Investigation of Perfluoroalkyl Acids in Taihu Lake: Occurrence, Transport and Environmental Risk Assessment

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Abstract The presence of perfluoroalkyl acids (PFAAs) in Taihu Lake, China has been determined in surface water and sediments. A polar organic chemical integrative sampler (POCIS) was successfully used to quantify the concentration of PFAAs in the surface water. The concentrations of PFAAs were estimated by POCIS in the field, ranged from 11.79 ng/L to 390.77 ng/L at the sampling locations. The concentrations of PFAAs in sediments were ranged from 0.52 ng/L to 13.58 ng/L. Perfluorooctanoate was the most abundant compound detected in Taihu Lake with mean concentration of 289.34 ng/L in water and 12.6 ng/g dw in sediments. Risk quotient posed by PFAAs were assessed for different aquatic organisms. The results indicated that PFAAs had no risk to aquatic organisms in Taihu Lake system.

1. Introduction
Perfluoroalkyl acids (PFAAs) are a group of very persistent organic compounds, which have been produced since 1950. They are widely used in industrial applications and consumer because of their unique amphiphilic properties [1]. Direct and diffuse sources of PFAAs to environment together with precursor degradation and stability leads to presence of PFAAs in the environment [2]. Recent reports have released that PFAAs have toxic potential to aquatic organisms [3]. To protect aquatic organisms from these compounds, more information is needed about their environmental potential effects.

Considering the potential effects of PFAAs in aquatic systems, there is an urgent need for their regular monitoring. Conventional sampling for PFAAs in water is primarily utilized active sampling techniques, but these techniques only provide a snapshot of the contamination and may miss fluctuations in pollutant levels [4]. To overcome drawbacks of active sampling, passive sampling device has been widely adopted for field campaigns. Passive samplers can be exposed for long time in the aquatic environment, leading to the accumulation of compounds inside the receiving phase. If the sampling rate (Rs) of the compounds is known, analysis of compounds amount trapped in the receiving phase can calculate the time-weighted average (TWA) concentration over a specific period [5]. Recently the passive sampler POCIS has been widely used to monitor many water soluble compounds in aquatic systems.

The objective of this study were (1) to monitor and compared the concentration of PFAAs in water from active and POCIS sampling, (2) to determine the concentrations of PFAAs in sediment, and (3) to evaluate the environmental implications of PFAAs on different aquatic organisms.

2. Materials and methods

2.1 Materials and reagents
Perfluoroalkyl acids (J&K Chemical Ltd., China) investigated in this work were dissolved in methanol (Merck, Germany). $^{13}$C-labeled PFOA (Wellington Laboratories, Canada) was diluted in methanol. POCIS were constructed as described by Kaserzon et al. (2012) [6]. The POCIS comprised of 200 mg of weak anion-exchange (WAX) sorbent, and was packed between two polyethersulfone membranes.

2.2 Calibration of passive sampler
To determine sampler rate of POCIS, the passive sampling device was exposed in a flow-through channel system. Flow rate in the channel system was 8.5 cm/s. PFAAs solution was added into tap water, and the concentration of the water was 1.0 µg/L. Twelve POCISs were exposed for 1, 2, 4, 7, 10, and 14 days (two for each exposure period). The retrieved POCISs were wrapped in aluminum foil, stored at 4°C. During this period the water in the tank was replaced at regular intervals to ensure minimal depletion of PFAAs.

2.3 Sample collection and extraction of target analytes

2.3.1 POCIS
Twelve cages were deployed in Taihu Lake, each cage contained three POCISs. Detail information on the sampling site is given in figure 1. After the exposure period, POCISs were wrapped in aluminum foil and then transported to the laboratory. POCISs were stored at 4°C until extraction.

POCIS was opened, and the sorbent in POCIS was transferred into an empty SPE cartridge with glass wool. 100 µL of isotope-labeled internal standard solution (5 ng/mL) was spiked into the sorbent. Elution was performed with 4 mL of 0.1 % (v/v) ammonia solution in methanol followed by 4 mL of methanol. The eluent was concentrated to near-dryness under nitrogen and then reconstituted to 1.0 mL in methanol. Final extracts were stored at 4°C until analysis by UPLC/MS-MS.

2.3.2 Water sample
Surface water samples (1L) were sampled from each sample site at initial deployment and retrieval. Water samples were extracted by Oasis WAX SPE cartridges (6 cc, 150 mg). Cartridges were preconditioned sequentially with 4 mL of 0.1 % (v/v) ammonia solution in methanol, methanol and water. Prior to extraction, the samples were passed through glass fiber filters, and then 100 µL internal standards (50 ng/mL) was added to them. Water samples were extracted using similar methods as POCIS samples.

2.3.3 Sediment sample
Sediment was taken from each site on the first day of POCIS deployment. Sediment was freeze-dried at -60°C for extraction. The sediment samples were extracted using pressurized liquid extraction (Thermo Fisher, Germany). The sediment samples (~ 2 g dry wet) were put into a 22 mL stainless steel extraction cell. Prior to extraction, 100 µL internal standards (50 ng/mL) was added and equilibrated for 12 h in
The dark at 4 °C. The sediment samples were extracted using methanol at 70 °C for 3 static cycles at 1500 psi, resulting in an extraction volume of 25 mL. The extracts were evaporated down to 1.0 mL under nitrogen and then filtered through a 0.22 μm PTFE syringe filter. Final extracts were stored at 4°C until analysis by UPLC/MS-MS. The recovery (n=3) for water and sediment samples were range from 65.1-123% and 79.4-112%, depending on different PFAAs.

