Investigating sources and pathways of perfluoroalkyl acids (PFAAs) in aquifers in Tokyo using multiple tracers

Keisuke Kuroda^{a*1}, Michio Murakami^b, Kumiko Oguma^a, Hideshige Takada^c, and Satoshi Takizawa^a

^a Department of Urban Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo, 113-8656, Japan

^b Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo, 153-8505, Japan

^c Laboratory of Organic Geochemistry (LOG), Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

* Corresponding author: 16-2 Onogawa, Tsukuba, Ibaraki, 305-8506 Japan, keisukekr@gmail.com, Phone: +81 29 850 2843, Fax: +81 29 850 2920

¹ Present address: Center for Environmental Risk Research, National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, Ibaraki, 305-8506 Japan

Abstract

We employed a multi-tracer approach to investigate sources and pathways of perfluoroalkyl acids (PFAAs) in urban groundwater, based on 53 groundwater samples taken from confined aquifers and unconfined aquifers in Tokyo. While the median concentrations of groundwater

21 PFAs were several ng/L, the maximum concentrations of perfluorooctane sulfonate (PFOS,
22 990 ng/L), perfluorooctanoate (PFOA, 1800 ng/L) and perfluorononanoate (PFNA, 620 ng/L)
23 in groundwater were several times higher than those of wastewater and street runoff reported
24 in the literature. PFAs were more frequently detected than sewage tracers (carbamazepine
25 and crotamiton), presumably owing to the higher persistence of PFAs, the multiple sources
26 of PFAs beyond sewage (e.g., surface runoff, point sources) and the formation of PFAs
27 from their precursors. Use of multiple methods of source apportionment including principal
28 component analysis-multiple linear regression (PCA-MLR) and perfluoroalkyl carboxyl acid
29 ratio analysis highlighted sewage and point sources as the primary sources of PFAs in the
30 most severely polluted groundwater samples, with street runoff being a minor source (44.6%
31 sewage, 45.7% point sources and 9.7% street runoff, by PCA-MLR). Tritium analysis
32 indicated that, while young groundwater (recharged during or after the 1970s, when PFAs
33 were already in commercial use) in shallow aquifers (<50 m depth) was naturally highly
34 vulnerable to PFAA pollution, PFAs were also found in old groundwater (recharged before
35 the 1950s, when PFAs were not in use) in deep aquifers (50–500 m depth). This study
36 demonstrated the utility of multiple uses of tracers (pharmaceuticals and personal care
37 products; PPCPs, tritium) and source apportionment methods in investigating sources and
38 pathways of PFAs in multiple aquifer systems.

39 **Keywords**

40 perfluoroalkyl acids (PFAs); groundwater; pharmaceuticals and personal care products
41 (PPCPs); tritium; sewage; source apportionment

42 **Abbreviations**

43 PFAs, perfluoroalkyl acids; PFSA, perfluorinated sulfonic acids; PFCA, perfluoroalkyl

44 carboxylic acids; PFHxS, PFHpS, PFOS, PFDS, PFHpA, PFOA, PFNA, PFDA, PFUnDA,
45 PFDoDA, PFTrDA and PFTeDA; PFAA abbreviations, see Section 2.3; FOSA,
46 perfluorooctane sulfonamide; AFFF, aqueous film-forming foams; PCA, principal component
47 analysis; PC, principal component; MLR, multiple linear regression; FS, PCA factor score;
48 PFCAR, perfluoroalkyl carboxyl acid ratio analysis; L-PFCAR, long/(long + short) PFCAR;
49 E-PFCAR, even/(even + odd) PFCAR; PPCPs, pharmaceuticals and personal care products;
50 TU, tritium unit; BGL, below ground level

51 **1. Introduction**

52 Perfluoroalkyl acids (PFAAs) are a group of compounds which have $C_nF_{2n+1}-R$ structure,
53 where R is carboxyl, sulfonic, sulfinic, phosphonic or phosphinic functional group (Buck et
54 al., 2011). PFAAs have been broadly used as surfactants for various industrial and consumer
55 products since the 1950s, because they are resistant to thermal, physical, chemical and
56 metabolic degradation owing to their strong carbon-fluorine bonds (Kissa, 2001). Due to their
57 water-soluble and persistent nature, PFAAs have been ubiquitously detected in various water
58 environments, including surface water (Huset et al., 2008; Murakami et al., 2008a; Nakayama
59 et al., 2010; Zushi et al., 2011), rainwater (Kim and Kannan, 2007; Scott et al., 2006),
60 drinking water (Mak et al., 2009; Quiñones and Snyder, 2009), wastewater (Huset et al.,
61 2008; Schultz et al., 2006; Sinclair and Kannan, 2006), and sediments (Higgins et al., 2005;
62 Sakurai et al., 2010; Zushi et al., 2010). The potential environmental and toxicological impact
63 of PFAAs has been a growing concern, for especially “long-chain” perfluorinated sulfonic
64 acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFSA) and perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$,
65 PFCAs) and their corresponding anions (OECD, 2011; USEPA, 2009), which have been
66 shown to be more bioaccumulative than their short-chain analogues (Conder et al., 2008;

67 Olsen et al., 2009).

68 Generally, PFAA pollution is more intense in urban areas than in remote areas, because of the
69 presence of major PFAA sources, including wastewater treatment plants (WWTPs) (Schultz
70 et al., 2006; Sinclair and Kannan, 2006) and nonpoint sources such as surface runoff (Houtz
71 and Sedlak, 2012; Kim and Kannan, 2007; Murakami et al., 2009b; Nguyen et al., 2011; Xiao
72 et al., 2012; Zushi and Masunaga, 2009; Zushi et al., 2008). In groundwater, extremely high
73 levels of PFAAs ($\mu\text{g/L}$ to mg/L level) have been found in fire training areas, owing to the use
74 of aqueous film-forming foams (AFFF) (Houtz et al., 2013; Moody and Field, 1999; Schultz
75 et al., 2004; Weiß et al., 2012). In other areas, groundwater studies have mainly focused on
76 assessing the impact of PFAAs on humans (Jin et al., 2009; Post et al., 2009; Quiñones and
77 Snyder, 2009) and wildlife (Plumlee et al., 2008) based on the detected PFAA concentrations.
78 These latter studies showed that, although PFAA levels in groundwater in general were not
79 currently alarming, concentrations in groundwater impacted by anthropogenic activities (e.g.,
80 WWTP effluents or industries) were close to levels that can produce adverse effects on human
81 health and the environment (Plumlee et al., 2008; Post et al., 2009). Therefore, in-depth
82 studies are required on source identification and apportionment of groundwater PFAAs
83 having multiple potential sources and on pathways of those PFAAs in the subsurface. In
84 groundwater, various factors, such as adsorption and production from precursors (Higgins and
85 Luthy, 2006; Murakami et al., 2009a), would be involved in PFAA occurrence during
86 long-term subsurface passage. However, PFAA distribution in aquifers and pollution
87 pathways has only been studied in detail in a coastal dune of the Rhine River (Eschauzier et
88 al., 2010), and the apportionment of multiple sources of groundwater PFAAs has only been
89 attempted in our previous study, examining 16 samples mostly from shallow unconfined

90 aquifers in Tokyo (Murakami et al., 2009a). The vertical and horizontal distribution, pollution
91 pathways, and source identification and apportionment of PFAAs, within complex aquifer
92 systems, have not yet been studied.

