 2005; Cai *et al.* 2012). Ten grams of each sediment sample were extracted with 20 mL methanol/dichloromethane (1:9 v/v) by using ultrasonic-assisted solvent extraction. The sample was ultra-sonicated for 10 min and then centrifuged for 10 min at 4,000 rpm and the supernatant was collected. The extraction was repeated twice more. The supernatants were evaporated to dryness and re-dissolved into hexane to a final volume of 1–2 mL in a rotary evaporator. The hexane extracts were purified through a silica gel column pretreated with 20 mL of hexane. The column was rinsed with 20 mL hexane/dichloromethane (3:7 v/v) and then eluted with 40 mL hexane/dichloromethane (8:2 v/v). The latter was collected and concentrated to dryness and re-dissolved in 1 mL methanol for analysis.

Instrument conditions

Separation and quantification of the target compounds was achieved by HPLC-mass spectrometry (HPLC-MS). Chromatographic analyses were performed in an Agilent 1100 HPLC

(Agilent, USA) with a ZORBAX SB-C8 column (2.1 mm \times 150 mm, 3.5 μm) using a gradient elution with mobile phase A: Milli-Q water and B: methanol. The injection volume was 1 μL . The HPLC column eluent was directed into the mass spectrometer. Mass spectrometric analysis was performed with an AB Sciex 4000 QTRAP mass spectrometer (AB Sciex, USA) equipped with an electrospray source in negative ionization mode and set to monitor NP (m/z 219.3 \rightarrow 133.3) and OP (m/z 205.3 \rightarrow 133.3) in multiple reaction monitoring mode. Both quantitative and confirmatory ions were used to identify NP and OP in samples.

Quality assurance and quality control

Quality assurance and quality control were used to ensure the accurate quantification of the target compounds. A procedural blank, a standard and a spiked matrix sample were set for each batch of 10 samples. Only a low concentration of NP (9.6 ng L^{-1}) was detected in the procedural blank and the blank value was subtracted. The average recoveries of NP and OP were 98% and 72% and their relative standard deviations (RSD) were 8.3% and 1.5%, in surface water, respectively. Their average recoveries were 86% and 78% and their RSD were 10% and 5.0% in surface sediments, respectively. The limits of detection (LOD) were set at S/N ratios ≥ 10 . For surface water, the LOD of NP and OP were 0.5 ng L^{-1} and 1.0 ng L^{-1} , respectively; for surface sediment, the LOD of NP and OP were 0.05 ng g^{-1} and 0.1 ng g^{-1} , respectively. The HPLC-MS exhibited satisfactory linearity ($R^2 > 0.99$) for all the analytes.

Ecological and human health risk assessment

The ecological risk assessment was carried out based on the United States Environmental Protection Agency (USEPA) ecological risk assessment framework (USEPA 1992). The ecological risk was calculated by the hazard quotient (HQ), which is calculated from the measured environmental concentration (MEC) and predicted no-effect concentration (PNEC) as shown in Formula (1):

$$\text{HQ} = \frac{\text{MEC}}{\text{PNEC}} \quad (1)$$

The maximum concentration of NP or OP in all water samples was used as the MEC, and the values are presented in Table 1. PNEC values are their predicted no-effect concentration for each selected species and were calculated either by dividing acute toxicity (LC₅₀ or EC₅₀) values by an assessment factor of 1,000 or chronic toxicity values by an assessment factor of 10 (Selvaraj *et al.* 2014). Some representative aquatic organisms were selected, and the acute or chronic toxicity data were derived from previous toxicological studies. Type of organism, toxicity endpoints and PNEC values are shown in Tables 2 and 3. HQ values higher than 1 indicate conditions of unacceptable risk of adverse effect on the target species.

