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Perfluoroalkyl substances in the Maltese environment – (II) sediments, soils and groundwater

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HIGHLIGHTS
• Occurrence and distribution of 7 perfluoroalkyl substances in the Maltese soil, sediment and groundwater were investigated.
• PFOS, PFOA and PFDA were the most abundant PFASs in soil and sediment with the highest PFAS concentration always being PFOS.
• All PFAS analysed were found in groundwater with PFOA being the most abundant.

GRAPHICAL ABSTRACT

ABSTRACT

The presence of perfluoroalkyl substances (PFASs) in sediments and groundwater on the Maltese Islands is reported here for the first time. Sediments and soil samples were collected from 24 sites and groundwater was collected from 10 boreholes. PFASs were extracted from water and solid samples using solid phase extraction. The extracts were then analysed using ultra performance liquid chromatography coupled to mass spectrometry in tandem (UPLC-MS/MS). All sediment, soil and groundwater samples were contaminated with at least one PFAS. PFOS (<LOQ = 5.91 ng/g), PFOA (<LOQ = 0.58 ng/g) and PFDA (<LOQ = 1.05 ng/g) were the major PFASs being detected in 100% of the sediment and soil samples. Meanwhile PFOA (<LOD = 2.68 ng/L) was the PFAS detected in all groundwater samples. The concentrations of PFASs observed in groundwater on the Maltese Islands were below the parameters set by the Directive 98/83/EC.

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1. Introduction

Polyfluoroalkyl or perfluoroalkyl substances (PFASs) are a class of persistent organic pollutants (POPs) which have been manufactured and used in various applications over 50 years. They owe their persistence in the environment, to the strength of the C—F bond
2. Materials and methods

PFASs are ubiquitous in the environment and have been detected in even the most remote areas including the Arctic (Martin et al., 2004; Shoeib et al., 2006) and the Antarctic (Giesy and Kannan, 2001; Schiavone et al., 2009). PFASs in the environment can cause ecological problems as reported by de Vries et al. (2017). In this study it was found that as PFASs, from a fire-fighting incident, proved toxic to organisms on Bontaire Island, Flamingos preying on these organisms disappeared from the area as prey organisms diminished.

In a recent publication (Sammut et al., 2017) our group showed how rainwater was precipitating PFASs on the Maltese Islands which also polluted the seasonal surface water on the islands. Through seepage in valleys and soils, the rain and surface water will find its way into groundwater (Gellrich et al., 2012). In Malta, groundwater is used for drinking and irrigation. In this way, PFASs can contaminate the food chain. Directive 98/83/EC of the European Commission sets the legal framework to protect human health from the adverse effects of any contamination of water intended for human consumption (European Commission, 2018). The parameter set by the same directive for PFASs (meaning each individual perfluoralkylsubstance) is 100 ng/L and for ∑ PFASs (meaning the sum of perfluoralkylsubstances) is 500 ng/L (European Commission, 2018). The toxicological hazards of PFASs for humans have been described (Butenhoff and Rodricks, 2015; Hekster et al., 2003) They have also been reported as endocrine disruptors (Jensen and Jeffers, 2008). A review of epidemiologic literature for PFOA by Steenland et al. (2010) revealed that animal data indicate that PFOA can cause a number of different tumours and may have toxic effects on the immune, liver, and endocrine systems. There are also fairly consistent indications of fairly positive correlations with high cholesterol and uric acid blood levels due to PFOS exposure.

This study complements the previous study conducted by the same authors on the presence of PFASs in surface- and rainwater (Sammut et al., 2017). There are no previous studies of perfluoralkyl substances in soil, sediments and groundwater on the Maltese Islands reported in the literature.

The main objective of this study is to assess the occurrence of 7 PFASs in surface sediments, soil and groundwater of the Maltese Islands and to relate the findings to the specific isolated location of the islands as well as their geological influence on infiltration mechanisms.

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 (IS) in methanol included 13C2-PFHxA, 13C4-PFHpA, 13C6-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 (Campro Scientific, Veenendaal, The Netherlands). Methanol (MeOH) of LC-MS grade was obtained from Scharlab, while ammonium acetate (AcNH4H2O: 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 18 MΩ-cm was prepared using the Elga Purelab Classic purification system.