93 Tracers are useful in analyzing groundwater hydrology and pollution. Tritium (^3H) is a
94 suitable hydrological tracer because it is a constituent of the water molecule. Using tritium,
95 young groundwater recharged after the 1950s–1960s can be differentiated from older
96 groundwater. Considering that PFAA mass production began in the 1950s, tritium can be a
97 useful tracer for identifying pathways of PFAAs in groundwater. Pharmaceuticals and
98 personal care products (PPCPs) are useful tracers of sewage in groundwater (Kuroda et al.,
99 2012; Nakada et al., 2008), and have been applied as sewage tracers to investigate PFAA
100 sources in surface and marine waters (Murakami et al., 2008a; Murakami et al., 2011), but not
101 yet in groundwater.

102 Regarding methods of PFAA source identification and apportionment in groundwater, PFCA
103 ratio analysis (PFCAR) (Nguyen et al., 2011; Simcik and Dorweiler, 2005), and statistical
104 approaches such as principal component analysis (PCA) and multiple linear regression (MLR)
105 (Furl et al., 2011; Murakami et al., 2011; Nguyen et al., 2011), are easy to apply, since they
106 do not require quantification of groundwater flow. Our previous study on Tokyo groundwater
107 demonstrated a PFAA source apportionment method using PFCAR, assuming that sewage
108 and street runoff were the major sources (Murakami et al., 2009a). The source apportionment
109 method, however, has been applied only to a limited amount of data, and hence must be
110 verified by other methods (e.g., statistical approaches) and with other data (e.g., sewage-tracer
111 PPCPs).

112 The aim of this study is to investigate the sources and pathways of city-wide groundwater

pollution by PFAAs in multiple aquifers in central Tokyo, using a multi-tracer approach and multiple methods of source apportionment. We examined 53 samples of groundwater from shallow to deep (<500 m depth) aquifers, and 5 samples of tap water. The occurrence of PFAAs in groundwater was compared with that of PPCPs measured in our parallel study (Kuroda et al., 2012), to investigate the sources and fate of PFAAs in the subsurface. In order to identify PFAA sources and their contribution to PFAAs in groundwater, PCA followed by MLR (PCA-MLR), and PFCAR, were applied. The source apportionment results using PCA-MLR and PFCAR were further verified by the reported concentrations of PPCPs and heavy metals in the same samples (Kuroda, 2010; Kuroda et al., 2012) and those of PFAAs and PPCPs in river water, wastewater, and street runoff samples in the region (Morimoto et al., 2011; Murakami et al., 2008a; Murakami et al., 2009b; Zushi et al., 2011). Then, the mechanisms and pathways of PFAA pollution in the aquifers were investigated using tritium analysis, together with data on aquifer depths and hydrogeological conditions. Finally, the utility of these tracers and source apportionment methods was evaluated.

2. Materials and methods

2.1. Site description

2.1.1 Study area and geology

Figure 1 shows the study area, central Tokyo, with surface geology (Tokyo Metropolitan Government, 2001). The study area's location and geological cross-sections (Tokyo Institute of Civil Engineering and Technology Research, 1996) are shown in Figure S1 (Supplementary Information: hereafter, SI). The geology and the groundwater flow are described elsewhere (Kuroda et al., 2012); briefly, Tokyo's geology is characterized by the loam-covered Pleistocene Musashino Terrace in the west and the alluvium-covered Holocene

Tokyo Lowland in the east (Endo, 1992; Tokyo Metropolitan Government, 2006). In the Terrace, the major unconfined aquifer is the gravel layer at 5–20 m below ground level (BGL). In the Lowland, the unconfined aquifer is the Yurakucho Layer at 0–40 m BGL. Beneath these unconfined aquifers, the Pleistocene Tokyo Layers, alternating layers of silt, sand and gravel, form a middle zone, between the Terrace and the Lowland, at 0–50 m BGL. The Plio-Pleistocene Kazusa Layers, consisting of alternating layers of sand, gravel and silt, are the lowermost (>30 m BGL) confined aquifers, lying beneath both the Terrace and the Lowland (Tokyo Institute of Civil Engineering and Technology Research, 1977).

2.1.2 Groundwater recharge

The unconfined aquifers are mainly recharged by rainwater infiltration (123 mm/year) and leakage from water mains (91 mm/year) (Watanabe et al., 2009). Unconfined groundwater flows into rivers (Tokyo Institute of Civil Engineering and Technology Research, 1977). Rainwater infiltration is small in the study area because of little permeable surface. As of 2006, the major land uses are housing and buildings (60%) and streets (23%), which have low permeability, and highly permeable land surfaces are minor (parks 6.6%, agricultural land 1.2%, bare land 0.9% and forest 0.1%) (Bureau of Urban Development, Tokyo Metropolitan Government). Exfiltration of sewage from leaky sewer pipes could be an additional source of recharge (19–38 mm/year) (Kuroda et al., 2012). The exfiltration was considered the main pathway of sewage into Tokyo's subsurface, based on PPCP detection (Kuroda et al., 2012; Nakada et al., 2008). Large-scale infiltration of untreated or treated wastewater by artificial aquifer recharge, bank filtration, or on-site sewage disposal, is not an issue, except for the natural recharge from the two small canals (the Senkawa Josui Canal and the Tamagawa Josui Canal; Figure 1) running through the elevated part of the Terrace, in which reclaimed

wastewater has been introduced. However, the elevated PPCP levels were not observed in the canals' vicinity and PPCPs were detected widely in the region (Kuroda et al., 2012). The residence time of the confined groundwater in Tokyo, at depths of 40–124 m BGL, was estimated to be 11–28 years, using tritium analysis (Imaizumi et al., 2000). This relatively short residence time, relative to the depth, can be explained by the geology (see Figure S1); the Tokyo Layers' aquifers are partially connected with the upper unconfined aquifers because of intermittent silt layers, allowing for recharge from the unconfined aquifers. The Kazusa Layers of <100 m depth are considered to be recharged within just a few kilometers from both the upper unconfined aquifers and the Tokyo Layers, because the alternating layers of the Kazusa Layers are in contact with those upper aquifers due to the Kazusa Layers' dip of approximately one degree from west to east, and from south to north ((Tokyo Institute of Civil Engineering and Technology Research, 1996) and Figure S1).

