

INVESTIGATION OF PERFLUORINATED COMPOUNDS IN FINAL LANDFILL SITE

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Abstract

In this study, to investigate behavior of Perfluorinated compounds (PFCs) in the final landfill site and the leachate treatment plant (LTP), we measured PFCs concentration of the waste and the monitoring well water samples in the final landfill site and the effluent samples from each treatment process. Target compounds were perfluorinated carboxylic acids (C4-C14, PFCAs) and perfluorinated alkyl sulfonates (C4, C6, C8, C10, PFASs). The analysis was conducted using LC/MS/MS with negative electrospray ionization.

PFCAs (C4-C14) and PFAS (C4) were detected in the waste samples, and PFOA was dominant compounds (26-28 µg/kg-wet). PFCAs (C4-C9, C12) and PFAS (C4) were detected in the well water samples, and PFBA was dominant compounds (2.5- 280 µg/L). PFCAs (C4-C9) and PFAS (C4) were detected in the effluent samples. These results indicate that long-chain PFCAs (C10-14) remain in the landfill. Additionally, the concentration levels of PFCs in LTP were decreased at the activated carbon treatment.

Introduction

PFCs such as perfluorinated octane sulfonate (PFOS) and perfluorinated octanoic acid (PFOA) have been found to be persistent, bioaccumulative, and entailing toxic properties¹. Furthermore, PFOA, PFOS and homologue compounds, PFCAs and PFASs, have been globally detected in human bloods^{2,3}, biota⁴, sea water⁵, and remote areas such as the Arctic⁶. PFCs pollution became recognized as a serious problem in the world, and, therefore, PFOS and perfluoro-1-octanesulfonyl Fluoride (PFOSF) were added as persistent organic pollutants (POPs)⁷.

PFCAs and PFASs are surfactants, and they are soluble in water and oil (aqueous solubility: PFOS 570mg/L, PFOA 3400mg/L). Hence, contamination of PFCAs and PFASs spread to the environment through the water easily. In many cases, occurrences of PFCs in the environment were originated from wastewater of factories or wastewater treatment plants (WWTP). Concentrations, behaviors, and variations of PFCs in WWTP were investigated⁸, and these results suggested that waste water effluent is a significant source of PFCs to the environment. On the other hand, highly concentrated PFCs were detected in leachate samples of final landfill sites^{9,10}. It was indicated that final landfill sites are one of the indirect sources of PFCs to the environment. However, behavior of PFCs in final landfill site, how PFCs flows out to the environment, was not clear. To assess potential sources and implement appropriate measures, investigating behavior of PFCs in final landfill site is needed.

In this study, to investigate behavior of PFCs in the final landfill site and the leachate treatment plant (LTP), we measured PFCs concentration of waste and well water samples in the final landfill site and effluent samples from each treatment process.

Material and method

Standards

Standard solution of PFCAs and PFASs mixture (PFAC-MXB) contained Perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA), Perfluorotridecanoic acid (PFTrDA), Perfluorotetradecanoic acid (PFTeDA), Perfluorobutane sulfonate (L-PFBS), Perfluorohexane sulfonate (L-PFHxS), Perfluorooctane sulfonate (L-PFOS), and Perfluorodecane sulfonate (L-PFDS) were purchased from Wellington laboratories. Standard solution of isotope-labelled PFCAs and PFASs mixture (MPFAC-MXA) contained Perfluoro-n-[¹³C₄]butanoic acid (MPFBA), Perfluoro-n-[1,2-¹³C₂]hexanoic acid (MPFHxA), Perfluoro-n-[1,2,3,4-¹³C₄]octanoic acid (MPFOA), Perfluoro-n-[1,2,3,4,5-¹³C₅]nonanoic acid, (MPFNA), Perfluoro-n-[1,2-¹³C₂]decanoic acid (MPFDA), Perfluoro-n-[1,2-¹³C₂]undecanoic acid (MPFUdA),

Perfluoro-n-[1,2-¹³C₂]dodecanoic acid (MPFDoDA), Sodium perfluoro-1-hexane[¹⁸O₂]sulfonate (MPFHxS), and Sodium perfluoro-1-[1,2,3,4-¹³C₄]octanesulfonate (MPFOS) were purchased from Wellington laboratories. The purity of the standard solutions was higher than 98%.

Sampling site and Sample collection

Sampling site in this study is sea reclamation type. The site is a controlled landfill type that has LTP.

The waste samples (muddy) in the final land fill site were collected from upper layer (approx. 3m below G.L.) and lower layer (approx. 7m below G.L.) in June, 2010, respectively.

The well water samples in the final land fill site were collected from the monitoring well of upper layer (approx. 5m below G.L.) middle layer (approx. 10m below G.L.), and lower layer (approx. 15m below G.L.), respectively.