2.4 Analysis of PFAAs
PFAAs concentrations were measured using an Agilent 1290 ultrahigh performance liquid chromatography (UPLC) system coupled with an Agilent 6400 triple quadrupole mass spectrometer (Agilent, USA) based on previously reported methods[7].

3. Results and discussion

3.1 Sampling rates and uptake kinetics
Passive sample to monitor containment in aquatic environment is becoming more and more important. In order to use the POCIS to estimate concentrations of contaminant in aqueous matrices, a sampling rate (Rs) must be obtained for the target compounds. The Rs can obtain from the laboratory experiment. The sampling rate can be calculated with the following Eq.(1) [8, 9]

\[ M = M_s C_s = R_s C_w t \]

where \( M_s \) is the mass of the sorbent, \( t \) is the POCIS exposure period. \( C_s \) and \( C_w \) are the concentrations of analyte in the sorbent and water, respectively.

Table 1 Sampling rates (Rs) of PFAAs at 8.5 cm/s flow velocities by POCIS

| Compound               | Abbreviation | Rs (L/d) | \( R^2 \) |
|------------------------|--------------|----------|-----------|
| Perfluorohexanoate     | PFHxA        | 0.05±0.003 | 0.99      |
| Perfluoroheptanoate    | PFHpA        | 0.05±0.002 | 0.99      |
| Perfluorooctanoate     | PFOA         | 0.06±0.004 | 0.99      |
| Perfluorononanoate     | PFNA         | 0.11±0.006 | 0.99      |
| Perfluorodecanoate     | PFDA         | 0.17±0.012 | 0.99      |
| Perfluoroundecanoate   | PFUdA        | 0.10±0.011 | 0.96      |
| Perfluorododecanoate   | PFDoA        | 0.06±0.010 | 0.99      |

POCIS sampling rates for PFAAs (Table 1) were obtained from laboratory experiment. These Rs values were used to calculate the concentration of PFAAs in water from Taihu Lake. Most of the Rs values in this work were significantly smaller than in other studies [10]. The differences of the Rs values are might be caused by water temperature, pH, the type of water used, as well as hydrodynamic conditions of each.

3.2 Occurrence of PFAAs in surface water
PFAAs concentrations were obtained with POCIS at each sampling site are summarized in figure 2. During the operation of passive sampler, active sampling was also used to measure the concentration of PFAAs. The target compounds were detected at all sampling sites using passive and active sampling. In Taihu Lake, the concentrations of total PFAAs in the surface water range of 451.66-752.85 ng/L. The predominant PFAAs were PFOA (243.12-390.77 ng/L, using POCIS) and PFHxA (71.95-193.12 ng/L, using POCIS), which accounted for 50.98% and 18.68% of total PFAAs, respectively.

The concentration of PFAAs from POCIS are higher than those from grab sampling. There were instances of both good and poor agreement between PFAAs concentrations measured from passive sampling and active sampling. POCIS provide a time-weighted average water concentration estimate over 14 days, while the grab samples represent a single point in time. The method detection limit of PFAAs using active sampling is higher than POCIS, and the results of active sampling show large
relative standard deviation.

![Figure 2 Distribution of PFAAs in waters from Taihu Lake](image)

### 3.3 Occurrence of PFAAs in sediment

The concentrations of PFAAs in sediment samples are shown in figure 3. Similar to the spatial distribution of PFAAs in water samplers, the sediment total PFAAs concentrations were higher in the north part of Taihu Lake than in south areas. The sediments total PFAAs concentrations from Taihu Lake ranged from 22.56 ng/g to 28.69 ng/g. The highest total PFAAs appeared at site S9, and the lowest total PFAAs at S2 in the Gonghu Bay. The PFAAs profiles in sediment, where PFOA was predominant. The level of PFOA from 12.15 ng/g to 13.58 ng/g, accounting for 51.5% of the total PFAAs on average in sediments. The level of long-chain PFAAs (C9-C12) such as PFNA, PFDA, PFUdA and PFDoA ranged from 0.88-2.03 ng/g, 0.87-1.92 ng/g, 1.11-1.53 ng/g and 0.52-1.64 ng/g, respectively.
3.4 Assessment of risk due to PFAAs

The environmental risk assessment of PFAAs can be evaluated from the risk quotient (RQ) [11]:

\[
RQ = \frac{MEC}{PNEC} \times \frac{MEC}{LC_{50}} \times \frac{AF}{AF}
\]

where MEC and PNEC are measured environmental concentration and the predicted no effect concentration, respectively. PNEC was obtained from the toxicity data divided by a security factor (AF) of 1000. In present work, the median lethal concentration (LC\(_{50}\)) or the median effective concentration (EC\(_{50}\)) for aquatic life were determined. The potential risk for ecological effects from contaminated water was assessed. The RQ were classified into three risk levels: >1, contamination in the area was of high risk, 0.1-1.0, medium risk, 0.01-0.1, low risk. As shown in figure 4, all RQ values for PFAAs were below 0.01. These results indicated that current concentrations of PFAAs in Taihu Lake are unlikely to cause risk to the relevant aquatic organisms.

4. Conclusions

This study investigated the distribution tendency of PFAAs in the water and in the sediment of Taihu Lake. The concentration of PFAAs in the water was evaluated by passive sampling techniques. POCIS has been proved as an effective tool to obtain the TWA concentrations of PFAAs. The total concentration of PFAAs were 454.55-753.85 ng/L in the water using POCIS. The level of PFAAs in sediments was 22.56-28.69 ng/g. Risk assessment results imply that PFAAs pose little risk to the relevant aqueous organisms.

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