Science of the Total Environment 645 (2018) 596–602

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Occurrence and distribution of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in natural forest soils: A nationwide study in China

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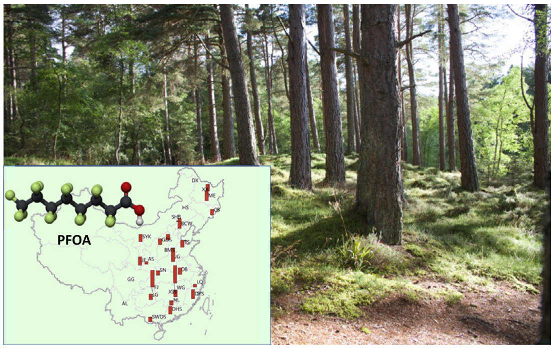
HIGHLIGHTS

- PFOA and PFOS levels in surface soils from 28 Chinese mountains forests were analysed.
- Levels of PFOA in Chinese natural mountains forests were up to 9.0 pg·g^{-1} dw.
- PFOA and its precursors were the major problem in Chinese natural forest soil.
- The occurrence of PFOA appears to be more dependent on the source than environmental factors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 May 2018
Received in revised form 9 July 2018
Accepted 12 July 2018
Available online xxxx

Editor: Jay Gan

Keywords:
PFOA
PFOS
Forest soil
Natural mountain
Altitude

ABSTRACT

Forests serve as the primary reservoir for organic carbon above ground. Previous studies have revealed that forest soils play key roles in the retention of persistent organic pollutants (POPs). In this study, the occurrence and distribution of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were investigated in 54 surface soil samples from 28 natural forested mountain sites across China between 2012 and 2013. The detection frequency of PFOA (70%) was significantly higher than that of PFOS (4%). PFOA levels ranged from <0.9 to 9.0 pg·g^{-1} dry weight (dw). Levels of PFOA and PFOS in forest soils were significantly lower than those in agricultural, urban and rural areas in China. Relatively high levels of PFOA were detected in Hubei Province (Jiugong Mountain, average: 3.4 pg·g^{-1} dw) and Jiangxi Province (Wugong Mountain, average: 4.4 pg·g^{-1} dw), where many domestic fluoropolymer manufacturers are located. PFOS was only detected in these two provinces (2.2 pg·g^{-1} dw and 2.7 pg·g^{-1} dw, respectively). From most of the surveyed mountains, the concentrations of PFOA increased with elevation. The lower temperature and greater precipitation probably made PFOA and its precursors available to transport and degrade more readily at higher altitude sites. A relatively higher level (1.9 ± 1.3 pg·g^{-1} dw) of PFOA was found in the broadleaf evergreen forest area, mainly due to the high industrial emissions, plant retention, and precipitation rate in this area. Source were the dominant factor controlling the spatial distribution of PFOA in natural forest soils in China.

1. Introduction

Perfluoroalkyl acids (PFAAs) are synthetic chemicals with wide applications that have been used industrially since the 1950s (Lindstrom

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https://doi.org/10.1016/j.scitotenv.2018.07.151
0048-9697/

et al., 2011; Tsai et al., 2002). They are persistent in the environment due to the stability of high-energy fluorocarbon (C—F) bonds (Xiao et al., 2015). Two representative PFAAs, namely, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), have proved to be bioaccumulative and toxic to many organisms (Ng and Hungerbühler, 2014). In 2009, PFOS and its related compounds were added in the Stockholm Convention under Annex B (UNEP, 2009). In 2015, PFOA and its related compounds were proposed for listing under the Convention and are under review (UNEP, 2015). Under the 2010/2015 PFOA Stewardship Program (USEPA, 2006), the production and use of PFOA and its related chemicals was eliminated by eight major fluoropolymer and telomer manufacturers. Nevertheless, the annual production of PFOA in China has increased to 150 t in 2013 (Li et al., 2015). In addition to the direct emission, the precursors of PFOA and PFOS were another source for the occurrence of PFOA and PFOS in the environment. Sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), and fluorotelomer alcohols (FTOHs) are the precursors of PFOA and PFOS (D'eon et al., 2006; Ellis et al., 2004). They are produced from perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer (FT)-based products and are also released as by-products during the manufacturing of PFOA and PFOS. These precursors have been assumed to be ultimately converted to PFOS/PFOA in the environment (Liu et al., 2017).

PFOS and PFOA have been widely detected in diverse environments around the world, such as the air (Dreyer et al., 2009), water (Lindim et al., 2016), sediments (Yang et al., 2013), and biota (Tao et al., 2006). In addition, PFOA and PFOS have been widely detected in areas far from PFAA emission sources, including the Arctic, Antarctic and the Tibetan Plateau (Cai et al., 2012; Llorca et al., 2012; Shi et al., 2010). Forests are the reservoirs for ~80% of organic aboveground carbon and play an important role in the global distribution of persistent organic pollutants (POPs) (Nizzetto et al., 2007; Bergknut et al., 2011). Forest soil is an important sink for POPs, and the levels and compositions of POPs in forest soils can indicate their emission and atmospheric deposition, and reflect their migration (Sweetman et al., 2005). Most natural forests are located far from the emission sources of PFAAs, and atmospheric transport and deposition are the central pathways for PFAAs in natural forests (Codling et al., 2014). Due to their low volatility, PFAAs were believed to combine with particulates to be transported long distances in the atmosphere (Hurley et al., 2004). The degradation of their precursors was shown to be another source for PFAAs in the areas far from the emission sources of PFAAs (Ellis et al., 2004).

