Doctoral Dissertation

博士論文

Distribution and behavior of perfluoroalkyl acid precursors in the aquatic environment and their importance in total perfluoroalkyl substances

水環境におけるパーフルオロアルキル酸前駆物質の分布と挙動及び全パーフルオロアルキル化合物に占める重要性

By
Ye Feng（叶 丰）

Graduate School of Environment and Information Sciences
Yokohama National University
Japan
国立大学法人 横浜国立大学大学院
環境情報学府

December, 2014

ABSTRACT

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 $\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}$ by oxidation ($\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$) against $\Sigma[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]_{\mathrm{before\ oxidation}}$ 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: $\Sigma\Delta\mathrm{PFCA} / (\Sigma\mathrm{PFAS}_{\mathrm{before}} + \Sigma\Delta\mathrm{PFCA})$. 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.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Prof. Shigeki Masunaga, for giving me the chance to learn and to do the research under him. His warm reply to my first touch through email is the start of the 6 years of my life in Japan. I am deeply grateful of his instructive advice and useful suggestions and the platform provided by him. All of that made me keep growing up.

I thank to Prof. Hiroyuki Matsuda and Prof. Satoshi Nakai who gave me valuable questions and comments during the time I staying in here. I am also grateful to Prof. Satoshi Nakai, Prof. Koichi Fujie, Prof. Masaru Oya and Associate Prof. Yoshihito Takeda for serving as members of the judge committee in my doctoral defense meeting. I thank Dr. Yasuyuki Zushi (former member of MNM laboratory) for the specific skills you taught me concerning the analysis of organic contaminants. I also thank Master student Junya Negishi for the help during the experiment. I acknowledge Ms. Mayumi Tamura for the invaluable support she provided during my stay in MNM Lab. and Mrs. Y. Gotoh who provided technical support in the MNM Lab.

Great thanks also go to my fellow PhD students and friends in MNM laboratory for all the fruitful discussions, good times and fun we had over the course of my time in Yokohama National University.

I am grateful for financial support by the River Fund for Young Scientists Grant (25−1263−008) from the River Foundation, Japan, and the Leadership Program in Sustainable Living with Environmental Risk (SLER) at Yokohama National University under the aid of Strategic Funds for the Promotion of Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology.

Finally, my love and thanks to my family for their spiritual and financial support throughout the 6 years when I stayed far away cross the ocean.

LIST OF TABLES

LIST OF FIGURES

LIST OF PUBLICATIONS

Feng Ye, Masahiro Tokumura, Mohammad S. Islam, Yasuyuki Zushi, Jungkeun Oh, Shigeki Masunaga, Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent − Case study of Tama River, Japan, Water Research, 67, 77-75, 2014.

Feng Ye, Yasuyuki Zushi, Shigeki Masunaga, Survey of perfluoroalkyl acids (PFAAs) and their precursors present in Japanese consumer products, Chemosphere. (Under Review)

Zushi, Y., Ye, F., Motegi, M., Nojiri, K., Hosono, S., Suzuki, T., Kosugi, Y., Yaguchi, K., Masunaga, S., Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo Bay basin of Japan. Environ. Sci. Technol., 45, (7), 2887-2893, 2011.

Zushi Y., Ye F., Motegi M., Nojiri K., Hosono S., Suzuki T., Kosugi Y., Yaguchi K., Masunaga S., Spatial distribution and loading amounts of particle sorbed and dissolved perfluorinated compounds in the basin of Tokyo Bay. Chemosphere, 88, (11), 1353-1357, 2012.

Md Saiful Islam, Md Kawser Ahmed, Mohammad Raknuzzaman, Md Habibullah-Al-Mamun, Feng Ye, Masahiro Tokumura, Shigeki Masunaga, Trace metals in different land-use soils in the capital city of Bangladesh and health risk assessment, Journal of Soil and Sediment. (Under review)

CONFERENCE PRESENTATIONS

Yasuyuki ZUSHI, **Feng YE**, Mamoru MOTEGI, Kiyoshi NOJIRI, Shigeo HOSONO, Toshinari SUZUKI, Yuki KOSUGI, Kumiko YAGUCHI, Shigeki MASUNAGA: Current Situation of PFC Pollution in the Basin of Tokyo Bay, Japan, Water and Environment Technology Conference Program and Abstracts, p. 9 (June 25-26, 2010 Yokohama National University, Yokohama, Japan)

Zushi Y, **Ye F**, Motegi M, Nojiri K, Hosono S, Suzuki T, Kosugi Y, Yaguchi K, Masunaga S: Survey of Perfluorinated Compound (PFC) Pollution in the Basin of Tokyo Bay Using the Simultaneous Analysis Method for 35 Types of PFCs, 30th International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2010) (2010.9.12-17; San Antonio, Texas, USA)

Y. Zushi, **F. Ye**, M. Motegi, K. Nojiri, S. Hosono, T. Suzuki, Y. Kosugi, K. Yaguchi, S. Masunaga: Spatial Distribution and Loadings of Particle Sorbed and Dissolved Perfluorinated Compounds in the Basin of Tokyo Bay, SETAC North America 32nd Annual Meeting Abstract Book p. 60 (13–17 November 2011; Hynes Convention Center, Boston, Massachusetts, USA)

Ye F, Zushi Y, Masunaga S: Analysis of perfluorinated compounds (PFCs) in commercial products, 32nd International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2012) Organohalogen Compounds Vol. 74, 251-254 (2012) (2012.8.26-31; Cairns, Australia)

F. Ye, M. Tokumura, J. Oh, S. Masunaga, Y. Zushi: Quantitation of Perfluoroalkyl Acid Precursors in Tama River, Japan, Society of Environmental Toxicology and Chemistry North America 34th Annual Meeting (2013.11.17–21; Nashville, TN, USA)

頭士泰之，**Ye Feng**，益永茂樹，茂木守，野尻喜好，細野繁雄，鈴木俊也，小杉有希，矢口久美子：東京湾流域河川における残留性有機フッ素化合物(PFCs)の汚染全容調査　～38 種 PFC 類縁体の一斉分析手法の適用～、第 44 回日本水環境学会年会講演集，p. 547（2010.3.15-17、福岡大学 七隈キャンパス）

頭士泰之、**Ye Feng**、益永茂樹、茂木守、野尻喜好、細野繁樹、鈴木俊也、小杉有希、矢口久美子：東京湾流域における河川懸濁物中 PFCs 濃度の空間分布実態、第 45 回日本水環境学会年会講演集 p.430（2011.3.18-20; 北海道大学札幌キャンパス）

Feng YE、頭士泰之、益永茂樹：製品に含有される残留性有機フッ素系化合物（PFCs）の分析手法の検討、第 45 回日本水環境学会年会講演集 p.702（2011.3.18-20; 北海道大学札幌キャンパス）

頭士泰之，**Ye Feng**，茂木守，野尻喜好，細野繁雄，鈴木俊也，小杉有希，矢口久美子，益永茂樹：東京湾流域河川における溶存態・懸濁態 PFCs の空間分布及び輸送量、第 20 回環境化学討論会講演要旨集, 186-187 (2011.7.16-18; 熊本県立大学)

Ye Feng，頭士泰之，益永茂樹：市販製品に含有される残留性機フッ素化合物（PFCs）の分析、第２１回環境化学討論会要旨集(CD 版) p. 829-830 (2012.7; 愛媛県県民文化会館)

小谷健輔、**Ye Feng**、益永茂樹：市販製品に含有される残留性有機フッ素化合物の直接曝露とリスク評価、平成 24 年度室内環境学会学術大会講演要旨集 p. 214-215 (2012.12.15-16；東海大学高輪キャンパス)

F. Ye, 徳村雅弘, S. ISLAM, 頭士泰之, 呉正根, 益永茂樹: 都市河川と下水処理水におけるパーフルオロアルキル酸前駆体の分布とその重要性：多摩川における事例研究, 第 17 回日本水環境学会シンポジウム講演集，331-336（2014.9.8-10; 滋賀県立大学）

1. Review of the basic information of perfluoroalkyl acids and their precursors

1.1 Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are known to have useful properties, such as chemical inertness, water proof, lubricity, non–stick, fire resistance, heat resistance. Due to these properties, they have been widely used since the 1950s in various commercial products, (e.g., upholstery, cookware, sports clothing, plastics, food handling equipment, medical equipment, motor oil additives, fire‑fighting foams, paints and inks) (Dinglasan–Panlilio and Mabury, 2006; Fiedler et al., 2010; Kissa, 2001; Sinclair et al., 2007).

Among the PFASs, PFOS (perfluorooctane sulfonic acid) and PFOA (Perfluorooctanoic acid) have been studied most. They have all carbon–hydrogen (C–H) bonds replaced by the carbon–fluorine (C–F) bonds and attached with sulfate or carboxylate group as the functional group. (Giesy and Kannan, 2002; Renner, 2001; Schultz et al., 2003)

In 1999, high concentrations of PFOS were (detected and) reported in the serum of fluorochemical production employees. After this incident, PFOS and PFOA have drawn lots of attentions of researchers. And monitoring of PFASs had started globally.

The monitoring of PFAAs started for PFOS and PFOA, then the number of target compounds increased gradually. As there are numerous PFAAs, however, monitored chemicals are only part of PFASs. Especially PFAA precursors have not been well monitored. This may underestimate the existence of PFASs and lead to inefficient PFAS management. For example, without the management of PFAA precursors, which will decompose into PFAAs in the environment, the regulation on PFAAs becomes less effective. For the better management of PFASs, the information of all the PFASs will be required. Therefore, this study aims to fill the information gap of PFAA precursors in aquatic environment for avoiding inefficient management of PFASs.

In the chapter I, the basic information on PFASs, including structure, classification, use, manufacturing method, quantity, etc. of PFAAs and PFAA precursors were summarized.

1.2 Perfluoroalkyl acids

PFAAs are important both because they are highly persistent substances that have been directly emitted to the environment or are formed indirectly from the environmental degradation or metabolism of precursor substances, and because they (or their salts) are or have been used in a wide variety of industrial and consumer applications (Buck et al., 2011). Depending on acid strength (pK_a value), PFAAs will dissociate to a greater or lesser extent to their anions in aqueous environmental media, soils, or sediments. The protonated and anionic forms have very different physicochemical properties. For perfluoroalkyl carboxylic acids, there is an ongoing debate regarding what is the environmentally relevant pK_a, with measured and estimated values varying by several log units for PFOA (Burns et al., 2008; Cheng et al., 2009; Goss, 2008; Rayne and Forest, 2010).

1.2.1 Structure and families of perfluoroalkyl acids

As the name of PFAAs, these compounds have all H atoms on all C atoms in the alkyl chain attached to the functional group have been replaced with F. Phosphate, carboxylate or sulfate group is attached to the end of perfluoroalkyl chain, as the functional group. Then the family of PFAAs includes perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids (**Table 1-1**, **Figure 1-1**). The most frequently discussed PFAAs were PFCAs and PFSAs, which are the family of PFOA and PFOS, respectively.

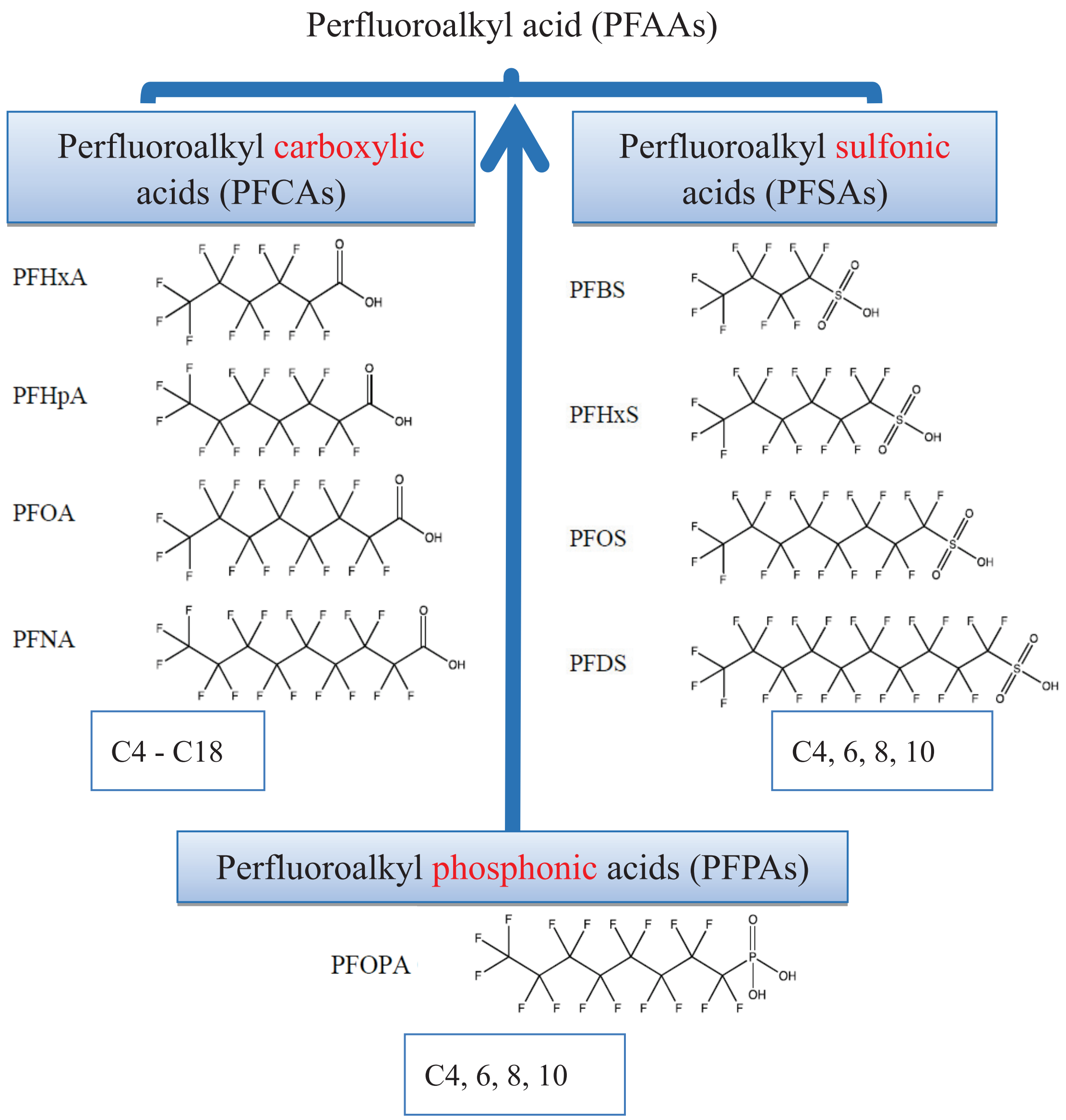


Figure 1-1 the classification and structures of perfluoroalkyl acid (PFAAs)

1.2.2 Uses of perfluoroalkyl acids

C-F bond distance is shorter than those of other halogens, PFAAs with more F, replacing H, have less C-F bond distance. The intermolecular interaction of perfluoroalkyl substances is weakened and this significantly lowers the surface tension and boiling point, and causes low refractive index, and non-stickiness. Therefore, they have properties excellent in heat resistance, chemical resistance, water and oil repellency, etc., and have been manufactured as surfactant for wide range of uses. Such as PFAAs used in aqueous film-forming foam, is because they are stable in acid or alkali which make them to form stable emulsion or foam as emulsifier or foaming agent. PFAAs containing aqueous film-forming foam make the time of fire extinguishing shorter significantly (CMC CO., Ltd, 2001). The uses of PFAAs are showed in **Table 1-1**.

Table 1-1 Uses, names, and structures of Perfluoroalkyl acids (PFAAs) compounds for which all H atoms on all C atoms in the alkyl chain attached to the functional group have been replaced with F (Buck et al., 2011)

	Classification and chemical structure	**CnF2n+1R, where R =**	**Uses**
Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids (PFCAs)[a]	-COOH	Surfactant
	Perfluoroalkyl carboxylates (PFCAs)[a]	-COO−	
	Perfluoroalkane sulfonic acids (PFSAs)[b]	$-SO_3H$	
	Perfluoroalkane sulfonates (PFSAs)[b]	$-SO_3^-$	
	Perfluoroalkane sulfinic acids (PFSIAs)[b]	$-SO_2H$	Intermediate environmental transformation product
	Perfluoroalkyl phosphonic acids (PFPAs)[c]	$-P(=O)(OH)_2$	Surfactant
	Perfluoroalkyl phosphinic acids (PFPIAs)[c]	$-P(=O)(OH)(C_mF_{2m+1})$	Surfactant

[a] Substances originating by either electrochemical fluorination (ECF) or fluorotelomer processes

[b] Substances originating by ECF

[c] Substances originating by fluorotelomer processes.

The most representative PFAAs are PFOS and PFOA, and OECD (Organisation for Economic Co-operation and Development) has done survey on the use of PFOS, PFOA and their related substances. For the detail of the uses of perfluoroalkyl acids, please refer to "1.2.5.2 Uses of PFOS and PFOA".

1.2.3 Manufacturing method of perfluoroalkyl acids

There are two main methods for manufacturing PFAAs: electrochemical fluorination (ECF) and telomerization (Buck et al., 2011). PFCAs were originated by either electrochemical fluorination (ECF) or fluorotelomer processes, PFSAs were originated by ECF, and PFPAs were originating by fluorotelomer processes.

In the ECF process, organic compounds are dissolved or dispersed in liquid fluorinated hydrocarbon, and apply electrical current for fluorination. Then PFAAs are generated by all the hydrogen atoms of the organic compounds replaced by fluorine atoms. Produced PFAAs have carbon chain of even or odd different length depending on the starting organic compounds. Sometimes branched-chain may also occur.

In the process of telomerization, perfluoroalkyl compound, most commonly pentafluoroethyl (or perfluoroethyl) iodide, C_2F_5I (PFEI), is reacted with unsaturated compound tetrafluoroethylene $CF_2 = CF_2$ (TFE) to yield telomers. The characteristics of telomer molecule are that it combines perfluorinated carbon chain and short carbon chain (commonly two carbon atom with hydrogen atoms), and that always have straight chain with even number of carbon atoms on it.

1.2.4 Quantity of production of perfluoroalkyl acids

According to OECD survey in 2009 (OECD, 2011), the total amount of PFOA present in products as unreacted residual was less than 1.5 tons in 2008. Based on the reported data, the number of PFCA-related chemicals (23 chemicals) and PFOA-related chemicals (12 chemicals) manufactured and/or present in products was larger than the PFSA (3 chemicals) and PFOS (4 chemicals) groups of chemicals. From the survey response, the most commonly reported use of products containing perfluorinated chemicals appears to be in the production of water/oil repellent products. No common uses across all four groups were noted except for antireflective coating products for photolithography that used PFOS, PFSA or PFOA products. Products containing PFOS and related substances were not reported to be used in fire fighting products. Very small quantities of perfluorinated chemicals were released to air or water systems compared to landfill or off-site transfer for incineration.

Table 1-2 List of Perfluoroalkyl acids produced in 2009 (OECD, 2011)

Substance	Mass quantity of the substance as a residual or impurity in products
PFOS and related substances	< 3.5tonnes
PFSA and related substances	< 0.5 tonnes
PFOA and related substances	< 5.5 tonnes
PFCA and related substances	< 1.5 tonnes

Quantity of production of PFAAs that have been reported in the OECD survey 2009 is shown in Table 1-2. These results represent of 34 industrialised countries in North and South America, Europe and the Asia and Pacific region, as well as the European

Commission:

(1) European Union member states (21 Countries)

United Kingdom, Germany, France, Italy, Netherlands, Belgium, Luxembourg, Finland, Sweden, Austria, Denmark, Spain, Portugal, Greece, Ireland, Czech Republic, Hungary, Poland, Slovakia, Estonia, Slovenia.

(2) Other (13 countries)

Japan, United States, Canada, Mexico, Australia, New Zealand, Switzerland, Norway, Iceland, Turkey, South Korea, Chile, Israel.

1.2.5 Historical issue – PFOS and PFOA

1.2.5.1 Physical and chemical properties of PFOS・PFOA

The contamination by PFAAs appears different from the other earlier pollutants. It is caused by their specific property, manufacture method and use of these compounds. Physical and chemical properties of PFOS and PFOA are shown in Table 1-3 (Ministry of the Environment Government of Japan, 2008).

Water solubility

In the structures of PFOS and PFOA, carboxylic acid or sulfonic acid as a hydrophilic group connects to the perfluoroalkyl chain. Perfluoroalkyl group acts as an electron-attracting group which strengthens the acidity make them into strong acid. They present in the environment in ionized states and exhibit high water solubility. Therefore, it is thought to be distributed more to the water in the environment. The details of water solubility of PFOS and PFOA are shown in Table 1-3.

The perfluorooctanoate anion is highly water-soluble and has negligible vapor pressure, whereas perfluorooctanoic acid has very low water solubility and sufficient vapor pressure to partition out of water into air (Kaiser et al., 2005; Webster and Ellis, 2010; Webster et al., 2010).

Table 1-3 physical and chemical property of PFOS and PFOA (Ministry of the Environment Government of Japan, 2008)

PFOS	
Melting point	> 400 ˚C
Boiling point	–
Specific gravity	≈0.6, ≈1.1 (lithium salt), ≈1.1 (ammonium salt), ≈1.1 (Jeffrey diethanolamine salt)
Vapor pressure	6.4×10^{-3} mmHg (Acid, 25 ˚C, calculated by MPBPWIN) (＝0.85Pa),

	1.43×10^{-11} mmHg (25 ˚C, calculated by MPBPWIN) (=1.9×10-9 Pa)
Partition coefficient (1–octanol / water) (log Kow)	–
Dissociation constant (pKa)	2.5(acid)、2.80 (acid)
Water-soluble (water solubility)	519 mg/L (20±0.5˚C)、680 mg/L (24～25˚C)、 570 mg/L、370 mg/L (fresh water)、 12.4 mg/L (unfiltered seawater)、25 mg/L (filtered seawater)、12.4 mg/L (natural seawater、22～23 ˚C)、 20.0 mg/L (3.5% NaCl solution、22～24 ˚C)

PFOA	
Melting point	54.3 ˚C (acid), 157～165 ˚C
Boiling point	188 ˚C (acid, 760 mmHg), 189 ˚C (acid, 736 mmHg)
Density	1.792 g/cm^3 (acid, 20 ˚C) 0.6～0.7 g/cm^3 (bulk density)
Vapor pressure	0.031 mmHg (=4.2 Pa) (acid, 25˚C, extrapolated value), 0.02 mmHg (=3 Pa) (acid, 20˚C, extrapolated value), 6×10^{-5} mmHg (=8×10^{-3} Pa) (20˚C, extrapolated value)
Partition coefficient (1-octanol / water) (log Kow)	–
Dissociation constant (pKa) of	2.5 (acid), 2.80 (acid)
Water-soluble (water solubility)	9.5×10^3 mg/L (acid, 25˚C)

Value showed as the ammonium salt except the ones marked with “(acid)”

Acid dissociation constant

The reported acid dissociation constant values of PFOA are differ between literatures, e.g. 3.8 (Burns et al., 2008), 1.3 (Kutsuna and Hori, 2008), nearly 0 (Goss, 2008). Even though, PFOA is present in ionized states rather than acid states in environment. However, pH of the rainwater was detected as low as 4.5 near factory, and the pH varied in the mist of sea water (Armitage et al., 2009), which is considerably due to the higher portion of acid. It is described that, the acid dissociation constant of PFOS to be 1 or less (OECD, 2002). And PFOS presents as ionized states basically.

1.2.5.2 Uses of PFOS and PFOA

After the regulations of PFOS, there is little information available on the usage of PFOS and PFOA. The usage information shown in this section was selected from OECD survey (2005) before the regulations of PFOS (OECD, 2005).

PFOS

According to the OECD survey (2005), responses indicated the use of PFOS or related raw chemicals in industrial processes only. No domestic uses for the raw chemicals were noted. The processes identified were metal plating and electronic etching operations, semiconductors, metal coatings, in wax or other polishing agents, cleaning agents, in sealants or as a chemical intermediate. Chemicals were present in products in proportions ranging from 0.001% - 50%. For uses in electronic etching or metal plating, PFOS or related chemicals were noted as present at 5% - 25%. Table 1-4 showed the results of Survey on Use of PFOS and related Substances of countries.

Essential Uses

The essential uses reported by individual countries for PFOS and related chemicals are as ingredients in fire fighting foams (Class B fires), aircraft hydraulic fluids, chromium plating (mist suppressants), anti-reflective or photoresist agents in semiconductor photolithography and anti-static, surfactant or adhesion control agents in photographic processes.

New Uses

No new uses were reported.

Table 1-4 Results of Survey on Use of PFOS and PFOS related Substances from ORCD (2005)

Country	Known Uses of the Chemical
Australia	aqueous film forming foam (AFFF) and alcohol type fire fighting foams
Belgium	Photographic industry, electronics industry (semi-conductors), aviation hydraulic fluids
Finland	metal plating and photolithography processes in semiconductor industry as well as hydraulic fluids for aircrafts
New Zealand	aviation hydraulic fluid and in certain photographic and electronic applications
Switzerland	Photolithography & semiconductors, Hydraulic fluids, Metal coating

UK	chromium plating (mist suppressants), semiconductors (photolithography), aviation hydraulic fluids, and photographic anti-static agents (UK is confident that alternatives either exist or can be developed except for aviation hydraulic fluids)
US	In 2002 (67 FR 72854), the U.S. excluded from regulation PFOS-related substances used (1) as an anti-erosion additive in fire-resistant phosphate ester aviation hydraulic fuels; (2) as a component of a photoresist substance, or as a component of an anti-reflective coating; (3) in coatings for surface tension, static discharge, and adhesion control; or (4) as an intermediate only to produce other chemical substances
EU	Use category: Fixing agents, Flame retardants and fire preventing agents, Foaming agents, Impregnation agents, Intermediates, Solvents, Other

PFOA

Responses indicated only industrial use and no domestic use of raw PFOA and related chemicals. Noted uses for these chemicals were as polymer processing aids in photographic film, as reagents, as surfactants and for semiconductors. Products containing PFOA and related chemicals were used only for industrial purposes. No domestic uses were noted. The specific industrial uses were as metal coatings (eg. non-stick cookware), surface coatings, textile treatments, additives for plastic resins and aqueous dispersions and for glass fibre impregnation. **Table 1-5** showed the results of Survey on Use of PFOA and related Substances of countries.

Table 1-5 Results of Survey on Use of PFOA and PFOA-related substances from ORCD (2005)

Country	Known Uses of the Chemical
France	Surfactant in the polymerisation process of polyvinylidene fluoride
Germany	Essential emulsifier for polymerisation of fluoropolymers
Italy	Polymer processing aids, photographic film. Polymer processing aids, photographic film
Japan	Semiconductors, etc. Polymer production, etc.

	Surfactant, etc.
Poland	Reagent
US	Manufacture of fluoropolymer dry resins and aqueous dispersions
Switzerland	Paints, auxiliary. Textile cleaning g^{-1}eneral chemical/flux agent

1.2.5.3 Toxicity

PFOA and PFOS, which are very stable, are recognized as the final degradation product of their rated compounds in the natural environment (Giesy and Kannan, 2001). The reported half-life of PFOS in human serum is as long as 8.70 years and PFOA is 4.37 years (Burris et al., 2002).

Acute toxicity

The acute toxicity of PFOS was tested by oral dose of the potassium salt of PFOS to rat. The most observed symptoms were hypoactivity, hypotonia of extremities, ataxia, coloring (yellow) of the genitourinary part at autopsy, hyperemia of glandular mucosa and expansion of stomach and lung congestion. (U.S.EPA, 1978a)

The acute toxicity of PFOA was reported that it irritated eyes, skin and respiratory tract, and sticking to skin caused redness and pain, entering the eye caused blurred vision, Inhaling caused sore throat and cough, and oral dose caused nausea and abdominal pain, vomiting (IPCS, 2005).

Chronic toxicity

For middle－ and long－term toxicity of PFOS, the dose to rat or mouse showed peroxisome proliferative effect of the liver. Potassium salt of PFOS at concentration of 0, 0.003, 0.01, 0.03, 0.1, 0.3%（0, 2, 6, 18, 60, 200 mg/kg/day） was dosed to every groups consisted with five male and five female Sprague-Dawley rats, for 90 days. The result showed the survival time until 100% lethal rate is 7－8 days for 0.3% dose group, 8－14 days for 0.1 dose group, 13－28 days for 0.03% group (U.S.EPA, 1978b).

The middle－ and long-term toxicity of PFOA was observer as peroxisome proliferator, PFOA activates peroxisome proliferator-responsive receptor distributed in the organization of high fatty acid catabolism on the performance of a liver (PPARα), aggravates the reaction via the cytochrome P-450 and β oxidation of fatty acids, inhibit the secretory effect of cholesterol and very low density lipoprotein from the liver, the effects on the transport and metabolism of such lipids leads to fat accumulation in the liver and decrease of triglyceride and triglycerides in serum, and believed as the reason for causing hepatotoxicity, including liver cancer by promoting the reduction of cell death and cell proliferation. (Klaunig et al., 2003) (Kennedy et al., 2004) (U.S.EPA, 2005)

Ammonia salt of PFOA at concentration of 0, 0.001, 0.003, 0.01, 0.03, 0.1% (0, 0.56, 1.72, 5.64, 17.9, 63.5 mg/kg/day for male, and 0, 0.74, 2.3, 7.7, 22.36, 76.47 mg/kg/day for female) was dosed to every groups consisted with five male and five female Sprague-Dawley rats, for 90 days. The result showed suppression of body weight increasing was observed in males groups with dose concentration of 0.03% or higher, the body weight of male group with dose concentration of 0.1% was significantly decreased.

Relative weight of kidney were significantly increased in the male group of 0.01% or higher, however, the absolute weight in each group stayed in same level indicating no effect on the organizations. Absolute weight of the liver was significantly increased in the male group of 0.003% or higher, and in females at 0.1% group, relative weight was significantly increased in the male group of 0.03% or higher, and in females at 0.1% group.

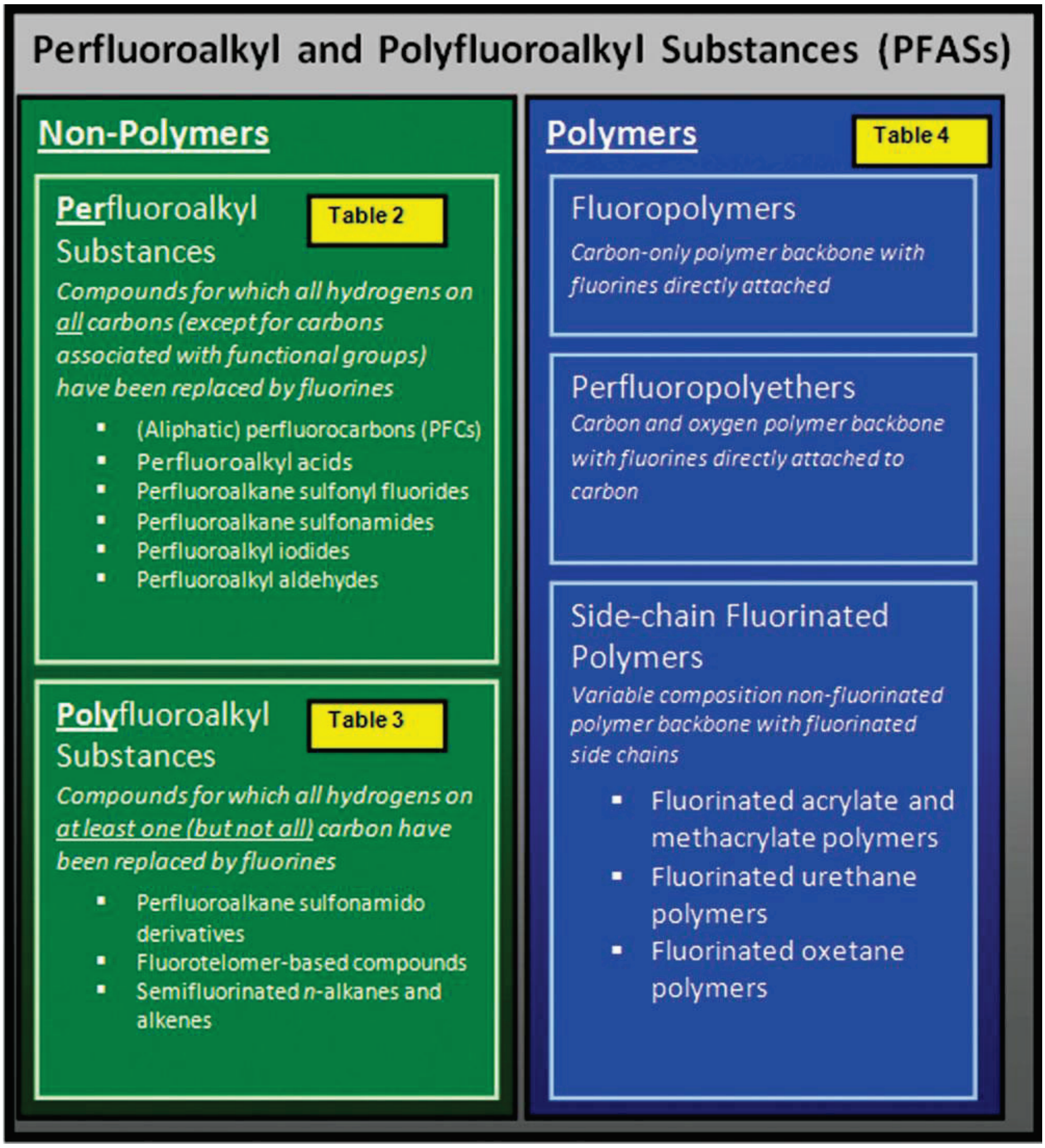
It were observed that fading of the color of liver surface for 0.1% male group, hepatocellular hypertrophy in 4/5, 5/5, 5/5 in groups of 0.01% or higher, and hepatocellular necrosis in 2/5, 2/5, 1/5, 2/5 in groups of 0.003% or higher (U.S.EPA, 1978c).

