Perfluorinated alkyl substances (PFASs) in northern Spain municipal solid waste landfill leachates

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Highlights

- This is the first study on PFASs occurrence in landfill leachates in Spain.
- PFOA, PFHpA and PFHxA were ubiquitously detected in raw and treated leachate.
- Leachate treatment by membrane bioreactors (MBR) gave rise to a different PFASs profile and in some cases to an increase of ∑PFASs concentration compared to raw leachate, likely due to generation of PFASs through precursor compounds.
- Estimated mass flow of 16 ∑PFASs discharged into the sewage system in northern Spain was 1209 g/year, from landfill sites that serve a 1.8 million population.

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Abstract

Landfill leachates have been recognized as significant secondary sources of poly- and perfluoroalkyl substances (PFASs). This study presents data on the occurrence and concentration of 11 perfluoroalkyl carboxylates (PFCAs) and 5 perfluoroalkyl sulfonates (PFSAs) in leachates from 4 municipal solid waste landfill sites located across northern Spain. To the best of our knowledge, this is the first report of the presence of PFASs in Spanish landfill leachates. Two of the landfill sites applied on-site treatment using membrane bioreactors (MBR), and its effect on PFASs occurrence is also reported. Total PFASs (∑PFASs) in raw leachates reached 1378.9 ng/L, while in treated samples ∑PFASs was approximately two-fold (3162.3 ng/L). PFCAs accounted for the majority of the detected PFASs and perfluorooctanoic acid (PFOA) was the dominant compound in raw leachates (42.6%), followed by shorter chain PFHxA (30.1%), PFPeA and PFBA. The age of the sites might explain the PFASs pattern found in raw leachates as all of them were stabilized leachates. However, PFASs profile was different in treated samples where the most abundant compound was PFHxA (26.5%), followed by linear perfluorobutane sulfonate (L-PFBS) (18.7%) and PFOA (17.7%). The overall increase of the PFASs content as well as the change in the PFASs profile after the MBR treatment, could be explained by the possible degradation of PFASs precursors such as fluorotelomer alcohols or fluorotelomer sulfonates. Using the volume of leachates generated in the landfill sites, that served 1.8 million people, the discharge of 16 ∑PFASs contained in the landfill leachates was estimated as 1209 g/year.

Keywords: perfluoroalkyl substances (PFAS), landfill leachate, perfluorooctanoic acid (PFOA), perfluoroalkyl carboxylates, perfluoroalkyl sulfonates.

1. Introduction

Poly- and perfluoroalkyl substances (PFASs) have been synthesized and widely used in different industrial and commercial applications since the 1950s such as surfactants, coatings, water repellents for leather and textiles, metal plating and fire-fighting foams, among others (Busch et al., 2010; Dauchy et al., 2012; Yan et al., 2015). The high-energy C-F bonds convert PFASs into non-biodegradable, highly persistent and bio-accumulative compounds when they contain long alkyl chains (Prevedouros et al., 2006), and on the other hand, they are difficult to remove using conventional treatment methods (Quiñones and Snyder, 2009). These compounds have been regulated in the last decade (OJ L372, 2006). Perfluoroctane sulfonate (PFOS) has been classified as a PBT (persistent, bioaccumulative and toxic) chemical (OECD, 2002), being included in the Stockholm Convention list of persistent organic pollutants (POPs) (UNEP, 2009) as well as in the European Directive 2013/39/EU as a priority substance in the field of water policy (OJ L226, 2013). Additionally, perfluorooctanoic acid (PFOA) has been recently proposed by the European Union for listing under the Stockholm Convention (OJ L104, 2015).

Municipal solid waste landfills receive consumer products, which are susceptible to contain PFASs (Eggen et al., 2010).Therefore, it is likely that PFASs can be released and reach landfill leachates with the potential of migration to the surrounding aquatic environment and in particular groundwater (Paul et al., 2009; Yan et al., 2015). Furthermore, recent studies have demonstrated that landfills are, similarly to wastewater treatment plants (WWTP), emission sources of semivolatile PFASs to the ambient air (Ahrens et al., 2011; Weinberg et al., 2011). Studies on PFASs in municipal landfill leachates have been conducted mainly in three regions all over the world: North America (Huset et al., 2011; Benskin et al., 2012; Li et al., 2012; Gewurtz et al., 2013; Allred et al.; 2014; Clarke et al., 2015), Europe (Woldegiorgis et al., 2006; Kallenborn et al., 2008; Eggen et al., 2010; Busch et al., 2010; Perkola et al., 2013) and China (Zhang et al., 2014; Yan et al., 2015). All the studies performed in Europe correspond to northern and central European countries. Recently, a study on PFASs has been published dealing with landfill leachates in Australia (Gallen et al., 2016). The number of PFASs monitored varies from one study to another. The most frequently analysed PFASs in landfill leachates are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). Although there is a significant variability in the occurrence and patterns of PFASs among studied landfills, short chain PFASs (C_4-C_8 chain length) dominate the distribution profiles. Data on PFASs occurrence in leachates have revealed concentrations of PFASs among the highest levels in environmental waters, although still lower than PFASs concentrations found in aqueous film forming foam (AFFF)-impacted groundwater collected from military training areas (Filipovic et al., 2015, Schaefer et al., 2015). To the best of our knowledge, no previous studies have been carried out either in Spain or in other southern European countries concerning PFASs monitoring in leachate samples.

Leachate handling typically involves treatment either on-site or at a WWTP (Benskin et al., 2012; Yan et al., 2015) but the extent to which these processes reduce

PFASs is not well-known due to the fact that only few studies have reported the fate of PFASs during leachate treatment processes (Busch et al., 2010 and Yan et al., 2015). However, it is worth noticing that in some cases a net increase in PFASs concentrations was observed after activated sludge treatment of landfill leachates (Busch et al., 2010).

The aim of the present study was to investigate the occurrence and distribution pattern of PFASs (11 PFCAs and 5 PFSAs) on municipal solid waste landfill leachates from four different landfill sites located in northern Spain. Special attention was paid on the influence of the leachate treatment process because of the fact that in two of the sites both raw and treated leachate samples were studied. Further, a comparison of the results obtained with reported PFASs data on municipal landfill leachates was accomplished.

2. Materials and methods

2.1. Standards and reagents

Two different certified standard solutions were purchased from Wellington Laboratories (Guelph, Ontario, Canada): PFC-MXA and PFS-MXA, containing PFCAs and PFSAs, respectively at individual concentrations of 2 μg/mL. The analytical standard MPFAC-MXA of 2 μg/mL, also from Wellington Laboratories, was used as internal standard (IS). A detailed list of the target analytes, internal standards, acronyms, formulas and purities of the standards is given in Table S1. Evolute WAX (6cc, 200mg, 50µm) solid phase extraction (SPE) cartridges were purchased from Biotage and Oasis HLB (6cc, 200mg, 30µm) SPE cartridges were acquired from Waters (Milford, MA, USA). Bulk ENVI-Carb sorbent (100 m^2/g, 120/400 mesh) was purchased from Supelco (Bellefonte, MA, USA). All solvents were UPLC-MS quality and Milli-Q water was used throughout.

2.2. Landfill sites and leachate characterization

Leachate samples were collected from 4 different municipal landfill sites in March 2015. An overview of the landfill sites, including estimated volume of leachate generated per year, the status of the sites, the leachate treatment process when applied and the characterization of samples is shown in Table 1.

