Occurrence, distribution and seasonal variation of organophosphate flame retardants and plasticizers in urban surface water in Beijing, China

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The occurrence, spatial distribution and seasonal variation of 14 organophosphate esters (OPEs) were investigated in urban surface water (river and lake water) from July 2013 to June 2014 in Beijing, China. Sewage influent and effluent samples, as well as rainwater and road runoff samples were also analyzed as the potential sources of OPEs in surface water. Tris(2-chloro-1-methylethyl) phosphate (TCP) and tris(2-chloroethyl) phosphate (TCEP) were the most abundant OPEs with the average concentrations of 291 ng L⁻¹ and 219 ng L⁻¹, respectively. Relatively high concentrations of OPEs were detected in rivers located at southern and eastern urban of Beijing, which was probably attributed to the treated and untreated sewage discharge. Besides, higher levels of OPEs were observed in urban surface water in the summer, and the wet deposition (rainfall) was confirmed to be an important factor for this observation. Risk assessment showed low or medium risk of OPEs for the organisms (algae, crustacean and fish).

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1. Introduction

As the major replacement for polybrominated diphenyl ethers (PBDES), organophosphate esters (OPEs) are utilized as flame retardants in a large variety of consumer products such as plastics, textiles, electronic equipment, industrial materials and furniture (Reemtsma et al., 2008; Yang et al., 2014). Chlorinated-OPEs are the predominant compounds for this application (Reemtsma et al., 2008). Apart from being used as flame retardants, OPEs are also applied as plasticizers, antifoaming or anti-wear agents in lacquers, hydraulic fluids, floor polishing agents, and non-ionic extractants in hydrometallurgy (Marklund et al., 2005a; Salamova et al., 2014a). In general, there is a considerable variation in the physical and chemical properties of OPEs. As shown in Table S1, these chemicals exhibit a wide range of logKow values (from −0.65 to 9.49). Additionally, OPEs can be classified as semi-volatile compounds with Henry’s law constant values ranged from $2.92 \times 10^{-10}$ to $1.98 \times 10^{-8}$ atm m³ mol⁻¹ (Wensing et al., 2005). Although the atmospheric half-lives of OPEs are below 2 days (from <1 to 21.3 h), their occurrence in precipitation in the North Sea atmosphere and Arctic, indicates that they can undergo long range atmospheric transport (LRAT) (Möller et al., 2012; Shoieb et al., 2014).

Considering that OPEs are generally not chemically bonded to materials, these compounds could be slowly released into surrounding environment by volatilization, leaching and abrasion (Yang et al., 2014). According to previous reports, several OPEs have been detected in the aquatic (Cristale et al., 2013a; Martinez-Carballo et al., 2007; Venier et al., 2014), terrestrial (David and Seiber, 1999; Fries and Mihajlovic, 2011; Mihajlovic and Fries, 2012), and atmospheric environment (Möller et al., 2012; Möller et al., 2011; Salamova et al., 2014b). Additionally, potential adverse effects of OPEs to the ecosystem and human health have also been pointed out in previous studies (Kim et al., 2011; Meeker et al., 2013; Reemtsma et al., 2008). The reports associated with human exposure have demonstrated the reduction of sperm counts and hormone levels due to the exposure to TPhP and TDCP (Meeker and Stapleton, 2010). TCEP and TDCP are considered as carcinogens and potential neurotoxicants (Cequier et al., 2015; Salamova et al., 2014a), and may cause acute or chronic adverse effects to aquatic
organs (Cristale et al., 2013a; Kim et al., 2011). TCPP is also a suspected carcinogen (Reemtsma et al., 2008), and TnBP has neurotoxic properties after chronic exposure (Reemtsma et al., 2008). TPhP and 2-ethylhexyl diphenyl phosphate (EHDP) reveal potentially bioaccumulative and toxic role to aquatic ecosystem (Kim et al., 2011; Sundkvist et al., 2010).

The occurrence and fate of OPEs in aquatic environment is of concern since these compounds can massively reach surface water from industrial and domestic sewage discharge (Fries and Puttmann, 2003; Martinez-Carballo et al., 2007) and atmosphere deposition (Bacaloni et al., 2008; Möller et al., 2011; Regnery and Püttmann, 2009). The discharge of industrial and domestic sewage is considered as the major source of OPEs in surface water (Reemtsma et al., 2008). Some alkyl-OPEs such as trimethyl phosphate (TMP) and triethyl phosphate (TEP), have been well removed in sewage treatment plants (STPs), whereas the chlorinated-OPEs are not subjected to the significant removal, which are, thus, discharged with effluents into rivers (Bester, 2005; Marklund et al., 2005a; Meyer and Bester, 2004). Besides, atmosphere deposition has been pointed to be another important source of OPEs in surface water environment (Möller et al., 2011; Regnery and Püttmann, 2009). The OPEs at levels from ng L\(^{-1}\) to µg L\(^{-1}\) have been detected in many rivers in Germany (Andresen et al., 2004; Fries and Puttmann, 2001; 2003; Regnery and Püttmann, 2010), Aire River in UK (Cristale et al., 2013a), volcanic lakes in Italy (Bacaloni et al., 2008), and rivers in Austria (Martinez-Carballo et al., 2007), as well several rivers in China (Wang et al., 2015, 2014, 2011).