1.3 PFAA precursors

The PFAA precursors which contain PFAA in molecular are considered to be numerous. A study have identified more than 115 molecular structures of polyfluorinated surfactants in industrial blends (used to coat food paper and board packaging, and in packaging) from the European Union, the Unites States of America, and China (Trier et al., 2011). Those potential precursors that eventually decompose into PFOS and other perfluoroalkyl acids (PFAAs) such as perfluorooctanoic acid (PFOA) are still being used and have not been studied in detail.

1.3.1 Structure and families

The PFAA and their precursors, which contain PFAA molecule structurally, are all belong to perfluoroalkyl and polyfluoroalkyl substances（PFASs). PFASs are divided into 3 large families: perfluoroalkyl substances, polyfluoroalkyl substances, polymers (Buck et al., 2011). The perfluoroalkyl substances family (compounds listed in APPENDIX **Table A1-1**), composed by PFAAs and other non-polymer, are defined as aliphatic substances for which all of the H atoms attached to C atoms in the nonfluorinated substance from which they are notionally derived have been replaced by F atoms, except those H atoms whose substitution would modify the nature of any functional groups present. Most of the PFAA precursors known are belong to the perfluoroalkyl substances family (compounds listed in **Table A1-1**) and polyfluoroalkyl substances family (compounds listed in **Table A1-2**) in **Figure 1-2**. For the rest family: polymers family (compounds listed in Table A1-3), it is well accepted that they generally have very different physical, chemical, and biological properties than discrete chemical substances of low molecular weight (e.g., methyl methacrylate versus poly[methyl methacrylate]). There are various definitions of a polymer, but the basic concept describes a substance consisting of molecules characterized by the sequence of one or more types of monomer unit. (Buck et al., 2011)。



Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

Non-Polymers

Perfluoroalkyl Substances

Table 2

Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines

- (Aliphatic) perfluorocarbons (PFCs)
- Perfluoroalkyl acids
- Perfluoroalkane sulfonyl fluorides
- Perfluoroalkane sulfonamides
- Perfluoroalkyl iodides
- Perfluoroalkyl aldehydes

Polyfluoroalkyl Substances

Table 3

Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines

- Perfluoroalkane sulfonamido derivatives
- Fluorotelomer-based compounds
- Semifluorinated *n*-alkanes and alkenes

Polymers

Table 4

Fluoropolymers

Carbon-only polymer backbone with fluorines directly attached

Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers

Variable composition non-fluorinated polymer backbone with fluorinated side chains

- Fluorinated acrylate and methacrylate polymers
- Fluorinated urethane polymers
- Fluorinated oxetane polymers

Figure 1-2 Classification hierarchy of environmentally relevant perfluoroalkyl and polyfluoroalkyl substances (PFASs) (Buck et al., 2011)

1.3.2 Uses of Perfluoroalkyl acids precursors

To the author's knowledge, there is only number of studies found about the uses of PFAA precursors. PFAA precursors such as phosphate fluorosurfactants, perfluorooctane sulfonamide were used as commercial fluorochemical (D'eon and Mabury, 2011). PFAA precursors were detected in commercial products such as food packaging (Trier et al., 2011) and water proof agent (Herzke et al., 2012). It seems PFAA precursors are more used for commercial usage, while PFAAs are used only for industrial purposes, referred to OECD survey (OECD, 2005).

A study on commercial products pointed out that FTOHs are used to treat paper to improve its moisture and oil barrier properties as well as a waterproofing agent for textiles, particularly for outdoor clothing. And FTSs are used among other fluorotelomers in fire fighting foam for their film forming properties and the ability to decrease fuel absorption.(Herzke et al., 2012)

It was known that telomers are produced and used commercially as mixtures, in which the typical length of the chains is between four and eighteen carbon atoms (NMR Publisering, 2013).

In a study, Buck et al. (2011) showed in usage lists that majority of precursors are used as "major raw material for surfactant and surface protection products" and the second majority are "intermediate environmental transformation product". (see **Table A1-1**, **Table A1-2** and **Table** A1-3)

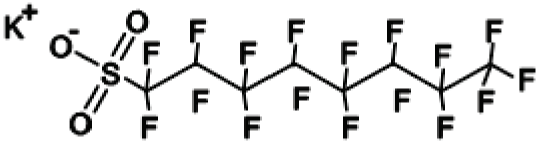
1.4 Regulations

We summarized the information of regulations of PFASs from Stockholm Convention, USEPA and Ministry of the Environment, Government of Japan. We found most of the regulations are focused on PFAAs such as PFOS and PFOA. Comparing to them, number of regulations toward PFAA precursors is very a few.

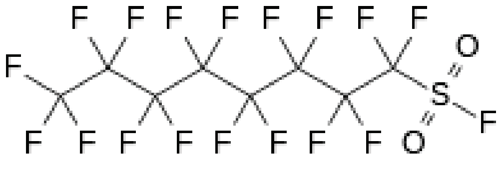
1.4.1 Stockholm Convention on Persistent Organic Pollutants

In May of 2009, PFOS, its salts and perfluorooctane sulfonyl fluoride (POSF) were added to the Annex B of the Stockholm Convention and classified as Persistent Organic Pollutants (POPs).

The structure of potassium salt of PFOS (CAS No.1763-23-1):



and (POSF, CAS No.307-35-7), the major raw material used to manufacture PFOS**:**



Detail of the regulation of PFOS, its salts and PFOS-F can be found at below:
http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx
http://chm.pops.int/Implementation/Exemptions/Articlesinuse/tabid/452/Default.aspx

1.4.2 USEPA

- **2010/15 PFOA Stewardship Program**

In 2006, EPA and the eight major companies in the industry launched the 2010/15 PFOA Stewardship Program, in which companies committed to reduce global facility emissions and product content of PFOA and related chemicals by 95 percent by 2010, and to work toward eliminating emissions and product content by 2015. Information of Stewardship Program: http://www.epa.gov/oppt/pfoa/pubs/stewardship/

- **Long-Chain Perfluorinated Chemicals Action Plan**

On December 30, 2009, EPA posted four action plans, including an action plan on long-chain perfluorinated chemicals (LCPFCs). The LCPFCs action plan outlines actions that would further reduce exposure to LCPFCs by addressing their use in products from sources other than the eight companies participating in the stewardship program.

Target compounds: PFSA sub-category includes perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonic acid (PFOS), other higher homologues, and their salts and precursors. The long-chain PFCA sub-category includes PFOA, other higher homologues, and their salts and precursors. Some of those potential long-chain PFAC precursors include chemicals known commercially as fluorotelomers.

Details of this plan can be obtained at the website of USEPA shown below:

http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html

- **Significant New Use Rule (SNUR),**

On September 30, 2013, EPA published a final Significant New Use Rule (SNUR), to ensure that 1) the Agency is notified prior to any new use of long-chain perfluoroalkyl carboxylate (LCPFAC) chemical substances as part of carpets or carpet treatment products and 2) EPA has the opportunity to review the use and, if necessary, take action to restrict the use. Details of this rule can be obtained at USEPA website shown below:

http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPPT-2012-0268-0034

1.4.3 Ministry of the Environment Government of Japan (MOE)

- **CSCL regulation, Order for Enforcement and Ministerial Ordinances**

On 1st April 2010, PFOS, its salts and perfluorooctane sulfonyl fluoride (POSF) were added to the “Specified Chemical Substances of Category A”. The list of category A of

“act on the evaluation of chemical substances and regulation of their manufacture, etc.” (CSCL) can be obtained at site below:
http://www.env.go.jp/chemi/kagaku/kisei/class1.html

On 27th Dec. 2002, PFOA was added to the “Chemical Substances subject to Type II Monitoring”. The list of Chemical Substances in Type II monitoring can be obtained from the Web site below:
http://www.env.go.jp/chemi/kagaku/kisei/2kanshi.html

On 31th May 2007, the PFCAs with carbon-chain longer than 11 were added to the “Chemical Substances” subject to Type I Monitoring. The list of chemical substances belonging this category can be obtained at Web site below:
http://www.env.go.jp/chemi/kagaku/kisei/1kanshi.html

- **Law concerning Pollutant Release and Transfer Register / PRTR Law**

PFOS was added to the “Class I Designated Chemical Substance” in PRTR Law. The list of chemical substances in this class can be obtained from the Web site below:
http://www.env.go.jp/chemi/prtr/archive/target_chemi/01.pdf

1.5 Conclusion

In the chapter 1, the basic information of PFAAs and their precursors was reviewed, especially for PFAA precursors limited information could be found. The collected information was introduced for comprehensively understanding the family and classification of PFAAs and their precursors as well as the status them including their uses and regulations.

2. Global pollution situation of PFAAs and limited information of PFAA precursors

2.1 Aquatic environment

In the aquatic environment, Yamashita et al. have conducting a global survey during 2002-2004 in the central to eastern Pacific Ocean (19 locations), South China Sea and Sulu Seas (five), north and mid Atlantic Ocean (12), and the Labrador Sea (20)(Yamashita et al., 2005). The results showed that the concentration of PFOS and PFOA in surface seawater ranged between 500 pg / L - 100 pg / L, in the open sea of the Atlantic, which indicating the pollution of manmade compound have spread to the open ocean of the Pacific Ocean where have no human activity (**Figure 2-1**).

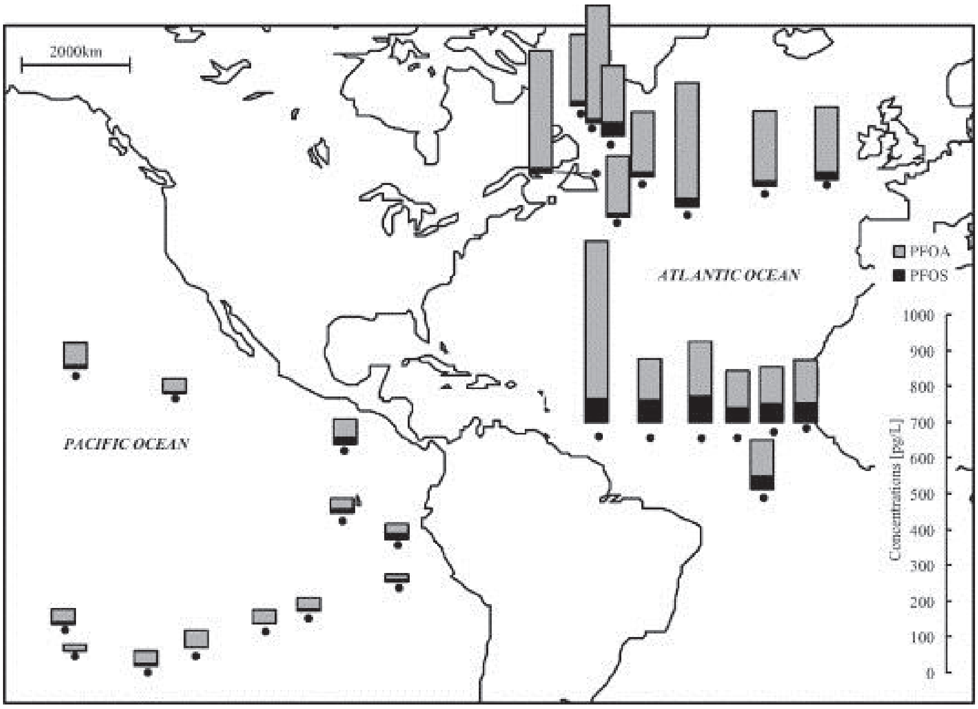


Figure 2-1 Concentrations of PFOS and PFOA in surface seawater of the Atlantic Ocean and Eastern Pacific Ocean (Yamashita et al., 2005)

The pollution situation of Japan showed concentration as high as 250 ng L^{-1} in Tokyo Bay and Osaka Bay, and as high as 20 ng L^{-1} in northern Kyushu area and the west Seto Inland Sea. The concentration in Japan area is about 1000 times higher than the open sea, which indicated the serious pollution in the closed aquatic environment (**Figure 2-2**). At the same time, the observed pollution at coastal area indicating the flows from rivers to ocean may be the main contribution of the PFAAs in the ocean.

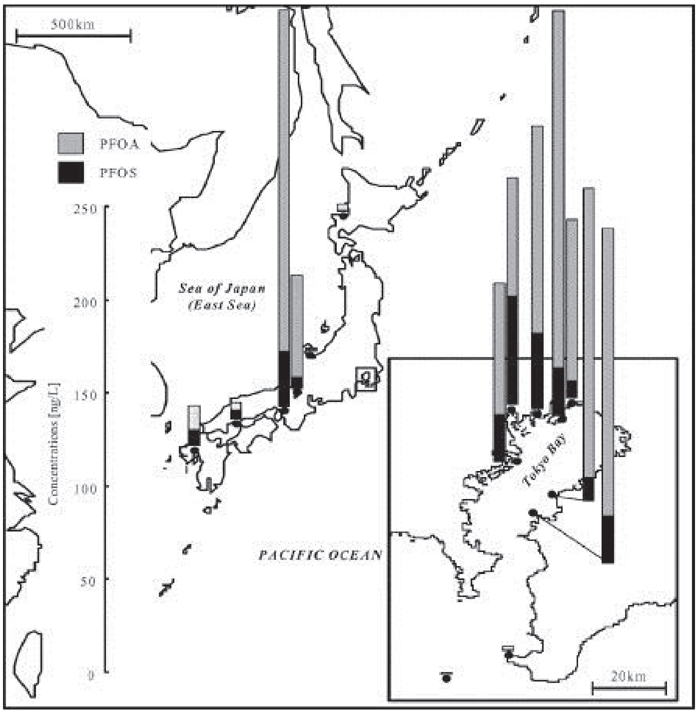


Figure 2-2 Concentrations of PFOS and PFOA in surface seawater from Tokyo Bay and coastal Japan (Yamashita et al., 2005)

Furthermore, the results from another study in ocean and coast area showed that relatively higher concentration in coast water than sea water (**Table 2-1**). Comparing concentrations in sea water from Asia, America, in Europe, it is noted that higher concentration levels of PFOA were observed in Korea and Tokyo Bay, and PFOS in the Great Lakes of the United States and Tokyo Bay. The variations of the concentration in the coastal area should be explained by their point sources.

Table 2-1 PFAAs water concentrations published in the scientific literatures

Area	PFOS [ng L^{-1}]	PFOA [ng L^{-1}]	Reference
River water			
Tennessee River (partially downstream of a fluorchemical production plant)	30.3–144	<25–598	Hansen et al., 2002
River Elbe	7.9	9.0	Theobald et al., 2011
Lake water			
Great Lakes, USA	21–70	27–50	Boulanger et al., 2004
Sea water			
Central Atlantic Ocean	0.038–0.073	0.1–0.15	Yamashita et al., 2004

South China Sea	0.008–0.11	0.16–0.42	Yamashita et al., 2004
Eastern Pacific Ocean	0.054–0.078	0.14	Yamashita et al., 2004
Central to Western Pacific Ocean	0.00l–0.005	0.015–0.035	Yamashita et al., 2004
Arctic and sub-arctic ocean water, Canada	0.010–0.424	0.007–0.234	Yamashita et al., 2004
Tokyo Bay	12.7–25.4	154–192	Yamashita et al., 2004
Coastal waters of Korea	0.04–730	0.24–320	So et al., 2004
Coastal waters of Hong Kong	0.09–3.1	0.73–5.5	So et al., 2004
Pearl River Delta and South China Sea	0.02–12	0.24–16	So et al., 2004
Open North Sea	0.048–0.43	0.084–0.77	Theobald et al., 2011
Coastal North Sea	0.28–3.1	0.54–5.9	Theobald et al., 2011
Western Baltic Sea	0.33–0.90	0.47–1.05	Theobald et al., 2011

2.2 Atmospheric environment

Among the PFASs, mainly the volatile ones were investigated in atmospheric environment. And many of the volatile PFASs are the precursors of PFAAs.

Li et al. have conducted research in Asian area including India, Japan and China. In Japan, the highest PFASs concentration was detected in Tokyo. Apart from Tokyo, the concentrations of PFASs were quite uniform, with the ratio of the highest to lowest measured values (H/L ratio) less than 10. Strong correlations($r > 0.95$, $p < 0.01$) of PFCs were observed for all the Japanese samples. The correlation indicated similar emission sources and environmental processes. In India, the variations of concentration were large, and this should be resulted from point sources. Clear differences in PFASs composition were seen compared to those in Japan.

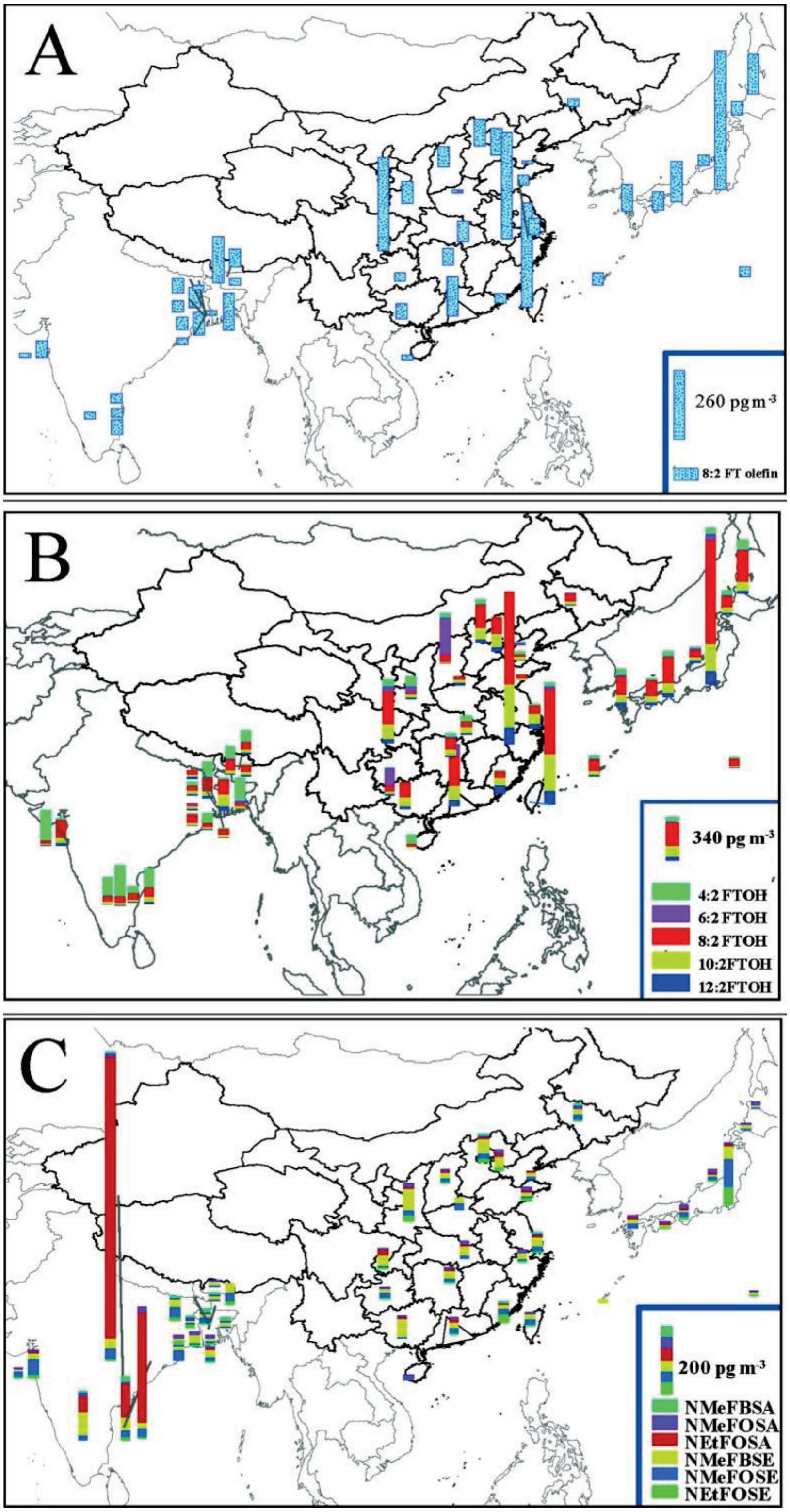


Figure 2-3 Spatial distribution of 8:2 FTO (A), FTOHs (B), and FOSAs and FOSEs (C)

Greater proportions of 4:2 FTOH to total FTOH, and NEtFOSA and NMeFBSE to total FOSA and FOSE were found in India than in Japan. (See **Figure 2-3**) Moreover, the patterns were also different between the samples collected in South India and North India, suggesting the different industrial activities. In China, very high level of 10:2 FTOH 8:2 FTOH, and 8:2 FTOH were detected at the developed cities. High correlation with the population density was observed. Higher concentrations of 6:2 FTOH were measured at the cities with the largest coal and mine industries in China. PFASs were considered to be used in lubricants in the mining machinery (Li et al., 2011).

Shoeib et al. (2006) conducted a survey in the Arctic atmosphere. Air concentrations (pg/m^3) of 8:2 FTOH, in urban locations in North America and Europe, ranged from 40 to 150 and 33 to 326, respectively and for the Toronto samples, the mean 8:2 FTOH air concentration was (41 ± 18 pg/m3) (n = 3), approximately 3 times higher than the mean concentration of 14.9 pg/m3 detected in Arctic air. (See **Figure 2-3**)

For the cruise samples, 8:2 FTOH, 10:2 FTOH, and MeFOSE were above the detection limit in all samples, while 6:2 FTOH and EtFOSE were quantifiable in 10/20 and 12/20 samples, respectively. MeFOSEA was not detected in any of the samples analyzed. The highest concentrations of FTOHs in the cruise samples were for 8:2 FTOH (5.8-26 pg/m^3) followed by 10:2 FTOH (1.9-17 pg/m^3) and 6:2 FTOH (BDL to 6.0 pg/m^3). 8:2 FTOH represents 50-70% of the total FTOHs.

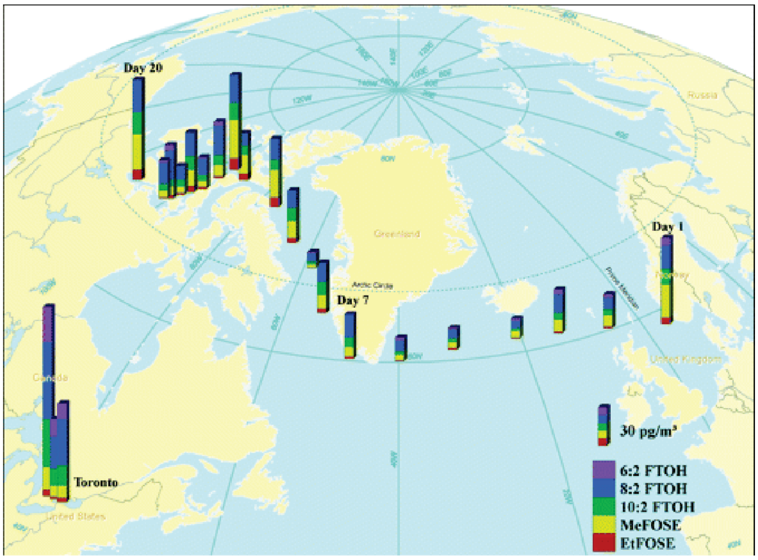


Figure 2-4 Total air concentrations (sum of gas phase and particle phase) for FTOHs and PFASs across the North Atlantic Ocean and Canadian Archipelago and in Toronto, Canada. (Shoeib et al., 2006)

2.3 Soil

Soils are the critical link between global atmospheric and hydrologic processes where both local and distant contaminants can accumulate and be released into aquatic and terrestrial communities, because PFAS concentrations in soils will influence ground and surface water, wildlife, and crops (Strynar et al., 2012). However, there are fewer studies on soil compared to aquatic and atmospheric environment. Emmett et al. (2006) reported that the concentration of PFOA detected in the blood of people was 100 times higher than the PFOA in well water they were drinking.

Strynar et al. (2012) have made preliminary observations about the occurrence of the PFASs in soils in different parts of the world consisting of 10 samples from each of 6 nations (United States, China, Japan, Norway, Greece, and Mexico). For representing a wide range of chemical and physical characteristics for evaluation, care was taken to exclude soils from areas with known PFC contamination and/or in the vicinity of industries known to use PFASs. The most commonly detected PFCs were PFOS > PFOA > PFDoA > PFHpA > PFHxA. PFOS was measured above the LOQ in 48% of the samples, with a maximum concentration of 10.1 ng g^{-1}. The second most common compound was PFOA measured above the LOQ in 28% of the samples with the highest concentration of 31.7 ng g^{-1}. There was at least one PFC detected above the LOQ in 58.3% of the soil samples. The soils originating from the United States had quantifiable concentrations of PFCs in every sample (10/10) while only one of the ten soils from China had (1/10) quantifiable levels of PFCs. On a national basis, the number of soils (max n = 10) with quantifiable concentrations of PFCs were: USA (10) > Mexico (9) > Japan (7) > Norway (6) > Greece (2) > China (1). The results from the ten highest soil sample concentrations determined were summarized in **Table A1-4**.

In the sediments of Taihu Lake China, PFOA was detected 0.16 (0.02 – 0.52) ng g^{-1} (Yang et al., 2011) and had similar concentration levels with the results of Dianchi Lake China ND – 0.71 ng g^{-1} (Zhang et al., 2012). Slightly lower concentration was found in the Daliao River system with a mean concentration of 0.12 (0.09 – 0.17) ng g^{-1} dw (Bao et al., 2009) and in the rivers of San Francisco Bay, USA with a mean concentration of 0.25 (n.d. – 0.625) ng g^{-1} dw (Higgins et al., 2005). Higher concentration was reported in Kyoto River in Japan with the concentration of 1.30 – 3.90 ng g^{-1} dw (Senthilkumar et al., 2007). Much higher concentration was reported in Huangpu River in Shanghai (So et al., 2007) and Haihe River in Tianjin (F. Li et al., 2011), China, where a mean concentration of PFOA was found to be 34.60 (5.20 – 203) ng g^{-1} and 1.80 (0.90 – 3.70) ng g^{-1} dw, respectively. For the concentration of PFOS in sediments, it were reported with similar concentrations level in Taihu Lake China 0.11 (0.09 – 0.14) ng g^{-1} dw) (Yang et al., 2011), Roter Main River, Germany 0.201 (0.09 – 0.348) ng g^{-1} (Becker et al., 2008), Daliao River China 0.21 (0.06 – 0.37) ng g^{-1} (Bao et al., 2009), and Dianchi Lake China 0.07 – 0.83 ng g^{-1} (Zhang et al., 2012). Higher concentration was reported in the San Francisco Bay, USA (n.d. – 3.76 ng g^{-1} dw) (Higgins et al., 2005) Haihe River, China 5.20 (1.80 – 7.30) ng g^{-1} dw) (F. Li et al., 2011), and Orge River, France (mean concentration of 4.30 ng g^{-1} dw) (Labadie and Chevreuil, 2011). The results of those studies were summarized in **Table 2-2**.

Table 2-2 Concentrations of PFOS and PFOA in sediment (ng g^{-1} dw) samples around the world

Sampling	Year	n	Concentration		References
			PFOS	PFOA	
Yangtzi River Estuary, China	2008	4	72.9–536.7	NA	Pan and You, 2010
Orge River near Paris, France	2010	12	4.3 ± 0.3	<0.07	Labadie and Chevreuil, 2011
Estuarine and coastal areas of Korea	2008	12	Nd-2.0	Nd-2.0	Naile et al., 2010
Several River of Japan	2005	9	Nd-3.9	Nd-6.4	Senthilkumar et al., 2007
Daliao River system of northeast China	2008	10	0.06–0.37	0.09–0.17	Bao et al., 2009
San Francisco Bay, USA	2004	17	n.d.-3.76	n.d.-0.625	Higgins et al., 2005
Yangtzi River near Shanghai	2009	9	ND-0.46	0.20–0.64	Bao et al., 2010
Zhujiang River, Guangzhou, China	2009	22	n.d.–3.1	0.09–0.28	Bao et al., 2010
Taihu Lake, China	2009	32	0.06–0.31	<0.02–0.52	Yang et al., 2011
Haihe River, Tianjin China	2010	16	1.76–7.32	0.92–3.69	F. Li et al., 2011
Dianchi Lake, China	2010	26	0.07–0.83	ND-0.71	Zhang et al., 2012

2.4 Objectives of this study

The objectives of my studies are clarification of the situation of PFASs including PFAAs and their precursors. Some of these compounds are used in various uses, including commercial uses and essential uses, and some of them are under regulations. Conflicts have appeared between the benefit of using these compounds and the health risk of them. The management that considers the conflicts is needed, however the lack of information became the bottleneck of that. My studies focused on the PFAA precursors including the ones beyond regulation and will decompose into regulated PFAAs. I conducted the studies in urban river and domestic sewage treatment plant for clarifying the PFAAs and their precursors in the aquatic environment where are the linkage of human activity and nature system. The results of these studies are believed to providing baseline information on the occurrence and distribution of potential PFAA precursors for policy management.

The objectives were shown in Chapters:

Chapter 1 Review of the basic information of perfluoroalkyl acids and their precursors:

To review the base information of PFAAs and their precursors, especially information of PFAA precursors is limited. This information is for comprehensively understanding "what they are", "how they are used", and "How they are regulated now".

Chapter 2 Global pollution situation of PFAAs and limited information of PFAA precursors

To review the research results about PFAA and part of PFAA precursors in environment of the world prior to our study, for better understanding the macroscopic pollution situation of PFAAs and their precursor.

Chapter 3 Applying a new method for quantitation of precursors

The introduction of the detail information of the oxidation method which applied in our studies in Chapter 4 and 5, and of the test results of this method in our laboratory to show the applicability of the method for our study.

Chapter 4 Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent

To show the first date set of quantified concentration and compositions of total PFAA precursors in river water

To clarify the spatial distribution in the Tama River this composed of approximately 50% sewage treatment plant effluent

To investigate the contribution to PFAA precursors from domestic wastewater

To recommend the necessity of controlling the PFAA precursors, for more effectively controlling PFOS and PFOA in the aquatic environment

Chapter 5 Existence, mass balance and transformation of perfluoroalkyl acids and their precursors in sewage treatment plant

To investigate the impact of PFAA precursors in STP

To show the major sources of PFAA, by investigating the STP influent

To clarify the efficiency of removal of PFAA precursors by ozonation and chlorination treatment

To clarify the mass load for investigating the behavior of PFAA and PFAA precursors in STP

To clarify the PFASs removal ability of STP is underestimated or not
To provide base information for PFASs policy management

3. Applying a new method for quantitation of precursors

This study applied a recently developed method for investigating the impact from PFAA precursors. This chapter introduced the mechanism and testing results of this method. Following that, we conducted replication for testing this method before applying it to the environmental samples. The results of our testing were summarized in this chapter.

