



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



I. Fuertes<sup>b,1</sup>, S. Gómez-Lavín<sup>a,1</sup>, M.P. Elizalde<sup>b</sup>, A. Urtiaga<sup>a,\*</sup>

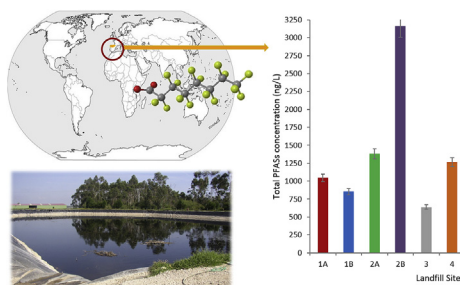
<sup>a</sup> Department of Chemical and Biomolecular Engineering, University of Cantabria, Av. De Los Castros s/n., 39005, Santander, Spain

<sup>b</sup> Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country, Apdo 644, 48080, Bilbao, Spain

## 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.
- Treatment by membrane bioreactors varied the PFASs profile and eventually to an increase of  $\sum$ PFASs compared to raw leachate.
- Estimated mass flow of 16  $\sum$ PFASs discharged was 1209 g/year, from landfill sites that serve a 1.8 million population.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 August 2016

Received in revised form

17 October 2016

Accepted 19 October 2016

Available online 28 October 2016

Handling Editor: I. Cousins

### Keywords:

Perfluoroalkyl substances (PFAS)

Landfill leachate

Perfluorooctanoic acid (PFOA)

Perfluoroalkyl carboxylates

Perfluoroalkyl sulfonates

## 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 (PFASs) 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 ( $\sum$ PFASs) in raw leachates reached 1378.9 ng/L, while in treated samples  $\sum$ 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  $\sum$ PFASs contained in the landfill leachates was estimated as 1209 g/year.

© 2016 Elsevier Ltd. All rights reserved.

\* Corresponding author.

E-mail address: [urtiaga@unican.es](mailto:urtiaga@unican.es) (A. Urtiaga).

<sup>1</sup> Both authors contributed equally to the manuscript.

## 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). Perfluorooctane 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., 2012a,b; Li et al., 2012; Gewurtz et al., 2013; Allred et al., 2014; Clarke et al., 2015), Europe (Woldegiorgis et al., 2006; Kallenborn et al., 2004; Eggen et al., 2010; Busch et al., 2010; Perkola and Sainio, 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<sub>4</sub>–C<sub>8</sub> 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., 2012a,b; 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; 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 (6 cc, 200 mg, 50 µm) solid phase extraction (SPE) cartridges were purchased from Biotage and Oasis HLB (6 cc, 200 mg, 30 µm) SPE cartridges were acquired from Waters (Milford, MA, USA). Bulk ENVI-Carb sorbent (100 m<sup>2</sup>/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.

Download English Version:

<https://daneshyari.com/en/article/5746596>

Download Persian Version:

<https://daneshyari.com/article/5746596>

[Daneshyari.com](https://daneshyari.com)