The effluent samples in LTP were collected from each treatment process in November, 2010. The sampling points are showed in Fig.1.

All samples were collected and stored glass bottles. All samples were kept refrigerated at 4°C until analysis.

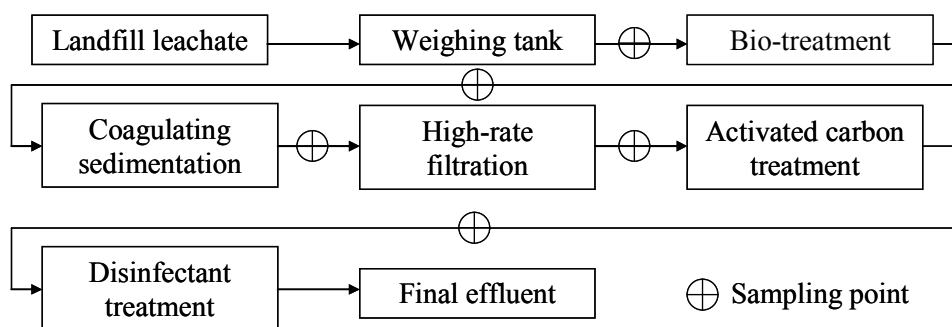


Fig.1 Leachate treatment process and sampling point

Sample preparation and analysis

The waste sample was centrifuged for 10min at 3000rpm. The residue was transferred to glass tube, and 20µL of MPFAC-MXA (each 100 ng/mL in methanol) as internal standard were added. After added 10mL of methanol, the sample was extracted by sonication for 10min. After centrifuged for 10min at 3000rpm, the extraction was transferred to new glass tube. The extraction process was repeated three times. The combined extraction was concentrated under gentle nitrogen stream to 5mL. After this, the concentrated solution was diluted to 100mL of distilled water, and 10 µL of formic acid was added. The solution was extracted with Solid Phase Extraction (PFC II, Wako Pure Chemical Industries). After the analyte-loaded, the cartridge was eluted 5mL of 0.1% ammonium/methanol. The eluted solution was concentrated under gentle nitrogen stream to 1mL.

The water and effluent sample were spiked with 20µL of MPFAC-MXA (each 100 ng/mL in methanol), as internal standard, and then 10µL of 10% formic acid in distilled water were added. The sample was extracted with SPE (PFC II, Wako Pure Chemical Industries). The following operation was conducted in the same method of the waste sample.

The each final solution was analyzed by liquid chromatography (LC)-tandem mass spectrometer (MS/MS) using Xevo TQ (Waters) coupled with ACQUITY UPLC (Waters). Analysis was conducted using negative electrospray ionization with multiple reaction monitoring. 10mM ammonium acetate and acetonitrile were used for LC mobile phase. Analytical column was ACQUITY UPLC BEH (C18, 2.1×50mm, 1.7µm, Waters). Separation of instrument blank was performed using a retention gap column (ACQUITY UPLC BEH (C18, 2.1×10mm, 1.7µm, Waters)).

Instrumental limits of detection (LODs) and limits of quantification (LOQs)

The instrumental limits of detection (LODs) were defined empirically as the concentration producing a signal to noise ratio of 3, and the limits of quantification were defined as the concentration producing a signal to noise ratio of 10. Preparation blanks of all analytes were not detected (<LOD).

Results and discussion

PFCs in waste, well water, and effluent samples

Table 1 shows the concentrations of PFCs in the waste, well water, and effluent samples. PFCAs (C4-C9) and L-PFBS were detected in all samples. Long-chain PFCAs (C10-C14) were detected in the waste samples. PFDoDA (<LOQ) was detected in the well water sample of middle layer. L-PFOS was detected in only the well water sample of middle layer. PFOA was dominant compound in the waste samples. The maximum concentration of PFOA in the waste samples was 28µg/kg-wet. In contrast, PFBA was dominant compound in the well water samples. The maximum concentration of PFBA in the well water samples was 280µg/L. The concentration patterns of PFCs were similar to the monitoring well water in the landfill. However, PFOA was dominant compound in the effluent samples except the activated carbon treatment effluent sample. The different was thought to be due to different sampling time, or different sampling location: LTP and the monitoring well are in a different place. Long -chain PFCAs (C10, C11, C13, C14) were not detected in the well water samples and effluent samples (Fig.2). These results indicate that long-chain PFCAs remain in the landfill.

PFCAs concentration of well water samples of middle layer were high compared with the other layer samples. This result indicates that the area in surrounding the monitoring well of middle layer was hot spot of waste contained high level PFCs.