The sites were located in northern Spain across a longitudinal distance of about 400 km and served a population of nearly 1.8 million inhabitants. All landfill sites are placed in river basins that flow to the Bay of Biscay (northeast of Atlantic Ocean) According to the Statistical Classification of Economic Activities (NACE, 2008) , all the studied landfill sites were used for treatment and disposal of non-hazardous municipal solid waste from residential urban areas. Raw leachate grab samples (2 L) were collected before the leachate was pumped off either to the on-site treatment facilities or to the municipal water sewage system for treatment in the local WWTP. Additionally, at two of the studied sites treated leachate grab samples (2 L) were collected from the effluent of the leachate treatment facilities. The leachate treatment was similar in both landfill sites and consisted of an external membrane bioreactor (MBR) unit that integrated a two-stage biological process with an ultrafiltration (UF) unit. The biological process consisted of an aerobic and anaerobic nitrifying pressurised reactor that reduced the ammonia content by its conversion into nitrogen gas. At the same time the organic matter content was reduced, mainly the biodegradable fraction. Then, the biologically treated leachate entered an UF unit provided with tubular membrane modules to separate the biomass from the treated leachate. All grab samples were collected in polypropylene (PP) bottles pre-washed with methanol, and polytetrafluorethylene (PTFE) based materials were avoided throughout the sampling and analysis to prevent potential sample contamination.

2.3. Sample preparation

Untreated and treated leachates were filtered with 0.7 µm fiberglass filters (GFF, ChmLab) to eliminate particulate matter. An aliquot of 70 mL of each leachate sample was spiked in duplicate with IS MPFAC-MXA (30 ng of each analyte, see Table S1) prior to solid phase extraction (SPE) in order to correct losses and matrix effect.

SPE was previously optimised as described in Supplementary material. According to these results, leachate samples were extracted using SPE Evolute WAX cartridges conditioned with 5 mL methanol and 5 mL Milli-Q water. After leachates loading, cartridges were washed with 3 mL of 2% formic acid and 3 mL of Milli-Q water:methanol (95:5 v/v). Then they were dried under vacuum and finally PFASs were eluted with 8 mL of 1% ammonia (NH_3) in methanol.

Extracts were cleaned up using dispersive carbon sorbent (Envicarb) to remove the co-eluted interfering compounds according to the method suggested by Powley et al. (2005). Briefly, 100 mg of EnviCarb activated carbon and 50 µL of glacial acetic acid were added in a centrifuge tube and vortex mixed along with the sample extract for 30 s. Centrifugation was carried out at 11000 rpm and extracts were then filtered (0.22 µm) and transferred to a 15 mL PP tube to be further evaporated until dryness under a gentle stream of dry nitrogen gas. The final volume was adjusted to 200 µL of Milli-Q water:methanol (70:30 v/v) prior to injection.

2.4. Instrumental analysis and quantification

The purified sample extracts were analyzed using an Agilent 1260 series high performance liquid chromatography (HPLC) system coupled to a Quattro Micro triple quadrupole (QqQ) mass spectrometer (MS/MS, Waters, Milford, MA, USA) with an electrospray ionization (ESI) interface operated in the negative ionization mode. A Kinetex Phenomenex C18 column (50 x 2.1 mm x 2.6µm) at 35 ºC was used for the analytical separation. The mobile phase consisted of Milli-Q water (A) and methanol (B), both containing 2 mmol/L ammonium acetate, that was flowed at an operating flow rate of 0.2 mL/min in gradient mode. Further details about the instrumental analysis and quantification method by HPLC-MS/MS is described in the Supplementary material.

Dilutions from the stock standard solutions were prepared in methanol/water (70:30 v/v) at 7 concentration levels ranging from 5 ng/mL to 400 ng/mL and calibration curves were built in order to calculate the PFAS concentrations in real samples and to control the linear range of the instrumental response.

Quality control and validation of the method were made using internal standards and recovery rates, method blanks, calibration linearity. Limits of detection (LOD) as well as repeatability are summarized in Table S2 . Values of LOD were estimated as the lowest concentration of each PFAS compound in the leachate solution giving a peak area equal to the blank signal plus three times the standard deviation of the blank. Intra day repeatability, expressed as relative standard deviation (RSD) percentage, was obtained through five measurements of the standard mixture of the compounds (50 ng/mL) during a day. Recovery rates of internal standards detected in real samples ranged from 54.5 % (MPFDA, n=12) to 80 % (MPFNA, n=12). Reported concentrations were corrected with recoveries of IS.

3. Results and discussion

3.1. *PFASs content in landfill leachates*

3.1.1. Total concentration of PFASs

In the six landfill leachate samples, 8 of the 16 PFASs were detected. Comparison between PFASs concentrations in the different landfill sites is illustrated in Figure 1a (raw data about PFASs concentration are provided in Table S3 of supplementary material). PFASs total concentrations (∑PFASs) in raw leachate samples ranged from 639.2 ng/L (site 3) to 1378.9 ng/L (site 2). Regarding treated samples, the variation range was wider. The lower ∑PFASs was found in site 1 (856.0 ng/L) while in site 2 it reached up to nearly four-fold the concentration in site 1 (3162.3 ng/L). It is worthy to note that sampling method can influence the measured concentrations of PFASs. In this work, grab samples were collected and it means that in the two sites where the MBR treatment was applied, the treated leachate sample did not correspond exactly to the raw leachate collected at the same site, since the residence time of leachate in the MBR/UF unit was not taken into account.

Overall, PFCAs accounted for the majority of the fluorochemicals quantified in the leachate samples from all the studied sites. This is consistent with data reported from leachates in US, Germany or Denmark (Bossi et al., 2008; Busch et al., 2010; Huset et al., 2011). The total concentration of PFCAs (∑PFCAs) ranged from 595.7 ng/L in sample 3 up to 2578.4 ng/L in sample 2B, meanwhile the sum of PFSAs concentrations (∑PFSAs) ranged from non-detected in samples 1A and 1B to 583.9 ng/L in sample 2B.

The discharge rate of 16 ∑(PFCAs+PFSAs) into the aqueous environment was estimated by multiplying the PFASs concentrations by the annual average volume of leachate generated in each site (Table 1). The estimated discharge rate ranged from 65.6 g/year in site 3 to 835 g/year in site 2, with an accumulated 16 ∑PFASs mass flow of 1209 g/year from the four studied landfill sites that serve a population of approximately 1.8 million in northern Spain. The results showed an average discharge of PFASs rate of 672 µg/year*inhabitant.

3.1.2. Individual concentration of PFASs

Figure 1b shows an overview of the mass fraction contribution of individual compounds in each sample. In general terms, PFOA was the dominant compound in untreated leachate samples. With a mean contribution to the total mass fraction of 42.6%, the concentration of PFOA was the highest one among all measured PFASs in untreated leachate samples 1A and 3. Nevertheless, in samples 2A and 4, PFHxA and PFBS respectively, showed concentrations slightly over their PFOA content.

