

# Contamination Profile of Perfluorinated Compounds (PFCs) in Ambient Water Surrounding a Major Producer in Central China

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## Introduction

The ongoing production of regulatory organofluorine products (e.g. PFOS, PFOA) in China has received great concerns, especially due to the potential release of long chain perfluorinated compounds (PFCs) [1,2]. A previous study in 2010 has revealed the significant contamination of PFASs in a major producer of PFOS and related chemicals in central China [3]. In recent years, the product lines of Chinese producers have been changed a lot due to the pressure from both international treaties and local regulations, which might cause the changes of local PFCs contamination. For example, some short chain PFCs have been developed as the alternatives to long-chain C8 compounds [4]. In the present study, the contamination profile of PFCs in ambient water surrounding the major producer in the previous report was updated.

## Material and Methods

### *Chemicals and materials*

The mass labeled internal standard obtained from Wellington Laboratories (Guelph, ON, Canada) and contained M4-PFBA, M5-PFPeA, M2-PFHxA, M4-PFHpA, M2-PFOA, M4-PFOA, M5-PFNA, M2-PFDA, M2-PFUnA, M2-PFDoA, M3-PFBS, M4-PFHxS and M4-PFOS. M2-PFOA was used as injection standard. HPLC grade methanol, acetone and n-hexane were purchased from Duksan (Kyoungkido, Korea). The other material includes: Sampling bottles (1L, PP), ultrapure water (18 M $\Omega$ ·cm, Millipore, MA, USA), acetic acid reagent (HPLC grade), ammonia solution (25% in H<sub>2</sub>O), Oasis HLB cartridges (200 mg/6ml, Waters, MA), adjustable micropipettes (100-1000  $\mu$ L, 20-200 $\mu$ l) and microfiber filter (47mm, Whatman, Kent, UK).

### *Sampling strategy*

N=42 samples were collected near the major producer in Hubei Province China. Different onsite (groundwater S2 (n=16), downstream river S3 (n=17), recycling pond S4 (n=1), plant waste water effluent S5 (n=1), tap water S6 (n=1), rainfall well S7 (n=1) and offsite (local reservoir S1 (n=4), upstream river S8 (n=1) location were selected to highlight the effect of manufacturing activities and ultimate release of contaminants to the Yanshui river. During 14 days sampling period precipitation was also recorded to highlight temporal trends. Field blanks were also collected from S1, S2 and S3 location. The selected sampling locations are presented Fig 1 (a).

### *Pretreatment, instrumental analysis, Quality assurance and Quality Control (QA/QC)*

All the water samples were filtered through 47mm glass microfiber filter and pH was adjusted (5-7). The 500ml of water was spiked with 50 ng mass labeled internal standard (0.5  $\mu$ g/ml). Then allowed to stay for 30 min. Further extracted by solid phase extraction (SPE) using oasis HLB cartridge to reduce matrix interfere. The complete procedure adopted was following: HLB cartridges were preconditioned with 4ml of 0.5 % ammonia methanol, methanol and ultrapure water respectively. After loading sample (at rate of 1drop/sec), cartridge was washed with 4ml of sodium acetate solution a dried for 1 hour. The sample was eluted with 3ml of methanol and 2ml of 0.5 %

ammonia methanol solution. Final volume was adjusted to 0.5 ml by gentle nitrogen stream and known amount of 50 ng injection standard (M2-PFOA, 0.5 µg/ml) was added prior to instrumental analysis.

The quantification of ionic compounds was performed by using ultra-high performance liquid chromatography (UltiMate® 3000 UHPLC, Dionex) along with mass spectrometer (API 3200, AB Sciences). A ZORBAX Eclipse C18 XBD column (5 µm × 2.1 mm × 150 mm) was used for the separation of target compounds at 30°C temperature. Analyst 1.5.1 software and Chromeleon 6.80 workstation were used. The mixture of 10 mmol/L NH<sub>4</sub>AC (A) and methanol (B) was used as the mobile phase, with the flow rate of 0.35 mL/min. Further 10 µl of sample was injected for quantification of 12 target PFAAs.

QA/QC procedures were strictly followed during sampling, extraction and final analysis. Glass ware and Teflon coated lab ware was completely avoided. For the quantification purpose internal standard calibration method was used. Method detection limits (MDLs) were calculated ranging from 0.6-2.9 ng/L. The blanks were below the MDLs except PFOS and PFHxA which were less than 5% of field samples. The calculated recoveries of mass labeled internal standard were ranging from 50-150%.

