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Occurrence and screening-level risk assessment of organophosphate ester flame retardants and plasticizers in 40 rivers around the Bohai Sea, north China

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ABSTRACT: As an alternative of polybrominated diphenyl ethers (PBDEs), environmental level and risk assessment about organophosphate esters (OPEs) are required as the worldwide demand for OPEs has been increasing every year. This study focused on the spatial distribution and screening-level risk assessment of organophosphate ester flame retardants and plasticizers in 40 major rivers entering into the Bohai Sea, north China. Water samples were filtrated by glass fiber filters, then extracted by liquid-liquid extraction, and analyzed by gas chromatography-mass spectrometry (GC-MS) for 15 different OPE congeners and one synthetic intermediate triphenylphosphine oxide (TPPO). The sum of the OPE (ΣOPE) concentrations in 40 rivers

ranged from 10 to 1566 ng L^{-1}, with the mean ΣOPE concentration of 344 ng L^{-1}. Tri(1-chloro-2-propyl) phosphate (TCPP) (range: 5-921ng L^{-1}, with a mean concentration of 186 ng L^{-1}) and tri(2-choroethyl) phosphate (TCEP) (range:1 – 418 ng L^{-1}, mean:88 ng L^{-1}) were the most abundant OPEs in river waters of North China. It is noted that the concentration levels of TPPO (range: <LOD – 5852 ng L^{-1}, mean: 224 ng L^{-1}) were much higher than those reported in the Elbe, Germany. The riverine inputs of target organophosphorus compounds were estimated to be 8.0 t yr^{-1} for Liaodong Bay, 3.6 t yr^{-1} for Bohai Bay and 1.7 t yr^{-1} for Laizhou Bay, respectively. In addition, a screening-level risk assessment was conducted with RQ ranging from 0.0004 to 0.1129, which indicated no significant risk presented in all the 40 rivers. However, for these potentially persistent and bioaccumulative compounds, a refined and long-term risk assessment needs to be carried on.

Brief: Organophosphate ester flame retardants and plasticizers are ubiquitous in the aquatic environment and subject to emerging contaminants discharged into the coastal environment.

INTRODUCTION

Organophosphate esters (OPEs) have been used as flame retardants and plasticizers for decades due to their excellent physicochemical properties. Since brominated flame retardants (BFRs) have been gradually restricted worldwide due to the environmental concerns, OPEs, as an alternative of BFRs, have been increasingly used in many industrial applications and household products. Halogenated (chlorinated) OPEs are predominantly used as flame retardants in furniture, textiles, mattresses, electronics (e.g., televisions, cell phones), and even children products such as strollers, sleepwear and baby clothing.[1-5] Non-halogenated OPEs are mostly applied as plasticizers, antifoaming agents and additives.[1,2] Another organophosphorus

compound triphenylphosphine oxide (TPPO) is extensively employed as synthetic intermediate in pharmaceutical products and as ligand for many transitional metals.[6]

Organophosphorus flame retardants are listed in the High Production Volume Chemicals (HPVC) programme.[7] The global consumption of OPEs amounted to 500 000 t in 2011 and expected to reach 680.000 t in 2015.[8] In China, the production of PFRs (phosphorus flame retardants) was estimated to be 100 000 t in 2011 and demands for PFRs was expected to increase every year by 15%.[8] Since OPEs are not chemically bonded to polymeric materials and typically water soluble, they can easily leach out of the material into the environment via volatilization, abrasion, and dissolution.[9] Large production and consumption of OPEs resulted in high detection frequency in both domestic circumstance (air and dust) and nature environment (water, air and sediment) over the past decade.[9,10]

Halogenated OPEs have been proved to be persistent in the environment and resistant to hydrolysis in neutral pH.[10] Risk assessment with respect to human health for OPEs has not yet been completed.[10,11] Nevertheless, the draft on the risk assessment of tri(2-chloroethyl)phosphate (TCEP) recognized it's carcinogenicity, high toxicity and environmental persistence.[12] Furthermore, tri (dichloropropyl) phosphate (TDCPP) had been proved to be carcinogenic, and tri(1-chloro-2-propyl) phosphate (TCPP) and tributoxyethyl phosphate (TBEP) were also suspected carcinogens.[13,14] New York prohibited use of TCEP in children care products under the age of 3 from December 1, 2013.[15] After New York city, Washington will prohibit the use of TCEP and TDCPP in children products and home furniture in July 1, 2014.[16]

Considering the toxic effects of these compounds, together with the limited reports on the occurrence of OPEs in the environment, it is worthy to collect more information on these contaminants to fill our knowledge gaps of the fate of OPEs in the environment.

Bohai Sea is an enclosed inner sea of China, with huge amount of domestic sewage and industrial waste water pouring into it every day. Rivers are the major source/pathway responsible for the pollutants into the sea. According to a recent report about the water quality in the rivers emptying into the China coastal seas, all the 11 routine monitored rivers emptying into the Bohai Sea were equal to or lower than Level IV National Environmental Quality Standards for Surface Water, 5 of 11 rivers had even exceed the Level V standards.[17]

To investigate the distribution characteristics and fluxes of emerging organic compounds in the rivers around the Bohai Sea, 40 major rivers were selected. The rivers were chosen based on their length, water loading volume, pollution status according to previous studies and the total water volume of these 40 rivers accounted for about 96 % of these rivers emptying into the Bohai Sea and northern Yellow Sea, for detailed information see Table S1.

In the river basin areas, it has been subject to heavy anthropogenic influences owing to the high speed development of the agriculture, industry and economy during the past ca. 50 years.[18] There is one of the most important heavy industrial complexes in Northeast Asia, including chemical (flame retardants production), petrochemical, pharmaceutical, steel-iron, and machinery industries.[18] Nearly 100 billion tons of river water carried kinds of organic pollutants including OPEs flowing into the Bohai Sea in a year. Moreover, phosphorus is a key nutrient for marine phytoplankton and microbial communities, OPEs as a kind of organic phosphorus may play an important role in biogeochemical cycle of phorsphorus.[19] In the Bohai Sea, the limiting nutrients of phytoplankton was changed from nitrogen in the early 1980s to nitrogen-phosphorus in the late 1980s, and then to phosphorus after the 1990s.[20] Therefore, it is more worthy to estimate the riverine input of organic phosphorus such as OPEs.

