# OCCURRENCE OF FLUOROALKYL SURFACTANTS IN WATER FROM SRI LANKA

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**Abstract**
In this study, we simultaneously analyzed twenty fluorochemicals including fluorotelomers in water samples collected from Sri Lanka. The method included by a solid phase extraction coupled with high performance liquid chromatography interfaced to high-resolution mass spectrometry. Concentration of PFOS and PFOA were ranged from 0.66-47 and 0.83-12.4 ng $L^{-1}$, respectively. Analysis also showed the presence of fluorooctane acetate, N-EtFOSAA, in all the locations with a concentration range of 0.034-4.1 ng $L^{-1}$. THPFOS which is one of the active ingredients in AFFF, also found in all the samples with a mean value of 0.64 ng $L^{-1}$. This is the first report to show that concentrations of perfluorinated surfactants from surface waters in Sri Lanka are similar to those concentrations found in many developed nations.

**Introduction**
Widespread occurrence of wide variety of perfluorinated compound (PFCs) in humans, wildlife, and the environment has been reported even in remote regions far from sources.[1] Studies show that nearly all people have some PFCs in their blood, regardless of age.[2] The way PFCs get into human blood is not well known. However, their analogy to natural fatty acids seems to be disrupted number of fatty acid related gene functions in animal body.[3]
So far majority of published documents for contamination of these compounds was found to be focused on developed countries where as number of studies in developing countries are scarce. Earlier we have reported concentrations of fluorinated compounds in human blood and seminal plasma from different populations in Sri Lanka.[4] In this study, concentrations of twenty fluorinated compounds were measured in coastal and inland waters from Sri Lanka. It included, six perfluoroalkyl sulfonates, ten perfluoroalkyl carboxylic acids, two fluorooctane acetates, one each fluorooctane sulfonamides, and fluorinated telomer carboxylic acid.

**Materials and Methods**
**Sample collection**
In September, 2005 10 water samples from 0.5 m depth were collected into clean polypropylene sampling bottles (500 ml) from water bodies alone the western coastline. Additional fresh water samples were taken from the Kandy Lake located in the center of the country, from 0.5 and 3m depth (figure 1). These samples were refrigerated, transported to Japan and kept at 4 ºC until analysis.
Twenty poly- and perfuorinated compounds were examined in this study. The purity of the standards was ≥ 95%. All the chemicals were selected from the stocks from the National Institute of Advance Industrial Sciences and Technology (AIST), Japan. Details of theses chemicals have been noted in elsewhere.[5-7]
Compound analyzed:
PFASs (perfluoroalkyl sulfonates): PFEtS: $F(CF_2)_2SO_3^-$, PFPrS: $F(CF_2)_3SO_3^-$, PFBS: $F(CF_2)_4SO_3^-$, PFHxS: $F(CF_2)_6SO_3^-$, PFOS: $F(CF_2)_8SO_3^-$, THPFOS: $F(CF_2)_6(CH_2)_2SO_3^-$
PFASs (perfluoroalkyl carboxylic acids): PFHxA: $F(CF_2)_5COO^-$ , PFHpA: $F(CF_2)_6COO^-$, PFOA: $F(CF_2)_3COO^-$, PFNA: $F(CF_2)_8COO^-$, PFDA: $F(CF_2)_9COO^-$, PFUnDA: $F(CF_2)_{10}COO^-$, PFDoDA: $F(CF_2)_{11}COO^-$, PFTeDA: $F(CF_2)_{13}COO^-$, PFHxDA: $F(CF_2)_{15}COO^-$, PFOcDA: $F(CF_2)_{17}COO^-$
fluorinated telomers: *N*-EtFOSAA: $F(CF2)_8SO_2N(C_2H_5)(CH_2COO)^-$, *N*-EtFOSA: $F(CF2)_8\ SO_2N(C_2H_5)^-$ , PFOSA: $F(CF_2)_8SO_2NH^-$, 8:2FTUCA: $F(CF_2)_7CF{=}CHCOO^-$