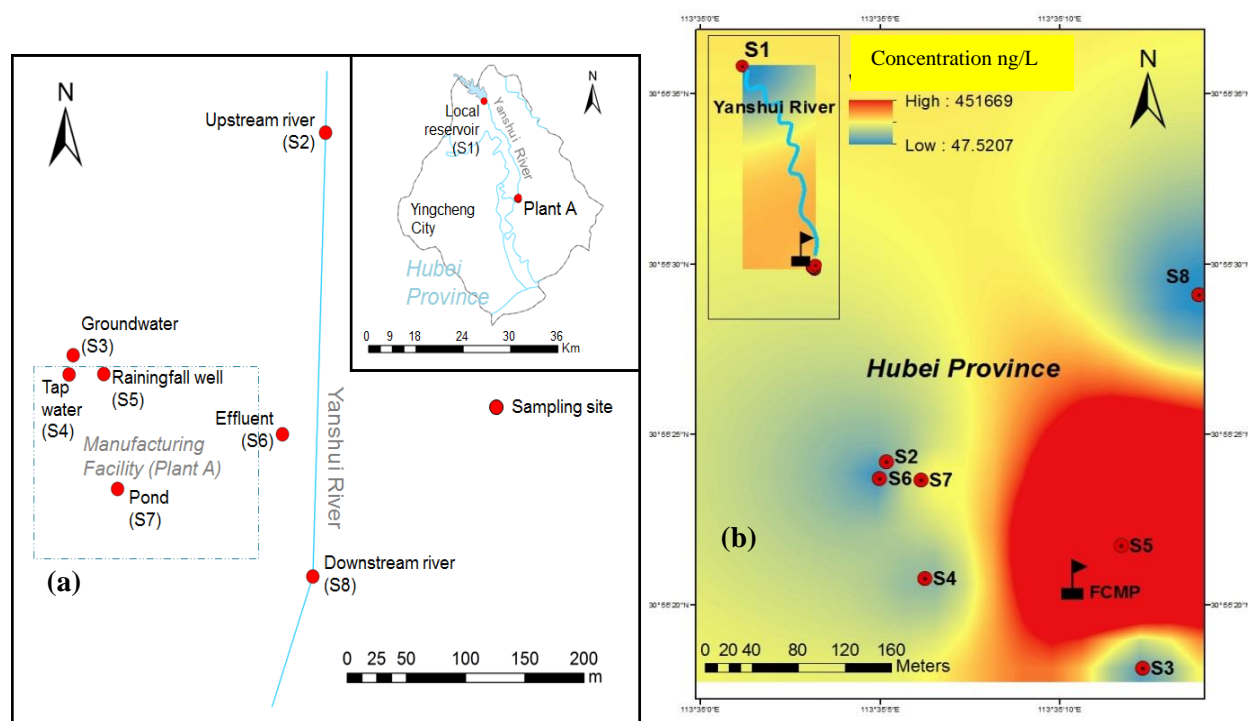


Fig.1 (a) Map of sampling site and (b) Concentration profile

## Result and Discussion

### *Detected levels of PFCs in water samples*

The detected concentration of 12 selected PFCs range from n.d.-17619 ng/L, as shown in Table 1. The highest concentration was determined in the waste water effluent directly discharged to the Yanshui River ( $\sum_{12}\text{PFASs}$  = 469561 ng/L). This river was the receiving water body of the industrial wastewater discharged by the main producer. The detected concentration in downstream water was raised up to 12602 ng/L as compared to offsite upstream area (18 ng/L). Also other water bodies have been contaminated by PFCs including recycling pond (25833 ng/L), rainfall well (74229 ng/L), and the ground water (2458 ng/L). The contamination profile is presented in Fig 1(b). The detected level of PFCs were higher than most of previously published reports from China [4-6]. Moreover, during 14 days sampling campaign high precipitation was observed on 8<sup>th</sup>, 9<sup>th</sup> and 10<sup>th</sup> day. During these days the observed concentrations in the groundwater samples were correspondingly lower. This indicates that rainwater is affecting the concentrations in groundwater maybe by dilution. On the other hand, no such dilution trend was observed for downstream surface water, which might mainly be affected by industrial emission. Furthermore the correlation from downstream water was estimated between short (PFBS) and long (PFOA) chain compounds and determined weak positive correlation ( $p < 0.01$ ,  $R^2 = 0.570$ ) indicate that the source of these two pollutants maybe same and mainly the FCPF.