Considering the widely application of OPEs in buildings, vehicles, electronics and plastics, more consumption of these compounds was expected in urban city, especially in large city with a dense population, and the urban surface water may suffer serious contamination of OPEs. So far, only one study focused on the occurrence and distribution of OPEs in urban surface water from Germany (Regnery and Püttmann, 2010), hence, more information should be collected to fill our knowledge gaps of the occurrence and distribution of OPEs in urban surface water from densely populated cities. Moreover, temporal variation of OPEs in aquatic environment should be further investigated since the seasonal trend was uncertain in previous studies (Bacaloni et al., 2008; Regnery and Püttmann, 2010).

According to the data from European flame retardants association (EFRA), China is one of the most flame retardants-consuming countries, accounting for approximately 20% of global consumption (EFRA, 2012). It is estimated that the annual yield of OPEs had reached 70,000 tons in 2007 and was predicted to increase by 15% annually in China (Wei et al., 2015). Accordingly, their universal usages may lead to widespread pollution of OPEs in China.

Beijing is one of the most populated and developed cities in China, with total dimension of 16410.54 km\(^2\) and a huge population of 21.516 million. The aim of this study was to investigate the occurrence and distribution of OPEs in urban surface water from densely populated city. To this end, levels of 14 OPEs in surface water covering almost the whole urban of Beijing, China were studied. Besides, spatial distribution and seasonal variation from July 2013 to June 2014 of the target compounds in surface water were also investigated. Additionally, sewage influent and effluent, rainwater and road runoff samples were collected and analyzed as the potential sources of OPEs in urban surface water. Finally, environmental risk of OPEs in surface water was evaluated to explore the impact of these chemicals on aquatic organisms.

2. Materials and methods

2.1. Materials and reagents

Seven alkyl phosphates, including TMP, TEP, TnBP, tri-iso-butyl phosphate (TIBP), TBEP, tripropyl phosphate (TPPrP) and tri(2-ethylhexyl) phosphate (TEHP), and three chlorinated alkyl phosphates (TCEP, TCPP and TDCP), and four aryl phosphates, including TPhP, tri-m-cresyl phosphate (TCrP), cresyl diphenyl phosphate (CDPP) and EHDP, were obtained from Dr. Ehrenstorfer GmbH (Germany) as target OPEs, and detailed information was listed in Table S1 (Supplementary material). TMP-d\(_9\), TEP-d\(_{15}\) and TPPrP-d\(_{21}\) obtained from C/D/N Isotopes Inc. (USA), TnBP-d\(_{27}\) and TPhP-d\(_{15}\) purchased from Cambridge Isotope Laboratories (UK), and TCPP-d\(_{18}\) supported by Toronto Research Chemicals Inc. (Canada) were used as internal standards (IS). HPLC grade acetonitrile and dichloromethane (DCM) were provided by Fisher Scientific (USA). Ultrapure water (18.3 M\(\Omega\)) was produced by a Milli-Q Gradient system (Milipore, Bedford, USA).

Individual stock solution with the concentration of 1000 mg L\(^{-1}\) was prepared in acetonitrile, and mixed stock solution containing all analytes was prepared in acetonitrile at the concentration of 10 mg L\(^{-1}\). All stock solutions were kept in an –20 °C refrigerator. Calibration solutions (0.05–1000 µg L\(^{-1}\)) used in routine application were prepared in acetonitrile/water (4:6).

2.2. Sampling

2.2.1. Urban surface water

River and lake water samples were collected at 34 sampling sites in the urban of Beijing monthly from July 2013 to June 2014 (except December 2013 and January 2014 in frozen period). A total of 340 water samples (surface layer, 0.2 m depth) were obtained in 10 sampling campaigns. In order to fully understand the occurrence of OPEs in surface water in Beijing, all of the major rivers and lakes in the urban areas are included in this study. As shown in Fig. 1, the samples L1-L8 were collected from lakes in various parks. The sampling sites R1-R8 belong to Chang River, and sampling sites R9-R11 belong to Tonghui River, while the samples R12-R17 were collected from Liangshui River and its tributaries, and samples R18-R21 were collected from Qing River and its tributaries. The rest sampling sites R22-R26 were located at Beixiao River, Xiba River, Liangma River, Baijialou Sewer and Xiaotaihou River, respectively.

2.2.2. Wastewater

Additionally, seven STPs (A-G) in the urban of Beijing were also marked in Fig. 1. Influent and effluent water samples were collected as 24 h composite samples by using automatic samplers with sampling interval of 2 h from STP A in October 2013. The plant employs conventional activated sludge treatments to remove biologically degradable organic materials, and the secondary effluent was discharged into the Qing River.

2.2.3. Rain water

A total of 10 rain water samples were collected from June to August 2013 using a stainless steel box (area 1 m\(^2\), height 30 cm) placed at monitoring station in Beijing teaching botanical garden. This sampling site located in the central urban of Beijing, which near the sampling site L4.

