DISTRIBUTION CHARACTERISTICS OF PERFLUOROCARBOXYLATES (PFCAs) AND PERFLUOROALKLYSULFONATES (PFASs) IN DOMESTIC SEWAGE TREATMENT PLANTS IN KOREA

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Introduction

In 2009, perfluorooctanesulfonate (PFOS) and its salts were listed in Annex B of the Stockholm Convention of POPs and their use is restricted. PFCs have properties of persistent organic pollutants (POPs) such as persistent, bioaccumulation and long range transport. Therefore, the perfluorinated compounds (PFCs) including perfluorocarboxylates (PFCAs) and perfluoroalklysulfonates (PFASs) are recognized as an important emerging pollutant, presently. PFCs have been produced and used in the worldwide as consumer products for the past five decades but since 2000, their manufacturing and use are reduced and restricted due to the toxicity of PFCs. PFCAs and PFASs 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, PFCAs and PFASs are normally detected in the domestic sewage and in the sludge of the treatment plant and the detected compounds were very various according to the plants. The treatment plants have no any process to reduce and remove PFCs and in the processes of the plant the high-molecular-weight PFCs could be changed to low-molecular-weight PFCs or reverse 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. Therefore, to observe the behavior of PFCAs and PFASs in the process of a plant the influent, effluent and sludge of the 25 domestic sewage treatment plants in Korea were investigated in this study.

Materials and methods

(1) Plant

There are 2,770 public domestic sewage treatment plants in Korea (2009) and the plants are classified two groups based on the treatment capacity with above or below 500m^3/day. The plants with below 500m^3/day are much more than that with above 500m^3/day, but most domestic sewage generated in Korea is treated using plants with capacity above 500m^3/day (about 85%). Therefore, to investigate the plants with capacity above 500m^3/day were selected and separated according to the amount of industrial wastewater (below 60%) flowing public domestic sewage treatment plant.

(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 sewage, final effluent sewage and final discharged sludge of each 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 10454.1). ES 10394.1 is KSTM for PFCs in influent sewage/wastewater or effluent sewage/wastewater of treatment plant using LC/MS/MS and ES 10454.1 is KSTM for PFCs in soil/sludge/sediment using LC/MS/MS. The sample bottle with polypropylene (PP) was used and the sample was collected 3 times in a day. The samples were keeping in a freezer and analyzed in a week after sampling. To extract of PFCs in samples the solid phase extraction (SPE) and to analyze the isotopes of PFCs as internal standard were used. The analyzer was LC/MS/MS with electro-spray ionization (ESI) and multiple-reaction monitoring (MRM).

Results and discussion

(1) Concentration of PFCs in the influent sewage

The total concentrations of PFCs (11 target compounds) in the influent sewage of 25 treatment plants were 4.8-502.8 ng/L (85.0 ng/L). According to the plant the total concentration of PFCs and the distribution of target compounds in the influent sewage were very varied. However, in most plants PFOA or PFOS was high detected compound and the low molecular weight compounds (C6-C8) were detected mainly in most plants. Comparing PFOS with PFOA, PFOS was the dominant compounds in the 14 treatment plants and PFOA was the dominant compounds in the 11 treatment plants. The inflow rate of industrial wastewater was affected by the total concentration of PFCs in influent sewage. In the plants 1-16 the industrial wastewater was flowing 0-2%, 20-30% in the plants 17, 18, 21, 24, 25 and 40-60% in the plants 19, 20, 22, 23. The total concentrations of PFCs in the plants 1-16 and 17, 18, 21, 24, 25 were not clearly distinguished by difference of the inflow rate of industrial waste water. However, the total concentrations of PFCs in the plants 19, 20, 22, 23 were very higher than that in the plants 1-16 and 17, 18, 21, 24, 25. Although the concentration of PFCs in plants 19, 20, 22, 23 were very high, the dominant compound in plants 19, 20, 22, 23 was PFOA or PFOS, like others. Therefore, it was estimated that the character of the sewage flowing into a treatment plant was more important factor than the inflow rate of industrial wastewater to decide the distribution of target compounds. However, it was estimated also that the inflow rate of industrial wastewater flowing into a domestic sewage treatment plant was one important factor to decide the concentration of PFCs.

(2) Concentration of PFCs in the effluent sewage

The total concentrations of PFCs (11 target compounds) in the effluent sewage of 25 treatment plants were 6.3-484.0 ng/L (72.5 ng/L). According to the plant the total concentration of PFCs and the distribution of target compounds in the effluent sewage were very varied. In most plants PFOA or PFOS was high detected compound and the low molecular weight compounds (C6-C8) were detected mainly in most plants, like as influent sewage. Comparing PFOS with PFOA, PFOS was the dominant compound in the 9 treatment plants and PFOA was the dominant compound in the 16 treatment plants. The detected compounds in the effluent sewage were similar from that in the influent sewage, but the distribution of compounds in influent sewage and effluent sewage was a little difference. The high inflow rate (above 40%) of industrial wastewater was affected by the total concentration of PFCs in the effluent sewage like as influent sewage. However, the concentration of PFCs in the effluent sewage of plant 20 was not high, although in the plant 20 the industrial wastewater was flowing above 50%. And also, comparing the influent sewage with the effluent sewage, the concentration of PFCs in the effluent sewage of plant 20 was decreased remarkably. Therefore, it was estimated that the character of the sewage discharged from a treatment plant was based on the character of the sewage flowing into a treatment plant. It means that by treatment process or time the PFCs could not be removed, but changed between compounds.

(3) Concentration of PFCs in the sludge

The total concentrations of PFCs (11 target compounds) in the sludge of 25 treatment plants were 4.0-347.7 ng/g (92.4 ng/g). According to the plant the total concentration of PFCs and the distribution of target compounds in the sludge were very varied. In most plants PFOS was high detected compound and the high- molecular-weight compounds (C8-C11) were detected mainly in most plants. The detected compounds and distribution of compounds in the sludge were very dissimilar from that in the influent and effluent sewage. The high inflow rate (above 40%) of industrial wastewater was affected by the total concentration of PFCs in sludge like as influent and effluent sewage. Therefore, it was estimated that the character of the sludge discharged from a treatment plant was not based on the character of the sewage into a treatment plant, but the physical and chemical properties of PFCs. In other words, it was guessed that during the treatment of the sewage in a plant the PFCs were changed or reacted in the solid-phase. It means that by treatment process or time the PFCs could not be removed, but changed between compounds.

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