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## **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  $\Sigma$ PFASs concentration compared to raw leachate, likely due to generation of PFASs through precursor compounds.
- Estimated mass flow of 16  $\Sigma$ 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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26 **Perfluorinated alkyl substances (PFASs) in northern Spain municipal**  
27 **solid waste landfill leachates**

28

29 **Abstract**

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

49 discharge of 16  $\Sigma$ PFASs contained in the landfill leachates was estimated as 1209  
50 g/year.

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

53

## 54 **1. Introduction**

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

70 Municipal solid waste landfills receive consumer products, which are susceptible  
71 to contain PFASs (Eggen et al., 2010). Therefore, it is likely that PFASs can be released

72 and reach landfill leachates with the potential of migration to the surrounding aquatic  
73 environment and in particular groundwater (Paul et al., 2009; Yan et al., 2015).  
74 Furthermore, recent studies have demonstrated that landfills are, similarly to wastewater  
75 treatment plants (WWTP), emission sources of semivolatile PFASs to the ambient air  
76 (Ahrens et al., 2011; Weinberg et al., 2011). Studies on PFASs in municipal landfill  
77 leachates have been conducted mainly in three regions all over the world: North  
78 America (Huset et al., 2011; Benskin et al., 2012; Li et al., 2012; Gewurtz et al., 2013;  
79 Allred et al.; 2014; Clarke et al., 2015), Europe (Woldegiorgis et al., 2006; Kallenborn  
80 et al., 2008; Eggen et al., 2010; Busch et al., 2010; Perkola et al., 2013) and China  
81 (Zhang et al., 2014; Yan et al., 2015). All the studies performed in Europe correspond to  
82 northern and central European countries. Recently, a study on PFASs has been  
83 published dealing with landfill leachates in Australia (Gallen et al., 2016). The number  
84 of PFASs monitored varies from one study to another. The most frequently analysed  
85 PFASs in landfill leachates are perfluoroalkyl carboxylic acids (PFCAs) and  
86 perfluoroalkyl sulfonic acids (PFSAs). Although there is a significant variability in the  
87 occurrence and patterns of PFASs among studied landfills, short chain PFASs (C<sub>4</sub>-C<sub>8</sub>  
88 chain length) dominate the distribution profiles. Data on PFASs occurrence in leachates  
89 have revealed concentrations of PFASs among the highest levels in environmental  
90 waters, although still lower than PFASs concentrations found in aqueous film forming  
91 foam (AFFF)-impacted groundwater collected from military training areas (Filipovic et  
92 al., 2015, Schaefer et al., 2015). To the best of our knowledge, no previous studies have  
93 been carried out either in Spain or in other southern European countries concerning  
94 PFASs monitoring in leachate samples.

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

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

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

## 107 **2. Materials and methods**

### 108 *2.1. Standards and reagents*

109 Two different certified standard solutions were purchased from Wellington  
110 Laboratories (Guelph, Ontario, Canada): PFC-MXA and PFS-MXA, containing PFCAs  
111 and PFSAs, respectively at individual concentrations of 2 µg/mL. The analytical  
112 standard MPFAC-MXA of 2 µg/mL, also from Wellington Laboratories, was used as  
113 internal standard (IS). A detailed list of the target analytes, internal standards, acronyms,  
114 formulas and purities of the standards is given in Table S1. Evolute WAX (6cc, 200mg,  
115 50µm) solid phase extraction (SPE) cartridges were purchased from Biotage and Oasis  
116 HLB (6cc, 200mg, 30µm) SPE cartridges were acquired from Waters (Milford, MA,  
117 USA). Bulk ENVI-Carb sorbent (100 m<sup>2</sup>/g, 120/400 mesh) was purchased from Supelco  
118 (Bellefonte, MA, USA). All solvents were UPLC-MS quality and Milli-Q water was  
119 used throughout.

