



Delivery of unprecedented amounts of perfluoroalkyl substances towards the deep-sea



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HIGHLIGHTS

- We have found perfluoroalkyl substances (PFASs) in marine sinking particles.
- Dense shelf water cascading enhances PFAS transfer towards greater depths.
- Specific interactions of PFASs with particles play a major role in their downward flux.

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ABSTRACT

The finding of perfluoroalkyl substances (PFASs) in particles sinking to the deep northwestern Mediterranean Sea confirms the role of the latter as ballast for the transfer of pollutants to the deep sea. The transfer of particulate matter down to the deep is enhanced during atmosphere-driven, high-energy physical oceanographic processes like dense shelf water cascading (DSWC), which is caused by winter surface heat losses and evaporation. Here we present data from samples collected during winter 2012, when dense shelf water formation and subsequent cascading triggered the flushing of large amounts of PFASs through a submarine canyon to depths in excess of 1000 m. The finding of quantifiable concentrations of long-chain PFOA, PFOS and PFNA substances and significantly high concentrations of the short-chain substances PFHxA and PFBA indicates that these compounds, sorbed onto particulate matter, are quickly and directly transferred to the ocean's interior, thus highlighting the role of DSWC in removing those pollutants from the coastal ocean. Eventually, uncertainties about our results arising from the limited number of samples available are counterbalanced by their intrinsic value as intense DSWC events, like the one in 2012, occur only every 5–7 years in the study area, which seriously restricts sampling opportunities. Our results add PFASs to the list of persistent organic pollutants like polychlorinated biphenyls, chlorobenzenes or polycyclic aromatic hydrocarbons known to be conveyed to the deep marine environment.

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1. Introduction

Since the late 1940s perfluoroalkyl substances (PFASs), consisting of a hydrophobic alkyl chain, partly or fully fluorinated, and a hydrophilic end group, have been extensively manufactured for a number of industrial and consumer applications such as oil, stain and water repellents for textiles and paper products, insecticides, surfactants, fluoropolymers, metal plating and cleaning, and lubricants (Prevedouros et al., 2006; Buck et al., 2011 and references therein). Due to their high bioaccumulation, persistence and toxic properties (Key et al., 1997; Giesy and Kannan, 2002; Beach et al., 2006) studies of PFAS emission sources,

occurrence in environmental matrices and biological effects are of the utmost interest.

PFASs have been released for decades into the environment both from direct and indirect sources. Direct emissions occur after the discharges at production sites, while indirect emissions mainly result from the formation of specific PFAS by transformation of perfluoroalkyl based products and residues from the galvanizing and paper industries and, specially, from waste water treatment plants (WWTPs) (Llorca et al., 2012). Once in the environment, the physicochemical properties of each substance drive their partitioning, degradation and transport ability (Ahrens et al., 2011). Long-chain substances, such as perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), with 6 or more perfluorinated carbons, have a greater tendency to bioconcentrate and/or bioaccumulate than their short-chain analogues (Martin et al., 2003). In 2006, the

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world's eight main fluorochemical manufacturers committed to strongly reduce the emissions of PFOA and related chemicals and to cease their production by 2015. In May 2009, PFOS and related salts were included in the global list of persistent organic pollutants (POPs) under the Stockholm Convention. They were listed in Annex B of the Convention, which means that parties must take measures to restrict the production and use of the chemical, except for permitted uses. Subsequently, the production of perfluorochemicals has recently shifted to shorter chain compounds, which are less toxic and non-bioaccumulative (Conder et al., 2008). They are nonetheless persistent and the fate of their degradation products is still unknown.

PFASs have been detected in all environmental compartments such as air (Xie et al., 2013), soils and sediments (Higgins et al., 2005), freshwater (Kim and Kannan, 2007; Clara et al., 2009), coastal waters (So et al., 2004; Sanchez-Avila et al., 2010), open ocean waters including remote areas such as the Arctic Ocean (Cai et al., 2011; Yamashita et al., 2008) and biota (Kelly et al., 2009). Some recent studies have reported short-chain compounds in freshwater and beach sediments too (Llorca et al., 2012; Yeung et al., 2013). Although it has been hypothesized that most of the PFASs released so far reside in the oceans (Prevedouros et al., 2006; Cousins et al., 2011), their occurrence in particles settling to the deep sea has not been established to date. In this context, semi-enclosed seas, like the Mediterranean Sea, behave as land-derived pollutant collectors (Albaiges, 2005; Salvadó et al., 2012).