2.2.4. Road runoff water

A total of 43 road runoff samples were collected at 5 sampling sites at the main road of Beijing (the 2nd ringroad, 3rd ringroad and 4th ringroad) from June to August 2013. On each occasion, one composite road runoff sample was obtained using a 40-L stainless steel container below the road storm sewer from each site. All of water samples were collected in glass bottles (500 mL) rinsed with methanol and dried in advance. Immediately after being transported to the laboratory, the samples were stored at 4 °C and treated by SPE within two days. Before SPE procedure, water
samples were filtered through GF/C glass fiber filters (1.2 µm, Whatman, UK) to remove suspended particulate matters.

2.3. Methods

OPEs were analyzed by an Ultimate 3000 HPLC system (ThermoFisher, USA) coupled with an API 3200 triple-quadrupole mass spectrometer equipped with an electrospray ion source (ESI) (Applied Biosystems/MDS SCIEX, USA). The separation of the analytes was carried out on Acclaim Mixed-Mode HILIC-1 column (2.1 mm × 150 mm; i.d., 5.0 µm) (ThermoFisher, USA) at a flow rate of 0.25 mL min⁻¹. Ultrapure water (A) and acetonitrile (B) were applied as mobile phase with the gradient as follows: initial 40% B with the maintenance for 1.0 min, sequential linear increase to 60% B in 4 min; following increase to 100% B in 3 min and hold for 7 min; then, the gradient return to the initial condition of 40% B in 0.2 min and hold for 6.8 min to allow for equilibration. The electrospray ionization was operated in the positive ion mode under multiple reaction monitoring (MRM) with the ion spray voltage of 5.0 kv and source temperature of 600 °C. Individual MS/MS parameters for each compound are listed in Table S2 (Supplementary material).

Water samples were extracted and cleaned by solid phase extraction (SPE) with an ENVI-18 cartridge (6 ml, 500 mg, Supelco). Cartridges were conditioned with 5 mL of acetonitrile and 5 mL of ultrapure water sequentially. Then, 200 mL of water samples were passed through at a flow rate of 4 mL min⁻¹. The cartridges were rinsed with 10 mL of ultrapure water, dried for 30 min, and finally eluted with 6 mL of 25% DCM in acetonitrile. The eluent was finally concentrated down to approximately 0.4 mL at 37 °C under a stream of N₂ and diluted to a final volume of 1 mL with ultrapure water.

2.4. Quality control

As shown in Table S3 (Supplementary material), the calibration curves were measured for all 14 OPEs with constant amount of IS (10 ng), and a good linearity (R = 0.9877–0.9969) was obtained for the analytes in a wide concentration range. The limits of detection (LODs, S/N ≥ 3) ranged from 0.3 to 16 ng L⁻¹ after extraction of 200 mL of water sample. The recovery rate of 68.5–113.2% was observed for river water samples, with the RSD lower than 15% (n = 4), and recovery rate of 64.8–103.9% was detected for wastewater samples, with the RSD lower than 15.9% (n = 4). The low recovery rates of some OPEs may be due to their tendency to volatilize or adsorb onto bottles during the sample pretreatment procedure. The application of IS could compensate for these loss to some extent.

Five field blank samples made from ultrapure water (1 L) was included in river water, lake water, wastewater, rainwater and road runoff sampling and shipped back to the laboratory with the
samples. Additionally, during the analysis of each batch of samples, at least one lab procedure blank should be prepared from ultrapure water. Six OPEs, including TEP, TCEP, TCPP, TnBP, TiBP and TBEP, were detected in the lab procedure blanks with concentrations lower than 10 ng L\(^{-1}\). While the concentrations of TEP, TCEP and TCPP, when detected, in field blanks were in the range of 5–25 ng L\(^{-1}\). Therefore, results for all analytes were blank corrected by subtraction of mean blank values from the raw OPEs values in water samples. In addition, in order to monitor the stability of the system, a 10 ng L\(^{-1}\) standard was set as the quality control concentration and checked every 10 injections.

2.5. Risk characterization

The risk of OPEs for aquatic organisms was evaluated by the determination of risk quotient (RQ) values, as described by several previous reports (Cristale et al., 2013a; Li et al., 2012; Sanchez-Avila et al., 2012; Santos et al., 2007). RQ value of each compound in water was calculated using the following formula:

\[
RQ = \frac{\text{MEC}}{\text{PNEC}}
\]  
(1)

\[
\text{PNEC} = \frac{\text{LC50} \text{ or EC50}}{f}
\]  
(2)

Where MEC is the measured environmental concentration; PNEC is the predicted no effect concentration; LC\(_{50}\) or EC\(_{50}\) is the lowest median effective concentration value obtained from available literature, and \(f\) is an appropriate standard assessment factor. In this study, the toxicological data (LC\(_{50}\) or EC\(_{50}\)) for algae, crustacean and fish obtained from available literature, and an assessment factor of 0.1 were used for RQ calculation (European Commission, 2003).