3.1 Introduction of the recently reported oxidation method

3.1.1 Mechanism

Tsao and Wilmarth (1959) showed that at pH values above 12, thermolysis rapidly converts the $S_2O_8^{2-}$ ion into the sulfate radical ($SO_4^{-\bullet}$), which is then quickly converted to $^{\bullet}OH$, shown by the reaction at blow. The PFAA precursors are converted to PFCAs with the corresponding perfluorinated chain length. Gauthier and Mabury (2005) and Plumlee et al. (2009) showed that the PFOA was not oxidized appreciably by the $^{\bullet}OH$.

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-\bullet} \qquad \text{(Reaction 1)}$$

$$SO_4^{-} + OH^{-} \rightarrow SO_4^{2-} + {}^{\bullet}OH \qquad \text{(Reaction 2)}$$

Based on the aforementioned observations, Houtz and Sedlak (2012) developed a new method for quantifying the total concentration of PFAA precursors in urban runoff. In brief, water samples were exposed to hydroxyl radicals ($^{\bullet}OH$) generated by the thermolysis of persulfate ($S_2O_8^{2-}$) under basic pH conditions. The PFAA precursors were transformed to PFCAs with the corresponding perfluorinated chain length, showed in Figure 3-1. The concentrations of the total PFAA precursors could be inferred by comparing the PFCA concentrations before and after oxidation.

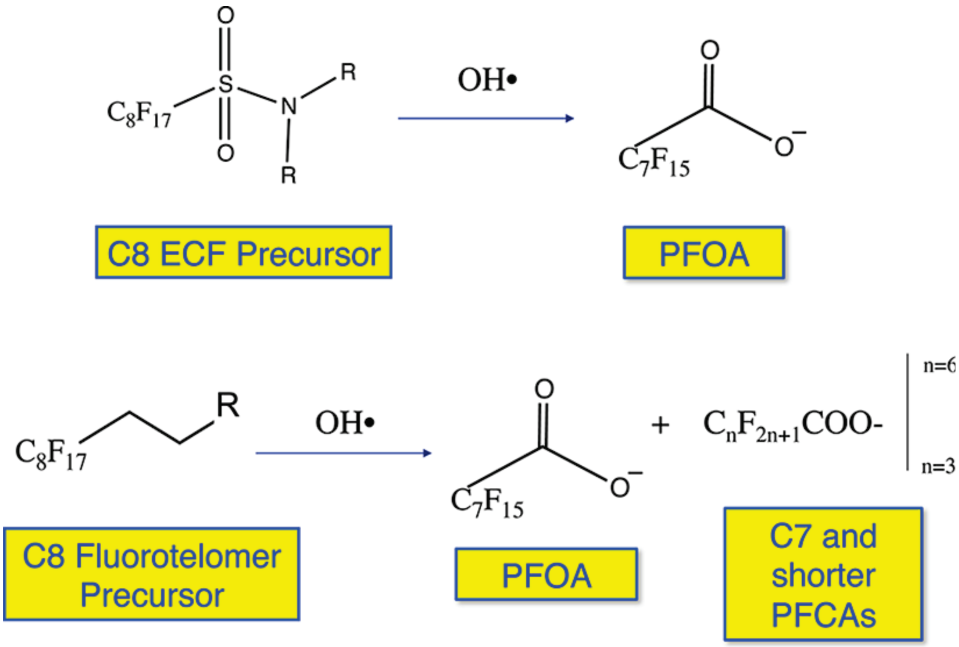


Figure 3-1 PFAA precursors were transformed to PFCAs with the corresponding perfluorinated chain length by hydroxyl radicals under pH > 12 conditions (Houtz and Sedlak, 2012)

3.1.2 *Effect from NaOH and heat to precursors*

Test result of Houtz and Sedlak (2012) confirmed that PFOS and PFOA will not be affected during oxidation treatment. Heated controls containing a suite of sulfonamide precursors without added persulfate or NaOH indicated no loss of precursors upon heating (**Figure 3-2**). The author also mentioned the presence of NaOH without added persulfate did not affect the concentrations of precursors during heating.

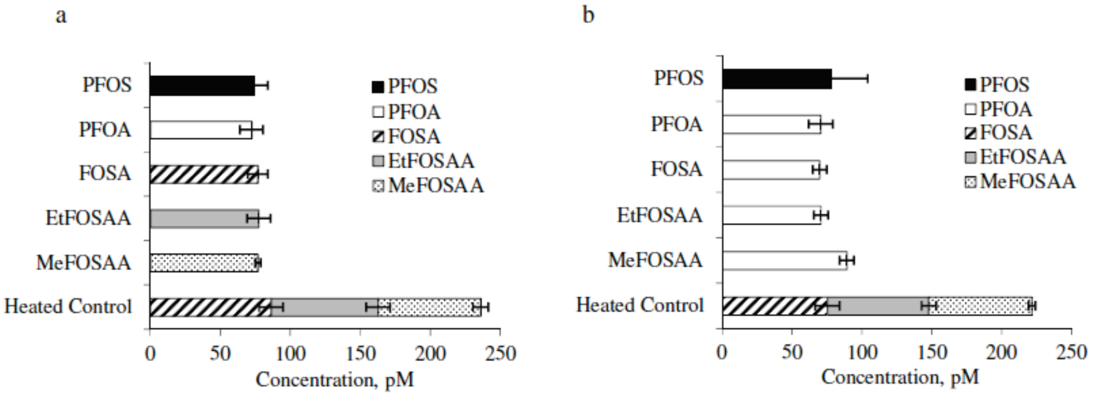


Figure 3-2 Concentrations of C8 perfluorooctane sulfonamide-containing precursors and PFOS and PFOA in individual HPLC-grade water reactors (n=4 per compound) before (a) and after (b) oxidation with 20 mM persulfate and 50 mM NaOH; heated precursor

controls did not contain persulfate and no NaOH was added (Houtz and Sedlak, 2012).

3.1.3 Effect of persulfate concentration on the conversion of PFCA precursors

This test was conducted by several HPLC water and stormwater samples subjected to treatment with aliquots of persulfate of different concentration. Concentration of PFCAs showed no change with different concentration of presulfate, indicating that excess persulfate did not affect the concentrations of PFCAs. To ensure complete conversion of precursors in stormwater samples, a total use of 60 mM of persulfate was decided in subsequent runoff samples.

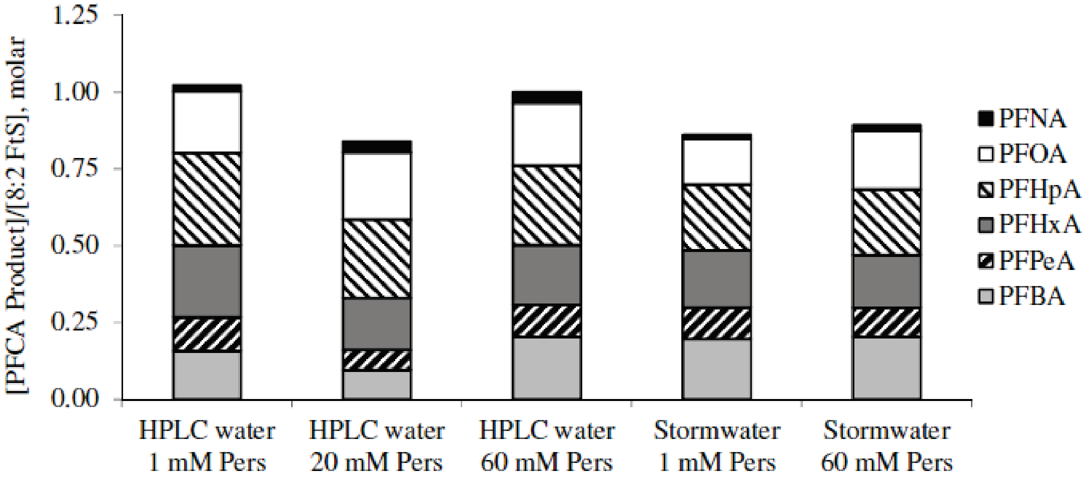


Figure 3-3 The distribution of PFCA products produced from the thermolysis of aqueous samples containing 10 nM 8:2 FtS under the following conditions: 8:2 FtS amended to HPLCgrade water containing 1 mM, 20 mM, and 60 mM persulfate and 8:2 FtS amended to a January 2011 stormwater sample containing 1 mM persulfate and 60 mM persulfate. TOC = 5 mg/L in stormwater (Houtz and Sedlak, 2012).

3.1.4 Reaction time required for complete oxidative conversion of PFCA precursors

The test of conversion of precursors into PFCAs was conducted by using N-MeFOSAA, FOSA, 6:2 FtS and 8:2 FtS in HPLC–grade water in the presence of 5 mM persulfate and 50 mM NaOH over time at 85 °C. N-MeFOSAA and FOSA was converted completely around 30 minutes (**Figure 3-4**) and 6:2 FtS and 8:2 FtS was around 40 minutes (**Figure 3-5**). This indicated conversion of the precursors will be completed within 1 hour. It is considered that reaction time of 6 hours was decided in subsequent tests on runoff samples to ensure complete conversion of precursors in stormwater samples.

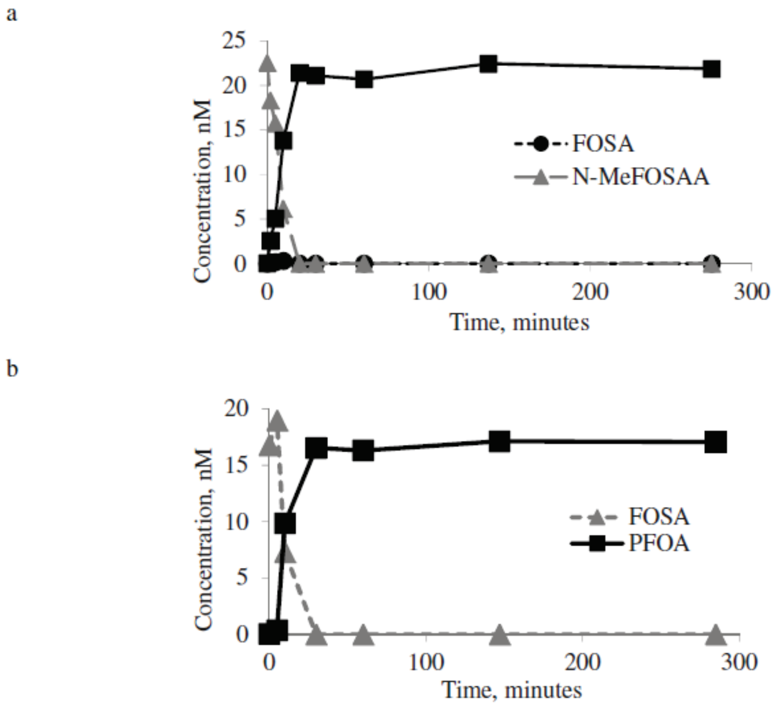


Figure 3-4 Conversion of *N*-MeFOSAA (a) and FOSA (b) in HPLC–grade water in the presence of 5 mM persulfate and 50 mM NaOH over time at 85 °C (Houtz and Sedlak, 2012)

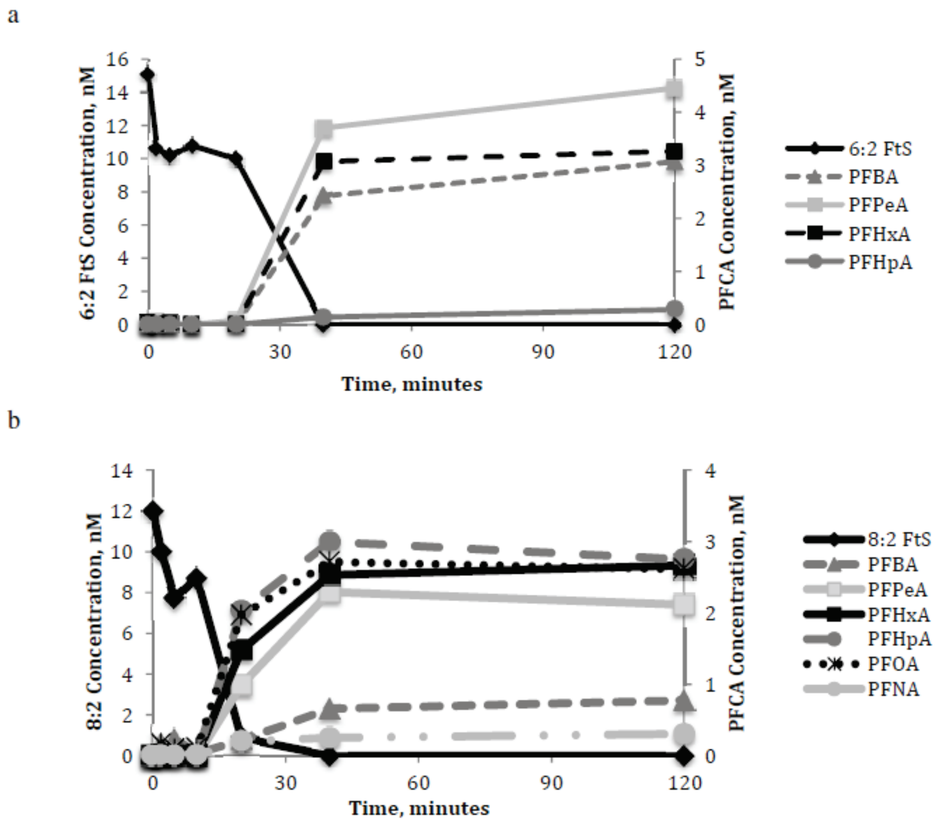


Figure 3-5 Conversion of 6:2 FtS (a) and 8:2 FtS (b) in HPLC –grade water in the presence of 5 mM persulfate and 50 mM NaOH over time at 85 °C (Houtz and Sedlak, 2012).

3.2 Test for the oxidation method by this study

To conduct this oxidation method, only water bath and reagent are needed. In brief, unfiltered water samples were transferred to HDPE bottles. Sample was added with potassium persulfate (60 mM) and NaOH (150 mM). The HDPE bottles were placed in a temperature–controlled oil bath at 85 °C for 6 h, as shown in **Figure 3-6**. Then, the samples were cooled to room temperature in an ice bath prior to pH adjustment. The pH of the samples was adjusted between 5 and 9 by concentrated HCl prior to the extraction.

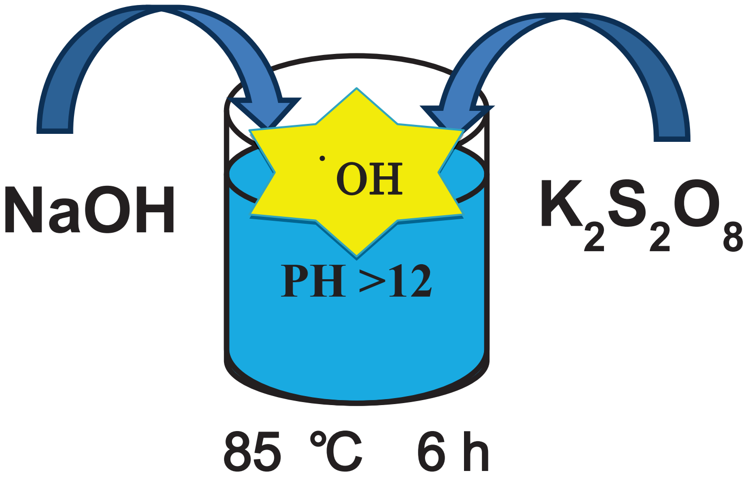


Figure 3-6 The method for oxidation of PFAA precursors

For testing the oxidation method, we conducted test experiments by using PFAA precursors in the presence of 60 mM persulfate and 150 mM NaOH prior to oxidation. Heated controls containing a suite of sulfonamide precursors without added persulfate indicated no loss of precursors upon heating.

3.2.1 Confirmation of the time of oxidative conversion

The essential time for oxidation treatment were tested by using mixture of 8:2 FTCA, 8:2 FTUCA, NMeFOSAA, NEtFOSAA and FOSA in ultra-pure water in the presence of 60 mM persulfate and 150 mM NaOH over time (30, 60, 90, 120 and 300 minutes, respectively) at 85 °C. The yielded PFCAs were analyzed, result showed in **Figure 3-7**, indicating all the precursors completed conversion within 1 hour. Six hours of oxidation treatment should be enough to ensure complete conversion of precursors in samples of this study.

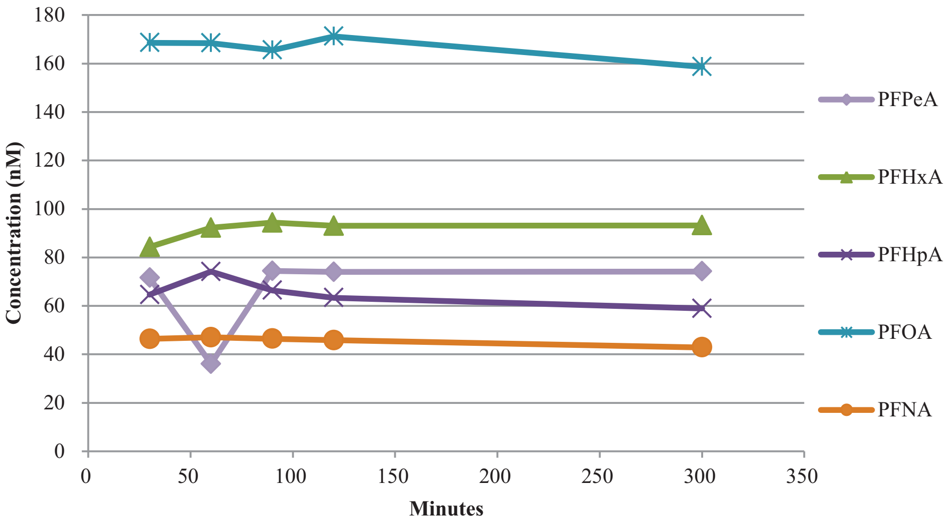


Figure 3-7 Yield of PFCA by oxidation treatment from PFAA precursors mixture (8:2 FTCA, 8:2 FTUCA, NMeFOSAA, NEtFOSAA and FOSA) in ultra-pure water in the presence of 50 mM persulfate and 150 mM NaOH over time at 85 °C.

3.2.2 Confirmation of oxidative conversion

Oxidation of solutions of the precursors (n=3), NMeFOSAA, 6:2 FTCA, 8:2 FTCA, di-SAmPAP, each produced a suite of PFCAs of varying chain lengths (**Table 3-1, Figure 3-8**). The sum of the PFCAs detected after complete oxidation of each precursor compound accounted 107%±3%, 85%± %, 105%± 1%, 35%± 35%.

Similar to the result by the method developed by Houtz and Sedlak (2012), C8 sulfonamides type precursors yielded PFOA nearly 100%, and n:2 fluorotelomer precursors yield a mixture of C4 to C(n + 1) PFCAs.

Houtz and Sedlak (2012) used n:2 Fts and 8:2 diPAP type fluorotelomer precursors which yielded 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 (**Table 3-1**). Although n:2 FTCA and n:2 Fts were fluorotelomers, they may have much different property, e.g. n:2 FTCA was reported as intermediate environmental transformation product while n:2 Fts was reported to be used as surfactant and environmental transformation product (Buck et al., 2011).

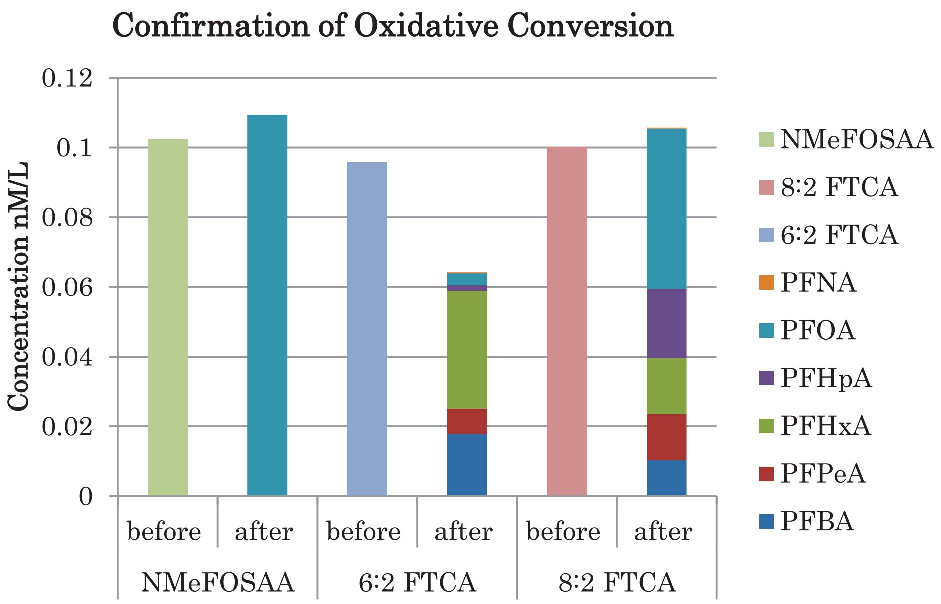


Figure 3-8 Confirmation of oxidative conversion of 3 PFAA precursors (n=3) to PFCAs.

Table 3-1 Confirmation of molar yields of PFCAs from 3 PFAA precursors (n=3), thermolyzed in the presence of persulfate.

Starting precursor compound (n=3)	ΔPFBA/ [precursor]	ΔPFPeA/ [precursor]	ΔPFHxA/ [precursor]	ΔPFHpA/ [precursor]	ΔPFOA/ [precursor]	ΔPFNA/ [precursor]	Total
NMeFOSAA					107% ±07		107% ±07
6:2 FTCA	19% ±9%	14% ±4%	50% ±0%	2% ±%%			85% ±5%
8:2 FTCA	10% ±0%	13% ±3%	16% ±6%	20% ±0%	46% ±6%	0% ±0.2%	105% ±05%

3.2.3 Blank for operation control of oxidation treatment

Heated blanks are used as the operation control of oxidation treatment and solid-phase extract for analysis PFCAs yielded from precursors. However, PFCAs was detected (> 5 ng L^{-1}) from heated blanks, while low concentrations (< 0.5 ng L^{-1}) were detected from solid-phase extraction, indicating there are some contamination in the oxidation treatment operation. Therefore, some tests were conducted to search the cause of the contamination.

First test was the comparison of yielded PFCAs by using the blanks with or without heat and oxidation agents in oxidation treatment (n=3). The results showed that the blank detected with higher concentration of PFCAs (>5 ng L^{-1}) are with heat and oxidation agents, which indicted the detected PFCAs were yielded from PFAA precursors existing in oxidation agents or ultra-pure water (**Figure 3-9**).

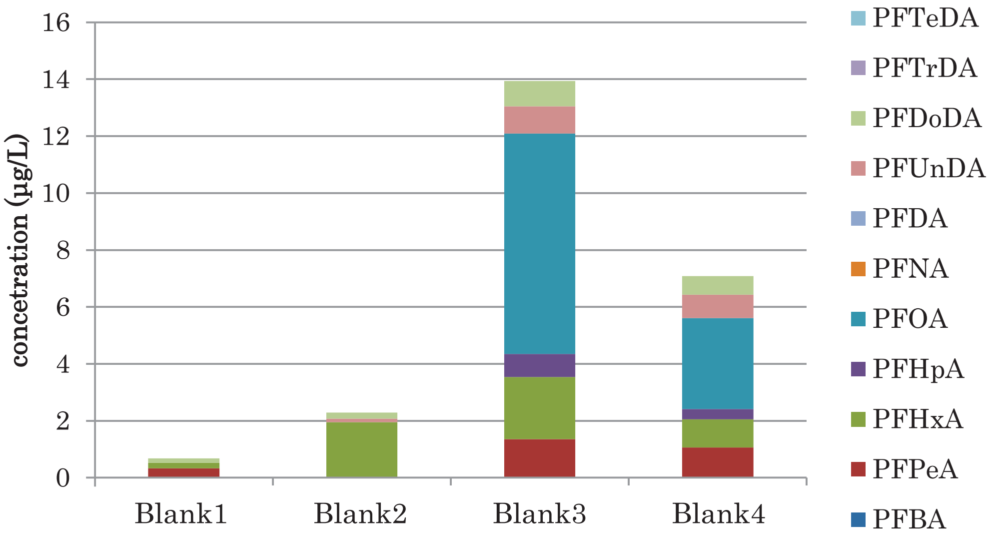


Figure 3-9 Comparison of yielded PFCAs from precursors as contamination in heated blanks (n=3).

Blank 1: Ultra-pure water with no reagent & no heat

Blank 2: Ultra-pure water with reagent & no heat

Blank 3: Ultra-pure water with reagent & heat

Blank 4: Bottled pure water with reagent & heat

The second blank tests were conducted to check the contamination in oxidation agents and ultra-pure water (**Figure 3-10**). Blank B2 and B4 had one more oxidation treatment than blank B1 and B3, for checking the contamination from oxidation treatment. The results showed that PFCAs were detected in all the blanks. In the blanks with or without additional oxidation, PFCAs were detected in the same concentration level, indicating much lower contamination (<1 ~ >2.5 ng L^{-1}) in oxidation agents, which are added into samples for oxidation treatment, than the contamination from ultra-pure water. For the samples added with ultra-pure water during the oxidation treatment, the contaminations from water were excluded. Therefore, we analyzed once-oxidized water and twice-oxidized water then used the increased part as operation control of oxidation treatment for each batch analysis.

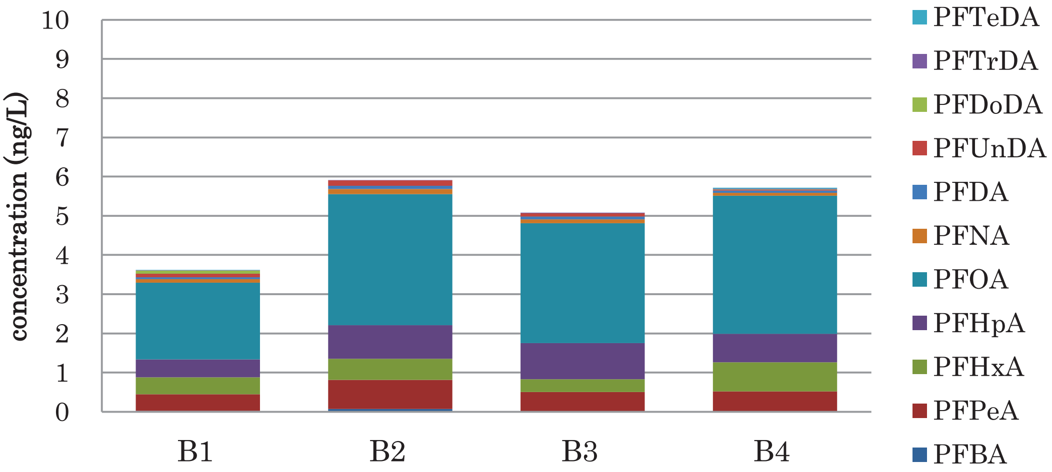


Figure 3-10 Comparison of yielded PFCAs from precursors as contamination in blanks using different ultra- pure water and oxidation agents (n=3)

B1: blank oxidized once & using new oxidation agents

B2: blank oxidized twice& using new oxidation agents

B3: blank oxidized once & using old oxidation agents

B4: blank oxidized twice & using old oxidation agents

3.3 Conclusion

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. Houtz and Sedlak (2012) used n:2 Fts and 8:2 diPAP type fluorotelomers which yielded C(n − 1) PFCA as the most abundant product followed by C(n) PFCA. In our study the most dominated product was C(n) PFCA from n:2 FTCA. This difference may not affect the estimation of PFAA precursors significantly in this study.

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

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

4. Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent

4.1 Introduction

Limited information is available on the PFAA precursors which decompose into per- and polyfluorinated alkyl substances. Thus, in this study, we studied the total PFAA precursor concentrations in the Tama River, which is one of the major rivers in Tokyo. According to the Bureau of Sewerage, Tokyo Metropolitan Government (2012), up to 50% of the river water was composed of sewage treatment plant (STP) effluents. Hence, we applied the proposed method to demonstrate the increase of PFCAs by the oxidation of PFAA precursors (Δ[PFCAs]). This method converts both PFCA and PFSA precursors into PFCAs, which is a potential source of PFAAs in river water. We showed the spatial distribution of PFAAs, including the Δ[PFCAs] from the PFAA precursors in urban river water and STP effluents. The importance of these PFAA precursors as a potential source of PFAA was determined by estimating the ratio of the PFCAs formed against PFAAs originally present ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}] / \Sigma[\text{PFAAs}]_{\text{before oxidation}}$), and the importance of controlling the PFAA precursors was examined. To our knowledge, this is the first study that quantified the potential of PFCA forming in river water and showed the spatial distribution of potential concentration of PFAAs precursors in urban river water and STP effluent samples. This study also provides baseline information on the occurrence and distribution of potential PFAA precursors.

4.2 Materials and Methods

4.2.1 Sample collection

Sampling was conducted in the Tama River basin (**Figure 4-1**), and according to the Bureau of Sewerage, Tokyo Metropolitan Government (2012), the middle and downstream water reportedly consisted of approximately 50% STP effluents. Twelve river water samples and 3 STP effluent samples were collected from upstream to downstream sites of the main river and its upstream tributaries on 7th Oct. 2013 (**Table** 4-1). There was no rain on and before the day of sampling. Therefore, the influence of rainfall on the water flow was found to be minimal. Most of the river water samples were collected from the center of the river. The STP effluent samples were collected from the outflow of the plant connected to the river. Field records were made during the sampling, including pH, EC, color etc. showed in **Table A1-6**. The collected samples were decanted into methanol-rinsed 3 L high density polyethylene (HDPE) bottles and were kept in ice for up to 12 h. Upon arrival at the laboratory, the samples were stored at 4 °C until analysis. Care was taken to avoid the usage of any PTFE–coated materials.

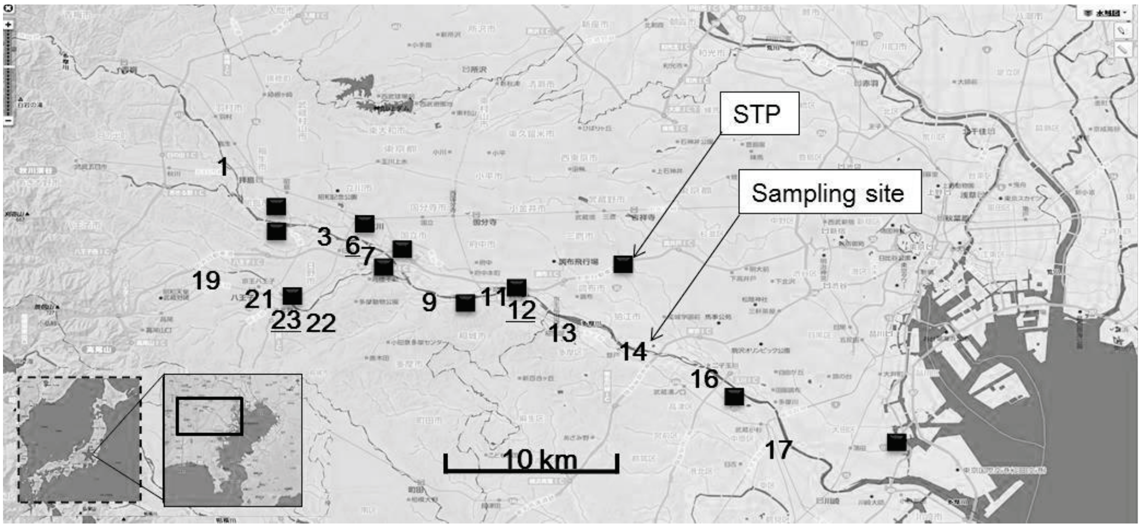


Figure 4-1 Map of the Tama River (Tokyo) showing sampling locations.
Boxes represent sewage treatment plants (STPs). The numbers with underline represent the sampling sites for STP effluents, and the others represent the sampling sites for river water.