In the present study, OPEs were analyzed to determine their occurrence in aqueous phase and their profiles in different rivers. In addition, the riverine input of OPEs into the Bohai Sea was

estimated and a risk assessment was conducted to evaluate the influence of OPEs. To the best of our knowledge, this is the first study of organophosphate esters (OPEs) in aqueous environment around Bohai Sea and the first report of environmental distribution of TPPO in China.

EXPERIMENTAL SECTION

Study area and sampling. Water samples were collected in 40 major rivers around the Bohai Sea and the north Yellow Sea in August 2013. The locations of sampling sites were shown in Figure 1. The total watershed area is up to 1 412 581 km^2, nearly 15% of China (Table S1).[21] The water sampling procedure was conforming to the Chinese National Standard -Technical Specifications Requirements for Monitoring of Surface Water and Waste Water (HJ/T91 2012) and changed with small modifications. In brief, sampling sites were chosen as close as the river mouth but avoided to the influence of salt water. In most of the rivers in this study, there are floodgates/dams near the river mouth to prevent the sea water intrusion during high tide period and also to keep the fresh water level high. Water samples were collected across the floodgates/dams and in some cases across the bridges. In each river, one transection with 3 to 5 points according to the river width was set, and a 10 L stainless steel bucket was used to collect the surface water. Three to five 10-L water samples were mixed together in one 60 L stainless steel bucket and one liter of mixed water was kept frozen in PET bottles prior to extraction. All the sampling buckets and PET bottles were rinsed with acetone in a clean-lab, and then river water three times on the spot.

Analysis. The water samples were filtrated by glass fiber filters (GFF, Φ: 47 mm, pore size: 0.7 μm). The filtrate was added with an aliquot of surrogate standard solution (D_{27} TnBP and D_{15} TPhP) and then extracted with 50 ml dichloromethane for 3 times. The extracts were combined and then concentrated to 150 μL for GC-MS analysis. 500 pg $^{13}C_6$-PCB 208 was added into each

sample as injection standard. The samples were analyzed by GC-MS (Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer) equipped with a PTV (programmed temperature vaporizer) injector. The GC separation was performed with a HP-5MS column (length: 30 m, ID: 0.25 mm; film: 0.25 μm, J&W Scientific). The PTV (2μL injection volume with a pulse pressure of 20 psi for 2 min and inlet temperature of 280 °C) was operated in PTV pulse splitless mode 50 °C (2 min) → 5 °C/min → 170 °C (5 min) →10 °C/min → 230 °C (5 min) → 5 °C/min → 270 °C → 30 °C/min →300 °C (10 min). The quadrupole was maintained at 150 °C and the ion source of the mass spectrometer was operated at 230 °C at 70 eV electron impact (EI). Selected masses of fragment ions for quantification and quantitation were listed in Table S1. The response factors were derived from the calibration curves (8-points) made for response ratio between target compounds and surrogate standards (0-5000 ng mL^{-1}).

This study covered 16 organophosphorus compounds: three halogenated (chlorinated) alkyl phosphates, including tris(1-chloro-2-propyl) phosphate (TCPP), tris(2-choroethyl) phosphate (TCEP), and tris(dichloroisopropyl) phosphate (TDCPP); ten non-halogenated alkyl phosphates, including trimethyl phosphate (TMP), triethyl phosphate (TEP), tri-*iso*-propyl phosphate (TiPrP), tri-*n*-propyl phosphate (TPrP), tri-*iso*-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TBP), tripentyl phosphate (TPeP), trihexyl phosphate (THP), tris(2-butoxyethyl) phosphate (TBEP), and tris(2-ethylhexyl) phosphate (TEHP); two aryl phosphates, including tricresyl phosphate (TCP), and triphenyl phosphate (TPP) and also the synthetic intermediate triphenylphosphine oxide (TPPO). Their acronym, chemical structures, applications, toxicity and CAS No. were given in Table 1.

Quality Assurance/Quality Control (QA/QC). The recoveries of spiked experiments were from 67 ± 2% (TPPO) to 95 ± 8% (TCEP) for 15 target organophosphorus compounds with a mean recovery of 81.4% (n=5), except from DMP (36 ± 2%). A method blank with each sample

batch (six samples) was included. The mean blanks were between 7 ± 3 (TPPO) to 235 ± 102 (TCPP) pg/L. The instrumental limit of detection (LOD) was defined as three times the signal-to-noise (S/N=3) and ranged from 0.1 pg (TnBP) to 6 pg (TBEP). The method detection limit (MDL) was defined as the mean field blank concentrations plus three times the standard deviation (3σ) of the field blanks and ranged from 0.018 (TPPO) to 0.55 (TCPP) pg/L (Table S2). All concentrations of organophosphorus compounds in this paper were not corrected for recoveries.

RESULTS AND DISCUSSION

Concentration and distribution characteristics. OPEs were detected in all samples with water phase concentrations decreasing as follows: TCPP (4.59~921 ng L^{-1}, mean: 187.20 ng L^{-1}), TCEP (1.29~268 ng L^{-1}, mean: 81 ng L^{-1}), TEP (<LOD~350 ng L^{-1}, mean: 43.6 ng L^{-1}), T*i*BP (<LOD~218 ng L^{-1}, mean: 13 ng L^{-1}). TPPO was up to 5850 ng L^{-1} in concentration. The detailed concentration data was listed in Table 2. Fig 2 presents the concentrations of TCPP, TCEP and TPPO in sampling rivers from northeast (Yalu River) to south (Jiahe River) around Bohai Sea. The distribution patterns of TCPP and TCEP are similar, which may indicate they came from the same source. What was worth noting, TPPO was detected with concentration <LOD to 370 ng L^{-1} in the samples except Jiehe River and Yalu River. It was up to 1280 ng L^{-1} and 5850 ng L^{-1} in Jiehe River and Yalu River, respectively, far higher than the rest of the rivers. In terms of rivers, Yalu River, Jiehe River, Jiahe River, Xiaoling River and Liugu River were the most contaminated by OPEs and TPPO, with a total concentration of 6079 ng L^{-1}, 2300 ng L^{-1}, 1590 ng L^{-1}, 1350 ng L^{-1}, and 1100 ng L^{-1}, respectively.