**Chemical analysis**
Concentrations of fluorochemicals in waters were measured by a solid phase extraction method described

elsewhere.[5,6] The method simultaneously accommodated more target analytes including telomere alcohols, telomere acids, and sulfonamides. Extractions were carried out Oasis® WAX (Waters Co., 150mg/6cc) solid-phase cartridges. The cartridges were preconditioned by eluting 4 mL each of 0.1% $NH_4OH$/methanol, methanol, and milli-Q water, in sequence. The aliquot of 500 mL water sample was passed through the cartridge at a rate of 1 drop/s and eluate was discarded. Then the cartridge was washed by 25 mM sodium acetate (pH 4) and dried by centrifuging the cartridge at 3000 rpm for 2min. Then target analytes were eluted with 4mL of methanol and 4mL of 0.1% $NH_4OH$/methanol in to two separate fractions. The fractions were concentration under a gentle stream of high-pure grade nitrogen gas, and then transferred to polypropylene vials for chemical analysis.

**Instrumental analysis and quantification**

Analysis of fluorochemicals were performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), comprising an Agilent HP1100 liquid chromatograph interfaced with a Micromass® (Beverly, MA) Quattro Ultima Pt mass spectrometer operated in the electrospray negative ionization mode.[5,6] Concentrations were not adjusted for the purity of standards or recovery. The mean procedural blank and recovery of analytics are given in Table 1.

**Results and Discussion**

The concentrations of fluorinated compounds measured in Sri Lankan waters are shown in Table 1. All the water samples contained detectable concentrations of PFOS (0.65-44 ng $L^{-1}$), PFUnDA (0.018-0.13 ng $L^{-1}$), PFDA (0.11-0.5 ng $L^{-1}$), PFNA (0.23-0.61 ng $L^{-1}$), PFOA (1.07-12.4 ng $L^{-1}$), PFHpA (0.26-2.03 ng $L^{-1}$), PFHxA (0.33-2.17 ng $L^{-1}$), THPFOS (0.055-2.8 ng $L^{-1}$), and *N*-EtFOSAA (0.034-4.1 ng $L^{-1}$). PFHS (<0.016-1.14 ng $L^{-1}$), PFOSA (<0.016-7.5 ng $L^{-1}$), PFBS (<0.016-1.18 ng $L^{-1}$), PFDoDA (<0.016-0.041 ng $L^{-1}$) were detected in 83%, 75%, 33%, and 25% of the samples, respectively. Seven other target compounds were not detected in any location. The greatest concentration of PFOS (44 ng $L^{-1}$) was found in location B2, from the narrow water way connected to the larger water bodies of the Bire Lake. Additionally, most of compounds including PFOSA, PFHxA and N-EtFOSAA also detected in greater concentrations in B2 compared to other locations. The Bire Lake is a eutrophic and virtually stagnated water body located in the very center of the Colombo city, surrounded by the most populated and busiest area. The highest PFOS concentration found in B2 was greater than Tokyo Bay (13-25 ng $L^{-1}$), and number of water bodies from the New York State (0.8-13 ng $L^{-1}$).[5,8] The perflurooctanesulfonyl flurode (POSF)-based fluoro chemicals in surface treatments and fire fighting foams would explain elevated PFOS contamination in water.[8] The highest PFOSA concentration (7.5 ng $L^{-1}$) was also detected from the same location of B2 where the greatest PFOS concentration was found. The average concentrations of most the compounds analyzed from the waters of Lake Bire had higher concentrations compared to other locations suggesting that potential source of those compounds may out come of the release of sewage effluents into the Lake. Next to Lake Bire system, Kirillapone canal (KE 1), Kandy Lake, Hamilton Canal and Kelani River (H samples) and Negombo Lagoon had mean PFOS concentrations in descending order, respectively. Kirillapone canal and Kandy Lake are also surrounded by highly populated areas. The lowest PFOS concentration was found in Negombo Lagoon. The Negombo Lagoon has high water exchange through the narrow inlets which are connected to the sea from the North side, could reduce the retention time of contaminant in the water profile. For instance, mean concentration of PFOS found in Negombo Lagoon was within the recorded PFOS concentrations in coastal waters from Hong Kong (0.27-3.1 ng $L^{-1}$), China (0.46-2.5 ng $L^{-1}$) and Korea (0.17-3.1 ng $L^{-1}$) .[7]