Table 4-1 Information of sampling sites

Sampling site	Type of Sampling site	Sampling time	Sampling place in river	Location in World Geodetic System
1	Main river	13:30	center	35.732429, 139.32106
3	Main river	14:05	center	35.694145, 139.373864
7	Main river	15:52	left	35.67391, 139.427229
9	Main river	16:15	center	35.658534, 139.439353
11	Main river	16:40	center	35.652414, 139.488169
13	Main river	17:19	center	35.64408, 139.525613
14	Main river	17:53	center	35.62507, 139.568593
16	Main river	18:43	right	35.600297, 139.638955
17	Main river	19:10	center	35.58545, 139.668808
19	Branch river	13:03	center	35.680324, 139.300136
21	Branch river	12:08	center	35.666989, 139.337866
22	Branch river	11:45	center	35.655821, 139.355996
23	STP effluent flowing into a branch river	11:24	center	35.655126, 139.355167
6	STP effluent flowing into the main river	14:39	center	35.685178, 139.410321
12	STP effluent flowing into the main river	17:06	center	35.654193, 139.512459

4.2.2 Oxidation of PFAA precursors

The oxidation treatment method, mentioned in Chapter 3, was used for oxidizing PFAA precursors in river samples. 125 mL unfiltered water samples were transferred to 125 mL HDPE bottles. One sample from each site was subsampled in triplicate (n=3) and was added with 2 g (60 mM) of potassium persulfate and 1.9 mL of 10 N NaOH (150 mM). The HDPE bottles were placed in a temperature–controlled oil bath (Personal H–10 SH; TAITEC, Saitama, Japan) at 85 °C for 6 h. Then, the samples were cooled to room temperature in an ice bath. The pH of the samples was adjusted between 5 and 9 by concentrated HCl prior to the extraction.

Flow of oxidation treatment:

Unfiltered water into 125ml bottle (in triplicate)

↓←Add 2 g (60 mM) of potassium persulfate and 1.9 mL of 10 N NaOH (150

mM) (pH above 12)
↓ Shake the mixture gently
↓ place the bottle into oil bath 85 °C, 6 hour
Cool down ← adjust pH between 5～9 by HCL

4.2.3 Extraction and analysis

Extractions of river samples were conducted after oxidation for "After oxidation group" and directly for "Before oxidation group" as showed in **Figure 4-2**.

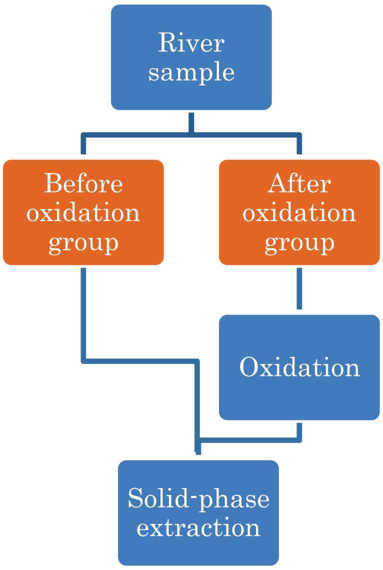


Figure 4-2 Analysis flow for river sample

Isotope–labeled surrogate standards (**Table 4-4**) were added to the samples and blanks prior to the extraction in order to correct their recovery rates for each batch analysis. The original samples (before oxidation) and the samples obtained after the oxidation treatment were subjected to solid phase extraction (SPE) (Oasis WAX SPE cartridges, 6 cm^3, 150 mg, 30 μm; Waters, Milford, MA) which was a modified procedure of that reported by Taniyasu et al. (2005). The cartridges were preconditioned with 4 mL of 0.1% NH_4OH (in CH_3OH), CH_3OH, and ultra–pure water, respectively. Both the original and oxidized samples were pulled through the SPE cartridges under vacuum using a gum tube connected to a SPE manifold (GL Sciences, Tokyo, Japan). After sample loading, the HDPE bottles were rinsed with 4 mL of 50% CH_3OH in ultra–pure water, which was also pulled through the SPE cartridges for extraction. After extraction, the cartridges were rinsed with 4 mL of ultra–pure water and dried.

Following the drying step, the SPE cartridges were eluted with 2 mL of CH_3OH followed by 2 mL of 0.1% NH_4OH in CH_3OH. The eluate was evaporated to 400 μL to avoid the loss of the target compounds during the drying process. The concentrations of the 14 PFAAs and 3 precursors of PFOS and PFOA (**Table 4-4**) were quantified by high performance liquid chromatography (HPLC, Agilent 1100LC, Agilent Technologies, Palo Alto, CA, USA) interfaced with a tandem mass spectrometer (MS/MS; Micromass Quattro, Waters, Milford, MA, USA).

Flow of solid-phase extraction:

Sample
↓ ←Inject with isotopically labeled surrogate standards 20uL of 200 ug/L
↓ ←Load sample to solid phase extraction cartridge (Oasis Wax 6 cm3, 150 mg, 30 um)
↓ Rinse bottle
↓ Dry cartridge
↓ Elute analyte from cartridge
↓ Concentrate the elutes
↓ Filtration
Analyze by LC-MSMS

4.2.4 Quantitation

Quantitation was conducted by use HPLC and MS/MS. The information the methods of HPLC (**Figure 4-3, Table 4-2**) and MS/MS are showed blow (**Table 4-3, Table 4-4):**

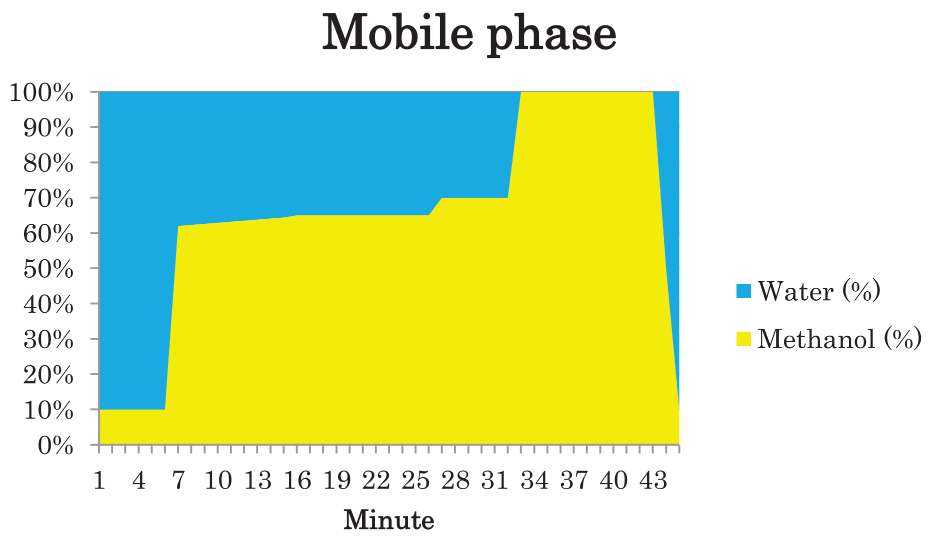


Figure 4-3 Gradient of Mobile phase in HPLC over time for analyzing

Table 4-2 Condition of HPLC analysis

HPLC	Condition
Instrument	:HP1100 (Agilent)
Guard column	:None
Column	:Zorbax XDB C-18 (150 mm × 2.1 mm, aperture size 5 μm)
Mobile Phase A	:10mM Ammonium acetate aq.
Mobile Phase B	:Methanol
Gradient	:Time (min) 0 - 5 - 15 - 25 - 31 - 42 - 44.5
	:B(%) 10 - 62 - 65 - 70 - 100 - 50 - 10
Flow Rate	:0.2 ml/min
Column Temp.	:40 ˚C
Injection Volume.	:10 μL

Table 4-3 Condition of MS/MS analysis

MS/MS	Condition
Instrument	:Quattro Ultima
Ionization Mode	:ESI
Capillary Voltage	:2.5 kV
Scan Type	:MRM

Table 4-4 MS Parameters used for individual target compounds

Native standard	precursor ion	product ion	cone (V)	collision (eV)	Purity	Labeled standard	precursor ion	product ion	cone (V)	collision (eV)	Purity
PFBA	212.7	168.7	35	13	> 98%	[^{13}C$_2$]PFBA	216.7	171.7	35	13	> 98%
PFPeA	262.7	218.7	35	9	> 98%	[^{13}C$_2$]PFHxA	314.7	269.6	35	9	> 98%
PFHxA	312.7	268.7	35	10	> 98%						
PFHpA	362.7	318.7	35	10	> 98%						
PFOA	412.7	368.7	35	10	> 98%	[^{13}C$_4$]PFOA	416.7	371.6	35	10	> 98%
PFNA	462.7	418.7	35	10	> 98%						
PFDA	512.7	468.7	35	11	> 98%						
PFUnDA	562.7	518.7	35	11	> 98%	[^{13}C$_2$]PFDoDA	614.6	569.6	45	13	> 98%
PFDoDA	612.7	568.7	35	13	> 98%						
PFTrDA	662.7	618.7	35	13	> 98%						
PFTeDA	712.7	668.7	35	13	> 98%						
PFBS	298.7	98.7	35	25	> 98%	[^{13}C$_4$]PFOS	502.7	98.7	35	35	> 98%
PFHxS	398.7	98.7	35	35	> 98%						
PFOS	498.7	98.7	35	35	> 98%						
PFDS	598.7	98.7	35	45	> 98%						
8:2 FTCA	476.7	392.7	35	18	> 98%	[^{13}C$_2$]8:2 FTCA	478.7	393.6	35	18	> 98%
PFHxPA	398.7	78.7	35	25	> 98%	Cl-PFHxPA	414.7	78.7	35	30	> 98%
PFOPA	498.7	78.7	35	35	> 98%						
FOSA	497.7	77.7	35	30	> 98%	[^{13}C$_2$]FOSA	505.9	77.9	35	30	> 98%
SAmPAP	629.7	58.7	35	40	90%	[^{13}C$_2$]8:2diPAP	993	545	35	25	>98%

4.2.5 Estimation of PFAA precursors

The produced Δ[PFCAs] values upon oxidation were used for estimating the total concentrations of the PFAA precursors. The maximum and minimum concentrations of the C8 and C6 PFAA precursors (as PFOA and PFHxA, respectively) were calculated, and from these concentrations, the probable PFAA precursors were assessed by the method developed by Houtz and Sedlak (2012). However, it is difficult to perform oxidation tests for all the available precursors, and hence, the estimation of the total precursor concentration cannot avoid uncertainty. Therefore, we considered increased concentration of PFCAs (by oxidation) as the indicator of PFAA precursor concentrations in water samples.

4.2.6 Quality assurance/Quality control

4.2.6.1 Method Recovery test

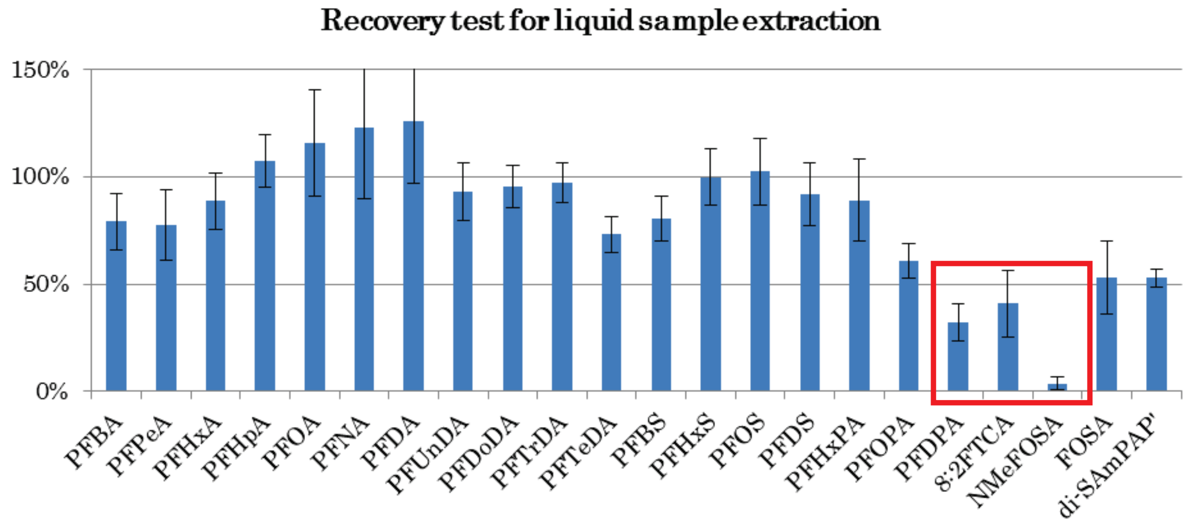


Figure 4-4 Recovery rates of spiked chemicals for solid-phase extraction in water sample (n=3).
Error bars represent the standard deviation.

The recovery of extraction of target compounds in samples was tested. The test was conducted by using water sample and divided it into two groups: one was spiked with standard mixture the anther was not. By comparing the difference of the concentrations of those two groups, the actual detected concentration of spiked standard can be calculated. The final concentration of spiked standard after concentrating will be 10 μg/L when no loss occurred.

The recoveries of target compounds except 8:2 FTCA, PFDPA and NMeFOSA ranged 53 - 126%. Due to the low recoveries of PFDPA (32%) and NMeFOSA (4%) in this method, these compounds were not quantitated. For 8:2 FTCA (41%), although its recovery was lower than 50%, we quantitated it as a reference value.

4.2.6.2 Blank for operation control

As tested in section "3.2.3", increased concentration of the PFCAs such as PFBA and PFOA were observed in the blank tests conducted with ultra–pure water. Therefore, the blanks were oxidized twice and the further increase in the PFCA concentrations was determined. The contamination from pure water and that from oxidation process (oxidizing reagent solution) could be distinguished from the above tests. As pure water was not used during the sample analysis, the blank values obtained in the oxidation process were used to correct the measured values for each batch analysis.

Blanks blow were used for every analysis batch:
Operation blank for oxidation treatment (n = 3 sets of once-oxidated and twice-oxidated water)
Operation blank for solid-phase extraction (n = 3)
Blank for LC-MSMS (n = 2)

4.2.6.3 Method validation

Most of the samples were analyzed in triplicate and the median values were used for further studies because outliers were sometimes observed among the triplicate values.

Bottles were invert 3 times for subsampling from sampling bottles.

The LOD was calculated by using the 3 × value of signal / noise (S/N). The detected concentrations lower than LOD were regarded as not detected.

Including the spiked sample recovery test, blank test, direct extraction and oxidation treatment mention above, all the samples was finished within 21 days after sampling day.

4.2.6.4 Statistical methods

Statistical significance was computed using the *t* test. Welch's t test was used to determine the difference in the ratios of Δ[PFCA] to $[\mathrm{PFCAs}]_{\text{before oxidation}}$ in river water and STP effluent samples. Paired samples *t* test was used to test the difference in the total concentrations of the paired samples before and after oxidation, and to determine the ratios of Δ[PFCA] to $[\mathrm{PFCAs}]_{\text{before oxidation}}$ for individual PFCA in upstream, downstream, and STP effluent samples. The difference was deemed to be significant when the p was < 0.05.

4.4 Results and Discussion

4.4.1 Concentration of PFAAs and their precursors before oxidation

The concentration of the 15 PFAA and 3 PFAA precursors before oxidation in the river water samples were 3.9–38 ng L^{-1} (average = 23 ng L^{-1}) (**Table A1-7**). The most prevalent PFAAs in the river water samples were PFOS (0.54–8.0 ng L^{-1}, average = 5.1 ng L^{-1}), PFOA (0.59–5.7 ng L^{-1}, average = 3.7 ng L^{-1}), PFHxA (0.25–5.0 ng L^{-1}, average = 3.0 ng L^{-1}), and perfluorononanoate (PFNA) (0.26–5.0 ng L^{-1}, average = 2.8 ng L^{-1}). A study conducted by Zushi et al. (2011) reported that in 2009 two sites (a site close to site 17 and a site same as site 13 of this study) exhibited a PFOS concentration of 20 and 18 ng L^{-1}, PFOA concentration of 12 and 9 ng L^{-1}, and PFNA concentration of 64 and 58 ng L^{-1}. These previously reported concentrations were higher by more than two times for PFOS and PFOA, and around 10 times for PFNA than those in sites 17 and 13 of this study. Murakami et al. (2008) reported that the high PFNA concentrations were due to the industrial production of PFCAs in Japan. In this study, the lower concentrations of PFNA were observed, which indicated that its use had decreased because of increased focus on PFOS, PFOA and their related compounds.

In the spatial distribution of the Tama River, an increase in the total concentration of the PFAAs and its precursors before oxidation was observed from sampling sites 1 to 17 of the main river and 19 to 22 of its branch (**Figure 4-5a**). Sites 1 (3.9 ng L^{-1}) and 19 (4.4 ng L^{-1}) were located at the upstream of the main river and one main branch, respectively and they exhibited the lowest total concentrations in each stream. In the study by Zushi et al. (2011), a similar concentration level (2.7 ng L^{-1}) was observed in the site that was approximately 8 km upstream of site 1 in this study. According to Zushi and Masunaga (2011), the increase in the total concentration of the PFAAs was observed at sites where the population density was higher than that in the upper stream. This is explained by the high correlation between the dissolved perfluoroalkyl compound concentrations and population density.

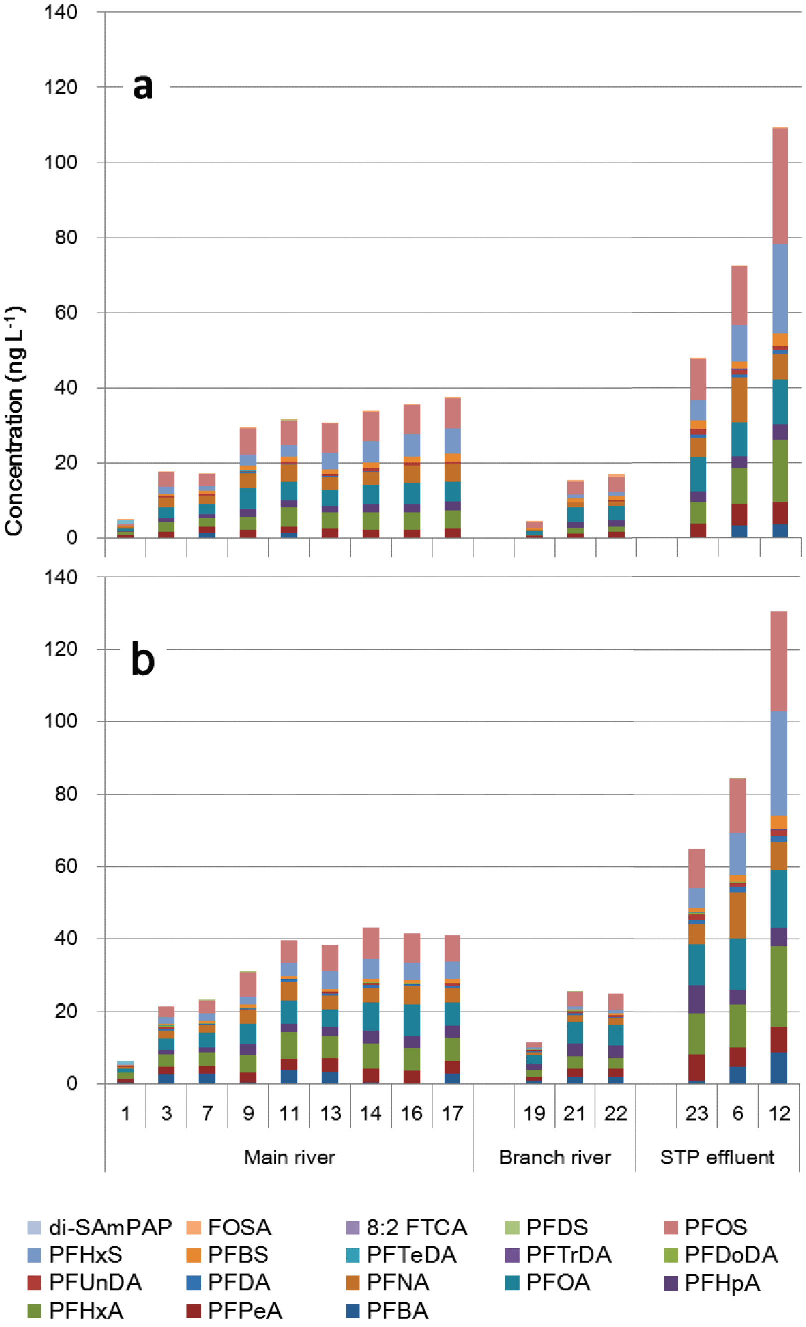


Figure 4-5 Concentration of perfluoroalkyl acids (PFAAs) before and after oxidation. a) PFAAs (n = 16) and their precursors (n = 3) before oxidation in all sampling sites. b) PFAAs and their precursors after oxidation in all sampling sites.

The total concentrations of the 15 PFAAs and 3 PFAA precursors before oxidation in the STP effluent samples (sites 23, 6 and 12) were 48–109 ng L^{-1} (average = 76 ng L^{-1}) (**Figure 4-5a**). The most prevalent PFAAs were PFOS (11–31 ng L^{-1}, average = 19 ng L^{-1}), PFHxS (5.6–24 ng L^{-1}, average = 13 ng L^{-1}), PFHxA (5.8–17 ng L^{-1}, average = 11 ng L^{-1}), and PFOA (9.0–12 ng L^{-1} , average = 10 ng L^{-1}). The comparison of median concentrations showed that the concentrations of the PFAAs in the effluent samples were 2 to 5 times higher than those in the river water samples. Among all the samples, site 12 showed the highest total concentration (109 ng L^{-1}) for both the river water and STP effluent samples. Zushi et al. (2011) showed that the effluents of STPs which were located in different rivers in Tokyo had higher total concentrations than the river water. Based on the above results, it was concluded that the STP effluents were the larger source of PFAAs in the aquatic environment.

The total concentrations of the C8 PFAA precursors, namely 8:2 fluorotelomer carboxylic acid, *N*-methyl perfluorooctane sulfonamide (NMeFOSA), FOSA, and di-perfluorooctane sulfonamidoethanol-based phosphate measured prior to oxidation were 0.04–0.61 ng L^{-1} and the concentrations were much lower than those of the total concentrations of the PFCAs and PFSAs (**Table A1-7**). Lower total concentrations of the precursors were observed in the effluent (average = 0.09 ng L^{-1}) than in river water (average = 0.23 ng L^{-1}) samples. Among the analyzed PFAA precursors, the FOSA was the most commonly detected compound with concentrations as high as 0.61 ng L^{-1} (site 22). The other three C8 precursors were not detected (< 0.06 ng L^{-1}) in the samples except for NMeFOSA, which was detected at site 1. The low concentrations of the PFAA precursors and a relatively high concentration of FOSA were observed in studies by Motegi et al. (2013) and Zushi et al. (2011), which were conducted on the major rivers in Tokyo. Therefore, it was concluded that the use of PFNA decreased out and no remarkable changes were observed in the concentration of routinely analyzed C8 precursors between 2009 and 2013.

4.4.2 Concentration of PFAA precursors estimated by the oxidation of samples

Oxidation treatment of the river water samples produced a considerable amount of the PFCAs which led to the increase of total concentrations of the PFAAs (**Table A1-7** and **Figure 4-5b**). The oxidation method converted both the PFCA and PFSA precursors into PFCAs, which was a potential source of PFAAs in river water. The concentrations of the PFCAs after oxidation treatment included the originally existed PFCAs as well as those formed from the oxidation of the precursors (Δ[PFCAs]) (**Figure 4-6**). The total concentration of the PFCAs with 4–12 perfluoroalkyl carbon chains which were produced upon oxidation ($\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$) were 2.1 to 19 ng L^{-1} (average = 8.8 ng L^{-1}, **Table 4-5**). As reported by Houtz and Sedlak (2012), the PFCAs with carbon chains having more than 12 carbons did not increase significantly, and the sulfonates were not formed from the oxidation of the PFAA precursors. The three most increased PFCAs were of the following order: PFHxA (average Δ[PFHxA] = 2.1 ng L^{-1}) > PFOA (average Δ[PFOA]= 1.9 ng L^{-1}) > PFBA (average Δ[PFBA] = 1.8 ng L^{-1}) (**Table 4-5**). The total concentrations of PFAAs were significantly different before and after oxidation ($p < 0.05$), indicating the existence of PFAA precursors in the environment. Notably, the observed large percentage of Δ[PFBA] among $\Delta[\text{PFCA}]_{\text{C4-C12}}$ may be due to its shorter carbon chain which can be formed from various precursors with longer carbon chains (**Figure 4-6**). In most of the samples, the $\Delta[\text{PFCA}]_{\text{C4-C12}}$ by oxidation could not be explained by the degradation of the four PFAA precursors measured before oxidation.

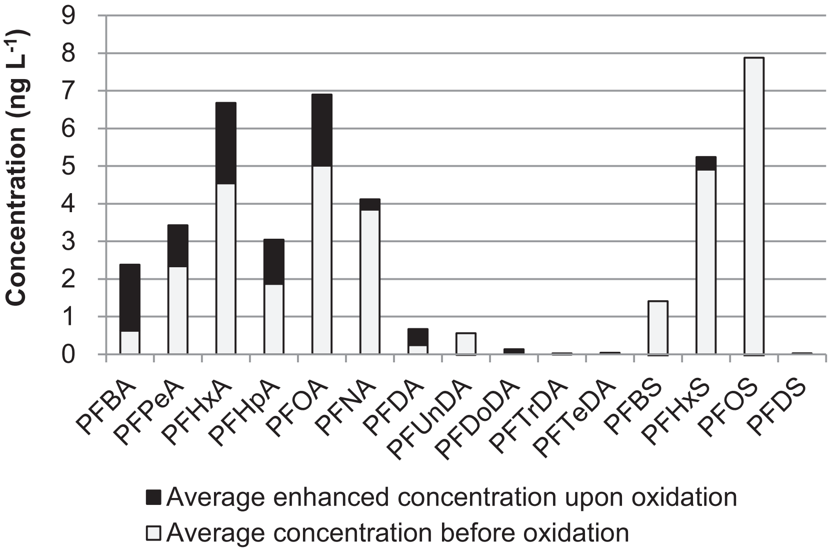


Figure 4-6 PFAA before and after oxidation, gray bar shows average concentration of all sites before oxidation and black bar shows the elevated part by oxidation.

The spatial distribution of PFCA formation potential in river water is shown in **Figure 4-7.** The increased concentrations of the PFCAs by oxidation ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]$) increased in the upstream along the river flow but did not change much in the middle to lower reach of the river. The concentrations of $\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]$ were 2.1–9.5 ng L^{-1}, and the average concentrations of the upstream and downstream sites were 6.5 and 8.1 ng L^{-1}, respectively (**Table 4-5**). At the sampling site 1, which was the most upstream site of the main river, the lowest concentrations of $\Sigma\Delta[\text{PFCAs}_{\text{C4-C12}}]$ were observed, while the highest concentrations were observed in site 14 at the downstream of the main river. These results indicate that increased concentrations of the PFAA precursors exist in the middle to lower reach than the upstream of the river. While the concentrations of $\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]$ increased in the lower reach of the main river (**Figure 4-7**), the ratios of the PFCAs formed against PFAAs originally present ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]$ / $\Sigma[\text{PFAAs}]_{\text{before oxidation}}$) were much higher in the upstream of the main

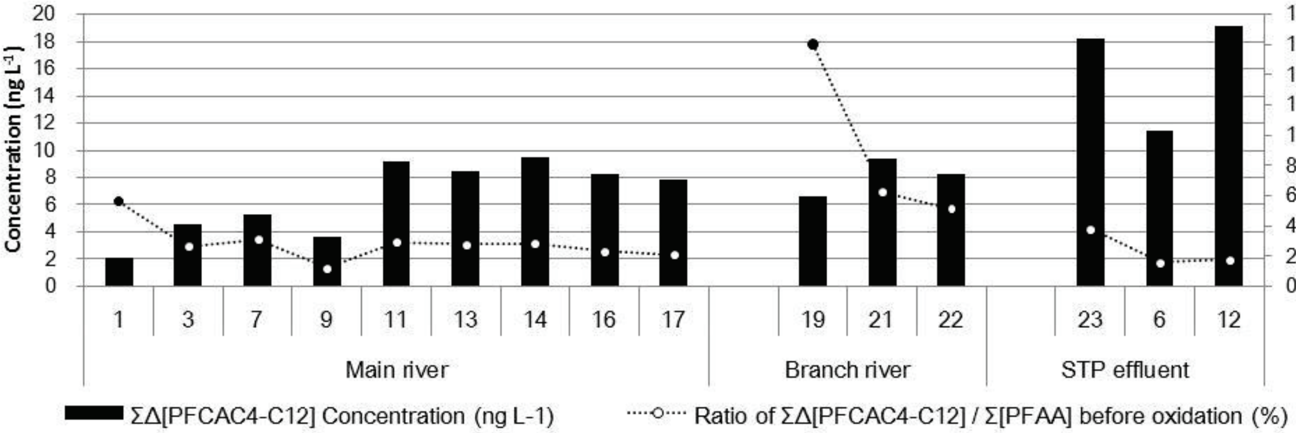


Figure 4-7 Total perfluorinated carboxylic acid concentrations upon oxidation (ng L^{-1}) ($\Sigma\Delta[PFCA_{C4\text{-}C12}]$) and the ratio (%) of their concentration to that of the total perfluoroalkyl acids before oxidation ($\Sigma[PFAA]_{\text{before oxidation}}$).

Table 4-5 Increased concentration of perfluorinated carboxylic acids (PFCAs, ng L^{-1}) upon oxidation in samples, the ratio of increased total PFCAs to perfluoroalkyl acids (ΣPFAAs) before oxidation, and the ratio of increased individual PFCA to PFCA before oxidation

River water / STP effluent	Main / Branch	Increased concentration of PFCAs												Ratio of ΣΔ[PFCA $_{C4-C12}$] / Σ[PFAAs] $_{before\ oxidation}$	Ratio of Δ[PFCA]/[PFCA]$_{before\ oxidation}$								
		Sampling sites	Δ[PFBA]	Δ[PFPeA]	Δ[PFHxA]	Δ[PFHpA]	Δ[PFOA]	Δ[PFNA]	Δ[PFDA]	Δ[PFUnDA]	Δ[PFDoDA]	ΣΔ[PFCA $_{C4-C12}$]	Σ[PFAAs] $_{Before\ oxidation}$		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
River water	Main river	1	0.32	0.52	0.73	0.00	0.51	0.00	0.00	0.00	0.00	2.1	3.7	56%	-	71%	89%	0%	87%	0%	-	0%	-
		3	2.6	0.54	0.78	0.15	0.32	0.00	0.00	0.17	0.00	4.6	17	26%	-	33%	30%	16%	11%	0%	0%	36%	-
		7	1.4	0.74	1.2	0.52	1.4	0.00	0.00	0.00	0.00	5.2	17	31%	104%	52%	46%	51%	55%	0%	0%	0%	-
		9	0.47	0.43	1.5	0.78	0.00	0.12	0.29	0.00	0.00	3.6	29	12%	-	21%	46%	35%	0%	3%	150%	0%	-
		11	2.4	1.5	2.5	0.38	1.5	0.52	0.46	0.00	0.00	9.2	31	29%	175%	89%	49%	22%	29%	11%	196%	0%	-
		13	3.3	1.5	1.8	0.71	0.40	0.47	0.23	0.04	0.00	8.5	30	28%	-	64%	41%	45%	9%	14%	120%	9%	-
		14	0.40	1.8	2.0	1.3	2.9	0.54	0.42	0.00	0.00	9.5	34	28%	-	85%	43%	61%	59%	15%	287%	0%	-
		16	0.00	1.4	1.7	1.2	3.0	0.42	0.56	0.00	0.00	8.2	35	23%	-	66%	37%	54%	53%	9%	321%	0%	-
		17	2.7	1.2	1.4	0.96	1.3	0.00	0.00	0.21	0.00	7.8	37	21%	-	53%	29%	43%	24%	0%	0%	51%	-
	Average		1.5	1.1	1.5	0.67	1.3	0.23	0.22	0.05	0.00	6.5	26	28%	139%	59%	45%	36%	36%	6%	134%	11%	-
	Branch river	19	0.95	0.69	1.6	1.3	1.6	0.56	0.00	0.00	0.00	6.6	4.1	160%	-	147%	618%	633%	179%	211%	-	-	-
		21	2.0	1.1	2.0	1.8	2.2	0.00	0.00	0.38	0.00	9.4	15	63%	-	91%	147%	103%	58%	0%	-	241%	-
		22	2.0	0.64	1.5	1.5	2.3	0.34	0.00	0.00	0.00	8.3	16	51%	-	42%	102%	79%	69%	23%	-	0%	-
	Average		1.6	0.81	1.7	1.5	2.0	0.30	0.00	0.13	0.00	8.1	12	69%	-	93%	289%	272%	102%	78%	-	120%	-
STP effluent		23	0.80	3.7	5.7	4.8	2.4	0.40	0.30	0.18	0.00	18	48	38%	-	100%	98%	165%	26%	8%	44%	12%	-
		6	1.6	0.00	2.1	1.3	4.9	0.66	0.93	0.00	0.00	11	72	16%	50%	0%	22%	43%	53%	6%	110%	0%	-
		12	5.3	0.99	5.6	1.3	3.7	1.0	0.69	0.49	0.00	19	109	18%	158%	16%	34%	32%	31%	15%	68%	47%	-
	Average		2.6	1.5	4.5	2.4	3.7	0.70	0.64	0.22	0.00	16	76	21%	104%	39%	51%	80%	37%	10%	74%	20%	-
River & effluent	Average		1.8	1.1	2.1	1.2	1.9	0.34	0.26	0.10	0.00	8.8	33	40%	122%	62%	95%	92%	50%	21%	118%	28%	-

Table 4-6 Concentrations of individual perfluorinated carboxylic acids before oxidation ([PFCAs]$_{\text{before oxidation}}$), after oxidation ([PFCAs]$_{\text{after oxidation}}$), their differences (Δ[PFCAs]) and their ratios (Δ[PFCA]/[PFCA]$_{\text{before oxidation}}$) in upstream, downstream and sewage treatment plant effluent samples.

