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Temporal-spatial distributions and ecological risks of perfluoroalkyl acids (PFAAs) in the surface water from the fifth-largest freshwater lake in China (Lake Chaohu)

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ABSTRACT

To investigate the residues, compositions, distributions and potential ecological risks of perfluoroalkyl acids (PFAAs), water samples were collected seasonally between August 2011 and November 2012 from 20 sites in Lake Chaohu and its tributary rivers. The mean concentration of total PFAAs (TPFAAs) was 14.46 ± 6.84 ng/L. PFOA was the predominant contaminant (8.62 ± 4.40 ng/L), followed by PFBA (2.04 ± 1.16 ng/L) and PFHxA (1.23 ± 1.50 ng/L). The TPFAAs concentrations peaked in August 2012 in each area, except for the western river. The opposite spatial trends were found for PFOA and PFOS in both the lake and river areas. Except for PFOS and PFUdA, the levels of TPFAAs and PFAAs were significantly related to the composition of fluorescent dissolved organic matter (FDOM) but not related to total DOM expressed by dissolved organic carbon (DOC). The risk of PFOS determined by a species sensitivity distribution model was notably above that of PFOA.

1. Introduction

Perfluorochemicals, particularly perfluoroalkyl acids (PFAAs), have been produced and used for more than 50 years (Giesy and Kannan, 2001) and have been widely applied in fire-fighting foams, carpets, paints, oil-resistant coatings for food contact paper, textiles, and leather (Giesy et al., 2002; Begley et al., 2005; Gewurtz et al., 2009). PFAAs are stable, persistent, and difficult to degrade in the environment because of their strong C—F bond (Key et al., 1997). In May 2009, perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride were listed in the Annex B of the Stockholm Convention text (SCPOPs 2009).

There are many studies examining the distribution and composition of PFAAs in surface water (Boulanger et al., 2004; So et al., 2004; Clara et al., 2009; Murakami et al., 2009; De Silva et al., 2011; Sun et al., 2011; Wang et al., 2012; Zhou et al., 2012; Flores et al., 2013; Hong et al., 2013; Yu et al., 2013; Zhou et al., 2013); however, studies on the effect factors, such as the water environmental factor and the composition of dissolved organic matter, are limited (Ahrens et al., 2009). Additionally, numerous researchers have focused on human exposure to PFAAs (such as in breast milk, drinking water, and food) and health risks (Lau et al., 2007; ATSDR, 2009), but there is a lack of studies concerning their ecological risks. Therefore, it is necessary to conduct relevant research to fully understand the environmental behavior, the toxic effects, and the risks of PFAAs.

Lake Chaohu is the fifth-largest freshwater lake and one of the most eutrophic lakes in China, with a water area of approximately 760 km^2. Our previous studies showed that persistent organic pollutants (POPs) were at high concentration levels; for example, the concentrations of PAHs were 150.3 ± 31.4 ng/L in the water and 60.85 ± 46.17 ng/m^3 in the air (Qin et al., 2013a, 2013b), the concentration of OCPs was 132.4 ± 432.1 ng/L in the water (Liu et al., 2013; Ouyang et al., 2013), and the concentrations of BDEs were 713.8 ± 368.9 pg/g in the sediment and 86.2 ± 59.4 pg/m^3 in the air (He et al., 2013a, 2013b, 2014b). However, there is still a lack of research on PFAAs in Lake Chaohu. The primary purposes of this study are (1) to perform a seasonal investigation into the

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occurrence, composition and temporal-spatial variation of PFAAs in the surface water, (2) to explore the effects of water environmental factors and dissolved organic matter on the PFAAs residues and their distribution in the surface water, and (3) to evaluate the individual and combined ecological risks of PFAAs in the surface water.

2. Materials and methods

2.1. Measurement of PFAAs in the water

The water samples from twenty sites in Lake Chaohu and the surrounding rivers (Fig. 1) were collected in August 2011, November 2011, February 2012, May 2012, August 2012, and November 2012. The detail information on the site distributions and water sampling were presented in the Text S1 in the Supporting Information (SI).

The water sample preparation followed a published method (Taniyasu et al., 2005; Wang et al., 2014) with several modifications (please see the Text S2 in the SI for the details). The samples were analyzed using an Agilent 1290 Infinity HPLC System coupled with an Agilent 6460 triple quadrupole LC/MS System (Agilent Technologies, USA). A Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 3.5 μm, Agilent Technologies, USA) was used, and the column temperature was 40 °C. An ammonium acetate solution at 2 mM (solvent A) and acetonitrile (solvent B) were used as mobile phases. Gradient conditions were: 5 μL sample was injected at a flow rate of 0.3 ml/min, starting with 80% A and 20% B, and the condition was held for 13 min, then increased to 90% B at 14 min. The source gas (N_2) flow rate and temperature were maintained at 9 L/min and 350 °C, respectively. The MS/MS was operated under negative ESI modes.

