



Quantitative trace analysis of polyfluorinated alkyl substances (PFAS) in ambient air samples from Mace Head (Ireland): A method intercomparison

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ABSTRACT

A method intercomparison study of analytical methods for the determination of neutral, volatile polyfluorinated alkyl substances (PFAS) was carried out in March, 2006. Environmental air samples were collected in triplicate at the European background site Mace Head on the west coast of Ireland, a site dominated by 'clean' westerly winds coming across the Atlantic. Extraction and analysis were performed at two laboratories active in PFAS research using their in-house methods. Airborne polyfluorinated telomer alcohols (FTOHs), fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs) as well as additional polyfluorinated compounds were investigated. Different native and isotope-labelled internal standards (IS) were applied at various steps in the analytical procedure to evaluate the different quantification strategies. Field blanks revealed no major blank problems. European background concentrations observed at Mace Head were found to be in a similar range to Arctic data reported in the literature. Due to trace-levels at the remote site, only FTOH data sets were complete and could therefore be compared between the laboratories. Additionally, FOSEs could partly be included. Data comparison revealed that despite the challenges inherent in analysis of airborne PFAS and the low concentrations, all methods applied in this study obtained similar results. However, application of isotope-labelled IS early in the analytical procedure leads to more precise results and is therefore recommended.

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1. Introduction

During recent years, concern regarding polyfluorinated alkyl substances (PFAS) has increased due to their persistence, bio-accumulative properties, potential toxicity and ubiquitous presence in the environment. The determination of these industrial chemicals in human blood (Hansen et al., 2001; Yeung et al., 2006) and organisms from remote locations such as the Arctic (Giesy and Kannan, 2001; Smithwick et al., 2005) and the Southern Ocean (Tao et al., 2006) has been reported in numerous studies.

Nevertheless, the major issue for regulation of this new and emerging group of environmental contaminants is the investigation of sources and transport pathways for PFAS. How do persistent ionic compounds like perfluorooctane sulfonate (PFOS) and perfluorocarboxylates (PFCAs) reach remote regions far from

production and emission areas? The so-called 'precursor hypothesis' proposed by Ellis et al. (2003, 2004) mentions indirect long-range atmospheric transport via neutral, volatile precursors such as fluorotelomer alcohols (FTOHs) as a possible transport pathway. Atmospheric oxidative transformation might eventually degrade airborne FTOHs to PFCAs and lead to their precipitation (Ellis et al., 2004). In addition, biotransformation may occur after inhalation or ingestion of precursor PFAS (Dinglasan et al., 2004). Alternatively, direct release and long-range waterborne transport of ionic PFAS to remote locations by means of oceanic currents were postulated by Prevedouros et al. (2006).

Regarding the precursor theory, air monitoring data from North America (Martin et al., 2002; Stock et al., 2004; Shoeib et al., 2004, 2005; Piekartz et al., 2007; Loewen et al., 2008), Europe (Jahnke et al., 2007a,b; Barber et al., 2007; Dreyer et al., 2008), Japan (Piekartz et al., 2007; Oono et al., 2008), the Arctic (Shoeib et al., 2006; Stock et al., 2007) and remote locations in the Southern East Atlantic (Jahnke et al., 2007c) have recently emerged. However, analysis of airborne PFAS at low levels is hampered by analytical challenges due to their unusual physical–chemical properties and relatively high volatility compared to 'classical' semi-volatile contaminants such as polychlorinated biphenyls. Additionally, the lack of standardisation of analytical protocols may limit data comparability between different laboratories. Isotope-labelled (IL)

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internal standards (IS) have only recently become available for these chemicals. Most of the previously published studies used native IS, a method less precise than using IL IS, and an intercomparison exercise is necessary to compare results obtained using the different quantification strategies.

The only PFAS interlaboratory comparison studies carried out previously did not include air analysis (van Leeuwen et al., 2006; Longnecker et al., 2008). A method intercomparison was performed applying two different air sampling methods simultaneously at the same location (Jahnke et al., 2007b). However, these samples were extracted and analysed in the same laboratory.

The scope of this study was to perform a method intercomparison of the trace determination of neutral, volatile PFAS including FTOHs, applying quantification using IL IS or native standards (NS). The European Monitoring and Evaluation Program (EMEP) and Global Atmospheric Watch (GAW) station Mace Head on the west coast of Ireland was chosen to provide European background levels of these emerging environmental contaminants. A two-week sampling campaign was carried out in March, 2006. Samples were shipped to two different European laboratories active in PFAS research and with considerable experience in analysis of airborne PFAS: GKSS Research Centre Geesthacht (GKSS), Germany and Lancaster University (LU), UK. At these laboratories, samples were processed and analysed applying the respective in-house analytical protocols.

Additionally, European background levels of neutral, volatile PFAS as determined in this study were set into context with published data from metropolitan Hamburg, Germany (Jahnke et al., 2007b) and Arctic air concentrations (Shoeib et al., 2006; Stock et al., 2007; Jahnke, 2007).

