



Per- and polyfluoroalkyl substances in the Western Mediterranean Sea waters



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HIGHLIGHTS

- First study on the dissolved PFASs in the open Western Mediterranean Sea waters.
- PFHxA, PFHpA, PFOA, PFHxS and PFOS were the most abundant compounds.
- Atlantic inflow and river discharge are likely the most important sources.
- Open sea PFAS levels were lower than those detected along the coast of Spain.
- Concentrations of PFHxA, PFHpA and PFHxS were higher than in the Atlantic Ocean.

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ABSTRACT

The spatial and temporal distribution of per- and polyfluoroalkyl substances (PFASs) in the open Western Mediterranean Sea waters was investigated in this study for the first time. In addition to surface water samples, a deep water sample (1390 m depth) collected in the center of the western basin was analyzed. Perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorohexanesulfonate (PFHxS) and perfluorooctanesulfonate (PFOS) were detected in all samples and were the dominant PFASs found. The sum of PFAS concentrations (Σ PFASs) ranged 246–515 $\mu\text{g/L}$ for surface water samples. PFASs in surface water had a relatively homogeneous distribution with levels similar to those previously measured in the Atlantic near the Strait of Gibraltar, in water masses feeding the inflow to the Mediterranean Sea. Higher concentrations of PFHxA, PFHpA and PFHxS were, however, found in the present study. Inflowing Atlantic water and river/coastal discharges are likely the major sources of PFASs to the Western Mediterranean basin. Slightly lower (factor of 2) Σ PFASs was found in the deep water sample (141 $\mu\text{g/L}$). Such a relatively high contamination of deep water is likely to be linked to recurring deep water renewal fed by downwelling events in the Gulf of Lion and/or Ligurian Sea.

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1. Introduction

During recent years, several per- and polyfluoroalkyl substances (PFASs) have been recognized as ubiquitous environmental contaminants. Some perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonates (PFASs) are priority substances for research and regulation because of their persistence, bioaccumulative potential, global distribution and toxicity. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), for example, are

routinely measured in terrestrial, freshwater and marine environments, including biota (Buck et al., 2011; Giesy and Kannan, 2001; Houde et al., 2011, 2006; Yamashita et al., 2005), and their toxicity and bioaccumulation is well documented (Beach et al., 2006; Conder et al., 2008; Lau et al., 2007). In 2000, a major global manufacturer announced the phase-out of PFOS and related compounds (3M, 2000). Six years later, the world's major fluorochemical manufacturers committed to substantially reduce emissions and product content of PFOA, its precursors and PFASs with longer aliphatic chains (U.S. EPA, 2015). The European Union banned most uses of PFOS and related compounds in 2008 (European Commission, 2006). In 2009, PFOS and its precursor perfluorooctane sulfonyl fluoride (PFOSF) were added to the annex B of

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the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2009) resulting in global restriction of their production and use. Furthermore, the Stockholm Convention recently recommended PFOA to be listed as a persistent organic pollutant (POP) (UNEP, 2015).

For over 60 years, PFASs have been used as emulsifiers, lubricants, components of fire-fighting foams, stain and soil repellent agents, textiles, electronics, food packaging and detergents (Kissa, 2001). The unique physicochemical properties of PFASs make their replacement difficult. Known fluorinated alternatives to long-chain PFASs belong essentially to two categories: i) shorter chain homologues; and ii) functionalized perfluoropolyethers (Wang et al., 2015). Although some of those alternatives (e.g. shorter chain PFASs) are less bioaccumulative (Conder et al., 2008) and less toxic (Borg and Hakansson, 2012), they may still pose risks to humans and the environment (Wang et al., 2015).

PFASs have been emitted to the environment from direct sources (i.e. emissions from manufacture, product use and disposal) but they can also be formed in the environment as degradation products of some polyfluorinated precursors (e.g. fluorotelomer alcohols, polyfluoroalkyl phosphates, polyfluorinated amides/sulfonamides and their derivatives) (Buck et al., 2011; Dinglasan et al., 2004; Ellis et al., 2004; Jackson et al., 2013; Martin et al., 2006; Wallington et al., 2006) primarily as a result of atmospheric reaction with OH radicals and/or biodegradation. Known sources of PFASs to the aquatic environments include effluents from industrial and residential waste water (Arvaniti and Stasinakis, 2015), landfill effluents (Kallenborn et al., 2004), contaminated wet atmospheric depositions (Dreyer et al., 2010; Scott et al., 2006), and runoff from contaminated soils (Lindstrom et al., 2011). Due to the carboxylic/sulfonic acid groups PFCAs and PFASs are less volatile and more soluble in water than legacy POPs such as PCBs or organochlorine pesticides. As a result, marine waters are their main environmental reservoirs. Transport to the deep waters and burial into sediments were identified as final sinks of the environmental burden of persistent PFASs (Prevedouros et al., 2006; Sanchez-Vidal et al., 2015; Yamashita et al., 2008; Zaraitalabad et al., 2013).