2.2. Sampling sites and sample collection

Surface sediment samples were collected between the months of June and August 2015. During these months most of the valleys would have little or no surface water left. The sediments were collected in pre-cleaned polypropylene (PP) bottles and always included the top 10 cm of sediment. The approximate mass of each sample was 50 g and any stones and vegetation were removed. The surface soil samples were collected between the same months and in the same manner as that described for sediment samples. The PP bottles were stored in a cooling box during the time at the field and later stored in a fridge at 4 °C until analysis. A total of 24 sediment samples were collected, 10 of which were collected from valleys in Gozo, while 15 were collected from valleys situated in Malta (Fig. 1). These sediments were from valleys that were used for surface water sample collection by Sammut et al. (2017). Six samples from Malta were soil samples collected from random small urban fields. Groundwater samples were collected by the Malta Water Services Corporation personnel in pre-cleaned polypropylene (PP) bottles with a capacity of 1.0 L. A total of 10 groundwater samples were collected from different areas on the island of Malta during the months of November and December 2015 and January 2016 (Fig. 2). The collection sites are the most commonly used extraction sites by the Corporation for water extraction as well as for sampling for water quality analysis. All boreholes are under pumping conditions and therefore there was no need for well purging. The bottles and screw-caps were rinsed with methanol and dried before use to minimize contamination. The bottles were then rinsed three times with 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 was 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 the same as the sample.

2.3. Solid phase extraction

2.3.1. Sediment/soil extraction

Waters Oasis® HLB Plus Short Cartridge, with 225 mg Sorbent per Cartridge, and 60 μm particle size were used for SPE extraction and used in accordance with the Waters PFC Analysis Kit for ACQUITY UPLC System Guide (2009). Prior to use, the extraction cartridge was preconditioned by passing 10 mL of MS grade methanol at a flow rate of <10 mL/min followed by 10 mL of 18 MΩ water.

The methanol extraction previously described by Lorenzo et al. (2015) is used here. Prior to carrying out the methanol extraction, 5 g of soil or sediment samples were spiked with 150 μL of 0.599 ng/mL IS. The soil or sediment was then extracted three times using 10 mL of methanol, vortexed, sonicated for 15 min, and centrifuged at 965 rcf for 15 min. The volume was then reduced to 5 mL under Nitrogen and made up to 100 mL of 18 MΩ ultra-pure water added. The conditioned cartridge was then loaded with the 100 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 set to 35 °C. The methanol eluent (300 μL) was delivered to a UPLC sample vial. The target sample mixture is 1:3 eluent/water.

2.3.2. Groundwater extraction

Waters Oasis® HLB Waters cartridges were also used for groundwater extraction. Preconditioning and elution of cartridges were performed as for sediment and soil extraction described above. However, in this case the conditioned cartridge was 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.
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 C18, 2.1 × 50 mm column, OASIS HLB cartridges and vials and PFASs standards. The PFC Isolator Column is 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. For groundwater, a seven-point calibration curve at 0.33, 0.66, 1.29, 2.62, 5.2, 10.4 and 20.83 ng/ml while for sediments, a six-point calibration curve at 2.08, 3.33, 6.46, 13.13, 26.04 and 52.08 ng/ml was used for the quantification with good linearity over this concentration range ($R^2 > 0.9979$). An exemplar calibration curve is presented in Fig. S1 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 soil free of PFASs (for sediment and soil) and 18 MΩ− water free of PFASs (for groundwater) spiked with the target compounds. Percent

![Map of Malta showing the locations from which sediments was collected between May and August 2015.](image-url)
recoveries for internal standards in groundwater and sediments were always within the range of 70%–130%.