2.2. Sampling locations

For PFAA analysis, we collected 53 groundwater and 5 tap water samples (Figure 1), between October 2007 and October 2009. Of the groundwater samples, 32 originated from unconfined aquifers (10–30 m BGL), 3 from springs (flowing from ambient unconfined aquifers), and 18 from confined aquifers (20–500 m BGL). The non-spring groundwater samples were taken from existing wells for emergency use, public baths and drinking water. The method for identifying sampled aquifers is described in S1 (SI), and the basic information on the groundwater samples is shown in Table S1 (SI). PFAAs in 8 of the 53 sites investigated in this study had been measured in 2006 (Murakami et al., 2009a). The major source of Tokyo's water supply is river water that is typically treated by flocculation, sedimentation and sand filtration. Ozonation and granular activated carbon are also employed to treat a part of the

total supply volume (Bureau of Waterworks, Tokyo Metropolitan Government). Tritium levels were analyzed in 15 of the 53 groundwater samples. At 7 locations, both tritium and PFAA samples were simultaneously taken; and the other 8 tritium samples were separately taken in 2009.

2.3. Sampling and analysis of PFAAs and FOSA

We analyzed four PFSAAs and eight PFCAs: perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTTrDA) and perfluorotetradecanoate (PFTeDA). Perfluorooctane sulfonamide (FOSA), which is considered a precursor of PFAAs (Prevedouros et al., 2005), was also measured. The details of sampling, analytical methods, and chemical used are given elsewhere (Murakami et al., 2008a; Nishikoori et al., 2011). Briefly, the collected sample waters were filtered through pre-baked glass-fiber filters (GF/F, pore size: 0.7 μ m; Whatman) and stored at 5 °C until analysis. PFAAs and FOSA in the 0.7 μ m-filtrate (1000 mL) were concentrated by solid-phase extraction (SPE); after filtration, 13 C-labeled PFOS, 13 C-labeled PFOA and 13 C-labeled PFDA were spiked into aliquots of samples, and then the samples were passed through Sep-Pak Plus tC18 cartridges (Waters) preconditioned with 20 mL methanol and then 10 mL distilled water. A flow rate of <10 mL/min was maintained. The cartridges were washed with 7 mL 30% (v/v) methanol in distilled water, and then with 7 mL 55% (v/v) methanol in distilled water that was acidified with 4 M HCl to pH 2.0–2.5. The target compounds were eluted with 20 mL methanol. The samples had a good diffusion within

methanol. The eluate was concentrated to 500 μ L, and PFAAs and FOSA in the methanol were analyzed by liquid chromatography–tandem mass spectrometry (LC-MS/MS: Agilent 1100 and TSQ Quantum) with a Zorbax Rx-C8 column (Agilent) in electrospray negative ionization mode. A gradient mobile phase of 0.5 mM ammonium acetate in distilled water and 0.5 mM ammonium acetate in acetonitrile was used. At a flow rate of 0.3 mL/min, the mobile phase gradient was ramped from 20% to 100% 0.5 mM ammonium acetate in acetonitrile in 5 min, maintained at 100% for 11 min, and then ramped down again to 20%. The capillary temperature was maintained at 350 °C. Ions were monitored in selected reaction monitoring mode. Monitored parent and product ions are listed in Table S2. PFHxS, PFHpS and PFOS were recovery-corrected with ^{13}C -PFOS. PFHpA, PFOA and PFNA were recovery-corrected with $^{13}\text{C}_2$ -PFOA. PFDA, PFUnDA, PFDoDA, PFTrDA and PFTeDA were recovery-corrected with ^{13}C -PFDA. PFDS and FOSA were not recovery-corrected; this was because their concentrations without recovery-correction using ^{13}C -compounds showed better reproducibility and recovery than the case with recovery-correction.

With every batch of samples (usually five), distilled water was brought to the field and analyzed as a travel blank. The LOQs (limits of quantification) were set at the larger values of either three times of the travel blank concentrations or the lowest calibration standard, and were 0.25–3.7 ng/L.

2.4. Sampling and analysis of tritium

Tritium was measured using a low-background liquid scintillation counter (LSC-LB5, Hitachi Aloka Medical, Ltd.) following electrolytic enrichment of tritium by a factor of about 25 using Fe-Ni electrodes. The LOQs were 0.2–0.3 tritium unit (TU), and relative standard deviation of samples was within $\pm 5\%$. The tritium measurements were conducted at

Geo-Science Laboratory Co. Ltd., Nagoya, Japan.

2.5. Quality control and quality assurance of PFAAs and FOSA

The reproducibility and recovery tests were performed in this study for quality control and assurance by using WWTP effluent ($n = 4$; Tables S3 and S4). Relative standard deviation (RSD) were less than 23%, while that of PFDS, PFHpA and PFUnDA ranged 29–43%, probably due to large experimental errors associated with low concentrations (0.8–5.3 ng/L). Indeed, RSD in PFAA-spiked WWTP effluent were only less than 14% except for PFTeDA (21%). The recovery rates of PFAAs spiked into the WWTP effluent were within $100 \pm 15\%$ for majority of PFAAs and for FOSA. The recovery rates of PFHxS were higher (128%) and those of PFUnDA (74%) were lower, perhaps due to the difference in magnitude of ionization from labeled surrogate compounds. Regarding groundwater samples, recovery-correction would work well, since the average recoveries of the labeled surrogates in WWTP effluent (185% for ^{13}C -PFOS, 123% for $^{13}\text{C}_2$ -PFOA and 105% for ^{13}C -PFDA in QA/QC experiments) and those in groundwater samples (230% for ^{13}C -PFOS, 121% for $^{13}\text{C}_2$ -PFOA and 102% for ^{13}C -PFDA) were similar, and the recoveries of most PFAAs and FOSA were within an acceptable range in recovery test using WWTP effluent. Moreover, compared to the wide range of PFAA concentrations in groundwater samples measured (<0.25 –1800 ng/L), the experimental errors would not be a major concern.