## 120 2.2. Landfill sites and leachate characterization

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

125 The sites were located in northern Spain across a longitudinal distance of about  
126 400 km and served a population of nearly 1.8 million inhabitants. All landfill sites are  
127 placed in river basins that flow to the Bay of Biscay (northeast of Atlantic Ocean)  
128 According to the Statistical Classification of Economic Activities (NACE, 2008) , all  
129 the studied landfill sites were used for treatment and disposal of non-hazardous  
130 municipal solid waste from residential urban areas. Raw leachate grab samples (2 L)  
131 were collected before the leachate was pumped off either to the on-site treatment  
132 facilities or to the municipal water sewage system for treatment in the local WWTP.  
133 Additionally, at two of the studied sites treated leachate grab samples (2 L) were  
134 collected from the effluent of the leachate treatment facilities. The leachate treatment  
135 was similar in both landfill sites and consisted of an external membrane bioreactor  
136 (MBR) unit that integrated a two-stage biological process with an ultrafiltration (UF)  
137 unit. The biological process consisted of an aerobic and anaerobic nitrifying pressurised  
138 reactor that reduced the ammonia content by its conversion into nitrogen gas. At the  
139 same time the organic matter content was reduced, mainly the biodegradable fraction.  
140 Then, the biologically treated leachate entered an UF unit provided with tubular  
141 membrane modules to separate the biomass from the treated leachate. All grab samples  
142 were collected in polypropylene (PP) bottles pre-washed with methanol, and  
143 polytetrafluorethylene (PTFE) based materials were avoided throughout the sampling  
144 and analysis to prevent potential sample contamination.

145        *2.3. Sample preparation*

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

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

156            Extracts were cleaned up using dispersive carbon sorbent (Envicarb) to remove  
157 the co-eluted interfering compounds according to the method suggested by Powley et al.  
158 (2005). Briefly, 100 mg of EnviCarb activated carbon and 50 µL of glacial acetic acid  
159 were added in a centrifuge tube and vortex mixed along with the sample extract for 30 s.  
160 Centrifugation was carried out at 11000 rpm and extracts were then filtered (0.22 µm)  
161 and transferred to a 15 mL PP tube to be further evaporated until dryness under a gentle  
162 stream of dry nitrogen gas. The final volume was adjusted to 200 µL of Milli-Q  
163 water:methanol (70:30 v/v) prior to injection.

164        *2.4. Instrumental analysis and quantification*

165            The purified sample extracts were analyzed using an Agilent 1260 series high  
166 performance liquid chromatography (HPLC) system coupled to a Quattro Micro triple  
167 quadrupole (QqQ) mass spectrometer (MS/MS, Waters, Milford, MA, USA) with an



168 electrospray ionization (ESI) interface operated in the negative ionization mode. A  
169 Kinetex Phenomenex C18 column (50 x 2.1 mm x 2.6 $\mu$ m) at 35 °C was used for the  
170 analytical separation. The mobile phase consisted of Milli-Q water (A) and methanol  
171 (B), both containing 2 mmol/L ammonium acetate, that was flowed at an operating flow  
172 rate of 0.2 mL/min in gradient mode. Further details about the instrumental analysis and  
173 quantification method by HPLC-MS/MS is described in the Supplementary material.

174 Dilutions from the stock standard solutions were prepared in methanol/water  
175 (70:30 v/v) at 7 concentration levels ranging from 5 ng/mL to 400 ng/mL and  
176 calibration curves were built in order to calculate the PFAS concentrations in real  
177 samples and to control the linear range of the instrumental response.

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

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### 193 3. Results and discussion

#### 194 3.1. PFASs content in landfill leachates

##### 195 3.1.1. Total concentration of PFASs

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

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

215 The discharge rate of 16  $\Sigma$ (PFCAs+PFASs) into the aqueous environment was  
216 estimated by multiplying the PFASs concentrations by the annual average volume of  
217 leachate generated in each site (Table 1). The estimated discharge rate ranged from 65.6  
218 g/year in site 3 to 835 g/year in site 2, with an accumulated 16  $\Sigma$ PFASs mass flow of  
219 1209 g/year from the four studied landfill sites that serve a population of approximately  
220 1.8 million in northern Spain. The results showed an average discharge of PFASs rate of  
221 672  $\mu\text{g}/\text{year}\cdot\text{inhabitant}$ .

### 222 3.1.2. Individual concentration of PFASs

223 Figure 1b shows an overview of the mass fraction contribution of individual  
224 compounds in each sample. In general terms, PFOA was the dominant compound in  
225 untreated leachate samples. With a mean contribution to the total mass fraction of  
226 42.6%, the concentration of PFOA was the highest one among all measured PFASs in  
227 untreated leachate samples 1A and 3. Nevertheless, in samples 2A and 4, PFHxA and  
228 PFBS respectively, showed concentrations slightly over their PFOA content.