3. Results and discussion

3.1. Occurrence of PFASs in sediments and soils

In a previous study conducted by the same authors, it was established that all surface and rainwater samples were contaminated with at least one PFAS on the Maltese Islands (Sammut et al., 2017). Although the islands are scarred from end to end by valleys, there are no permanent rivers or lakes on the Maltese Islands. In winter, during times of high rainfall, most of these are filled with fresh water. However, most dry up in summer, and only some watercourses may have fresh water running all year round. The water which accumulates in these

![Malta Map](image)

Fig. 2. Map of Malta showing the locations from which groundwater was collected during December 2015 and January 2016.

| Methodological detection limit (LOD) and quantification limit (LOQ) for sediment and groundwater. |
|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|
| PFAS     | Limit of detection (LOD) - sediment/soil (ng/g) | Limit of quantitation (LOQ) - sediment/soil (ng/g) | Limit of detection (LOD) - groundwater (ng/L) | Limit of quantitation (LOQ) - groundwater (ng/L) |
|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|
| PFHxS    | 0.40                                              | 0.50                                              | 0.02                                              | 0.04                                              |
| PFOS     | 0.02                                              | 0.04                                              | 0.03                                              | 0.04                                              |
| PFHxA    | 0.23                                              | 0.25                                              | 0.03                                              | 0.04                                              |
| PFHpA    | 0.03                                              | 0.04                                              | 0.03                                              | 0.04                                              |
| PFDA     | 0.02                                              | 0.04                                              | 0.03                                              | 0.04                                              |
| PFNA     | 0.05                                              | 0.04                                              | 0.03                                              | 0.04                                              |
| PFDA     | 0.20                                              | 0.40                                              | 0.02                                              | 0.06                                              |

1 – Wied il-Ghasel borehole (Naxxar)  2 – Macedonija borehole (Mosta)  3 – Balal borehole (Naxxar)
4 – Wied Bordi borehole (t o Mosta)  5 – Qattara borehole (t o Rabat)  6 – Mgieri borehole (Luqa)
7 – Fawwara borehole (Siggiewi)  8 – Farrugia borehole (Siggiewi)  9 – Zurrieq road borehole (1 o Zurrieq)
valleys is then utilised by farmers to water their crops during the summer months. The release of PFASs into surface waters from industrial sources is insignificant in Malta since these do not exist. Therefore, the sources of PFASs in Malta would be expected to be rainfall, dust (from street run off) and disposal of PFASs containing substances (Sammut et al., 2017). In addition, landfills which are well known for their contribution of PFASs to soil and groundwater (Hammid et al., 2018) would also be a source in Malta. Prior to Malta’s accession to the EU in 2004, Malta had one large uncontrollable landfill covering an area of 280 m² and a height of 60 m (Wasteserve Malta, 2018). On May 12, 2004, in accordance with European Directives, and which Malta was then obliged to follow, the uncontrolled landfills located in Maghlab in Malta and Qortin in Gozo were closed (Wasteserve Malta, 2018). At about the same time, engineered landfills were introduced and designed to protect the surrounding environment from the landfill leachate (Wasteserve Malta, 2018). Malta also had two other landfills which were in Wied Fuliża, Zurrieq and in Luqa that were closed in 1996 and 1970 respectively (Wasteserve Malta, 2018).

The majority of the PFAs are acids having very low dissociation constants, therefore in the environment they are most often present in their anionic form (Pancras et al., 2016; Buck et al., 2011). It would be expected that due to their low volatility and low sorption coefficients most of the PFAs remain in solution when they reach surface water, although there will be some partitioning to sediments (Ahrens et al., 2011; Zareitalabad et al., 2013). Locally therefore, surface water in valleys during the wet months will be the primary source of PFASs to the sediments. Meanwhile PFASs present in rainwater and any other water such as tap water or groundwater will be the primary source to soil. The chain-length and functional group of PFASs determines their fate and transport as they move through the environment (Higgins and Luthy, 2006; Ahrens and Bundschuh, 2014). Therefore shorter-chain carboxylates such as PFBA, PFPeA and PFHxA are expected to preferentially partition into soil rather than water as they adsorb more readily to the organic matter in the soil (Scher et al., 2018). Furthermore, the short-chain sulfonates PFBS and the long-chain carboxylate PFOA are expected to lie in between the above 2 groups mentioned in terms of solubility and mobility due to their chain length and functional group combination (Scher et al., 2018).