2.6. Source apportionment of PFAAs using PCA-MLR and PFCAR

We investigated the source contributions to the elevated levels of $\Sigma 5\text{PFAAs}$ (where ‘ $\Sigma 5\text{PFAAs}$ ’ denotes the sum of the respective concentrations of PFOS, PFOA, PFNA, PFDA and PFUnDA) in groundwater, using PCA-MLR and PFCAR. The methods of PCA-MLR and PFCAR are described in S2.1 and S2.2, respectively. Briefly, in PCA-MLR, PFAA

concentrations were transformed into a dimensionless standardized form (Larsen and Baker, 2003; Thurston and Spengler, 1985). PCA was performed using a correlation matrix with a varimax rotation, retaining principal components (PCs) whose eigenvalues were greater than 1 (Harrison et al., 1996). MLR was done using the PCA factor scores (hereafter, FSs) as independent variables and Σ PFAs as dependent variables. The mean source contributions for all samples were estimated from the ratio of regression coefficients. The source contributions for any given sample were estimated using regression coefficients and its FSs. In PFCAR, two concentration ratios using four PFAs (PFOA, PFNA, PFDA and PFUnDA) were used: the long/(long + short) ratio ((PFDA + PFUnDA)/ Σ 4PFAs: L-PFCAR) and the even/(even + odd) ratio ((PFOA + PFDA)/ Σ 4PFAs: E-PFCAR). These two ratios significantly differ between wastewater and street runoff (Murakami et al., 2009b). The contributions of sewage and street runoff were estimated as follows:

$$R_{GW} = a \times R_{ww} + b \times R_{SR} \quad (1)$$

where R_{GW} , R_{WW} , and R_{SR} are L-PFCAR or E-PFCAR in groundwater in this study, WWTP influent, and street runoff (Murakami et al., 2009b), respectively, and a and b are the contributions (%) from sewage and street runoff, respectively ($a + b = 100\%$). We assumed that street runoff was the representative and dominant PFA source of surface runoff compared with other runoffs (e.g., roof runoff), because PFA concentrations in street runoff were more than 1 order of magnitude higher than those in rainfall (Murakami et al., 2009a; Murakami et al., 2009b). In order to verify the source apportionment methods above, these methods were also applied to river water, wastewater and street runoff samples reported in and around the study area for a reference (hereafter, ‘the reference samples’; S2.3 for details).

3. Results and discussion

3.1. Occurrence and concentration of PFAAs in groundwater and tap water

We observed widespread pollution by PFAAs in groundwater (Figure 1 for the spatial distribution; Figure 2 (a) for the detection rate; Figure 2 (b) for the distribution of concentration; Tables S1 for the measured values). PFAAs were detected above the LOQs in 96% of the groundwater samples. In these samples, PFHxS, PFOS, PFHpA, PFOA, PFNA and PFDA were the most prevalent, being found in more than 77% of the samples. Among the PFCAs, those with ≤ 9 fluorinated carbons (PFHpA, PFOA, PFNA and PFDA) were higher both in detection rate and concentration than those with longer carbon chains (PFUnDA, PFDODA, PFTrDA and PFTeDA). This would be partly because PFCAs with relatively longer chains are more hydrophobic and likely to be preferentially adsorbed onto solid phases (Higgins and Luthy, 2006; Murakami et al., 2009a). In our previous study, in which artificial street runoff was passed through soil columns, breakthroughs of PFOA, and afterward of PFNA, were observed, while breakthroughs of PFDA and PFUnDA were not clearly observed over 169 days of infiltration (Murakami et al., 2009a). Figure S2 shows the comparison of PFOS, PFOA, PFNA and PFDA levels in the eight groundwater samples investigated both in 2006 (Murakami et al., 2009a) and in 2007 (this study). Compared to the levels of PFOS and PFOA, those of PFNA and PFDA showed greater deviation between in 2006 and 2007. The good agreement between the respective levels of PFOS and PFOA in the eight groundwater samples the two sampling campaigns would indicate continuous groundwater pollution by those PFAAs, and possibly indicate adsorption equilibrium of both PFOS and PFOA in the subsurface.

Figure 1. Occurrence of PFAAs in groundwater and tap water with surface geology (2001) in Tokyo. (2-column fitting image)

Figure 2. The detection rate (a) and concentration (b) of PFAAs and FOSA in groundwater in Tokyo. In (a), the detection rate of Σ PFAAs means the detection rate of any one of PFAAs

analyzed. (1-column fitting image)

Table 1 shows the PFAA concentration ranges in the groundwater and tap water measured in this study, compared with those reported in rivers (Murakami et al., 2008a), wastewater (WWTP influent and secondary effluent) (Murakami et al., 2008a; Murakami et al., 2009b) and street runoff (Murakami et al., 2009b), which represent major environmental media containing appreciable levels of PFAAs in Japan. The median concentration of PFOS in groundwater (5.7 ng/L) was higher than in Japanese rivers (0.97 ng/L (Murakami et al., 2008a)), however that of PFOA was lower in groundwater (8.5 ng/L) than in rivers (35 ng/L), partly because of suspected point sources of PFOA (e.g., industries) discharging wastewater into the rivers (Murakami et al., 2008a). For the other PFAAs, the median concentration in groundwater was generally similar to that in rivers. The median concentration of groundwater PFAAs in Tokyo was one order of magnitude lower than that in San Jose, California, and that in New Jersey, where groundwater was impacted by anthropogenic activities (WWTP effluent and PFOA-related facilities, respectively) (Plumlee et al., 2008; Post et al., 2009). The median PFAA levels in Tokyo groundwater were comparable to those in European groundwater (Eschauzier et al., 2010; Loos et al., 2010).

While the median PFAA concentrations in groundwater were typically several ng/L, the range in concentration was very large. The maximum concentrations of PFOS (990 ng/L), PFHpA (61 ng/L), PFOA (1800 ng/L), PFNA (620 ng/L) and FOSA (96 ng/L) in groundwater were several times higher than those of wastewater and street runoff (Murakami et al., 2009b) in Tokyo and those of groundwater in the US (Plumlee et al., 2008; Post et al., 2009; Quiñones and Snyder, 2009), Europe (Eschauzier et al., 2010; Loos et al., 2010) and China (Jin et al., 2009). The spatial distribution of PFAAs in groundwater (Figure 1) shows that only a few

sites, namely, GW0907 (Σ PFAAs 1900 ng/L), GW1806 (1900 ng/L) and GW0308 (820 ng/L), were severely polluted. Their PFAA levels exceeded several international guidelines. Two groundwater samples exceeded the USEPA Provisional Health Advisory value of PFOS (200 ng/L) and a groundwater sample did that of PFOA (400 ng/L). Furthermore, PFOS concentrations in 5 samples exceeded a proposed guideline (50 ng/L) for the protection of trophic level IV avian species that consume organisms in equilibrium with the water (Rostkowski et al., 2006). Therefore, care should be taken if those groundwaters are directly used for drinking purposes, landscaping or replenishing rivers.

While samples from unconfined aquifers and springs were all positive with PFAAs, even confined aquifers had high detection rates (89%; Figure 2(a)). The median levels of PFAAs from confined aquifer samples were generally only less than one order of magnitude lower than those of unconfined aquifers and springs (Figure 2(b)). The distributions of detection rates and concentrations of PFAAs were very similar among the aquifer types. Moreover, extremely high concentrations of PFOS and PFOA were found in both aquifer types.