When calculating the risk quotient on the basis of Health risk limits (PFOS, PFOA: 70 ng/l, PFBS: 7000 ng/L), the hazard ratio (HR) of long chain compounds (both tap and ground water) exceeds 1, while HR of PFBS was less than 1 in current scenario. Such result suggests that long-chain PFCs should be regarded as the priority currently.

**Table 1. Concentration profile (ng/L) of selected PFCs from ambient water of FCPF**

|       | Reservoir (S1) | Groundwater (S2) | Downstream river (S3) | Recycling pond (S4) | Plant's wastewater outfall (S5) | Tap water (S6) | Rainfall well (S7) | Upstream river (S8) |
|-------|----------------|------------------|-----------------------|---------------------|---------------------------------|----------------|--------------------|---------------------|
| PFHxA | 6.7            | 10595.2          | 656.1                 | 5097.7              | 15977.9                         | 48.4           | 5286.4             | 1.8                 |
| PFHpA | 1.2            | 1706.5           | 514.8                 | 835.5               | 10220.8                         | 6.2            | 985.1              | n.d.                |
| PFOA  | 7.4            | 1624.2           | 1441.1                | 780.6               | 27736.4                         | 15.5           | 1869.7             | 4.3                 |
| PFNA  | 0.7            | 4.2              | 6.3                   | 9.0                 | 370.6                           | 0.5            | 11.4               | n.d.                |
| PFDA  | n.d.           | n.d.             | 2.5                   | n.d.                | 289.5                           | n.d.           | 37.1               | n.d.                |
| PFBS  | 8.9            | 4410.2           | 4582.2                | 10332.6             | 170619.1                        | 293.8          | 25302.2            | 3.3                 |
| PFPeS | 0.1            | 612.8            | 612.4                 | 361.0               | 28624.0                         | 2.7            | 1321.3             | n.d.                |
| PFHxS | 1.1            | 2153.8           | 1130.8                | 1097.7              | 35439.4                         | 16.3           | 14187.1            | 0.7                 |
| PFHpS | 1.1            | 175.3            | 204.6                 | 265.0               | 14385.0                         | 1.8            | 1327.0             | n.d.                |
| PFOS  | 19.8           | 3297.9           | 3439.2                | 7002.9              | 163009.3                        | 77.4           | 23601.0            | 8.3                 |
| PFNS  | 0.5            | 6.9              | 10.3                  | 25.0                | 2408.9                          | n.d.           | 201.4              | n.d.                |
| PFDS  | n.d.           | 2.8              | 2.0                   | 26.5                | 480.9                           | n.d.           | 100.0              | n.d.                |

### *Effects of the product line adjustment*

Present data depicted that contamination profile of PFCs varied a lot. Short chain PFCs were dominant in the current scenario. Regarding the percentage contribution of individual compounds, the most dominant species was PFBS (36%). The detected concentration of PFBS in ambient water (294 ng/l – 170619 ng/L) was also exceeding than most of previously cited data [5, 6]. The concentration of PFHxS was ranging from (0.7 ng/L - 35439 ng/L) contributing 9% of all the detected PFCs. Such high detected level of short chain compounds draw attention to these contaminants.

The observed shift towards short chain PFCs may be due to multiple reasons. For instance, the restricted use of long-chained PFCs by governmental and private actors, extensive use of C4-based compounds in manufacturing process (*N*-methyl perfluorobutane sulfonate) as compared to C8-based compound and considering short chained contaminants as alternative [7]. Short chain contaminants have long-range transportation and their lower hydrophobicity making them easier to enter to groundwater and ultimately drinking water.

For the selected major producer, the small-scale trial production of PFBS (perfluorobutane sulfonate) and PFHxS (perfluorohexane sulfonate) began as early as 2008. While in recent five years, the production scale expanded significantly. Last year (2016), the production of PFBS and PFHxS has scaled up to 20 t/a and 10 t/a respectively. So the change found in the contamination of PFCs is consistent with the product line adjustment in this producer.

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