Area	Sites		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	ΣΔ[PFCA $_{\text{C4-C12}}$]
Upstream	1, 3, 7, 19, 21 and 22	[PFCA]before oxidation	0.23	1.2	1.5	1.00	2.3	1.4	0.02	0.21	0.00	7.9
		[PFCA]after oxidation	1.8	1.9	2.8	1.8	3.7	1.6	0.34	0.35	0.12	14
		Δ[PFCA]	1.5	0.70	1.3	0.84	1.4	0.16	0.33	0.14	0.12	6.5
		Ratio of Δ[PFCA]/[PFCA]$_{\text{before oxidation}}$	672%	61%	86%	84%	60%	11%	-	-	-	-
Downstream	9, 11, 13, 14, 16 and 17	[PFCA]before oxidation	0.23	2.1	4.5	2.0	5.2	4.2	0.16	0.55	0.00	19
		[PFCA]after oxidation	1.8	3.4	6.3	2.9	6.7	4.4	0.58	0.31	0.10	27
		Δ[PFCA]	1.6	1.3	1.8	0.89	1.5	0.19	0.42	-0.24	0.10	7.6
		Ratio of Δ[PFCA]/[PFCA]$_{\text{before oxidation}}$	672%	62%	40%	44%	29%	4%	-	-	-	-
STP effluent	6, 12 and 23	[PFCA]before oxidation	2.2	5.1	11	3.3	10	8.0	0.85	1.3	0.00	41
		[PFCA]after oxidation	4.8	6.6	15	5.7	14	8.7	1.5	1.4	0.21	58
		Δ[PFCA]	2.6	1.4	4.5	2.4	3.7	0.70	0.64	0.10	0.21	16
		Ratio of Δ[PFCA]/[PFCA]$_{\text{before oxidation}}$	118%	27%	42%	74%	36%	9%	75%	8%	-	-
All sites	1, 3, 6, 7, 9, 11, 13, 14, 16, 17, 19, 21, 22 and 23	[PFCA]before oxidation	0.62	2.3	4.5	1.9	5.0	3.8	0.24	0.56	0.00	19
		[PFCA]after oxidation	2.4	3.4	6.7	3.0	6.9	4.1	0.67	0.54	0.13	28
		Δ[PFCA]	1.8	1.1	2.1	1.2	1.9	0.28	0.43	-0.02	0.13	8.9
		Ratio of Δ[PFCA]/[PFCA]$_{\text{before oxidation}}$	282%	46%	47%	63%	38%	7%	-	-	-	-

river and in the branch river (56% and 160% at sites 1 and 19, respectively) than the other sites of the river (**Figure 4-7** and **Table 4-5**). According to Lei et al. (2004), this could be due to the existence of relatively important sources of PFAA precursors other than the STP effluents, such as atmospheric deposition of volatile fluorinated precursors or untreated sewage in the upstream of the river, where the river water flow is less. According to Ahrens et al. (2011), volatile precursors were emitted from the STPs and landfill sites to the atmosphere.

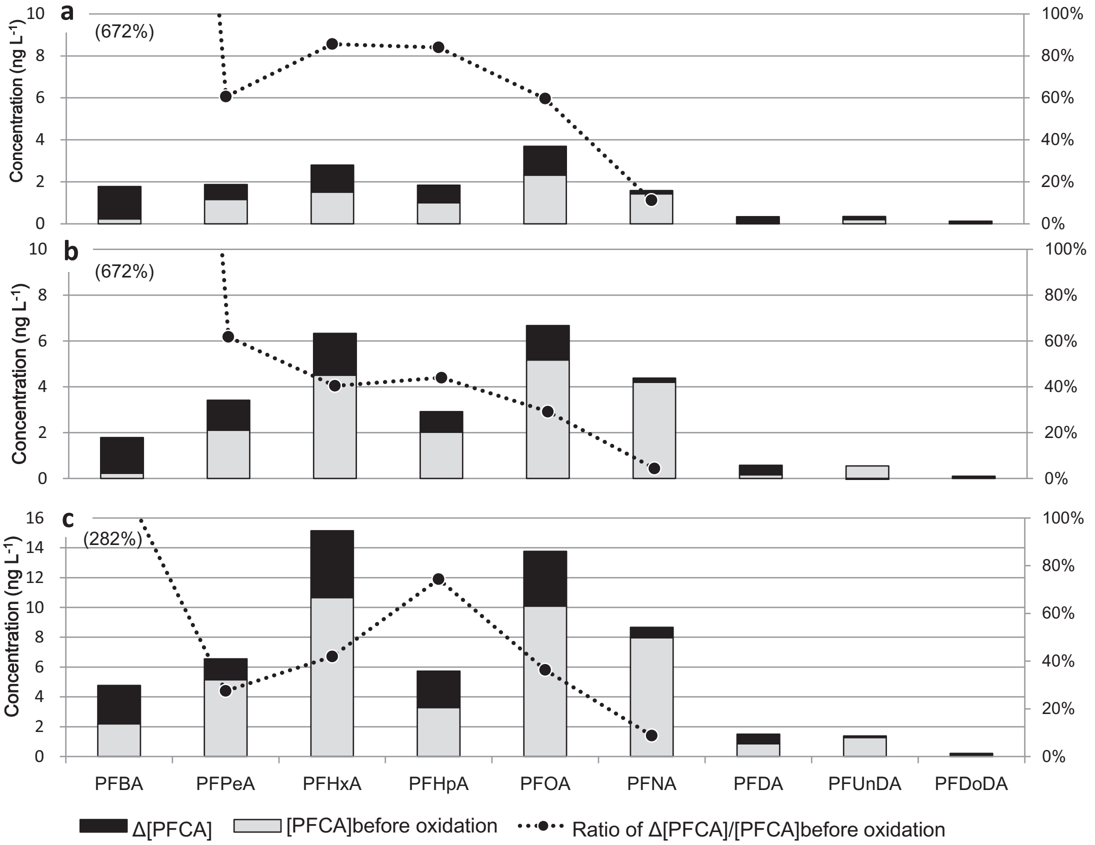


Figure 4-8 Concentrations (ng L^{-1}) of perfluorinated carboxylic acids before oxidation ($[PFCAs]_{\text{before oxidation}}$); increased concentrations after oxidation ($\Delta[PFCAs]$) and the ratio of their concentrations (%) ($\Delta[PFCAs] / [PFCAs]_{\text{before oxidation}}$).

a) Upstream river water samples (average of sites 1, 3, 7, 19, 21, and 22).

b) Downstream river water samples (average of sites 9, 11, 13, 14, 16, and 17).

c) Sewage treatment plant effluent samples (average of sites 6, 12, and 23).

The difference in the ratios of individual PFCA ($\Delta[PFCA]/[PFCA]_{\text{before oxidation}}$) in all the upstream (sites 1, 3, 7, 19, 21, 22) and downstream (sites 9, 11, 13, 14, 16, 17) sites of the river and STP effluents (sites 23, 6, 12) are shown in **Figure 4-8a-c** and **Table 4-6**. For the

PFCAs with a carbon chain length of 4 and 5 carbons, similar ratios were observed for all the sites, while for those with chain lengths of 6 to 9 carbons, the ratios decreased significantly ($p < 0.05$) from the upstream to downstream sites. These results implied that there could be different sources of PFAA precursors with different carbon chain lengths.

The concentrations of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ in the 3 STP effluent samples (site 23, 6, 12) were 18, 11, and 19 ng L^{-1} (average = 16 ng L^{-1}), respectively (**Table 4-5**). Increased concentrations of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ were observed in the STP effluents compared to the river water samples (**Figure 4-7**). These results indicated that the STP effluents were one of the major sources of the PFAA precursors in the aquatic environment. However, the ratios of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ to $\Sigma[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]_{\text{before oxidation}}$ in the STP effluents (average = 0.21) were slightly lower than those in the river water samples (average of main river = 0.28 and branch river = 0.69) (**Figure 4-7** and **Table 4-5**), whereas the differences were not statistically significant ($p > 0.05$). The elevated concentration and the lower ratios of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ in the STP effluents indicated the degradation of precursors during the sewage treatment process. This observation supported the studies by Shivakoti et al. (2010) and Sun et al. (2012), which showed the increase of PFAAs during the sewage treatment process.

The average ratios of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ in the river water samples were 28% and 69% for the main and branch rivers, respectively. These ratios were much higher than that of the previous studies by Benskin et al. (2012), Motegi et al. (2013), Murakami et al. (2009), and Zushi et al. (2011) on aquatic environment in which the individual precursors were determined. Hence, it can be concluded that the previous studies underestimated the occurrence of the PFAA precursors in the aquatic environment and that a greater number of precursors beyond the commonly measured ones existed.

The type of C8 PFAA precursors can be PFOS precursor or PFOA precursor. This was estimated by the method described by Houtz and Sedlak (2012). According to this method, the C8 precursors existed as PFOS precursors when the estimated maximum of [C8 PFAA precursors] was closer to Δ[PFOA]. In most of the samples investigated in this study, the majority of the C8 precursors existed as "PFOA precursors" (**Table 4-7**) while the "PFOS precursors" were majorly estimated to be present in the urban runoff samples in California (Houtz and Sedlak, 2012). The difference in the results could be due to the difference in the PFAA precursor use in the two countries or to the difference types of samples (river water and urban runoff).

The type of C6 PFAA precursors can be PFHxS precursor or fluorotelomer-based precursor. This was estimated by the method described by Houtz and Sedlak (2012). According to this method, the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA], the greater is the probability of the PFHxS precursors; conversely, the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA]/0.19, the greater is the probability of the C6 fluorotelomer–based (i.e., PFHxA) precursors. The C6 precursors were estimated likely present as "PFHxS precursors" in one third of the samples, while the "C6 fluorotelomer–based precursors" were likely present in two thirds of the sampling sites investigated in this study (**Table 4-7**). However, according to Houtz and Sedlak (2012), the "C6 fluorotelomer–based precursors" were estimated as the likely type of precursors in urban runoff samples in California. The difference in the results could be due to the different usage of PFAA precursors or to the different types of samples (river water and urban runoff).

4.5 Conclusion

To our knowledge, this is the first study on the spatial distribution and importance of PFAA precursors in the urban river water and STP effluent. The importance of PFAA precursors in river water was revealed by its significant ratio of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ against $[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]_{\text{before oxidation}}$ (average = 28% and 69% for main and branch river respectively) ($p < 0.05$). Therefore, the commonly measured precursors were only a part of the total precursors present in the environment. The ratios of $\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$ against $\Sigma[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]_{\text{before oxidation}}$ 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.

Table 4-7 Predicted minimum and maximum concentrations of C6 and C8 precursors based on the increase of perfluoroalkyl acids (PFAAs) by oxidation of PFAA precursors (ng L^{-1} as PFHxA and PFOA, respectively) and the probable precursor types in river water samples

		C8 precursors as PFOA				C6 precursors as PFHxA				
	Sampling sites	Estimated concentration		Estimated precursor type*		Estimated concentration		Estimated precursor type**		
		Minimum	Maximum	Maximum/ Δ[PFOA]	Probable precursor type	Minimum	Maximum	|Maximum - Δ[PFHxA]|	|Maximum - Δ[PFHxA]/0.19|	Probable precursor type
Main river	1	0.51	0.51	100%	PFOS	0.73	2.8	2.0	1.1	C6 fluorotelomer-based
	3	0.89	0.32	280%	PFOA	0.62	2.9	2.1	1.2	C6 fluorotelomer-based
	7	3.4	1.4	243%	PFOA	0.57	4.0	2.9	2.1	C6 fluorotelomer-based
	9	0.00	0.00	0%	-	0.64	3.2	1.7	4.7	PFHxS
	11	2.9	0.86	200%	PFOA	2.0	8.2	5.7	4.7	C6 fluorotelomer-based
	13	2.0	0.00	500%	PFOA	1.0	7.6	5.8	2.0	C6 fluorotelomer-based
	14	8.0	2.3	273%	PFOA	0.53	9.0	6.9	1.7	C6 fluorotelomer-based
	16	7.4	2.5	251%	PFOA	0.38	7.3	5.6	1.6	C6 fluorotelomer-based
	17	4.9	1.3	382%	PFOA	0.35	6.3	4.9	1.2	C6 fluorotelomer-based
Branch river	19	6.5	0.93	409%	PFOA	0.13	4.3	2.7	4.0	PFHxS
	21	9.0	2.2	419%	PFOA	0.00	6.3	4.3	4.2	C6 fluorotelomer-based
	22	7.9	1.9	337%	PFOA	0.00	4.0	2.5	3.9	PFHxS
	Average	4.5	1.2	-	-	0.58	5.5	-	-	-
STP effluent	23	12	1.9	500%	PFOA	0.35	20	14	10	C6 fluorotelomer-based
	6	9.7	4.2	198%	PFOA	0.66	2.1	0.00	8.9	PFHxS
	12	8.6	2.5	232%	PFOA	4.2	9.5	3.9	20	PFHxS
	Average	10	2.9	-	-	1.7	11	-	-	-

* The closer the estimated maximum of [C8 PFAA precursors] is to Δ[PFOA], the greater the proportion of likely PFOS precursors according to Houtz and Sedlak (2012).

** The closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA], the greater the proportion of likely PFHxS precursors are; conversely, the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA]/0.19, the greater the proportion of likely C6 fluorotelomer-based (i.e., PFHxA) precursors are, according to Houtz and Sedlak (2012).

5. Existence, mass balance and transformation of perfluoroalkyl acids and their precursors in sewage treatment plant

5.1 Introduction

In chapter 4, I investigated the PFAA and their precursors in urban river. The importance of the effluent of sewage treatment plant (STP) as the source of these compounds was indicated. Thus, a study focused on the STP. The impact of PFAA precursors in STP as the major sources of PFAAs was investigated in STP influents. Efficiency of removal of PFAA precursors by ozonation and chlorination treatment was studied. Also the mass loads in STPs were investigated for clarifying the behavior of PFAAs and their precursors in STPs. Furthermore, whether the PFASs removal ability of STP is underestimated or not was investigated to provide basic information for better PFASs management policy.

5.2 Method

5.2.1 Sample collection

Sampling was conducted in 3 STPs of Yokohama city of Japan. The influent, treated sewages at individual processes, final effluent, and active sludge, etc., as shown in **Table 5-2**, were collected in May 2014. There was no rain from more than 2 day before sampling. Therefore, the influence of rainfall on the flow quantity was minimal. Most of the samples were collected as composite sample, effluent and sludge were collected by grab sampling. There are not composite sampler for effluent and sludge in these STPs, because they are considered to be well mixed over time already. The collected samples were decanted into methanol-rinsed 2 L high density polyethylene (HDPE) bottles and were kept in ice for less than 2 h. Samples were not filtered prior to extraction based on previous reports of chain-length dependent sorption of PFASs to glass fiber or nylon filters (45−60% sorption for PFDS, PFTriDA, and PFTeDA using Nylon and 25−30% sorption for PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFDS using glass fiber) (Labadie and Chevreuil, 2011). Suspended solids (SS) were separated from the influents and sledge samples by centrifuge upon arrival at the laboratory, for preventing the decomposition of target compounds. For the other samples, including treated sewage and final effluent, the SS were not separated because they were too little to collect by centrifuge. The separated SS were dried by vacuum freeze drying equipment and kept in -20 °C, and liquid samples were stored at 4 °C.

Care was taken to avoid the usage of any PTFE–coated materials.

Table 5-1 Composition of influent at sampling STPs.

STP	Cooling water (indirect)	Cooling water (direct)	Planting waste water	Acid or alkali washing water	Other washing water	Domestic waste water	Supernatant of sludge adjusting tank	Total Influent
T	96	190	242	1587	3882	164843	5270	176110
S	166	11	2.0	201	613	34557	3042	38592
K	548	76	6.0	177	5561	207599	6707	220674
			Proportion					**Total**
T	0.055%	0.11%	0.14%	0.90%	2.2%	94%	3.0%	100%
S	0.43%	0.029%	0.0052%	0.52%	1.6%	90%	7.9%	100%
K	0.25%	0.034%	0.0027%	0.080%	2.5%	94%	3.0%	100%

Table 5-2 Information on sampling STPs

STP	Time	Sewerage system	Designed population capita	Type of sample		Sewage Treatment system	Name of sample	Daily flow m^3/d
T	8th May for grab 7th May for composite	Separated	597100	Inf.	Composite	-	TI	176110
				T.S.	Composite	Mixture of AOAO and Standard	TT12	47700
					Composite	Mixture of pseudo AO, Standard, AOAO	TT34	106100
					Composite	A2O	TT5	22300
				Eff. (Cl)	Composite	Chlorination	TC12	47700
					Composite	Chlorination	TC34	106100
					Composite	Chlorination	TC5	22300
				Eff. (O, Cl)	Grab	Ozonation and Chlorination	TO	4290
				A.S.	Grab	-	TS	2160
S	8th May for grab 7th May for composite	Separated	180000	Inf.	Composite	-	SI	38592
				T.S.	Composite	Standard	STA	18108
					Composite	AO	STB	18718
				Eff. (Cl)	Composite	Chlorination	SCA	18108
					Composite	Chlorination	SCB	18718
				A.S.	Grab	-	SS	476
K	12th May	Combined	546000	Inf.	Composite	-	KI	220674
				T.S.	Composite	Mixture of Standard and A_2O	KTA	223574
					Composite	A_2O	KTB	
				Eff. (Cl)	Grab	Chlorination	KC	215324
				Eff. (O)	Grab	Ozonation	KO	5191
				A.S.	Grab	-	KS	1720

Inf.: influent; T.S.: treated sewage; Eff.: effluent; Eff. (O): effluent after ozonation; Eff. (Cl): effluent after chlorination; A.S.: sludge in adjusting tank;

5.2.2 Oxidation of PFAA precursors

The oxidation treatment method, mentioned in Chapter 3 and also used for river samples, was used for oxidizing PFAA precursor in sewage and sludge samples. For liquid part of samples 50 mL unfiltered liquid were transferred to 125 mL HDPE bottles. For solid part of samples, extracts in NH_4OH in methanol was dried in 125 ml HDPE bottles by nitrogen gas and added with 50 ml ultra-pure water. Sample from each sampling site was subsampled in triplicate (n=3) before added with 0.7 g (60 mM) of potassium persulfate and 0.63 mL of 10 N NaOH (150 mM). The HDPE bottles were placed in a temperature–controlled oil bath (Personal H–10 SH; TAITEC, Saitama, Japan) at 85 °C for 6 h. Then, the samples were cooled to room temperature in an ice bath. The pH of the samples was adjusted between 5 and 9 by concentrated HCl prior to the extraction.

Flow of oxidation treatment:

Unfiltered liquid sample 50 ml into 125ml bottle (in triplicate) or dried extracts of solid sample added with 50 ml ultra-pure water
↓←Add 0.7 g (60 mM) of potassium persulfate and 0.63 mL of 10 N NaOH (150 mM) (pH above 12)
↓Shake the mixture gently
↓Place bottles into oil bath 85℃, 6 hour
Cool down ← adjust pH between 5～9 by HCL

5.2.3 Extraction and analysis

Extractions of STP samples were separated by liquid and solid part of samples. The detail of the experiment flow was shown in **Figure 5-1**.

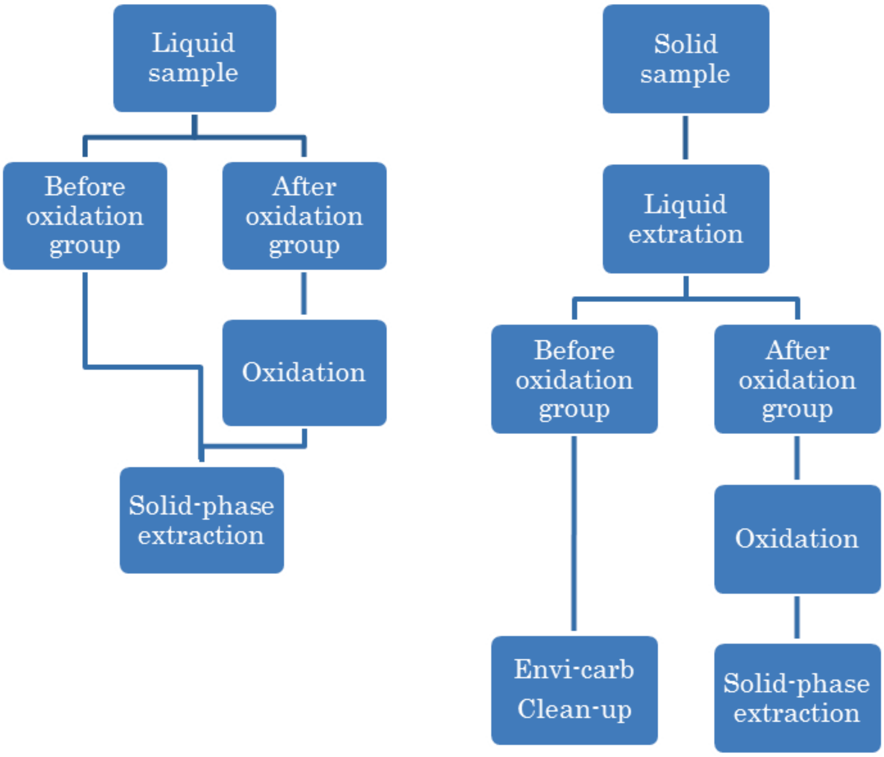


Figure 5-1 Analysis flow of STP samples.

5.2.3.1 Extraction of liquid sample

Solid-phase extraction applied for liquid sample was used for samples including sewage samples and the liquid part of influent and sludge. Explanation was omitted here, because it is the same with the extraction of river water samples in section 4.2.3 showed in the flow at blow.

Experiment flow of solid-phase extraction:

Sample
↓←Inject isotopically labeled surrogate standards 20uL of 200 ug/L
↓←Load sample to solid phase extraction cartridge (Oasis Wax 6 cm^3, 150 mg, 30 µm)
↓Rinse bottle
↓Dry cartridge
↓Elute analyte from cartridge
↓Concentrate the elutes
↓Filtration
Analyze by LC-MSMS

5.2.3.2 Extraction of solid sample

Solid-liquid extraction

Dried Solid samples separated from sludge and influent samples by centrifuge were collected 0.1 g and 0.02 g, respectively, putted into 15 ml tube, and spiked with 4 ng of labeled internal standards. All samples were extracted in triplicate. 0.1% NH_4OH in methanol was added for extraction, 2.5 and 7 ml respectively. Tubes were vortexed for 30 seconds, sonicated for 30 min, and shaken at 300 rpm for 20 mins. The extract was separated from the soil by centrifugation at 4000 rpm for 5 min. The supernatants for solid-phase extraction were transferred to a new 15 mL centrifuge, and for oxidation were transferred to 125 ml HDPE bottles. Extractions were repeated two more times to ensure complete removal of all PFAA and their precursors.

Analysis flow of solid-liquid extraction:

Dried Solid samples in 15mL centrifuge tube
↓ Added 2.5 mL (for influent) or 7 ml (for sludge) of 0.1% NH4OH(Methanol)
↓ 30s Vortex
↓ 20min 30-35℃ sonicate
↓ 20min 300 rpm shake
↓ 5min 4000rpm centrifuge
↓ Transfer supernatant to 125 ml HDPE bottle (before oxidation group) or 15 ml centrifuge tube (after oxidation group)
×repeat 2 more time

Solid-phase extraction

Solid-phase extraction applied for liquid sample was used for samples including sewage samples and the liquid part of influent and sludge. Explanation was omitted here, because it is the same with the extraction of river water samples in section 4.2.3 showed in the flow at blow.

Analysis flow of solid-phase extraction:

Sample
↓←Inject isotopically labeled surrogate standards 20uL of 200 ug/L
↓←Load sample to solid phase extraction cartridge (Oasis Wax 6 cm^3, 150 mg, 30 μm)
↓Rinse bottle

↓Dry cartridge
↓Elute analyte from cartridge
↓Concentrate the elutes
↓Filtration
Analyze by LC-MSMS

5.2.4 Quality assurance/Quality control

5.2.4.1 Method Recovery test

The method recovery was tested for the extraction of target compounds in solid samples by solid-liquid extraction prior to solid- phase extraction. The test was conducted by using solid samples and divided them into two groups: one group was spiked with standard mixture the other was not. By comparing the difference of the concentrations of those two groups, the actual detected concentration of spiked standard was calculated. The final concentration of spiked standard after concentration was expected to be 10 μg/L when no loss occurred.

The recoveries of the target compounds except for PFTrDA, PFTeDA and PFDPA were 51 - 108%. The recoveries of PFTrDA, PFTeDA and PFDPA were lower than 50% in this method. Therefore, these compounds were not quantitated.

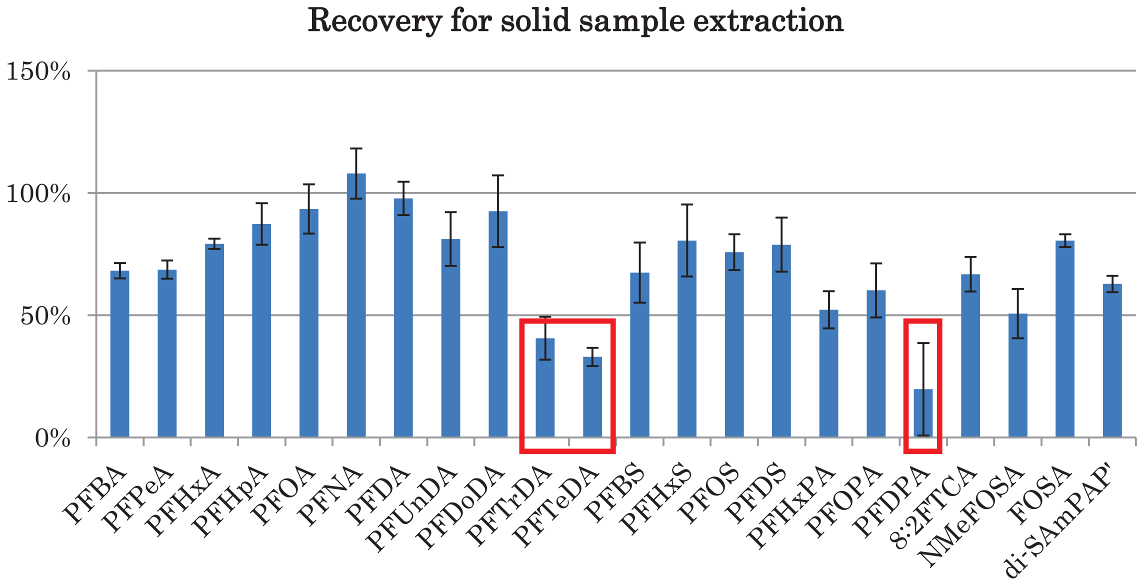


Figure 5-2 Recovery rates of spiked chemicals in the extraction of solid samples (n=3). The error bars represent the standard deviation.

5.2.4.2 Blank for operation control

As tested in section “3.2.3”, increased concentration of the PFCAs such as PFBA and PFOA were observed in the blank tests conducted with ultra–pure water. Therefore, the blanks were oxidized twice and the further increase in the PFCA concentrations was determined. The contamination from ultra-pure water and that from oxidation process (oxidizing reagent solution) could be distinguished from the above tests. As ultra-pure water was not used during the sample analysis, the blank values obtained in the oxidation process were used to correct the measured values for each batch analysis.

Blanks below were used for analysis:

- Operation blank for oxidation treatment (n = 3 sets of once-oxidated and twice-oxidated water)
- Operation blank for solid-phase extraction for liquid sample (n = 3)
- Operation blank for solid-liquid extraction followed by solid-phase extraction for solid samples (n = 3)
- Operation blank for solid-liquid extraction followed by clean-up for solid samples (n = 3)
- Blank for LC-MSMS (n = 2)

5.2.4.3 Method validation

Most of the samples were analyzed in triplicate and the median values were used for further studies, because outliers were sometimes observed among the triplicate values.

Bottles were inverted 3 times for subsampling from sampling bottles.

The LOD was calculated by using the 3 × value of signal / noise (S/N). The detected concentrations lower than LOD were regarded as not detected.

Including the spiked sample recovery test, blank test, direct extraction and oxidation treatment mention above, analyses of the liquid samples and solid samples were finished within 6-15 days and 12-17 days, respectively, after the day of the sampling.

5.3 Result and Discussion

5.3.1 Concentration of PFAAs and their precursors before oxidation

Concentration. The concentrations of the PFAAs and their precursors before oxidation in the liquid part of samples were 25 to 82 ng L^{-1} and in the solid part were 3.7 to 997 ng L^{-1} (**Table A1-8**). The four most abundant PFASs (in average concentration), in liquid phase of STP T, S, and K were PFOA = 9.5, 17, 15 ng L^{-1}, PFNA = 9.0, 8.2, 10 ng L^{-1}, PFHxA = 6.2, 6.0, 6.9 ng L^{-1} and PFOS = 4.7, 6.3, 8.9 ng L^{-1}, respectively. The four most abundant PFASs in solid phase were PFUnDA (2.5 – 520 ng L^{-1}), PFDA (<0.43 – 205 ng L^{-1}), PFOS (<3.1 – 145 ng L^{-1}) and PFDoDA (<1.1 – 70 ng L^{-1}). Among the four most abundant PFASs mentioned above, PFPA was not observed, and PFOS was the only PFSA, and the rest were all PFCAs.

PFAAs in liquid phase. The PFASs with carbon chain C6-C9 were the most prevalent. PFOA, PFNA and PFOS were observed as the most abundant PFASs in liquid phase in this study, and this is consistent with finding of previous studies (Murakami et al., 2009; Shivakoti et al., 2010). Comparing with those previous studies, the concentrations of PFOA, PFNA and PFOS were lower in this study; especially PFOS decreased most among the three. For example, in one of those previous studies: the concentrations of PFOS, PFOA and PFNA were 14 – 336 ng L^{-1}, 14 – 41 ng L^{-1}, and 13 – 70 ng L^{-1} in influents and 42 – 635 ng L^{-1}, 10 – 68 ng L^{-1}, and 17 – 94 ng L^{-1} in effluents, respectively (Murakami et al., 2009). In my previous study on Tama River in Japan and in the other studies on STPs in Japan, PFOS were detected as the most prevalent PFASs in the river water samples (Murakami et al., 2009; Shivakoti et al., 2010). The lower concentrations in the samples of this study could be explained by the regulations and actions toward PFOS, PFOA and long chain perfluorinated chemicals around 2009 and 2010. In this study relatively higher concentration of PFHxA was observed which was not found prevalent in other studies. The appearance of PFHxA may be due to its shorter chain and used as the substitute of PFOS and PFOA, or due to decomposition from longer chain precursors such as 6:2 FTOH. The detected PFOS (1.2 – 12 ng L^{-1}) was in relatively lower concentration compared with PFOA, PFNA and PFHxA. Two PFPAs analyzed were observed in relatively low concentrations (PFHxPA was <0.25 to 4.1 ng L^{-1} and PFOPA was <0.53 to 3.2 ng L^{-1}). Compared with PFSA and PFCA, this group of compounds was detected in relatively lower concentrations. These results showed similar concentration levels with the previous studies on river waters in Japan (median concentration of PFHxPA was lower than 0.15 ng L^{-1}, arithmetic mean = 0.28 ng L^{-1}) (Zushi et al., 2011) and Canada (PFHxPA, PFOPA, and PFDPA arithmetic mean concentrations were 1.2, 3.4, and 0.66 ng L^{-1}, respectively) (D'eon et al., 2009). The similar concentration levels detected from river environment and STPs indicated that there should be other sources contributing PFPAs in river environment.