In tap water, only PFAAs with ≤ 9 fluorinated carbons (PFHxS, PFOS, PFHpA, PFOA, PFNA and PFDA) and FOSA were detected with concentrations in the order of several ng/L, similar to the median concentrations of these PFAAs in groundwater (Figure 1 for spatial distribution; Table S5 for the measured values). The frequent detection of those PFAAs with relatively short carbon chains in tap water has been reported in several studies (Mak et al., 2009; Quiñones and Snyder, 2009). It has been shown that the treatment methods employed in Tokyo's water supply—flocculation, sedimentation, sand filtration, ozonation and granular activated carbon—are ineffective in removing PFOS and PFOA (Takagi et al., 2011).

3.2. Comparison of PFAA and PPCP levels

In order to investigate the sources and fate of PFAAs in the subsurface, PFAA levels were compared to PPCP levels measured in our parallel study (Kuroda et al., 2012). The groundwater in Tokyo was contaminated by sewage, as confirmed by PPCP detection (Kuroda et al., 2012; Nakada et al., 2008). Figure 3 shows the comparison of PFOS and PFOA levels in aquifers with the levels of two PPCPs (carbamazepine and crotamiton; Table S1) which are known as conservative tracers of sewage (Clara et al., 2004; Nakada et al., 2008). The comparison of PFHpA and PFNA and the two PPCPs is shown in Figure S3. In these Figures, the PFAA and PPCP levels in river waters in Japan, and secondary effluents in Tokyo (Murakami et al., 2008a), are also shown. In rivers in Japan, the primary source of PFOS, PFHpA and PFNA was inferred to be secondary effluents (Murakami et al., 2008a). With regard to PFOA, while secondary effluents were suggested as the primary source in most rivers, there was evidence of a significant contribution from point sources other than WWTPs (e.g., industries) to the remarkably high PFOA level in several rivers (Murakami et al., 2008a).

Figure 3. Comparison of PFOS and PFOA with carbamazepine (a, b) and crotamiton (c, d) in groundwater in this study, river waters in Japan (Murakami et al., 2008a), and secondary effluent in Tokyo (Murakami et al., 2008a) in the literature. (2-column fitting image)

Sewage was inferred to be a major source of PFAAs in some groundwater samples in which both PFAAs and the sewage-tracer PPCPs were detected, and the groundwater data were distributed around the data points of rivers and secondary effluents. Other groundwater samples, however, showed a different PFAA distribution than was found in samples from

371 rivers and secondary effluents; the ratio of PFAA to PPCP abundance was greater in the
372 groundwater samples than in the river and secondary effluent samples. Moreover, 30–42% of
373 the groundwater samples were positive only for PFAAs, while PPCPs were below the LOQs
374 in those samples. There are three possible reasons for the higher abundance and detection
375 rates of PFAAs compared to PPCPs. First, subsurface attenuation of PFAAs may be slower
376 than that of PPCPs. The residence time of confined aquifers of 40–124 m depth were
377 estimated to be 11–28 years (Imaizumi et al., 2000) and that of unconfined aquifers and
378 springs would be shorter. The half-life of carbamazepine in groundwater is typically 5–10
379 years (Drewes et al., 2003; Massmann et al., 2008). The half-life of crotamiton has not yet
380 been quantified, although it has been shown to be shorter than that of carbamazepine (Kuroda
381 et al., 2012). On the other hand, PFAAs are the end-products of manufacturing process of
382 perfluoroalkyl and polyfluoroalkyl substances, and thereby highly recalcitrant to
383 biodegradation, owing to their very strong carbon-fluorine bonds. Therefore, higher
384 PFAA/PPCP ratios with crotamiton than that with carbamazepine found in samples with high
385 levels of PFAAs might be attributed to the lesser half-life of crotamiton. Second, detection of
386 PFAAs at appreciable levels, despite the absence of PPCPs, may indicate the contribution of
387 other sources than sewage (e.g., surface runoff and point sources) to groundwater PFAAs.
388 Third, PFAAs might be formed from precursors while passing through soils. Formation of
389 PFAAs from precursors under biologically active conditions was indicated in the activated
390 sludge process (Guerra et al., 2014; Schultz et al., 2006; Sinclair and Kannan, 2006) and in
391 soil-water systems (Murakami et al., 2013; Murakami et al., 2008b). It has been shown that
392 urban runoff also contained PFAA precursors in a significant amount (Houtz and Sedlak,
393 2012). In the present study, FOSA was detected at only 19% of groundwater samples and it

was detected in samples with high levels of PFOS and PFOA (Figure S4).

Adsorption to soils may have a minor effect on subsurface attenuation of the four PFAAs (PFOS, PFHpA, PFOA and PFNA) and the two PPCPs. Similar to PFOS and PFOA, the concentrations of the two PPCPs in Tokyo groundwater were unchanged between in 2006 and 2007 (Kuroda et al., 2012). Therefore, during the long-term continuous pollution of groundwater, adsorption equilibrium on the subsoil would have been reached for PFOS, PFOA, carbamazepine, crotamiton and perhaps PFHpA, whose carbon chain is shorter than PFOA. In our previous soil column percolation experiments using secondary effluents, breakthroughs of the two PPCPs were observed (Shinohara et al., 2006). Adsorption on soil might have influenced the attenuation of PFNA, especially in the samples that had lower PFNA/carbamazepine ratios than those of rivers and secondary effluent. For PFAAs whose carbon-chains are longer than PFNA, adsorption to soils would have been a major issue, as stated in section 3.1 and Figure 2. Temporal changes in PFAA and PPCP consumption would not have influenced greatly to the relative abundance of PFAAs in groundwater, which should be older than the PFAAs in rivers and secondary effluents. While annual PFAA consumption data are not available, the time-trend of PFAA usage in Tokyo may be estimated from PFAA levels in Tokyo Bay sediments (Zushi et al., 2010). Between 1990 and 2004, the ratio of PFAA concentrations in Tokyo Bay sediments to carbamazepine consumption (Ministry of Health, 1990–2004) did not change significantly (Figure S5).

Based on the observed PFAA levels (~several ng/L) in tap water, leakage from water mains may provide the background levels, but would not account for the elevated levels of PFAAs in groundwater. However, surface runoff may be a source of elevated PFAAs in groundwater, along with sewage. In Japan, street runoff and storm water runoff contain high levels of

PFAAs (e.g., maximum PFNA 172 ng/L; Table 1), causing non-point PFAA pollution in urban surface waters (Murakami et al., 2009b; Nishikoori et al., 2011; Zushi and Masunaga, 2009; Zushi et al., 2008). PFAA concentrations in rainwater in Tokyo area were only at low ng/L levels (Kwok et al., 2010; Murakami et al., 2009b; Nishikoori et al., 2011).

