DETERMINATION OF PERFLUOROALKYL SUBSTANCES (PFASs) IN DRINKING WATER FROM THE NETHERLANDS AND GREECE.

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Introduction

Perfluoroalkylated substances (PFASs) are organic chemicals that possess thermal, chemical and biological stability, non-flammability and surface-activity properties[1, 2]. Their unique properties enable them to persist in the environment and bioaccumulate in living organism, and to biomagnify in the food chain. PFASs have been detected in environmental matrices (air, dust, sewage, rivers, oceans etc.)[3-5], food products (fish, chicken, eggs, milk, drinking water etc.) and food packages[6-10] and also in biological matrices (blood, breast milk)[11, 12]. Routes through which humans are exposed to PFASs are e.g. inhalation and consumption of food products, drinking water and inhaling household dust, regardless the fact that the exact mechanism comprises an issue of further research. Some studies demonstrate the consumption of drinking water as one of the most important routes of exposure, as there is a correlation between the consumption rate of PFASs contaminated water and the PFASs' concentration in human serum[13, 14]

In the present study the concentrations of PFASs in drinking water samples (tap and bottled water) from the Netherlands and Greece were determined in an effort to evaluate, compare and explain the levels of contamination in both countries. In a PFASs dietary exposure assessment for Dutch consumers some years ago[6], the contribution from drinking water was based on estimated PFASs levels due to the lack of measured drinking water PFASs levels. These estimated levels can now be replaced by real measured values coming from this study. To our knowledge, this is the first study presenting PFASs' levels in tap and bottled water samples from Greece, and it is an important contribution to the existing body of literature. The sampling points for the tap water samples were chosen based on the origin of the water (groundwater, surface water) used for the preparation of drinking water, in order to distinguish differences among contamination levels. For the analysis of these samples, a liquid chromatography-tandem mass spectrometer (LC-MS/MS) and isotope dilution method were applied. In the present study 11 PFASs: perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorobutane sulfonate (PFBuS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS) were quantifiied.

Materials and methods

Drinking water samples were collected from the Netherlands and Greece from August 2013 until January 2014. Tap water samples were collected using prewashed bottles (rinsed with MeOH) and then stored at 4^{o}C until the analysis. The different brands of bottled water were collected from supermarkets in both countries and were also stored in the refrigerator (4^{o}C) until the analysis. For each water sample, 250 ml were fortified with 25 µl of Mass-Labelled *PFCAs and PFSAs* Solution/Mixture (MPFAC-MXA, purchased from Wellinghton laboratories) 100 ng/ml and homogenised. Solid phase extraction (SPE) was performed by using weak anion exchange Oasis WAX cartridges[9, 15]. SPE cartridges were eluted with 3 ml NH_4OH in acetonitrile (ACN) and the collected extract was centrifuged for 10 min at 10000 rpm at 20^{o}C. After centrifugation, the supernatant was evaporated till dryness under N_2. The dry residue was dissolved in 675 µl of 2 mM ammonium acetate in H_2O, 300 µl of ACN and 25 µl of $^{13}C_8$-PFOS solution 100 ng/ml. The final solution was transferred into a vial for analysis by LC-MS/MS.

For the analysis of all the water samples, LC-MS/MS was used, based on a Shimadzu LC system with a Acquity UPLC BEH C18 analytical column (50mm * 2.1mm i.d., 1.7 um, Waters). In addition, a Symmetry C18 column (50mm * 2.1mm i.d., 5 um, Waters) was used as guard column in order to isolate and delay interferences from the LC system. The chromatographic gradient was operated at a flow rate of 0.400 mL/min starting from 75% 2 mM ammonium acetate in water (A) to 100% ACN (B) in 6 min. The LC system was connected to a triple quadrupole MS (AB SCIEX QTRAP 5500 SYSTEM, Applied Biosystem - Analytical Technologies), equipped

with a Turbo Spray source operating in negative mode. The analyses were performed with a multiple reaction monitoring (MRM) method that monitored two mass transitions (parent ion/product ion) for every analyte except for PFPeA.
The limit of detection (LOD) was determined as 3 times the signal to noise ratio and it was set at 0.2 ng/l for all the compounds, and the recoveries were ranging between 85-115% for all the mass-labelled compounds except for the $^{13}C_2$-PFUnA (60-80%). Quality-control (QC) standards (one blank water sample and two spiked water samples at the concentrations of 0.05 ng/ml and 1 ng/ml) were analysed in every batch of samples, controlling in this way the repeatability of the analytical method.