Human health risk was estimated according to margin of safety (MOS) level and tolerable daily intake (TDI), considering the intake of water from the rivers as a potential exposure pathway. MOS was calculated by applying Formula (2):

$$\text{MOS} = \frac{\text{Drinking water guideline}}{\text{HC}} \quad (2)$$

where HC is the highest detected concentration of NP or OP in the riverine outlets. The drinking water guidelines were derived from the literature (Nielsen *et al.*

1999). When the MOS value is greater than 1, no health risk is expected, while MOS < 1 indicates a possible health risk.

The exposure of adults and infants for NP and OP could be estimated by applying the quantity of drinking water consumed according to the USEPA: 2 L per day for 60 kg adults and 1 L per day for 10 kg infants (USEPA 2006). The estimation was performed as follows:

$$\text{Adult exposure } (\mu\text{g/kg bw/day}) = \frac{\text{HC} \times 2}{60} \quad (3)$$

$$\text{Infant exposure } (\mu\text{g/kg bw/day}) = \frac{\text{HC} \times 1}{10} \quad (4)$$

The adult exposure is compared with the human reference dose and TDI to estimate the safety status.

The drinking water contribution to TDI was calculated according to Formula (5) (Liu *et al.* 2013):

$$\text{Contribution to TDI } (\%) = \frac{\text{Adult exposure}}{\text{TDI}} \times 100 \quad (5)$$

where TDI is obtained from the studies shown in Table 4.

Table 1 | Concentrations of NP and OP in riverine water (ng L⁻¹) and surface sediments (ng g⁻¹ dw) from the six riverine outlets of the PRE

Sites	APs	January 2013 ^a		April 2013 ^a		July 2013	
		Water	Sediment	Water	Sediment	Water	Sediment
S1	NP	2,105 ± 89	14 ± 2	97 ± 14	10 ± 4	8,450 ± 240	30 ± 12
	OP	262 ± 11	0.4 ± 0.1	8.8 ± 4.0	0.3 ± 0.1	6,940 ± 330	8.8 ± 1.7
S2	NP	810 ± 30	22 ± 2	65 ± 9	23 ± 6	1,740 ± 200	46 ± 19
	OP	86 ± 47	0.8 ± 0.1	4.3 ± 1.2	0.6 ± 0.2	1,265 ± 137	5.2 ± 0.7
S3	NP	960 ± 55	20 ± 2	79 ± 20	8.7 ± 3.1	2,050 ± 129	92 ± 27
	OP	124 ± 4	0.5 ± 0.03	5.3 ± 0.7	0.3 ± 0.1	1,718 ± 59	42 ± 11
S4	NP	1,970 ± 60	31 ± 0.7	58 ± 14	61 ± 2	6,710 ± 40	30 ± 18
	OP	359 ± 10	1.1 ± 0.2	6.2 ± 2.3	2.7 ± 0.8	9,970 ± 70	2.7 ± 2
S5	NP	2,531 ± 24	40.1 ± 3.6	36 ± 2	17 ± 12	6,690 ± 343	28 ± 10
	OP	400 ± 6	1.4 ± 0.3	2.8 ± 0.8	0.5 ± 0.3	5,580 ± 260	5.7 ± 2.0
S6	NP	3,366 ± 152	25.4 ± 5.2	61 ± 21	42 ± 8	16,200 ± 80	55 ± 5
	OP	581 ± 21	0.8 ± 0.1	7.2 ± 4.2	0.8 ± 0.1	15,700 ± 200	4.9 ± 2.8
S7	NP	2,843 ± 21	95 ± 7	390 ± 233	36 ± 7	9,630 ± 120	72 ± 20
	OP	504 ± 14	3.0 ± 0.6	23 ± 14	2.0 ± 0.8	8,270 ± 470	4.2 ± 1.1

The data are presented as mean ± standard error.

^aThe data in January and April are cited from our previous study (Chen *et al.* 2014).

