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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 ΣPFAS concentrations than ones travelling over sea or having rain events prior to sampling.

GRAPHICAL ABSTRACT
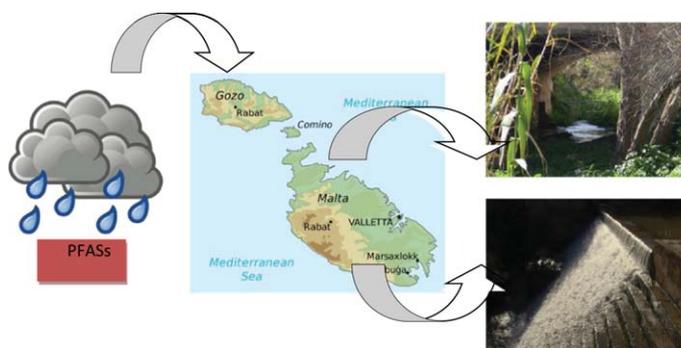
ARTICLE INFO

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 ΣPFAS 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; Góralcazyk 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 hydrospheric 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 Siġġiewi, Baħrija 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 km^2; Malta covers 246 km^2 and Gozo 67 km^2. 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 $^{13}C_2$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_8$-PFOA, $^{13}C_5$-PFNA, $^{13}C_6$-PFDA, $^{18}O_2$-PFHxS and $^{13}C_8$-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 (AcNH$_4$: 77.08 g/mol; 98%) and sodium thiosulfate pentahydrate (Na$_2$S$_2$O$_3$·5H$_2$O: 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.
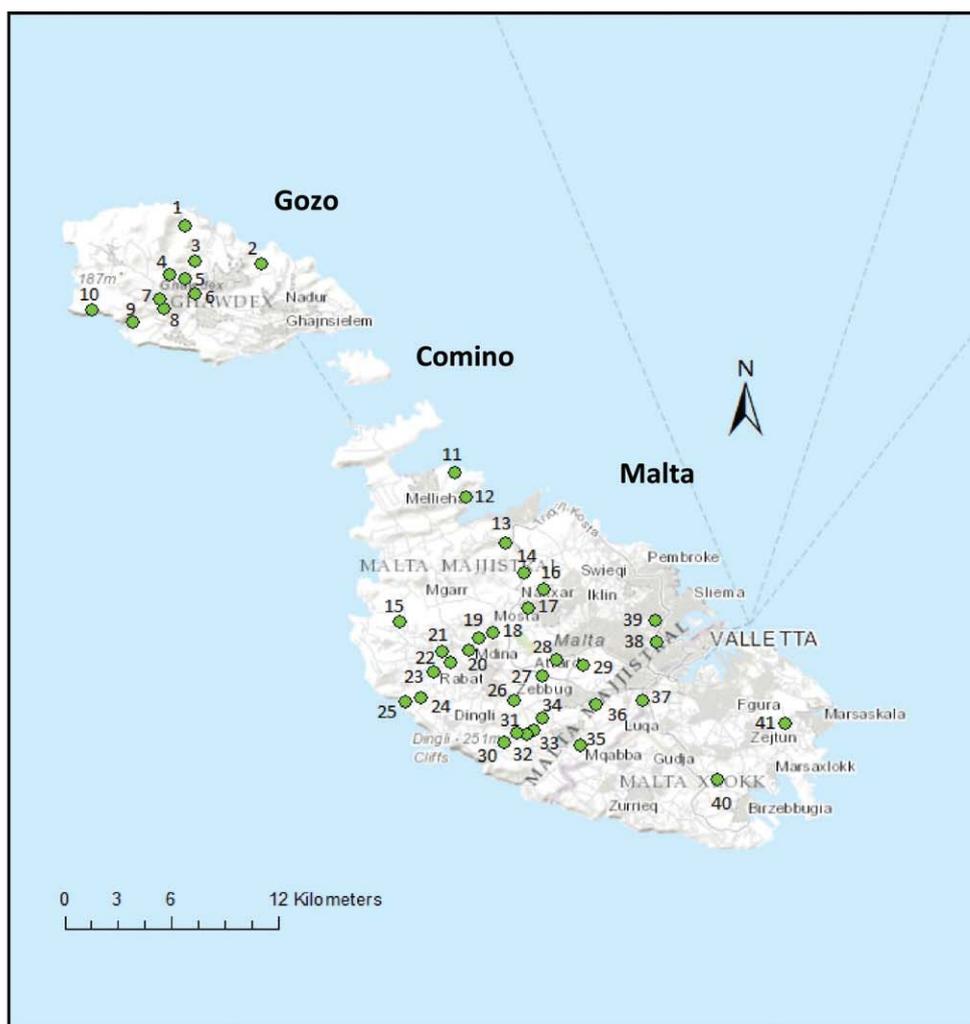
1 - Wied l-Infern	2 - Wied Ramla l-Ħamra	3 - Wied Marsalforn
4 - Wied ta` Sara	5 - Wied tal-Grazzja	6 - Wied ta` Żejta
7 - Wied il-Lunzjata	8 - Għajn tal-Ħasselin	9 - Wied Xlendi
10 - Għadira ta` Sarraflu	11 - Wied l-Imġiebaħ	12 - Wied tal-Mistra
13 - Wied Qannotta	14 - Wied Għajn Rihana	15 - Wied Santi
16 - Wied il-Għasel	17 - Wied Speranza	18 - Wied il-Qlegħja (lower)
19 - Wied l-Armla	20 - Wied il-Qlegħja (Chadwick Lakes)	21 - Wied Għomor
22 - Wied tal-Fiddien	23 - Wied il-Busbies	24 - Wied Liemu
25 - Wied ir-Rum	26 - Wied l-Isqof	27 - Wied Incita (Żebbuġ)
28 - Wied ta` Rmiedi	29 - Wied is-Sewda	30 - Wied Girgenti
31 - Wied il-Luq	32 - Wied Ħesri (upper)	33 - Wied Ħesri (lower)
34 - Wied San Anton	35 - Wied Xkora	36 - Wied Qirda
37 - Wied il-Kbir	38 - Msida Reservior	39 - Wied Għollieqa
40 - Saptan	41 - Wied iz-Ziju	

