Direct Measurement Of Perfluoroalkylated Surfactants In The Great Lakes Water Samples

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Introduction

Considerable effort has been made in the last few years to determine the level of perfluorinated surfactants contamination in the environment, particularly perfluoroalkylated acids. The unique physicochemical properties of the perfluorinated compounds contributed to their large industrial and household use over the last 50 years. These chemicals are part of a large number of surface treatment and surfactant formulations such as fire-fighting foams, special cleaners, mining surfactants and insecticides. A recent report[1] showed higher values of perflourooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) than the values determined earlier[2] for the Great Lakes and has created a scientific debate[3,4].

This paper presents the first report of a direct determination of perfluorinated surfactants from water samples at the parts-per-trillion (ng/L) level, eliminating the extraction/concentration steps used in the previous studies[1,5]. The goal of the investigation was to determine the level of selected perfluorinated surfactants in Great Lakes waters using a simple method, with minimal manipulation of the original sample. Results are reported for PFOS ($C_8F_{17}SO_3^-$) and PFOA ($C_7F_{15}CO_2^-$) in water samples from Lake Ontario, Lake Erie and Lake Huron, quantified with internal standard and standard addition methods. Samples from 11 different locations were analyzed in triplicate.

Experimental Section

Standards and Chemicals

Potassium perfluorohexane sulfonate (PFHxS, 99.9%), potassium PFOS (86.4%) and heptadecafluorooctane sulfonamide (PFOSA, 99.9%) were provided by the 3M Company (St Paul, MN, USA). Standards of perfluoroheptanoic acid (PFHpA, 99%), PFOA (96%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUnA, 95%) and perfluorododecanoic acid (PFDoA, 95%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Optima grade methanol and HPLC grade water were obtained from Fisher Scientific (Toronto, ON, Canada).

Two internal standards were used, ^{13}C mass-labeled PFOA ($^{13}C_2$-PFOA, Perkin-Elmer Life Sciences, Boston, MA, USA) and ^{13}C mass-labeled PFDA ($^{13}C_2$-PFDA, Wellington Laboratories, Guelph, ON, Canada).

Water Samples

One liter samples were collected at a depth of 1.5 m from Lake Ontario (LO-1 – LO-7), Lake Erie (LE-1 – LE-3) and Lake Huron (LH-1) at off shore and near shore locations in September 2004 and stored in polypropylene bottles at 4 °C. Aliquots of 300 µL from the water samples were mixed with an equal volume of MeOH containing the internal standards $^{13}C_2$-PFOA and $^{13}C_2$-PFDA giving final concentrations of 20 fg/µL and 50 fg/µL, respectively. The sample/MeOH mixtures were filtered using Mini-UniPrep^{TM} syringeless filter devices having 0.2 µm polypropylene (PP) filter media and PP housings (Whatman, Forham Park, NJ, USA). Preliminary tests were also performed using 0.45 µm PP and 0.2 µm Nylon Mini-UniPrep^{TM} syringeless filter devices.

Five 100 mL replicates collected from one Lake Ontario location (LO-2) were spiked with $^{13}C_2$-PFOA and $^{13}C_2$-PFDA, concentrated using ENVI-18 (6 mL, 1g C18) solid phase extraction (SPE) cartridges (Supelco, Oakville, ON, Canada), eluted with MeOH, evaporated to dryness and reconsituted in 1 mL solvent 1:1 MeOH/water. Three 100 mL aliquots were similarly processed after spiking them with a perfluoroalkylated surfactants solution for an addition of 1 ng for each analyte (final concentration - 10 ng/L).

Instrumental Analysis by LC/MS/MS

Analysis of target analytes (PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS and PFOSA) was performed using a high performance liquid chromatograph-tandem mass spectrometer system (HPLC-MS/MS), consisting of an Agilent 1100 Series liquid chromatograph coupled with a 4000QTRAP triple quadrupole mass spectrometer (Applied Biosystems - MDS Sciex, Concord, ON, Canada). Water and methanol solvents (0.01 M ammonium acetate) were passed through an Agilent degasser (G1379A) and delivered by the binary pump system (G1312A) at a total flow rate of 250 µL/min. One hundred microliter (100 uL) aliquots of the original water sample/MeOH mixes were injected by the Agilent autosampler (G1313A) through a C18 guard column (2mm i.d. x 4 mm, Phenomenex, Torrance, CA, USA) with chromatographic separation performed on a Genesis C18 column (2.1

mm i.d. x 50 mm, 4µm; Chromatographic Specialties, Brockville, ON, Canada). Target analyte separation was obtained in 4 minutes under isocratic conditions with a mobile phase consisting of 80% methanol and 20% water. The mass spectrometer was operated in negative electrospray ionization multiple reactions monitoring (MRM) mode. After optimizing the source/gas related parameters, the ion spray voltage was maintained at -4500 V, the turbo ion spray was operated at 400 °C, with the nebulizer gas at 45 psi and the turbo gas maintained at 60 psi. Prior to this study the instrument analyzed only samples having less than 5 pg/ µL of each perfluorinated compound, to prevent instrumental contamination.