In the northwestern Mediterranean, two atmospheric-driven hydrodynamic processes have been recognized as the major particle transport mechanisms from coastal and shelf environments to the deep-sea: dense shelf water cascading (DSWC) and wave storms (Canals et al., 2006; Palanques et al., 2006; Sanchez-Vidal et al., 2012). Such processes transport particles mainly through submarine canyons, which act as preferential conduits for cross-margin sediment transfer (Canals et al., 2013; Puig et al., 2014). In particular, the Cap de Creus submarine canyon has been identified as the main off-shelf pathway for sedimentary particles being resuspended from the Gulf of Lion during high-energy, atmospheric-driven events (Palanques et al., 2006). Previous studies have reported the presence of organochlorine compounds (Salvadó et al., 2012, 2013) and anthropogenic trace elements (Cossa et al.,

2014) in the Cap de Creus Canyon, therefore representing a key site for assessing the transfer of pollutants to the deep-sea ecosystems.

The objective of this study is to provide the first evidence ever of PFASs downward fluxes in the ocean. Time series of particle fluxes were obtained in the Cap de Creus Canyon during a period characterized by moderate storms and a major DSWC event. 21 PFASs were considered, including 13 perfluoroalkyl acids, 4 perfluorosulfonates, 1 sulfonamide and 3 perfluorophosphonic acids. We aim to investigate the relevance of PFAS fluxes to the deep sea and to assess the role of deep continental margins and basins as their ultimate sink.

2. Material and methods

2.1. Sample and data collection

Instrumented moorings were deployed during winter 2011–12 at 300 and 1000 m depth in the axis of the Cap de Creus Canyon (stations CCC300 and CCC1000, Fig. 1). The CCC300 mooring was equipped with a Technicap sediment trap placed at 25 m above the bottom (mab) and an Aanderaa RCM-9 current meter placed at 5 mab. The CCC1000 mooring was equipped with a Technicap sediment trap deployed at 25 mab and a Nortek Aquadopp current meter placed at 23 mab.

Despite the fact that there are many documented accuracy issues (e.g. Gardner, 2000; Buesseler et al., 2007), sediment traps are the only tool for directly collecting sinking particles during their transit to the deep sea. The sequential sampling sediment traps used in this study were Technicap PPS3 (0.125 m² collecting area) and PPS4 (0.05 m² collecting area) models with a cylindro-conical collection funnel and 12 polypropylene collecting cups (Heussner et al., 1990), which were set to rotate every 15 days. Sampling intervals were set at 30 min for current meters. The arrival of large amounts of material in February 2012 clogged the sediment trap at CCC1000, which prevented obtaining further samples beyond this date.

Before the deployment the cups were cleaned with 0.5 N HCl, rinsed with ultrapure water and filled with buffered 5% (v/v) formaldehyde solution in 0.45 µm filtered seawater. This poisoning solution prevents degradation of trapped particles and limits the disruption of swimming

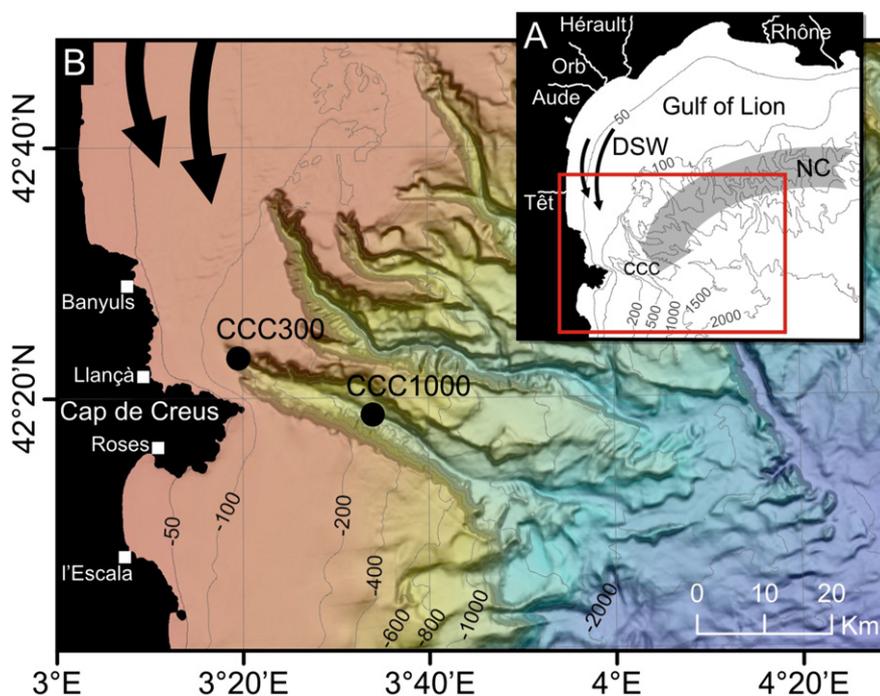


Fig. 1. A, General bathymetric map of the Gulf of Lion with main rivers. The coarse grey arrow shows the direction of the mesoscale along-slope Northern Current (NC), while the thin black arrows over the shelf illustrate the flow of dense-shelf water (DSW). B, Location of the instrumented mooring lines in the Cap de Creus Canyon (CCC) at 300 (CCC300) and 1000 (CCC1000) m of water depth.

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