In risk assessment studies, common criteria for risk levels are established by interpreting RQ values: RQ < 0.1 indicates low risk to aquatic organisms; 0.1 ≤ RQ ≤ 1 indicates medium risk; RQ ≥ 1 indicates high risk (Hernando et al., 2006; Van Doorslaer et al., 2014; Verlicchi et al., 2012).

3. Results and discussion

3.1. Levels of OPEs in urban surface water

All of 14 OPEs were detected in river and lake water samples in the urban of Beijing, and the total OPEs (\(\sum\text{OPEs}\)) varied between 3.24 and 10,945 ng L\(^{-1}\) (Table 1), which is significantly higher than those detected in lake water samples from less populated cities of Germany (Regnery and Puttmann, 2010), reflecting heavy anthropogenic impacts on the contamination of OPEs in urban surface water from densely populated city. The concentration-percent composition of 14 OPEs in the surface water in this study was shown in Fig. S1. TCPP and TCEP were the most abundant compounds, and their concentration-percent composition ([TCPP]+[TCEP]) accounted for 28.2–83.1% of the total, with an average of 56.7%. The result can be expected giving that TCPP and TCEP are widely used in flexible and rigid polyurethane foam (PUF), rubber and textile coatings (Marklund et al., 2003, 2005a). Additionally, the chlorinated OPEs were reported to be more persistent in the environment than the non-chlorinated OPEs (Reemtsma et al., 2008). Then, TMP, TEP and TBP were the secondary abundant OPEs in surface water, and their concentration-percent composition ([TMP]+[TEP]+[TBP]) accounted for 11.6–63.2% of the total, with an average of 34.1%.

In the present study, TCPP, TCEP, TMP, TEP and TBEP were detected with the frequency of 80–98% in the river and lake water in Beijing (Table 1). As summarized in Table 2, most of these levels were higher than those detected in rivers around the Bohai Sea, China (Wang et al., 2015), Oder River (Fries and Puttmann, 2003), Elbe River (Bollmann et al., 2012) and lake water samples (Regnery and Puttmann, 2010) from Germany, as well as those in surface water from Austria (Martinez-Carballo et al., 2007), Rhine River in Netherlands (Bollmann et al., 2012) and volcanic lake waters from central Italy (Bacaloni et al., 2008). TCEP concentration in surface water from Beijing was similar to that detected in Songhua River (Wang et al., 2011) and Pearl River Estuaries, China (Wang et al., 2014), and the levels of TCPP and TBEP in this study were similar to those detected in the Spanish rivers (Cristale et al., 2013b) and Pearl River Estuaries, China (Wang et al., 2014), but the TBEP level was lower than that in Aire River in UK (Cristale et al., 2013a).

Two structural isomers, TnBP and TiBP, were observed at similar average levels of 19.6 (≤LOD-256) and 23.3 (≤LOD-169) ng L\(^{-1}\), and detection frequency of 85% and 94%, respectively. These concentrations were similar to those detected in rivers around the Bohai Sea, China (≤LOD-218 ng L\(^{-1}\)) (Wang et al., 2015), Danube River (20–110 ng L\(^{-1}\)), Schwechat River (82 ng L\(^{-1}\)) and Liesz River (75 ng L\(^{-1}\)) in Austria (Martinez-Carballo et al., 2007), Elbe River (2–50 ng L\(^{-1}\)) (Bollmann et al., 2012) and urban lake waters (≤LOQ-122 ng L\(^{-1}\)) (Regnery and Puttmann, 2010) in Germany, but lower than those detected in Songhua River, Northeast China (87–960 ng L\(^{-1}\)) (Wang et al., 2011), rivers in Spain (≤LOD-1200 ng L\(^{-1}\)) (Cristale et al., 2013b), Albano lake in Italy (≤LOQ-784 ng L\(^{-1}\)) (Bacaloni et al., 2008) and other rivers in Germany (100–1510 ng L\(^{-1}\); 69–1044 ng L\(^{-1}\)) (Fries and Puttmann, 2001, 2003).

TPhP was detected with the frequency of 75% and average concentration of 4.49 (≤LOD-96.3) ng L\(^{-1}\) in urban surface water in Beijing, which was similar to those detected in most of other sites (Andresen et al., 2004; Cristale et al., 2013a; Martinez-Carballo et al., 2007; Wang et al., 2011). In good agreement with literature, TPhP, TEHP, TCrP, CDPP and EHDPP were found with low concentration (≤LOQ-40.3 ng L\(^{-1}\)) and frequency (≤50%) in the surface water in Beijing. However, high concentration of 951 ng L\(^{-1}\) for TPhP was detected in Vico lake in Italy (Bacaloni et al., 2008), implying the different production and application patterns of OPEs in different areas.