2. Experimental

2.1. Materials and methods

The analytical standards used in this study including acronyms, CAS numbers and suppliers are listed in Table 1. Whilst the GKSS method (Jahnke et al., 2007d) only included 6:2 FTOH, 8:2 FTOH,

10:2 FTOH, *N*-methyl/ethyl fluoroctane sulfonamide (NMe/EtFOSA) and *N*-methyl/ethyl fluoroctane sulfonamidoethanol (NMe/EtFOSE), the LU method (Barber et al., 2007) additionally investigated 4:2 FTOH, 12:2 FTOH, fluorotelomer olefins (6:2 FTOlefin, 8:2 FTOlefin, 10:2 FTOlefin and 12:2 FTOlefin), fluoroctane sulfonamide (FOSA) as well as *N*-methyl fluorobutane sulfonamide and sulfonamidoethanol (NMeFBSA/NMeFBSE). Method detection limits (MDLs) of the commonly analysed compounds are given in Table 2. For details on how MDLs were derived, we refer to Jahnke et al. (2007d) and Barber et al. (2007). At both laboratories, reagents and solvents were of highest commercially available quality and used as received.

The methods for sampling, extraction and analysis used in this study have been described in detail elsewhere, including extensive method validation data (Jahnke et al., 2007d; Barber et al., 2007). Briefly, all analytical protocols included the enrichment of the target analytes on glass fibre filters (GFFs, providing an estimate of the analyte fraction present in the particulate phase) and XAD-2 resin sandwiched between two polyurethane foam slices (PUF/XAD-2/PUF, representing the fraction in air associated with the gaseous phase) by means of high-volume air samplers. The GFFs and PUF/XAD columns were extracted separately with ethyl acetate (EtOAc), concentrated and analysed by gas chromatography coupled to mass spectrometry using chemical ionisation (GC/CI-MS). Positive chemical ionisation (PCI) was applied for quantification of the analytes, while negative chemical ionisation (NCI) was used qualitatively. The complete GC/CI-MS methods are described in Jahnke et al. (2007d) and Barber et al. (2007). Important characteristics of the different methods are given in Table 2.

2.2. Internal standards

Two spiking strategies were examined: (1) spiking IL IS at the sampling site just prior to sampling which results in whole method recoveries including 'breakthrough' losses during sampling (GKSS), and (2) spiking IL IS (strategy 2 a) or NS (strategy 2 b) prior to extraction giving extraction method efficiencies only (LU). By

Table 1
Analytical standards, their acronyms and CAS numbers, suppliers and purities used in the GKSS method (Jahnke et al., 2007d) and the LU method (Barber et al., 2007).

Target analyte	Acronym	CAS no.	Supplier and purity (GKSS)	Supplier and purity (LU)
1H,1H,2H-perfluoro-1-octene	6:2 FTOlefin	25291-17-2	n.a.	Interchim, Montluçon, Cedex, France/>97%
1H,1H,2H-perfluoro-1-decene	8:2 FTOlefin	21652-58-4	n.a.	Interchim, Montluçon, Cedex, France/>97%
1H,1H,2H-perfluoro-1-dodecene	10:2 FTOlefin	30389-25-4	n.a.	Interchim, Montluçon, Cedex, France/>97%
1H,1H,2H-perfluoro-1-tetradecene	12:2 FTOlefin	67103-05-3	n.a.	Interchim, Montluçon, Cedex, France/>97%
1H,1H,2H,2H-perfluoro-1-hexanol	4:2 FTOH	2043-47-2	n.a.	Matrix Scientific, Columbia, SC, USA/97%
1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH	647-42-7	Lancaster Synthesis, Frankfurt a.M., Germany/97%	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH	678-39-7	Lancaster Synthesis, Frankfurt a.M., Germany/97%	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH	865-86-1	Lancaster Synthesis, Frankfurt a.M., Germany/97%	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
1H,1H,2H,2H-perfluoro-1-tetradecanol	12:2 FTOH	39239-77-5	n.a.	donation DuPont/no information on purity available
<i>N</i> -methyl nonafluorobutane sulfonamide	NMeFBSA	n.a.	n.a.	donation 3M/no information on purity available
<i>N</i> -methyl nonafluorobutane sulfonamidoethanol	NMeFBSE	n.a.	n.a.	donation 3M/no information on purity available
<i>N</i> -methyl heptadecafluoroctane sulfonamide	NMeFOSA	31506-32-8	donation 3M, Germany/no information on purity available	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
<i>N</i> -ethyl heptadecafluoroctane sulfonamide	NEtFOSA	4151-50-2	ABCR, Karlsruhe, Germany/95%	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
<i>N</i> -methyl heptadecafluoroctane sulfonamidoethanol	NMeFOSE	24448-09-7	donation 3M, Germany/no information on purity available	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%
<i>N</i> -ethyl heptadecafluoroctane sulfonamidoethanol	NEtFOSE	1691-99-2	donation Mabury group at University of Toronto, Ontario, Canada/97%	donation 3M/no information on purity available
Heptadecafluoroctane sulfonamide	FOSA	754-91-6	n.a.	Wellington Laboratories Inc., Guelph, Ontario, Canada/>98%

n.a., Not available.

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