

## PERFORMANCES OF WASTEWATER TREATMENT PROCESSES ON REMOVAL OF PERFLUORO CHEMICALS (PFCs)

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### Abstract

Perfluorochemicals (PFCs) are widely used in industries, but some of them are suspected as persistent, bioaccumulated and toxic chemicals. Some studies implied that current treatment processes might be ineffective to remove PFCs from wastewater. Periodical surveys were conducted in a municipal wastewater treatment plant (WWTP) in Japan to estimate performance of treatment facilities to remove 15 kinds of PFCs. Behavior of these PFCs can be classified into "Medium", "Long", and "Short" patterns according to their carbon chain lengths. "Medium" PFCs, such as PFOA, PFNA and PFOS, are primary contaminants in this WWTP and poorly removed by whole process. PFCs in "Long" and "Short" patterns were removed by activated sludge process coupled with clarifiers in the WWTP. Ozonation and activated carbon filtration seems ineffective to remove these PFCs.

### Introduction

Perfluorochemicals (PFCs) are widely applied as surfactants, repellents, additives, fire-fighting foams, polymer emulsifiers and insecticides for almost half a century<sup>1</sup>. However some PFCs are suspected as persistent, bioaccumulated and toxic (PBT), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which are globally distributed in water environment, air, soil, biota, food and human body<sup>2,3</sup>. For example, some river water and drinking water in Japan have been polluted at very high concentration of PFOA<sup>4,5</sup>. Results of environmental monitoring indicated ineffective removal of PFCs in drinking water treatment facilities<sup>6,7</sup>. Occurrences of PFCs in WWTP effluents have been reported in US, Europe and Japan, which implied that WWTP might be an important source of PFCs in environment. The investigated WWTPs seemed ineffective to remove PFCs, especially for PFOS and PFOA<sup>8,9</sup>, which were accumulate in activated sludge<sup>8,10</sup> and increased in aqueous concentration in some processes. In this study, six times of surveys were conducted periodically in a municipal WWTP in Kinki area in Japan to study behavior of PFCs and estimate performances of wastewater treatment processes on removal of these PFCs.

### Materials and Methods

The periodical surveys were conducted in a WWTP near Lake Biwa six times from Aug. 17 to Dec. 7 in 2006. This WWTP consists of four series of activated sludge process in parallel. Partial stream of the 4th series was introduced to advanced treatment processes including ozone contactor and biological activated carbon (BAC) filter. Samples were collected at nine sites along the process; influent (Inf) of WWTP, primary clarifier effluent (PC), activated sludge (AS), return sludge (RS), secondary clarifier effluent (SC), sand filtration effluent (SF), ozonation effluent (O3), BAC filtration effluent (BF) of the 4th series, and the effluent (Eff) of WWTP. Samples in Inf, Eff, PC, and SC were collected by auto samplers every hour in a day and mixed together to get composite samples. At the other sites, grab samples were taken in the early morning of the sampling date. All of the samples were stored in 2-liter polyethylene terephthalate (PET) bottles and transferred to laboratory after sampling as soon as possible. The wastewater sample was firstly filtrated by 1 $\mu$ m glass fiber filtration paper (GF/B, Whatmann), and the filtrate was pretreated by solid phase extraction (SPE) process with weak anion exchange (WAX) cartridge (Oasis<sup>®</sup>, Waters). The elution was rebuilt in 50% (v/v) acetonitrile solvent. The sludge sample was centrifuged by 3000 rpm for 30 minutes to separate supernatant and condensed sludge. The supernatant was applied by the WAX-SPE process, the same method as that for wastewater samples. The condensed sludge was applied to an accelerated solid extractor (ASE-200, Dionex) and the extract was cleaned up by the WAX-SPE process. Extraction of suspended solid in wastewater samples followed the same method with condensed sludge. Analysis of PFCs in particulate phase of samples at SC, SF, O3, BAF and Eff was not conducted because of the very low concentrations of suspended solid at these sites (<1 mg/L). Fifteen kinds of PFCs were studied in this paper, including twelve kinds of perfluorocarboxylic acids (PFCAs, F(CF<sub>2</sub>)<sub>n-1</sub>COO<sup>-</sup>) and three kinds of perfluoroalkyl sulfonates (PFASs, F(CF<sub>2</sub>)<sub>n</sub>SO<sub>3</sub><sup>-</sup>). Investigated PFCAs

contained PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTeDA, PFHxDA, PFOcDA with carbon length of 4~12, 14, 16, and 18. Investigated PFASs contained PFBuS, PFHxS and PFOS with carbon chain length of 4, 6 and 8 respectively. All PFC standards were purchased from Wako Pure Chemical Industries Ltd. and Tokyo Chemical Industry Co. with purities of 95~98%. A single-component stock solution was prepared in 10g/L for every 15 PFCs in pure methanol, and then, the multi-component solution was prepared by diluting single stock solutions into 50% acetonitrile solvent. PFC concentrations were calculated by gross mass without correction by their purities.