The PFAS concentrations in sediments and soils collected from 24 different locations from Malta and Gozo are shown in Table 2. All sediments and soil samples were contaminated with at least one PFAS. As expected, PFASs having >7 carbons were the predominant ones, PFOA (~LOQ – 5.91 ng/g), PFOA (~LOQ – 0.58 ng/g), and PFDA (LOQ – 1.05 ng/g) were found in 100% of the samples. PFOA as predicted above was present in lower concentrations than PFOS. PFNA (ND – 0.88 ng/g) was detected in all but one sample (Wied Sera, Sediment 5). PFHpA (ND – < LOQ), PFHxS (ND – 0.12 ng/g) and PFHxAs (ND – 0.48 ng/g) were detected in trace amounts (<0.50 ng/g). These values were comparable to data reported by other studies (Campos et al., 2015 and Rankin et al., 2016).

In terms of cumulative PFAS concentrations (i.e. considering the sum of the seven PFASs analysed), the highest was found in Zebbug (Soil 22, 8.50 ng/g), Msida (Soil 20, 3.82 ng/g), Wied il-Ghasel (Sediment 12, 3.71 ng/g), Wied Lunzjata (Sediment 6, 3.51 ng/g), Mosta (Soil 14, 3.47 ng/g) and Chadwick Lakes (Sediment 16, 3.41 ng/g). Wied il-Ghasel and Chadwick Lakes are two connected valleys and are located on the main island, Malta (Fig. 3). Wied Speranza which lies between these two also had a relatively high cumulative PFAS concentration (Sediment 13, 2.24 ng/g).

It is interesting to note that in all the samples with high cumulative PFAS concentration, the highest PFAS concentration was always PFOA (Table 2). This high PFOA level in sediments can be attributed to Stormwater runoff. It is a known fact that stormwater carries various pollutants from the urban watershed such as nutrients and pesticides from landscaped areas, heavy metals, brake and tire wear, and organic pollutants (Baun et al., 2006; Davis et al., 2001; Eriksson et al., 2007). Previous studies have shown that PFASs, in particular PFOs and PFOA concentration in stormwater runoff is higher than they are in rainfall (Xiao et al., 2012; Kim and Kannan, 2007). Although stormwater runoff studies were not performed in Malta, the previous study on rain and valley water revealed higher PFAS concentration in valley water than rainfallwater (Sammut et al., 2017) which was consistent with previous studies. In most cases valley water on the Maltese Islands are composed of stormwater runoff as can be seen in Fig. 4. Contributors to PFOS on particles in stormwater have been attributed to street dust and vehicular traffic (Murakami and Takada, 2008) and also debris of commercial food packaging or other products which may contain PFOS (Jahnke and Berger, 2009; Paul et al., 2009). The PFOS present in the stormwater ends up in the valleys with both valleys having significant levels of PFOS detected in surface water (Sammut et al., 2017). Due to its properties the PFOS will preferentially partition into the soil rather than water.

PFOS was also found to have the highest concentration in the 6 soil samples collected from urban gardens. This is consistent with a study conducted by Scher et al. (2018) in which outdoor tap water, garden soil, and garden produce were analysed from 20 homes in Minnesota. PFOS was found to have the highest median concentration in soil. The concentration of PFOS varied as follows: Zebbug (Soil 22, 5.01 ng/g) > Msida (Soil 20, 1.86 ng/g) > Mosta (Soil 14, 1.68 ng/g) > St Paul’s Bay (Soil 10, 0.63 ng/g) > Mtarfa and Bahrija (Soil 18 and 15, 0.26 ng/g respectively). One contribution to the presence of PFOS in urban soil can also be attributed to the well-water which is used for watering the plants and trees in home gardens. Most Maltese homes are furnished with a well which is an excavated structure created in the ground. Rainwater flows into the wells from rooftops carrying with it any dust or dirt and in some rare cases also from road run-off. Rooftops of most Maltese homes are commonly coated with water resistant paints and other roof treatment compounds. Water repellent paints are a typical field for PFAS application with PFOS being the main PFAS in the investigated paint samples (Herzke et al., 2012).
Fig. 5 shows that high PFOS concentration in urban soil was localised to areas with medium to dense built-up areas and soil sealing between 30% to 80%. Meanwhile low PFOS concentration was localised to areas with arable land or sclerophyllous vegetation. In built-up areas, stormwater will have limited dispersal due to soil sealing (hence the higher risk of flooding in such areas). Therefore, the water remains on roads collecting dust and other material related to vehicular traffic, which eventually ends up in urban soil. On the other hand, in green areas, stormwater will have greater dispersal and little will remain on roads. In addition, in such areas input from vehicular traffic and street dust is less.

