



## Determination of Perfluoroalkyl Substances in Municipal Landfill Leachates from Beijing, China

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Perfluoroalkyl substances (PFASs) that accumulate in landfills are a potential source of PFASs *via* leaching into the surface or groundwater environment. In the study, 10 PFASs, including PFHxA, PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFOS were determined in untreated and treated landfill leachates at three landfill sites in Beijing, China. The results showed that PFHxA, PFHpA, PFOA and PFOS were detected in untreated leachates of three landfill sites. The PFASs in treated leachates depended on the different treatment systems. In the full scale treatment, after the biological treatment and reverse osmosis processing, the leachate showed the lowest concentrations and highest removal efficiencies of PFHxA, PFHpA, PFOA and PFOS, followed by landfill leachate after the treatment using biological treatment, microfiltration and activated carbon. The leachate only treated by biological treatment had the highest concentrations and lowest removal efficiencies of PFASs. The ratio of PFHxA, PFHpA and PFOA concentration of leachate to Beijing tap water was 53.4, 4.5 and 132, respectively. The results indicate that municipal landfill leachate is the potential source pollution of PFASs.

**Keywords:** Landfill leachate, Perfluoroalkyl substances, Perfluorooctanoate, perfluorooctane sulfonate.

### INTRODUCTION

Perfluoroalkyl substances (PFASs) have been widely used in industrial and commercial applications for several decades as surfactants, emulsifiers, fire retardants and polymer additives. They are highly stable, bio-accumulative and resistant to degradation in the environment<sup>1,2</sup>. Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are the most commonly used and most often found PFASs in the environment<sup>3</sup>. The maximum solubility of PFOA, PFOS is 3400 mg/L and 570 mg/L in water<sup>4</sup>. According to the literature, these compounds have been detected in wastewater, surface water, groundwater and even tap water throughout the world<sup>5,6</sup>. Because of their global distribution, environmental persistence, bioaccumulation and toxicity, PFOA and PFOS have increasingly attracted global attention<sup>7,8</sup>. In 2009, PFOS was added to the persistent organic pollutants (POPs) list of the Stockholm convention.

Few studies document the association of PFASs with municipal solid wastes, in part, because of difficulties in handling such heterogeneous material. Municipal solid wastes in landfills are subject to chemical reactions and degradation processes that may result in PFOA and PFOS containing in leachates<sup>9</sup>. To date, data for up to only 12 PFASs in leachate are available<sup>10,11</sup>. Therefore, more investigation and systemic data are still required for better understanding of PFASs pollution in leachates.

The objective of this study is to investigate the occurrence of PFASs, including PFHxA, PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFOS, in untreated and treated landfill leachate from three landfill sites in Beijing, China. Special attention is focused on the influence of different treated methods in full scale treatment in relation to the concentration level and contribution of individual PFASs. Further, a comparison of PFASs concentrations in untreated and treated leachates is established.

### EXPERIMENTAL

Perfluorohexanoic acid (PFHxA,  $\geq 98\%$ ), perfluorohexane sulfonate (PFHxS,  $\geq 98\%$ ), perfluoroheptanoic acid (PFHpA, 96%), perfluorooctanoic acid (PFOA, 95%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 96%), perfluoroundecanoic acid (PFUnDA, 96%), perfluorododecanoic acid (PFDoDA, 96%), perfluorotridecanoic acid (PFTrDA, 96%) and perfluorooctane sulfonate (PFOS,  $\geq 98\%$ ) were obtained from Alfa Aesar Co., Ltd. The internal standard substance <sup>13</sup>C<sub>4</sub>-PFOS (MPFOS,  $\geq 98\%$ ) and <sup>13</sup>C<sub>4</sub>-PFOA (MPFOA,  $\geq 98\%$ ) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All standards and stock solutions were prepared in methanol (Fisher Scientific, Pittsburgh, PA, USA) and stored in polypropylene (PP) tubes or vials at 4 °C.

Methanol (HPLC grade) was obtained from Fisher Scientific (U.S.A). Ammonium acetate (97 %) and ammonium hydroxide (analytical grade; v/v, 50 %) were purchased from Alfa Aesar (Ward Hill, MA, USA). Sodium hydroxide (super grade, > 98 %) and acetic acid (analytical grade,  $\geq 99.5$  %) were obtained from Beijing Chemical Reagent Factory (China). Pure water was produced by a Milli-Q Advantage A10 system (Millipore, Billerica, MA, USA).

**Leachate samples:** All untreated and treated landfill leachate samples were collected during April 2013 and stored in high-density polyethylene bottles. Sample bottles were kept on ice and brought to the laboratory within 4 h collection. All leachate samples were stored at 4 °C and were extracted within 4 weeks of sampling. The leachate samples were taken from three municipal landfill sites in Beijing, China. A description of the landfill sites including volume of leachate, the cleaning treatment process of leachate and status of the landfill sites are presented in Table-1.