Fig. 1. Map of the Maltese Islands showing the locations from which surface water was collected during February and March 2015.

Prior to carrying out solid phase extraction, water samples were spiked with 150 µL of 0.599 ng/mL I.S. The conditioned cartridge was then loaded with 500 mL of water at a flow rate of approximately 5 mL/min. Residual water in the sorbent was removed by passing nitrogen through the cartridge for approximately 20 min.

For elution, 2 mL of methanol was passed through the cartridge at a flow rate of 1 mL/min and the solvent collected in a 15 mL PP centrifuge tube. The extract was concentrated by evaporating to a total of 500 µL using a nitrogen/bath evaporator with the temperature set to 35 °C. The methanol eluent (300 µL) was delivered to a PP UPLC sample vial. The target sample mixture is 1:3 eluent/water.

2.4. Chromatographic conditions

The samples were analysed using the Waters® ACQUITY UPLC® System with the TQ-D Detector (UPLC-MS/MS). The data were acquired using MassLynx™ Software, v.4.1. Incorporated into MassLynx Software, IntelliStart™ Software technology was used to optimise MRM scan parameters. PFASs are present in many components of laboratory instruments and trace levels of PFASs can leach out. In addition, PFASs have also been detected in common HPLC solvents and in laboratory water, therefore analysis of PFASs requires great care. For this reason the Waters® ACQUITY® PFC Analysis Kit was installed and used. This

kit contains PEEK solvent lines, stainless steel tubing, screws, ferrules, filters, a PFC Isolator Column, an ACQUITY UPLC BEH C$_{18}$ 2.1 × 50 mm column, OASIS HLB cartridges and vials and PFASs standards. The PFC Isolator Column was placed in-line between the solvent mixer and the injector. The chromatographic conditions including the optimal MRM conditions used for each compound are presented in Tables S2, S3 and S4 in the Supporting Information.

2.5. Quantification and quality control

Quantification was performed by the internal standard method. A seven-point calibration curve at 0.33, 0.66, 1.29, 2.62, 5.2, 10.4 and 20.83 ng/mL was used for the quantification with good linearity over this concentration range (R^2 > 0.9979). The calibration curves for each PFAS analysed are presented in Figs. S1 to S7 in the Supporting information. Instrumental blanks consisting of 25% methanol in water was injected between each sample and in addition a Field Reagent Blank was incorporated with each batch of water samples. None of the instrumental blanks and field reagent blanks showed any contamination. The limits of detection and quantification of the analytical method were calculated with the minimum concentration of analyte that produced a signal-to-noise ratio (S/N) of 3:1 and 10:1, respectively (Table 1). Percent recoveries were determined using 18 MΩ/cm water free of PFASs spiked with the target compounds (Table 1). Percent recoveries for internal standards in surface water and rain water were always between the ranges of 70%–130%.