Results and discussion
Drinking water samples were collected from the Netherlands (37 tap water samples and 5 bottled water samples) and Greece (43 tap water samples and 5 bottled water samples). The sampling points of the tap water in the two countries are illustrated in Figure 1.

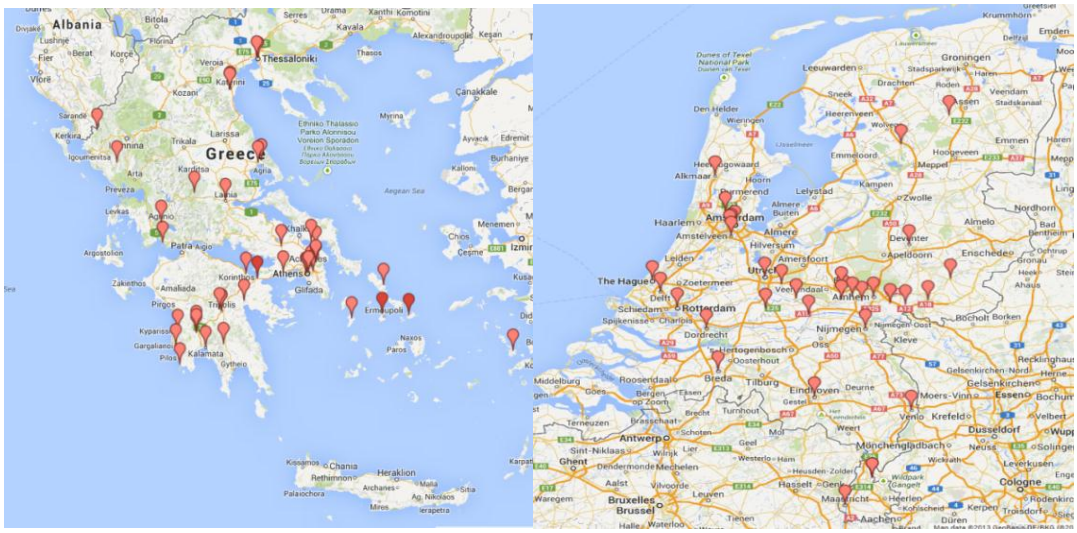

Fig. 1. Drinking water sampling points in Greece (left panel) and in the Netherlands (right panel). Maps were generated using Google Maps (www.googlemaps.com)

The concentrations of PFASs were summarized. In 18 (out of 37) samples from the Netherlands, PFASs were detected above the LOQ (0.6 ng/L). This was also the case for 9 (out of 43) samples from Greece. PFASs levels in drinking (tap) water from the Netherlands were higher in comparison to the Greek ones (Table 1). The ∑PFASs in the Greek samples ranged between <LOQ to 5.9 ng/L, with the highest concentrations in water from three Aegean islands, Mykonos (PFASs sum: 5.9 ng/L), Kalymnos (PFASs sum: 4.8 ng/L) and Syros (PFASs sum: 3.6 ng/L) and also from one town in Peloponnisos, Tripoli (PFASs sum: 5.7 ng/L). On the Aegean islands there is no industrial activity. Possibly the detected levels can be attributed to other factors including human activities which increase at the islands during the summer period due to tourism. Also, contribution from water supplying systems cannot be excluded. The ∑PFASs in the Dutch samples ranged between <LOQ and 53.5 ng/L, with a maximum concentration detected in the area around the Amsterdam Schiphol airport. It is not clear why the levels at Schiphol airport were the highest observed in this study. Apart from Schiphol, the most contaminated samples from the Netherlands originated from the surrounding areas of Amsterdam and Rotterdam, two densely populated cities. This is in agreement with the results of previous studies in Europe, where the highest concentrations of PFASs were also detected in drinking water samples originated from the most industrialized cities[16-18]. A likely explanation for these elevated PFASs levels in the western part of the Netherlands is that tap water is sourced mainly from river water which is contaminated with PFASs. In the eastern part of the Netherlands, drinking water is sourced from groundwater, which probably explains why the PFAS levels in these water samples were lower, mostly <LOQ (Figure 2).
In the present study, considering the drinking water sourced from Dutch surface water, the short chain PFASs, especially PFBuS, PFHxS, PFPeA, PFHxA, PFHpA, and PFOA, and in some places PFOS, were detected most frequently, while the longer chain PFASs (C>8) were rarely detected (Figure 2). These results are in accordance

