INFLUX AND EFFLUX OF PERFLUORINATED COMPOUNDS (PFCs) IN THE WASTEWATER TREATMENT PLANTS IN KOREA

Song G-J[1*], Song K-B[2], Seok K-S [2],Moon Y-H[1], Joo J-H[1], Lee A-Y[1]

[1] Institute of Environmental and Energy Technology, POSTECH, Pohang, Kyoung-buk, South Korea; [2] National Institute of Environmental Research, Incheon, South Korea

Introduction

The perfluorooctanesulfonate (PFOS) and its salts were listed in Annex B of the Stockholm Convention of POPs in 2008 and their use is restrictednow. PFCs have properties of persistent organic pollutants (POPs): persistent, bioaccumulation and long range transport. Therefore, the perfluorinated compounds (PFCs) are now recognized as an important emerging pollutant.PFCs have been produced and used in the worldwide as consumer products for the past five decades but since 2000, their manufacturing and use have been reduced and restricted due to their toxicity of PFCs. PFCs have very high solubility in water and high absorbability in soil or sediment/sludge with high content of organic carbon. Due to the chemical and physical properties such as the high solubility in water and high absorbability in soil or sediment/sludge with high content of organic carbon, PFCsare normally detected in the domesticand/or industrial wastewater. Nowadays, the wastewater treatment plants have no any process to reduce or remove PFCs, because PFCs emitted from wastewater treatment plants are not regulated by law in Korea.Therefore, to estimate the influx and efflux ofPFCs in wastewater treatment plantsthe PFCs in influent and effluent were investigated in the 25 domestic and 15 industrial wastewater treatment plants.

Materials and methods

(1) Plant

There are 2,770 public domestic wastewatertreatment plants (DWTPs)and 46,860 industrial wastewater treatment plants (IWTPs)in Korea.Most of thedomestic wastewater is treated in plants with a capacity of over 500m^3/day (about 85%). Therefore, for investigation the plants with capacity above 500m^3/day were selected and separated according to the amount of industrial wastewater (below 60%) flowing public domestic wastewater treatment plant. The industrial wastewater treatment plants are classified into 5 groups based on the treatment capacity with over 2,000m^3/day (class 1), 700-2,000m^3/day (class 2), 200-700m^3/day (class 3), 50-200m^3/day (class 4) and below 50m^3/day (class 5). Although there are more plants of class 4-5 than those of class 1-3, most industrial wastewater (over 80%) is treated in class 1-3 plants. Therefore, for investigation the plants of classes 1-3 were selected and classified industry.The classified industries were the paper and pulp manufacturing industry, the electricity and electronic industry, the chemical products manufacturing industry and metal products manufacturing industry. And also the 5 industrial wastewater treatment plants that treat various types of industrial wastewater from large industrial complex were investigated.

(2) Target compounds and samples

The target compounds were 8 PFCAs(perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid and perfluorotridecanoic acid) and 3 PFASs (perfluorohexane sulfonate, perfluorooctane sulfonate and perfluorodecane sulfonate). The samples were first influent and final effluent in a plant.

(3) Sample collection and analysis

The sampling and analysis were based on the Korean Standard Testing Methods (KSTM) for PFCs (ES 10394.1). ES 10394.1 is the KSTM for PFCs in influent sewage/wastewater or effluent sewage/wastewater of treatment plants using LC/MS/MS. Asample bottle with polypropylene (PP) was used and the sample was collected 3 times in a day. The samples kept in a freezer and analyzed in a week after sampling.PFCs in samples were extracted with the solid phase extraction (SPE) and the isotopes of PFCs as internal standard were used to analyze 11 target compounds. The analyzer was LC/MS/MS with electro-spray ionization (ESI) and multiple-reaction monitoring (MRM).

Results and discussion

(1) Influx and efflux of PFCs in the domestic wastewater treatment plants (DWTPs)

The total concentrations of PFCs (11 target compounds) in the influent and the influx of PFCs were 4.8-502.8 ng/L (85.0 ng/L) and 0.196-107.665 g/day ($15.371_{avg.}$ g/day), respectively. The influx of PFCs showed large differenceaccording to the plant. Usually, the influx of PFCs in the plant with a high inflow rate of industrial wastewater was high. However, some plants showed the high influx of PFCs although the inflow rate of industrial wastewater was zero or very low. Those plants were located in the capital or metropolitan areas. Among the 11 target compounds the influx of PFOA and PFOS was 5.5-73.4% ($35.1_{avg.}$%) and 3.7-89.2% ($38.2_{avg.}$%), respectively. Although the influx of PFOA and PFOS was significantly varied according to the plant, the total influx of PFOA and PFOS in many plants showed over 50%. The total concentrations of PFCs (11 target compounds) in the effluent and the efflux of PFCs were 6.3-484.0 ng/L (72.5 ng/L) and 0.131-95.985 g/day ($11.963_{avg.}$ g/day), respectively. The efflux of PFCs showed also varied according to the plant. The efflux was influenced not always by influx. In many plants the efflux was higher than influx, and the distribution of 11 target compounds in influx and efflux was very different. Among the 11 target compounds the efflux of PFOA and PFOS was 11.9-64.4% ($34.3_{avg.}$%) and 3.2-76.7% ($31.7_{avg.}$%), respectively. Although the efflux of PFOA and PFOS was very different according to the plant, the total efflux of PFOA and PFOS in many plants was over 50% like as influx of PFOA and PFOS.