Table 1 Concentration of PFCs in waste, well water, effluent sample

	Waste [µg/kg-wet]		Well water sample [µg/L]			Effluent sample [µg/L]				
	Upper layer	Middle layer	Upper layer	Middle layer	Lower layer	Weighing tank effluent	Bio-treatment effluent	Sedimentation effluent	Filtration effluent	Activated carbon treatment effluent
PFBA	2	1.9	7.2	280	2.5	3.1	2.7	2.5	2.7	2.4
PFPeA	1	1.1	2.2	220	1.7	1.9	1.5	1.4	1.5	1.7
PFHxA	1.7	1.9	2.6	140	1.1	2.1	2	1.9	2.1	1.6
PFHpA	0.89	1.5	0.71	23	0.58	0.69	0.56	0.58	0.65	0.37
PFOA	28	24	0.87	66	0.77	3.8	2.7	3.2	3.3	0.55
PFNA	2.1	3.6	0.52	0.69	0.12	0.09	0.037	0.043	0.044	0.0054
PFDA	2.1	4.4	ND	ND	ND	ND	ND	ND	ND	ND
PFUnDA	1	3.8	ND	ND	ND	ND	ND	ND	ND	ND
PFDoDA	0.72	5.3	ND	<0.6	ND	ND	ND	ND	ND	ND
PFTTrDA	0.68	3.4	ND	ND	ND	ND	ND	ND	ND	ND
PFTeDA	0.47	3.3	ND	ND	ND	ND	ND	ND	ND	ND
LOD of PFCA	0.1	0.1	0.01	0.2	0.01	0.01	0.01	0.01	0.01	0.001
LOQ of PFCA	0.3	0.3	0.03	0.6	0.03	0.03	0.03	0.03	0.03	0.005
L-PFBS	<0.5	<0.5	2.1	<1	0.54	0.66	0.61	0.4	0.64	0.27
L-FHxS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L-PFOS	ND	ND	ND	1.1	ND	ND	ND	ND	ND	ND
L-PFDS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
LOD of PFAS	0.2	0.2	0.02	0.4	0.02	0.02	0.02	0.02	0.02	0.002
LOQ of PFAS	0.5	0.5	0.05	1	0.05	0.05	0.05	0.05	0.05	0.005

ND: Not detection (<LOD)

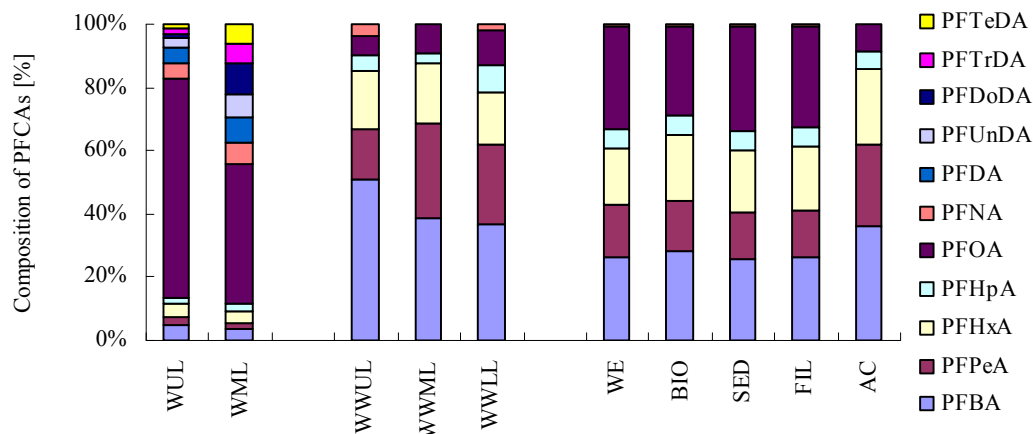


Fig.2 Composition of PFCAs in the samples; WUL = waste of upper layer, WML = waste of middle layer, WWUL = well water of upper layer, WWML = well water of middle layer, WWLL = well water of lower layer, WE = weighting tank effluent, BIO = bio-treatment effluent, SED = sedimentation effluent, FIL = filtration effluent, and AC = activated carbon treatment effluent.

Behavior of PFCs in LTP

The concentration levels of PFCs were decreased at the activated carbon treatment, and this result indicates that activated carbon treatment is effective for removal of PFCs in leachate. Other reserches^{10, 11} also had reported similar results. However, short-chain PFCAs was not removal at the activated carbon treatment process. The concentration of PFOA and PFNA decreased from the filtration effluent to the activated carbon treatment effluent by one digit, on the other hand, the concentration of PFBA, PFPeA, PFHxA, and PFHpA were not changed. Absorbability of activated carbon for short-chain PFCAs might be low.

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