



Perfluoroalkyl substances in the Maltese environment – (I) surface water and rain water



G. Sammut^a, E. Sinagra^{a,*}, R. Helmus^b, P. de Voogt^{b,c}

^a Department of Chemistry, University of Malta, Malta

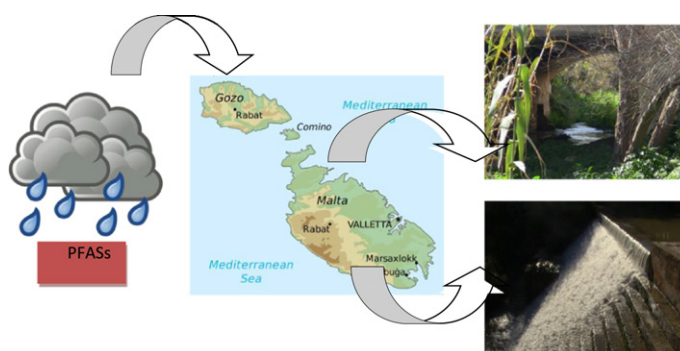
^b IBED, University of Amsterdam, Amsterdam, Netherlands

^c KWR, Watercycle Research Institute, Nieuwegein, Netherlands

HIGHLIGHTS

- The occurrence and distribution of 2 perfluorosulfonates and 5 perfluorocarboxylates in the Maltese surface and rain water were investigated.
- PFOA and PFOS were the most abundant PFASs in surface water.
- Except for a few samples PFAS concentrations and PFAS composition in precipitation were quite uniform suggesting common sources.
- Air masses from source regions yielded rain with higher Σ PFAS concentrations than ones travelling over sea or having rain events prior to sampling.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of perfluoroalkyl substances (PFASs) in rain water on the Maltese Islands is reported here for the first time and an extensive survey of these substances in surface water also reported. The Maltese archipelago lies at the centre of the Mediterranean Sea and consists of three main inhabited islands: Malta, Gozo and Comino. Surface water was collected from 41 valleys during the months of February and March 2015 at the peak of the wet season. Rain water was collected during the months of December 2014, February, August, September and October 2015. PFASs were extracted from the water samples using solid phase extraction and the extracts were then analysed using ultra performance liquid chromatography coupled to mass spectrometry in tandem (UPLC-MS/MS). All surface and rain water samples were contaminated with at least one PFAS. PFOS (<LOD – 8.6 ng/L) and PFOA (ND – 16 ng/L) were the two major PFASs being detected in 100% and 95% of the surface waters respectively. The Σ PFAS concentrations in rain water ranged between 0.38 ng/L (1st October 2015) and 6 ng/L (21st February 2015). The Maltese archipelago is surrounded by sea and disconnected from any other mainland; therefore the results confirm that remote environments can become contaminated by PFASs from rain events depending on wind prevailing trajectories.

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* Corresponding author at: Room 109, Chemistry & Pharmacology Building, University of Malta, Msida.
E-mail address: emmanuel.sinagra@um.edu.mt (E. Sinagra).

1. Introduction

No one can deny the fact that the last five decades have seen a tremendous growth in public, scientific and governmental interest in the environmental effects of persistent organic pollutants (POPs). POPs are chemical substances that resist environmental breakdown, therefore accumulating in the environment and have the capability of long-range transport (Jones and de Voogt, 1999). In addition, they also have the capability of bioaccumulating in human and animal tissues with a negative consequence on human and animal health (Gascon et al., 2013). Initially, the focus was more on POPs that contained chlorine and bromine, such as chlorofluorocarbons (CFCs) and polychlorinated biphenyls (PCBs) (Key et al., 1997). However during the past years an awareness has risen on a new type of POP that contain an alkyl chain, typically between 4 and 12 carbon atoms, with all or most hydrogen atoms replaced by fluorine. These are referred to as *polyfluoroalkyl or perfluoroalkyl substances* (PFASs).

As one would expect, the increased awareness in perfluoroalkyl substances contributed to a surge in publications in the literature which is constantly growing. PFASs have been detected in a variety of environmental matrices from around the globe. These include surface waters (Skutlarek et al., 2006; Taniyasu et al., 2003; Loos et al., 2007; Möller et al., 2010; Heydebreck et al., 2015), oceans (Ahrens et al., 2010a,b; Yamashita et al., 2008; Wei et al., 2007; So et al., 2004), fish (Lacina et al., 2011; Nania et al., 2009; Llorca et al., 2009; Schuetze et al., 2010; Svihlikova et al., 2015), milk (Lacina et al., 2011), human milk (Barbarossa et al., 2013; Kuklenyik et al., 2004; So et al., 2006; Tao et al., 2008a,b; Guzmàn et al., 2016), human blood (Kuklenyik et al., 2004; Kannan et al., 2004; De Silva and Mabury, 2006; Góralczyk et al., 2015), rain water (Dreyer et al., 2010; Mahmoud et al., 2009), drinking water (Eschauzier et al., 2013a,b, 2012; Ullah et al., 2011), food samples (Vestergren et al., 2012; Domingo et al., 2012), food packaging (Begley et al., 2005; Still et al., 2013), vegetables (Herzke et al., 2013; Felizeter et al., 2012; Stahl et al., 2009; Lechner and Knapp, 2011), air (Shoeib et al., 2004; Stock et al., 2004; Arkadiusz et al., 2007), dust (Domingo, 2012; Shoeib et al., 2005), sludge (Eschauzier et al., 2012), soils (Prevedouros et al., 2006; Rankin et al., 2016), sediments (Clara et al., 2009; Lorenzo et al., 2016), arctic environment (Shoeib et al., 2006; Young et al., 2007; Stock et al., 2007) and polar bears (de Silva and Mabury, 2004; Smithwick et al., 2005, 2006), amongst others.