3. Results and discussion

3.1. Occurrence of PFASs in water

The Water Operations Unit of the Water Services Corporation (WSC) is responsible for all distribution and groundwater operations in the Maltese Islands. The Maltese tap water consists approximately of 50% groundwater and 50% desalinated water produced from sea water. The groundwater is rainwater that permeates the ground and slowly seeps through porous rock until it reaches the aquifer. Therefore, rainwater alone which falls on the ground and the rainwater which accumulates as surface water during the winter months can be considered as being sources of PFASs in groundwater. As a consequence, the PFASs in groundwater can be considered as being one source of PFASs in drinking water although contamination that can occur during tap water production should also be considered. Apart from contaminating the groundwater, surface water may end up in the sea since rivers are in fact considered as the main vehicle for transporting contaminants to the sea (Sanchez-Avila et al., 2010; McLachlan et al., 2007). Malta, being an island in the Mediterranean Sea which is an enclosed basin, contributes minimally to river run-off and effluent discharges which are identified as the main culprit of pollution. To evaluate the possible contamination of surface waters which may eventually contaminate groundwater, used for drinking water production, agriculture and husbandry, different surface samples from Malta and Gozo were assessed.

Table 1
Methodological detection limit (LOD) and quantification limit (LOQ) and mean recoveries of the target compounds.

PFAS	Limit of detection (LOD)	Limit of quantitation (LOQ)	Mean recovery (n = 3)
PFHxS	0.02 ng/L	0.04 ng/L	91%
PFOS	0.03 ng/L	0.04 ng/L	98%
PFHxA	0.02 ng/L	0.04 ng/L	72%
PFHpA	0.02 ng/L	0.04 ng/L	76%
PFOA	0.03 ng/L	0.04 ng/L	73%
PFNA	0.02 ng/L	0.04 ng/L	73%
PFDA	0.02 ng/L	0.06 ng/L	75%

3.1.1. Occurrence of PFASs in surface waters

The release of PFASs into surface waters from industrial sources is insignificant in Malta since these do not exist. Therefore, the sources of PFASs would be expected to be rainfall, dust (from street run off) and disposal of PFASs containing substances. The PFAS concentrations in surface waters collected from 41 different valleys from Malta and Gozo is shown in Table 2. All 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. These values were comparable to data reported by Loos et al. (2009) for the 3 Maltese valleys that these workers surveyed. In the same study, PFOA and PFOS were also identified as the major PFAS contaminant present in European Rivers (detected in 97% and 94% of samples respectively). Other studies, concerning these substances in European rivers (McLachlan et al., 2007; Möller et al., 2010), have shown that concentrations of PFOA and PFOS are similar to those found in this present study. Unlike the concentrations detected on the Maltese Islands, European rivers were found to have concentrations as high 97 ng/L and 1371 ng/L for PFOA and PFOS respectively. The fact that the concentrations in the Maltese Islands are lower is attributed to the fact that there is no industrial source of these substances and that the surface waters in Malta are not linked to any of the European rivers.

In the present study, other major PFAS were perfluoroalkylcarboxylic acids PFHxA (ND – 17 ng/L) and PFHpA (ND – 11 ng/L) being detected in 92% and 90% of the surface waters respectively. PFHxS (88%), PFNA (85%) and PFDA (66%) were detected in trace concentrations (<5 ng/L).

In terms of cumulative PFAS concentrations (i.e. considering the sum of the seven PFASs analysed), the highest were found in Wied Sara (Valley 4, 35 ng/L) and Wied tal-Grazzja (Valley 5, 33 ng/L) (Fig. 2). These two valleys, located in Gozo, are connected (Fig. 2) and both have high concentrations of PFHxA (17 ng/L and 15 ng/L) and PFHpA (11 ng/L and 10 ng/L). Both valleys are surrounded by agriculture land and are in a rural area (Fig. 2). Simcik and Dorweiler (2005) proposed that the ratio of PFHpA/PFOA is indicative of atmospheric PFAS sources when greater than one and of non-atmospheric sources associated with urban areas when the value is lower than one. The same study also showed that the ratio increased as the location of the surface waters increased in distance from urban areas. Both valleys have a ratio > 1, which is indicative of atmospheric PFAS sources. The high concentrations of PFHxA and PFHpA may also be an indication of these originating from the same source. Wang et al. (2014) estimated a continuous increase in the global emissions for 6:2 FTOH which is a volatile precursor of PFHxA and PFHpA. In fact, 6:2 FTOH is a major raw material being used to replace 8:2 FTOH in the production of FTOH-based products (Zhao et al., 2013). It has an estimated atmospheric lifetime of 50 days (Piekarz et al., 2007) and has been detected in the gas phase in European air samples (Barber et al., 2007).

