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Spatial distribution and partitioning behavior of selected poly- and perfluoroalkyl substances in freshwater ecosystems: A French nationwide survey

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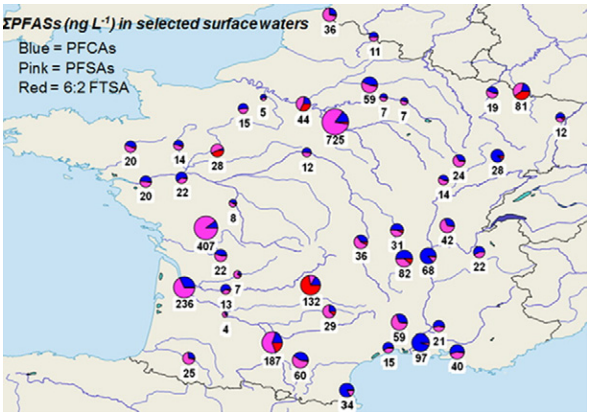
HIGHLIGHTS

- A large-scale survey of PFASs in 133 French rivers and lakes is reported.
- Descriptive statistics, correlations and partitioning coefficients were determined.
- Non-detects were taken into account using functions from the NADA R-package.
- Hot spots of PFAS contamination were found near large urban and industrial areas.
- Sediment levels were partly controlled by grain size and organic carbon content.

GRAPHICAL ABSTRACT



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ABSTRACT

The spatial distribution and partitioning of 22 poly- and perfluoroalkyl substances (PFASs) in 133 selected rivers and lakes were investigated at a nationwide scale in mainland France. ΣPFASs was in the range < LOD–725 ng L^{-1} in the dissolved phase (median: 7.9 ng L^{-1}) and <LOD–25 ng g^{-1} dry weight (dw) in the sediment (median: 0.48 ng g^{-1} dw); dissolved PFAS levels were significantly lower at "reference" sites than at urban, rural or industrial sites. Although perfluorooctane sulfonate (PFOS) was found to be the prevalent compound on average, a multivariate analysis based on neural networks revealed noteworthy trends for other compounds at specific locations and, in some cases, at watershed scale. For instance, several sites along the Rhône River displayed a peculiar PFAS signature, perfluoroalkyl carboxylates (PFCAs) often dominating the PFAS profile (e.g., PFCAs > 99% of ΣPFASs in the sediment, likely as a consequence of industrial point source discharge). Several treatments for data below detection limits (non-detects) were used to compute descriptive statistics, differences among groups, and correlations between congeners, as well as log K_d and log K_{oc} partition coefficients; in that respect, the Regression on Order Statistics (robust ROS) method was preferred for descriptive statistics computation while the Akritas–Theil–Sen estimator was used for regression and correlation analyses. Multiple regression results

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suggest that PFAS levels in the dissolved phase and sediment characteristics (organic carbon fraction and grain size) may be significant controlling factors of PFAS levels in the sediment.

1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are surfactants that have been used since the 1950s in manifold industrial applications, including metal plating, fluoropolymer processing aids, textiles, and firefighting foams (Prevedouros et al., 2006; Ahrens and Bundschuh, 2014). However, it was not until the last decade that their environmental fate and ecotoxicology aroused the interest of the scientific community (Kannan, 2011). Since then, PFASs have been reported in biotic and abiotic compartments worldwide, including remote polar areas (Houde et al., 2011). Of all the PFASs currently investigated, perfluorooctane sulfonate (PFOS) remains the most emblematic, due to its ubiquitous character and adverse effects (Lau et al., 2007). Numerous papers have reported on the highly bioaccumulative potential of PFOS in biota (Houde et al., 2011) as well as on its persistence (Olsen et al., 2007). These properties led to the classification of PFOS as a Persistent Organic Pollutant (POP) in 2009, under the framework of the Stockholm Convention (UNEP-POPS-COP.4-SC-4-17). Since then, the use of PFOS-containing products has been drastically restricted by the EU (e.g., PFOS-based aqueous film forming foams being banned since June 2011). However, a number of industrial sectors such as electroplating, photolithography or hydraulic fluids for aviation still benefit from derogations until a non-toxic substitute is available (2010/757/EU Commission Regulation). Other PFASs, which have not been added yet to the listing of POPs in the Stockholm Convention, may also be cause for concern, especially medium and long-chain carboxylates (Wolf et al., 2012; Buhrke et al., 2013).