TCPP and TCEP were the most abundant OPEs in most of the rivers, while the sum of their concentrations ([TCPP] + [TCEP]) ranged from 41 to 98% (average 80%) of the Σ_{15}OPEs compositions (Fig 3). This behavior is in agreement with studies in Pearl River.[9] It may be

158 attribute to that TCPP and TCEP were two of the most common products of halogenated
159 phosphate esters and that they appeared to be the most recalcitrant in water.[10] However, TCEP
160 was not amid the most abundant OPEs in German rivers, for instance, Elbe, Rhineand four river
161 systems in Hessen.[22, 23] The difference could be explained by the industrial replacement of TCEP
162 by TCPP in Europe in the 1990s.[24] In this study, there was no reflection of the shift in usage from
163 TCEP to TCPP in China. TEP, TiBP, TDCPP, TBP, TPP and TBEP presented intermediate
164 concentration, ranging from <LOD to 350 ng L^{-1}. It may reflect the widespread distribution of
165 this family of contaminants in rivers influenced by anthropogenic pressures, as reported for other
166 sites previously. TMP, T*i*PrP, TPrP, TPeP, THP, TEHP and TCP were detected at the lowest
167 concentration or not detected out in most of the rivers. The different pattern of OPEs may
168 attribute to their difference in physicochemical properties and consequent difference in
169 accumulation features and degradability as well as difference in production and employment.
170 In addition, 37 of sampling rivers flowing into three bays of the Bohai Sea, namely, Liaodong
171 Bay, Bohai Bay and Laizhou Bay. It could be shown that the average concentrations of OPEs in
172 rivers flowing into Laizhou Bay (681 ng L^{-1}) were 1.2 times higher than in rivers flowing into
173 Liaodong Bay (545 ng L^{-1}) and more than 3.8 times higher than in rivers flowing into Bohai Bay
174 (180 ng L^{-1}). It was suggested that rivers flowing through the OPEs production sources
175 contributed to the high values.
176 There are very limited reports about TPPO in river water. Still, concentration of TPPO in this
177 study （0.70-5850 ng L^{-1}) was far higher than in Elbe (Germany, 10-40 ng L^{-1}) and in three
178 Volcanic Lakes (Italy, 2 ±1 ng L^{-1}).[1, 25] Although the concentration of TPPO was much lower in
179 contrast to this study it was assessed as one of the major organophosphorus compound. Since the
180 study area was one of the most important heavy industrial complexes in China, including

chemical, petrochemical, pharmaceutical, steel-iron, and machinery industries,[18] it may exert severe pressure on the environment.

To our knowledge, limited reports about the occurrence of OPEs in river water were available throughout the world. Concentrations of selected OPEs and TPPO in others studies in river water were listed in Table 3. In contrast to those published previously, organophosphorus compounds contamination in China maintained high level but not higher than UK. What's more, priority attention should be given to TPPO contamination.

Riverine input into the Bohai Sea. According to the samples concentrations and the annual runoff, the total riverine input of OPEs was estimated to be 18 t yr^{-1} and the total riverine input of TPPO was estimated to be 113 t yr^{-1}(Table S3). It's generally considered that riverine runoff plays an important role for the transportation of anthropogenic pollutants from terrestrial source to the ocean.[26] Liaodong Bay received relatively high riverine input of OPEs and TPPO with 8.0 t yr^{-1} in comparison to the Bohai Bay (3.6 t yr^{-1}) and Laizhou Bay (1.7 t yr^{-1}).

As we all know, river discharges are an important nutrient sources including phosphate for Bohai Sea. Especially for the phosphorus limitation trend of Bohai Sea, not only inorganic phosphate from riverine input is important but also the organic phosphate, for instance, organophosphorus compound, may make a difference.[20]

Risk assessment. As discussed earlier, China is facing severe organophosphorus compounds contamination. The risk assessment for river water organisms was estimated according to the water concentration of the most abundant and intermediate concentration organophosphorus compounds (TCPP, TCEP, TPPO, TEP, TiBP, TDCPP, TBP, TPP, and TBEP) and L(E)C_{50} of Daphnia *magna* and fish (only for TPPO), following the recommendation of the Technical Guidance Document on Risk Assessment.[27] Risk quotients were calculated according to:

$$RQ = \frac{MEC}{PNEC} = \frac{MEC}{EC_{50}/f}$$

Where MEC means environmental concentration, PNEC is the predicted no effect concentration, and f is the security factor or uncertainty factor. A value of 1000 is adopted in this work.[27] Data was interpreted by the maximum probable risk for ecological effects from river water was followed as recommended by.[28] It indicates no significant risk for RQ < 1.0, indicates a small potential for adverse effects for 1.0 ⩽ RQ < 10, and indicates significant potential for adverse effects for 10 ⩽RQ <100. In other words, the exposure point concentration is equal to or one hundred times greater than the risk screening benchmark. It is indicated that potential adverse effects should be expected when RQ equal of great than 100.

The toxicological relevant concentrations (LC50 or EC50) used for RQ calculations are summarized in Table S4, and the RQs results calculated for each compound in the rivers are listed Table S5. RQs for TCPP, TCEP, TEP, TiBP, TDCPP, TBP, TPP, and TBEP varied from 0 to 0.02 for daphnia magna. RQs for TPPO varied from 0.00001 to 0.11 for fish. As a consequence, no significant risk (RQ < 1) was estimated along all the 40 rivers for daphnia magna (TPPO for fish).