(2) Influx and efflux of PFCs in theindustrial wastewater treatment plants (IWTPs)

The total concentrations of PFCs (11 target compounds) in the influent and the influx of PFCs were4.3-4188.0ng/L (414.0ng/L) and 0.185-437.177 g/day ($34.265_{avg.}$ g/day), respectively.Plants 1-4 were treated the paper and pulp manufacturing industry wastewater, the plants 5-7 were treated the electricity and electronic industry wastewater, the plants 8-9 were treated chemical products manufacturing industry wastewater, the plant 10 was treated the metal products manufacturing industry wastewater and the plants 11-15 were treated the mixed various industrial wastewater in large industrial complexes. However, the influx of PFCs significantly varied according to the plant and showed no trend according to the industry. Among the 11 target compounds the influx of PFOA and PFOS was 0.3-65.3% ($12.3_{avg.}$%) and 0.0-98.3% ($2.2_{avg.}$%), respectively.The influx of PFOA and PFOS also greatly varied depending on the industry. The total concentrations of PFCs (11 target compounds) in influent and the efflux of PFCswere16.9-7627.3ng/L (611.4ng/L) and 0.030-62.426 g/day ($8.589_{avg.}$ g/day), respectively. The efflux of PFCs also showed very variations according to the plantand not any trend according to the industry. The efflux was influenced not always by influx. In many plants the efflux was higher than influx. Among the 11 target compounds the efflux of PFOA and PFOS was 0.2-70.7% ($2.0_{avg.}$%) and 0.0-98.6% ($15.1_{avg.}$%), respectively.

From the results, it was known that a lot of PFOA and PFOS was existed in the domestic wastewater and emitted from DWIPs, but PFOA and PFOS in industrial wastewater was varied depending on the manufacturing process or product. Furthermore, it was estimated that in the processes of the plant the PFCs were not removed or reducedthrough the difference between influx and efflux of PFCs in each plant, butthrough the distribution of 11 target compounds in influx and efflux in each plantthe high-molecular-weight PFCs could be changed to low-molecular-weight PFCs or reversed because of the chemical and physical properties such as the high solubility in water and high absorbability in soil or sediment/sludge with high content of organic carbon.

(2)Estimation of discharge load of PFCs in effluent of the wastewater treatment plants in Korea

The discharge load of PFCs (11 target compounds)in effluent of the wastewater treatment plants in Korea was estimated by the discharge load of PFCs in effluent of the DWTPs and the IWTPs in Korea. The discharge load of PFCs in effluent of the DWTPs in Korea was calculated with PFCs average concentration in effluent of 25 plants and the discharge amount of the treated domestic wastewater in Korea. The discharge load of PFCs in effluent of the IWIPs in Korea was calculated with PFCs average concentration in effluent of 15 plants and the discharge amount of the treated industrial wastewater in Korea.The discharge load of PFCs in effluent of the wastewater treatment plants in Korea was estimated about1.910 ton/yr (about 1.239 ton/yr (65%) in effluent of DWTPs and about 0.671 ton/yr (35%) in effluent of the IWTPs). The discharge load of PFOA and PFOS in effluent of the wastewater treatment plants in Korea was estimated about 0.366 ton/yr (about 0.340 ton/yr (93%)

in effluent of DWTPs and about 0.026 ton/yr (7%) in effluent of the IWTPs) and about 1.115 ton/yr (about 0.528 ton/yr (47%) in effluent of DWTPs and about 0.587 ton/yr (53%) in effluent of IWTPs).

From the results, it was known that onemajor emission source of PFCs is the DWTPs in Korea and PFOS was discharged 3 times more than PFOA. And also most of thePFOA was discharged from the DWTPs. Comparing the result in this study with other results in foreign countries the estimated discharge load of PFCs in Korea was not high.

References

1.Ministryof Environment of Korea. (2010);*The Korean Standard Testing Method of POPs*
2.Ministryof Environmentof Korea. (2010);*Statistical data of the domestic sewage in Korea*
3.Ministryof Environmentof Korea. (2010) *Statistical data of the industrial wastewater in Korea.*
4.OECD.(2002);*Hazard Assessment of Perfluorooctane Sulphonate (PFOS) and Its Salts*
5.OECD. (2006);*OECD Workshop on Perfluorocarboxylic acids (PFCAs) and Precursors*
6.Bommanna G, Kenneth S, Ewan S, Kurunthachalam S, Kurunthachalam K. (2007); *Water Research*41: 4611-4620
7.Michio M, Eiji I, Hiroyuki S, Kentaro K, Yuki M, Arata H, Hideshige T. (2008); *Environ Sci Technol*. 42: 6566-6572
8.Lin YC, Panchangam SC, Lo CC. (2009); *Environ Sci Technol*. 157: 1365-1372
9.Alexander GP, Kevin CJ, Andrew JS. (2009);*Environ Sci Technol*. 43: 386-392
10.Armiatage JM, Schenker U, Scheringer M, Martin JW, Macleod M, Cousins IT. (2009);*Environ Sci Technol*. 43: 9274-9280
11.Yu J, Hu J, Tanaka S, Fujii S. (2009);*Water Research*43: 2399-2408