RESULTS AND DISCUSSION

Occurrence and levels of NP and OP in riverine waters

Concentrations of NP and OP in surface water samples from the six riverine runoff outlets are shown in Table 1. They were detected in all samples analyzed, indicating that they were ubiquitous contaminants. The concentration of NP was observed at a relatively high level in riverine water, ranging from 1,740 to 16,200 ng L⁻¹ in July. Nevertheless, the concentration of OP, ranging from 1,265 to 15,700 ng L⁻¹, was found to be 1.03–17.03-fold lower than NP except for the value at S4, which was similar to other studies being about 4–73-fold lower than NP (Renner 1997; Yang *et al.* 2005). It indicates that products leaching from the Pearl River system contain mostly NP ethoxylates. NP and OP have maximum concentrations at S6 (HM), which is around the Pearl River power plants and HM ferry terminal. Consider the fact, the water courses draining into the HM outlet run through some large urban areas including Guangzhou, Dongguan and Huizhou. In particular, Guangzhou is a densely populated and highly industrialized city and Dongguan has a developed manufacturing industry, including printing, pleather and bleaching and dyeing houses. Therefore, the busy industrial and economic activities gave rise to the HM outlet receiving much more domestic and industrial wastewater, which was the important source of AP contaminants. However, lower concentrations were observed at S2 (JT), which was located in areas with relatively dispersed populations and less influenced by human activities. Besides, the NP and OP in the eastern estuaries were detected at relatively higher concentrations than those in western estuaries. This was probably due to the fact that riverine runoff was an important contributor for anthropogenic pollution transported from terrestrial sources into oceans. Wang *et al.* (2014) also reported that the annual input of OPEs from eastern estuaries (HM, JM, HQ, and HE) in general was more than from western outlets (MD, JT, HT, and YM), for the water courses draining into eastern estuaries run through several large manufacturing centers, including Guangzhou and Dongguan.

As shown in Table 1, the concentrations of NP described in our previous study were in the range of 810–3,366 ng L⁻¹ and 36–390 ng L⁻¹ in January and April for riverine water,

respectively; the concentrations of OP ranged from 86 to 581 ng L⁻¹ and from 2.8 to 23 ng L⁻¹ respectively in January and April (Chen *et al.* 2014), suggesting that the concentrations of APs in July were higher than those in January followed by those in April. The highest concentrations were detected in July, due to NP and OP being the main biodegradation products of APEOs, while the high temperature of water in July accelerates the degradation rate of APEOs by microorganisms. In addition, the heavier use of pesticide products in summer may also be a reasonable explanation for the highest concentration in July. The concentrations of NP and OP found in January being higher than those in April may be accounted for by the dilution effect of the higher rainfall in April, as was explained in previous work (Chen *et al.* 2014). Heavy rainfall might facilitate much more contaminant flow into outlets via surface runoff, and it was evident that the dilution effect is more predominant than surface runoff.

Comparing with rivers around the world, such as in Wang *et al.* (2012) on the Yellow River (China) and Heemken *et al.* (2001) on the Elbe River (Germany), it is found that the peak concentration of NP in the present study was higher than in many other reports. However, concentrations in the Ter River (80–17,500 ng L⁻¹; Céspedes *et al.* 2008) were similar to that detected in our work and concentrations in the Anioia and Cardener tributaries (Spain) were much higher (<150–37,300 ng L⁻¹; Céspedes *et al.* 2005). OP concentrations were higher than those obtained in some China studies. In the international rivers, Elbe (Germany), Sumidagawa (Japan) and Ter (Spain), OP was found at lower concentrations (Heemken *et al.* 2001; Isobe *et al.* 2001; Céspedes *et al.* 2008), whereas concentrations in the Anioia and Cardener tributaries (Spain) were much higher (<90–21,900 ng L⁻¹; Céspedes *et al.* 2005). The results reveal that the Pearl River system has been significantly polluted by NP and OP.