Regarding point sources, only GW1806, with a remarkably high PFOA concentration (1800 ng/L), was possibly polluted by point sources; in this case, sources such as industrial facilities. There was a storage space for industrial wastes within 100 m away from the well, but its usage of fluorochemicals was not known. In several rivers in Japan, where point sources other than WWTPs (e.g., industries) have been suggested as the major sources of PFOA (Murakami et al., 2008a), distinctively PFOA-dominated PFAA compositions have been reported (PFOA/PFOS: 13–703; PFOA/PFNA: 28–163; and %PFOA (PFOA/(PFOA, PFNA, PFDA and PFUnDA)): 90–99%). Such compositions were not found in other rivers (0.33–16, 0.7–6.2, 35–78%), in wastewater (0.08–2.9, 0.4–1.4, 26–55%), or in street runoff (1.8–16, 2.0–7.4, 44–65%), in Japan (Murakami et al., 2008a; Murakami et al., 2009b). In groundwater, only GW1806 had such a PFOA-dominated composition (269, 244, 99%). In tributaries of the Rhine River, contaminated organic waste applied in agricultural areas was a suspected source of specifically elevated PFOA (Skutlarek, 2006). In Tokyo, however, biosolids are unlikely sources of PFAAs because agricultural land is located only in peripheral areas, and biosolids application is not a common practice.

3.3. Source apportionment of PFAAs in groundwater

In PCA-MLR using 5PFAAs (PFOS, PFOA, PFNA, PFDA and PFUnDA) in 53 groundwater samples as input data, 3 PCs were obtained. Table S6 shows the rotated component matrix and loadings after rotation. On the basis of the PFAA profiles observed in Japan and

comparison with the reference samples, PCs 1–3 were interred to be sewage, street runoff and point sources, respectively (S2.1). Figures 4 (a) and (b) show the FSs and source contributions of PCs resulted from PCA-MLR, for the 10 groundwater samples which had the highest Σ 5PFAAs, respectively. On the basis of regression coefficients from MLR, the mean percent contribution to Σ 5PFAAs was 44.6% sewage, 9.7% street runoff and 45.7% point sources. When input data for PCA was changed (i.g., 5PFAAs and carbamazepine as input variables; groundwater samples and the reference samples as input samples), the FS distribution and source contributions of the 10 groundwater samples did not change greatly (S3).

In PFCAR, both L-PFCAR and E-PFCAR gave consisitent estimates of sewage-street runoff source apportionment in four groundwater samples, including those from the two most contaminated sites (GW0907 and GW0308), where sewage was the principal source of pollution (Figures 4(c) and 4 (d)). Those results were very similar to PCA-MLR results, when PC3 was regarded as a member of sewage group. On the other hand, in the 6 groundwater samples with lesser Σ 5PFAAs, the E-PFCAR results were different from the results of the other two methods; namely, in 5 out of the 6, L-PFCAR indicated sewage as the principal source. In our previous soil column percolation experiments, the effluents showed a lesser L-PFCAR result, and a greater E-PFCAR result, in comparison with the influents, owing to the preferential partitioning of PFDA and PFUnDA over PFOA and PFNA during soil passage (Murakami et al., 2009a). Therefore, L-PFCAR may overestimate, and E-PFCAR may underestimate the contribution of sewage to Σ 5PFAAs in groundwater (Murakami et al., 2009a). Meanwhile, L-PFCAR gave reasonable source estimation for the reference samples (Figure S9). Moreover, L-PFCAR and PCA-MLR gave consistent results. It was therefore indicated that PCA-MLR and L-PFCAR were more viable than E-PFCAR in source

apportionment of Σ 5PFAAs in groundwater. With L-PFCAR, the respective fractions of Σ 5PFAAs attributed to sewage and street runoff were 82% and 18% of the sum of Σ 5PFAAs in the 10 groundwater samples.

To further validate the above-mentioned source apportionment methods, the source apportionment results were compared with concentrations of carbamazepine (Kuroda et al., 2012) and heavy metals (Kuroda, 2010) measured in the same samples, using Spearman's rank-order correlation analysis (Table S8). The heavy metals, Cd, Co, Cr, Cu, Ni and Zn, were contained in urban runoff at high concentrations (Han et al., 2006; Joshi and Balasubramanian, 2010). The results showed that PCA-MLR and L-PFCAR are viable methods for estimating the contribution of sewage and street runoff in groundwater. The original Σ 5PFAAs before source-apportionment positively correlated with carbamazepine, Ni and Zn. PCA-MLR and L-PFCAR results, however, gave a more reasonable correspondence with carbamazepine and heavy metals. PC1, PC3 and the Σ 5PFAAs fractions attributed to sewage by L-PFCAR had positive correlations with only carbamazepine. On the other hand, PC2 and the street runoff-attributed Σ 5PFAAs fractions by L-PFCAR correlated with several heavy metals. Furthermore, the sum of PC1 and PC3 turned out to have a stronger correlation with carbamazepine than PC1 or PC3 alone; this would be because multiple PPCPs were detected at relatively high concentrations in point source-suspected GW1806 (Kuroda et al., 2012). This could also suggest a close relationship between point source-derived PFAAs and sewage. On the other hand, the source-attributed Σ 5PFAAs fractions estimated by E-PFCAR did not have reasonable correlations with carbamazepine or heavy metals. E-PFCAR was possibly not an appropriate source apportionment method, due to the greater error resulting from the difference in E-PFCAR, relating street runoff and WWTP influent (street

runoff/WWTP influent = $0.72/0.45 = 1.6$ times), being smaller than that in L-PFCAR (0.26/0.03 = 8.7 times). At stations GW0907 and GW1101, the larger fraction of sewage-attributed $\Sigma 5\text{PF}AAs$ estimated by E-PFCAR could be attributed to this small dynamic range of E-PFCAR.

To wrap up, both PCA-MLR and L-PFCAR were viable methods for sewage-street runoff source apportionment. Moreover, PCA-MLR enabled estimation of point source-derived PFAs. Both methods suggested sewage and point sources as the dominant sources of $\Sigma 5\text{PF}AAs$ in severely contaminated groundwater, with street runoff being a relatively minor source.

Figure 4. Source apportionment of 10 groundwater samples with the highest $\Sigma 5\text{PF}AAs$ by PCA-MLR (a: factor scores; b: contribution of sources), L-PFCAR (c) and E-PFCAR (d).

3.4. Pathways of PFAAs in aquifers, based on tritium analysis

Tritium is a radioactive isotope of hydrogen, with a half-life of 12.33 years (Lucas and Unterweger, 2000), and is useful in differentiating young groundwater, recharged after the 1950s and 1960s, from old groundwater (see Figure S9).