The higher abundance of PFOA could be consequence of the commercial history of C8-based production of PFCAs (Prevedouros et al., 2006; Oliaei et al., 2010; Huset et al., 2011). PFOA was used as processing acid in certain polymerization processes, and subsequently its presence has been reported in consumer products as an unreacted residual material (Eggen et al., 2010). According to the age of landfill sites and the characterization of the leachates (Table 1), all the studied samples could be considered as stabilized leachates (Alvarez-Vazquez et al., 2004; Kurniawan et al., 2005). Taking into account that consideration, it was expected to find high concentrations of PFOA and PFHxA because of the discharge of consumer products with high contents of these PFASs for a long time and actually, these two PFASs were the only ones detected in every landfill leachate sample. Furthermore, the contribution of fluorotelomer precursor degradation to PFCAs has been reported by many authors (Wang et al. 2011; Benskin et al. 2012; Filipovic and Berger, 2015) and could be other important PFASs source in landfill leachates. It would also explain to a certain extent the predominance of PFCAs among ∑PFASs.

All of the predominant PFASs, except PFOA, are considered short-chain PFCAs/PFSAs, with 6 or less perfluorinated carbons (Buck et al., 2011). Long-chain PFCAs (PFNA, PFUdA, PFDoA and PFTrDA) and long-chain PFSAs (L-PFHpS and L-PFDS) were below the detection limit in every leachate sample. It should be noted that PFCAs with 9 or more carbons and PFOS adsorb considerably more strongly to organic solids than some of the shorter chain PFASs , which tend to leak off municipal solid wastes. This is consistent with the higher aqueous solubility and lower sediment-water partition coefficients of the short-chain homologues compared to the PFASs with longer perfluoroalkyl chain (Higgins and Luthy, 2006).

Regarding PFSAs, L-PFOS was only detected in raw leachate sample 3. The high amount of L-PFBS detected in samples from site 4, where PFOS was not detected, could be attributed to the fact that PFOS and other PFOS-based compounds, included in the Stockholm Convention list of POPs, have been phased out since 2002. Their use has been increasingly substituted by other alternatives such as L-PFBS (Oliaei et al., 2010; Eggen et al., 2010). Furthermore, the considerable concentration of L-PFBS in raw leachates from site 4 (529.6 ng/L) could indicate that a higher load of more recent wastes has been disposed of in this landfill site.

3.2. Effect of MBR treatment on PFASs

The MBR treatment reduced effectively ammonia and COD, as observed in Table 1. However, it failed to remove PFCAs and PFSAs as it is illustrated in Figure 2. This increase of PFASs concentration is in agreement with the results reported by Gewurtz et al. (2013), who concluded that the on-site treatment did not decrease the concentration of PFOA and PFOS in landfill leachates from 10 Canadian municipal solid waste landfill. However, that work did not detail the type of leachate treatment applied at the landfill site, and only PFOS and PFOA levels were reported. Similarly, Busch et al. (2010) and Yan et al. (2015) reported the evidence of higher PFASs levels in landfill leachates after biological treatment. According to most monitoring studies, PFCAs and PFSAs seem not to be consistently removed during secondary biological treatment (Arvaniti and Stasinakis, 2015). The predominant high energy carbon-fluorine bond makes these compounds inherently recalcitrant to biodegradation treatments (Kwon et al., 2014).

Looking at individual compounds, PFHpA concentrations slightly increased after treatment, from 78.4 ng/L in untreated sample 2A, to 101.6 ng/L in sample 2B. Similarly, PFHxA concentration increased from 692.7 ng/L in untreated sample 2A, to 840.5 ng/L in sample 2B. Moreover, the concentration of PFPeA increased significantly after the treatment applied in site 2, from 23.3 ng/L to 330.6 ng/L. The increase in the concentration of PFHxA and PFPeA could be explained by the degradation of unknown precursors such as 6:2 fluorotelomer alcohols and fluorotelomer sulfonates, and the persistence of the perfluoroalkyl carboxylates obtained as degradation products, which has been already reported for biological treatment in WWTPs (Arvaniti and Stasinakis, 2015; Loganathan et al., 2007; Sinclair and Kannan, 2006). As a result of its increasing use, 6:2 fluorotelomer sulfonate (6:2 FTS) has been detected in landfill leachates from municipal solid waste in U.S (Huset et al., 2011; Allred et al., 2014) in concentrations up to 470 ng/L. 6:2 FTS has been found to be biodegraded in wastewater treatment facilities into PFHxA and PFBA (Wang et al., 2011). Although 6:2 FTS was not included as target analyte in this study, its likely presence in the raw leachate could explain the substantial appearance of PFBA in treated sample 2B, and the increase of PFHxA content. However, further research is needed to verify this assumption.

Other compounds like L-PFBS, were measured after the treatment with concentrations as high as 584.5 ng/L. This might be attributed to the increasingly use of some sulphonamides. D'Eon et al. (2006) reported the transformation of N-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE) into PFBA and PFBS by atmospheric reaction with hydroxyl radicals. Huset et al. (2011) detected sulphonamides in landfill leachates. The most abundant was the C4-based Me-FBSAA and they argued that based on the biodegradation of analogous N-ethyl perfluorooctane sulfonamidoacetic acid (N-Et-FOSAA) found by Rhoads et al. (2008), N-methyl perfluorobutane sulfonamidoacetic acid (Me-FBSAA) could be a precursor to PFBS resulting from degradation of Me-FBSE.

3.3. Comparison to international PFASs concentrations

Although there are few available data on PFASs occurrence in landfill leachates all over the world, a substantial variability is found in the reported concentrations among landfills, and to a less extent in the patterns distribution. The data are collected and summarized in Table 2 to provide the basis for comparison and correspond to studies carried out in landfill sites from 4 global regions: North America (Huset et al., 2011; Benskin et al., 2012; Li et al., 2012; Gewurtz et al., 2013; Allred et al.; 2014), Europe (Woldegiorgis et al., 2006; Kallenborn et al., 2008; Eggen et al., 2010; Busch et al., 2010; Perkola et al., 2013), China (Zhang et al., 2014 and Yan et al., 2015) and Australia (Gallen et al., 2016). The data obtained in the present study are also included. Most of the published studies deal with leachates from the two first regions and the total PFASs concentrations reported in raw leachates ranged from a few to thousands ng/L. It is also noticeable, that the European studies were performed in Northern and Central Europe, while we are unaware of any studies assessing PFAS in landfill leachates in the southern European countries. The differences among the reported contamination levels are mainly due to the different type and number of analysed compounds and the specific characteristics of each landfill site. Differences in individual PFASs concentration could be explained by different usage of these compounds and different regulation among the studied regions (Busch et al., 2010). Based on these arguments, comparisons of the concentration levels should be considered cautiously.