229 The higher abundance of PFOA could be consequence of the commercial history  
230 of C8-based production of PFCAs (Prevedouros et al., 2006; Oliaei et al., 2010; Huset  
231 et al., 2011). PFOA was used as processing acid in certain polymerization processes,  
232 and subsequently its presence has been reported in consumer products as an unreacted  
233 residual material (Eggen et al., 2010). According to the age of landfill sites and the  
234 characterization of the leachates (Table 1), all the studied samples could be considered  
235 as stabilized leachates (Alvarez-Vazquez et al., 2004; Kurniawan et al., 2005). Taking  
236 into account that consideration, it was expected to find high concentrations of PFOA  
237 and PFHxA because of the discharge of consumer products with high contents of these  
238 PFASs for a long time and actually, these two PFASs were the only ones detected in

239 every landfill leachate sample. Furthermore, the contribution of fluorotelomer precursor  
240 degradation to PFCAs has been reported by many authors (Wang et al. 2011; Benskin et  
241 al. 2012; Filipovic and Berger, 2015) and could be other important PFASs source in  
242 landfill leachates. It would also explain to a certain extent the predominance of PFCAs  
243 among  $\Sigma$ PFASs.

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

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

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263           3.2. *Effect of MBR treatment on PFASs*

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

277           Looking at individual compounds, PFHpA concentrations slightly increased  
278 after treatment, from 78.4 ng/L in untreated sample 2A, to 101.6 ng/L in sample 2B.  
279 Similarly, PFHxA concentration increased from 692.7 ng/L in untreated sample 2A, to  
280 840.5 ng/L in sample 2B. Moreover, the concentration of PFPeA increased significantly  
281 after the treatment applied in site 2, from 23.3 ng/L to 330.6 ng/L. The increase in the  
282 concentration of PFHxA and PFPeA could be explained by the degradation of unknown  
283 precursors such as 6:2 fluorotelomer alcohols and fluorotelomer sulfonates, and the  
284 persistence of the perfluoroalkyl carboxylates obtained as degradation products, which  
285 has been already reported for biological treatment in WWTPs (Arvaniti and Stasinakis,  
286 2015; Loganathan et al., 2007; Sinclair and Kannan, 2006). As a result of its increasing  
287 use, 6:2 fluorotelomer sulfonate (6:2 FTS) has been detected in landfill leachates from

288 municipal solid waste in U.S (Huset et al., 2011; Allred et al., 2014) in concentrations  
289 up to 470 ng/L. 6:2 FTS has been found to be biodegraded in wastewater treatment  
290 facilities into PFHxA and PFBA (Wang et al., 2011). Although 6:2 FTS was not  
291 included as target analyte in this study, its likely presence in the raw leachate could  
292 explain the substantial appearance of PFBA in treated sample 2B, and the increase of  
293 PFHxA content. However, further research is needed to verify this assumption.

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

### 304 *3.3. Comparison to international PFASs concentrations*

305 Although there are few available data on PFASs occurrence in landfill leachates  
306 all over the world, a substantial variability is found in the reported concentrations  
307 among landfills, and to a less extent in the patterns distribution. The data are collected  
308 and summarized in Table 2 to provide the basis for comparison and correspond to  
309 studies carried out in landfill sites from 4 global regions: North America (Huset et al.,  
310 2011; Benskin et al., 2012; Li et al., 2012; Gewurtz et al., 2013; Allred et al.; 2014),  
311 Europe (Woldegiorgis et al., 2006; Kallenborn et al., 2008; Eggen et al., 2010; Busch et

312 al., 2010; Perkola et al., 2013), China (Zhang et al., 2014 and Yan et al., 2015) and  
313 Australia (Gallen et al., 2016). The data obtained in the present study are also included.  
314 Most of the published studies deal with leachates from the two first regions and the total  
315 PFASs concentrations reported in raw leachates ranged from a few to thousands ng/L. It  
316 is also noticeable, that the European studies were performed in Northern and Central  
317 Europe, while we are unaware of any studies assessing PFAS in landfill leachates in the  
318 southern European countries. The differences among the reported contamination levels  
319 are mainly due to the different type and number of analysed compounds and the specific  
320 characteristics of each landfill site. Differences in individual PFASs concentration could  
321 be explained by different usage of these compounds and different regulation among the  
322 studied regions (Busch et al., 2010). Based on these arguments, comparisons of the  
323 concentration levels should be considered cautiously.

