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Poly- and perfluoroalkylated substances (PFASs) in water, sediment and fish muscle tissue from Lake Tana, Ethiopia and implications for human exposure

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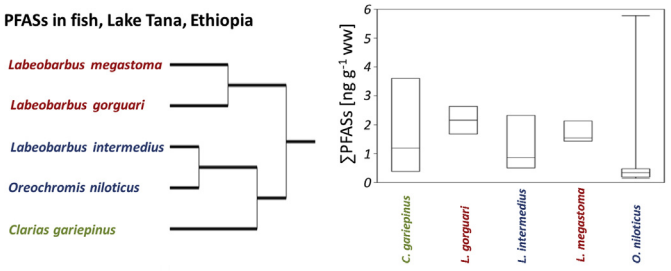
HIGHLIGHTS

- PFCAs were predominant in water (68%), sediment (91%), and fish (71%).
- PFAS levels are higher in piscivorous compared to non-piscivorous fish species.
- PFAS sorption depends on the CF_2 moiety and functional group for sediment or biota.
- PFAS levels were generally low and potential risks to humans are not expected.

GRAPHICAL ABSTRACT



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ABSTRACT

Lake Tana is Ethiopia's largest lake and there are plans to increase the harvest of fish from the lake. The objective of this study was to assess the levels of poly- and perfluoroalkyl substances (PFASs) in different compartments of the lake (water, sediment, and fish muscle tissue), and its implications for human exposure. The results showed higher PFAS concentrations in piscivorous fish species (*Labeobarbus megastoma* and *Labeobarbus gorguari*) than non-piscivorous species (*Labeobarbus intermedius, Oreochromis niloticus* and *Clarias gariepinus*) and also spatial distribution similarities. The ∑PFAS concentrations ranged from 0.073 to 5.6 ng L^{-1} (on average, 2.9 ng L^{-1}) in surface water, 0.22–0.55 ng g^{-1} dry weight (dw) (on average, 0.30 ng g^{-1} dw) in surface sediment, and non-detected to 5.8 ng g^{-1} wet weight (ww) (on average, 1.2 ng g^{-1} ww) in all fish species. The relative risk (RR) indicates that the consumption of fish contaminated with perfluorooctane sulfonate (PFOS) will likely not cause any harmful effects for the Ethiopian fish eating population. However, mixture toxicity of the sum of PFASs, individual fish consumption patterns and increasing fish consumption are important factors to consider in future risk assessments.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are persistent, bioaccumulative and toxic (PBT) substances of concern for environmental and human health (Ahrens and Bundschuh, 2014). PFASs have been widely used, for example, as stain repellents in commercial applications such as textile, paper, and household products over the past 50 years (Buck et al., 2011). Sources of PFASs to the environment include sewage treatment plant (STP) effluents, landfill effluents, and fire training facilities (Ahrens, 2011). STPs are also not effective in removing PFASs from wastewater since PFASs were detected at similar or higher concentrations in STP effluent when compared to the STP influent (Schultz et al., 2006).

An important exposure pathway for human intake of these substances is fish of both freshwater and marine origin (Dórea, 2008). PFASs have been widely investigated in fish of Europe (Berger et al., 2009; Labadie and Chevreuil, 2011), South America (Quinete et al., 2009) and Asia (Yang et al., 2012). There is however, a lack of knowledge of PFASs in African aquatic ecosystems and the potential exposure to humans (Hanssen et al., 2010; Mudumbi et al., 2014; Orata et al., 2008). Lake Tana, the largest lake in Ethiopia and the origin of the Blue Nile, is of interest for investigation of substances with PBT characteristics since production of fish from the lake is predicted to increase. Different hazardous health effects related to PFASs have been reported the aquatic ecosystem and humans, e.g. endocrine-disrupting effects, hepatotoxicity, immunotoxicity and reproductive toxicity (Ahrens and Bundschuh, 2014; Borg et al., 2013; Du et al., 2013). However, little is known about the levels of PFASs in the fish that will be produced.

The aim of this study was to assess *i)* the spatial distribution of PFASs in Lake Tana, Ethiopia, *ii)* the distribution of PFASs in five different fish species, *iii)* solid/liquid partition and bioconcentration behaviour of individual PFASs, and *iv)* the human health risk from PFASs if fish consumption increases. In this study, we collected surface water, sediment and fish muscle tissue samples from Lake Tana in October 2014. The risk of human exposure to perfluorooctane sulfonate (PFOS) was estimated based on a comparison of human fish consumption and pollutant levels in fish from Lake Tana relative to established international guidelines.