Quantitation was performed using internal standards and standard additions. Standards mixtures containing 0.5, 1, 2, 5, 10, 20, 50 and 100 ng/L (fg/uL) were used to create calibration curves for each analyte. Peak area counts were corrected based on the internal standard ($^{13}C_2$-PFOA) response. For both PFOS and PFOA the equations obtained had the correlation coefficient r^2=0.999. For each sample 3 replicates and 3 standard additions (+2, +5 and +10 fg/µL) were analyzed, with 3-4 injections from each one of them. The results reported for the standard addition method are based on the peak area counts from three aliquots and three standard additions (2, 5 and 10 ng/L) for each sample. The values determined with the standard addition method for the SPE processed samples are based on the peak area counts of five aliquots and one standard addition (10 ng/L) for three aliquots from a Lake Ontario sample (LO-2).

Results and Discussion

Mini-UniPrep^{TM} syringeless filter devices were tested with Nylon and polypropylene (PP) filtering media. The Nylon filter is more suited to analyzing PFHpA, PFOA, PFNA and PFDA, since it retained minimal amounts of these analytes from 1 - 100 fg/µL standard solutions. For the same reason the PP filter is more suited to analyzing sulfonates (PFHxS, PFOS and PFOSA) and longer chain perfluorinated acids (PFUnA, PFDoA). Using PP vials without filtration would avoid the loss of all analytes on filtering media but the instrument would be exposed to particulates present in the samples. When samples were less diluted with MeOH (0-10%), the analytes were retained completely on the filtering media. Therefore samples were mixed 1:1 with MeOH to minimize losses on the filtering media and maintain a low limit of detection (LOD) for the analytes.

The analytes monitored in all samples were: PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS and PFOSA. The limit of detection (LOD) for all the analytes were between 1 and 4 ng/L. PFOS and PFOA were detected in all lake samples tested with the exception of the Lake Huron sample. No PFOA was detected in the Lake Huron sample (Figures 1 and 2).

The large level of PFOA in blanks reported in the previous studies[1,5] was not observed in our study. The major differences between our method and the previous ones are the lack of preconcentration steps and the isocratic conditions used for the separation. No peaks were observed in the blanks when the volume injected was 10 µL or less. The mismatch of the MeOH content between the mobile phase and the sample injected was identified as factor which creates disturbances in the background level and small peaks of PFOA in the blanks, especially when relatively large volumes of 100 µL were injected. The peak observed in the blank is directly affected by the difference in MeOH content and the volume injected.

Matrix effects were observed in all real samples tested based on monitoring the peak area counts of the two internal standards. The analytes with less retention were more affected, including the $^{13}C_2$-PFOA internal standard. The effect was less evident for the second internal standard $^{13}C_2$-PFDA. The decrease in area counts for the mass-labeled analytes is a good indication of the matrix effects since they are not present in any real sample.

The values determined for PFOS with the standard addition method were 1-4 ng/L lower than the values determined based on the internal standard. This trend was not evident for PFOA where the differences between the values determined with the two methods were smaller (0-2 ng/L), although relatively large standard deviations (SD) for the internal standard method were observed. A lower level of PFOS (Figure 3) was determined from the 5 SPE replicates but the value determined using the standard addition method is similar to the values determined with direct injection. This effect was not observed for PFOA because the matrix affects the non-chromatographically separated labeled and native PFOA in the same manner. $^{13}C_2$-PFOA is clearly not the best candidate for quantifying PFOS, but at this time there are no mass-labeled sulfonates available.

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References

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Figure 1: Concentrations of PFOA determined from the eleven water samples from the Great Lakes.