The sediments with the least cumulative PFAS concentration were at L-Ghadira ta’ Sarraflu (Sediment 9, 0.24 ng/g) and Wied Incita (Sediment 19, 0.20 ng/g). L-Ghadira ta’ Sarraflu is a very important habitat since it is one of the very few natural pools in the Maltese Islands where water accumulates and persists even during the hot summer months when most other freshwater dries up (Fig. 6). Therefore in this case, the sediment was taken just above the water line as it was at the time of sampling. Here PFOS (PFNA and PFHpA also) had a concentration of <LOQ while PFDA was the only quantifiable PFAS with a concentration of 0.24 ng/g. PFOA had a concentration of <LOD while PFHxA and PFHxS were not detected. This is consistent with their fate and
Fig. 5. Urban Atlas. The darker red areas indicate higher dense urban areas and greater soil sealing (http://geoserver.pa.org.mt/publicgeoserver, PA, 2018).

Fig. 6. L-Ghadira tà Sarafu.
transport in the environment and a study conducted previously by Chen et al. (2016). Chen et al. (2016) examined reversible and irreversible sorption of several PFASs to bed sediments from an urban reservoir. They found that PFNA, PFDA and PFOS strongly sorb to sediments and acted predominantly as irreversible sinks. PFOA and PFHxS were moderately sorbing and short-chained PFASs such as PFHxA are not significantly sorbed.

Wied Incita sediment meanwhile had a PFOS concentration of 0.2 ng/g which was the only quantifiable PFAS. Unfortunately, the sediment here had a recent activity which could have influenced the result. Sediment had been unearthed and moved. In addition, the position from where the sample was taken was a point where the source was fields and green area and little to no influence from road run-off. This can explain the low PFOS concentration.

3.2. Occurrence of PFASs in groundwater

The Water Operations Unit of the Water Services Corporation (WSC) is responsible for all distribution and groundwater operations in the Maltese Islands (Water Services Corporation, 2018). In Malta, tap water consists approximately of 43% groundwater and 57% desalinated water produced by reverse osmosis plants from sea water (Water Services Corporation, 2018). Therefore, groundwater represents a potential PFAS exposure pathway either through direct ingestion of contaminated drinking water or indirect ingestion of PFAS in crops irrigated with the contaminated 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. The presence of PFASs in rainwater and surface water has already been confirmed in the previous study (Sammut et al., 2017), while the presence of PFASs in soil has been discussed above. Therefore, it would be expected that PFASs would also be found in groundwater.

The Maltese Islands are composed of two porous and fractured limestones (Pedley et al., 1976), namely the Miocene Upper Coralline Limestone (UCL) and the Oligocene Globigerina-Lower Coralline Limestone (GL-LCL) (Stuart et al., 2010) (Fig. 7).

The UCL crops out mainly in the north and west of the Maltese islands and varies in thickness from 30 to 90 m. The LCL is found in a substantial part of the Maltese islands and is generally up to 210 m thick. The two limestones are separated by a layer of clayey and marly material known as Blue Clay formation which in some places also has the thin Greensand formation above it (Stuart et al., 2010). The Blue Clay formation is 20–65 m thick and acts as an aquitard, although some groundwater stored in the perched aquifers of the UCL does seep to the underlying Main Sea Level (MSL) aquifer in the LCL (Sapiano et al., 2006). From a structural point of view, the main island of Malta is divided into the northern and the central/southern regions by the major fault line known as Victoria Fault. Hence, south of this fault, the UCL aquifer is perched vertically above the LCL aquifer which are separated by the Blue Clay. The lower aquifer is in direct contact with seawater which results in the development of a classic ‘Ghyben-Herzberg’ lens (Stuart et al., 2010). Each aquifer has different porosities which would determine the speed of seepage. Stuart et al. (2010) estimated the groundwater residence time on the Maltese mainland was between 15 and 40 years.