LC-ESI-MS/MS was applied to measure PFCs in pretreated samples. Reverse phase column of Zorbax XDB-C<sub>18</sub> (150×2.1mm, 5μm) with guard column XDB-C<sub>8</sub> (10×2.1mm, 5μm) was used as LC stationary phase. Pure water with pH buffer of 10 mM CH<sub>3</sub>COONH<sub>4</sub> (solvent A) and pure acetonitrile (solvent B) were applied as LC mobile phase. In order to clean up LC column and accelerate PFCs elution, a gradient flow was applied by varying solvent A : B from 50:50 to 0:100 in 1~7 minute, keeping constant at 0:100 to 10 minute, and returning back to 50 : 50 in one minute. Daughter ions of [C<sub>n</sub>F<sub>2n+1</sub>]<sup>-</sup> for PFCA and [SO<sub>3</sub>]<sup>-</sup> for PFASs were detected and quantified in selected ion mode at specific *m/z*. PFC concentrations in range of 5~150 μg/L and their specific peak areas had linear relationship (*R*<sup>2</sup>>0.99) with 10 μL of injection volume. Each sample was spiked with 20 ng/L PFC multi-component standard before SPE or ASE process to estimate process recoveries. Detection limits for each PFC was in range of 8~16 ng/L with one thousand times concentration by SPE. Process recovery rates for each PFCs were 40~60% for PFCA (*n*=4~6,11,12,16,18) and PFBuS, 76 ~ 79% for PFCA (*n*=7,10,14) and PFOS, and 112~122% for PFCA (*n*=8,9) and PFHxS.

Table 1 PFC concentrations in influent, final effluent and BAC effluent, ng/L

PFCs, ng/L	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA
Inf (Aqu.)	<b>24</b> (10~57)	<b>55</b> (11~83)	<b>31</b> (ND~93)	<b>79</b> (30~116)	<b>95</b> (24~237)	<b>125</b> (15~340)	<b>15</b> ND~51)	<b>23</b> (ND~39)
Inf (Par.) <sup>a</sup>	<b>7</b>	<b>5</b>	<b>11</b>	<b>12</b>	<b>38</b>	<b>20</b>	<b>27</b>	<b>101</b>
Eff (WWTP)	<b>5</b> (ND~13)	<b>10</b> (6~22)	<b>14</b> (10~36)	<b>26</b> (9~114)	<b>98</b> (45~159)	<b>104</b> (50~364)	<b>12</b> (6~50)	<b>14</b> (9~19)
BAC (4th) <sup>b</sup>	<b>7</b> (ND~10)	<b>19</b> (5~63)	<b>12</b> (ND~27)	<b>23</b> (5~82)	<b>64</b> (32~109)	<b>84</b> (44~386)	<b>16</b> (7~40)	<b>13</b> (8~18)
	PFDoA	PFTeDA	PFHxDA	PFOcDA	PFBuS	PFHxS	PFOS	
Inf (Aqu.)	<b>22</b> (ND~186)	<b>92</b> (5~161)	<b>22</b> (5~128)	<b>47</b> (16~91)	<b>125</b> (40~262)	<b>18</b> (ND~36)	<b>19</b> (4~212)	
Inf (Par.)	<b>224</b>	<b>336</b>	<b>77</b>	<b>57</b>	<b>61</b>	<b>19</b>	<b>82</b>	
Eff (WWTP)	<b>21</b> (9~67)	<b>15</b> (ND~101)	<b>7</b> (ND~68)	<b>8</b> (ND~63)	<b>26</b> (7~49)	<b>10</b> (7~29)	<b>31</b> (18~53)	
BAC (4th)	<b>12</b> (8~49)	<b>11</b> (ND~29)	<b>10</b> (3~162)	<b>10</b> (6~57)	<b>31</b> (8~88)	<b>12</b> (7~61)	<b>29</b> (22~110)	

Note: *a*, PFC in particulate phase, averaged by last two surveys. Others were averaged by five surveys.  
*b*, effluent of partial stream in 4th series.

## Results and Discussion

**Table 1** shows average values and concentration ranges of each PFC in influent, final effluent and BAC effluent of investigated WWTP. PFC concentrations in particulate phase (ng/g dry) were uniformed with aqueous phase (ng/L) in same volume by multiplying concentrations of PFC and suspended solids. Maximum value among the six surveys was excluded from average values to reduce effects from shock loadings. All PFCs were detected in the WWTP influent, among which PFOA, PFNA, PFTeDA were dominant in aqueous phase with concentrations of 95, 125 and 92 ng/L respectively. In final effluent and BAC effluent, PFOA and PFNA were dominant in all investigated PFCs, and not ineffectively removed by current treatment processes.