Although no significant risk was observed to the aquatic organisms considering short-term exposure, organophosphorus compounds are potentially persistent in water. Concentration of TCEP is still relatively high in Europe (Table 3) even though it had been replaced by TCPP 20 years ago. Moreover, it had been proved that organophosphorus flame retardants can be accumulated in biota. Therefore, more detection and risk assessment of organophosphorus compounds in aquatic ecosystem for either short-term or long-term should be carried on.

Environmental implication. This study was carried out screening-level occurrence and risk assessment for OPEs in rivers flowing into the Bohai Sea, which located in one of the most

important heavy industrial complexes in Northeast Asia with heavy anthropogenic influences owing to the high speed development of the agriculture, industry and economy during the past 50 years. Chlorinated OPE, e.g. TCPP and TCEP were the most abundant OPEs in river waters of North China, indicating the influence of large production and consumption of chlorinated OPE in the regions around Bohai Sea. Priority should be given to TPPO due to its relatively high concentration in river waters and the report that it is harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Though no significant risk was estimated for OPEs along all the 40 rivers for daphnia magna (TPPO for fish), considering the large production and consumption of OPEs in China and the fact that New York and Washington have already restricted the usage of TCEP and TDCPP, there is a need to conduct more studies on occurrence and risk assessment of organophosphate ester (OPE) flame retardants and plasticizers in the aquatic ecosystem and coastal environment.

ASSOCIATED CONTENT

Supporting information

Additional figures and tables are given in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Bollmann, U. E.; Moller, A.; Xie, Z.; Ebinghaus, R.; Einax, J. W., Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water research* **2012,** *46*, (2), 531-8.
2. Regnery, J.; Puttmann, W., Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. *Water research* **2010,** *44*, (14), 4097-104.
3. Stapleton, H. M.; Klosterhaus, S.; Eagle, S.; Fuh, J.; Meeker, J. D.; Blum, A.; Webster, T. F., Detection of Organophosphate Flame Retardants in Furniture Foam and U.S. House Dust. *Environmental science & technology* **2009,** *43*, 7490-7495.
4. Salamova, A.; Ma, Y.; Venier, M.; Hites, R. A., High Levels of Organophosphate Flame Retardants in the Great Lakes Atmosphere. *Environmental Science & Technology Letters* **2014,** *1*, (1), 8-14.
5. CTIF http://www.cefic-efra.com/index.php/furniture-a-textile/introduction (Oct.14),
6. Fuheng, H.; Wang, L.; Shuangfei, C., Solubilities of Triphenylphosphine Oxide in Selected Solvents. *J. Chem. Eng.* **2009,** *54*, 1382-1394.
7. Veen, I. v. d.; Boer, J. d., Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012,** *88*, (10), 1119-53.
8. Ou, Y. X., Developments of organic phosphorus flame retardant industry in China. *Chemical Industry and Engineering Progress* **2011,** *30*, (1), 210-215.
9. Wang, X.; He, Y.; Lin, L.; Zeng, F.; Luan, T., Application of fully automatic hollow fiber liquid phase microextraction to assess the distribution of organophosphate esters in the Pearl River Estuaries. *The Science of the total environment* **2014,** *470-471*, 263-9.
10. Reemtsma, T.; Quintana, J. B.; Rodil, R.; Garcı´a-López, M.; Rodrı´guez, I., Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *TrAC Trends in Analytical Chemistry* **2008,** *27*, (9), 727-737.
11. Waaijers, S. L.; Hartmann, J.; Soeter, A. M.; Helmus, R.; Kools, S. A.; de Voogt, P.; Admiraal, W.; Parsons, J. R.; Kraak, M. H., Toxicity of new generation flame retardants to Daphnia magna. *The Science of the total environment* **2013,** *463-464*, 1042-8.
12. *European Commission, EU Risk Assessment Report, Tris (2-chloroethyl) phosphate, TCEP, Draft* 2006.
13. WHO, Environmental Health Criteria 209. In *Flame Retardants: Tris(chloropropyl) phosphate and Tris(2-chloroethyl) phosphate*, Geneva,Switzerland, 1998.

14. WHO, Environmental Health Criteria 209. In *Flame Retardants: Tris(2-butoxyethyl) phosphate, Tris(2-ethylhexyl) phosphateand Tetrakis (hydroxymethyl) phosphonium salts*, Geneva,Switzerland, 2000.
15. Prohibits the manufacture, distribution, and sale of child care products containing TRIS. In *NY A06195*, 2011.
16. Toxic-Free Kids and Families Act :An act relating to flame retardants. In *ESHB 1294*, 2013.
17. SOA, Marine Environmental Information, section 8 (total 21),State Oceanic Administration People's Republic of China. In 2013; Vol. 2014.
18. Men, B.; He, M.; Tan, L.; Lin, C., Distributions of polychlorinated biphenyls in the Daliao River estuary of Liaodong Bay, Bohai Sea (China). *Mar Pollut Bull* **2014,** *78*, (1-2), 77-84.
19. Jiménez, J. C.; Berrojalbiz, N.; Pizarro, M.; Dachs, J., Organophosphate ester (OPE) flame retardants and plasticizers in the open Mediterranean and Black Seas atmosphere. *Environmental science & technology* **2014,** *48*, (6), 3203-9.
20. Liu, H.; Yin, B. S., Numerical investigation of nutrient limitations in the Bohai Sea. *Marine environmental research* **2010,** *70*, (3-4), 308-317.
21. Cui, Z. Study on Scheme of Total Emission Control of Main Chemical Pollutants in 13 Cities around Bohai Sea. PhD thesis, Ocean University of China, 2008.
22. Quednow, K.; Püttmann, W., Organophosphates and Synthetic Musk Fragrances in Freshwater Streams in Hessen/Germany. *Clean – Soil, Air, Water* **2008,** *36*, (1), 70-77.
23. Wang, X. W.; Liu, J. F.; Yin, Y. G., Development of an ultra-high-performance liquid chromatography-tandem mass spectrometry method for high throughput determination of organophosphorus flame retardants in environmental water. *Journal of chromatography. A* **2011,** *1218*, (38), 6705-11.
24. Quednow, K.; Puttmann, W., Temporal concentration changes of DEET, TCEP, terbutryn, and nonylphenols in freshwater streams of Hesse, Germany: possible influence of mandatory regulations and voluntary environmental agreements. *Environmental Science and Pollution Research* **2009,** *16*, (6), 630-640.
25. Bacaloni, A.; Cucci, F.; Guarino, C.; Nazzari, M.; Samperi, R.; Lagana, A., Occurrence of Organophosphorus Flame Retardant and Plasticizers in Three Volcanic Lakes of Central Italy. *Environ. Sci. Technol.* **2008,** *42*, 1898-1903.
26. Regnery, J.; Puttmann, W., Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. *Chemosphere* **2010,** *78*, (8), 958-64.
27. European Commission, Technical Guidance Document in supportof Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. 2nd Edition. In Bureau, E. C., Ed. Ispra, Italy, 2003.
28. Wentsel, R. S.; Thomas, W.; Point, L.; Simini, M.; Checkai, R. T.; Ludwig, D., *Tri-service procedural guidelines for ecological risk assessments*. Defense Technical Information Center: 1996.
29. Etter, M. C.; Baures, P. W., Triphenylphosphine Oxide as a Crystallization Aid. *J. Am. Chem. SOC* **1987,** *110*, 639-640.
30. Yan, X.; He, H.; Peng, Y.; Wang, X.; Gao, Z.; Yang, S.; Sun, C., Determination of Organophosphorus Flame Retardants in Surface Water by Solid Phase Extraction Coupled with