Mean PFOA concentration (6.8 ng $L^{-1}$) in the Kandy Lake, which was the only location where samples collected from an inland fresh water system, greater than all other locations. The Kandy Lake is surrounded by the second largest city in Sri Lanka, where industrial influences may be less than in the Bire Lake. In contrast, mean PFOA concentration in the Kandy Lake was 2.7 folds greater than that of PFOS concentration (2.5 ng $L^{-1}$). Similar contamination pattern was found in surface waters in New York State. [8] This pattern may be indicative of different sources of flurochemical contamination between Colombo and Kandy area. Sinclear *et al*.[8] suggested that greater PFOA contamination may arise from the use of fluoropolymers and telomer alcohols. PFOA is an essential wetting agent in the production of polytetrafluoroethylene (PTFF) (kennedy, 2004).[22] PTFE also used in number of household utensils including non-stick cookware and other products such as food packaging, clothing, and carpeting.

Two perfluoro precursors, *N*-EtFOSAA and PFOSA, were detected in the water samples in the range of 0.034-4.1 and <0.016-7.5 ng $L^{-1}$. Data for *N*-EtFOSAA and PFOSA in water are scarce. The precursor concentrations found here are similar to those reported data in the Great Lakes for *N*-EtFOSAA (<2.2-11 ng $L^{-1}$) and PFOSA (<0.3-1.3 ng $L^{-1}$). THPFOS, (0.055-2.8 ng $L^{-1}$) has been reported in all the locations from Sri Lankan waters. The THPFOS concentration found in Kandy Lake was 14-folds lower than that in the Bire Lake. Fluorotelomer sulfonates such as THPFOS are active ingredients of fluorocarbon-based surfactants used in aqueous film-forming foams (AFFF).

The mean concentrations of other perfluoro compounds were minor. PFHpA, PFHxA, PFHS, PFBS, PFNA, PFDA, PFUnDA, PFDoDA were, respectively, 5-, 7-, 7-, 14-, 18-, 28-, 100-, and 167-folds less than the mean concentration of PFOS.

PFOS concentration in Bire Lake in Colombo city was few folds greater than other locations, where as Kandy Lake contained elevated PFOA concentration suggesting different sources into two water bodies. This report provides first set of data for contamination of fluorinated chemicals found in waters from South Asian region. The PFOS and PFOA concentration found in Sri Lankan waters fall within the concentration ranges of those reported for surface waters from most of developed nations including the United State and Japan.

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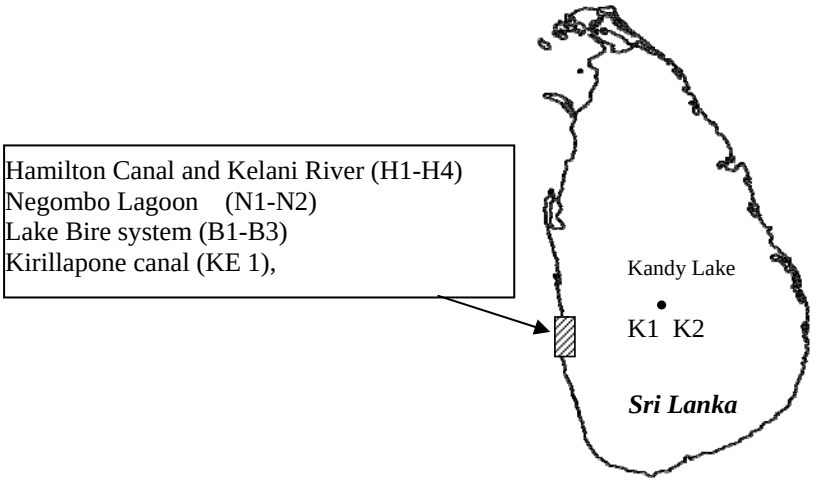