The concentrations of PFASs obtained for the northern Spain landfill leachates fell in the low range of previously reported levels for leachates from municipal solid waste landfill sites in Europe, taking into account for the comparison the 16 PFASs studied in this work. In Europe, Busch et al. (2010) reported minimum concentrations of ∑PFASs (16) of 146.1 ng/L in raw leachates from one landfill site in Germany and Perkola et al. (2013) reported 402.8 ng/L for Nordic leachates in Finland. Our results (average 1082 ng/L) are lower than the concentrations found by Eggen et al. (2010) in Norway (4157 ng/L) and by Woldegiorgis et al. (2006) in Sweden (26454 ng/L). Compared to PFASs contamination in leachates from Australia, our results are similar to the PFASs concentration detected by Gallen et al. (2016) in eight closed landfill sites (1365 ng/L). However, they are lower than the ∑PFASs (16) found by Gallen et al. (2016) in 6 operational sites in Australia (5254 ng/L), the ∑PFASs (16) reported in leachates from U.S. by Allred et al. (2016) in 6 landfill sites (6156 ng/L) or by Huset et al. (2011) in four lined landfill sites in U.S. (2253-6157 ng/L). In the last case, landfill sites received biosolids from WWTP to be disposed of together with the domestic wastes, and in the study by Allred et al. (2014) some of the studied sites also accepted biosolids. However, the top range PFASs concentrations (based on 11 PFASs) reported in raw leachates was found in China, where the PFASs concentrations ranged from 7280 ng/L to 292000 ng/L (Yan et al., 2015). This value was found in an active site in Shanghai, which is one of the most industrialized and urbanized regions in China. In fact, the PFASs contamination level at that landfill was even higher than the values from sites receiving industrial wastes (Yan et al., 2015).

Regarding treated leachates, despite the fact that final concentrations are more dependent on the type and efficiency of the applied treatment, the average PFASs concentrations in our study (2009 ng/L) are again more consistent with the results reported for European leachates by Busch et al. (2010) after the application of different treatment processes such us reverse osmosis, activated carbon, nanofiltration and biological treatment in twenty sites (average ∑PFASs (16) 1335 ng/L). Similar treatment technologies were applied to Chinese leachates (Yan et al., 2015). However, PFAS concentrations reached 111,000 ng/L.

The presence of PFASs in Spain has been reported in several type of samples, such as coastal and surface waters, sediments and sewage sludge (Gómez-Canela et al., 2011; Sánchez-Avila et al., 2010; Flores et al., 2013; Llorca et al., 2011; Gómez-Canela et al., 2012). Comparing the results presented in this study with the significantly lower reported PFASs levels in other type of samples in Spain allowed us to elucidate that landfill sites seem to be a critical environmental compartment in the life cycle of these pollutants.

4. Conclusions

The occurrence and distribution pattern of PFASs (11 PFCAs and 5 PFSAs) in landfill leachates from Spain was studied for the first time by collecting grab samples in 4 different municipal solid waste landfill sites located across northern Spain. Both, raw and treated leachates were studied. Total Σ(PFCAs + PFSAs) concentration ranged from 639.2 ng/L to 1378.9 ng/L in raw leachates, while in treated samples total PFASs ranged from 856 ng/L to 3162.3 ng/L. PFCAs were most abundant than PFSAs, and among them PFOA and PFHxA were the predominant compounds. All leachate samples had the common characteristic that shorter chain PFASs were greater in abundance than their respective longer chain homologues. The MBR treatment process was not effective to remove PFASs from the studied leachates. In one site, the total PFASs concentration in the MBR effluent was two-fold the concentration in the raw leachate, and a net generation of some PFCAs was observed. This could be explained by the persistence of PFCAs against biodegradation and to the probable biotransformation of precursor compounds such as flurotelomer alcohols and sulphonamides into PFCAs. The estimation of the 16 ∑(PFCAs+PFSAs) discharge rate due to the annual volume of leachate generated in the 4 studied landfill sites was 1209 g/year, or alternatively an average discharge rate of 672 µg (PFCAs+PFSAs)/year*inhabitant. Further research should be carried out to study the presence of PFCAs precursors and the fate during each step of the leachate treatment process.

5. Acknowledgement

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6. Appendix. Supplementary Material

Supplementary data associated with the sample preparation and instrumental analysis, as well as the complete set of PFASs concentrations, can be found in this section.

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Table 1. Summary information of the municipal solid waste landfill sites, the treatment processes and the characterization of leachate samples (Source for data of leachate amount and landfill site status: Spanish Register of Emissions and Pollutants Sources, PRTR-Spain, http://www.prtr-es.es/informes)

Landfill site	**Amount of leachate (m^3/year)**	**Status**	**Treatment process [a]**	**Leachate sample code**	**pH**	**Conductivity (mS/cm)**	**TOC[c] (mg/L)**	**NH_4^+ (mg/L)**	**Cl^- (mg/L)**
1	219,000	Active old site	None	1A	7.8	7.8	1003	417	1012
			MBR/UF	1B	8.0	4.6	238	21.7	1007
2	264,054	Active old site	None	2A	8.5	9.5	2613	846	1870
			MBR/UF	2B	7.0	4.5	491	45.9	1788
3	102,670	Inactive old site, closed in 2014	None	3	8.2	8.1	741	492	1286
4	95,261	Inactive old site, closed in 2015	None	4	7.9	4.5	971	535	967

[a] MBR: Membrane Bioreactor, UF: Ultrafiltration; [c] TOC: Total Organic Carbon

Table 2. Summary of international reported PFASs concentrations in municipal solid waste landfill leachates. ΣPFASs was calculated using the reported concentrations of only PFASs compounds found in the samples analyzed in the present study.

Region - Country		**Concentrations in landfill leachates (ng/L)**															
		PFBA	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTeDA**	**PFBS**	**PFHxS**	**PFOS**	**ΣPFASs**	**Comments**	***Reference***
North America	Canada (n=30)	120-660(327)	630-1800(980)	670-2500 (1411)	240-690 (439)	300-1500 (649)	31-450 (146)	40-1100 (294)	<3-120 (<29.5)	1.5-16 (<4.8)	<1.5-5.1 (<2.1)	44-190 (94)	85-540 (323)	220-4400 (1094)	5793.4	"Flow through leachate". Untreated Landfill A.	Benskin et al., 2012[a]
	Canada (n=3)	70	880	650	380	210	15	10	<3	<1.4	<1.5	28	220	80	2543	"Recirculated leachate" Untreated. Landfill B	Benskin et al., 2012[a]
	Canada (n=28)			695		439								279	27-21300 (2950)	Average concentrations	Li et al., 2012 [a]
	U.S. (Gulf Coast)	1700	1100	790	328	490	23	15	0.4	0.2	0	750	700	160	6056.6	Untreated leachates. Wastes: MSW[b], C&D[c] and industrial wastes.	Huset et al., 2011[a]
	U.S. (Pacific Northwest)	170	120	270	100	1000	22	14	0	6	1.2	280	160	110	2253.2		
	U.S. (West Coast)	1400	1500	620	340	900	28	23	0.1	0.8	9	810	430	97	6157.9		
	U.S. (Mid-Atlantic States)	430	730	360	170	380	20	0.3	0	0	2	280	170	56	2598.3		
	U.S. (Mid-Atlantic States)	250	500	350	150	490	19	11	9.5	0.7	0.7	390	200	91	2461.9		
	U.S. (Mid-Atlantic States. D6)	540	470	430	170	720	26	18	0.9	0.2	13	890	360	140	3778.1		
	U.S. (site A)	670	650	1800	940	1300	55	31	n.d	<LOQ	n.d	380	830	170	6156	MSW[b] (since 1999)	Allred et al., 2014[a]
	U.S. (site B1)	3500	1300	1700	1100	910	11	6.3	n.d	n.d	n.d	61	730	220	6038.3	MSW[b] (1975- 1999)	
	U.S. (site B2)	1500	1600	2200	1900	1200	27	6.8	n.d	n.d	n.d	86	560	140	7719.8	MSW[b] (since 1999)	
	U.S. (site C)	3700	3200	8900	3100	5000	290	200	26	29	5.6	3200	1100	590	25640.6	MSW[b] (since 2009)	