Gas Chromatography-Mass Spectrometry. *Chinese Journal of Analytical Chemistry* **2012,** *40*, (11), 1693-1697.
31. Cristale, J.; Katsoyiannis, A.; Sweetman, A. J.; Jones, K. C.; Lacorte, S., Occurrence and risk assessment of organophosphorus and brominated flame retardants in the River Aire (UK). *Environmental pollution* **2013,** *179*, 194-200.
32. Cristale, J.; Katsoyiannis, A.; Chen, C.; Jones, K. C.; Lacorte, S., Assessment of flame retardants in river water using a ceramic dosimeter passive sampler. *Environmental pollution* **2013,** *172*, 163-9.
33. Cristale, J.; Garcia Vazquez, A.; Barata, C.; Lacorte, S., Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk assessment. *Environment international* **2013,** *59*, 232-43.
34. Martinez-Carballo, E.; Gonzalez-Barreiro, C.; Sitka, A.; Scharf, S.; Gans, O., Determination of selected organophosphate esters in the aquatic environment of Austria. *The Science of the total environment* **2007,** *388*, (1-3), 290-9.
35. Kim, S. D.; Cho, J.; Kim, I. S.; Vanderford, B. J.; Snyder, S. A., Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water research* **2007,** *41*, (5), 1013-21.
36. Haggard, B. E.; Galloway, J. M.; Green, W. R.; Meyer, M. T., Pharmaceuticals and other organic chemicals in selected north-central and northwestern Arkansas streams. *J. Environ. Qual.* **2006,** *35*, (4), 1078-1087.

Figure caption

Figure 1: Sampling sites in the 40 rivers around the Bohai Sea

Figure 2: Occurrence of TCPP, TCEP and TPPO in 40 sampling rivers in ng L^{-1}around the Bohai sea from northeast (Yalu River) to south (Jiahe River)

Figure 3: Percentage composition of 15 OPEs in the river water

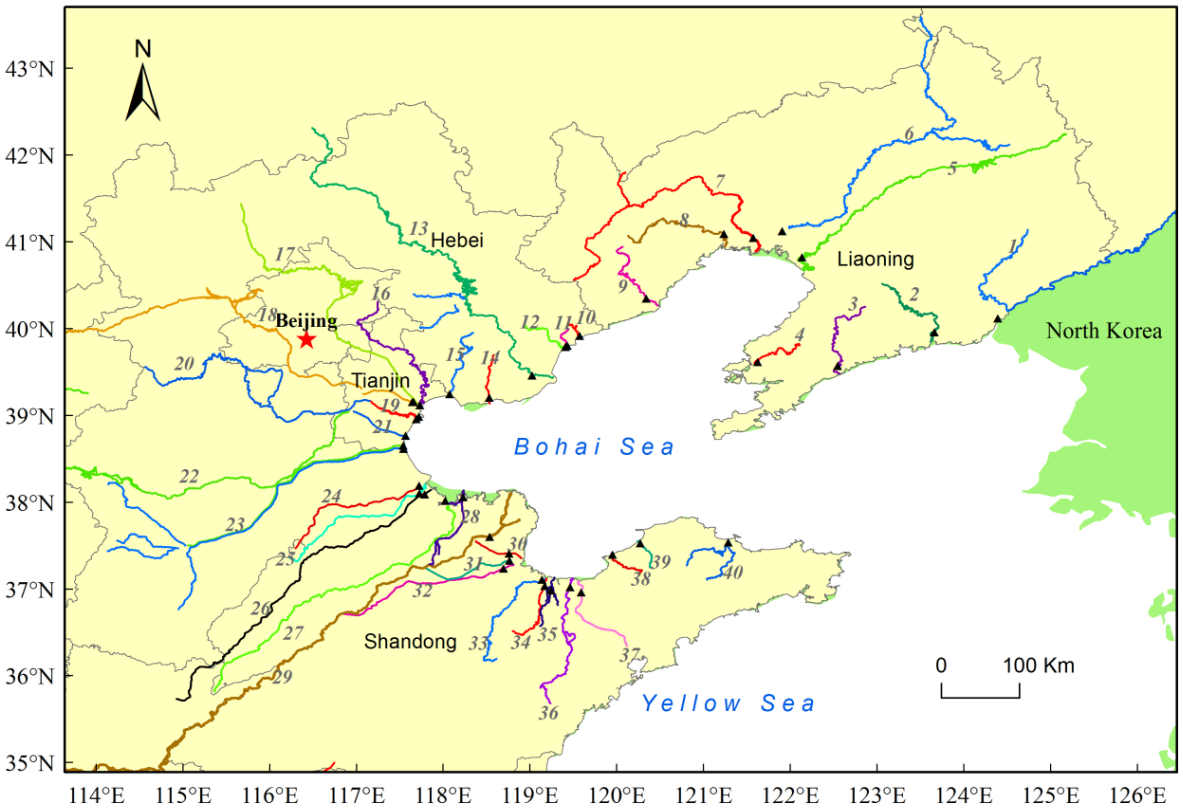
Table title

Table 1: The chemical structures, applications, toxicity, CAS No. and physicochemical. properties (log K_{OW}: n-octanol-water partition coefficient, WS: water solubility, VP: vapor pressure) of the OPEs and TPPO in this study