Due to their elevated persistence in air and water, many PFASs are detected also in pristine areas including the open sea. Two main transport pathways were proposed to account for the presence of PFASs in remote areas: i) long-range atmospheric transport of volatile neutral precursors degraded in remote regions (Ellis et al., 2004; Stock et al., 2007; Young et al., 2007); and ii) direct transport of ionic PFASs by oceanic currents or by means of sea spray (Armitage et al., 2009a; Prevedouros et al., 2006; Wania, 2007). While the atmospheric inputs are the main drivers of contaminations by PFASs in inland environments (Benskin et al., 2011; Schenker et al., 2008; Young et al., 2007), oceanic advection is the dominant pathway to remote marine environments (Armitage et al., 2006, 2009a, 2009b).

Investigating PFAS distribution in offshore marine environments is useful to elucidate transport mechanisms and assess background environmental contamination levels. Pioneering work by Yamashita et al. showed widespread occurrence of PFOA and PFOS in the global oceans (Yamashita et al., 2008, 2005). Several studies have further focused on gathering data on a broader range of PFASs in open ocean waters along global transects (Ahrens et al., 2010b, 2009; Benskin et al., 2012a, 2012b; Cai et al., 2012; González-Gaya et al., 2014) and the North Sea (Ahrens et al., 2010a; Theobald et al., 2011).

The present study focused, for the first time, on the open Mediterranean Sea. Despite being enclosed by land, the Mediterranean Sea is a deep oligotrophic ocean with surface water influenced by inflow from the Atlantic Ocean through the Gibraltar

strait and with a water mass circulation path that, similarly to that of a large ocean, is essentially controlled by convective processes and evaporation. Inflow from rivers has very little influence on water properties and transport (especially in the western basin). This influence is limited to near-shore locations where a few medium-sized river estuaries are found. Surface water in the west basin of the Mediterranean primarily originates from the Atlantic water inflow through the Gibraltar strait and thereby is referred to as Modified Atlantic Water (MAW). The aims of the study were: i) to assess for the first time PFAS water contamination in open Mediterranean surface water; ii) to assess spatial variability of PFAS concentrations in surface water; iii) to assess seasonal differences; and iv) to compare PFAS levels and profiles with previous data from Spanish coast (Sánchez-Avila et al., 2010) and inflowing Atlantic water (Ahrens et al., 2010b, 2009; Benskin et al., 2012b; González-Gaya et al., 2014). The overall rationale for this study was to gather information useful to infer on the transport pathways controlling PFAS levels in the Mediterranean Sea surface water.

2. Materials and methods

2.1. Sample collection

In order to obtain spatially integrated PFAS concentration data, several (7–14) surface water grab samples were collected in selected sampling areas (volume of individual spot sample varied between 350 and 700 mL). These were pooled prior to extraction to form an aggregated sample of about 5 L. Samples were collected during two cruises in spring (MEDOCC14) and autumn (EMSO-MEDIT_02 + ICHNUSSA2014) 2014 from the Italian research vessel Urania. Integrated samples were collected along route lengths of approximately 50–120 km (3–8 h time integration). Details on sample collection including exact coordinates, sampled volumes, temperature and salinity of individual sampling locations can be found in the Supporting Information (Tables S1 and S2).

A total of 6 aggregated samples were collected during the first cruise in March–April 2014 and 10 aggregated samples during the cruise conducted in November 2014 (Fig. 1). In one case a single deep water sample was collected 50 km south of Sardinia at the depth of 1390 m using a Niskin bottle deployed on a CTD rosette.

Water samples were collected into 5 L pre-cleaned amber glass bottles using the ship water inlet positioned at 4 m below sea surface. The sampling train and pump were made of PVC and metal with no fluoropolymer parts. No pre-filtration of the samples was performed during collection. Before usage, the bottles were pre-cleaned using Decon 90 (Decon Laboratories Limited, Hove, UK), Milli-Q water and rinsed with methanol (MeOH) at least three times.

Immediately after merging the samples from different spot locations in equal volumes, solid phase extraction (SPE) was performed directly on board.

2.2. Chemicals, reagents and standards

The analytical standards for eighteen target compounds (10 PFCAs, 5 PFASs, FOSA, MeFOSE and EtFOSE) and twelve isotopically-labelled standards ($^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_4$ PFOA, $^{13}\text{C}_8$ PFOA, $^{13}\text{C}_5$ PFNA, $^{13}\text{C}_2$ PFDA, $^{13}\text{C}_2$ PUnDA, $^{13}\text{C}_2$ PFDoDA, $^{18}\text{O}_2$ PFHxS, $^{13}\text{C}_4$ PFOS, $^{13}\text{C}_8$ PFOS, dMeFOSE, dMeFOSE) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). The standards were supplied in the form of methanolic solutions. Working solutions at different concentrations were prepared by appropriate dilution of these solutions in MeOH and HPLC grade water. All isotopically-labelled standards except $^{13}\text{C}_8$ PFOA and $^{13}\text{C}_8$ PFOS were used as internal standards and were added before instrumental analysis to

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