**Sample preparations:** Fluoropolymer materials were avoided throughout the analysis, including Teflon bottles and Teflon-lined caps. The extraction of leachate samples was performed using solid-phase extraction (SPE) as described by Taniyasu *et al.*<sup>12</sup>, with modifications. Briefly, 0.5 L filtered leachate samples were extracted using 500 mg hydrophilic-lipophilic balance (500 mg, 6 cc HLB) cartridges (Waters, USA). The HLB extracts in 4 mL methanol were diluted with 6 mL dichloromethane and applied to Sep-Pak plus silica cartridges (1 g, waters). The silica cartridges were preconditioned with 5 mL dichloromethane/methanol (60:40 v/v). The diluted extracts were loaded onto the silica cartridges and collected into a polypropylene tube. The extract was evaporated to dryness under a gentle nitrogen stream and reconstituted in 0.5 mL methanol/aqueous ammonium hydroxide (0.01 %) solution (70:30 v/v). The leachate extracts were filtered by a 0.2  $\mu\text{m}$  nylon syringe filter to remove fine particles and then stored at -20 °C until analysis.

**Chemical analysis:** The identification of the PFASs in the leachate samples was accomplished with a high performance liquid chromatograph with an electrospray ionization tandem mass spectrometer (HPLC-ESI/MS/MS) operated in negative mode. Separation was achieved on a dionex acclaim 120 C18 column (4.6 mm i.d.  $\times$  150 mm length, 5  $\mu\text{m}$ ; Dionex, Sunnyvale, CA, USA) with an injection volume of 10  $\mu\text{L}$ . A 10 min dualistic gradient at a flow rate of 1 mL/min was adopted which began with 28 % 50 mM  $\text{NH}_4\text{OAc}$ . The  $\text{NH}_4\text{OAc}$  was reduced to 5 % at 4 min before returning to 28 % at 7 min. The quantitative analyses were conducted using ESI/MS/MS (API 3200; Applied Biosystems/MDS SCIEX US).

**Quality assurance and quality control:** Polytetrafluoroethylene (PTFE) materials were removed from the equipment, or replaced with stain steel or PEEK vessels. Polypropylene

(PP) or glass tubes and containers were rinsed with methanol and water before use.

MillQ water samples (0.02 L, n = 10) were spiked with 1 ng target standards, then treated following the same procedures as the leachate samples. The PFASs were extracted with recoveries of between 95 and 128 %. The results indicated the SPE extraction is sufficient to support quantitative extraction. Duplicate matrix spikes were prepared for leachate samples. The leachate samples (0.5 L, n = 10) were spiked with 2 ng target standards, left for 0.5 h and passed through the extraction procedure. The recoveries were in the range of 77 and 126 %, which indicated sufficient reproducibility.

The linearity was evaluated using eight different concentrations covering a range of 50-20,000 ng/L. Each concentration was spiked with 5 ng of  $^{13}\text{C}_4$ -PFOS as the internal standard. Analysis and quantification were performed using analyst 1.4.1 software (API 3200; applied biosystems/MDS SCIEX, US). Standard curves were prepared using a quadratic "1/x<sup>2</sup>" weighted regression. The calibrations showed strong linearity with correlation coefficients > 0.99. The limits of detection (LODs) were determined on the basis of a signal-to-noise ratio of 3 (S/N = 3) or greater, which were 0.15 ng/g for PFHxA, PFHxS and PFOS, 0.5 ng/g for PFHpA, PFOA and PFNA, 0.7 ng/g for PFUnDA and PFDoDA and 1 ng/g for PFDA and PFTA, respectively. The lowest concentrations of the standard calibration were repeatedly injected and the peak areas showed good reproducibility with the relative standard deviation (RSD) below 11 % (n = 7). The eight-point standard calibration was conducted before and after each analysis. PFASs of 1  $\mu\text{g/L}$  were injected during the analysis for calibration verification and to ensure the sensitivity stability.

Blanks were prepared using Milipore water together with leachate samples and tap water samples. The blank value for PFOA analyzed together with landfill leachate was 10 ng/L, while PFOA blank value was not detected when analyzed together with tap water. Other PFASs blank values were not detected when analyzed together with landfill leachate and tap water. The concentrations of the samples were corrected by the blank concentration.

SPSS 13 software was used for statistical analysis. Concentrations below LOD were assigned as  $\text{LOD}/\sqrt{2}$  during the calculations. A Pearson correlation analysis was used to examine possible correlations among various PFASs in samples and that between PFASs concentrations with other parameters such as different site and age of landfill. The Kolmogorov-Smirnov test (one-sample K-S test) was conducted to test the normality of the data set.

