EVALUATION OF PERFLUOROALKYL COMPOUNS IN KOREAN WASTEWATER TREATMENTS PLANTS

Rui Guo[1], Eung sun Lee[1], Ji-Hyun Lee[2], Won jin Sim[1], Jeong-Eun Oh[1*]

[1]Environmental Analysis Laboratory, Department of Environmental Engineering, Pusan National University, Pusan, Korea, [2]Korea Testing &Research Institute, Ulsan, Korea

Abstract

Recent studies have shown that the wastewater treatment plant (WWTP) is a significant source of perfluoroalkyl compounds (PFCs) in natural water. In this study, 11 PFCs were analyzed in influent and effluent wastewater and sludge samples in 15 municipal, 4 livestock and 3 industrial WWTPs in Korea. The observed distribution pattern of PFCs differed between the wastewater and sludge samples. Perfluorooctane sulfonate (PFOS) was dominant in the sludge samples, whereas perfluorooctanoic acid (PFOA) was dominant in wastewater. PCA and cluster analysis results provided an explanation for this variation in PFC distribution patterns in the aqueous and sludge samples. The perfluoroalkylsulfonate (PFAS) concentrations tended to decrease after treatment in most WWTPs, whereas the removal of perfluoroalkylcarboxylic acids (PFCAs) was insignificant during treatment.

Introduction

PFCs are man-made chemicals used as surfactants, polymers, plastic additives and in a variety of other applications. These compounds are environmental ubiquitous and have been detected in air, water and biota samples worldwide.[1-5]

Discharge of wastewater from municipal wastewater treatment plants (WWTPs) is recognized as one of the principal routes for the introduction of PFCs into aquatic environments and many studies have examined the distribution and the fate of PFCs during wastewater treatment processes.[6-9] However, limited data are available on the PFCs concentrations in various activated sludge processes and most of these studies investigated small numbers of WWTPs or analyzed only PFOS and PFOA. [10, 11]

In this study, we analyzed 11 PFCs in sludge, influent and effluent from various types of WWTP in Korea and evaluated the levels, distribution and fate of PFCs. Also, removal efficiency of PFCs during treatment was accessed and multivariate statistical analysis was performed to evaluate the relationship between the PFC concentrations and the sample types. To the best of our knowledge, this is the first study reporting PFC levels in Korean WWTPs.

Materials and Methods

All perfluorochemicals including PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFBS, PFHpS, PFOS, PFDS, perfluoro-n-[1,2,3,4-13C4]octanoic acid (MPFOA, internal standard), were purchased from Wellington Laboratories (Guelph, ON, Canada). All solvents and reagents were HPLC grade.

Standard addition method was used to compensate for sludge matrix interference. Sludge samples extraction and cleanup steps used herein were referred to that described earlier with a few modifications.[9] Wastewater samples were extracted as described before.[12]

A Micromass Quattro tandem LC/MS/MS system was used to analyze the extract. Confirmation of analyte identity was accomplished through multiple reaction monitoring and the optimized parameters were list in Table 1.

Quantitation for wastewater was performed using an internal standard calibration curve and seven calibration standards (0.1-10.0ng/mL) were prepared. The coefficient of determination (R^2) was greater than 0.99 and the deviation of every point from the standard was less than 20%.

Table 1 MS/MS parameters and ions monitored for PFCs

Compound	Primary ion (m/z)	Product ion (m/z)	Cone voltage (V)	Collision energy (eV)
PFBS	299	99	40	30
PFHpS	449	99	50	50
PFOS	499	99	55	55
PFDS	599	99	50	50
PFHxA	313	269	15	10
PFOA	413	369	15	10
PFNA	463	419	15	11
PFDA	513	469	20	10
PFUdA	563	519	20	11
PFDoA	613	569	20	14

Results and Discussion

1. PFCs in wastewater and sludge

No PFCs were detected in livestock wastewater and sludge samples, indicating that livestock WWTPs were not the source of PFCs to natural water bodies. PFOA was the dominant compounds and its concentrations ranged from 2.3 to 614.7ng/L and 3.4 to 590.9ng/L in influent and effluent, respectively. PFOS was the second dominant compound in the wastewater with levels of 0.89~39.9ng/L and 0.9~16.7ng/L in the influent and effluent, respectively. (shown in Figure 1A). In the influent wastewater, an even>odd carbon PFCA pair pattern was observed, in which PFHxA>PFHpA, PFOA>PFNA, PFDA>PFUdA, due to the PFCAs biodegradation from FTOH.