In Figure 5, Σ PFAAs was compared with well depths and tritium indicators (concentration data in Table S9). Tritium samples at <50 m depth had concentrations of 1.7–4.2 TU, which suggested that the samples contained young groundwater likely recharged during or after the 1970s (see Figure S9). PFAAs were detected in all these samples, and at high concentrations in some. Since PFAAs had already been in widespread use before the recharge of the aquifers, the water may have been polluted before or shortly after recharge near the ground surface (e.g., by atmospheric sources, infiltration of surface runoff, or sewer exfiltration). As discussed above, the pollution sources of the groundwater samples with very high maximum PFAA levels were associated with sewage. As was the case with PPCPs (Kuroda et al., 2012), the large variation in the observed PFAA concentrations could be explained by locally-occurring pollution mechanisms, such as sewer exfiltration, and by the large variation in PFAA source levels and the degree of dilution.

The other two tritium analysis samples (GW1213: 130 m depth; and GW4001: 500 m depth) both contained old groundwater (0.4 TU and <0.3 TU, respectively), which had been recharged before the 1950s. Therefore, it was not surprising that no PFAAs were detected at GW1213, because PFAAs were not yet in use when the groundwater was recharged. However, PFAAs were detected at GW4001. In addition, caffeine, a labile marker of sewage (Buerge et al., 2003), was detected, at 11 ng/L, in this sample (Kuroda et al., 2012). Since it is highly unlikely that the caffeine had persisted for more than 50 years, it is likely that

GW4001, and perhaps other PFAA-positive deep groundwater samples, were contaminated due to defects in well casings, which would allow contamination by young groundwater from the upper aquifers.

Figure 5. ΣPFAAs with depth of wells and concentration of tritium. (1-column fitting image)

3.5. PPCP analysis, tritium analysis, PCA-MLR and L-PFCAR as means of evaluating groundwater pollution by PFAAs

This study demonstrated the utility of PPCP analysis, tritium analysis, PCA-MLR, PFCAR, and their combined use in investigating the sources and pathways of PFAA pollution in multiple aquifer systems. PPCPs served as indicators of pollution by sewage in individual groundwater samples. Moreover, they were useful in obtaining a general idea of the sources of, and processes involving, PFAAs in groundwater, and in validating source apportionment

538 methods. Quantitative source assessment of individual samples, however, would be difficult
539 using PPCPs alone in the study site, because the relationship between PPCPs and
540 sewage-attributed PFAAs was not linear, because of several factors involving the relationship
541 between PPCPs and PFAAs in groundwater (section 3.2); the correlation between
542 concentrations of PPCPs and sewage-attributed Σ 5PFAAs was significant but not strong
543 enough (maximum $\rho = 0.64$; Table S8) for such quantitative assessment. Moreover, PPCP
544 concentrations were below the LOQs in GW0308, which was considered to be severely
545 polluted by sewage. In contrast, in a site where WWTP effluent was recharged into an aquifer
546 through a lagoon, carbamazepine was shown to be an effective quantitative tracer of sewage
547 within a residence time of two years (Gasser et al., 2010). This contrast would be partly
548 owing to attenuation of PPCPs over the (presumably) longer residence times involved in the
549 present study, and partly to random mixing of PFAAs and PPCPs in the Tokyo sewers. For
550 source assessment of individual groundwater samples, PCA-MLR and L-PFCAR are viable
551 methods. In this study, while both methods enabled source apportionment between sewage
552 and street runoff, PCA-MLR was useful in distinguishing point source-derived PFAAs with
553 anomalous PFAA compositions. Both methods require PFAA profiles of potential PFAA
554 sources, which might vary among countries and regions. Tritium analysis was useful in
555 distinguishing old groundwater that theoretically does not contain PFAAs. Therefore, the
556 pollution mechanisms involving young groundwater (e.g., sewer exfiltration, infiltration of
557 street runoff) and old groundwater (e.g., defects of well structure) were indicated by a
558 combined use of tritium and PPCP analyses.

559 More generally, since groundwater is characterized by a long residence time, countermeasures
560 and regulatory actions against PFAA pollution, such as PFAA-use reduction, production

phaseout and short-chain PFAA shift, may eventually achieve low PFAA levels in groundwater. Meanwhile, PFAA levels in deep aquifers may increase due to the legacy of past PFAA use, production from precursors, or contamination by young groundwater. Therefore, continuous monitoring of PFAAs in aquifers, using the above-mentioned tracers and source apportionment methods, would seem essential work for the future.

4. Conclusions

The ubiquitous occurrence of PFAAs in samples from all types of aquifers, at almost all depths, showed the high vulnerability of Tokyo's aquifers to pollution by PFAAs. While PFAAs' median concentrations were low (several ng/L), a few of groundwater samples had high levels of PFAAs (up to 1800 ng/L). PFAAs were more frequently detected than sewage-tracer PPCPs, carbamazepine and crotamiton. Sources of severe PFAA pollution were inferred as sewage and point sources by using PCA-MLR and L-PFCAR. A combined use of tritium and PPCPs indicated the pollution mechanism of both shallow young groundwater recharged after 1950s (sewer exfiltration, infiltration of street runoff) and deep old groundwater recharged before 1950s (detects of well structure). Overall, PPCP analysis, tritium analysis, PCA-MLR and L-PFCAR were shown to be useful in investigating sources and pathways of multi-sourced PFAAs in multiple aquifer systems.

Acknowledgments

The authors thank the members of Laboratory of Urban Water Systems, the University of Tokyo, the members of Laboratory of Organic Geochemistry, Tokyo University of Agriculture and Technology, and the local government officers for their help in sample collection and analysis. This study was supported in part by Grant-in-aid for Scientific Research (#22404012) and Research Fellowships for Young Scientists (#21-04295) from

584 Japan Society for the Promotion of Science, and a CREST project grant for ‘Development of
585 Well-balanced Urban Water Use System Adapted for Climate Change’ from the Japan
586 Science and Technology Agency.
587