3.2. Spatial variation

Mann–Whitney’s tests were used for statistical analysis to investigate the spatial variation of concentrations for OPEs. Five

Table 1

Levels (ng L\(^{-1}\)) of OPEs in urban surface water samples in Beijing, China.

| Analytes    | Mean   | Median | Max.   | Min.   | Fre. (%) |
|-------------|--------|--------|--------|--------|----------|
| TMP         | 144    | 48.3   | 9497   | <LOD  | 88.2     |
| TEP         | 88.7   | 47.5   | 2072   | <LOD  | 94.7     |
| TPnP        | 0.02   | <LOD   | 3.59   | <LOD  | 1.4      |
| TCEP        | 219    | 104    | 5698   | <LOD  | 95.8     |
| TPnHp       | 4.49   | 1.31   | 96.3   | <LOD  | 74.8     |
| TCPP        | 291    | 174    | 1742   | <LOD  | 99.4     |
| CDPP        | 0.43   | 0.03   | 4.85   | <LOD  | 48.5     |
| EHDPP       | 0.38   | <LOD   | 40.3   | <LOD  | 6.7      |
| TCrP        | 0.18   | <LOD   | 4.29   | <LOD  | 37.5     |
| TBP         | 116    | 22.8   | 3617   | <LOD  | 90.2     |
| TDCP        | 46.3   | 23.2   | 855    | <LOD  | 79.8     |
| TEHP        | 0.91   | <LOD   | 23.5   | <LOD  | 41.7     |
| TnBP        | 19.6   | 10.1   | 256    | <LOD  | 84.9     |
| TiBP        | 23.3   | 14.1   | 169    | <LOD  | 93.6     |
| Alkyl-OPEs  | 392    | 218    | 9761   | 0.21   |          |
| CI-OPEs     | 556    | 323    | 6537   | <LOD  |          |
| Acyl-OPEs   | 5.48   | 1.82   | 96.3   | <LOD  |          |
| Total       | 954    | 569    | 10,945 | 3.24   |          |

* Concentration below the limit of detection (LOD).
target compounds, including TPrP, EHDP, TCrP, TEHP and CDPP, were not evaluated due to their low detection frequencies (<50%). In this study, statistical analysis revealed that significant differences were observed in the \( \sum \text{OPEs} \) concentrations among different sampling sites \((p < 0.05)\). As illustrated in Fig. 2, the levels of OPEs detected in all lakes were similar to those detected in the Chang River \((p > 0.05)\), but much lower than those detected in other rivers \((p < 0.05)\). In general, the lakes and Chang River are used for leisure and entertainment, where the discharge of wastewater and surface runoff are strictly controlled \((p < 0.05)\). Furthermore, the upstream of the Chang River and some lakes (site L1-L3) is an important drinking water source for Beijing residents, and has been protected by the fence. On the contrary, the other rivers (except Chang River) are usually located near the outlet of STPs, and flow through a densely populated and highly industrialized urban area in Beijing, which may be heavily impacted by large amounts of STP effluents and industrial wastewaters. Therefore, the different sources and functions of the surface water contributed to the different levels of OPEs in the lakes and rivers.

As for the rivers (except Chang River), no significant difference of \( \sum \text{OPEs} \) concentrations was observed for Tonghui River, Liangshui River and Qing River \((p > 0.05)\), whereas the three rivers present significant lower levels than the other rivers located in the eastern urban \((p < 0.05)\). As shown in Fig. 2, the highest concentrations of TPrP was detected in Xiaotaihou River (R26), which were almost 1–2 orders of magnitudes higher than those detected in other rivers. TPrP is very polar and volatile OPE with the log Kow of -0.65 and vapor pressure of 8 \times 10^{-11} \text{torr} at 25°C \((\text{Reemtsma et al., 2008})\); it was found to be well removed in sewage treatment process \((84–100\%)\) \((\text{Marklund et al., 2005a})\). Therefore, the high level of TPrP in Xiaotaihou River may be due to other point sources, which needs to be further investigated. In addition, the highest level of TBEP was detected in Biaojialou Sewer (R25), followed by Tonghui River (R11). TBEP was widely used in floor polish and floor waxes, and has been frequently detected in wastewater with the concentration up to 35,000 and 30,000 ng L\(^{-1}\) in influent and effluent samples \((\text{Marklund et al., 2005a})\), respectively. It is known that the site R11 in Tonghui River situated at the downstream of STP D which is the greatest STP in Beijing with the treatment capacity of 1000 000 m\(^3\) d\(^{-1}\). And the Biaojialou Sewer may receive direct discharge of untreated domestic sewage from nearby residents. Therefore, the highest levels of TBEP in Biaojialou Sewer and Tonghui River may be due to the heavy discharge of domestic sewage.