Region - Country		Concentrations in landfill leachates (ng/L)															
		PFBA	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTeDA**	**PFBS**	**PFHxS**	**PFOS**	**ΣPFASs**	**Comments**	***Reference***
	U.S. (site D)	800	1600	1300	460	150	12	9.8	n.d	n.d	n.d	310	64	39	3944.8	MSW[b] (since 2003)	
	U.S. (site E)	69	54	190	62	180	11	8.9	n.d	n.d	n.d	38	45	25	613.9	MSW[b] (since 1996)	
	Canada (n=10)					50.3 - 1590								<9.5 - 744		Untreated leachates	Gewurtz et al., 2013
	Canada (n=10)					42-4750								<9.8 - 2070		Treated leachates	
Australia	Australia (n=28)	220-890 (532.5)		360-5700 (1635.6)	130-3500 (925.6)	20-100 (684.7)	14-89 (48.8)	2-57 (26.4)	0.72-18 (9.5)	13-28 (19.7)	27-29 (28)	74-840 (395.2)	7.6-1900 (513.6)	95-1100 (438.4)	4819.6	Operational landfill leachate	Gallen et al., 2016
	Australia (n=32)	47-1600 (504.0)		12-410 (144.1)	2.2-210 (64.5)	19-670 (170.6)	0.25-9.6 (4.2)	<LOQ	<LOQ	<LOQ	25-25 (25.0)	7.2-250 (71.8)	0.95-1300 (208.4)	37-870 (174.5)	1367.1	Closed landfill leachate	
Asia	China (Raw Leachate)	1100-9270	609-6530	146-4430	75.4-5830	281-214000	<LOQ-381	<LOQ-18.8				1600-41600	<LOQ-479	1150-6020	7280-292000	Raw Leachate	Yan et al.,2015 [a]
	China (Bioreactor supernatant)	1000-8500	478-5290	103-3710	37.4-2560	543-70900	1.8-76.7	<LOQ-50				1180-18300	2.7-242	238-717	4570-111000	Bioreactor supernatant	
	China (UF[1] effluent)	93.4-1590	<LOQ-1100	<LOQ-3030	<LOQ-2840	670-48300	<LOQ-91.3	<LOQ				872-21000	<LOQ-121	49-374	2130-79000	Ultrafiltration effluent	
	China (RO[2] effluent)	<LOQ-6.7	<LOQ	<LOQ	<LOQ	30.7-94.8	<LOQ-1.6	<LOQ				22.4-83.4	<LOQ-2.1	11-21.9	98.4-190	Reverse osmosis effluent	
Europe	Sweden (n=4)	<12-30(7.5)		<7-310 (77.5)	7.70-260(197.5)	38-1000(537)	<18-100(43.5)	<20-220(82.5)	<5.9-<59			<0.5-110(37.3)	12-1800 (518)	32-1500 (555)	2087.8	Treated leachates	Woldegiorgis et al., 2006 [a]
	Sweden (n=1)	<1300		<300	<600	4200	<680	<410	<430			<34	8900	9600	<25154	Untreated leachates	
	Norway, Finland (n=9)			26.4-697		91.3-516	3.5-61.3					5.64-112	11.6-158	30.2-187	201-1537		Kallenborn et al.,2004 [a]
	Norway	<185		590-757	215-277	532-767	310-539	<75	<29	<25		<5	89-281	455-2920	2191-6123 (4157)	Untreated leachates Aqueous phase	Eggen et al., 2010 [a]
	Norway	<LOD		<LOD	<LOD	2.76-4.05	<LOD	<LOD	<LOD	<LOD		<LOD	0.05-0.15	7.28-33.9	10.53-38.43 (24.5)	Untreated leachates (2006) Particles	Eggen et al., 2010 [a]

Region - Country	Concentrations in landfill leachates (ng/L)														
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	ΣPFASs	Comments	*Reference*
Finland (n=2)			49-200 (120)		76-270(170)		2-3.7 (2.8)						87-140 (110)		Untreated leachates	Perkola et al., 2013
Estonia (n=2)			600		600		<0.5						100		Biological treated leachate	Nakari et al., 2011
Germany (n=2)			150		200		<0.5						50		Biological and ozonation treated leachate	
Sweden (n=2)			2900		2000		<0.5						1500		Biological and phytoremediation treated leachate	
Polen (n=2)			800		700		200						400		Untreated leachate	
Finland (n=2)			200		250		<0.5						150		Untreated leachate	
Denmark (n=2)			700		100		<10						<10		Untreated leachate	
Germany (n=20)	<LOD-2968 (458)	<LOD - 829	<LOD - 2509 (234)	<LOD - 280 (48)	<LOD - 926 (145)	<LOD - 80.1 (7.3)	<LOD - 55.1(6)	<LOD - 2.98 (0.36)	<LOD - 2.45	<LOD - 0.41	<LOD - 1356 (220)	<LOD - 178(22.2)	0.01-235(30.9)	4-8059 (1335.3)	Treated leachates	Busch et al., 2010 [a]
Germany (n=1)	52.97	18.36	19.07	5.57	22.68	<LOD	0.46	<LOD	<LOD	<LOD	15.3	3.46	8.23	146.1	Raw leachates	
Holland (n=2)	76-244 (150)		44-70(56)	20-21(20)	63.6-76(69.8)	<LOQ					17-20(18)	11-12(11)	9.6		Landfill leachate plume	Eschauzier et al., 2013
Holland (n=2) Site OW1-f3	1010-1280(1200		506-670(570)	214-318(320)	1657-2444(2050.5)	<LOQ					62-104 (91)		110		Landfill leachate plume	
North Spain (n=4)	22-86(61)	<LOD-267(73)	102-692(325)	<LOD-78(20)	387-584(461)	<LOD-6(1.5)	<LOD	<LOD	<LOD	<LOD	<LOD-529(132)	<LOD	<LOD-43(11)	639-1379 (1082)	MSW, raw leachate	This study
North Spain (n=2)	<LOD-794(397)	136-330(233)	224-849(532)	60-102(80)	199-512(356)	<LOD	<LOD	<LOD	<LOD	<LOD-68	167-584(376)	<LOD	<LOD	856-3162 (2009)	MSW, treated leachate	

[a] The authors report data on more PFASs compounds than the PFASs included in this summary; [b]MSW (municipal solid wastes); [c]C&D (construction and demolition wastes). Reported values in brackets correspond to mean values; n, number of samples