324         The concentrations of PFASs obtained for the northern Spain landfill leachates  
325 fell in the low range of previously reported levels for leachates from municipal solid  
326 waste landfill sites in Europe, taking into account for the comparison the 16 PFASs  
327 studied in this work. In Europe, Busch et al. (2010) reported minimum concentrations of  
328  $\Sigma$ PFASs (16) of 146.1 ng/L in raw leachates from one landfill site in Germany and  
329 Perkola et al. (2013) reported 402.8 ng/L for Nordic leachates in Finland. Our results  
330 (average 1082 ng/L) are lower than the concentrations found by Eggen et al. (2010) in  
331 Norway (4157 ng/L) and by Woldegiorgis et al. (2006) in Sweden (26454 ng/L).  
332 Compared to PFASs contamination in leachates from Australia, our results are similar  
333 to the PFASs concentration detected by Gallen et al. (2016) in eight closed landfill sites  
334 (1365 ng/L). However, they are lower than the  $\Sigma$ PFASs (16) found by Gallen et al.  
335 (2016) in 6 operational sites in Australia (5254 ng/L), the  $\Sigma$ PFASs (16) reported in  
336 leachates from U.S. by Allred et al. (2016) in 6 landfill sites (6156 ng/L) or by Huset et

337 al. (2011) in four lined landfill sites in U.S. (2253-6157 ng/L). In the last case, landfill  
338 sites received biosolids from WWTP to be disposed of together with the domestic  
339 wastes, and in the study by Allred et al. (2014) some of the studied sites also accepted  
340 biosolids. However, the top range PFASs concentrations (based on 11 PFASs) reported  
341 in raw leachates was found in China, where the PFASs concentrations ranged from  
342 7280 ng/L to 292000 ng/L (Yan et al., 2015). This value was found in an active site in  
343 Shanghai, which is one of the most industrialized and urbanized regions in China. In  
344 fact, the PFASs contamination level at that landfill was even higher than the values  
345 from sites receiving industrial wastes (Yan et al., 2015).

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

354       The presence of PFASs in Spain has been reported in several type of samples,  
355 such as coastal and surface waters, sediments and sewage sludge (Gómez-Canela et al.,  
356 2011; Sánchez-Avila et al., 2010; Flores et al., 2013; Llorca et al., 2011; Gómez-Canela  
357 et al., 2012). Comparing the results presented in this study with the significantly lower  
358 reported PFASs levels in other type of samples in Spain allowed us to elucidate that  
359 landfill sites seem to be a critical environmental compartment in the life cycle of these  
360 pollutants.



#### 361 **4. Conclusions**

362 The occurrence and distribution pattern of PFASs (11 PFCAs and 5 PFSA) in landfill  
363 leachates from Spain was studied for the first time by collecting grab samples in 4  
364 different municipal solid waste landfill sites located across northern Spain. Both, raw  
365 and treated leachates were studied. Total  $\Sigma$ (PFCAs + PFSA) concentration ranged from  
366 639.2 ng/L to 1378.9 ng/L in raw leachates, while in treated samples total PFASs  
367 ranged from 856 ng/L to 3162.3 ng/L. PFCAs were most abundant than PFSA, and  
368 among them PFOA and PFHxA were the predominant compounds. All leachate samples  
369 had the common characteristic that shorter chain PFASs were greater in abundance than  
370 their respective longer chain homologues. The MBR treatment process was not effective  
371 to remove PFASs from the studied leachates. In one site, the total PFASs concentration  
372 in the MBR effluent was two-fold the concentration in the raw leachate, and a net  
373 generation of some PFCAs was observed. This could be explained by the persistence of  
374 PFCAs against biodegradation and to the probable biotransformation of precursor  
375 compounds such as fluoroalcohol and sulphonamides into PFCAs. The  
376 estimation of the 16  $\Sigma$ (PFCAs+PFSA) discharge rate due to the annual volume of  
377 leachate generated in the 4 studied landfill sites was 1209 g/year, or alternatively an  
378 average discharge rate of 672  $\mu\text{g}$  (PFCAs+PFSA)/year\*inhabitant. Further research  
379 should be carried out to study the presence of PFCAs precursors and the fate during  
380 each step of the leachate treatment process.

381

#### 382 **5. Acknowledgement**

383 The authors thank financial support from the Spanish Ministry of Economy and  
384 Competitiveness (Project CTM2013-44081-R).

385

386 **6. Appendix. Supplementary Material**

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

389

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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 <sup>3</sup> /year)	Status	Treatment process <sup>a</sup>	Leachate sample code	pH	Conductivity (mS/cm)	TOC <sup>c</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)	Cl <sup>-</sup> (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

<sup>a</sup> MBR: Membrane Bioreactor, UF: Ultrafiltration; <sup>c</sup> TOC: Total Organic Carbon