Concentrations of all PFCs were summed up (=ΣPFC) to observe a general pattern of PFCs at each sampling site. **Figure 1** shows the mass fluxes of ΣPFC, which were calculated with product of concentration and flow rate at each site. Italic numbers represented mass fluxes in whole WWTP, and others represented mass flux in the 4th series. Mass fluxes of ΣPFC in particulate phase were shown by numbers in brackets. In this survey, 150 g in aqueous phase and 210 g in particulate phase were daily introduced to WWTP, equal to 450 ng per capita per day. After treatment by overall processes, about 80% of ΣPFC were removed from influent and 69 g residual ΣPFC were discharged into lake water. If only aqueous phase was considered, removal efficiency was as low as 54%.

In the 4th series, 50 g/day  $\Sigma$ PFC were totally introduced and 80% of them were removed by a combined process of PC, ASP and SC. Distribution coefficient of  $\Sigma$ PFC in particulate phase to aqueous phase was 9 in aeration tank and 12 in return sludge, indicating very strong accumulation of PFCs in activated sludge. Sand filtration, ozonation and biological activated carbon filtration seemed unable to reduce  $\Sigma$ PFC effectively.

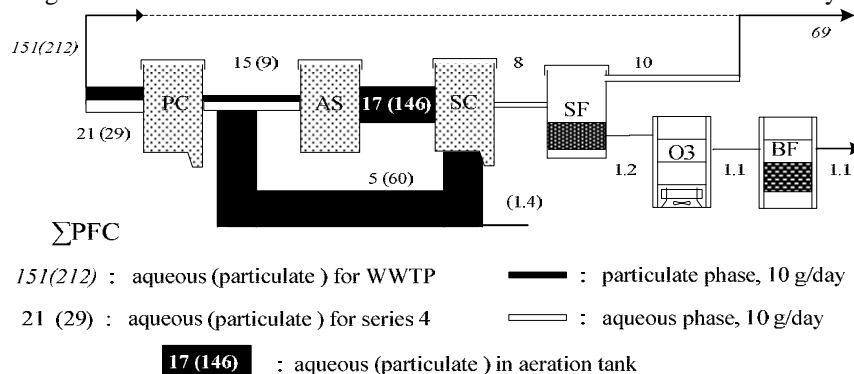


Figure 1 Mass flux of  $\Sigma$ PFC in WWTP

Table 2 Patterns of PFC behavior in WWTP

	<i>Medium PFCs</i>	<i>Long PFCs</i>	<i>Short PFCs</i>
PFCs included	PFOA, PFNA, PFOS PFCA(8-9), PFAS(8)	PFDA, PFUnA, PFDoA, PFTeDA, PFHxDA, PFOcDA PFCA(10~12, 14, 16, 18)	Other PFCs PFCA(4-7), PFAS(4-6)
Description	PFCs break through WWTP process with poor treatment	High loading on particles in influent. Removed by PC-ASP-SC.	Less toxic and bioaccumulated. Removed by PC-ASP-SC.
Influent Concentration	<b>Moderate</b> 100~150ng/L 10~80% on SS	<b>High</b> 100~420ng/L >80% on SS	<b>Weak</b> 30~50ng/L 10~50% on SS
Removal by PC	<b>Moderate</b> 39 ~ 52%	<b>Strong</b> 45 ~ 81%	<b>Weak</b> 3 ~ 62%
Removal by ASP	<b>Negative</b> -110 ~ -13%	<b>Effective</b> 31 ~ 83%	<b>Positive</b> 10 ~ 77%
Overall removal in aqueous	<b>Poor &amp; negative</b> -51 ~ 33%	<b>Positive</b> 37 ~ 78%	<b>Effective</b> 61 ~ 71%
Overall removal in aqu. & part.	<b>Poor</b> 42 ~ 71%	<b>High</b> 90 ~ 97%	<b>Moderate</b> 68 ~ 82%

In order to understand general behavior of PFCs, all investigated PFCs were classified into three groups of “*Medium*”, “*Long*” and “*Short*” according to their carbon chain lengths. **Table 2** shows the similar behavior of PFCs in the same pattern. **Figure 2** shows aqueous and particulate concentrations of typical PFC in each group, such as PFHxA as “*Short*”, PFOA and PFOS as “*Medium*”, and PFTeDA as “*Long*”.