A total of 10 groundwater samples were analysed (Fig. 2). All groundwater samples were contaminated with at least one PFAS (Table 3). PFOA (<LOD – 2.68 ng/L) was the major PFAS, being detected in 100% of groundwater samples. This was followed by PFHxS (ND – 2.22 ng/L) being detected in 70% of groundwater samples. PFDA was not detected in any of the groundwater samples, and PFNA was detected in only one groundwater sample. This is consistent with their transport properties in the environment since shorter chained PFASs have a lower sorption potential to particles, their mobility is higher and their transport through soil to groundwater is faster (Gellrich et al., 2012). Long-chain PFASs such as PFDA and PFNA would preferentially partition into the soil.

In terms of cumulated PFAS concentrations (considering the sum of the seven PFASs analysed) the highest was found in Mgieret groundwater (Borehole 6, 11.2 ng/L). Except for PFDA which was ND, the Mgieret groundwater was also the only sample where all PFASs were found in quantifiable amounts. The location of this groundwater may explain the high cumulated PFAS concentration. These include in order of effect:

(i) It is located 600 m downstream from a now disused landfill (Fig. 8). The area used to be the island’s rubbish dump until 1970s before the government decided to use Maghtab (Wasteserve Malta, 2018).

(ii) The main airport (Luqa airport) is located 940 m upstream from
the groundwater location (Fig. 8). Within the perimeter of the airport, there is also the training grounds for the fire brigade. The airport was an extension of an earlier airport that served military and civil purposes from 1957 until 1992 when the new airport was inaugurated. The type of foam concentrate used is 6% AFFF and the amount used for training is limited and is approximately 100 L/month (personal communication). This activity was conducted prior to 2003 when 3 M stopped using PFOS in its firefighting foam concentrate.

(iii) The location of the groundwater is adjacent to Route 8, which is a busy vehicular road therefore, road runoff contributes to the contamination. It is also located downstream from an urban area contributing further to road runoff contamination.

(iv) The geological formation in the area from where the groundwater was sampled consisted of Globigerina Limestone (Fig. 8) which is porous having a primary permeability of 32–40% (Stuart et al., 2010). However, this may not be a significant factor.

Sampling sites with the least cumulated PFAS concentrations having either low or non-detectable concentrations of PFASs were Macedonia (Borehole 2), Wied Bordi (Borehole 4), Qattara (Borehole 5) and Favwara (Borehole 7). All these are located in ‘remote’ areas on the island of Malta and/or in areas where the hydrogeology indicates a lower percentage porosity. The other sampling sites had cumulated PFAS concentrations ranging from 1.2 ng/L to 2.69 ng/L. There appears to be a general trend of increasing PFAS concentration in samples of groundwater depending on four factors:

1. how far from an urban area and whether it is downstream from this urban area; the closer to the urban, area the higher the PFAS concentration.
2. road run-off: the heavier the vehicular traffic in the area the higher the PFAS concentration.
3. past or current use of AFFF and.
4. the presence of any landfills in the surrounding area.

4. Conclusions

After a previous study by this group showed that the remote and therefore pristine Maltese Islands are contaminated by PFAS through precipitation, this study establishes a link between rain and surface water and sediment and groundwater. Sediments in valleys previously filled with surface water that originated from rain water and road runoff, were found to be contaminated with PFASs. Soils from fields and urban gardens were also found to be contaminated. The accumulation of PFASs in sediments and soil eventually seep into the groundwater.

<table>
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<tr>
<th>Borehole</th>
<th>PFHxS (ng/L)</th>
<th>PFOS (ng/L)</th>
<th>PFHxA (ng/L)</th>
<th>PFHpA (ng/L)</th>
<th>PFOA (ng/L)</th>
<th>PFNA (ng/L)</th>
<th>PFDA (ng/L)</th>
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Fig. 8. The map shows the urban atlas of the area. ▲ = the location where fire training took place; ▲ = the location of borehole ▲ = the location of disused landfill.
system contaminating it with PFASs. The concentrations of PFASs observed in groundwater on the Maltese Islands were below the parameters set by the Directive 98/83/EC.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.04.403.

References