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

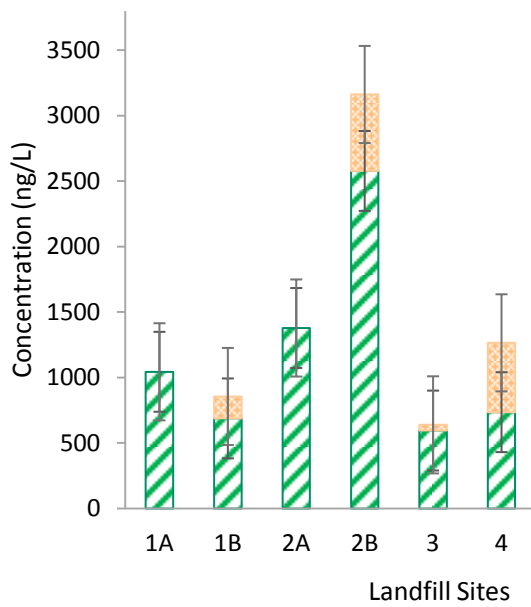
Region - Country		Concentrations in landfill leachates (ng/L)														Comments	Reference
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	$\Sigma$ PFASs		
North America	Canada (n=30)	120-660(327)	630-1800(980)	670-2500(1411)	240-690(439)	300-1500(649)	31-450(146)	40-1100(294)	<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 <sup>a</sup>
	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 <sup>a</sup>
	Canada (n=28)			695		439								279	27-21300(2950)	Average concentrations	Li et al., 2012 <sup>a</sup>
	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 <sup>b</sup> , C&D <sup>c</sup> and industrial wastes.	Huset et al., 2011 <sup>a</sup>
	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 <sup>b</sup> (since 1999)	Allred et al., 2014 <sup>a</sup>
	U.S. (site B1)	3500	1300	1700	1100	910	11	6.3	n.d	n.d	n.d	61	730	220	6038.3	MSW <sup>b</sup> (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 <sup>b</sup> (since 1999)	
	U.S. (site C)	3700	3200	8900	3100	5000	290	200	26	29	5.6	3200	1100	590	25640.6	MSW <sup>b</sup> (since 2009)	

Region - Country		Concentrations in landfill leachates (ng/L)														Comments	Reference
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	ΣPFASs		
	U.S. (site D)	800	1600	1300	460	150	12	9.8	n.d	n.d	n.d	310	64	39	3944.8	MSW <sup>b</sup> (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 <sup>b</sup> (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 <sup>a</sup>
	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 <sup>1</sup> 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 <sup>2</sup> 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 <sup>a</sup>
	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 <sup>a</sup>
	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 <sup>a</sup>
	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 <sup>a</sup>

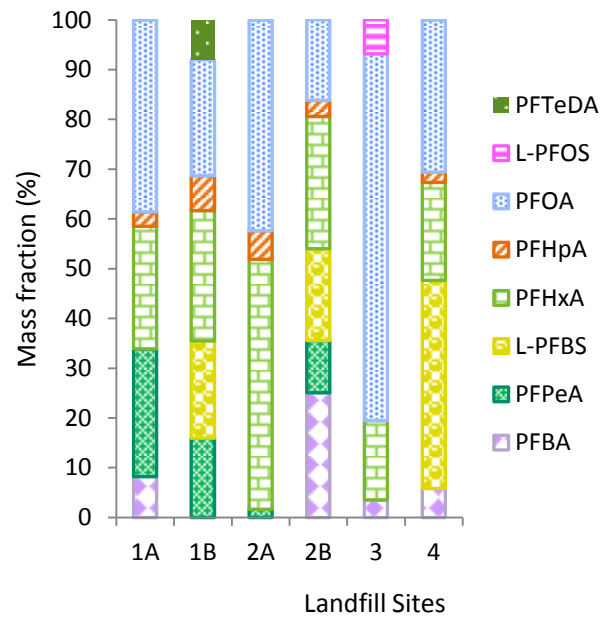
Region - Country	Concentrations in landfill leachates (ng/L)														Comments	Reference
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	ΣPFASs		
Finland (n=2)			49-200 (120)		76- 270(170)		2-3.7 (2.8)						87-140 (110)		Untreated leachates	Perkola et al., 2013
Estonia (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 <sup>a</sup>
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(120 0		506- 670(570)	214- 318(320)	1657- 2444(205 0.5)	<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	<LOD	856-3162 (2009)	MSW, treated leachate	