with previous studies[17, 19-20]. A potential explanation is that the short chain PFASs are less efficiently removed by the water purification procedures. This suggests that water purification procedures should be adapted in order to remove also shorter chain PFASs[21].

As far as the bottled water samples are concerned, they all originated from ground wells and no PFASs were detected.

The currently found levels in drinking water from Greece and the Netherlands should be combined with levels of PFASs in food products to examine if they could pose a risk to human health, taking into account the established TDI levels by EFSA (150 ng/kg b.w. for PFOS, 1500 ng/kg b.w. for PFOA)[22]. However, EFSA TDI levels do not take into account other short chain PFASs. Up to now, it is unknown what the consequences for the human exposure of these short chain substances are.

Table 1. Concentrations (ng/L) of PFASs in drinking (tap) water from the Netherlands and Greece

∑PFASs concentration (ng/L)	No. samples (n)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	Median (ng/L)
Netherlands					
<LOQ - 15	26	<LOQ	7.5	0.6	1.4
15-30	8	17.4	29.9	25.3	24.7
30-55	3	30.9	53.5	38.8	32.1
Greece					
<LOQ - 2	38	<LOQ	0.8	0.1	0.8
2-6	5	2.4	5.9	4.5	5.3

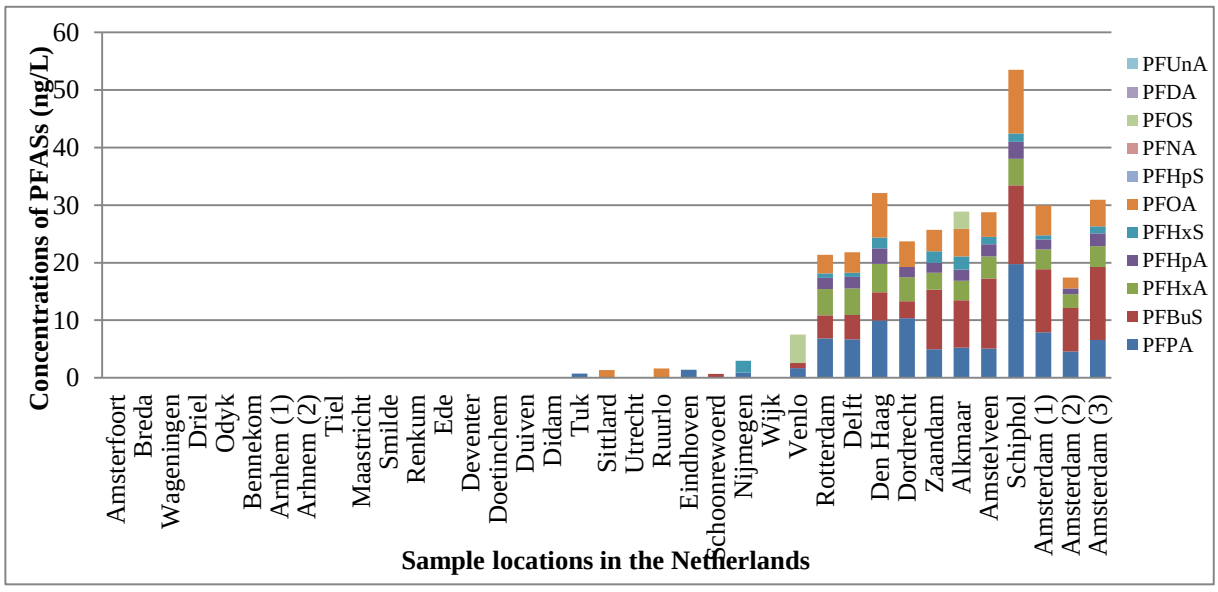

Figure 2. Concentrations of individual PFASs (ng/L) in the drinking (tap) water samples from the Netherlands

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