A high cumulative PFAS concentration was also found at the Għajn tal-Ħasselin (Valley 8; 33 ng/L). However, the sample from this location, contained the highest concentration of PFOA (16 ng/L). Although this is not a valley, it consists of 16th century arched shelters built over the springs where women wash their clothes to this day. The waste water from the Għajn tal-Ħasselin flows into the nearby valleys which include Wied Xlendi and Wied Lunzjata. The PFHpA/PFOA ratio of the Għajn tal-Ħasselin is 0.12 while that of Wied Xlendi and Wied Lunzjata 0.32 and 0.14 respectively. This is indicative of non-atmospheric sources which include road-run off and its proximity to urban areas. In addition, the washing of clothes may have an important role on the sources of PFASs in the Għajn tal-Ħasselin and consequently in the nearby valleys. It has been shown that losses from consumer products such as clothing during use and disposal contributes to the indirect emissions of precursors degrading to stable PFCAs and PFSAs (3M, 2000; Paul et al., 2009; Supreeyasunthorn et al., 2016).

In Malta, Wied Għollieqa and Msida Reservoir contained the highest cumulative PFAS concentrations (Valley 39; 26 ng/L and Valley 38;

Table 2

PFAS's concentrations determined in surface waters from different samples collected from Malta and Gozo. (ND – not detected, <LOD – below limit of detection and <LOQ – below limit of quantitation).

Valley	PFHxS (ng/L)	PFOS (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	Σ
1	1.26	0.31	0.35	0.29	0.31	0.62	ND	3.14
2	1.36	0.39	0.43	0.41	0.57	0.63	ND	3.79
3	1.33	0.15	0.63	0.28	0.88	0.60	ND	3.87
4	2.47	0.84	17.04	11.20	2.78	0.69	<LOD	35.02
5	2.40	0.85	15.25	10.54	3.36	1.21	<LOD	33.61
6	1.39	1.78	1.26	0.76	3.00	0.92	2.71	11.82
7	1.47	2.23	1.04	1.08	7.45	1.75	3.36	18.38
8	2.02	5.28	2.72	1.95	16.24	1.66	2.94	32.81
9	1.81	1.07	0.69	1.55	2.30	<LOD	2.77	10.19
10	1.30	1.34	3.67	3.26	7.63	3.44	3.24	23.88
11	ND	0.48	ND	0.31	0.36	ND	ND	1.15
12	1.56	1.17	<LOQ	0.17	0.47	0.77	2.70	6.84
13	ND	0.28	0.31	0.29	ND	ND	2.61	3.49
14	1.34	0.17	0.34	ND	0.31	0.62	2.62	5.40
15	1.13	<LOD	ND	ND	ND	ND	ND	1.13
16	1.47	1.18	0.50	0.06	1.08	0.96	2.90	8.15
17	1.41	1.04	0.50	0.30	1.82	0.85	2.66	8.58
18	1.42	0.93	0.43	0.09	1.87	ND	2.70	7.44
19	1.36	0.72	0.48	<LOQ	0.47	0.75	2.65	6.43
20	1.44	0.70	0.50	ND	0.27	0.74	2.78	6.43
21	1.21	0.25	0.38	ND	0.58	0.63	ND	3.05
22	1.22	0.22	0.39	0.47	0.46	0.55	ND	3.31
23	ND	0.08	0.29	0.29	0.23	ND	ND	0.89
24	1.59	0.66	0.47	0.09	0.49	0.73	ND	4.03
25	1.11	0.18	ND	0.28	0.16	ND	ND	1.73
26	1.22	0.08	0.34	0.35	0.36	0.56	ND	2.91
27	1.76	1.42	0.49	0.66	1.83	1.34	2.86	10.36
28	1.50	1.16	0.26	0.42	1.79	0.90	2.92	8.95
29	1.62	2.35	0.19	0.34	3.17	1.06	2.89	11.62
30	1.40	0.12	0.41	0.38	0.49	0.76	ND	3.56
31	1.24	0.15	0.28	0.29	0.29	0.52	2.67	5.44
32	1.18	0.09	0.33	0.36	0.42	0.70	ND	3.08
33	ND	0.25	0.43	0.18	0.63	0.67	2.67	4.83
34	1.26	0.57	0.47	0.33	0.48	0.65	ND	3.76
35	1.27	1.45	0.12	0.75	4.55	1.25	3.53	12.92
36	1.56	1.52	0.20	1.32	3.44	1.71	3.16	12.91
37	1.50	3.58	0.59	1.25	3.39	1.17	3.39	13.62
38	1.63	3.11	0.70	0.48	9.87	2.52	3.23	21.54
39	1.91	8.60	1.95	1.15	7.08	1.48	4.23	26.4
40	ND	0.11	0.26	0.71	1.84	1.17	2.79	6.88
41	1.54	2.76	0.26	1.45	5.15	2.43	4.40	17.99
Σ	53.66	49.62	54.95	42.84	97.87	37.01	75.38	411.33