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

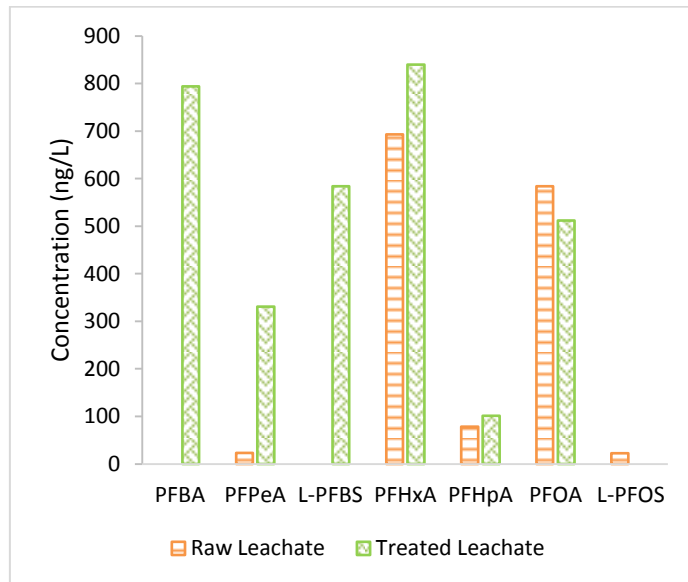
a)



b)





**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)



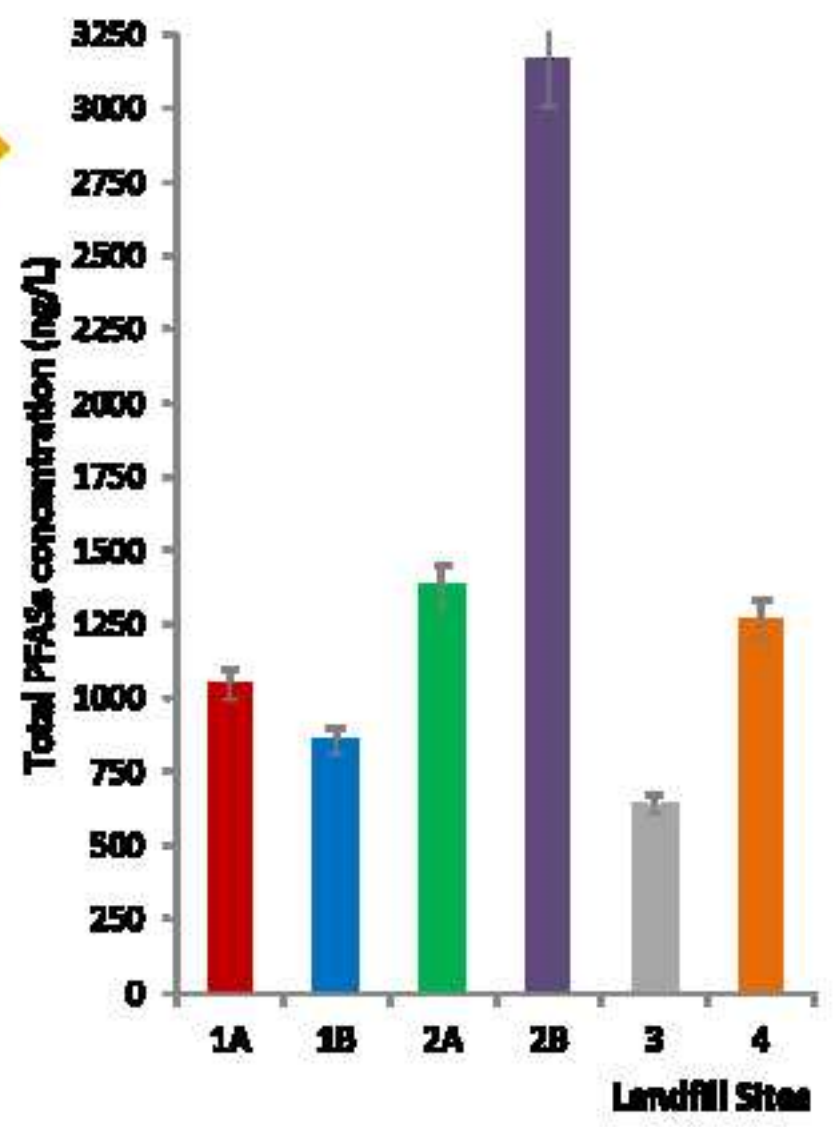
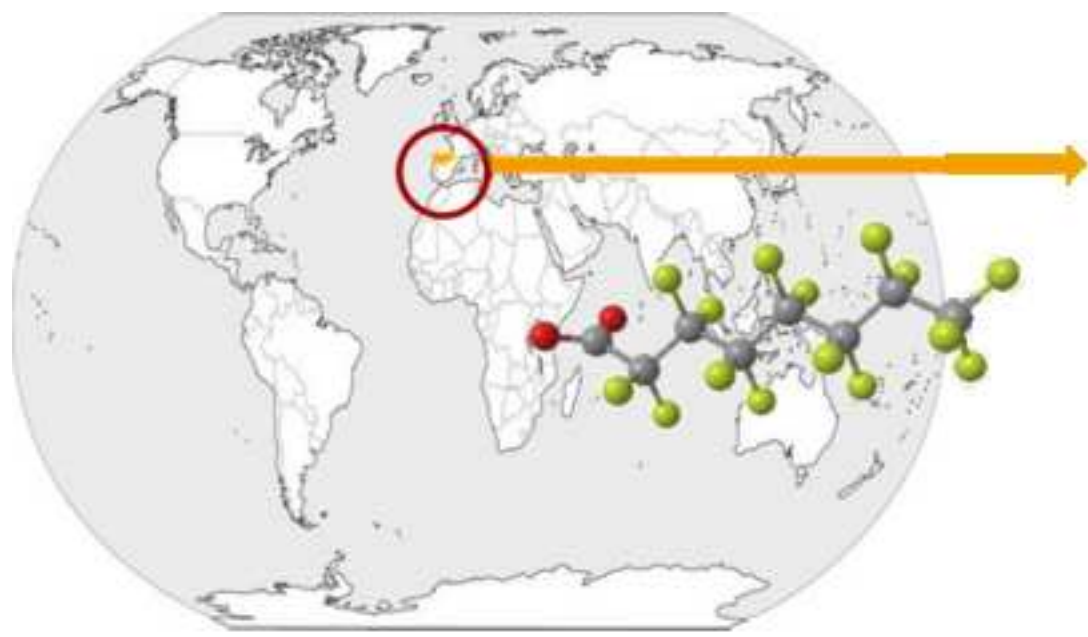
**Figure 2.** Individual PFASs concentrations before and after leachate treatment in site 2.