Two major sources have been described for the distribution of PFASs in the environment (Buck et al., 2011). The first is direct sources which refer to the manufacture and use and disposal of PFASs. The second is indirect sources which refer to the formation of a PFAS by transformation of precursor substances in the environment, wildlife or humans. Two transport pathways of PFASs have also been suggested, namely hydro-spheric and atmospheric (Kim and Kannan, 2007). Sources of PFASs in surface water have been identified as street run off (Murakami et al., 2009), discharge of fire-fighting foam (Moody et al., 2002), landfill leachates (Moody and Field, 1999; Eschauzier et al., 2013b) and degradation of precursor compounds (Ellis et al., 2004). Rainfall also plays a part how PFASs end up in surface water since it has been described as being the most effective scavenger for the removal of atmospheric pollutants (Al-Khashman, 2005; Migliavacca et al., 2005). It has also been shown to be an effective scavenger for PFASs in the atmosphere (Kwok et al., 2010). Two types of scavenging processes have been described (Manoli et al., 2000): (i) in-cloud scavenging and (ii) below-cloud scavenging.

The only study of perfluoroalkyls substances in the Maltese environment was by Loos et al. (2009). The study reported results from surface water samples obtained from 3 valleys in the Maltese Islands namely; Wied il-Luq in Siggiewi, Bahrija Valley in Rabat and Wied il-Lunzjata in Fontana. The European wide study reported the results of analysis of PFHxA, PFHpA, PFOA, PFNA, PFOS, PFDA, and PFUNA. Only PFOA and PFOS were detected in appreciable amounts and these only in Wied il-

Luq on the island of Malta. There are no reports of perfluoroalkyl substances in rain water precipitating on the Maltese Islands.

The main objective of this study is to assess the occurrence of 7 PFASs in surface water and rain water in the Maltese Islands. The archipelago consists of three inhabited islands, namely Malta, Gozo and Comino and two tiny uninhabited islands. The land area of the Maltese Islands covers just over 316 km²; Malta covers 246 km² and Gozo 67 km². The coastline of Malta is 137 km long while that of Gozo is 43 km, both islands having a variety of bays, creeks and stretches of cliffs. Surface water was analysed from several valleys found on the two principal islands. The Maltese islands have no permanent rivers or lakes. However, the islands are scarred from end to end by valleys. During times of high rainfall, most of these are filled with fresh water and although most dry up in summer, some watercourses may have fresh water running all year round. The water which accumulates in these valleys is then utilised by farmers to water their crops during the summer months.

2. Materials and methods

2.1. Chemicals and standards

The target analytes included two perfluorosulfonates which were PFHxS and PFOS and five perfluorocarboxylates which included PFHxA, PFHpA, PFOA, PFNA and PFDA. Internal Standards (I.S.) in methanol included ¹³C₂-PFHxA, ¹³C₄-PFHpA, ¹³C₈-PFOA, ¹³C₅-PFNA, ¹³C₆-PFDA, ¹⁸O₂-PFHxS and ¹³C₈-PFOS. A list with abbreviations of the non-labelled and labelled standards is shown in Table S1 of the Supporting information (SI).

The analytical standards and labelled standards were provided as a mixture in methanol by Prof. De Voogt and his team and had originally been procured by Campro Scientific, Veenendaal, The Netherlands. Methanol (MeOH) of LC-MS grade was obtained from Scharlab, while ammonium acetate (AcNH₄; 77.08 g/mol; 98%) and sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O; 248.18 g/mol; >99.5%) were obtained from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water having a conductivity of 18 MΩ/cm was prepared using the Elga Purelab Classic purification system.

2.2. Sampling sites and sample collection

Surface water samples were collected during the months of February and March 2015 at the peak of the wet season. A total of 41 samples were collected, 10 of which were collected from valleys in Gozo, while 31 were collected from valleys situated in Malta (Fig. 1). Rain water was collected during 8 different rainfall events from the locality of Zebbug, Malta. Water samples (surface and rain water) were collected in pre-cleaned polypropylene (PP) bottles with a capacity of 1.0 L. The bottles and screw-caps were rinsed with methanol and dried before use to minimize contamination. The bottles were then rinsed three times with the water to be sampled on-site prior to collecting the water. Water suspected to contain free chlorine was tested and if present approximately 80 mg of sodium thiosulfate pentahydrate were added. Samples were kept chilled during transportation and then stored at or below –20 °C in the laboratory until analysis. Before extraction, samples were allowed to thaw and reach room temperature. A Field Reagent Blank (FRB) was also handled with each sample set and treated exactly in the same manner as a sample.

2.3. Solid phase extraction

PFAS were extracted from water samples using the Waters Oasis® HLB Waters cartridges based on the method described by Waters® (2009). The cartridge was pre-conditioned by passing 10 mL of MS grade methanol at a flow rate of <10 mL/min followed by 10 mL of 18 MΩ/cm water.

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