21 ng/L respectively). Msida Reservoir has the second highest concentration of PFOA (9.9 ng/L) followed by Wied Ghollieqa (7.1 ng/L). The Msida Reservoir is not a valley, however it collects rain water and runoff water from nearby streets. Wied Ghollieqa is a valley and is situated in a populated urban area, also collecting rain water from nearby streets. The streets surrounding the Msida Reservoir and Wied Ghollieqa have heavy traffic which could be a contributing factor to the high

concentration of PFOA. Kim and Kannan (2007) found high concentrations of PFOA in surface runoff water collected at a site influenced by heavy traffic. The PFHpA/PFOA ratios here are both <1 (0.16 and 0.05 respectively) therefore confirming the contribution of non-atmospheric sources as being more important.

The valley with the least cumulative PFAS concentrations was Wied il-Busbies (Valley 23; 0.89 ng/L) followed by Wied Santi (Valley 15; 1.1 ng/L) and Wied L-Imġiebaħ (Valley 11; 1.1 ng/L). All these are located in 'remote' areas on the island of Malta. The PFHpA/PFOA ratios here are >1 for Wied il-Busbies and Wied Santi (1.26 and ND) and ~1 (0.86) for Wied L-Imġiebaħ implying an atmospheric source of the PFASs.

There appears to be a general trend of increasing PFAS concentration in samples of surface waters gathered from valleys downstream (rural to urban). This trend was observed more starkly for PFOS and PFOA (Fig. 3). Apart from the urban effect, the variations could be attributed to the different flow rates and volumes of water at each point which may contribute to the dilution or concentration of certain PFASs.

3.1.2. Comparison between Malta and Gozo surface water

There may be several factors which influence the presence of contaminants such as PFASs in surface water. These include the solubility of the PFAS and the respective sediment-water partitioning coefficient as well as the geological features of the valley system. Surface flow and water residence times also have an effect on the concentration of contaminants. Low surface flow and longer water residence times lead to higher solute concentrations in water courses. However, such data is absent for the Maltese islands. Like other Mediterranean rivers, valleys on the Maltese islands are strongly affected by dry periods after which flooding can occur and contaminants in the sediment are resuspended into the river water (Farre and Thomaidis, 2014).

The median concentrations in Malta and Gozo surface water are shown in Table 3.

These were compared using the Kruskall-Wallis test. No significant differences were found between Malta and Gozo surface water with regards to the median concentrations of PFHxS, PFOS, PFNA and PFDA, suggesting that these four PFASs come from the same source such as rainfall. On the other hand, the median concentrations of PFHxA, PFHpA and PFOA in Gozo surface water were significantly higher than the median concentrations of PFHxA, PFHpA and PFOA in Malta surface water. The difference could be influenced by two factors:

(i) Rainfall: Rainfall and wind data show that Gozo receives more rainwater than Malta and that most of the rain approaches on Malta from the northwest (after passing on Gozo). This could influence the concentration of PFASs on both islands since it has been shown that most of the PFASs (75%) are scavenged at the beginning of a rainfall event (Taniyasu et al., 2003). In addition, there are differences on the scavenging rates between PFCAs and PFSAs which could be related to their different