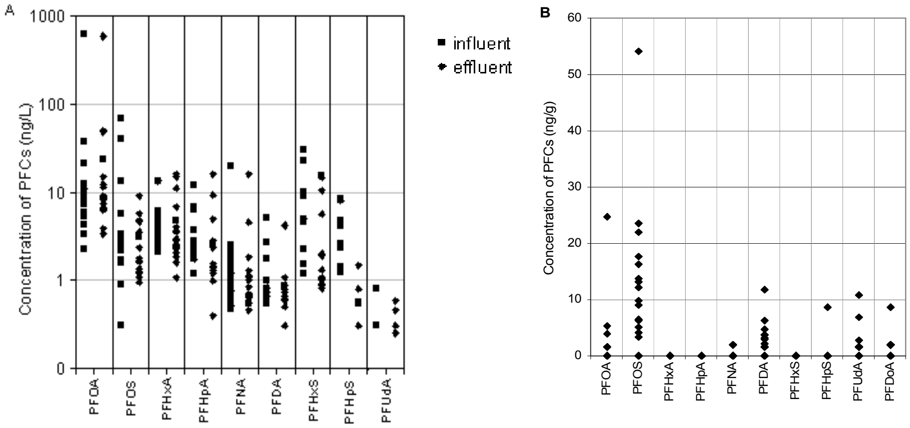

Figure 1 Concentration of PFCs in (A) wastewater and (B) sludge of WWTPs,

the y-axis of A in logarithmic scale

The highest concentration of PFOA (614.7ng/L) was detected in the influent of one of industrial wastewater treatment plant (I-WWTP), which treated mixed wastewater from pharmaceutical, paper and battery manufacturers. The other I-WWTPs that treated wastewater from pharmaceutical manufacturers only did not show high PFOA levels (8.9ng/L and 4.3ng/L for I-2 and I-3, respectively), indicating the high levels of PFOA were not due to pharmaceutical wastewater but rather to wastewater from paper or battery manufacturers. Relatively high concentrations of PFOA, PFOS, PFHxA, PFHpA, PFNA, and PFDA were determined in the influent of two WWTPs, treating mixture of domestic and industrial wastewater. Maybe industrial wastewater was the direct reason for the higher PFC concentration in the influent. The PFOS concentrations in influents from other STPs that treat 100% domestic sewage were low, suggesting that the domestic wastewater accounted for the low PFOS concentration compared to the industrial wastewater.

PFOS was the dominant PFCs in the sludge of all WWTPs, ranged from 3.3 to 54.1 ng/g dry weight (dw), followed by PFDA (<1.5 ~11.8ng/L) and PFUdA <(1.5-10.8ng/g) (Figure 1 B). PFOA was detected in 10 of 15 STP samples, with a concentration ranging from <1.5 to 5.3 ng/L, while PFDA and PFUdA were detected in 14 of 15 STPs. PFHxA, PFHpA and PFHxS were not detected in any of the sludge samples, and PFHpS was detected in only one sludge sample. Therefore, the PFCs levels in wastewater in Korea were not higher than those in foreign countries. The total concentrations of PFOA and PFNA in the influent were 7-200 times higher than those of PFDA and PFUdA, while PFDA and PFUdA concentrations in the sludge samples were 1-6 times higher than those of PFOA and PFNA. The results confirmed the preference of long-chain PFCAs to partition to sludge, which was consistent with the increased sediment-water partition coefficient with increased chain length.[13]

Yu et al. reported that the partition coefficient, i.e., the Kd value, of PFOS for primary sludge and activated sludge was 3 times higher than that of PFOA, resulting in a much greater amount of PFOS being adsorbed onto the sludge compared to PFOA. They also attributed the high variations in Kd value for PFOS and PFOA to the different retention time of aqueous and solid streams in primary and secondary clarifiers.[14]

For this reason, PFOS was dominant the PFCs in the sludge samples and much more PFOS was adsorbed onto the sludge than PFOA in this study.

2. Relationship between wastewater and sludge
The relationships among the concentrations of PFCs in sewage wastewater and sludge were investigated using PCA and cluster analysis.

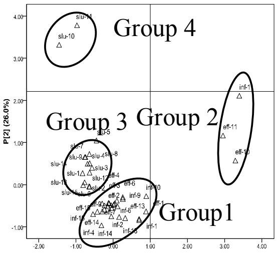

Figure 2 The relationships of concentration of PFCs in wastewater and sludge samples

