論　文　要　旨 Dissertation Abstract

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論文題目 Dissertation Title	Distribution and behavior of perfluoroalkyl acid precursors in the aquatic environment and their importance in total perfluoroalkyl substances

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are used in various applications, including industrial, commercial, and household uses and some of them are categorized into so called essential uses. But some of them are under regulations due to their persistent and toxic nature. There are conflicts between benefit of their use and health risk due to their exposure. Therefore management schemes that can cope with these conflicts are needed to be implemented. However lack of information is the bottleneck of appropriate management action. In this study, I focused on the perfluoroalkyl acid (PFAA) precursors that are not currently under regulation and that will decompose eventually into the regulated PFAAs in the environment. The target media of this study are urban river water and domestic sewage. Sewage treatment plants are the links of human activity and natural system in this case, river water. Sewage treatment plants are expected to remove the PFAAs, but the fates of PFAA precursors have hardly been known. It is believed that the results of this study will provide important information on the occurrence and distribution of PFAA precursors for the construction of better management policy.

The contents and obtained knowledge of each chapter were concluded below:

Chapter 1

In the chapter 1, the base information of PFAAs and their precursors was reviewed, especially for PFAA precursors limited information could be found. This information was introduced for comprehensively understanding “what they are”, “how they are used”, and “How they are regulated”.

Chapter 2

By reviewing the previous research results about PFAA and part of PFAA precursors in environment of the world, showed the macroscopic pollution situation of PFAAs and their precursor. The concentration levels and existence in the whole globe of these compounds were concluded. Comparing with the PFAAs, the limitation of the information of their precursors was shown by those results.

Chapter 3

The oxidation method converting all the PFAA precursors into PFCAs was introduced in this chapter. Test result in of this method in this study confirmed that injected precursors were all converted into PFCAs. The produced PFCAs detected had the proportions similar with the results of Houtz and Sedlak (2012), except for fluorotelomer precursors that Houtz and Sedlak (2012) used n:2 Fts and 8:2 diPAP type which yielded PFCA with carbon chain $n-1$ (C($n-1$) PFCA) as the most abundant product and followed by C(n) PFCA, however, in our study the most dominated product was C(n) PFCA from n:2 FTCA. This exception may not affect the estimation of impact of PFAA precursors.

The excess amount of oxidation agents and duration of oxidation treatment were used, in method of Houtz and Sedlak (2012), and which were considered enough to convert the PFAA precursors in common environmental samples.

The introduced and tested method in this chapter was applied for the studies in Chapters 4 and 5.

Chapter 4

The importance of PFAA precursors in river water was revealed by significant difference in the total concentrations of PFAAs before and after oxidation ($p < 0.05$). Therefore, the commonly measured precursors were only a part of the total precursors present in the environment. The ratios of sum of increased $PFCA_{C4\text{-}C12}$ by oxidation ($\Sigma\Delta[PFCA_{C4\text{-}C12}]$) against $\Sigma[PFCA_{C4\text{-}C12}]_{before\ oxidation}$ found in the STP effluent samples were lower (average = 21%) than those found in the river water (average = 28% and 69%) samples, which implied that the precursors might have decomposed into PFAAs during the sewage treatment process. On the other hand, higher ratios were observed in the upstream water samples which indicated the existence of emission sources other than the STP effluents.

This study showed that although the treatment process converting a part of the PFAA precursors into PFAAs, STPs were important sources of precursors to the Tama River. Further studies on the original sources of precursors are required to reduce the emission of PFAA and their PFAA precursors in the aquatic environment.

Chapter 5

The importance of PFAA precursors in STPs was revealed by its significant percentage of PFCAs formed: $\Sigma\Delta PFCA / (\Sigma PFAS_{before} + \Sigma\Delta PFCA)$. Therefore, the commonly measured precursors were only a part of the total precursors present in the STPs. The percentage of PFCAs formed in effluents of STP T (56, 48, 46, 47%), S (39, 15%) and K (42, 31%) were shown, which indicated PFAAs and their precursors existed at a level that cannot be neglected. This implied that concentration of the precursors that will eventually degrade into PFAAs in the environment is significant. PFAA precursors were estimated as the dominant PFASs in solid phase of STP indicating that the use of biosolid made from sludge of STP may contribute to emission of PFAA into environment and then to food chain.

Similar concentration levels and percentage of PFCAs formed indicated the removals of PFAA precursors are ineffective in ozonation and chlorination treatment.

Comparing with influent, 80, 77and 75% of estimated load of PFAAs after treatment tank decreased in STP T, S and K, respectively. STP reduces large amount of PFASs by the sole or combination of the follow reasons: a) striping of volatile PFAA precursors into atmosphere in aeration tank, b) lower mount of PFAA production from precursors by bio-decomposition comparing with oxidation method, and c) PFAAs and their precursors were absorbed on sludge which will be send to outside. These means the removal of PFASs in STP will be underestimated if only water phase is considered.

The estimation of type of precursors used in Japan showed that PFHxS precursors are the major C6 precursor, and PFOA precursors are the major PFAA precursors which contribute the PFOA in environment.