Figures 1 and

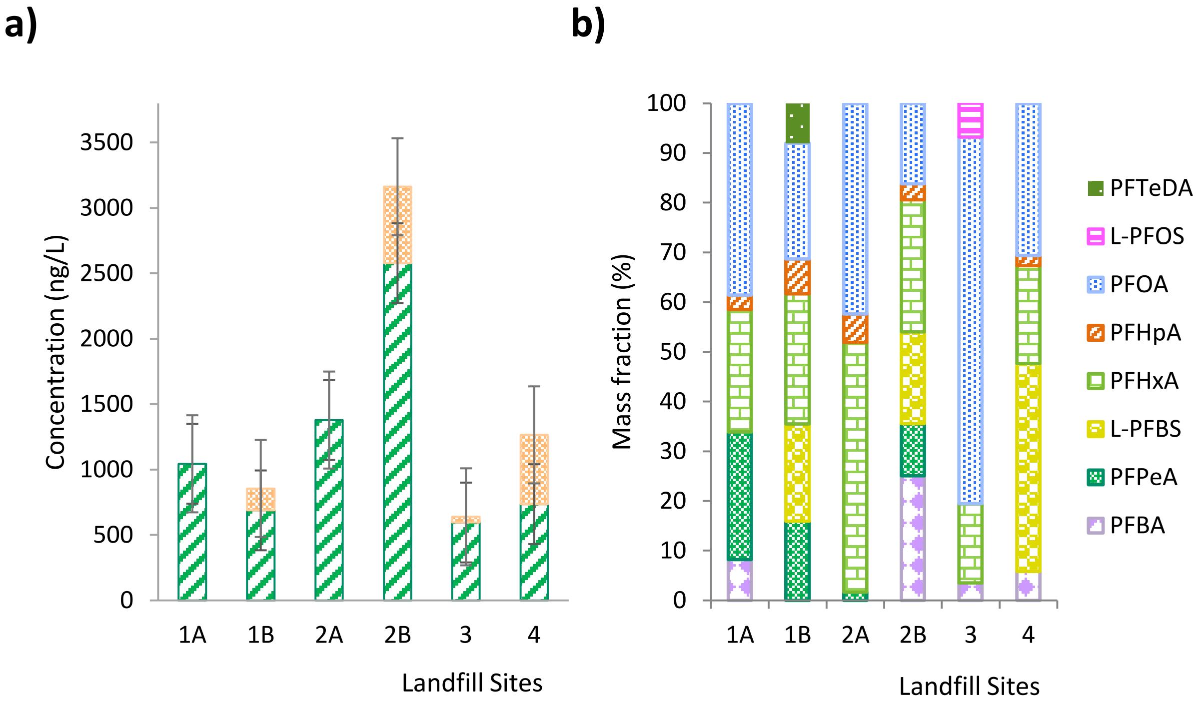


Figure 1. ▨ PFCAs concentrations, ▩ PFSAs concentration and total concentration of PFASs as sum of PFCAs and PFSAs (a); mass fractions of individual PFASs in landfill leachate samples from the different study sites (b)

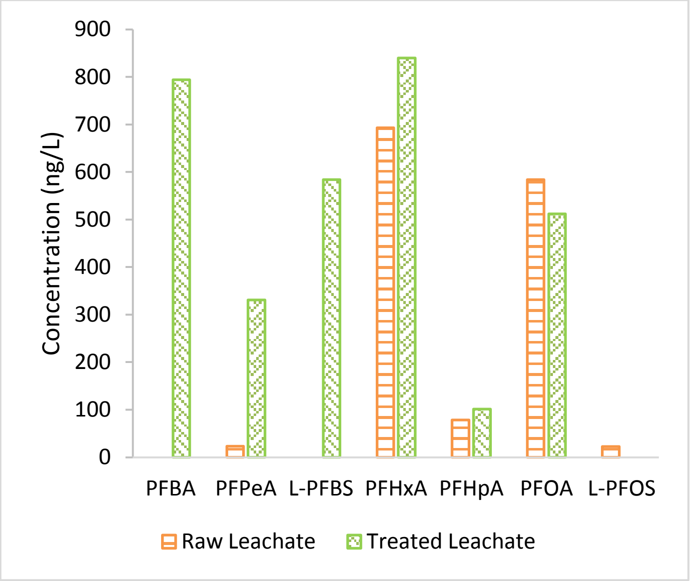


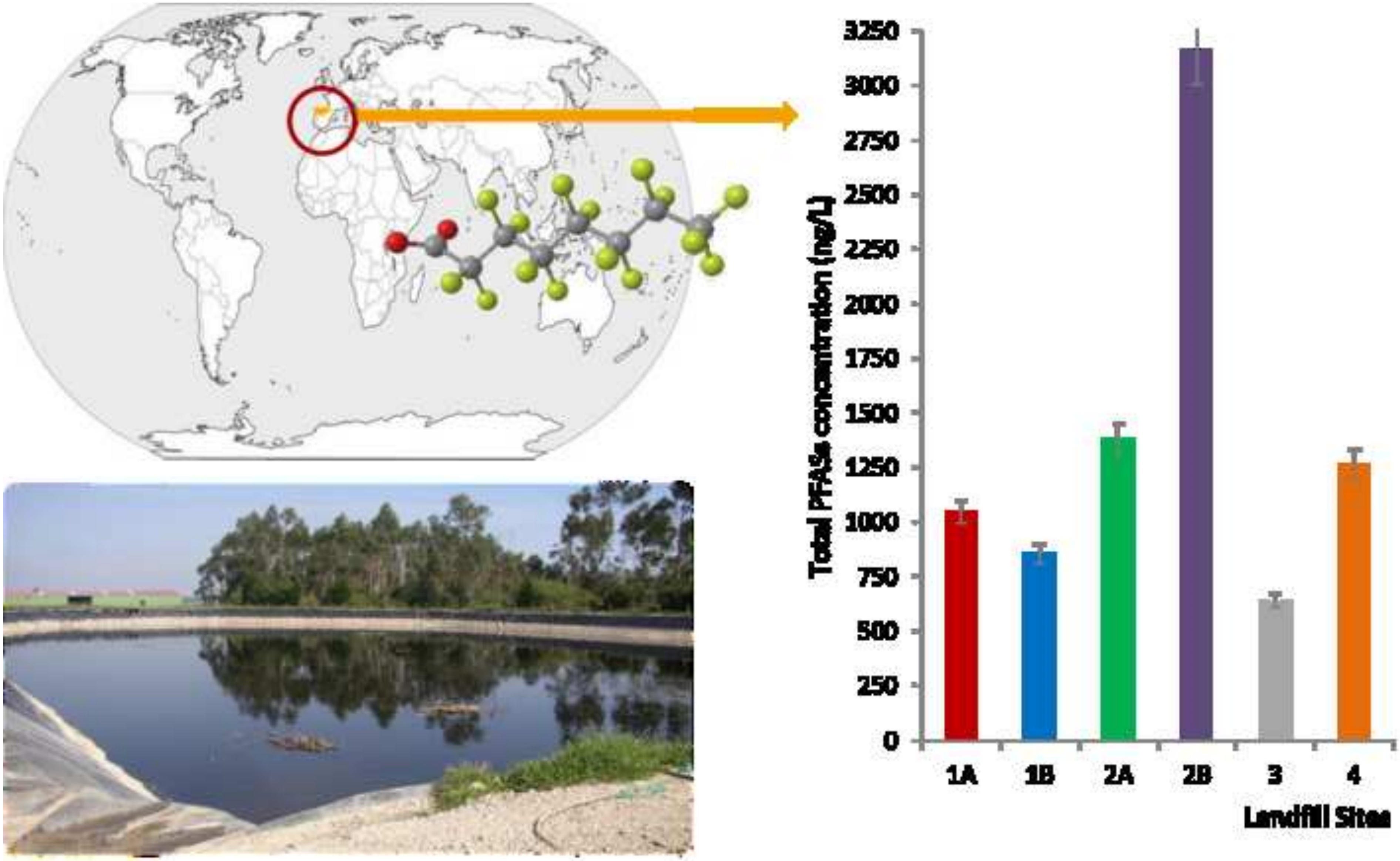
Figure 2. Individual PFASs concentrations before and after leachate treatment in site 2.