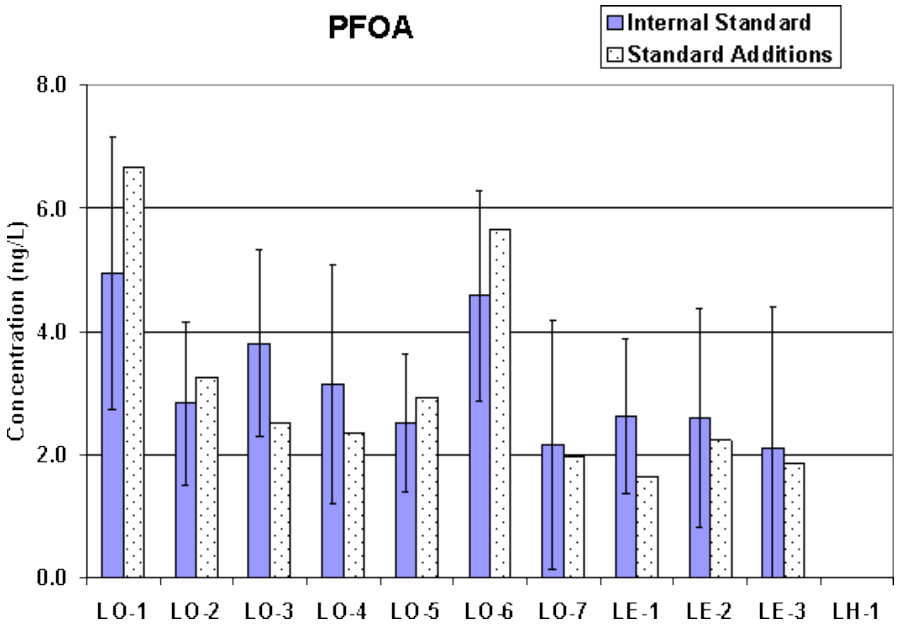


Figure 2: Concentrations of PFOS determined from the 11 water samples from the Great Lakes:

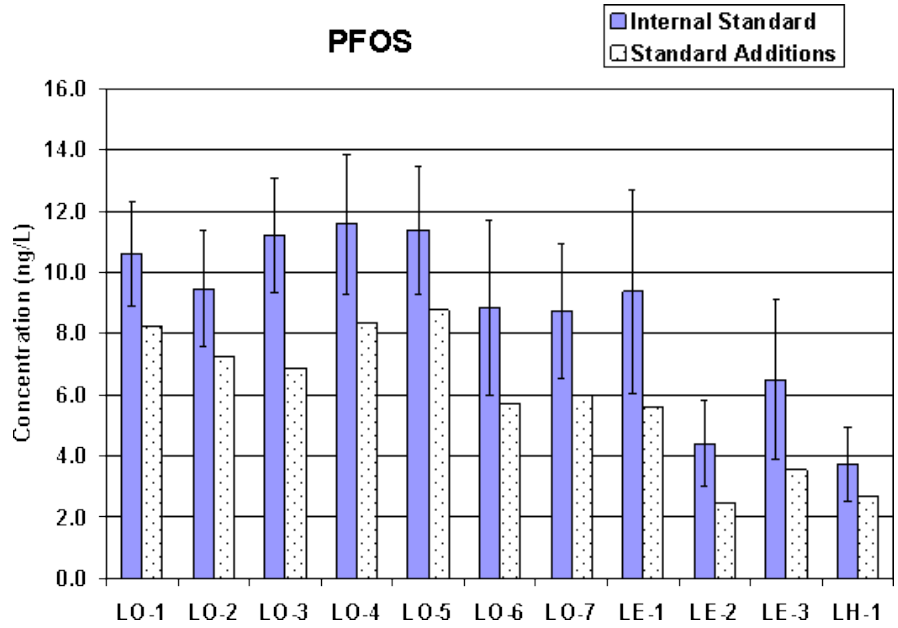
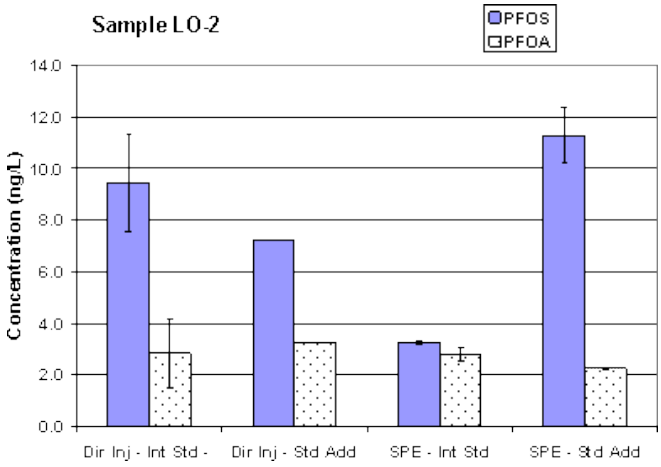


Figure 3: Concentrations of PFOS and PFOA determined in sample LO-2 from Lake Ontario; internal standard and standard addition methods were used for both, direct injection and SPE processed samples:


Sample LO-2
PFOS
PFOA
Concentration (ng/L)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Dir Inj - Int Std -
Dir Inj - Std Add
SPE - Int Std
SPE - Std Add