Fig. 2. Sampling points for *Wied Sara* and *Wied Tal-Grazzja* (on the island of Gozo) which are connected.
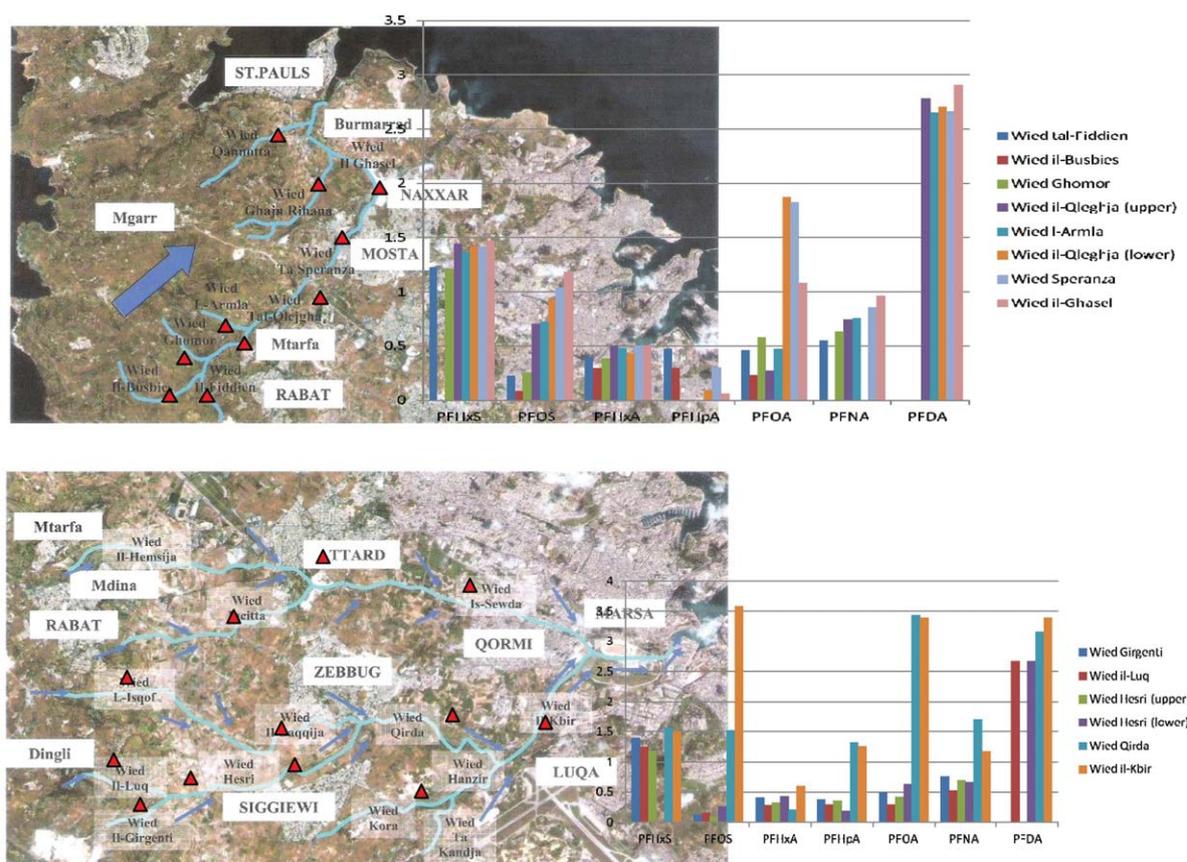
Fig. 3. The two principal valley systems in Malta (Source: Valley Management Section, Works and Infrastructure Department, Ministry for Transport and Infrastructure). (▲ = sample collection sites). The graphs on the right show the concentrations of the PFAS (in ng/L).

physiochemical properties (Taniyasu et al., 2003). These authors observed that short chain PFCAs are scavenged early and rapidly during a rainfall event while long chain PFCAs and PFSAs (since they are less water soluble and therefore sorbed more strongly to atmospheric particles) are scavenged later. This could explain why the concentration of the three soluble PFASs (PFHpA, PFHxA and PFOA) is significantly higher in Gozo than in Malta.

(ii) Properties of valleys: Although there has been no surface flow and residence time studies on the valley systems in Malta and Gozo, it was observed that the valley system in Malta tends to be more connected and longer, therefore providing more flow than the valleys from which water was collected in Gozo. This would imply an accumulation of PFASs in water courses in Gozo which leads to a higher concentration of the substances. In addition, the perfluorinated sulfonic acids (PFOS and PFHxS) and the longer chain PFASs (PFNA and PFDA) have higher sediment-water partitioning coefficients than the corresponding and shorter chain carboxylic acids (PFOA, PFHpA and PFHxA) (de Voogt and Saez, 2006; Higgins and Luthy, 2006). Therefore it would be expected that PFHpA, PFHxA and PFOA would readily dissolve in the surface water following the first rain.