Until now, only a few surveys have addressed PFAS environmental contamination at nationwide or larger spatial scale. For instance, Loos et al. (2009) targeted 122 rivers in Europe, although the focus was not put exclusively on PFASs. However, by compiling these data with other values from the literature, a first estimate of PFOS and perfluorooctanoate (PFOA) European discharges was calculated (Pistocchi and Loos, 2009). Clara et al. (2009) evaluated the occurrence of perfluoroalkyl sulfonates (PFSAs), carboxylates (PFCAs) and sulfonamides at national level, including sediments from 7 Austrian lakes and the river Danube, while Kwadijk et al. (2010) investigated the spatial distribution, sediment–water distribution coefficient, and bioaccumulation factor of 15 selected PFASs across 21 locations in The Netherlands. Boiteux et al. (2012) provided a first nationwide review of PFAS contamination in French raw and treated water for human consumption. In France, PFASs have been reported at relatively high levels in urban hydrosystems such as the River Seine and the River Orge (mean $\sum$PFASs $=$ 55 ng L^{-1} and 73 ng L^{-1}, respectively) (Labadie and Chevreuil, 2011a,b), perfluorohexane sulfonate (PFHxS) and PFOS being the dominant congeners at these sites, and perfluorohexanoate (PFHxA) and PFOA the main PFCAs, as was also observed near the mouth of the river Seine (McLachlan et al., 2007). Labadie and Chevreuil (2011a) reported on the bioaccumulation propensity and tissue-distribution of a wide range of PFASs in fish (European chub), while Munschy et al. (2013) investigated PFAS spatial distribution in shellfish along French coasts, pointing to contrasting PFAS patterns between the Atlantic and Mediterranean coasts. Human exposure to PFAS was assessed in a 2007 French survey, PFOS and PFOA being among the most frequently reported PFASs (detection frequency > 90%) in breast milk, at times reaching levels above 300 ng L^{-1} (Antignac et al., 2013).

In this context, the present study aimed at investigating PFAS occurrence and partitioning in mainland France surface water bodies. As part of the implementation of a national action plan on aquatic environment pollution (October 2010), the French Ministry of Ecology decided to launch an innovative and comprehensive approach under the Water Framework Directive (WFD) (2000/60/EC), in order to provide relevant information to update the lists of substances to be included in future monitoring schemes. A vast prospective campaign took place in spring–autumn 2012, which focused not only on potentially contaminated sites (i.e. urban or industrial) but also on supposedly pristine reference sites. Descriptive statistics of PFAS levels or molecular patterns were calculated for this comprehensive dataset which included 333 water and 129 sediment samples. The information was then summarized with the help of artificial neural networks via a Kohonen mapping (Giraudel and Lek, 2001). So far, the PFAS-focused literature has only yielded a few papers dealing with data below detection limits (non-detects) (De Solla et al., 2012; Jaspers et al., 2013; Rigét et al., 2013; Lam et al., 2014). Given the substantial number of observations that fell below detection limits in the present work, specific statistical treatments were implemented to compute descriptive statistics and to examine correlations between PFASs. An alternative method to determine log K_d and log K_{oc} partitioning coefficients taking into account non-detects is also reported in this paper, along with the investigation of factors controlling PFAS sediment levels.

2. Materials and methods

2.1. Investigated compounds

Four different groups of PFASs were targeted: perfluoroalkyl carboxylates, sulfonates, sulfonamides and sulfonamide acetic acids, as well as one fluorotelomer. A total of 22 individual molecules and a cluster of branched PFOS isomers, hereafter referred to as Br-PFOS, were therefore determined. Note that, in this paper, L-PFOS refers to the linear isomer, while “PFOS” refers to the sum of L-PFOS and Br-PFOS. Target analytes, as well as full details on chemicals, standards and consumables are indicated in the Supplementary information (SI).

2.2. Sampling strategy

Water and sediment samples were collected at 133 locations, including 115 sampling points located in rivers and 18 in lakes (Fig. 1). River sampling sites were classified into five main types (SI Table S1) by the Direction de l'Eau et de la Biodiversité (DEB, French Ministry of Ecology): reference, farmland, industrial, urban, and “poor ecological status”, the latter reflecting low occurrence of aquatic plants and biota. Three campaigns were set up to collect water samples from rivers, leading to a number of 315 water samples. The first campaign took place in April–June 2012, the second one in September 2012, and the third one in November–December 2012. In contrast, a unique water sample was collected for each lake (June 2012). At each sampling site, a 1 L high density polyethylene (HDPE) bottle previously washed in the laboratory was rinsed 3 times with the site surface water, filled to the brim, sealed, and stored in a cooling box (5 ± 3 °C), pending shipment to the laboratory within 24 h. Sediment samples ($n = 129$) were collected during a single sampling campaign (August–November 2012). Only the top layer (1 to 5 cm depth) of the sediment was sampled, in agreement with guidance document #25 of the WFD.

2.3. Sample reception and pre-treatment

Water samples were passed through GF/F (0.7 μm) Whatman glass microfiber filters (previously baked at 450 °C for 6 h) using Nalgene® polyethylene filtration units and the filtrate was divided into two 500 mL aliquots stored in HDPE bottles; filtrates were kept at −20 °C until analysis.