Figure captions

Figure 1. ▨ PFCAs concentrations, ▩ PFSAs concentration and total concentration of PFASs as sum of PFCAs and PFSAs (a); mass fractions of individual PFASs in landfill leachate samples from the different study sites (b)

Figure 2. Individual PFASs concentrations before and after leachate treatment in site 2.

Graphical Abstract



Supplementary Material

Perfluorinated alkyl substances (PFASs) in northern Spain municipal solid waste landfill leachates

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Sample Preparation

1. Solid phase extraction (SPE)

Four different SPE approaches were performed in order to optimize target analyte recoveries. A set of blanks, untreated leachate and spiked leachate samples were tested in duplicate according to each SPE approach. The spiked leachate samples consisted of 5 mL of sample from site 1 diluted in 20 mL of Milli-Q water and spiked with 25 µL of PFC-MXA and PFS-MXA standards. Blanks consisted of Milli-Q water and the sample volume was 25mL in all cases. Two different SPE cartridges were tested: Evolute WAX (weak anion exchange, 6cc, 200mg, 50µm) cartridges and Oasis HLB (6cc, 200mg, 30µm) cartridges. In every SPE approach, sample and reagent loading rates were fixed at approximately 1 drop/sec to achieve better recoveries (Busch et al., 2010).

The first SPE approach (A) was a modification of the method detailed by Perkola et al. (Perkola et al., 2013) and was done with WAX cartridges. Preconditioning was performed with 5 mL methanol and 5 mL Milli-Q water. After samples loading, the cartridges were washed with 1 mL of 2% formic acid and 1 mL of Milli-Q water: methanol (95:5 v/v). Then, they were dried under vacuum during 2 hours, and finally the target compounds were eluted with 4 mL of 1% ammonia in methanol. A second SPE approach (B) was performed using a modification of the method proposed by Li et al. (Li et al., 2010) by using also WAX cartridges. Cartridges were conditioned with 10 mL of 1% ammonia in methanol, then 10 mL of methanol and finally 10 mL of 1% acetic acid. After the samples were loaded, the cartridges were washed with 10 mL of 2% formic acid and dried under vacuum during 2 hours. Finally, the target analytes were eluted with 2 mL of methanol and 2 mL of 1% ammonia in methanol.

SPE approaches C and D were carried out according to Zabaleta et al. (Zabaleta et al., 2014). SPE approach C was performed with WAX cartridges, conditioned with 5 mL methanol and 5 mL Milli-Q water. After loading the samples, cartridges were washed with 1 mL of 2% formic acid and 1 mL of Milli-Q water: methanol (95:5 v/v), and dried under vacuum during 2 hours. Finally, the target analytes were eluted with 4 mL of 2.5% ammonia in acetone. In the last SPE approach (D) samples were extracted with Oasis HLB cartridges. Before the extraction, samples were adjusted to a pH-value of 1 using hydrochloric acid. The cartridges were conditioned with 5 mL methanol and 5 mL Milli-Q water, previously adjusted to pH 1 in the same way as samples. After the samples were loaded, the cartridges were washed with 5 mL of Milli-Q water: methanol (95:5 v/v) and dried under vacuum during 2 hours. The target compounds were eluted with 8 mL of methanol.

1.1. Optimum SPE

The results of total recoveries (%) of target PFASs after the whole analytical method performing SPE according to approaches A, B, C and D to spiked samples (n=3) are shown in Figure S1a. SPE approach A provided the best recoveries, expressed as the average of total PFASs recovery percentage. SPE procedures B and C were clearly rejected because of the low PFASs recoveries. Procedure D using Oasis HLB cartridges was not selected not only because of the low PFASs recoveries but also because of the issue of clogging of the SPE cartridges.

Leachate sample volumes were then optimized by performing the SPE approach A to different landfill leachate sample volumes from site 1: 25, 70 and 250 mL, respectively. The eluting mixture volume was also incremented according to the increased leachate sample volume. The highest total PFASs concentration was obtained with a sample volume of 70 mL (1014 ng/L, Figure S1b, followed by the leachate volume of 25 mL (940 ng/L). A noteworthy feature of the SPE was that when a sample volume of 250 mL was extracted, the PFASs concentration measured sharply decreased to 250mL. This significant target analyte loss could be due to SPE cartridges breakthrough, likely caused by the combination of high chemical oxygen demand (COD), high chloride and specific conductance typical of landfill leachates (Table 1) that might have exceeded the anion exchange capacity of WAX SPE cartridges.

2. Instrumental analysis

The mobile phase in the HPLC system consisted of (A) Milli-Q water and (B) methanol, both containing 2 mmol/L ammonium acetate. The operating flow rate was 0.2 mL/min in gradient mode, starting with 90% A (held until 0.3 min) to be then linearly increased to 40 % until 11 min. After 7 min a step increase to 100% B was programmed until 24 min, which was held for 2 min to complete elution. The column was reconditioned for 13 minutes at the starting composition of 90 % A prior to the next injection. The injection volume was 10 µL. The detection was done with a triple quadrupole mass spectrometer (Quattro Micro, Waters) in a multiple reaction monitoring (MRM) acquisition mode. Nitrogen was used as nebulizer, drying, and collision gas. Electrospray negative ionization was carried out using a capillary voltage of 3.20 kV, a nitrogen gas flow rate of 450 L/h and a drying gas temperature of 300 ºC. Fragmentor voltages and collision energy were optimised for the different target analytes by injection of individual compounds. These results are listed in Table S2 together with the MS/MS transitions. The MassLynx Software v. 4.0 (Waters) was used for instrument control, data acquisition and processing.

Table S1. Target analytes and internal standards, acronyms, molecular formulas and standard

Standard PFS-MXA

Compound	Acronym	Formula	Purity %
Potassium perfluoro-1-butanesulfonate	L-PFBS	$C_4F_9SO_3K$	>98
Sodium perfluoro-1-hexanesulfonate	L-PFHxS	$C_6F_{13}SO_3Na$	>98
Sodium perfluoro-1-heptanesulfonate	L-PFHpS	$C_7F_{15}SO_3Na$	>98
Sodium perfluoro-1- octanesulfonate	L-PFOS	$C_8F_{17}SO_3Na$	>98
Sodium perfluoro-1-Perfluoro-decanesulfonate	L-PFDS	$C_{10}F_{21}SO_3Na$	>98

Standard PFC-MXA

Compound	Acronym	Formula	Purity %
Perfluoro-n-butanoic acid	PFBA	C_3F_7COOH	>98
Perfluoro-n-pentanoic acid	PFPeA	C_4F_9COOH	>98
Perfluoro-n-hexanoic acid	PFHxA	$C_5F_{11}COOH$	>98
Perfluoro-n-heptanoic acid	PFHpA	$C_6F_{13}COOH$	>98
Perfluoro-n-octanoic acid	PFOA	$C_7F_{15}COOH$	>98
Perfluoro-n-nonanoic acid	PFNA	$C_8F_{17}COOH$	>98
Perfluoro-n-decanoic acid	PFDA	$C_9F_{19}COOH$	>98
Perfluoro-n-undecanoic acid	PFUdA	$C_{10}F_{21}COOH$	>98
Perfluoro-n-dodecanoic acid	PFDoA	$C_{11}F_{23}COOH$	>98
Perfluoro-n-tridecanoic acid	PFTrDA	$C_{12}F_{25}COOH$	>98
Perfluoro-n-tetradecanoic acid	PFTeDA	$C_{13}F_{27}COOH$	>98