The PFAA precursors in liquid phase. The PFAA precursors were detected in similar concentration level, and the order of quantitated PFAA precursors by average concentration were di-SAmPAP (<0.01 to 1.5 ng L^{-1}), 8:2 FTCA (<0.66 to 0.99 ng L^{-1}) and FOSA (<0.02 to 0.35 ng L^{-1}). And they were much lower than concentrations of PFCAs and PFSAs (see **Table A1-8**). di-SAmPAP was the most commonly detected one and showed the highest concentrations among 3 precursors in adjusted sludge (sampling site SS and KS) and influent (KI) samples. Similarly the low concentration levels of the PFAA precursors, however, a relatively high concentration of FOSA were observed in studies by Motegi et al. (2013) and Zushi et al. (2011), which were conducted on the major rivers in Tokyo. To the best of author's knowledge, this is the first study detected di-SAmPAP in Japan.

In liquid phase of different process samples. In STP T and S, higher total concentrations of PFASs in treated sewages and effluents, after ozonation, chlorination or both, than influents were detected. PFHxA and PFOA increased around 2 to 4 folds (**Table A1-8**). In STP K, no significant increase was observed. Increase of PFASs in sewage treatment was also reported from number of previous studies. For example, increases of PFOA and PFNA in secondary effluents compared with influents were observed in results by Murakami et al. (2009) and Shivakoti et al. (2010). The observed increases in this study were considered as formation from precursors, which will be discussed in the next section. PFCAs with carbon chain 9-12 and PFSAs with carbon chain 4, 6 and 8 had significantly higher concentrations in liquid phase of sludge samples from adjusting tank, which may be resulted by the preferential partition of these compounds to sludge. In the samples of other process water in STPs, including treated sewage and effluent after ozonation, chlorination or both, similar total concentrations were observed as 38 – 59 ng L^{-1} except for samples "TO" after ozonation and chlorination treatment showed lowest concentration as 25 ng L^{-1}.

PFASs in solid phase. The PFASs with carbon chain C10 – C12 and C8 were the prevalent ones. The PFUnDA (2.5 – 520 ng L^{-1}) with carbon chain C11 showed the highest average concentration, and followed by PFDA (<0.43 – 205 ng L^{-1}). These results suggested the preferential partitioning of PFCAs to solid phase, which increases with the increase of carbon-chain length. PFDA and PFUnDA were also reported to be highly correlated in sludge samples in one STP in New York State, USA, and it was pointed out that these compounds are introduced through the decomposition of telomer precursors such as 10:2 FTOH (Sinclair and Kannan, 2006). However, in this previous study, PFOA was the most dominant in sludge. These different results may be due to the different sampling time. The latter study was conducted in 2004 and 2005 and more than 9 years earlier than this study. Emission of PFASs has been reduced during the past 9 years.

PFAA precursors in solid phase. The quantitated precursor concentrations were in the following order: 8:2 FTCA (<0.66 to 8.4 ng L^{-1}), di-SAmPAP (<0.01 to 4.9 ng L^{-1}) and FOSA (<0.02 to 1.8 ng L^{-1}). Their concentrations were much lower than PFCAs and PFSAs (see **Table A1-8**). These precursors were detected from both "solid" phase of influents and sludge in adjusting tank. The di-SAmPAP was considered to preferentially partition to sludge, but it showed relatively low concentrations in solid phase of the samples. This could be explained by the commercial use of this compound was not high in Japan or most of them already decomposed in sludge, because di-SAmPAP was only observed in influent (sampling sites TI and SI). FOSA was only detected in sludge in adjusting tank (sampling site KS), this may be formed by the decomposition from their precursors. Because they are reported to be used as raw material (Buck et al., 2011), which means they might not be used directly in products.

5.3.2 Importance of PFAA precursors estimated by the oxidation of samples

Elevated concentrations. Oxidation treatment of the STP samples produced considerable amount of the PFCAs which led to the increase of total concentrations of the PFAAs (**Table A1-9** and **Figure 5-3**). The oxidation converted both the PFCA and PFSA precursors into PFCAs, which was a potential source of PFAAs to aquatic environment. The concentrations of the PFCAs after oxidation treatment included the originally existed PFCAs as well as those formed from the oxidation of the precursors (Δ[PFCAs]). The total concentration of the PFCAs with 4–12 perfluoroalkyl carbon chains which were produced upon oxidation ($\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]$) were 9.0 to 4169 ng L^{-1} among all the samples (**Table A1-9**). As reported by Houtz and Sedlak (2012), the PFCAs with carbon chains having less than 9 carbons increased significantly, and the sulfonates were not formed from the oxidation of the PFAA precursors.

In liquid phase. The ranges of elevated total PFCA (Δ[PFCA]) concentrations in STP T, S and K were 22 to 295 ng L^{-1} (average = 65 ng L^{-1}), 9.0 to 146 ng L^{-1} (average = 48 ng L^{-1}) and 29 to 222 ng L^{-1} (average = 66 ng L^{-1}), respectively (**Table A1-9**). The impact of PFAA precursors in each sample was shown by the percentage of total elevated concentration against the total concentration after oxidation, which included the elevated concentration and the concentration before oxidation: $\Sigma\Delta\mathrm{PFCA} / (\Sigma\mathrm{PFAS}_{\mathrm{before}} + \Sigma\Delta\mathrm{PFCA})$ (hereafter, this ratio is referred as “Percentage of PFCAs formed”). The percentage of PFCAs formed in 3 STPs were 33 to 91% (average over different PFCAs = 50%) for STP T, 15 to 74% (average = 39%) for STP S and 30 to 79% (average = 45%) for STP K. The average Percentages of PFCAs formed for 3 STPs ranged from 39% to 50% (**Table A1-9**). These results indicated that the total PFAA precursors have similar concentration levels with the PFAAs in liquid phase of the samples, which implied that concentrations of the precursors that will eventually degrade into PFAAs in the environment are significant.

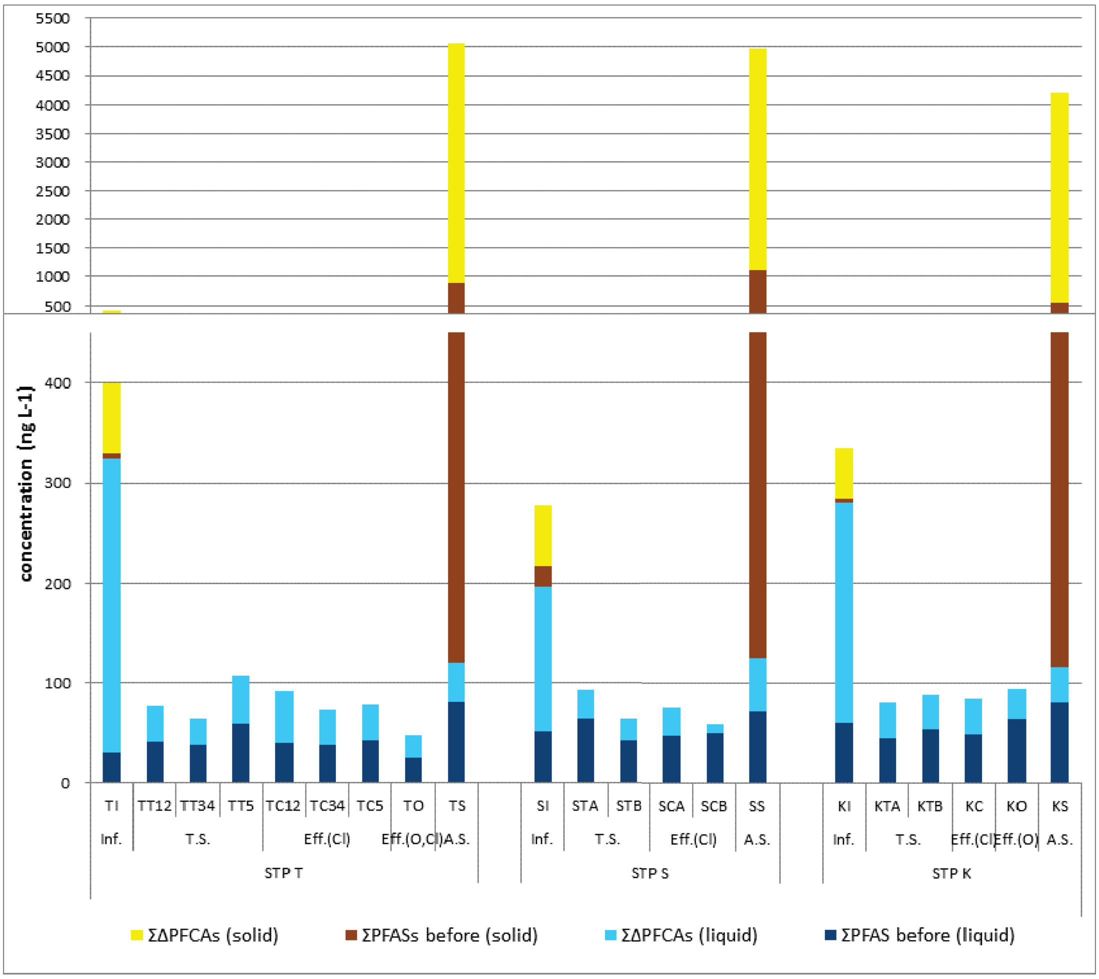


Figure 5-3 Concentrations of Σ[PFASs] before and after oxidation in all sampling sites. Dark and light blue bars represent the PFASs before oxidation and the elevated PFCAs after oxidation, respectively, in liquid phase of the samples. Dark and light yellow bars represent the PFASs before oxidation and the elevated PFCAs after oxidation, respectively, in solid parts of samples

In liquid phase of different process in STP. In influent samples, the concentrations of ΣΔPFCA were 295, 146 and 222 ng L^{-1} from 3 STP, which were much higher than average and the other samples. The Percentages of PFCAs formed of influents of STP T, S and K were 91, 74 and 79% respectively (**Table A1-9**). These high percentages indicated concentrations of PFAA precursors in influents may be much higher than PFAAs. The relatively abundant industrial wastewater in the influents were "other washing water" > "acid or alkali washing water" > "planting waste water" for STP T, "other washing water" > "acid or alkali washing water" > "cooling water (indirect)" for STP S, and "other washing water" > "Cooling water (indirect)" > "Cooling water (direct)" for STP K (**Table 5-1**).

Influent flows were dominated by "domestic waste water" which consisted 94, 94, 90% of the influent for STP K, T, S, respectively.

For the samples in other parts of STPs, including treated sewage, effluent (after ozonation, chlorination or both) and adjusted sludge, showed similar concentration levels and "percentage" of ΣΔPFCA ranged 21 to 54 ng L^{-1} and 30 to 56%, respectively, except sample "SCB" showed lowest value as 9.0 ng $L^{-1}$and 15%. These results indicated the removals of PFAA precursors are ineffective in ozonation and chlorination treatment.

In solid phase. The Δ[PFCA] concentrations (Percentage of PFCAs formed shown in brackets), of influents and sludge in adjusting tank were 70 (94%) and 4169 (85%) ng L^{-1} for STP T, 61 (79%) and 3843 (79%) ng L^{-1} for STP S, and 51 (95%) and 3660 (89%) ng L^{-1} for STP K, respectively (**Table A1-9**). Due to the difference of SS concentrations, the concentrations of sludge in adjusting tank are more than 50 times higher than influents. These results showed that precursors are dominating in solid phase of samples from STPs, and their Percentage of PFCAs formed is close to that of influent and higher than the rest of the liquid phase samples. Higher Percentage of PFCAs formed could be explained by the sediment/water partition coefficients, which tend to increase with number of CF_2 units (Higgins and Luthy, 2006; Kwadijk et al., 2010). The higher Percentage of PFCAs formed indicated the impact of the total PFAA precursors, as the potential source of PFAA. A recent study used biosolids-applied soil have reported biodegradation and plant uptake of PFCA precursor (Lee et al., 2014). PFAA precursors in solid part of STP as biosolid will contribute to more PFAA into environment and food chain.

Estimation of type of precursors. In liquid phase, the three most elevated PFCAs were Δ[PFHpA] (16 ng L^{-1}) > Δ[PFHxA] (11 ng L^{-1}) > Δ[PFOA] (9.9 ng L^{-1}) for STP T, Δ[PFHpA] (14 ng L^{-1}) > Δ[PFHxA] (12 ng L^{-1}) >Δ[PFBA] (8.8 ng L^{-1}) for STP S, and Δ[PFHpA] (18 ng L^{-1}) > Δ[PFHxA] (15 ng L^{-1}) > Δ[PFOA] (12 ng L^{-1}) for STP K. In solid phase, the three most elevated PFCAs were Δ[PFHpA] (757, 667and 705 ng L^{-1}) > Δ[PFHxA] (432, 379 and 334 ng L^{-1}) > Δ[PFPeA] (318, 314 and 284 ng L^{-1}) for STP T, S and K respectively. These concentrations were shown by the average concentration of samples in each STP (**Figure 5-4, Table A1-9**). The oxidation method used in this study was tested by four n:2 fluorotelomery precursors (6:2 FtS, 8:2 FtS, 6:2 diPAP and 8:2 diPAP) and showed that the Δ[PFCA] product formed in greatest yield was the $C(n - 1)$ Δ[PFCA] and the product formed in the second greatest yield was the $C(n)$ Δ[PFCA] (Houtz and Sedlak, 2012). In results of this study, greatest yield was Δ[PFHpA], which is C7, indicating dominating concentration of 8:2 fluorotelomery precursors in both liquid and solid phase of all STP samples.

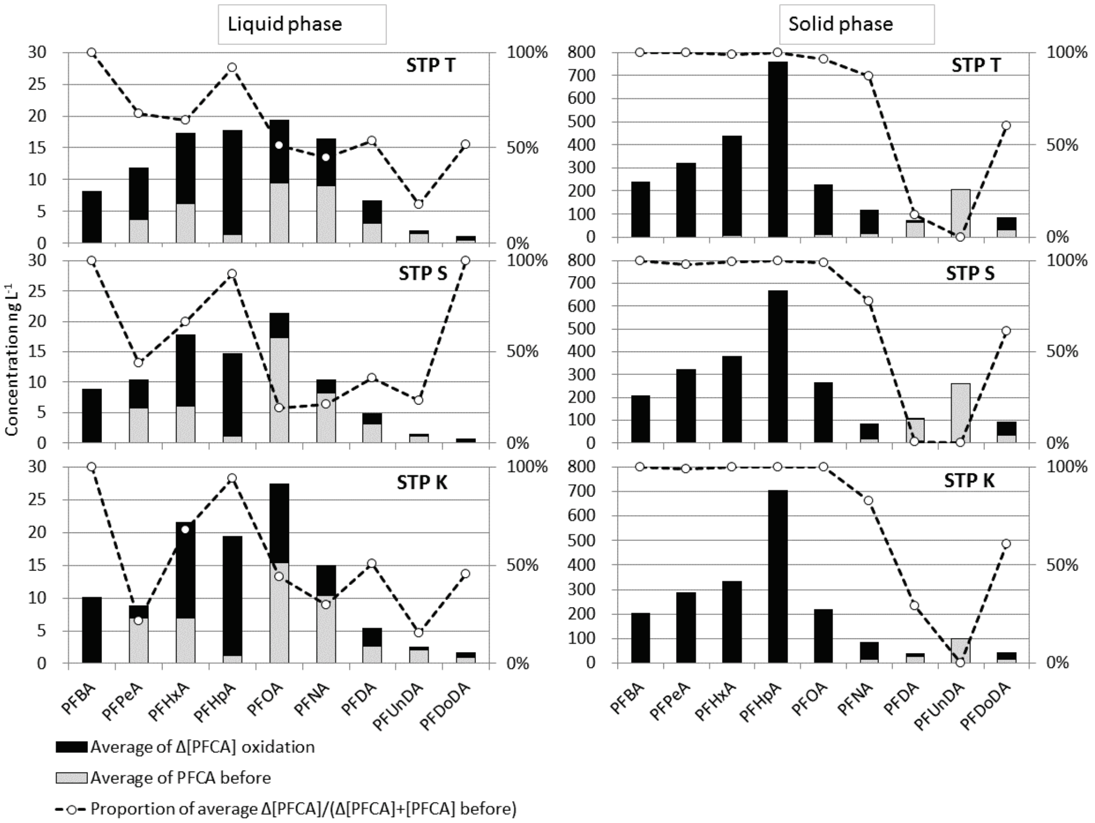


Figure 5-4 Concentrations (ng L^{-1}) of PFCAs before oxidation ($[PFCAs]_{before\ oxidation}$), their concentrations increased by oxidation (Δ[PFCAs]) and their proportion (%) of average Δ[PFCA]/(Δ[PFCA]+$[PFCA]_{before}$), in liquid and solid phase of all samples in SPT T, S and K.

The estimation of type of precursors was done by the method described by Houtz and Sedlak (2012). For C8 precursors, according to this method, the C8 precursors existed as PFOS precursors when the estimated maximum of [C8 PFAA precursors] was closer to Δ[PFOA]. In all the samples investigated in this study, the estimated likely precursor type was “PFOA precursor” (**Figure 5-3**). This result is consistent with our previous study on water river in Tokyo, Japan, while the “PFOS precursors” were majorly estimated in the urban runoff samples in California (Houtz and Sedlak, 2012). The difference in the results could be due to the difference in the PFAA precursor use in the two countries or to the difference types of samples (river water and urban runoff). A previous study in Japan reported that the effluent, containing high concentration of PFCAs (PFDA = 700 ng L^{-1}, PFOA = 600 ng L^{-1}, PFUdA = 400 ng L^{-1}), of a fiber dyeing process plant, where 8:2 FTOH and 10:2 FTOH used, is the resource of PFCA into environment and higher than 100ng L^{-1} of PFOA were detected from the river near this plant (Kawashita et al., 2014). These results suggested PFOA precursors are the major PFAS use in japan, which contribute the PFOA in environment.

For C6 precursors, according to this method of Houtz and Sedlak (2012), the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA], the greater is the probability of the PFHxS precursors; conversely, the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA]/0.19, the greater is the probability of the C6 fluorotelomer–based (i.e., PFHxA) precursors. In all of the STP samples, the type of C6 precursors were estimated as "PFHxS precursors" (**Table 4-7**), similarly, in our previous study PFHxS precursors were estimated as the likely type of precursors in one third of river samples of Tokyo, Japan, indicating "PFHxS precursors" are used as the major C6 precursor in Japan. While, according to Houtz and Sedlak (2012), the "C6 fluorotelomer–based precursors" were majorly estimated in most of the urban runoff samples in California. The difference in the results could be due to the different usage of PFAA precursors between Japan and USA.

Table 5-3 Predicted minimum and maximum concentrations of C6 and C8 precursors based on the increase of PFAAs by oxidation of PFAA precursors (ngL^{-1} as PFHxA and PFOA, respectively) and the likely precursors types in STP samples.

Sampling sites			C8 precursors				C6 precursors			
			Estimated mol concentration (nM L^{-1})		Estimated precursor type*		Estimated mol concentration (nM L^{-1})		Estimated precursor type**	
			Minimum	Maximum	Maximum/ Δ[PFOA]	likely type	Minimum	Maximum	|Maximum - Δ[PFHxA]/0.19|	likely type
Liquid part	**STP T**	**Inf.**	57.8	637.1	302%	**PFOA**	0.0	340.7	235	**PFHxS**
		T.S.	0.0	62.6	374%	**PFOA**	0.0	58.5	25	**PFHxS**
			12.0	55.4	383%	**PFOA**	0.0	71.1	21	**PFHxS**
			12.8	87.5	332%	**PFOA**	0.0	103.1	32	**PFHxS**
		Eff.(Cl)	0.0	101.1	500%	**PFOA**	0.0	60.6	47	**PFHxS**
			17.4	85.9	448%	**PFOA**	0.0	81.4	36	**PFHxS**
			7.1	76.7	365%	**PFOA**	0.0	99.3	29	**PFHxS**
		Eff.(O,Cl)	5.1	25.7	500%	**PFOA**	0.0	47.5	36	**PFHxS**
		A.S.	20.7	91.1	440%	**PFOA**	17.6	126.3	37	**PFHxS**
	STP S	**Inf.**	62.7	362.1	325%	**PFOA**	0.0	275.4	136	**PFHxS**
		T.S.	19.3	96.7	500%	**PFOA**	0.0	32.6	60	**PFHxS**
			8.1	40.7	500%	**PFOA**	0.0	0.0	41	**PFHxS**
		Eff.(Cl)	1.4	79.9	448%	**PFOA**	0.0	13.6	35	**PFHxS**
			4.2	33.5	500%	**PFOA**	0.0	0.0	21	**PFHxS**
		A.S.	34.3	155.1	452%	**PFOA**	0.0	133.1	65	**PFHxS**
	STP K	**Inf.**	106.7	606.8	304%	**PFOA**	0.0	120.6	230	**PFHxS**
		T.S.	0.0	35.4	500%	**PFOA**	0.0	0.0	48	**PFHxS**
			0.0	101.7	500%	**PFOA**	0.0	0.0	59	**PFHxS**
		Eff.(Cl)	13.2	66.1	500%	**PFOA**	0.0	0.0	52	**PFHxS**
		Eff.(O)	0.0	28.4	500%	**PFOA**	0.0	0.0	24	**PFHxS**
		A.S.	17.5	87.3	500%	**PFOA**	0.0	71.1	44	**PFHxS**
Solid part	**STP S**	**Inf.**	35.2	152.3	302%	**PFOA**	0.0	114.2	55	**PFHxS**
		A.S.	1720.4	10008.1	316%	**PFOA**	0.0	7056.5	3714	**PFHxS**
	STP T	**Inf.**	20.9	177.9	371%	**PFOA**	0.0	150.5	70	**PFHxS**
		A.S.	2426.7	11387.0	316%	**PFOA**	0.0	7813.1	4231	**PFHxS**
	STP K	**Inf.**	14.2	144.6	430%	**PFOA**	0.0	92.2	61	**PFHxS**
		A.S.	2158.0	9383.6	278%	**PFOA**	0.0	6781.1	3247	**PFHxS**

*The closer the estimated maximum of [C8 PFAA precursors] is to Δ[PFOA], the greater the proportion of likely PFOS precursors (Houtz and Sedlak, 2012).

**The closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA], the greater the proportion of likely PFHxS precursors are; conversely, the closer the estimated maximum of [C6 PFAA precursors] is to Δ[PFHxA]/0.19, the greater the proportion of likely C6 fluorotelomer-based (i.e., PFHxA) precursors are (Houtz and Sedlak, 2012).

5.3.3 Mass balance

Daily mass loads were calculated for investigating the mass balance of both PFAAs and PFAA precursors in STP. Concentrations used for calculation for mass balance were total concentrations of PFAAs after oxidation. The daily mass loads of influents and treated sewages were shown in Figure 5-5. However, significant decrease of mass load after oxidation between influents and treated sewages were observed. The ratios of mass after and before treatment tank ((T.S. + A.S. + Supernatant)/Inf.) of STP T, S and K were 35, 53 and 37%, respectively. The lower mass after treatment tank could not explained by the removal of sludge to outside, even it showed the removal of PFASs by sludge in adjusting tank were the similar or one second the amount (11, 2.3 and 7.2 g/d for STP T, S and K, respectively) with effluent (14, 2.3 and 17 g/d for STP T, S and K, respectively).

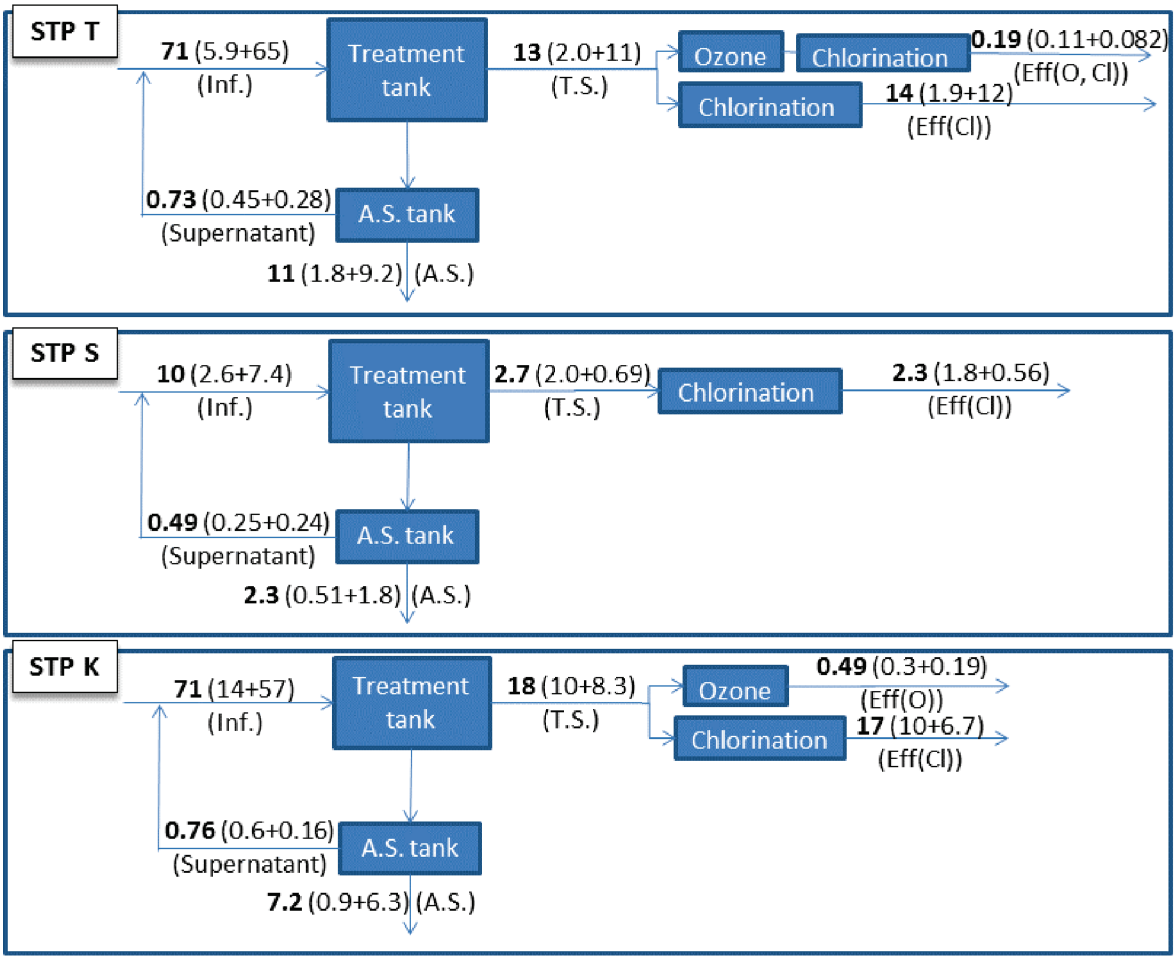


Figure 5-5 The mass loads (ng d^{-1}) of PFASs in STPs shown in figure as PFASs (PFAAs + PFAA precursors). The mass loads of PFAAs calculated from the concentrations of PFAAs before oxidation. The mass loads of PFAA precursors calculated from the

concentrations of the elevated PFAAs by oxidation.

The decrease of mass load could be explained by two possible reasons. One is that influent containing high proportion of volatile PFAA precursors which are stripped into atmosphere in aeration tank. This hypothesis could be supported by these studies: Rhoads et al. (2008) who have predicted the behavior of one kind of volatile PFAA precursor (N-EtFOSE) in STP: 76% is stripped into the atmosphere, 5% sorbs to waste solids, 13% undergoes transformation to N-EtFOSAA, and 6% is discharged in the wastewater effluent; And detection of PFASs in atmosphere near STP was also reported (Ahrens et al., 2011).

Another possible reason for the decrease of mass load was considered from the studies done on the metabolites of PFAA precursors. Dasu et al. (2013) have shown 8:2 FTS metabolites with a production of PFOA up to 4.5 mol% with the forest soil. In the prediction of Rhoads et al. (2008), little production of PFOS from one kind of volatile PFAA precursor (N-EtFOSE) was predicted. However, by the method in this study using $^{\bullet}$OH, for example, produce PFOA from 8:2 FtS as 21 mol% (Houtz and Sedlak, 2012). These results indicating bio-decomposition produces lower mount of PFAAs from precursors comparing with the oxidation method by $^{\bullet}$OH, which could be the reason for mass decrease, and leaded to lower mass loads in treated sewage than influent.

The mass load of influents of STP T and K showed similar amount of PFAAs after oxidation, even the influent flow of STP T (176110 m^3/d) is about 80% of that of STP K (220674 m^3/d). The higher flow of industry wastewater, including “cooling water (direct)”, “planting waste water” and “acid or alkali washing water”, could be the source of PFASs. This result consisting with the result mention above that, one or all of these 3 industry waste influents could be the reason for higher “percentage” observed in STP T than the others.

The removal efficiencies in STP were indicated by mass load. Consistent mass load among of treated sewages and effluents were observed (**Figure 5-5**). This result was consistent with the previously reported results mentioned above, indicating that the removals of PFAA precursors are ineffective in ozonation and chlorination treatment.

However, decrease of mass load between influents and treated water showed different result with the previous studies, which did not consider the total mass load of PFAA precursors and showed that similar or higher PFAS concentrations in the effluent in comparison with the influent, indicating that conventional STPs are not effective for removal of PFASs (Murakami et al., 2009; Schultz et al., 2006; Sun et al., 2012) or STPs utilizing biological treatment process coupled with chlorination, ozonation, or activated carbon adsorption showed ineffective decreasing of PFASs (Shivakoti et al., 2010). This study estimated the percentage of decrease of PFASs by comparing the amount of total PFAAs after oxidation between effluent and influent. The results showed that 80, 77 and 75% of PFAAs were decreased in STP T, S and K, respectively. Indicating that STP reduces PFASs by sole or combination of the following mechanisms; a) strips the volatile PFAA precursors into atmosphere in aeration tank, b) decomposition of PFAA precursors into PFAAs in low production yield and other compounds by bio-decomposition in aeration tank, and c) absorption of PFAAs and their precursors into sludge and send outside.

5.4 Conclusion

To our knowledge, this is the first report on the mass balance and transformation of PFAAs and their precursors in STPs. The importance of PFAA precursors in STPs was revealed by its significant Percentage of PFCAs formed: $\Sigma\Delta$PFCA / (ΣPFAS$_{\text{before}}$ + $\Sigma\Delta$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 oxidation were reduced in STP T, S and K, respectively. STP reduces large amount of PFASs by the sole or combination of the follow reasons: a) volatile PFAA precursors are stripped into atmosphere in aeration tank, b) PFAA precursors are decomposed into PFAAs with low yield and other compounds by bio-decomposition in aeration tank, and c) PFAAs and their precursors were absorbed into sludge and 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 precursor which contribute the PFOA in environment.

6. Conclusion and recommendation

The conclusions and recommendations 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 $\text{PFCA}_{\text{C4-C12}}$ by oxidation ($\Sigma\Delta[\text{PFCA}_{\text{C4-C12}}]$)

against $\Sigma[\mathrm{PFCA}_{\mathrm{C4\text{-}C12}}]_{\text{before oxidation}}$ 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: $\Sigma\Delta\mathrm{PFCA} / (\Sigma\mathrm{PFAS}_{\mathrm{before}} + \Sigma\Delta\mathrm{PFCA})$. 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.

7. References

Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E.J., 2011. Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere. Environ. Sci. Technol. 45, 8098–8105. doi:10.1021/es1036173

Armitage, J.M., MacLeod, M., Cousins, I.T., 2009. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. Environ. Sci. Technol. 43, 1134–1140.