## RESULTS AND DISCUSSION

The measured PFAS concentrations in untreated leachate samples are shown in Table-2. As shown in Table-2, PFHxA,

TABLE-1  
CLEANING TREATMENT PROCESS OF LEACHATE AND STATUS

Landfill site	Volume of leachate (m <sup>3</sup> /d)	Treatment process*	Status	Sample of leachate (Sample number)
Site 1	500	BIO	active	treated (1) and untreated (1)
Site 2	200	BIO, RO	inactive, closed 2009	treated (1) and untreated (1)
Site 3	50	BIO, MF, AC	active	treated (1) and untreated (1)

\*BIO = biological treatment, RO = reverse osmosis, MF = microfiltration, AC = activated carbon. In site 2, the landfill is inactive

TABLE-2  
PFAS CONCENTRATIONS IN UNTREATED LEACHATE SAMPLES\* (ng/L)

PFASs	Landfill site					
	Site 1		Site 2		Site 3	
	Mean	Concentration range	Mean	Concentration range	Mean	Concentration range
PFHxA	2156	1906-2830	1658	1355-1984	1054	876-1260
PFHpA	875	726-1025	633	521-930	528	408-873
PFOA	3742	2560-4658	2489	1886-3145	1652	1211-2312
PFNA	nd	nd	nd	nd	nd	nd
PFDA	nd	nd	nd	nd	nd	nd
PFUdA	nd	nd	nd	nd	nd	nd
PFDoA	nd	nd	nd	nd	nd	nd
PFTTrA	nd	nd	nd	nd	nd	nd
PFHxS	nd	nd	nd	nd	nd	nd
PFOS	56	38-76	< 15	< 15	39	20-54

\*Number of samples analyzed: 4. Because of the relatively constant emission, the leachate samples were collected 4 times within 24 h and were well mixed with equal volume. "nd = not detected"

PFHpA, PFOA and PFOS were detected in leachate of all three landfill sites. The mean concentration of PFOA in leachate was higher than PFHxA, PFHpA and PFOS, while PFOS was the lowest amongst all PFASs. PFHxA, PFHpA and PFOA were the dominant PFAS contaminants in all three landfill sites. PFNA, PFDA, PFUdA, PFDoA and PFHxS were not detected in any of untreated leachates collected from the landfill sites.

**PFASs in treated leachate:** After different cleaning processes, PFHxA, PFHpA, PFOA and PFOS were detected in all three landfill sites (mean value, the number of samples analyzed was 4). A comparison of individual PFAS concentrations in treated leachates using different treatment systems is shown in Fig. 1. Table-3 summarizes PFAS removal efficiencies both in untreated and treated leachates.

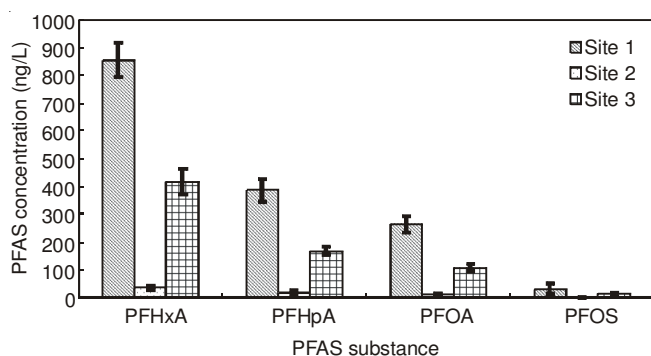


Fig. 1. PFAS concentrations in treated leachates of three different landfill sites. Site 1 treated by biological treatment, site 2 treated by biological treatment and reverse osmosis, site 3 treated by biological treatment, microfiltration and activated carbon

As shown in Fig. 1 and Table-3, effluent samples from site 2 landfill, after the treatment process of biological treatment and reverse osmosis, had the lowest concentrations and highest removal efficiencies of PFHxA, PFHpA, PFOA and PFOS, followed by site 3 landfill after the treatment process of biological treatment, microfiltration and activated carbon. Site 1 landfill leachate was only treated by the biological treatment process and had the highest concentrations and lowest removal efficiencies of PFASs. The explanation for this observation is possibly the different efficiencies of the treatment systems to remove PFASs from the leachate. Microfiltration, activated carbon and reverse osmosis are all advanced treatment methods

used after biological treatment. Reverse osmosis is a membrane-based treatment that uses semi-permeable membranes, which separate the leachate into a clean permeate and a contaminated residue. Microfiltration is a membrane filtration process that removes contaminants from leachate by passage through a microporous filter. activated carbon treatment is based on adsorption of contaminants to carbon and had been reported as a possible cleaning technique for removing PFAS from leachate.