**Figure captions**

**Figure 1.**  PFCAs concentrations,  PFSA concentration and total concentration of PFASs as sum of PFCAs and PFSA (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.



## 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  $\mu$ L of PFC-MXA and PFS-MXA standards. Blanks consisted of Milli-Q water and the sample volume was 25 mL in all cases. Two different SPE cartridges were tested: Evolute WAX (weak anion exchange, 6cc, 200mg, 50 $\mu$ m) cartridges and Oasis HLB (6cc, 200mg, 30 $\mu$ m) 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 °C. 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

<b>Standard PFS-MXA</b>			
Compound	Acronym	Formula	Purity %
Potassium perfluoro-1-butanesulfonate	L-PFBS	C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> K	>98
Sodium perfluoro-1-hexanesulfonate	L-PFH <sub>x</sub> S	C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> Na	>98
Sodium perfluoro-1-heptanesulfonate	L-PFH <sub>p</sub> S	C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub> Na	>98
Sodium perfluoro-1-octanesulfonate	L-PFOS	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> Na	>98
Sodium perfluoro-1-Perfluoro-decanesulfonate	L-PFDS	C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> Na	>98
<b>Standard PFC-MXA</b>			
Compound	Acronym	Formula	Purity %
Perfluoro-n-butanoic acid	PFBA	C <sub>3</sub> F <sub>7</sub> COOH	>98
Perfluoro-n-pentanoic acid	PFPeA	C <sub>4</sub> F <sub>9</sub> COOH	>98
Perfluoro-n-hexanoic acid	PFH <sub>x</sub> A	C <sub>5</sub> F <sub>11</sub> COOH	>98
Perfluoro-n-heptanoic acid	PFH <sub>p</sub> A	C <sub>6</sub> F <sub>13</sub> COOH	>98
Perfluoro-n-octanoic acid	PFOA	C <sub>7</sub> F <sub>15</sub> COOH	>98
Perfluoro-n-nonanoic acid	PFNA	C <sub>8</sub> F <sub>17</sub> COOH	>98
Perfluoro-n-decanoic acid	PFDA	C <sub>9</sub> F <sub>19</sub> COOH	>98
Perfluoro-n-undecanoic acid	PFUdA	C <sub>10</sub> F <sub>21</sub> COOH	>98
Perfluoro-n-dodecanoic acid	PFDoA	C <sub>11</sub> F <sub>23</sub> COOH	>98
Perfluoro-n-tridecanoic acid	PFT <sub>r</sub> DA	C <sub>12</sub> F <sub>25</sub> COOH	>98
Perfluoro-n-tetradecanoic acid	PFT <sub>e</sub> DA	C <sub>13</sub> F <sub>27</sub> COOH	>98
<b>Internal Standard MPFAC-MXA</b>			
Compound	Acronym	Formula	Purity %
Perfluoro-n- [ <sup>13</sup> C <sub>4</sub> ] butanoic acid	MPFBA	[2,3,4- <sup>13</sup> C <sub>3</sub> ]F <sub>7</sub> <sup>13</sup> COOH	>98
Perfluoro-n- [1,2- <sup>13</sup> C <sub>2</sub> ] hexanoic acid	MPFH <sub>x</sub> A	C <sub>4</sub> F <sub>9</sub> [2- <sup>13</sup> C]F <sub>2</sub> <sup>13</sup> COOH	>98
Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ] octanoic acid	MPFOA	C <sub>4</sub> F <sub>9</sub> [2,3,4- <sup>13</sup> C <sub>3</sub> ]F <sub>6</sub> <sup>13</sup> COOH	>98
Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ] nonanoic acid	MPFNA	C <sub>4</sub> F <sub>9</sub> [2,3,4,5- <sup>13</sup> C <sub>5</sub> ]F <sub>8</sub> <sup>13</sup> COOH	>98
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ] decanoic acid	MPFDA	C <sub>8</sub> F <sub>17</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	>98
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ] undecanoic acid	MPFUdA	C <sub>9</sub> F <sub>19</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	>98
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ] dodecanoic acid	MPFDoA	C <sub>10</sub> F <sub>21</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	>98
Sodium perfluoro-1-hexane [ <sup>18</sup> O <sub>2</sub> ] sulfonate	MPFH <sub>x</sub> S	C <sub>6</sub> F <sub>13</sub> S[ <sup>18</sup> O <sub>2</sub> ]ONa	>94
Sodium perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ] octanesulfonate	MPFOS	C <sub>4</sub> F <sub>9</sub> [1,2,3,4- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> SO <sub>3</sub> Na	>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).