Table 2: 16 target organophosphorus compounds concentrations in 40 rivers around Bohai Sea, north China

Table 3. Concentrations of selected OPEs and TPPO in different studies in river water in the world (ng L^{-1})

Figure 1:



No.	river	No.	river
1	Yalu River	21	Dagupaiwu River
2	Dayang River	22	Ziya River
3	Biliu River	23	Beipai River
4	Fuzhou River	24	Xuanhui River
5	Daliao River	25	Zhangweixin River
6	Liaohe River	26	Majia River
7	Daling River	27	Tuhai River
8	Xiaoling River	28	Chaohe River
9	Liugu River	29	Yellow River
10	Tanghe River	30	Guangli River
11	Daihe River	31	Zimai River
12	Yanghe River	32	Xiaoqing River
13	Luanhe River	33	Mihe River
14	Xiaoqinglong River	34	Bailang River
15	Douhe River	35	Yuhe River
16	Jiyun River	36	Weihe River
17	Chaobai River	37	Jiaolai River
18	Yongdingxin River	38	Wanghe River
19	Haihe River	39	Jiehe River
20	Duliujian River	40	Jiahe River

Figure 2:

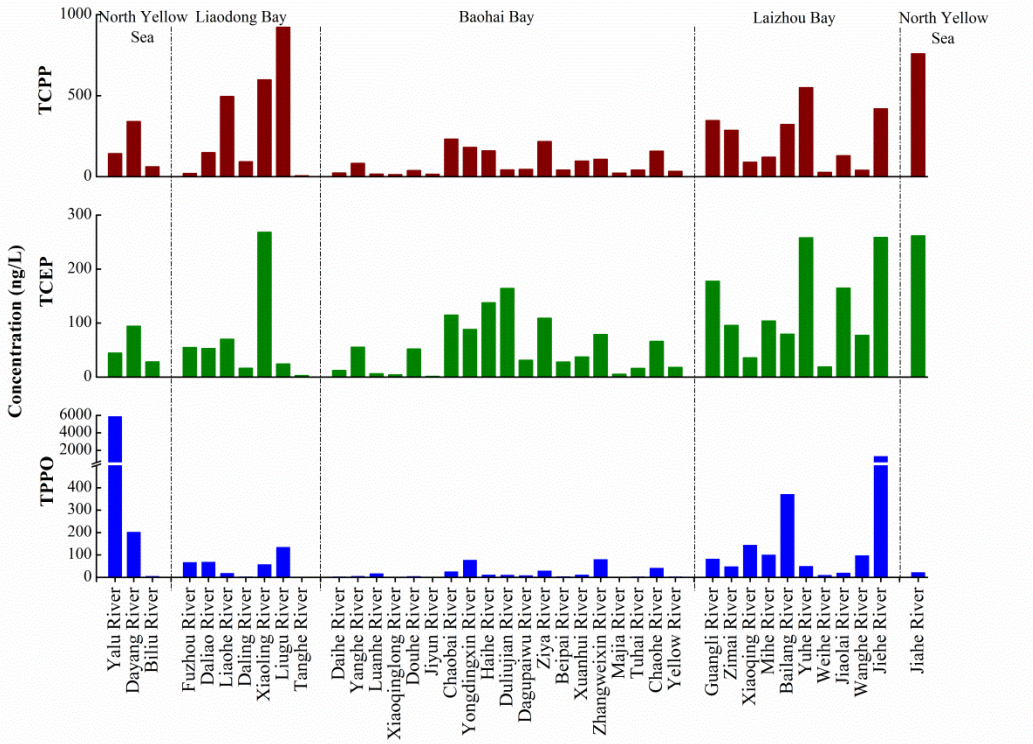

North Yellow Sea
Liaodong Bay
Baohai Bay
Laizhou Bay
North Yellow Sea
TCPP
TCEP
TPPO
Concentration (ng/L)
Yalu River
Dayang River
Biliu River
Fuzhou River
Daliao River
Liaohe River
Daling River
Xiaoling River
Liugu River
Tanghe River
Daihe River
Yanghe River
Luanhe River
Xiaoqinglong River
Douhe River
Jiyun River
Chaobai River
Yongdingxin River
Haihe River
Duliujian River
Dagupaiwu River
Ziya River
Beipai River
Xuanhui River
Zhangweixin River
Majia River
Tuhai River
Chaohe River
Yellow River
Guangli River
Zimai River
Xiaoqing River
Mihe River
Bailang River
Yuhe River
Weihe River
Jiaolai River
Wanghe River
Jiehe River
Jiahe River

Figure 3:

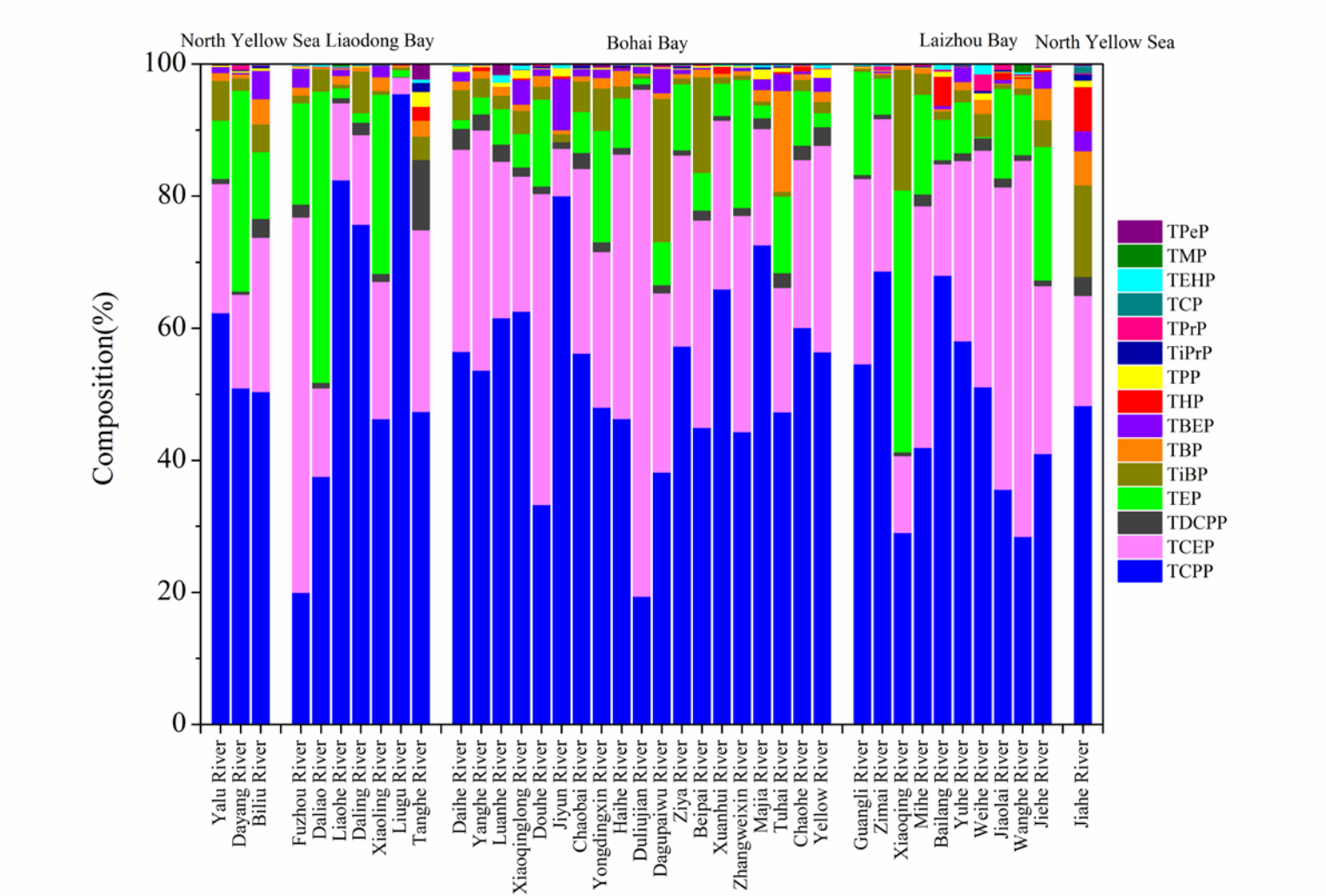
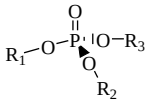
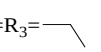
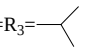

North Yellow Sea
Liaodong Bay
Bohai Bay
Laizhou Bay
North Yellow Sea
Composition(%)
100
80
60
40
20
0
TPeP
TMP
TEHP
TCP
TPrP
TiPrP
TPP
THP
TBEP
TBP
TiBP
TEP
TDCPP
TCEP
TCPP
Yalu River
Dayang River
Biliu River
Fuzhou River
Daliao River
Liaohe River
Daling River
Xiaoling River
Liugu River
Tanghe River
Daihe River
Yanghe River
Luanhe River
Xiaoqinglong River
Douhe River
Jiyun River
Chaobai River
Yongdingxin River
Haihe River
Duliujian River
Dagupaiwu River
Ziya River
Beipai River
Xuanhui River
Zhangweixin River
Majia River
Tuhai River
Chaohe River
Yellow River
Guangli River
Zimai River
Xiaoqing River
Mihe River
Bailang River
Yuhe River
Weihe River
Jiaolai River
Wanghe River
Jiehe River
Jiahe River

Table 1. The chemical structures, applications, toxicity, CAS No. and physicochemical. properties (log K_{OW}: n-octanol-water partition coefficient, W_S: water solubility, V_P: vapor pressure) of the OPEs and TPPO in this study

Acronym	Chemical structure 	Applications [1, 6, 29]	Toxicity [13, 14, 30, 4, 31]	phys.-chem. properties[1]	CAS no. [1]
TCPP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer	suspected carcinogenicity ; bioaccumulation； suspected toxicity;	log K_{OW} =2.59 W_S = 1.2 g L^{-1} V_P = 2.7·10^{-3} Pa	13674-84-5
TCEP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, lacquer/paint/glue, industrial processes	carcinogenicity ； neurotoxicity； suspected toxicity;	log K_{OW} =1.44 W_S = 7.0 g L^{-1} V_P = 8.2 Pa	115-96-8
TDCPP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, lacquer/paint/glue	carcinogenicity； neurotoxicity； higher acute toxicity than TCEP and TCPP	log K_{OW} = 3.65 W_S = 7.0·10^{-3} g L^{-1} V_P = 9.8·10^{-6} Pa	13674-87-8
TMP	$R_1=R_2=R_3=CH_3$	industrial processes(pharmaceutical, pesticide solvent and extractant)	n.a.	log K_{OW} = -0.65 W_S = 500 g L^{-1} V_P = 113 Pa	512-56-1
TEP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, industrial processes(raw materials of pesticides)	n.a.	log K_{OW} = 0.8 W_S = 500 g L^{-1} V_P = 52.4 Pa	78-40-0
T*i*PrP	$R_1=R_2=R_3=$ 	n.a.	n.a.	log K_{OW} = 2.12 W_S = 0.50 g L^{-1} V_P = 18.4 Pa	513-02-0
TPrP	$R_1=R_2=R_3=$ 	n.a.	n.a.	log K_{OW} = 1.87 W_S = 6.5 g L^{-1} V_P = 0.58 Pa	513-08-6
T*i*BP	$R_1=R_2=R_3=$ 	lacquer/paint/glue, anti-foaming agent, industrial processes	n.a.	log K_{OW} = 3.6 W_S = 1.6·10^{-2} g L^{-1} V_P = 1.71 Pa	126-71-6
TBP	$R_1=R_2=R_3=$ 	plasticizer, hydraulic fluid, floor covering, lacquer/paint/glue, anti-foaming agent,	suspected neurotoxicity	log K_{OW} = 4.0 W_S = 0.28 g L^{-1}	126-73-8