PP bottles were used, and polytetrafluoroethylene (PTFE) and other fluorinated materials were avoided during sampling, extraction and analysis. To ensure the reliability of the data, a field blank, solvent blank, and procedure blank were analyzed. Tests for the recovery of the method and the limit of detection were performed before the water sample analysis. The solvent blank was performed by using 100% methanol (HPLC grade) and run after 10 samples during the instrumental analysis. The field blank was prepared using Milli-Q water and stored in the same container as the samples. The procedure blank was also prepared by using Milli-Q water. Both the field blank and procedure blank were analyzed routinely to examine whether there was contamination during the sampling and extraction. There were no detectable PFAAs over the limit of quantification in all these blanks. The procedure recovery and matrix spike recovery tests were performed. For the procedure recovery, 10 ng mixtures of 17 native PFAAs standards were spiked into 1 L Milli-Q water and 1 L water samples. For the matrix spike recovery, mass labeled standards, including [1, 2, 3, 4 ^{13}C] PFBA, [1, 2, 3, 4 ^{13}C] PFOA, [1, 2 ^{13}C] PFDoA, [1, 2 ^{18}O] PFHxS, and [1, 2, 3, 4 ^{13}C] PFOS), were used (Table S1).

2.2. Other analyses

Other analyses including the dissolved organic carbon (DOC) and the three-dimensional spectra were presented in the Text S3 in the SI.

2.3. Ecological risk assessment of PFAAs in the water

The species sensitivity distribution (SSD) method was applied for the ecological risk assessment of PFAAs in the water. The general procedures and basic assumption of the SSD method were presented in the Text S4 in the SI. Based on the availability of the toxicity data, only two PFAA components, PFOA and PFOS, were selected. The chronic toxicity data (NOEC) of PFOA and PFOS to multiple aquatic species were collected from the database ECOTOX provided by the U.S. EPA (www.epa.gov/ecotox) (Table S2) (Kefford et al., 2011; Mu et al., 2014).

A software system, the Bayesian Matbugs Calculator (BMC), which was developed by our group (He et al., 2014a, 2014c) was applied to select the best SSD model (please see the Text S4 in the SI for the details). The log-normal distribution was identified as the best SSD model for PFOA and PFOS (Fig. 2). Fig. 2C shows that PFOS has much higher toxicity effects on aquatic species than that of PFOA under the same concentration. The hazardous concentration at 5% of species (HC_5) for PFOS (14.79 μg/L) is two orders of magnitude lower than that for PFOA (4087 μg/L).

The PAFs and multi-substance potentially affected fractions (msPAFs) could be calculated based on the SSD model for assessing the individual and combined ecological risk assessment of PFOA and PFOS (see 3.4 for details).

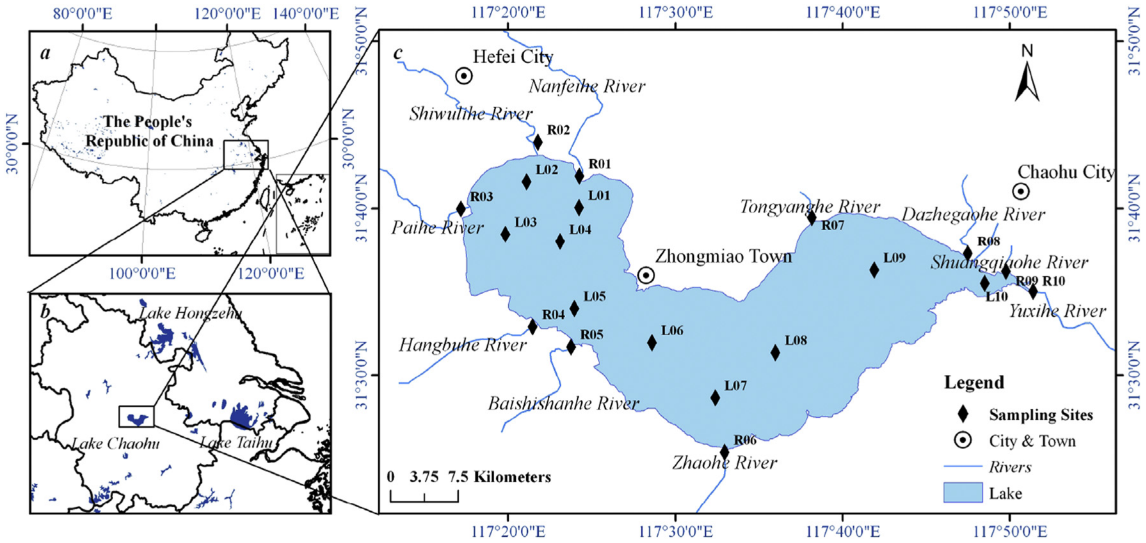

Fig. 1. The location of Lake Chaohu and the distribution of the sampling sites.