3.1.3. Occurrence of PFASs in rain water

The concentrations of PFASs in rain water collected during eight different rainfall events in Malta are summarised in Table 4. The rain water was always collected from the same area, Żebbuġ which is located in the central area of Malta.

PFASs were detected in all rain water samples. The ΣPFAS concentrations were between 0.38 ng/L (1st October 2015) and 6 ng/L (21st February 2015). PFDA was observed to have the highest cumulative concentration (average of 2.7 ng/L). This compound accounted for 43% of the determined PFASs and was detected in 6 of the 8 samples analysed. PFDA has previously been detected in arctic ice (Young et al., 2007) and since it is not produced in large quantities commercially, their presence was indicative of atmospheric oxidation. The source of PFDA would primarily be 10:2 FTOH (Young et al., 2007). The presence of FTOH in European outdoor air has been studied (Barber et al., 2007; Dreyer et al., 2009; Müller et al., 2002) and results show the presence of 8:2 FTOH and 10:2 FTOH at all sites sampled. Neutral PFASs have also been widely detected in indoor air which eventually diffuses to outdoor air. There are several sources for neutral PFASs which include residuals left over from the manufacturing process in several commercially available and industrially applied polymeric and surfactant materials (Barber et al., 2007) and also in waterproof jackets (Friends of the Earth Norway, 2006; Holmquist et al., 2016). PFHpA was found in all samples followed by PFOA which was detected in 7 out of 8 samples. PFHxS, PFOS and PFNA were each found in 6 out of 8 samples. The dominant atmospheric precursor to PFOA and PFNA is 8:2 FTOH (Young et al., 2007), while the atmospheric precursors to PFHpA are 6:2 FTOH and 8:2 FTOH (Ellis et al., 2004). The compound which was observed to have the lowest cumulative concentration was PFOS (average of 0.1 ng/L; ΣPFOS = 0.8 ng/L). The low concentration

Table 3
The median concentrations in Malta and Gozo surface water in ng/L.

	PFHxS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDA
Malta	1.36	0.66	0.34	0.31	0.49	0.74	2.67
Gozo	1.43	0.96	1.15	1.32	2.89	0.81	1.36

Table 4
PFAS's concentrations determined in rain water from 8 different rain events collected from Malta and Gozo.

Rain event	PFHxS (ng/L)	PFOS (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	Σ	Wind direction	Total rainfall (mm)
30/12/2014	1.11	0.07	0.29	0.29	0.24	0.61	2.65	5.26	15° (NNE)	47.6
18/02/2015	1.15	0.12	0.33	0.33	0.35	0.66	2.69	5.63	123° (ESE)	30.5
21/02/2015	1.12	0.27	0.32	0.33	0.68	0.86	2.72	6.30	284° (WNW)	35.4
12/08/2015	ND	0.26	ND	0.29	0.32	0.53	2.65	4.05	306° (NW)	6.5
09/09/2015	1.08	0.05	0.30	0.29	0.13	0.47	ND	2.32	16° (NNE)	10.3
01/10/2015	ND	ND	ND	0.29	<LOQ	ND	ND	0.38	136° (SE)	27.5
09/10/2015	1.09	ND	ND	0.28	ND	ND	ND	1.37	105° (ESE)	1.7
22/10/2015	1.08	0.05	0.29	0.38	0.22	0.99	2.73	5.74	296° (WNW)	8.8
Σ	6.63	0.82	1.53	2.48	2.03	4.12	13.44	31.05		

of PFOS observed in rainwater could be attributed to the phase out of PFOS-based chemicals since 2002.

The concentrations of all PFASs would be expected to vary together through time if they originated from the same source (Young et al., 2007). A graph of concentration of PFOA and PFNA at each rain event reveals a similar pattern (Fig. 4) suggesting that these two compounds come from the same source, likely the 8:2 FTOH (Young et al., 2007).

For all samples, seven ay air mass backward trajectories were calculated with the model Hysplit using NCEP's Global Data Assimilation System (GDAS) data with 1° latitude/longitude resolution provided by NOAA Air Resources Laboratory. Trajectories were calculated for a height of 500 m and an arrival time of 12 am in intervals of 24 h. The data include rainfall amount of the air masses that moved towards the measuring site. These are presented in Fig. S8 in the Supporting information.