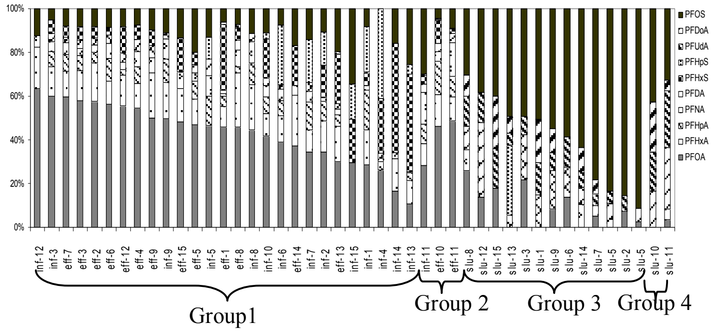

Figure 3 Composition percentages of PFCs in wastewater and sludge samples

Four different groups were observed (Figure 2). Group 1 comprised most of the influent and effluent samples (excluding inf-11, eff-10 and eff-11). Although the three wastewater samples in Group 2 had a similar distribution pattern to that of Group 1, they weren't clustered together with Group 1, as the total PFC concentrations were over 100ng/L in Group 2. Group 3 contained most of the sludge samples and only two sludge samples (slu-10 and slu-11) that treated a mixture of industrial and domestic wastewater together were grouped together as Group 4. Group 4 had high levels of PFUdA and PFDoA compared to the other sludge samples in Group 3.

The PFC compositions in each group are shown in Figure 3 with different distribution patterns being observed in each group. PFOA was dominant in wastewater and PFOS in sludge samples, indicating the different fates of these two PFCs in WWTPs, with PFOA being preferred in wastewater and PFOS in sludge.

The log Koc value (organic carbon-normalized distribution coefficient) seems to be one of the reasons for the distribution pattern and fates of PFOS and PFOA. Previous study also showed that the sulfonate moiety contributed an additional 0.23 log units to the measured distribution coefficient, compared to carboxylate analogs. Therefore, PFOS may partition on sludge in preference to PFOA, which generates the different dominant PFC pattern in sludge and wastewater samples.

3. Total removal efficiency

The fate of PFCs in the WWTPs was related with the functional groups. The concentration of PFHxS and PFHpS decreased by 34-68% and 43-100% respectively, and PFOS exhibited a positive removal efficiency of 44-78%, except for two cases that increased by 98-111%. For PFOA, the increased concentrations were generally observed after treatment, suggesting the presence of an additional PFOA source during the treatment. Other acids such as PFHxA, PFHpA, PFNA and PFDA showed either poor removal results or a wide range in this study. Overall, the removal efficiency of PFASs was higher than that of PFCAs, which is related with the higher log Koc values of PFASs than those of carboxylate analogs. Therefore, the PFASs removal by sorption on sludge is more preferable than that of PFCAs and resulted in better PFAS removal than that of PFCAs and dominant PFOS in the sludge samples.

Acknowledgments

This work is financially supported by Korea Ministry of Environment (MOE) as “Human resource development Project for Waste to Energy”.

Reference

1. Saito N., Harada K., Inoue K., Sasaki K., Yoshinaga T. and Koizumi A. J. *Occup. Health* 2004; 46: 49.
2. Olsen G. W., Church T. R., Larson E. B., van Belle G., Lundberg J. K., Hansen K. J., Burris J. M., Mandel J. H. and Zobel L. R. *Chemosphere* 2004;54: 1599.
3. Boulanger B., Vargo J., Schnoor J. L. and Hornbuckle K. C. *Environ. Sci. Technol*. 2004; 38: 4064.
4. Saito N., Sasaki K., Nakatome K., Harada K., Yoshinaga T. and Koizumi A. *Environ. Contam. Toxicol*. 2003; 45: 149.
5. 3M, 2001. US. EPA Administrative Record AR226-1030a111.
6. Boulanger B., Vargo J.D., Schnoor J.L. and Hornbuckle K.C. *Environ. Sci. Technol*. 2005; 39: 5524.
7. Schultz M.M., Barofsky D.F. and Field,J.A. *Environ. Sci. Technol*. 2006; 40: 289.
8. Sinclair E. and Kannan K. *Environ. Sci. Technol*. 2006; 40: 1408.
9. Higgins C. P., Field J. A., Criddle C.S. and Luthy R. G. *Environ. Sci. Technol*. 2005; 39: 3946.
10. Bossi R., Strand J., Sortkjær O.and Larsen M.M. *Environ. Int*. 2008; 34; 443.
11. Becker A.M., Gerstmann S. and Frank H. *Chemosphere* 2008; 72: 115.
12. Murakami M., Shinobara H., Takada H., *Chemosphere* 2009; 74:487
13. Schultz M.M., Heggins C.P., Huset C.A., Luthy R.G., Barofsky D.F.and Field, J.A., *Environ. Sci. Technol*. 2006; 40: 7350.
14. Yu J., Hu J.Y., Tanaka S., Fujii S., *Water Research*, article in press.