Occurrence and levels of NP and OP in surface sediments

The concentrations of NP and OP in sediments are shown in Table 1. NP and OP were detected in all samples, with the concentration ranging from 28 to 92 ng g⁻¹ dw for NP and from 2.7 to 42 ng g⁻¹ dw for OP in July. Interestingly, NP concentrations were relatively higher than those of OP in the same sampling site, which were similar to those in the surface

Table 2 | Derived PNEC values for NP based on toxicity values in different organisms

Group/Common name	Species	Test	Aquatic organisms ($\mu\text{g L}^{-1}$)	PNEC ($\mu\text{g L}^{-1}$)	References
Crustacea	<i>Artemia sinica</i>	LC ₅₀ , 72 h	2.7	0.0027	Shaukat <i>et al.</i> (2014)
	<i>Daphnia magna</i>	LC ₅₀ , 48 h	157	0.157	USEPA (2005)
	<i>Tigriopus japonicus</i>	LC ₅₀ , 48 h	510	0.51	Marcial <i>et al.</i> (2003)
Fish	<i>Pimephales promelas</i>	LC ₅₀ , 96 h	136	0.136	TenEyck & Markee (2007)
	<i>Pseudochromis fridamani</i>	LC ₅₀ , 96 h	175	0.175	Hamlin <i>et al.</i> (2015)
	<i>Oryzias latipes</i>	LOEC ^a , 60 days	11.6	1.16	Seki <i>et al.</i> (2003)
Algae	<i>Selenastrum capricornutum</i>	Chronic value	1,013	101.3	Spehar <i>et al.</i> (2010)
Insecta	<i>Chironomus tentans</i>	NOEC ^b	42	4.2	Kahl <i>et al.</i> (1997)

^aLOEC, lowest observed effect level.

^bNOEC, no observed effect level.

water. The octanol/water partition coefficients ($\log K_{ow}$) of NP and OP are 4.48 and 4.12, respectively. Difference in partitioning behavior suggests that NP may have higher affinity and is more easily partitioned to sediment than OP, and it is coincident with concentration distributions between NP and OP. Similar to riverine water, higher levels of NP were observed in HM, whereas OP in HM and MD exhibited a higher concentration. The discharge of effluents from surrounding domestic sewage and wastewater treatment plants might be responsible for the higher concentration. Moreover, APs in riverine waters and surface sediments exhibit a similar seasonal trend with the higher concentration found in July.

Concentrations of NP in our study are somewhat lower than those found in China and in international studies, such as those of Isobe *et al.* (2001) in the Sumidagawa River (Japan). As for OP, higher concentrations have been detected in rivers in the PRD (China), Tyne and Tees estuaries (UK), Sumidagawa River (Japan) and the Elbe River (Germany) (Lye *et al.* 1999; Heemken *et al.* 2001; Isobe *et al.* 2001; Chen *et al.* 2006), while concentrations in the Yellow River (Wang *et al.* 2012), Tokyo Bay (Japan) (Isobe *et al.* 2001) and Yeongsan (South Korea) (Duong *et al.* 2009) were lower than those obtained in our work.

Ecological and human health risks of NP and OP

Risk assessment of aquatic organisms

The maximum concentrations of NP and OP in riverine water were used to assess aquatic toxicity by the HQ