The chlorinated-OPEs were detected in Qing River, Tonghui River, Liangshui River and other rivers in the eastern urban with high concentrations, and the highest level was detected in Xiba River (R23). Chlorinated-OPEs are mainly used as flame retardants in polyurethane foam (PUF) and rubber in domestic, public, and automotive products, as well as used in textile coatings \((\text{Abdallah and Covaci, 2014; van der Veen and de Boer, 2012})\). TCPP and TCEP are also the most abundant OPEs in influents of STPs, and even detected with higher concentration in effluents, suggesting their persistence in water \((\text{Bester, 2005; Marklund et al., 2005a; Meyer and Bester, 2004})\). So the ubiquitous occurrence of the chlorinated-OPEs in rivers may be explained by the widespread use of chlorinated-OPEs-containing products and their resistance to degradation. TPhP was the most frequently detected aryl-OPEs in this study, and the highest concentration was detected in Liangshui River (R14). In previous studies, TPhP has been frequently detected in STP influent and effluent samples with concentrations below 300 ng L\(^{-1}\) \((\text{Marklund et al., 2005; Martinez-Carballo et al., 2007; Meyer and Bester, 2004})\). Thus, the relatively high concentration of TPhP in Liangshui River is presumably attributed to the effluent discharge of STP E and F along this river.

Geographically, higher levels of OPEs were observed in the rivers located at eastern and southern urban of Beijing, where the STPs are mainly distributed. For instance, the sampling site R11 located at the downstream of STP D, accordingly, the levels of TCPP and TCEP were approximately twofold of those detected at the upstream sampling site (R10). In this study, the concentrations of OPEs were also analyzed in influent and effluent samples in one typical STP (STP A). As shown in Table 3, TCPP revealed the highest concentration of 465 ng L\(^{-1}\) in the influent, followed by TBEP.

| Sites                      | TEP           | TCEP         | TCPP         | TDCP         | TBEP         | TnBP         | TIBP         | TPHP         | Ref.                  |
|----------------------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|-----------------------|
| Surface water, Beijing     | 88.7 (LOD<2072) | 219 (LOD<5698) | 291 (LOD<1742) | 463 (LOD<855) | 116 (LOD<3617) | 19.6 (LOD<256) | 23.3 (LOD<169) | 4.49 (LOD<96.3) | This study            |
| Rivers around Bohai Sea,   | n.a.          | 1–268        | 5–921        | <LOD-44      | <LOD-47      | <LOD-81      | <LOD-218     | <LOD-16      | (Wang et al., 2015)   |
| China                      | n.a.          | 220–1160     | 150–1150     | n.a.         | n.a.         | n.a.         | n.a.         | n.a.         | (Wang et al., 2014)   |
| Pearl River Estuaries,     | n.a.          | 119–316      | 62–169       | <LOD-330     | <LOD-1800    | <LOD-200     | <LOD-4600    | 370          | (Bollmann et al., 2012) |
| China                      | n.a.          | 23, 61       | 85, 126      | n.a.         | <LOD<53      | 32, 17       | 10, 8        | n.a.         | (Bollmann et al., 2012) |
| Elbe river, Germany        | 6.99–33.9     | 5–20         | 40–250       | 6.4–30.8     | <LOD-80      | 2–7.5        | 10–50        | 0.3–4        | (Bollmann et al., 2012) |
| Rhine Delta, Netherlands   | 29.7–82.7     | 12–25        | 75–160       | 13.2–30.6    | 28–54        | 6–28         | 17–84        | 1–2         | (Bollmann et al., 2012) |
| Urban lake water, Germany  | 23, 61        | 85, 126      | n.a.         | <LOQ<53      | 32, 17       | 10, 8        | n.a.         | n.a.         | (Bollmann et al., 2012) |
| Aire river, UK             | 1–42          | <LOD-64      | 2–62         | 2–60         | 8–127        | 3–784        | 1–380        | 2–21        | (Bacaloni et al., 2008) |
| Navarra, Asturias, Spain   | <LOD-330      | <LOD-1800    | <LOD-200     | <LOD-4600    | 370          | 1200         | n.a.         | n.a.         | (Bacaloni et al., 2008) |
| Catalonia, Spain           | 1–42          | <LOD-64      | 2–62         | 2–60         | 8–127        | 3–784        | 1–380        | 2–21        | (Bacaloni et al., 2008) |
| Ruhr river, Germany        | 13–51         | 33–170       | 7–19         | 24–500       | 20–110       | n.a.         | 6–10         | n.a.         | (Martinez-Carballo et al., 2007) |
| Oder river, Germany        | 13–130        | <LOD-1236    | n.a.         | <LOD-1236    | 121–952      | 69–1044      | n.a.         | n.a.         | (Fries and Puttmann, 2003) |
| Pearl River, China         | n.a.          | <LOD-220     | n.a.         | 103–663      | 100–1510     | n.a.         | n.a.         | n.a.         | (Fries and Puttmann, 2003) |

\(^a\) Concentration below the limit of detection (LOD).
\(^b\) Not available.
\(^c\) Concentration below the limit of quantification (LOQ).

Table 2: Concentrations (ng L\(^{-1}\)) of selected OPEs in different studies in surface water.
(398 ng L\(^{-1}\)), TCEP (150 ng L\(^{-1}\)) and TnBP (120 ng L\(^{-1}\)). Corresponding levels for TCPP, TBEP, TCEP and TnBP in the effluent were 605, 103, 254 and 93.1 ng L\(^{-1}\), respectively. The high concentration of these pollutants in the influent and effluent samples seems to confirm our conjecture that treated and untreated sewage discharge is one of the important factors contributed to relatively high levels of OPEs in the surface water in eastern and southern urban of Beijing. Besides, it is expected that the surface water system in eastern and southern urban located in the downstream area will suffer more serious pollution of OPEs as rivers flow...
through Beijing from west to east, especially for the chlorinated OPEs that are supposed to be persistent in aquatic environment.