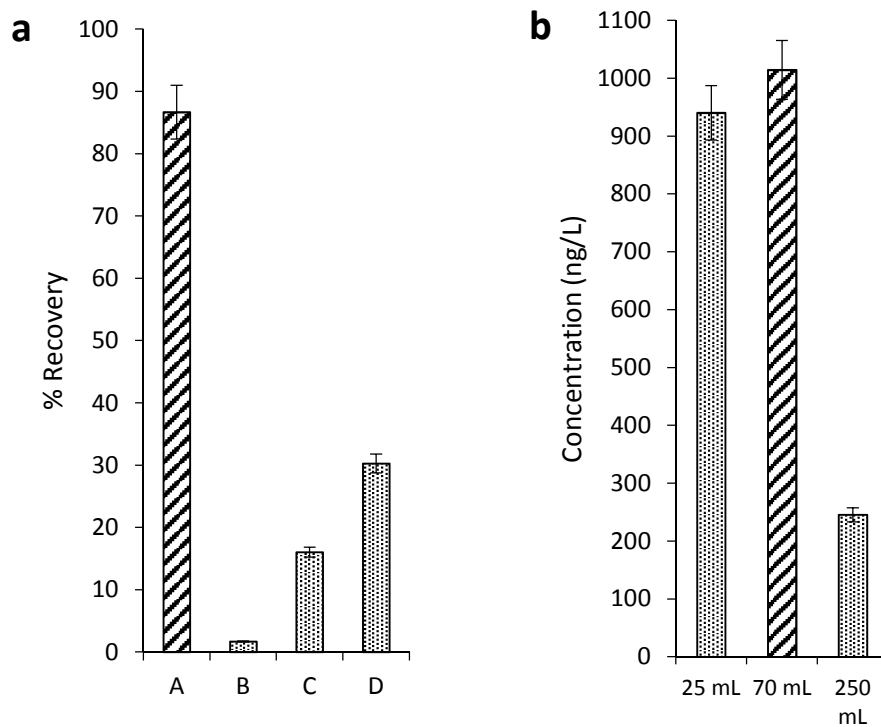
<b>Analytes</b>	<b>Precursor ion (m/z)</b>	<b>Product ion (m/z)</b>	<b>Fragmentor (V)</b>	<b>Collision energy (eV)</b>	<b>LOD (ng/L)</b>	<b>%RSD (n=5)</b>
<b>PFBA</b>	213	169	20	10	1.1	5.4
<b>PFPeA</b>	263	219	15	10	38.9	8.9
<b>PFHxA</b>	313	269/119	15	10/20	18.3	4.6
<b>PFHpA</b>	363	319/169	15	10/20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



**Table S3.** Concentration of individual PFASs, total PFASs, total PFCAs and total PFSAAs 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
PFTTrDA	<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
$\Sigma$ PFASs	1044.6	856.0	1378.9	3162.3	639.2	1265.8
$\Sigma$ PFCAs	1044.6	688.6	1378.9	2578.4	595.7	736.2
$\Sigma$ PFSAAs	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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