Previous studies on PFAAs in soils focused on agricultural lands (Rankin et al., 2016; Washington et al., 2010), residential areas (Li et al., 2010), and industrial areas (Jin et al., 2015; P. Wang et al., 2013). PFAA was reported at $pg \cdot g^{-1}$ dry weight (dw) levels (Strynar et al., 2012). Chinese forests are distributed in different vegetation regions, including broadleaf evergreen forests, temperate coniferous and broadleaf mixed forest, deciduous broadleaf forests, temperate grasslands, boreal forests, and alpine vegetation areas. The total forest area in China was 208 million ha, which covered 21.63% of Chinese land (State Forestry Administration of China, 2015). However, to the best of our knowledge, there was no report on PFAA levels in Chinese natural forest soils. PFOA and PFOS are non-volatile and persistent contaminants, and thus, once captured by the soil, it is difficult for them to reenter the atmosphere for migration (Brooke et al., 2004). The levels of PFOA and PFOS in natural forest soils can reflect the atmospheric transport from peripheral sources and the history accumulation of PFOA and PFOS.

Accordingly, in this study, 54 surface soil samples were collected from 28 background forested mountains across China, which are far away from cities and industrial plants, between 2012 and 2013. The aims were (i) to reveal the levels and spatial distribution of PFOA and PFOS in Chinese forest soils, and (ii) to investigate the influence of source and environmental factors on the distribution of PFOA and PFOS in forest soils.

2. Experimental section

2.1. Sampling

Fifty-four surface forest soil samples from 28 mountains across mainland China were collected between May 2012 and March 2013. Geodetic coordinates and meteorological parameters were noted as: longitudes ranging between 101.0° and 128.5°, latitudes ranging between 21.9° and 53.0°, altitudes ranging between 285 m and 4126 m, annual average temperatures ranging between −6 °C and 21 °C, and total precipitations ranging between 245 mm and 2006 mm. The geodetic coordinates and meteorological parameters in each site are shown in Table S1. The vegetation types include broadleaf evergreen forests, coniferous and broadleaf mixed forests, deciduous broadleaf forests, temperate grasslands, boreal forests, and alpine vegetation areas. All the sampling sites were chosen with a minimum distance of tens to several hundred km from typical industrial or civilian sources associated with PFOS and PFOA.

Before sampling, vegetation litter was carefully removed. A stainless-steel spade, which was pre-cleaned by methanol, was used to collect soil. The depth of the soil was approximately 10 cm. Three parallel samples were collected within a spacing of 5 m^2, and then mixed up. The soil samples were stored in 50 mL of polypropylene (PP) tubes, then sealed in PP bags and frozen at −20 °C. For transportation, the PP bags were placed in foam cases, which were filled with ice bags. The foam cases were delivered to the laboratory as soon as possible.

2.2. Chemicals

HPLC grade methanol and ammonium hydroxide (25%) were purchased from Sigma (St. Louis, USA). Ultrapure water was produced by a Milli-Q® Plus 185 system (Darmstadt, Germany). Native and ^{13}C-labelled PFOA and PFOS, which were used for calibration and as the internal standards (IS), respectively, were purchased from Wellington Laboratories (Ontario, Canada). ENVI-Carb graphitized carbon (250 mg, 3 cm) cartridges were purchased from Supelco (Bellefonte, USA). Hydrochloric acid was purchased from Sigma (St. Louis, USA). Nylon member filters were purchased from Pall Co. (New York, USA).

2.3. Extraction and analysis

Soil samples were freeze-dried for 72 h. Afterwards, large debris, such as stones, garbage, and plant roots, were picked up by tweezers. Samples were ground into powder using an agate mortar and then sieved through a 2-mm sieve. The details of the treatment referred to Zhao et al., with some modification (Z. Zhao et al., 2013).

The soil samples (1–3 g) were weighed into PP tubes pre-rinsed by methanol. Mass-labelled internal standards (2.5 ng, 50 pg/μL, 50 μL) were spiked into the soil samples, and then 15 mL of methanol was added. The soil samples were vortexed for 30 s and soaked for 30 min. After being sonicated for 30 min, the samples were centrifuged for 8 min at a speed of 3000 rpm. The supernatant was transferred to another PP tube for further treatment. The sonication was repeated twice, and the two supernatants were pooled. The pooled sample was concentrated to 2 mL under a gentle stream of high-purity nitrogen at 40 °C for further clean-up using ENVI-Carb cartridges. A cartridge was preconditioned by passing through 2 mL of methanol three times. A sample was then loaded onto the cartridge and the eluate was collected. The sample was further eluted by passing through 1 mL of methanol three times. The eluates were combined and concentrated to 0.5 mL under a gentle stream of high-purity nitrogen at 40 °C for further instrumental analysis. All samples were analysed in 3 duplicates.