Internal Standard MPFAC-MXA

Compound	Acronym	Formula	Purity %
Perfluoro-n- [$^{13}C_4$] butanoic acid	MPFBA	$[2,3,4\text{-}^{13}C_3]F_7{}^{13}COOH$	>98
Perfluoro-n- [1,2-$^{13}C_2$] hexanoic acid	MPFHxA	$C_4F_9[2\text{-}^{13}C]F_2{}^{13}COOH$	>98
Perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid	MPFOA	$C_4F_9[2,3,4\text{-}^{13}C_3]F_6{}^{13}COOH$	>98
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid	MPFNA	$C_4F_9[2,3,4,5\text{-}^{13}C_5]F_8{}^{13}COOH$	>98
Perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	MPFDA	$C_8F_{17}{}^{13}CF_2{}^{13}COOH$	>98
Perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid	MPFUdA	$C_9F_{19}{}^{13}CF_2{}^{13}COOH$	>98
Perfluoro-n-[1,2-$^{13}C_2$] dodecanoic acid	MPFDoA	$C_{10}F_{21}{}^{13}CF_2{}^{13}COOH$	>98
Sodium perfluoro-1-hexane [$^{18}O_2$] sulfonate	MPFHxS	$C_6F_{13}S[^{18}O_2]ONa$	>94
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate	MPFOS	$C_4\ F_9[1,2,3,4\text{-}^{13}C_4]F_8SO_3Na$	>98

Table S2. LC/MS/MS parameters for target analytes and internal standards, limits of detection (LOD) in leachates as well as intra day repeatability (%RSD) for target analytes (50 ng/mL).

Analytes	Precursor ion (m/z)	Product ion (m/z)	Fragmentor (V)	Collision energy (eV)	LOD (ng/L)	%RSD (n=5)
PFBA	213	169	20	10	1.1	5.4
PFPeA	263	219	15	10	38.9	8.9
PFHxA	313	269/119	15	10/20	18.3	4.6
PFHpA	363	319/169	15	10/20	17.1	4.5
PFOA	413	369/169	15	10/20	15.7	3.8
PFNA	463	419/219	15	15/20	50.3	11.3
PFDA	513	469/269	15	20/25	53.1	6.8
PFUdA	563	519/269	20	10/25	28.6	11.1
PFDoA	613	569/269	15	15/20	34.3	11.3
PFTrDA	663	619/169	15	20/45	34.6	10.2
PFTeDA	713	669/369	20	20/25	82.6	11.3
L-PFBS	299	99/80	45	25/25	66.6	4.9
L-PFHxS	399	99/80	50	25/40	33.1	1.4
L-PFHpS	449	99/80	50	25/45	30.6	8.8
L-PFOS	499	99/80	50	30/40	39.1	7.2
L-PFDS	599	99/80	60	35/35	86.3	10.5
MPFBA	217	172/58	20	15/20	32.9	6.8
MPFHxA	315	270/120	15	5/25	48.6	3.4
MPFHxS	403	103/84	50	30/35	41.4	5.1
MPFOA	417	372/172	15	15/25	14.0	2.9
MPFNA	468	423/223	15	15/25	10.0	3.4
MPFOS	503	99/80	60	40/45	82.3	5.6
MPFDA	515	470/170	15	15/40	22.6	4.3
MPFUdA	565	520/320	20	15/20	34.9	9.4
MPFDoA	615	570/169	20	15/45	6.9	11.4

Table S3. Concentration of individual PFASs, total PFASs, total PFCAs and total PFSAs in landfill leachate samples.

Analytes (ng/L)	**Landfill leachate samples**					
	1A	**1B**	**2A**	**2B**	**3**	**4**
PFBA	86.0	<LOD	<LOD	794.0	22.4	74.0
PFPeA	267.8	136.4	23.3	330.6	<LOD	<LOD
PFHxA	257.5	224.5	692.7	840.5	102.3	248.7
PFHpA	30.4	59.7	78.4	101.6	<LOD	26.0
PFOA	402.3	199.6	584.1	512.1	471.3	387.2
PFNA	<LOD*	<LOD	<LOD	<LOD	<LOD	<LOD
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	68.4	<LOD	<LOD	<LOD	<LOD
L-PFBS	<LOD	167.4	<LOD	584.5	<LOD	529.6
L-PFHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFOS	<LOD	<LOD	<LOD	<LOD	43.5	<LOD
L-PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
∑PFASs	1044.6	856.0	1378.9	3162.3	639.2	1265.8
∑PFCAs	1044.6	688.6	1378.9	2578.4	595,7	736.2
∑PFSAs	0	167.4	0	583.9	43.5	529.6

*<LOD: below limit of detection

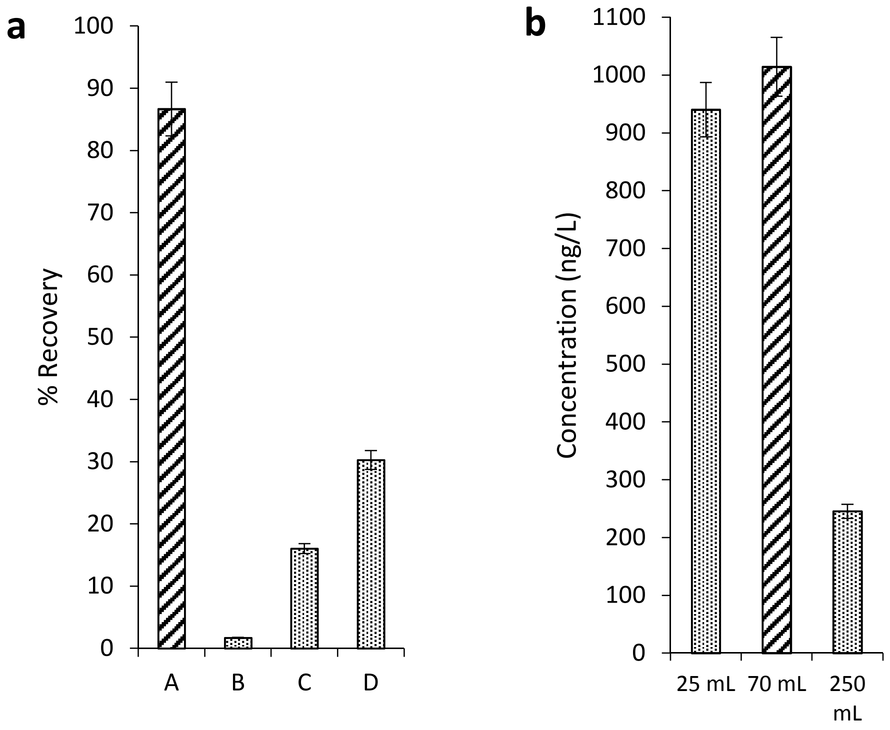

Figure S1. (**a**) Comparison of the total recoveries (%) of target compounds in spiked samples for the different extraction procedures A, B, C, and D; and (**b**) comparison of total PFASs concentration in real samples obtained after the application of SPE approach A with different leachate sample volumes. Experiments were carried out in triplicate.

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