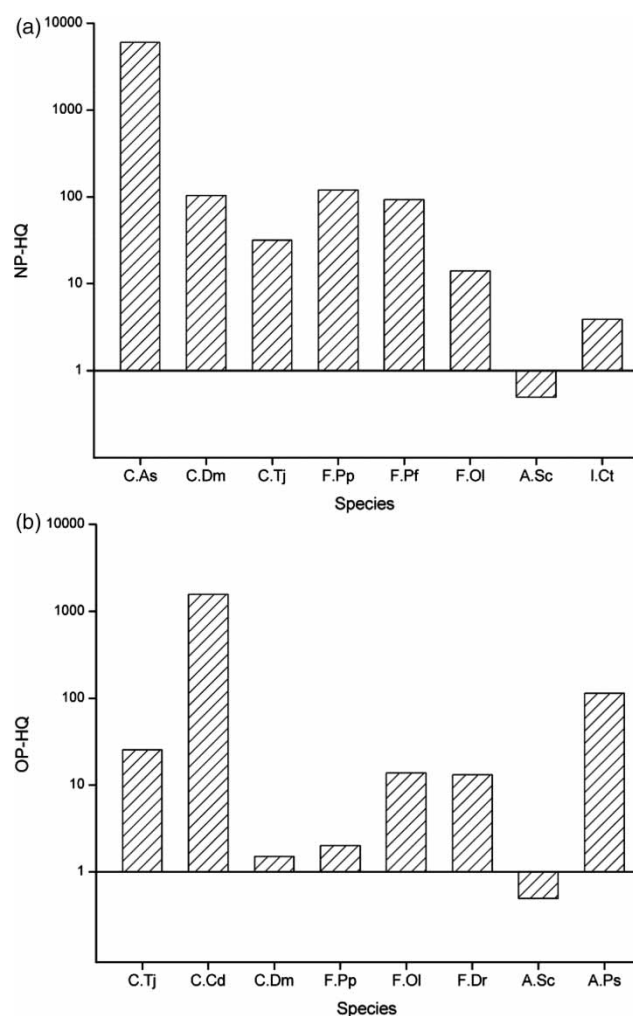


Figure 2 | Aquatic risk assessment of (a) NP and (b) OP in riverine waters based on HQ values (C – crustacean; F – fish; I – insect; A – algae; AS – *Artemia sinica*; Dm – *Daphnia magna*; Tj – *Tigriopus japonicus*; Pp – *Pimephales promelas*; Pf – *Pseudochromis fridamani*; Ol – *Oryzias latipes*; Sc – *Selenastrum capricornutum*; Ct – *Chironomus tentans*; Cd – *Ceriodaphnia dubia*; Dr – *Danio rerio*; Ps – *Pseudokirchneriella subcapitata*).

approach. The PNEC values for NP were derived for several organisms including crustaceans, insects, fish and algae, shown in Table 2. The NP_{PNEC} values for algae and insects were $101.3 \mu\text{g L}^{-1}$ and $4.2 \mu\text{g L}^{-1}$, respectively. In the case of crustaceans, the NP_{PNEC} values ranged from 0.0027 to $0.51 \mu\text{g L}^{-1}$. The NP_{PNEC} values for fish were in the range of 0.136– $1.16 \mu\text{g L}^{-1}$. Based on NP_{PNEC} values, it is inferred that animals are more sensitive than algae. For NP, the HQs of seven organisms were higher than 1 (Figure 2(a)). Among them, the HQ was 3.9 for insects and the HQs were in the ranges of 31.8–6,000 and 14.0–119 for crustaceans and fish, respectively. For algae, NP is not expected to pose any apparent risk as the HQs did not exceed 1. The maximum HQ was observed for the crustacean *Artemia sinica*. The results indicate that NP may have more impact on native crustacean populations.

The risk of OP to aquatic organisms was assessed for crustaceans, fish and algae, shown in Table 3. The OP_{PNEC} for crustaceans and fish were in the ranges of 0.01– $10.8 \mu\text{g L}^{-1}$ and 1.14– $7.7 \mu\text{g L}^{-1}$, respectively. In the case of algae, the OP_{PNEC} value ranged from 0.138 to

$100 \mu\text{g L}^{-1}$. Seven out of eight organisms have HQ values greater than 1 (Figure 2(b)). The calculated HQs for crustaceans and fishes were in the ranges of 1.5–1,570 and 2.0–13.8, respectively. Similarly, the river also did not pose a significant potential risk for the alga *Selenastrum capricornutum* (0.2). Based on the results, NP and OP posed a high risk to the relevant sensitive aquatic animals (excluding *S. capricornutum*).