It was previously reported that the PFAS concentrations in leachate ranged from a few ng to hundreds of ng per liter<sup>13,10,11</sup>. Generally, the concentration levels in this study are in a similar range as that reported in former studies<sup>11</sup>. Differences in concentration can be explained by different leachate water quality and treatment processes on landfills in different countries.

**Contrast of PFASs in leachate and tap water:** The PFASs in Beijing tap water were detected simultaneously in this study. PFHxA, PFHpA and PFOA were detected in the tap water at concentrations of 16 ng/L, 86 ng/L and 2 ng/L, respectively (mean value, the number of samples analyzed was 2). Compared with landfill leachate from site 1, the ratio of PFHxA, PFHpA and PFOA concentration of leachate and tap water is shown in Fig. 2.

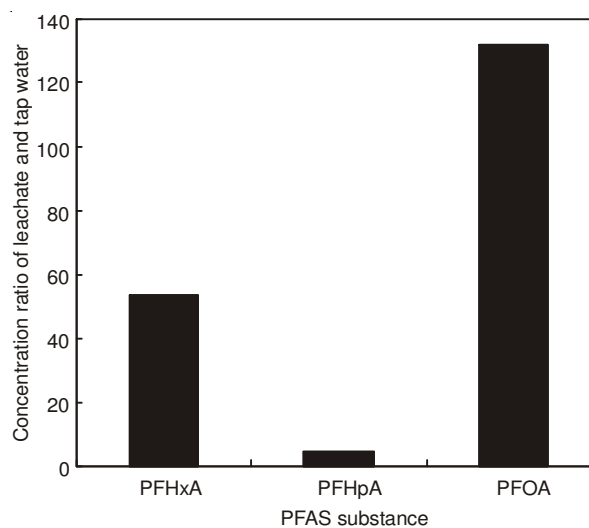


Fig. 2. Ratio of PFHxA, PFHpA and PFOA concentration of leachate and tap water

TABLE-3  
PFAS REMOVAL EFFICIENCIES BOTH IN UNTREATED AND TREATED LEACHATES

Landfill site	Site 1			Site 2			Site 3		
	Untreated leachates (ng/L)	Treated leachates (ng/L)	Removal efficiencies (%)	Untreated leachates (ng/L)	Treated leachates (ng/L)	Removal efficiencies (%)	Untreated leachates (ng/L)	Treated leachates (ng/L)	Removal efficiencies (%)
PFHxA	1906-2830	793-917	58.5-69.0	1355-1984	28-44	96.6-97.3	876-1260	372-464	60.5-63.0
PFHpA	726-1025	343-429	43.3-55.4	521-930	14-24	91.7-95.5	408-873	154-180	56.5-77.6
PFOA	2560-4658	232-294	89.5-93.2	1886-3145	8-16	99.2-99.4	1211-2312	93-123	89.8-94.1
PFOS	38-76	15-49	46.8-62.5	< 15	< 15	/	20-54	9-19	53.7-62.9

The ratios of PFHxA, PFHpA and PFOA concentration of leachate to tap water were 53.4, 4.5 and 132, respectively. Overall this indicates substantially higher levels of PFAS in the leachate, a potential source of PFASs which should be harm to humans and the wildlife. Although there are no concentration limits of PFASs in environmental quality standards or emission standards in China, the PFASs in the landfill leachate should be treated to prevent pollution of surface water and the groundwater environment.

### Conclusion

The PFASs, including PFHxA, PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA and PFOS were determined in untreated and treated landfill leachates. In the untreated leachates, PFHxA, PFHpA, PFOA and PFOS were detected in each of the three landfill sites tested. The PFHxA concentration in leachate varied between 876 and 2830 ng/L, the PFHpA concentration was 408-1025 ng/L and the PFOA concentration was 1211-4658 ng/L. The PFOS concentrations at landfill sites 1 and 3 were between 38-76 and 20-54 ng/L, respectively. PFHxA, PFHpA and PFOA were the dominant PFAS contaminants in the three landfill site leachates.

In the full scale treatment, after the biological treatment and reverse osmosis processing, the leachate showed the lowest concentrations and highest removal efficiencies of PFHxA, PFHpA, PFOA and PFOS, followed by landfill leachate after the treatment using biological treatment, microfiltration and activated carbon. The leachate only treated by biological treatment had the highest concentrations and lowest removal efficiencies of PFASs. The ratio of PFHxA, PFHpA and PFOA concentration of leachate to Beijing tap water was 53.4, 4.5 and 132, respectively. The results indicate that municipal landfill leachate is the potential source pollution of PFASs.

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