3.3. Seasonal variation

The statistical analysis (Friedman’s test) showed that the concentration of OPEs in urban surface water is significantly different from season to season depending on individual compound \((p < 0.05)\). The samples collected in the summer (July and August) showed higher levels of total OPEs, TCPP, TCEP, TMP and TEP, while lower levels of OPEs were detected during the winter (November and February) (Fig. 3). This result disagreed with previous study showing no significant seasonal trends for the OPEs in urban lake water samples from Germany (Regnery and Puttmann, 2010). It has been previously demonstrated that the proportions of OPEs in condensate and internal vehicle air reveal an increase when the temperature is increased (Regnery and Püttmann, 2009). The average temperature is about 30 °C in July and August (summer) in Beijing, while it is only about 10 °C and 5 °C in November and February (winter), respectively. Therefore, higher emission of OPEs, especially the more volatile OPEs (TMP, TEP, TCEP and TCPP etc.), from vehicles and buildings in summer than in winter can be expected.

In addition, high levels and detection frequency of OPEs have been observed in outdoor environment, including air particle matters (Möller et al., 2012; Salamova et al., 2014a, 2014b) and dust (Cao et al., 2014). It is probable that these pollutants in the outdoor air and dust are released into rivers along with wet deposition (rainfall) in the summer. Beijing is located in the north of China, with a temperate territorial semi-humid climate, and the most of precipitation occurs during the summer from July to August (Ren et al., 2013). Therefore, the high concentration of OPEs in urban

### Table 3
Levels (ng L\(^{-1}\)) of OPEs in influent, effluent, rainwater and road runoff samples in Beijing, China.

| Analytes | STP A | Rainwater (mean) | Road runoff (mean) |
|----------|-------|------------------|--------------------|
|          | Influent | Effluent | June (n = 3) | July (n = 3) | August (n = 4) | June (n = 11) | July (n = 12) | August (n = 20) |
| TMP      | 17.2    | 44.9    | 217        | 221        | 150       | 183        | 271        | 156         |
| TEP      | 46.9    | 64.1    | 107        | 85.8       | 81.9      | 239        | 348        | 226         |
| TCEP     | 150     | 254     | 3560       | 2270       | 2592      | 941        | 716        | 337         |
| TPhP     | 15.4    | 6.20    | 0.88       | 1.77       | 2.59      | 50.0       | 38.1       | 33.6        |
| TCPP     | 465     | 605     | 366        | 224        | 183       | 1488       | 1578       | 846         |
| CDPP     | <LOD\(^a\) | <LOD\(^a\) | <LOD<LOD<LOD | <LOD<LOD<LOD | <LOD\(^a\) | 16.5       | 11.1       | 9.37        |
| TGP      | 0.2     | <LOD\(^a\) | <LOD<LOD<LOD | <LOD<LOD<LOD | <LOD<LOD<LOD | 0.85       | 1.23       | 0.79        |
| TBEp     | 398     | 103     | 2.23       | 7.58       | 4.79      | 175        | 186        | 154         |
| TDCP     | 87.0    | 82.5    | <LOD<LOD<LOD | <LOD<LOD<LOD | <LOD<LOD<LOD | 242        | 109        | 71.5        |
| TEHP     | 7.10    | <LOD\(^a\) | 0.61       | 0.82       | 1.38      | 7.38       | 7.07       | 6.64        |
| TnBP     | 120     | 93.1    | 12.8       | 17.4       | 19.4      | 78.5       | 86.2       | 73.2        |
| TiBP     | 54.0    | 66.5    | 19.1       | 9.60       | 9.67      | 59.0       | 69.1       | 45.0        |

\(^a\) Concentration below the limit of detection (LOD).

Fig. 3. Seasonal variation of OPEs in urban surface water from July 2013 to June 2014.
surface water in July and August may be due to the input of rainwater enriching OPEs from the outdoor air and dust in the summer.

In this study, the concentrations of OPEs were also analyzed in rainwater and road runoff samples in Beijing from June to August (Table 3). TDCP was not detected in rainwater samples and TBEP was only detected in rainwater at low concentration level (2.23–7.58 ng L$^{-1}$), whereas the levels of TDCP and TBEP were up to 71.5–242 and 154–175 ng L$^{-1}$, respectively, in road runoff samples. Similar result was also obtained for TnBP, TEP and TPhP in rainwater and road runoff samples, suggesting that these OPEs possibly come from road dust rather than outdoor air. Compared to sewage effluent, much higher levels of TCPP, TCEP, TMP and TEP were detected in rainwater and road runoff samples, demonstrating the great contribution of rainfall to the presence of OPEs in urban surface water. The concentrations of TCEP detected in rainwater (2270–3560 ng L$^{-1}$) and TCPP detected in road runoff (846–1578 ng L$^{-1}$) were even one order of magnitude higher than those detected in STP effluent. This fact further confirms our hypothesis that wet deposition (rainfall) is an important factor for the occurrence of OPEs in aquatic environment.