Human health risk assessment

Drinking water is one of the important pathways of human exposure to APs, and surface water is often used as a direct or indirect source of drinking water. The consumption of drinking water containing chemicals even at a 1 ng L^{-1} level for a long time possibly affects human health (Snyder & Benotti 2010). The Pearl River is the important drinking water source for Guangzhou City and surrounding towns. Therefore, the human risk assessment was carried out according to the MOS level in drinking water and the TDI limit, shown in Table 4.

Table 3 | Derived PNEC values for OP based on toxicity values in different organisms

Group/Common name	Species	Test	Aquatic organisms ($\mu\text{g L}^{-1}$)	PNEC ($\mu\text{g L}^{-1}$)	References
Crustacea	<i>T. japonicus</i>	LC ₅₀ , 48 h	620	0.62	Marcial et al. (2003)
	<i>Ceriodaphnia dubia</i>	EC ₅₀ , 7 days	10	0.01	Isidori et al. (2006)
	<i>D. magna</i>	NOEC, 21 days	108	10.8	MOE Japan (2009)
Fish	<i>P. promelas</i>	NOEC, 96 h	77	7.7	IUCLID (2000)
	<i>O. latipes</i>	LOEC, 60 days	11.4	1.14	Seki et al. (2003)
	<i>Danio rerio</i>	NOEC, 38 days	12	1.2	Wenzel et al. (2001)
Algae	<i>S. capricornutum</i>	NOEC, 96 h	1,000	100	ABC (1984)
	<i>Pseudokirchneriella subcapitata</i>	EC ₅₀ , 72 h	138	0.138	MOE Japan (2009)

Table 4 | Human health risk assessment for the riverine water from the PRD

Parameter	Maximum concentration ($\mu\text{g L}^{-1}$)	Drinking water guidelines ($\mu\text{g L}^{-1}$)	MOS ($\mu\text{g kg}^{-1} \text{ day}^{-1}$)	Daily intake ($\mu\text{g kg}^{-1} \text{ bw day}^{-1}$)		Reference dose ($\mu\text{g kg}^{-1} \text{ day}^{-1}$)	TDI ($\mu\text{g kg}^{-1} \text{ day}^{-1}$)	Contribution for TDI (%)	
				Adult	Infant			Adult	Infant
NP	16.2	0.5 ^a	0.03	0.54	1.62	50 ^b	5.0 ^a	10.80%	32.40%
OP	15.7	–	–	0.52	1.57	–	–	–	–

^aNielsen et al. (1999).

^bUSEPA (2010).

The daily intake of NP through consuming drinking water varied between adults and infants. NP concentrations in the riverine waters were well above the drinking water guideline (~32–33 times) and the MOS was less than 1 (0.03). The daily intake for infants was three times larger than for adults, although infants are more vulnerable to these toxic substances. The daily intake value of NP is lower than the TDI of $5 \mu\text{g kg}^{-1} \text{bw}$ proposed by the Danish Institute of Safety and Toxicology (Nielsen *et al.* 1999). The concentrations were well below the human reference dose and their contributions to TDI were 10.80% and 32.40% for adults and infants, respectively (Table 4). It indicates that regular monitoring is indispensable. As to OP, it was not possible to assess the human health risk associated with its intake from drinking water consumption as no respective TDI is available.

CONCLUSIONS

In the present study, the occurrence of NP and OP in surface water and sediment from the six outlets of the PRE was investigated. Compared with OP, NP displays higher concentrations in all water and sediment samples. In addition, higher levels of NP and OP were found in HM. The levels of APs in surface water and sediment exhibit a similar seasonal distribution with the highest concentration in July, which may due to the degradation of their ethoxylated precursors under high temperature. All investigated compounds may pose high risks to a majority of aquatic organisms and have some adverse effects on human beings.

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