Except for a few samples, PFAS concentrations and PFAS composition in precipitation were quite uniform (Table 4) suggesting common sources. Precipitation samples 1, 2, 3 and 8 were characterised by elevated ΣPFAS concentration (>5 ng/L) whereas precipitation samples 4, 5, 6, and 7 had lower ΣPFAS concentration (<4 ng/L) and 1 or more PFAS not detected. Trajectory analysis of precipitation samples 1, 2, 3 and 8 show that prior to reaching the sampling point, the air masses travelled over source regions and may have contained large amounts of PFASs. On the contrary, trajectory analysis of precipitation samples 4, 5, 6 and 7 indicate that the majority of the air masses travelled over the sea and in some instances there was a rain event prior to reaching the sampling point. This may explain the low concentration or the absence of some PFASs since particle scavenging is most effective at the beginning of the precipitation event (Dreyer et al., 2010; Kwok et al., 2010). The first rain event will contain higher PFAS concentration due to in-cloud scavenging (the rain-out of PFASs dissolved in the cloud

Table 5
The median concentrations in surface water and rain water in ng/L.

	PFHxS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDA
Surface water	1.39	0.72	0.43	0.35	0.88	0.74	2.67
Rain water	1.09	0.06	0.29	0.29	0.23	0.59	2.65

droplet) in addition to below-cloud scavenging (the wash-out of PFASs present in the atmosphere) (Kwok et al., 2010).

3.1.4. Comparison between surface water and rain water

All surface water samples were collected during the months of February and March 2015, therefore included all rain water received during the first 3 rainfall events. The compounds detected in rain water were also detected in surface water. The high concentrations of PFDA detected in rainwater were also observed in surface water therefore indicating the source as being rainwater. The median concentrations in surface water and rain water are shown in Table 5.

The PFAS concentration in surface water was higher than those in rainfall, a pattern also observed previously between street runoff and rainfall (Murakami and Takada, 2008). This indicates that PFASs in surface waters are also derived from street dust and vehicle traffic (Murakami and Takada, 2008). Although street runoff was not analysed in this paper, it should be remembered that most of the street runoff in Malta and Gozo ends up in valleys. The median concentrations were compared using the Kruskall-Wallis test. No significant differences were found between surface water and rain water with regards to the median concentrations of PFHpA, PFNA and PFDA indicating that these have a common source. The source of PFHpA and PFNA is the atmospheric degradation of 8:2 FTOH while the source of PFDA is the atmospheric degradation of 10:2 FTOH (Young et al., 2007; Ellis et al., 2004).

4. Conclusions

This study has shown for the first time the presence of PFASs in rain water precipitating on the Maltese Islands. Furthermore, the study provides an extensive survey of Maltese surface waters for the presence of PFASs. It is unique due to the nature of the Maltese Islands. Being an island surrounded by the Mediterranean Sea, its water reservoirs are not connected through border crossing rivers carrying PFASs loads. Therefore, this study supports the notion that remote (and therefore also pristine) environments can become contaminated by PFASs from rain. The analyses of wind trajectories on the days leading to the rain episodes and correlation with the highest content of PFASs in rainwater, indicate that highest concentrations of the persistent organic pollutants are found in rainwater originating from north of the Maltese Islands.

The water collected from the seasonal reservoirs in the valleys of the Maltese Islands contained all the PFASs found in the rain water. However, some surface water contained PFASs not present in the rainwater. This suggests that some local anthropogenic activity has also had an input in the pollution.
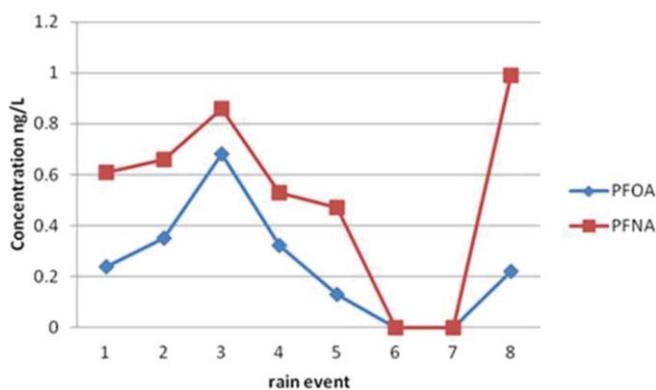

Fig. 4. Relationships between PFOA and PFNA in rain water collected from six rainfall events occurring in Malta in the period Dec 2014–Oct 2015.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.02.128.

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