Figure 1: Sampling Area

Table 1. Recovery and concentrations of perfluoroalkyl surfactants in waters in Sri Lanka (ng/L)

| | PFOS | PFHS | PFBS | PFOSA | PFDoDA | PFUnDA | PFDA | PFNA | PFOA | PFHpA | PFHxA | THPFOS | *N*-EtFOSAA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Average recovery | 90% | 101% | 92% | 97% | 102% | 108% | 110% | 100% | 100% | 116% | 117% | 108% | 97% |
| Cartridge blank | <0.016 | <0.016 | <0.016 | <0.016 | <0.016 | <0.016 | <0.016 | <0.08 | <0.08 | <0.08 | <0.08 | <0.016 | <0.016 |
| LOQ[a] | 0.016 | 0.016 | 0.016 | 0.016 | 0.016 | 0.016 | 0.016 | 0.08 | 0.08 | 0.08 | 0.08 | 0.016 | 0.016 |
| Negombo Lagoon | | | | | | | | | | | | | |
| N1 | 0.66 | 0.14 | <0.016 | <0.016 | <0.016 | 0.027 | 0.10 | 0.27 | 1.1 | 0.89 | 0.94 | 0.12 | 0.068 |
| N2 | 0.71 | 0.072 | <0.016 | <0.016 | <0.016 | 0.045 | 0.11 | 0.27 | 1.2 | 0.84 | 0.90 | 0.15 | 0.11 |
| Hamilton Canal & Kelani River | | | | | | | | | | | | | |
| H1 | 0.96 | 0.21 | 0.14 | <0.016 | <0.016 | 0.023 | 0.12 | 0.29 | 1.1 | 0.53 | 0.56 | 0.11 | 0.055 |
| H2 | 2.3 | 0.82 | 1.2 | 0.017 | <0.016 | 0.035 | 0.20 | 0.61 | 2.7 | 1.0 | 1.41 | 0.071 | 0.034 |
| H3 | 1.6 | 0.46 | 0.047 | 0.018 | <0.016 | 0.018 | 0.11 | 0.23 | 0.82 | 0.57 | 0.77 | 0.65 | 0.093 |
| H4 | 2.7 | 0.86 | 0.31 | 0.047 | <0.016 | 0.056 | 0.16 | 0.30 | 1.7 | 1.4 | 2.2 | 2.8 | 0.38 |
| Bire Lake | | | | | | | | | | | | | |
| B1 | 4.9 | 0.97 | <0.016 | 0.37 | 0.034 | 0.110 | 0.35 | 0.33 | 2.2 | 0.73 | 0.47 | 0.31 | 4.1 |
| B2 | 44 | 1.1 | <0.016 | 7.5 | 0.041 | 0.133 | 0.50 | 0.49 | 12.3 | 2.0 | 1.5 | 2.5 | 3.7 |
| B3 | 5.2 | 1.4 | <0.016 | 0.39 | 0.032 | 0.087 | 0.40 | 0.31 | 2.6 | 0.87 | 0.60 | 0.70 | 4.0 |
| Kirillapone Canal | | | | | | | | | | | | | |
| KE1 | 4.1 | 0.50 | <0.016 | 0.052 | <0.016 | 0.065 | 0.18 | 0.27 | 2.0 | 0.94 | 0.95 | 0.20 | 0.48 |
| Kandy Lake | | | | | | | | | | | | | |
| KN1 - 0.5m | 2.3 | <0.016 | <0.016 | 0.18 | <0.016 | 0.034 | 0.16 | 0.36 | 6.6 | 0.36 | 0.33 | 0.10 | 1.1 |
| KN2 - 3m | 2.6 | <0.016 | <0.016 | 0.19 | <0.016 | 0.077 | 0.16 | 0.31 | 7.0 | 0.26 | 0.36 | 0.055 | 0.98 |

[a]LOQ: Level of quantification