By comparing with RQ values of PBDEs (0.0013 and 0.0017) in the river of Shanghai, China (Zhao et al., 2012), higher RQ values of OPEs (maximum: 0.2782 for TBEP) were observed in the rivers of Beijing. Therefore, the risk of OPEs in rivers in Beijing should be of concern. In addition, the presence of OPEs in biota samples has been reported previously (Kim et al., 2011; Sundkvist et al., 2010), including TEHP, EHDPP, TPhP and TnBP, even the hydrophilic TEP (logKow = 0.80) and TCPP (logKow = 2.59) with low octanol-water partition coefficients (Reemtsma et al., 2008). Therefore, bioaccumulation and biomagnification of OPEs in biota from aquatic environment should be further investigated for a more comprehensive risk assessment.

### 4. Conclusion

In the present study, the occurrence and distribution of 14 OPEs in urban surface water of Beijing, China were explored. All of 14 OPEs were detected in the urban surface water samples, and TCEP and TCPP were the most abundant compounds followed by TMP, TEP and TBEP. The levels of these compounds in urban surface water in Beijing were higher than or similar to those detected in most of other sites in literature.

Spatial distribution of OPEs in urban surface water was also studied. Relatively high concentrations of OPEs were detected in other river samples than those detected in all lake waters and Chang River. Among several rivers, higher levels of OPEs were detected in the rivers located in southern and eastern urban of Beijing, which was probably due to the treated and untreated waste water systems and treated wastewater discharges. Most of these OPEs were detected in the urban surface water in Beijing in the summer, indicating a high concern of OPEs in these urban areas.

### Table 4

| Analytes          | Organisms                | L(EC)C50¹ (mg L$^{-1}$) | PNEC (ng L$^{-1}$) | RQs  |
|-------------------|--------------------------|-------------------------|--------------------|------|
| TCEP              | Algae (Scenedesmus subspicatus) | 51                      | 51,000             | 0–0.1117 |
|                   | Crustacean (Daphnia magna)| 330                     | 330,000            | 0–0.0173 |
|                   | Fish (Carassius auratus)  | 90                      | 90,000             | 0–0.0633 |
| TCDD              | Algae (Scenedesmus subspicatus) | 45                      | 45,000             | 0–0.0387 |
|                   | Crustacean (Daphnia magna)| 91                      | 91,000             | 0–0.0192 |
|                   | Fish (Poecilia reticulata)| 30                      | 30,000             | 0–0.0581 |
| TDCP              | Algae (Pseudokirchneriella subcapitata) | 39                      | 39,000             | 0–0.0219 |
|                   | Crustacean (Daphnia magna)| 4.2                     | 4200               | 0–0.2036 |
|                   | Fish (Carassius auratus)  | 5.1                     | 5100               | 0–0.1677 |
| TnBP              | Algae (Scenedesmus subspicatus) | 4.2                     | 4200               | 0–0.0609 |
|                   | Crustacean (Daphnia magna)| 3.65                    | 3650               | 0–0.0701 |
|                   | Fish (Carassius auratus)  | 8.8                     | 8800               | 0–0.0291 |
| TEP               | Algae (Scenedesmus subspicatus) | 34                      | 34,000             | 0–0.0050 |
|                   | Crustacean (Daphnia magna)| 11                      | 11,000             | 0–0.0153 |
|                   | Fish (Leuciscus idus)     | 20                      | 20,000             | 0–0.0084 |
| TBE                  | Algae (Scenedesmus subspicatus) | 900                     | 900,000            | 0–0.0023 |
|                   | Crustacean (Daphnia magna)| 350                     | 350,000            | 0–0.0059 |
|                   | Fish (Leuciscus idus)     | 2140                    | 2,140,000          | 0–0.0010 |
| TCPP              | Algae (Scenedesmus subspicatus) | 1                      | 1000               | 0–0.0963 |
|                   | Fish (Carassius auratus)  | 0.7                     | 700                | 0–0.1375 |
|                   | Crustacean (Daphnia magna)| 0.29                    | 290                | 0–0.0148 |
|                   | Fish (Leopemis macrochirius) | 0.27                    | 270                | 0–0.0159 |

¹ Acute toxicity (LC50 or EC50) data are obtained from (Verbruggen et al., 2005).
sewage discharge. Additionally, seasonal variation in the concentrations of OPEs in urban surface water was also observed, which revealed higher contamination in the summer (July and August). The high levels of OPEs detected in rainwater and road runoff samples (June to August) demonstrated that wet deposition was an important factor responsible for the high levels of OPEs in surface water in the summer season. Risk assessment based on acute toxicity data suggested the low or medium risk of OPEs to three aquatic organisms (algae, crustacean and fish). However, taking into account the high levels of OPEs in several sites in Beijing, long-term exposure and bioaccumulation of these pollutants in aquatic environment should be further explored.

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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.2015.11.008.

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