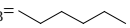
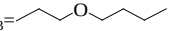
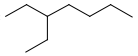
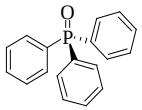
		industrial processes		V_P = 0.15 Pa log K_{OW} = 5.29	
TPeP	$R_1=R_2=R_3=$ 	n.a.	n.a.	$W_S = 3.3 \cdot 10^{-4}$ g L^{-1} $V_P = 2.2 \cdot 10^{-3}$ Pa	2528-38-3
THP	$R_1=R_2=R_3=$ 	n.a.	n.a.	n.a.	2528-39-4
TBEP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, fungus resistance, lacquer/paint/glue, anti-foaming agent	suspected carcinogenicity	log K_{OW} = 3.75 W_S = 1.1 g L^{-1} $V_P = 3.3 \cdot 10^{-6}$ Pa	78-51-3
TEHP	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, fungus resistance	n.a.	log K_{OW} = 9.49 $W_S = 6.0 \cdot 10^{-4}$ g L^{-1} $V_P = 1.1 \cdot 10^{-5}$ Pa	78-42-2
TCP	$R_1=R_2=R_3=$ 	flame retardant, hydraulic fluid, lacquer/paint/glue, industrial processes	n.a.	log K_{OW} = 5.11 $W_S = 3.6 \cdot 10^{-4}$ g L^{-1} $V_P = 8.0 \cdot 10^{-5}$ Pa	1330-78-5
TPP (TPhP)	$R_1=R_2=R_3=$ 	flame retardant, plasticizer, hydraulic fluid, lacquer/paint/glue	suspected neurotoxicity; high toxicity; bioaccumulation	log K_{OW} = 4.59 $W_S = 1.9 \cdot 10^{-3}$ g L^{-1} $V_P = 8.4 \cdot 10^{-4}$ Pa	115-86-6
TPPO		flame-retardant; ligand for many metals; solvent extraction; synthetic intermediate Crystallization Aid	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment	log K_{OW} = 2.83 $W_S = 6.3 \cdot 10^{-2}$ g L^{-1} $V_P = 3.47 \cdot 10^{-7}$ Pa	791-28-6

Table 2. 16 target organophosphorus compounds concentrations in 40 rivers around Bohai Sea, north China

Compound	Min (ng L^{-1})	Max (ng L^{-1})	Mean (ng L^{-1})	Median (ng L^{-1})	Detection rate (%)
TCPP	4.59	921	186	101	100
TCEP	1.29	268	80.2	54.9	100
TDCPP	0.19	44.5	4.34	2.57	100
TEP	0	350	43.0	13.4	93
T*i*BP	0.18	218	13.4	3.67	100
TBP	0.10	80.9	6.27	1.59	100
TBEP	0	47.2	4.21	1.17	73
THP	0	104	3.47	0.00	50
TPP	0	15.7	0.95	0.34	98
T*i*PrP	0	14.7	0.70	0.09	70
TPrP	0	5.06	0.63	0.20	75
TCP	0	15.0	0.39	0.00	95
TEHP	0	3.33	0.35	0.14	78
TPeP	0	3.07	0.17	0.02	58
TMP	0	1.63	0.08	0.00	5
TPPO	0.70	5850	224	19.8	100

Table 3. Concentrations of selected OPEs and TPPO in different studies in river water in the world (ng L^{-1})

River	Location	TCPP	TCEP	TEP	TiBP	TDCPP	TBP	TPP	TBEP	TPPO	Ref.
40 rivers	North China	5-921	1-268	<LOD-350	<LOD-218	<LOD-44	<LOD -81	<LOD-16	<LOD-47	<LOD -5852	This study
Pearl River Estuaries	South China	150-1150	220-1160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[9]
Songhua River	Northeast China	5-190	38-3700	5-190	n.a.	2-46	87-960	5-65	5-310	n.a.	[23]
Elbe	Germany	40-250	5-20	10-180	10-50	n.a.	2-8	<LOD-4	<LOD-80	10-40	[1]
Rhine	Germany	75-160	12-25	n.a.	17-84	n.a.	6-28	1-2	28-54	n.a.	[1]
Four streams	Germany	<LOD-2914	<LOD-557	n.a.	n.a.	<LOD-1284	<LOD-3889	n.a.	<LOD-1773	n.a.	[22]
Aire	UK	113-26050	119-316	n.a.	n.a.	62-149	n.a.	6-22	n.a.	n.a.	[31]
Aire	UK	4821	181	n.a.	n.a.	49	n.a.	17	n.a.	n.a.	[32]
Navarra，Asturias，Catalonia	Spain	<LOD-1800	<LOD-330	n.a.	<LOD-1200	<LOD-200	<LOD-370	<LOD-18	<LOD-4600	n.a.	[33]
Three rivers	Austria	33-170	13-130	13-51	n.a.	<LOD-19	20-110	<LOD-10	24-500	n.a.	[34]
three major rivers	South Korea.	n.a.	42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[35]
Arkansas streams	USA	n.a.	48-700	n.a.	n.a.	n.a.	31-560	n.a.	n.a.	n.a.	[36]

<LOD: below limit of detection; <LOQ: below limit of quantification; n.a.: not available