“*Medium*” PFCs have 8~9 carbons, such as PFCA(8~9) and PFOS. Typical behavior of “*Medium*” PFCs was their increasing aqueous concentrations in activated sludge process, and their poor or even negative removal by overall WWTP processes. Aqueous concentrations of PFOA and PFOS were almost doubled after activated sludge process. This behavior might be related to degradation of relative precursors by activated sludge<sup>8</sup>. As shown in **Fig. 2b** and **2c**, “*Medium*” PFCs were strongly accumulated in activated sludge. Ozonation and BAC filter seemed ineffectively to remove “*Medium*” PFCs. Because of their toxicity to aquatic lives and poor removal by conventional and advanced processes, “*Medium*” PFCs should be seriously concerned in WWTPs. “*Long*” pattern includes PFCA(10~18). Typical behavior of “*Long*” PFCs was their heavy loadings in influent and removal by activated sludge process. More than 80% of “*Long*” PFCs in WWTP influent were distributed on particles, which can be explained by their strong hydrophobic properties. As shown in **Fig. 2d**, “*Long*”

PFCs were very strongly accumulated in activated sludge and effectively removed by primary clarifier and activated sludge process. Long-chained PFCs are suspected to be more toxic than medium-chained PFCs. Fortunately, their strong hydrophobicity resulted in very low concentration in aqueous phase, and their particulate portion can be effectively removed by clarification.

Other PFCs in this study are allocated to “Short” group, including PFCA(4~7) and PFAS(4~6). “Short” PFCs were removed by current treatment processes. Short-chained PFCs are less toxic and bioaccumulated than medium-chained PFCs<sup>11</sup> and thus sometimes applied as alternatives. Therefore control of “Short” PFCs in this WWTP was not as urgent as “Medium” PFCs.

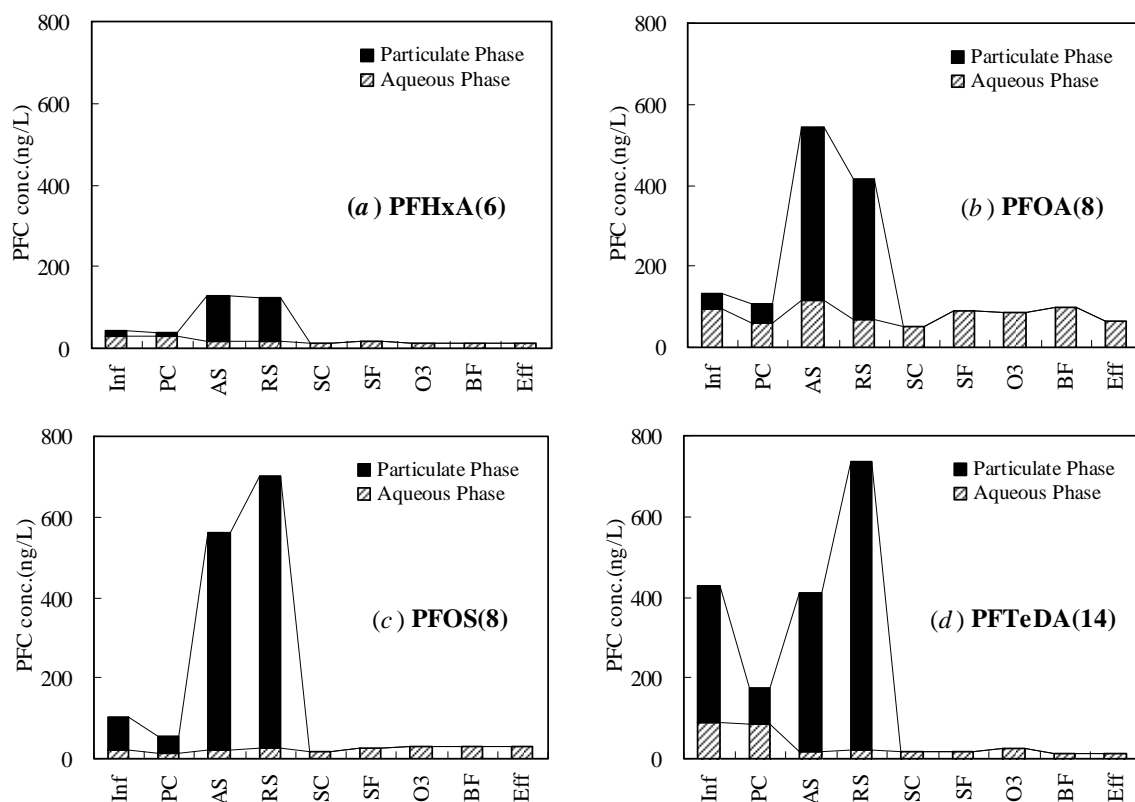


Figure 2 Aqueous and particulate concentrations of typical PFCs in a WWTP

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