2. Material and methods

2.1. Sampling sites

The sampling was performed in Lake Tana, located in the Amhara region in northwestern Ethiopia at around 1800 m above sea level. Lake Tana has an area of 3000–3600 km^2 (84 km long, 66 km wide) with a volume of 28 000 km^3 and a mean depth of 8 m (max 14 m). In total, 61 rivers and streams feed the lake, of which six are perennial and contribute more than 95% of the inflow. The only natural outflow is the Abbay River (Blue Nile River) in the southeastern part of the Bahir Dar Gulf (Ligdi et al., 2010). The 7 sampling sites included *i)* two sites in the south close to wastewater outlets, one near Bahir Dar prison (P) and one near Bahir Dar hospital (H), *ii)* one sample near the Cherechera lake level regulatory weir (C), which is located at the lake's outflow to the Blue Nile River, *iii)* one sample at the Yegashu river inlet in the northeast part of the bay, with very shallow water (depth 2 m) and surrounding agricultural land (Y), iv) one sample in the south close to the forested Zegi Peninsula, where a wood industry was situated (Z), *v)* two samples in the northern part of the lake, one was located near the center of Gorgora Town (G) and the other north of the town, close to the Dirma River (D) (for details see Fig. 1 and Supplementary Table S1).

2.2. Sampling

Fish samples ($n = 30$) were collected between October 11th and 25th, 2014, from five species: *Labeobarbus megastoma* (*L. megastoma*), *Labeobarbus intermedius (L. intermedius)*, *Labeobarbus gorguari* (*L. gorguari*), *Clarias gariepinus* aka African catfish (*C. gariepinus*) and *Oreochromis niloticus* aka Nile Tilapia (*O. niloticus*) (Supplementary Tables S2 and S3). The three *Labeobarbus* species were chosen due to their habitats and occurrence in the lake as well as their varying feeding habits, i.e. *L. megastoma* and *L. gorguari* are piscivorous and *L. intermedius* is omnivorous (Supplementary Table S4). The herbivorous *O. niloticus* is the most important fish in Ethiopia and stands for 60% of the commercial fishery in the country as well as 30% of the fishery in Lake Tana. The omnivorous *C. gariepinus* is also an important commercial fish as it is fast growing and thus a large protein source (Desta et al., 2007). All fish were weighed and measured (standard length) and directly dissected. The muscle sample was taken above the dorsal line, in between the dorsal and adipose fin. The samples were then carefully wrapped into aluminum foil and packed into a zip lock plastic bag together with an identification card. These samples were then frozen to −20 °C before transportation to Sweden.

Surface water and sediment samples were collected at five sites (i.e., P, H, C, Y, and Z). Surface water samples were collected as grab samples in plastic bottles and sediment samples were collected using a Van Veen Grab Sampler. After sampling, water and sediment samples were stored at −20 °C before transportation to Sweden.

2.3. Chemicals

In total, 26 PFASs were analyzed for four perfluoroalkane sulfonates (PFSAs) (PFBS, PFHxS, PFOS, PFDS), 13 perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), three perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA EtFOSA), two perfluorooctane sulfonamidoethanols (FOSEs) (MeFOSE, EtFOSE), three perfluorooctane sulfonamidoacetic acids (FOSAAs) (FOSAA, MeFOSAA, EtFOSAA) (purchased from Wellington Laboratories (ON, Canada)) and one fluorotelomer carboxylate (6:2 FTSA) (purchased from Chiron AS, Norway). In addition, 16 internal standards were used which were spiked before extraction (i.e. $^{13}C_8$-FOSA, d_3-MeFOSAA, d_5-EtFOSAA, d_3-MeFOSA, d_5-EtFOSA, d_7-MeFOSE, d_9-EtFOSE, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS) and one injection standard (InjS) was used ($^{13}C_8$-PFOA) (purchased from Wellington Laboratories (ON, Canada)).

2.4. PFAS analysis

Extraction and analysis of PFASs were performed using standardized and validated methods (Ahrens et al., 2010a, 2015). The muscle tissue samples were homogenized using Ultra-Turrax with a stainless steel probe in a 50 mL PP-tube. The extraction was performed using solid-liquid extraction (SLE). The water samples were filtrated (Whatman™ Glass Microfiber Filters GF/C™, 47 mm diameter, 1.2 μm) and extracted using solid phase extraction (SPE) using Oasis® WAX 6 cc cartridges, 6 cm^3, 500 mg, 60 μm (Waters). The extraction of the sediment samples was performed using SLE. The instrumental analysis was performed by high performance liquid chromatography (HPLC, Agilent Technologies 1200 Series, Palo Alto, CA, USA) with a triple quadrupole mass spectrometer interfaced with an electrospray ionization source in negative-ion mode ((−)ESI-MS/MS, Agilent 6460 Triple Quadrupole System, Palo Alto, CA, USA). Aliquots of 10 μL were injected on a Hypersil