Bao, J., Jin, Y., Liu, W., Ran, X., Zhang, Z., 2009. Perfluorinated compounds in sediments from the Daliao River system of northeast China. Chemosphere 77, 652–657. doi:10.1016/j.chemosphere.2009.08.018

Bao, J., Liu, W., Liu, L., Jin, Y., Ran, X., Zhang, Z., 2010. Perfluorinated compounds in urban river sediments from Guangzhou and Shanghai of China. Chemosphere 80, 123–130. doi:10.1016/j.chemosphere.2010.04.008

Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main river, Bayreuth, Germany. Environ. Pollut. 156, 818–820. doi:10.1016/j.envpol.2008.05.024

Benskin, J.P., Ikonomou, M.G., Gobas, F.A.P.C., Woudneh, M.B., Cosgrove, J.R., 2012. Observation of a Novel PFOS-Precursor, the Perfluorooctane Sulfonamido Ethanol-Based Phosphate (SAmPAP) Diester, in Marine Sediments. Environ. Sci. Technol. 46, 6505–6514. doi:10.1021/es300823m

Boulanger, B., Vargo, J., Schnoor, J.L., Hornbuckle, K.C., 2004. Detection of Perfluorooctane Surfactants in Great Lakes Water. Environ. Sci. Technol. 38, 4064–4070. doi:10.1021/es0496975

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, S.P., 2011. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. Integr. Environ. Assess. Manag. 7, 513–541. doi:10.1002/ieam.258

Bureau of Sewerage Tokyo Metropolitan Gvernment, 2012. Overview of works of Bureau of Sewerage Tokyo Metropolitan Gvernment, 2012. Bureau of Sewerage Tokyo Metropolitan Gvernment.

Burns, D.C., Ellis, D.A., Li, H., McMurdo, C.J., Webster, E., 2008. Experimental pKa determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa concentration dependence on laboratory-measured partitioning phenomena and environmental modeling. Environ. Sci. Technol. 42, 9283–9288.

Burris, J.M., Lundberg, J.K., Olsen, G.W., 2002. Determination of serum half-lives of several fluorochemicals (No. Interim Report #2). 3M Company.

Cheng, J., Psillakis, E., Hoffmann, M.R., Colussi, A.J., 2009. Acid Dissociation versus Molecular Association of Perfluoroalkyl Oxoacids: Environmental Implications. J. Phys. Chem. A 113, 8152–8156. doi:10.1021/jp9051352

CMC CO., Ltd, 2001. Market and Prospect of Fluorine Products. CMC CO., Ltd.

D'eon, J.C., Crozier, P.W., Furdui, V.I., Reiner, E.J., Libelo, E.L., Mabury, S.A., 2009. Perfluorinated phosphonic acids in Canadian surface waters and wastewater treatment plant effluent: Discovery of a new class of perfluorinated acids. Environ. Toxicol. Chem. 28, 2101–2107. doi:10.1897/09-048.1

D'eon, J.C., Mabury, S.A., 2011. Is Indirect Exposure a Significant Contributor to the Burden of Perfluorinated Acids Observed in Humans? Environ. Sci. Technol. 45, 7974–7984. doi:10.1021/es200171y

Dasu, K., Lee, L.S., Turco, R.F., Nies, L.F., 2013. Aerobic biodegradation of 8:2 fluorotelomer stearate monoester and 8:2 fluorotelomer citrate triester in forest soil. Chemosphere 91, 399–405. doi:10.1016/j.chemosphere.2012.11.076

De Silva, A.O., Allard, C.N., Spencer, C., Webster, G.M., Shoeib, M., 2012. Phosphorus-Containing Fluorinated Organics: Polyfluoroalkyl Phosphoric Acid Diesters (diPAPs), Perfluorophosphonates (PFPAs), and Perfluorophosphinates (PFPIAs) in Residential Indoor Dust. Environ. Sci. Technol. 46, 12575–12582. doi:10.1021/es303172p

Dinglasan-Panlilio, M.J.A., Mabury, S.A., 2006. Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials. Environ. Sci. Technol. 40, 1447–1453. doi:10.1021/es051619+

Emmett, E.A., Shofer, F.S., Zhang, H., Freeman, D., Desai, C., Shaw, L.M., 2006. Community Exposure to Perfluorooctanoate: Relationships Between Serum Concentrations and Exposure Sources. J. Occup. Environ. Med. 48, 759–770. doi:10.1097/01.jom.0000232486.07658.74

Fiedler, S., Pfister, G., Schramm, K.-W., 2010. Poly- and perfluorinated compounds in household consumer products. Toxicol. Environ. Chem. 92, 1801–1811. doi:10.1080/02772248.2010.491482

Gauthier, S.A., Mabury, S.A., 2005. Aqueous photolysis of 8:2 fluorotelomer alcohol. Environ. Toxicol. Chem. 24, 1837–1846. doi:10.1897/04-591R.1

Giesy, J.P., Kannan, K., 2001. Global Distribution of Perfluorooctane Sulfonate in Wildlife. Environ. Sci. Technol. 35, 1339–1342. doi:10.1021/es001834k

Giesy, J.P., Kannan, K., 2002. Peer Reviewed: Perfluorochemical Surfactants in the Environment. Environ. Sci. Technol. 36, 146A–152A. doi:10.1021/es022253t

Goss, K.-U., 2008. The pKa values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. 42, 456–458.

Hansen, K.J., Johnson, H.O., Eldridge, J.S., Butenhoff, J.L., Dick, L.A., 2002. Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River. Environ. Sci. Technol. 36, 1681–1685. doi:10.1021/es010780r

Herzke, D., Olsson, E., Posner, S., 2012. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study. Chemosphere 88, 980–987. doi:10.1016/j.chemosphere.2012.03.035

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. Environ. Sci. Technol. 39, 3946–3956. doi:10.1021/es048245p

Higgins, C.P., Luthy, R.G., 2006. Sorption of Perfluorinated Surfactants on Sediments†. Environ. Sci. Technol. 40, 7251–7256. doi:10.1021/es061000n

Houtz, E.F., Sedlak, D.L., 2012. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. Environ. Sci. Technol. 46, 9342–9349. doi:10.1021/es302274g

IPCS, 2005. Perfluorooctanoic acid. International Chemical Safety Cards.

Kaiser, M.A., Larsen, B.S., Kao, C.-P.C., Buck, R.C., 2005. Vapor Pressures of Perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic Acids. J. Chem. Eng. Data 50, 1841–1843. doi:10.1021/je050070r

Kawashita, H., Fukushima, A., Yoshikawa, M., 2014. Emission source and behavior of Perfluorinated Organic Copounds in Fukui Prefecture. 23rd Symp. Environ. Chem. Jpn. 447.

Kennedy, G.L., Jr, Butenhoff, J.L., Olsen, G.W., O'Connor, J.C., Seacat, A.M., Perkins, R.G., Biegel, L.B., Murphy, S.R., Farrar, D.G., 2004. The toxicology of perfluorooctanoate. Crit. Rev. Toxicol. 34, 351–384.

Kissa, E., 2001. Fluorinated Surfactants and Repellents. Marcel Dekker Inc.

Klaunig, J.E., Babich, M.A., Baetcke, K.P., Cook, J.C., Corton, J.C., David, R.M., DeLuca, J.G., Lai, D.Y., McKee, R.H., Peters, J.M., Roberts, R.A., Fenner-Crisp, P.A., 2003. PPARalpha agonist-induced rodent tumors: modes of action and human relevance. Crit. Rev. Toxicol. 33, 655–780. doi:10.1080/713608372

Kutsuna, S., Hori, H., 2008. Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298 K by means of an inert-gas stripping method with a helical plate. Atmos. Environ. 42, 8883–8892. doi:10.1016/j.atmosenv.2008.09.008

Kwadijk, C.J.A.F., Korytár, P., Koelmans, A.A., 2010. Distribution of Perfluorinated Compounds in Aquatic Systems in The Netherlands. Environ. Sci. Technol. 44, 3746–3751. doi:10.1021/es100485e

Labadie, P., Chevreuil, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ. Pollut. 159, 391–397. doi:10.1016/j.envpol.2010.10.039

Lee, H., Tevlin, A.G., Mabury, S.A., Mabury, S.A., 2014. Fate of Polyfluoroalkyl Phosphate Diesters and Their Metabolites in Biosolids-Applied Soil: Biodegradation and Plant Uptake in Greenhouse and Field Experiments. Environ. Sci. Technol. 48, 340–349. doi:10.1021/es403949z

Lei, Y.D., Wania, F., Mathers, D., Mabury, S.A., 2004. Determination of Vapor Pressures, Octanol−Air, and Water−Air Partition Coefficients for Polyfluorinated Sulfonamide, Sulfonamidoethanols, and Telomer Alcohols. J. Chem. Eng. Data 49, 1013–1022. doi:10.1021/je049949h

Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. Chemosphere 84, 265–271. doi:10.1016/j.chemosphere.2011.03.060

Li, J., Del Vento, S., Schuster, J., Zhang, G., Chakraborty, P., Kobara, Y., Jones, K.C., 2011. Perfluorinated Compounds in the Asian Atmosphere. Environ. Sci. Technol. 45, 7241–7248. doi:10.1021/es201739t

Ministry of the Environment Government of Japan, 2008. Environmental risk assessment of perfluorooctane sulfonic acid and Its salts. 環境省.

Motegi, M., Nojiri, K., Hosono, S., 2013. Investigation of PFOS, PFOA and their precursor pollution in rivers of Saitama prefectre (No. 10). Center for Environmental Science in Saitama.

Murakami, M., Imamura, E., Shinohara, H., Kiri, K., Muramatsu, Y., Harada, A., Takada, H., 2008. Occurrence and Sources of Perfluorinated Surfactants in Rivers in Japan. Environ. Sci. Technol. 42, 6566–6572. doi:10.1021/es800353f

Murakami, M., Shinohara, H., Takada, H., 2009. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs). Chemosphere 74, 487–493. doi:10.1016/j.chemosphere.2008.10.018

Naile, J.E., Khim, J.S., Wang, T., Chen, C., Luo, W., Kwon, B.-O., Park, J., Koh, C.-H., Jones, P.D., Lu, Y., Giesy, J.P., 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. Environ. Pollut. 158, 1237–1244. doi:10.1016/j.envpol.2010.01.023

NMR Publisering, 2013. Per and polyfluorinated substances in the Nordic Countries. Nordisk Ministerråd.

OECD, 2002. Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and Its Salts.

OECD, 2005. RESULTS OF SURVEY ON PRODUCTION AND USE OF PFOS, PFAS AND PFOA, RELATED SUBSTANCES AND PRODUCTS/ MIXTURES CONTAINING THESE SUBSTANCES.

OECD, 2011. OUTCOME OF THE 2009 SURVEY SURVEY ON THE PRODUCTION, USE AND RELEASE OF PFOS, PFAS, PFOA PFCA, THEIR RELATED SUBSTANCES AND PRODUCTS/MIXTURES CONTAINING THESE SUBSTANCES.

Pan, G., You, C., 2010. Sediment–water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River Estuary. Environ. Pollut. 158, 1363–1367. doi:10.1016/j.envpol.2010.01.011

Plumlee, M.H., McNeill, K., Reinhard, M., 2009. Indirect Photolysis of Perfluorochemicals: Hydroxyl Radical-Initiated Oxidation of N-Ethyl Perfluorooctane Sulfonamido Acetate (N-EtFOSAA) and Other Perfluoroalkanesulfonamides. Environ. Sci. Technol. 43, 3662–3668. doi:10.1021/es803411w

Rayne, S., Forest, K., 2010. Theoretical studies on the pKa values of perfluoroalkyl carboxylic acids. J. Mol. Struct. THEOCHEM 949, 60–69. doi:10.1016/j.theochem.2010.03.003

Renner, R., 2001. Growing concern over perfluorinated chemicals. Environ. Sci. Technol. 35, 154A–160A.

Rhoads, K.R., Janssen, E.M.-L., Luthy, R.G., Criddle, C.S., 2008. Aerobic Biotransformation and Fate of N-Ethyl Perfluorooctane Sulfonamidoethanol (N-EtFOSE) in Activated Sludge. Environ. Sci. Technol. 42, 2873–2878. doi:10.1021/es702866c

Schultz, M.M., Barofsky, D.F., Field, J.A., 2003. Fluorinated Alkyl Surfactants. Environ. Eng. Sci. 20, 487–501. doi:10.1089/109287503768335959

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006. Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. Environ. Sci. Technol. 40, 7350–7357. doi:10.1021/es061025m

Senthilkumar, K., Ohi, E., Sajwan, K., Takasuga, T., Kannan, K., 2007. Perfluorinated Compounds in River Water, River Sediment, Market Fish, and Wildlife Samples from Japan. Bull. Environ. Contam. Toxicol. 79, 427–431. doi:10.1007/s00128-007-9243-2

Shivakoti, B.R., Tanaka, S., Fujii, S., Kunacheva, C., Boontanon, S.K., Musirat, C., Seneviratne, S.T.M.L.D., Tanaka, H., 2010. Occurrences and behavior of perfluorinated compounds (PFCs) in several wastewater treatment plants (WWTPs) in Japan and Thailand. J. Environ. Monit. 12, 1255–1264. doi:10.1039/B927287A

Shoeib, M., Harner, T., M. Webster, G., Lee, S.C., 2011. Indoor Sources of Poly- and Perfluorinated Compounds (PFCS) in Vancouver, Canada: Implications for Human Exposure. Environ. Sci. Technol. 45, 7999–8005. doi:10.1021/es103562v

Shoeib, M., Harner, T., Vlahos, P., 2006. Perfluorinated Chemicals in the Arctic Atmosphere. Environ. Sci. Technol. 40, 7577–7583. doi:10.1021/es0618999

Sinclair, E., Kannan, K., 2006. Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants. Environ. Sci. Technol. 40, 1408–1414. doi:10.1021/es051798v

Sinclair, E., Kim, S.K., Akinleye, H.B., Kannan, K., 2007. Quantitation of Gas-Phase Perfluoroalkyl

Surfactants and Fluorotelomer Alcohols Released from Nonstick Cookware and Microwave Popcorn Bags. Environ. Sci. Technol. 41, 1180–1185. doi:10.1021/es062377w

So, M.K., Miyake, Y., Yeung, W.Y., Ho, Y.M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam, P.K.S., 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China. Chemosphere 68, 2085–2095. doi:10.1016/j.chemosphere.2007.02.008

So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K.S., 2004. Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea. Environ. Sci. Technol. 38, 4056–4063. doi:10.1021/es049441z

Strynar, M.J., Lindstrom, A.B., Nakayama, S.F., Egeghy, P.P., Helfant, L.J., 2012. Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils. Chemosphere 86, 252–257. doi:10.1016/j.chemosphere.2011.09.036

Sun, H., Zhang, X., Wang, L., Zhang, T., Li, F., He, N., Alder, A.C., 2012. Perfluoroalkyl compounds in municipal WWTPs in Tianjin, China—concentrations, distribution and mass flow. Environ. Sci. Pollut. Res. 19, 1405–1415. doi:10.1007/s11356-011-0727-6

Taniyasu, S., Kannan, K., So, M.K., Gulkowska, A., Sinclair, E., Okazawa, T., Yamashita, N., 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. J. Chromatogr. A 1093, 89–97. doi:10.1016/j.chroma.2005.07.053

Theobald, N., Caliebe, C., Gerwinski, W., Hühnerfuss, H., Lepom, P., 2011. Occurrence of perfluorinated organic acids in the North and Baltic seas. Part 1: distribution in sea water. Environ. Sci. Pollut. Res. Int. 18, 1057–1069. doi:10.1007/s11356-011-0451-2

Trier, X., Granby, K., Christensen, J., 2011. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environ. Sci. Pollut. Res. 18, 1108–1120. doi:10.1007/s11356-010-0439-3

Tsao, M.-S., Wilmarth, W.K., 1959. The Aqueous Chemistry of Inorganic Free Radicals. I. The Mechanism of the Photolytic Decomposition of Aqueous Persulfate Ion and Evidence Regarding the Sulfate–Hydroxyl Radical Interconversion Equilibrium. J. Phys. Chem. 63, 346–353. doi:10.1021/j150573a006

U.S.EPA, 1978a. Fluorad fluorochemical surfactant FC-95 acute oral toxicity (LD50) study in rats (No. Study No. 137-083).

U.S.EPA, 1978b. Ninety day subacute rat toxicity study (Study No. 137-085).

U.S.EPA, 1978c. Final report, ninety day subacute rat toxicity study on Fluorad® Fluorochemical FC-143, International Research and Development Corporation (No. Study No. 137-089). U.S.EPA.

U.S.EPA, 2005. Draft risk assessment of the potential human health effects associated with exposure to perfluorooctanoic acid and its salts.

Webster, E., Ellis, D.A., 2010. Potential role of sea spray generation in the atmospheric transport of perfluorocarboxylic acids. Environ. Toxicol. Chem. 29, 1703–1708. doi:10.1002/etc.228

Webster, E., Ellis, D.A., Reid, L.K., 2010. Modeling the environmental fate of perfluorooctanoic acid and perfluorooctanoate: An investigation of the role of individual species partitioning. Environ. Toxicol. Chem. 29, 1466–1475. doi:10.1002/etc.181

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of Perfluorinated Acids at Parts-Per-Quadrillion Levels in Seawater Using Liquid Chromatography-Tandem Mass Spectrometry. Environ. Sci. Technol. 38, 5522–5528. doi:10.1021/es0492541

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. Mar. Pollut. Bull. 51, 658–668. doi:10.1016/j.marpolbul.2005.04.026

Yang, L., Zhu, L., Liu, Z., 2011. Occurrence and partition of perfluorinated compounds in water and sediment from Liao River and Taihu Lake, China. Chemosphere 83, 806–814. doi:10.1016/j.chemosphere.2011.02.075

Zhang, Y., Meng, W., Guo, C., Xu, J., Yu, T., Fan, W., Li, L., 2012. Determination and partitioning behavior of perfluoroalkyl carboxylic acids and perfluorooctanesulfonate in water and sediment from Dianchi Lake, China. Chemosphere 88, 1292–1299. doi:10.1016/j.chemosphere.2012.03.103

Zushi, Y., Masunaga, S., 2011. GIS-based source identification and apportionment of diffuse water pollution: Perfluorinated compound pollution in the Tokyo Bay basin. Chemosphere 85, 1340–1346. doi:10.1016/j.chemosphere.2011.07.052

Zushi, Y., Ye, F., Motegi, M., Nojiri, K., Hosono, S., Suzuki, T., Kosugi, Y., Yaguchi, K., Masunaga, S., 2011. Spatially Detailed Survey on Pollution by Multiple Perfluorinated Compounds in the Tokyo Bay Basin of Japan. Environ. Sci. Technol. 45, 2887–2893. doi:10.1021/es103917r

8. Appendix

Table A1-1 Hierarchical overview of the nonpolymer polyfluoroalkyl substances: compounds for which all H atoms on at least one (but not all) C atoms have been replaced with F (Buck et al., 2011)

	Classification and chemical structure	**$C_nF_{2n+1}R$, where R =**	**Examples**	**Uses**
Perfluoroalkane sulfonamido substances[a]	*N*-Alkyl perfluoroalkane sulfonamides (MeFASAs, EtFASAs, BuFASAs)	$-SO_2NH(R')$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	*N*-Methyl perfluorooctane sulfonamide (MeFOSA), $C_8F_{17}SO_2N(CH_3)H$	Major raw material for surfactant and surface protection products
			N-Ethyl perfluorobutane sulfonamide (EtFBSA), $C_4F_9SO_2N(C_2H_5)H$	
			N-Butyl perfluorooctane sulfonamide (BuFOSA), $C_8F_{17}SO_2N(C_4H_9)H$	
	Perfluoroalkane sulfonamidoethanols (FASEs) and *N*-alkyl perfluoroalkane sulfonamidoethanols (MeFASEs, EtFASEs, BuFASEs)	$-SO_2N(R')CH_2CH_2OH$ where $R' = C_mH_{2m+1}$ (m = 0,1,2,4)	Perfluorooctane sulfonamidoethanol (FOSE), $C_8F_{17}SO_2NHCH_2CH_2OH$	Major raw material for surfactant and surface protection products
			N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE), $C_4F_9SO_2N(C_2H_5)CH_2CH_2OH$	
	N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates (MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs)	$-SO_2N(R')CH_2CH_2O\text{-}C(O)CH = CH_2$ and $-SO_2N(R')CH_2CH_2O\text{-}C(O)C(CH_3) = CH_2$ where $R' = C_mH_{2m+1}$ (m = 1,2,4)	*N*-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC), $C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OC(O)CH = CH_2$	Major raw material for surfactant and surface protection products
	Perfluoroalkane sulfonamidoacetic acids (FASAAs) and *N*-alkyl perfluoroalkane sulfonamidoacetic acids (MeFASAAs, EtFASAAs, BuFASAAs)	$-SO_2N(R')CH_2COOH$ where $R' = C_mH_{2m+1}$ (m = 0,1,2,4)	*N*-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), $C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	Intermediate environmental transformation product

Table A1-1 (Continued)

Fluorotelomer substancesb	Semifluorinated *n*-alkanes (SFAs) and alkenes (SFAenes)	-(CH2)mH and –CH = CH(CH2)m-2H, with *m* = 2–16 and *n* = 6–16	Perfluorohexylhexadecane (F6H16), F(CF2)6(CH2)16H	Ski wax; medical applications
	n:2 Fluorotelomer iodides (n:2 FTIs) (Telomer B)	-CH2CH2I	8:2 Fluorotelomer iodide (8:2 FTI), C8F17CH2CH2I	Major raw material for surfactant and surface protection products
	n:2 Fluorotelomer olefins (n:2 FTOs)	-CH = CH2	6:2 Fluorotelomer olefin (6:2 FTO), C6F13CH = CH2	Raw material for surfactant and surface protection products
	n:2 Fluorotelomer alcohols (n:2 FTOHs)	-CH2CH2OH	10:2 Fluorotelomer alcohol (10:2 FTOH), C10F21CH2CH2OH	Major raw material for surfactant and surface protection products
	n:2 Unsaturated fluorotelomer alcohols (n:2 FTUOHs)	-CF = CHCH2OH	8:2 Unsaturated fluorotelomer alcohol (8:2 FTUOH), C7F15CF = CHCH2OH	Intermediate environmental transformation product
	n:2 Fluorotelomer acrylates (n:2 FTACs) and methacrylates (n:2 FTMACs)	-CH2CH2OC(O)CH = CH2 and -CH2CH2OC(O)C(CH3) = CH2	8:2 Fluorotelomer acrylate (8:2 FTAC), C8F17CH2CH2OC(O)CH = CH2	Major raw material for fluorotelomer-based polymers used in surface protection products
	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates (PAPs)	(-CH2CH2O)xP(=O)(OH)3-x where *x* = 1 or 2	6:2 Fluorotelomer methacrylate (6:2 FTMAC), C6F13CH2CH2OC(O)C(CH3) = CH2 8:2 Fluorotelomer phosphate monoester (8:2 monoPAP), C8F17CH2CH2OP(=O)(OH)2	Surfactant and surface protection products
	n:2 Fluorotelomer aldehydes (n:2 FTALs) and unsaturated aldehydes (n:2 FTUALs)	-CH2CHO and -CF = CHCHO	8:2 Fluorotelomer phosphate diester (8:2 diPAP), (C8F17CH2CH2O)2P(=O)OH 8:2 Fluorotelomer aldehyde (8:2 FTAL), C8F17CH2CHO	Intermediate environmental transformation product

Table A1-1 (Continued)

	n:2 Fluorotelomer carboxylic acids (n:2 FTCAs) and unsaturated carboxylic acids (n:2 FTUCAs)		8:2 Fluorotelomer unsaturated aldehyde (8:2 FTUAL), C7F15CF = CHCHO	
		-CH2COOH and -CF = CHCOOH	8:2 Fluorotelomer carboxylic acid (8:2 FTCA), C8F17CH2COOH8:2 Fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), C7F15CF = CHCOOH	Intermediate environmental transformation product
	n:3 Saturated acids (n:3 Acids) and n:3 Unsaturated acids (n:3 UAcids)	-CH2CH2COOH and -CH = CHCOOH	7:3 Acid, C7F15CH2CH2COOH	Intermediate environmental transformation product
	n:2 Fluorotelomer sulfonic acids (n:2 FTSAs)		7:3 UAcid, C7F15CH = CHCOOH	
		-CH2CH2SO3H	8:2 Fluorotelomer sulfonic acid (8:2 FTSA), C8F17CH2CH2SO3H	Surfactant and environmental transformation product
Miscellaneous	Polyfluoroalkyl ether carboxylic acids	For example: -O(CmF2m)OCHF(CpF2p)COOH	4,8-Dioxa-3*H*-perfluorononanoate, CF3OCF2CF2CF2OCHFCF2COOH	Alternative fluoropolymer processing aid (as ammonium salt)

[a] Substances originating by electrochemical fluorination (ECF) process;

[b] Substances originating by fluorotelomer process.

Table A1-2 Hierarchical overview of fluoropolymers, perfluoropolyethers, and side-chain–fluorinated polymers (Buck et al., 2011)

		Example(s)	**Uses**
Fluoropolymers: Carbon-only polymer backbone with F directly attached to backbone C atoms		-(CF2CF2)n- Polytetrafluoroethylene (PTFE)	Plastics
		-(CH2CF2)n- Polyvinylidene fluoride (PVDF)	
		-(CH2CHF)n- Polyvinyl fluoride (PVF)	
		-(CF2CF2)n-(CF(CF3)CF2)m- Fluorinated ethylene propylene (FEP)	
Perfluoropolyethers (PFPEs): Ether polymer backbone with F atoms directly attached		F-(CmF2mO-)nCF3	Functional fluids, surfactants, and surface protection products
		HOCH2O-[CmF2mO-]nCH2OH	
		-where CmF2mO represents -CF2O-, -CF2CF2O-, and/or -CF(CF3)CF2O- units distributed randomly along the polymer backbone	
Side-chain–fluorinated polymers: Nonfluorinated polymer backbone with fluorinated side chains, ending in -CnF2n+1	Fluorinated acrylate and methacrylate polymers	Acrylate: Backbone-CH-C(O)O-X-CnF2n+1 Methacrylate: Backbone-C(CH3)-C(O)O-X-CnF2n+1 -where X is either -CH2CH2N(R′)SO2- with R′ = -CnH2n+1 (*n* = 0,1,2,4) or -CH2CH2-	Surfactants and surface protection products
	Fluorinated urethane polymers	Backbone-NHC(O)O- X-CnF2n+1 -where X is either -CH2CH2N(R′)SO2- with R′ = -CnH2n+1 (*n* = 0,1,2,4) or -CH2CH2-	Surfactants and surface protection products
	Fluorinated oxetane polymers	Backbone-CH2OCH2-R -where R = -CF3, -C2F5 or -CH2C4F9	Surfactants and surface protection products

Table A1-3 Hierarchical overview of the nonpolymer polyfluoroalkyl substances: compounds for which all H atoms on at least one (but not all) C atoms have been replaced with F**(Buck et al., 2011)**

	Classification and chemical structure	**CnF2n+1R, where R =**	**Examples**	**Uses**
Perfluoroalkane sulfonamido substances[a]	*N*-Alkyl perfluoroalkane sulfonamides (MeFASAs, EtFASAs, BuFASAs)	-SO2NH(R′) where R′ = CmH2m+1 (*m* = 1,2,4)	*N*-Methyl perfluorooctane sulfonamide (MeFOSA), C8F17SO2N(CH3)H	Major raw material for surfactant and surface protection products
			N-Ethyl perfluorobutane sulfonamide (EtFBSA), C4F9SO2N(C2H5)H	
			N-Butyl perfluorooctane sulfonamide (BuFOSA), C8F17SO2N(C4H9)H	
	Perfluoroalkane sulfonamidoethanols (FASEs) and*N*-alkyl perfluoroalkane sulfonamidoethanols (MeFASEs, EtFASEs, BuFASEs)	-SO2N(R′)CH2CH2OH where R′ = CmH2m+1 (*m* = 0,1,2,4)	Perfluorooctane sulfonamidoethanol (FOSE), C8F17SO2NHCH2CH2OH	Major raw material for surfactant and surface protection products
			N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE), C4F9SO2N(C2H5)CH2CH2OH	
	N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates (MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs)	-SO2N(R′)CH2CH2O-C(O)CH = CH2 and -SO2N(R′)CH2CH2O-C(O)C(CH3) = CH2where R′ = CmH2m+1 (*m* = 1,2,4)	*N*-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC), C8F17SO2N(C2H5)CH2CH2OC(O)CH = CH2	Major raw material for surfactant and surface protection products

Table A1-3 (Continued)

	Perfluoroalkane sulfonamidoacetic acids (FASAAs) and *N*-alkyl perfluoroalkane sulfonamidoacetic acids (MeFASAAs, EtFASAAs, BuFASAAs)	-SO2N(R′)CH2COOH where R′ = CmH2m+1 (*m* = 0,1,2,4)	*N*-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), C8F17SO2N(C2H5)CH2CO2H	Intermediate environmental transformation product
Fluorotelomer substances[b]	Semifluorinated *n*-alkanes (SFAs) and alkenes (SFAenes)	-(CH2)mH and –CH = CH(CH2)m-2H, with *m* = 2–16 and *n* = 6–16	Perfluorohexylhexadecane (F6H16), F(CF2)6(CH2)16H	Ski wax; medical applications
	n:2 Fluorotelomer iodides (n:2 FTIs) (Telomer B)	-CH2CH2I	8:2 Fluorotelomer iodide (8:2 FTI), C8F17CH2CH2I	Major raw material for surfactant and surface protection products
	n:2 Fluorotelomer olefins (n:2 FTOs)	-CH = CH2	6:2 Fluorotelomer olefin (6:2 FTO), C6F13CH = CH2	Raw material for surfactant and surface protection products
	n:2 Fluorotelomer alcohols (n:2 FTOHs)	-CH2CH2OH	10:2 Fluorotelomer alcohol (10:2 FTOH), C10F21CH2CH2OH	Major raw material for surfactant and surface protection products
	n:2 Unsaturated fluorotelomer alcohols (n:2 FTUOHs)	-CF = CHCH2OH	8:2 Unsaturated fluorotelomer alcohol (8:2 FTUOH), C7F15CF = CHCH2OH	Intermediate environmental transformation product

Table A1-3 (Continued)

	n:2 Fluorotelomer acrylates (n:2 FTACs) and methacrylates (n:2 FTMACs)	-CH2CH2OC(O)CH = CH2 and -CH2CH2OC(O)C(CH3) = CH2	8:2 Fluorotelomer acrylate (8:2 FTAC), C8F17CH2CH2OC(O)CH = CH2 6:2 Fluorotelomer methacrylate (6:2 FTMAC), C6F13CH2CH2OC(O)C(CH3) = CH2	Major raw material for fluorotelomer-based polymers used in surface protection products
	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates (PAPs)	(-CH2CH2O)xP(=O)(OH) 3-x where *x* = 1 or 2	8:2 Fluorotelomer phosphate monoester (8:2 monoPAP), C8F17CH2CH2OP(=O)(OH)2 8:2 Fluorotelomer phosphate diester (8:2 diPAP), (C8F17CH2CH2O)2P(=O)OH	Surfactant and surface protection products
	n:2 Fluorotelomer aldehydes (n:2 FTALs) and unsaturated aldehydes (n:2 FTUALs)	-CH2CHO and -CF = CHCHO	8:2 Fluorotelomer aldehyde (8:2 FTAL), C8F17CH2CHO 8:2 Fluorotelomer unsaturated aldehyde (8:2 FTUAL), C7F15CF = CHCHO	Intermediate environmental transformation product
	n:2 Fluorotelomer carboxylic acids (n:2 FTCAs) and unsaturated carboxylic acids (n:2 FTUCAs)	-CH2COOH and -CF = CHCOOH	8:2 Fluorotelomer carboxylic acid (8:2 FTCA), C8F17CH2COOH8:2 Fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), C7F15CF = CHCOOH	Intermediate environmental transformation product

Table A1-3 (Continued)

	n:3 Saturated acids (n:3 Acids) and n:3 Unsaturated acids (n:3 UAcids)	-CH2CH2COOH and -CH = CHCOOH	7:3 Acid, C7F15CH2CH2COOH 7:3 UAcid, C7F15CH = CHCOOH	Intermediate environmental transformation product
	n:2 Fluorotelomer sulfonic acids (n:2 FTSAs)	-CH2CH2SO3H	8:2 Fluorotelomer sulfonic acid (8:2 FTSA), C8F17CH2CH2SO3H	Surfactant and environmental transformation product
Miscellaneous	Polyfluoroalkyl ether carboxylic acids	For example: -O(CmF2m)OCHF(CpF2p)COOH	4,8-Dioxa-3*H*-perfluorononanoate, CF3OCF2CF2CF2OCHFCF2COOH	Alternative fluoropolymer processing aid (as ammonium salt)

Table A1-4 Measured concentrations (ng g^{-1}) in the ten soils with the highest total concentrations of PFASs (Strynar et al., 2012)

Description	PFTrDA	PFTeDA	PFDoA	PFUdA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFDS	PFOS	PFHS	PFBS	Total
RTP, NC (USA)	–	–	–	–	2.03	0.609	31.7	79.1	12.4	–	2.55	0.527	–	129
RTP, NC (USA)	–	–	–	–	0.958	–	15.6	34.1	5.36	–	0.606	–	–	56.6
Shinning Rock, NC (USA)	–	–	1.85	–	0.845	–	8.40	19.8	5.62	–	1.47	–	–	37.9
Osaka (Japan)	4.01	2.24	3.94	1.31	1.88	–	21.5	–	–	–	0.584	–	–	35.5
Houston, TX (USA)	–	–	–	–	–	–	2.66	6.12	2.96	–	2.16	–	–	13.9
Richmond, KY (USA)	–	–	1.73	–	–	–	2.14	4.61	1.71	–	1.60	–	–	11.8
W. Layfayette, IN (USA)	–	–	1.02	1.10	0.560	–	2.18	3.52	1.51	–	–	1.39	–	11.3
Mexico city (Mexico)	–	–	–	–	–	–	0.764	–	–	–	10.1	–	–	10.8
Hokkaido (Japan)	–	–	2.38	–	–	–	1.84			–	5.15	–	–	9.37
Laurel Fork, NC (USA)	–	–	1.44	–	–	–	1.35	1.56	0.945	–	2.52	–	–	7.81

Table A1-5 The supplier and purity of native standard and their related standard.

Classification	Abbreviation	Compound name	Supplier of standard and its purity
PFCAs (perfluoroalkyl carboxylic acids)	PFBA	Perfluorobutanoate	PFC-MXA Wellington Laboratories, 98%
	PFPeA	Perfluoropentanoate	
	PFHxA	Perfluorohexanoate	
	PFHpA	Perfluoroheptanoate	
	PFOA	Perfluorooctanoate	
	PFNA	Perfluorononanoate	
	PFDA	Perfluorodecanoate	
	PFUnDA	Perfluoroundecanoate	
	PFDoDA	Perfluorododecanoate	
	PFTrDA	Perfluorotridecanoate	
	PFTeDA	Perfluorotetradecanoate	
	$[^{13}C2]$PFHxA	Perfluoro-n-$[1,2-^{13}C2]$hexanoate	Wellington Laboratories, 98%
	$[^{13}C4]$PFOA	Perfluoro-n-$[1,2,3,4-^{13}C4]$octanoate	Wellington Laboratories, 98%
	$[^{13}C2]$PFDoDA	Perfluoro-n-$[1,2-^{13}C2]$dodecanoate	Wellington Laboratories, 98%
PFSAs (perfluoroalkyl sulfonic acids)	PFBS	Perfluorobutane sulfonate	Tokyo Chemical Ind., 98%
	PFHxS	Perfluorohexane sulfonate	Wellington Laboratories, 98%
	PFOS	Perfluorooctane sulfonate	Kanto Chemical, 98% including branched isomer
	PFDS	Perfluorodecane sulfonate	Wellington Laboratories, 98%
	$[^{13}C4]$PFOS	perfluoro-1-$[1,2,3,4-^{13}C4]$octanesulfonate	Wellington Laboratories, 98%
FTCAs (Fluorotelomer carboxylates)	8:2 FTCA	2-perfluorooctylethanoate	Wellington Laboratories, 98%
	$[^{13}C2]$8:2 FTCA	2-perfluorooctyl-$[1,2-^{13}C2]$-ethanoate	Wellington Laboratories, 98%
FOSAs (Perfluorooctane sulfonamides)	NMeFOSA	N-methylperfluoro-1-octanesulfonamide	Wellington Laboratories, 98%
	FOSA	Perfluorooctane sulfoneamide	Wellington Laboratories, 98%
	$[^{13}C8]$FOSA	Perfluoro-1-$[^{13}C8]$-octane sulfoneamide	Wellington Laboratories, 98%
	d5-NEtFOSA	N-deuterioethylperfluoro-1-octanesulfonamide	Wellington Laboratories, 98%
Polyfluorinated Phosphate Esters	SAm-PAP	Bis (N-ethyl perfluorooctane sulfonamido ethanol) phosphate	Industry material, 90%
	$[^{13}C4]$8:2 diPAP	$^{13}C4$-Bis(1H,1H,2H,2H perfluorooctyl phosphate	Wellington Laboratories, 98%

Table A1-6 Field record for sampling at Tama River.

2013/10/7 Temperature21～27℃

ID	Memo	Name	River	Latitude and longitude	Weather of yesterday	Weather	Time of sampling	Water temperature (℃)	Place of sampling in the river	Color	Smell	pH	EC (mS/cm)
19	near factory		branch(Asa river)	35.680324,139.300136	cloudy	sunny	13:03	21.3	center	×	×	7.86	0.12
21	after factory		branch(Asa river)	35.666989,139.337866	cloudy	sunny	12:08	24.3	center	×	×	5.8	0.07
22	after STP& factory		branch(Asa river)	35.655821,139.355996	cloudy	sunny	11:45	22.8	center	×	×	7.91	0.16
23	effluent	Kitano STP	effluent	35.655915, 139.354288	cloudy	sunny	11:24	24.3	center	×	×	7.31	0.16
1	background1		main Tama river	35.732429,139.32106	cloudy	sunny	13:30	22.5	center	×	×	8.61	0.12
3	after STP		main Tama river	35.694145,139.373864	cloudy	sunny	14:05	24.1	center	×	×	7.8	0.20
5			main Tama river	35.685361,139.407565	cloudy	sunny	14:25	24.1	center	×	×	7.87	0.28
6	Effluent	Kinshityo STP	effluent	35.685178,139.410321	cloudy	sunny	14:39	25.8	center	×	×	7.16	0.33
7	between STP		main Tama river	35.67391,139.427229	cloudy	sunny	15:52	24.9	left	×	×	7.8	0.27
9	between STP		main Tama river	35.658534,139.439353	cloudy	sunny	16:15	25.1	center	×	×	6.95	0.11
11	after STP		main Tama river	35.652414,139.488169	cloudy	sunny	16:40	25.6	center	×	×	7.33	0.23
12	Effluent	Kitatama No.1	effluent	35.654193,139.512459	cloudy	sunny	17:06	25.5	center	×	×	6.08	0.17
13	after STP		main Tama river	35.64408,139.525613	cloudy	sunny	17:19	25	center	×	×	6.73	0.10
14			main Tama river	35.62507,139.568593	cloudy	sunny	17:53	23.8	center	×	×	7.67	0.28
16	before STP		main Tama river	35.600297,139.638955	cloudy	sunny	18:43	23.5	right	×	×	7.59	0.24
17	after STP		main Tama river	35.58545,139.668808	cloudy	sunny	19:10	23.8	center	×	×	7.76	0.28

Maps: https://mapsengine.google.com/map/edit?gmp=msp&mid=zbmaxf6297TY.kL-kTX4E_vpE

Table A1-7 Concentration of perfluoroalkyl acids and their precursors in river water and sewage treatment plant effluent samples before and after oxidation (ng L^{-1})

Before / After oxidation	River water / STP effluent	Main / Branch	Sampling sites	PFAAs																PFAA precursors					Total
				PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	Σ[PFAAs]	8:2 FTCA	NMeFOSA	FOSA	di-SAmPAP	Σ[PFAA precursors]	
Before oxidation	River water	Main river	**1**	<0.31	0.73	0.82	0.21	0.59	0.46	<0.01	0.11	<0.09	<0.01	0.07	0.13	<0.14	0.54	0.04	3.7	<0.32	0.06	0.12	<0.01	0.18	3.9
			3	<0.31	1.6	2.6	0.95	2.8	2.6	0.08	0.47	<0.09	<0.01	<0.03	0.67	1.8	3.7	<0.02	17	<0.32	<0.01	0.15	<0.01	0.15	17
			7	1.4	1.4	2.5	1.0	2.5	2.4	0.02	0.40	<0.09	0.07	<0.03	0.64	1.5	3.0	<0.02	17	<0.32	<0.01	0.10	<0.01	0.10	17
			9	<0.31	2.1	3.3	2.2	5.7	3.8	0.19	0.46	<0.09	<0.01	0.06	1.4	2.9	6.9	0.05	29	<0.32	<0.01	0.13	<0.01	0.13	29
			11	1.4	1.6	5.0	1.7	5.0	4.6	0.23	0.64	<0.09	0.02	<0.03	1.2	3.1	6.7	0.10	31	<0.32	<0.01	0.17	<0.01	0.17	32
			13	<0.31	2.3	4.4	1.6	4.4	3.4	0.19	0.45	<0.09	<0.01	0.04	1.3	4.6	7.7	<0.02	30	<0.32	<0.01	0.13	<0.01	0.13	31
			14	<0.31	2.1	4.7	2.2	5.0	3.6	0.15	0.66	<0.09	0.03	0.04	1.5	5.7	7.8	<0.02	34	<0.32	<0.01	0.31	<0.01	0.31	34
			16	<0.31	2.2	4.6	2.2	5.6	4.7	0.17	0.68	<0.09	0.02	<0.03	1.6	5.9	7.7	<0.02	35	<0.32	<0.01	0.15	<0.01	0.15	35
			17	<0.31	2.4	5.0	2.2	5.3	5.0	0.04	0.42	<0.09	0.04	<0.03	2.0	6.8	8.0	0.04	37	<0.32	<0.01	0.40	<0.01	0.40	38
		Branch river	**19**	<0.31	0.47	0.25	0.20	0.88	0.26	<0.01	<0.06	<0.09	<0.01	<0.03	0.66	<0.14	1.4	<0.02	4.1	<0.32	<0.01	0.21	<0.01	0.21	4.4
			21	<0.31	1.2	1.4	1.8	3.7	1.4	<0.01	0.16	<0.09	<0.01	<0.03	0.95	0.94	3.6	<0.02	15	<0.32	<0.01	0.27	<0.01	0.27	15
			22	<0.31	1.5	1.5	1.8	3.4	1.5	<0.01	0.09	<0.09	<0.01	0.18	1.3	1.0	4.0	<0.02	16	<0.32	<0.01	0.61	<0.01	0.61	17
		Average		0.23	1.6	3.0	1.5	3.7	2.8	0.09	0.38	0.00	0.02	0.03	1.1	2.8	5.1	0.02	23	0.00	0.00	0.23	0.00	0.23	23
	STP effluent		**23**	<0.31	3.6	5.8	2.9	9.0	5.3	0.70	1.5	<0.09	<0.01	<0.03	2.4	5.6	11	<0.02	48	<0.32	<0.01	0.14	<0.01	0.14	48
			6	3.2	5.8	9.5	3.0	9.3	12	0.85	1.3	<0.09	0.13	<0.03	1.8	10	16	<0.02	72	<0.32	<0.01	0.08	<0.01	0.08	72
			12	3.4	6.0	17	4.0	12	6.7	1.0	1.0	<0.09	0.04	<0.03	3.5	24	31	<0.02	109	<0.32	<0.01	0.04	<0.01	0.04	109
		Average		2.2	5.1	11	3.3	10	8.0	0.85	1.3	0.00	0.05	0.00	2.6	13	19	0.00	76	0.00	0.00	0.09	0.00	0.09	76

Table A1-7 Concentration of perfluoroalkyl acids and their precursors in river water and sewage treatment plant effluent samples before and after oxidation (ng L^{-1}). (Continued)

Before / After oxidation	River water / STP effluent	Main / Branch	Sampling sites	PFAAs																PFAA precursors					Total
				PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	Σ[PFAAs]	8:2 FTCA	NMeFOSA	FOSA	di-SAmPAP	Σ[PFAA precursors]	
After oxidation	River water	Main river	**1**	0.32	1.2	1.6	<0.03	1.1	0.44	0.07	0.21	<0.09	<0.01	0.04	<0.08	<0.14	0.30	<0.02	5.3	-	-	-	-	-	5.3
			3*	2.6	2.2	3.4	1.1	3.2	2.3	0.35	0.64	0.13	<0.01	0.35	0.26	1.8	3.1	<0.02	21	-	-	-	-	-	21
			7	2.8	2.2	3.7	1.5	3.9	2.2	0.36	<0.06	0.11	<0.01	0.06	0.45	2.4	3.3	0.09	23	-	-	-	-	-	23
			9*	0.47	2.5	4.8	3.0	5.7	3.9	0.48	<0.06	0.10	<0.01	<0.03	0.73	2.4	6.5	0.06	31	-	-	-	-	-	31
			11*	3.8	3.1	7.5	2.1	6.5	5.1	0.69	<0.06	<0.09	<0.01	<0.03	0.99	3.7	6.1	<0.02	40	-	-	-	-	-	40
			13	3.3	3.8	6.3	2.3	4.8	3.9	0.43	0.49	<0.09	<0.01	<0.03	0.93	4.8	7.3	<0.02	38	-	-	-	-	-	38
			14*	0.40	3.9	6.8	3.5	7.9	4.1	0.57	0.76	0.15	<0.01	0.03	0.91	5.4	8.6	<0.02	43	-	-	-	-	-	43
			16*	<0.31	3.6	6.3	3.4	8.5	5.1	0.73	<0.06	0.20	<0.01	<0.03	0.85	4.8	8.0	<0.02	41	-	-	-	-	-	41
			17	2.7	3.6	6.4	3.2	6.6	4.1	0.57	0.63	0.17	<0.01	<0.03	0.89	4.9	7.4	<0.02	41	-	-	-	-	-	41
		Branch river	**19**	0.95	1.2	1.8	1.5	2.5	0.82	0.24	0.29	0.17	<0.01	<0.03	<0.08	0.54	1.4	<0.02	11	-	-	-	-	-	11
			21	2.0	2.3	3.3	3.6	5.8	1.9	0.57	0.54	0.19	<0.01	<0.03	0.38	0.90	3.9	0.10	25	-	-	-	-	-	25
			22	2.0	2.2	3.0	3.3	5.7	1.8	0.48	0.40	0.15	<0.01	<0.03	0.40	0.96	4.5	<0.02	25	-	-	-	-	-	25
		Average		1.8	2.6	4.6	2.4	5.2	3.0	0.46	0.33	0.11	0.00	0.04	0.57	2.7	5.0	0.02	-	-	-	-	-	-	-
	STP effluent		**23**	0.80	7.3	12	7.7	11	5.7	1.0	1.7	0.31	<0.01	0.08	1.2	5.7	11	<0.02	65	-	-	-	-	-	65
			6	4.8	5.4	12	4.2	14	13	1.8	0.94	0.22	0.03	<0.03	1.9	12	15	0.05	84	-	-	-	-	-	84
			12	8.7	7.0	22	5.3	16	7.7	1.7	1.5	0.09	0.17	<0.03	3.9	29	28	<0.02	131	-	-	-	-	-	131
		Average		4.8	6.6	15	5.7	14	8.7	1.5	1.4	0.21	0.06	0.03	2.3	15	18	0.02	38	-	-	-	-	-	38
	LOD			0.31	0.02	0.02	0.03	0.33	0.02	0.01	0.06	0.09	0.01	0.03	0.08	0.14	0.08	0.02	-	0.32	0.01	0.01	0.01	-	-

Table A1-8 Concentrations of PFAAs and their precursors in SPT samples before and after oxidation (ng L^{-1}).

Before/ After oxidation		STP	Type of sample	Ssampling site	PFAAs													PFAA precursors					Σ [PFASs]$_{before}$
					PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	PFHxPA	PFOPA	8:2FTCA	FOSA	di-SAmPAP	
Before oxidation	Liquid	STP T	Inf.	TI	<3.9	5.0	3.6	0.70	1.4	8.8	0.87	1.4	<0.29	2.3	0.86	4.0	<0.01	0.41	<0.53	0.99	<0.13	<0.16	30
			T.S.	TT12	<3.9	4.1	7.8	1.4	11	7.8	3.0	0.61	<0.29	0.80	<0.52	4.2	<0.01	<0.25	<0.53	<0.29	<0.13	<0.16	41
				TT34	<3.9	3.7	6.8	1.2	10	8.8	2.5	0.61	<0.29	0.80	<0.52	3.9	0.14	<0.25	<0.53	<0.29	<0.13	<0.16	39
				TT5	<3.9	6.3	9.1	2.4	13	12	4.0	1.3	0.49	2.2	0.86	6.4	<0.01	0.41	<0.53	<0.29	<0.13	<0.16	59
			Eff.(Cl)	TC12	<3.9	5.8	5.1	2.0	8.7	7.7	2.3	1.4	<0.29	2.6	0.86	3.5	<0.01	<0.25	<0.53	<0.29	<0.13	<0.16	40
				TC34	<3.9	4.3	6.1	1.4	12	7.2	1.6	0.61	<0.29	0.80	<0.52	3.8	<0.01	0.41	<0.53	<0.29	<0.13	0.26	38
				TC5	<3.9	2.3	6.7	1.4	11	7.5	3.1	1.3	0.49	2.4	0.86	4.7	<0.01	0.41	<0.53	<0.29	<0.13	<0.16	42
			Eff.(O,Cl)	TO	<3.9	1.6	3.3	1.0	7.6	4.4	1.1	<0.36	<0.29	4.0	0.86	1.2	<0.01	<0.25	<0.53	<0.29	0.22	<0.16	25
			A.S.	TS	<3.9	0.92	6.9	0.93	11	17	9.3	6.3	3.7	7.3	1.8	10	<0.01	4.1	0.88	0.48	<0.13	0.26	81
				Aaverage	0	3.8	6.2	1.4	9.5	9.0	3.1	1.5	0.51	2.6	0.68	4.7	0.02	0.64	0.10	0.16	0.02	0.06	44
		STP S	Inf.	SI	<3.9	2.8	5.0	1.2	11	8.6	3.2	1.5	0.49	4.2	8.5	4.5	<0.01	<0.25	<0.53	0.48	<0.13	0.26	52
			T.S.	STA	<3.9	5.1	9.1	1.8	25	7.4	3.2	0.61	<0.29	0.80	5.1	5.9	<0.01	<0.25	<0.53	<0.29	<0.13	<0.16	65
				STB	<3.9	5.1	5.8	1.5	15	4.4	1.2	0.61	<0.29	<0.48	2.7	6.8	0.13	<0.25	<0.53	<0.29	<0.13	<0.16	43
			Eff.(Cl)	SCA	<3.9	4.2	7.4	1.0	17	5.5	2.6	0.61	<0.29	0.80	2.5	4.3	<0.01	0.41	0.88	<0.29	<0.13	<0.16	47
				SCB	<3.9	10	5.9	1.1	15	5.1	2.1	0.61	<0.29	0.80	2.5	4.9	0.15	0.41	<0.53	<0.29	<0.13	1.0	51
			A.S.	SS	<3.9	2.9	3.8	0.68	19	15	7.5	2.3	<0.29	4.1	4.0	11	<0.01	<0.25	<0.53	<0.29	<0.13	1.5	72
				Average	0	5.8	6.0	1.1	17	8.2	3.1	1.1	0	1.7	3.7	6.3	0.14	0.21	0.67	0.08	0.04	0.65	56
		STP K	Inf.	KI	<3.9	7.4	4.1	0.44	13	12	2.1	1.9	<0.29	4.0	5.3	5.4	0.55	0.41	3.2	0.48	0.22	1.4	61
			T.S.	KTA	<3.9	6.4	5.7	1.5	12	8.8	1.2	0.61	<0.29	0.80	0.86	6.5	<0.01	0.41	<0.53	<0.29	0.22	0.26	46
				KTB	<3.9	5.8	6.2	1.1	9.3	12	2.2	1.6	<0.29	0.80	2.1	12	<0.01	<0.25	<0.53	<0.29	0.22	<0.16	54
			Eff.(Cl)	KC	<3.9	8.7	6.1	0.93	16	7.5	1.3	0.61	<0.29	0.80	0.86	5.7	<0.01	<0.25	<0.53	<0.29	<0.13	0.26	49
			Eff.(O)	KO	<3.9	5.1	9.1	1.8	25	7.4	3.2	0.61	<0.29	0.80	5.1	5.9	<0.01	<0.25	<0.53	<0.29	<0.13	<0.16	65
			A.S.	KS	<3.9	8.1	6.1	0.75	11	14	3.7	5.5	3.6	11	2.2	12	<0.01	0.41	<0.53	<0.29	<0.13	1.5	82
				Average	0	6.9	6.9	1.1	15	10	2.6	2.1	0.89	3.2	2.6	8.9	0	0.10	0	0	0.06	0.45	62
	Solid	STP T	Inf.	TI(S)	<0.30	1.0	4.2	0.99	3.8	<0.82	1.6	2.5	1.8	<0.31	<0.19	<3.1	<0.31	<0.01	<0.01	<0.66	<0.02	4.9	5.7
			A.S.	TS(S)	0.78	13	<0.11	1.6	1.9	38	205	520	70	<0.50	1.9	145	<0.49	<0.01	<0.01	<1.0	<0.04	<0.01	771
		STP S	Inf.	SI(S)	<0.30	0.98	<0.07	0.22	<0.71	<0.82	<0.43	2.5	<1.1	<0.31	<0.19	<3.1	0.51	<0.01	<0.01	<0.66	<0.02	1.5	21
			A.S.	SS(S)	<0.36	1.5	10	2.6	17	30	125	407	66	<0.38	0.97	103	<0.38	<0.01	<0.01	8.4	<0.03	<0.01	997
		STP K	Inf.	KI(S)	<0.30	0.17	<0.07	<0.13	<0.71	<0.82	<0.43	2.5	<1.1	<0.31	<0.19	<3.1	<0.31	<0.01	<0.01	1.1	<0.02	<0.01	3.7
			A.S.	KS(S)	<0.48	4.9	0.18	0.36	<1.2	30	56	198	33	0.85	2.9	106	1.7	<0.01	<0.01	<1.1	1.8	<0.01	435

(Continue)

Table A1-8 Concentrations of PFAAs and their precursors in SPT samples before and after oxidation (ng L-1). (Continue)

Before/ After oxidation		STP	Type of sample	Ssampling site	PFAAs															PFAA precursors			Σ [PFASs] after
					PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	PFDS	PFHxPA	PFOPA	8:2FTCA	FOSA	di-SAmPAP	
After oxidation		STP T	Inf.	TI	21	31	50	88	56	40	21	4.5	4.5	2.3	0.86	5.2	<0.08	<0.24	<0.56	-	-	-	327
			T.S.	TT12	6.5	7.6	13	8.4	21	12	3.5	0.61	<0.32	0.80	<0.48	4.2	<0.08	<0.24	<0.56	-	-	-	77
				TT34	6.5	8.0	11	7.2	11	12	3.6	0.61	<0.32	0.80	<0.48	3.6	<0.08	<0.24	<0.56	-	-	-	64
				TT5	6.5	13	16	13	18	22	5.9	0.61	<0.32	0.80	0.86	5.6	<0.08	<0.24	<0.56	-	-	-	102
			Eff.(Cl)	TC12	6.5	9.4	14	10	23	13	5.5	1.8	0.49	2.0	0.86	5.0	<0.08	<0.24	<0.56	-	-	-	92
				TC34	6.5	9.2	13	9.3	13	12	5.0	0.61	<0.32	1.9	0.86	4.3	<0.08	<0.24	<0.56	-	-	-	76
				TC5	6.5	8.3	13	10	16	11	3.8	1.2	0.49	2.2	0.86	3.9	<0.08	<0.24	<0.56	-	-	-	77
			Eff.(O,Cl)	TO	6.5	4.4	11	3.1	5.7	6.4	2.5	<0.4	<0.32	2.4	0.86	2.7	<0.08	<0.24	<0.56	-	-	-	45
			A.S.	TS	6.5	15	15	9.5	10	20	8.9	4.6	1.3	4.7	0.86	10	<0.08	<0.24	<0.56	-	-	-	108
		STP S	Inf.	SI	18	19	32	47	28	18	9.7	2.9	2.7	<0.48	1.7	3.5	<0.08	<0.24	<0.56	-	-	-	185
			T.S.	STA	6.5	7.0	21	9.8	19	7.2	3.9	0.61	<0.32	0.80	4.7	6.1	<0.08	<0.24	<0.56	-	-	-	87
				STB	6.5	5.0	13	4.8	10	6.5	2.7	0.61	<0.32	0.80	2.8	4.8	<0.08	<0.24	<0.56	-	-	-	58
			Eff.(Cl)	SCA	6.5	5.0	14	8.4	23	7.0	3.1	0.61	<0.32	0.80	2.6	5.7	0.01	<0.24	<0.56	-	-	-	77
				SCB	<3.9	3.1	10	3.8	16	5.6	2.8	0.61	<0.32	<0.48	2.4	6.0	0.05	<0.24	<0.56	-	-	-	51
			A.S.	SS	15	11	17	15	17	12	7.8	3.0	1.6	0.80	2.7	13	0.04	<0.24	<0.56	-	-	-	117
		STP K	Inf.	KI	18	15	49	83	46	29	13	4.2	3.5	<0.48	2.9	5.4	<0.08	<0.24	<0.56	-	-	-	270
			T.S.	KTA	6.5	5.7	15	4.4	26	9.7	3.0	0.61	0.49	0.80	2.3	7.0	0.02	<0.24	<0.56	-	-	-	82
				KTB	<3.9	1.9	17	9.5	22	13	3.5	1.6	0.49	<0.48	1.8	10.0	<0.08	<0.24	<0.56	-	-	-	82
			Eff.(Cl)	KC	16	5.8	16	6.4	13	11	2.7	0.61	<0.32	<0.48	2.2	6.6	<0.08	<0.24	<0.56	-	-	-	80
			Eff.(O)	KO	6.5	4.1	14	4.2	37	11	2.7	0.61	<0.32	0.80	4.1	8.8	<0.08	<0.24	<0.56	-	-	-	94
			A.S.	KS	13	12	15	8.0	11	15	4.8	2.6	0.49	0.80	2.1	13	0.06	0.41	<0.56	-	-	-	99
	Solid	STP T	Inf.	TI(S)	9.6	11	14	20	9.7	3.3	1.8	2.5	1.8	<0.31	<0.19	<3.1	<0.31	<0.01	<0.01	-	-	-	74
			A.S.	TS(S)	468	628	860	1496	439	228	140	390	162	11	<0.23	92	3.5	0.14	4.9	-	-	-	4923
		STP S	Inf.	SI(S)	6.7	11	15	22	9.2	4.1	2.9	2.5	3.8	0.52	<0.19	<3.1	<0.31	<0.01	<0.01	-	-	-	78
			A.S.	SS(S)	410	631	747	1314	519	164	139	328	182	0.83	0.50	158	10	13	13	-	-	-	4630
		STP K	Inf.	KI(S)	5.6	7.4	12	14	6.9	1.4	1.6	2.5	1.8	<0.31	<0.19	<3.1	<0.31	<0.01	<0.01	-	-	-	53
			A.S.	KS(S)	402	566	657	1396	433	172	77	194	82	0.85	<0.31	101	0.83	0.04	16	-	-	-	4098

Table A1-9 Elevated concentrations of PFCAs (ng L^{-1}) by oxidation, the "percentage" of ΣΔPFCA and the proportion of average ΔPFCAs.

	STP	Type of sample	Ssampling site	Δ[PFBA]	Δ[PFPeA]	Δ[PFHxA]	Δ[PFHpA]	Δ[PFOA]	Δ[PFNA]	Δ[PFDA]	\[PFUnDA	\[PFDoDA]	ΣΔ[PFCAs]	Σ [PFAA] before	"Percentage": ΣΔ[PFCA] / (Σ[PFAA]before+ΣΔ [PFCA])
Liquid	STP T	Inf.	TI	21	26	47	87	55	32	20	3.1	4.5	295	29	91%
		T.S.	TT12	6.5	3.5	5.0	6.9	9.3	4.1	0.51	0	0	36	41	46%
			TT34	6.5	4.2	4.5	6.0	0.89	3.0	1.1	0	0	26	39	40%
			TT5	6.5	6.9	6.7	11	4.8	10	1.9	0	0	48	59	45%
		Eff.(Cl)	TC12	6.5	3.6	9.3	8.4	14	5.2	3.2	0.36	0.49	51	40	56%
			TC34	6.5	4.9	7.3	7.9	0.63	4.7	3.4	0	0	35	38	48%
			TC5	6.5	5.9	6.1	8.7	5.0	3.5	0.67	0	0	36	42	46%
		Eff.(O,Cl)	TO	6.5	2.8	7.2	2.1	0	2.0	1.4	0	0	22	25	47%
		A.S.	TS	6.5	14	7.7	8.6	0	2.3	0	0	0	39	80	33%
			Average	8.1	8.0	11	16	9.9	7.4	3.6	0.38	0.55	65	44	50%
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	68%	64%	92%	51%	45%	54%	20%	52%			
	STP S	Inf.	SI	18	16	27	46	17	9.2	6.4	1.4	2.2	146	51	74%
		T.S.	STA	6.5	1.9	12	8.0	0	0	0.66	0	0	29	65	31%
			STB	6.5	0	7.7	3.4	0	2.1	1.5	0	0	21	43	33%
		Eff.(Cl)	SCA	6.5	0.81	6.8	7.4	5.9	1.5	0.55	0	0	29	47	39%
			SCB	0	0	4.1	2.8	0.91	0.51	0.71	0	0	9.0	50	15%
		A.S.	SS	15	7.9	13	14	0	0	0.38	0.61	1.6	54	71	43%
			Average	8.8	4.5	12	14	4.0	2.2	1.7	0.34	0.62	48	54	39%
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	44%	66%	93%	19%	21%	36%	23%	100%			
	STP K	Inf.	KI	18	7.2	44	83	33	18	11	2.2	3.5	222	59	79%
		T.S.	KTA	6.5	0	9.1	2.9	14	0.84	1.8	0	0.49	36	45	45%
			KTB	0	0	11	8.4	13	0.93	1.2	0.00	0.49	35	53	40%
		Eff.(Cl)	KC	16	0	9.8	5.5	0	3.6	1.4	0	0	36	49	42%
		Eff.(O)	KO	6.5	0	4.6	2.4	12	3.7	0	0	0	29	65	31%
		A.S.	KS	13	4.2	8.9	7.2	0	0.09	1.1	0	0	35	80	30%
			Average	10	1.9	15	18	12	4.5	2.7	0.37	0.74	66	59	45%
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	22%	68%	94%	44%	30%	51%	15%	45%			
Solid	STP T	Inf.	TI(S)	9.6	9.7	14	20	9.7	3.3	1.8	0	1.8	70	4.2	94%
		A.S.	TS(S)	468	627	849	1494	422	198	15	0	97	4169	762	0.85
			Average of Δ[PFCA] oxidation	239	318	432	757	216	101	8.3	-	49	2120	383	89%
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	100%	99%	100%	96%	87%	12%	-	60%			
	STP S	Inf.	SI(S)	6.7	9.9	11	21	5.4	4.1	1.3	0	2.0	61	16	79%
		A.S.	SS(S)	409	619	747	1312	517	126	0	0	112	3843	997	79%
			Average of Δ[PFCA] oxidation	208	314	379	667	261	65	0.63	-	57	1952	506	79%
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	98%	99%	100%	99%	78%	1%	-	61%			
	STP K	Inf.	KI(S)	5.6	7.3	12	14	6.9	1.4	1.6	0	1.8	51	2.6	95%
		A.S.	KS(S)	402	561	656	1396	433	141	21	0	49	3660	433	89%
			Average of Δ[PFCA] oxidation	204	284	334	705	220	71	11	-	25	1856	218	0.92
			Proportion of average Δ[PFCA]/(Δ [PFCA]+[PFCA] before)	100%	99%	100%	100%	100%	82%	29%	-	61%			