REFERENCES

- Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, et al. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environ. Assess. Manag.* 2011; 7: 513–541.
- Buerge IJ, Poiger T, Müller MD, Buser H-R. Caffeine, an anthropogenic marker for wastewater contamination of surface waters. *Environ. Sci. Technol.* 2003; 37: 691–700.
- Bureau of Urban Development, Tokyo Metropolitan Government (Website in Japanese); <http://www.toshiseibi.metro.tokyo.jp/>
- Bureau of Waterworks, Tokyo Metropolitan Government (Website in Japanese); <http://www.waterprofessionals.metro.tokyo.jp/index.html>
- Clara M, Strenn B, Kreuzinger N. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behavior of carbamazepine in wastewater treatment and during groundwater infiltration. *Water Res.* 2004; 38: 947–954.
- Conder JM, Hoke RA, Wolf Wd, Russell MH, Buck RC. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* 2008; 42: 995–1003.
- Drewes JE, Heberer T, Rauch T, Reddersen K. Fate of pharmaceuticals during ground water recharge. *Ground Water Monit. Rem.* 2003; 23: 64–72.
- Endo T. Confined groundwater system in Tokyo. *Environ. Geol. Water Sci.* 1992; 20: 21–34.
- Eschauzier C, Haftka J, Stuyfzand PJ, de Voogt P. Perfluorinated compounds in infiltrated River Rhine water and infiltrated rainwater in coastal dunes. *Environ. Sci. Technol.* 2010; 44: 7450–7455.
- Furl CV, Meredith CA, Strynar MJ, Nakayama SF. Relative importance of wastewater treatment plants and non-point sources of perfluorinated compounds to Washington State rivers. *Sci. Total Environ.* 2011; 409: 2902–2907.
- Gasser G, Rona M, Voloshenko A, Shelkov R, Tal N, Pankratov I, et al. Quantitative evaluation of tracers for quantification of wastewater contamination of potable water sources. *Environ. Sci. Technol.* 2010; 44: 3919–3925.
- Guerra P, Kim M, Kinsman L, Ng T, Alae M, Smyth SA. Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment. *J. Hazard. Mater.* 2014; 272: 148–154.
- Han YH, Lau SL, Kayhanian M, Stenstrom MK. Correlation analysis among highway stormwater pollutants and characteristics. *Water Sci. Technol.* 2006; 53: 235–243.
- Harrison RM, Smith DJT, Luhana L. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ. Sci. Technol.* 1996; 30: 825–832.
- Higgins CP, Field JA, Criddle CS, Luthy RG. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 2005; 39: 3946–3956.
- Higgins CP, Luthy RG. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 2006; 40: 7251–7256.
- Houtz EF, Higgins CP, Field JA, Sedlak DL. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* 2013; 47: 8187–8195.
- Houtz EF, Sedlak DL. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* 2012; 46: 9342–9349.
- Huset CA, Chiaia AC, Barofsky DF, Jonkers N, Kohler H-PE, Ort C, et al. Occurrence and mass flows of fluorochemicals in the Glatt Valley watershed, Switzerland. *Environ. Sci. Technol.* 2008; 42: 6369–6377.

- Imaizumi M, Komae T, Nihira S. Evaluation of recharge mechanism of confined groundwater using long term tritium concentration records in the metropolis of Tokyo. *J. Japan Soc. Eng. Geol.* (in Japanese with English abstract) 2000; 41: 87–102.
- Jin YH, Liu W, Sato I, Nakayama SF, Sasaki K, Saito N, et al. PFOS and PFOA in environmental and tap water in China. *Chemosphere* 2009; 77: 605–611.
- Joshi UM, Balasubramanian R. Characteristics and environmental mobility of trace elements in urban runoff. *Chemosphere* 2010; 80: 310–318.
- Kim S-K, Kannan K. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. *Environ. Sci. Technol.* 2007; 41: 8328–8334.
- Kissa E. *Fluorinated Surfactants and Repellants*, 2nd ed.; Marcel Dekker Inc.: New York, 2001.
- Kuroda K. Evaluation of potential of groundwater for the improvement of urban environments. dissertation, The University of Tokyo, 2010.
- Kuroda K, Murakami M, Oguma K, Muramatsu Y, Takada H, Takizawa S. Assessment of groundwater pollution in Tokyo using PPCPs as sewage markers. *Environ. Sci. Technol.* 2012; 46: 1455–1464.
- Kwok KY, Taniyasu S, Yeung LWY, Murphy MB, Lam PKS, Horii Y, et al. Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and several other countries. *Environ. Sci. Technol.* 2010; 44: 7043–7049.
- Larsen RK, Baker JE. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ. Sci. Technol.* 2003; 37: 1873–1881.
- Loos R, Locoro G, Comero S, Contini S, Schwesig D, Werres F, et al. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res.* 2010; 44: 4115–4126.
- Lucas L, L., Unterweger M, P. Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Stand. Technol.* 2000; 105: 541–549.
- Mak YL, Taniyasu S, Yeung LWY, Lu G, Jin L, Yang Y, et al. Perfluorinated compounds in tap water from China and several other countries. *Environ. Sci. Technol.* 2009; 43: 4824–4829.
- Massmann G, Sultenfuss J, Dunnbier U, Knappe A, Taute T, Pekdeger A. Investigation of groundwater residence times during bank filtration in Berlin: multi-tracer approach. *Hydrol. Processes* 2008; 22: 788–801.
- Ministry of Health, Labour and Welfare of Japan. The statistical yearbook of pharmaceutical industry productions trends, 1990–2004. (in Japanese)
- Moody CA, Field JA. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.* 1999; 33: 2800–2806.
- Morimoto T, Muramatsu Y, Takeshita A, Shimizu A, Murakami M, Takada H. Concentrations of water-soluble organic micropollutants and anthropogenic molecular markers in influent and effluent from sewage treatment plant. *J. Water Waste* (in Japanese with English abstract) 2011; 53: 635–646.
- Murakami M, Imamura E, Shinohara H, Kiri K, Muramatsu Y, Harada A, et al. Occurrence and sources of perfluorinated surfactants in rivers in Japan. *Environ. Sci. Technol.* 2008a; 42: 6566–6572.
- Murakami M, Kuroda K, Sato N, Fukushi T, Takizawa S, Takada H. Groundwater pollution by perfluorinated surfactants in Tokyo. *Environ. Sci. Technol.* 2009a; 43: 3480–3486.
- Murakami M, Morita C, Morimoto T, Takada H. Source analysis of perfluorocarboxylates in Tokyo Bay during dry weather and wet weather using sewage markers. *Environ. Chem.* 2011; 8: 355–362.

- Murakami M, Nishikoori H, Sakai H, Oguma K, Takada H, Takizawa S. Formation of perfluorinated surfactants from precursors by indigenous microorganisms in groundwater. *Chemosphere* 2013; 93: 140–145.
- Murakami M, Sato N, Anegawa A, Nakada N, Harada A, Komatsu T, et al. Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. *Water Res.* 2008b; 42: 2745–2755.
- Murakami M, Shinohara H, Takada H. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs). *Chemosphere* 2009b; 74: 487–493.
- Nakada N, Kiri K, Shinohara H, Harada A, Kuroda K, Takizawa S, et al. Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage. *Environ. Sci. Technol.* 2008; 42: 6347–6353.
- Nakayama SF, Strynar MJ, Reiner JL, Delinsky AD, Lindstrom AB. Determination of perfluorinated compounds in the upper Mississippi River basin. *Environ. Sci. Technol.* 2010; 44: 4103–4109.
- Nguyen VT, Reinhard M, Karina GY-H. Occurrence and source characterization of perfluorochemicals in an urban watershed. *Chemosphere* 2011; 82: 1277–1285.
- Nishikoori H, Murakami M, Sakai H, Oguma K, Takada H, Takizawa S. Estimation of contribution from non-point sources to perfluorinated surfactants in a river by using boron as a wastewater tracer. *Chemosphere* 2011; 84: 1125–1132.
- OECD, OECD portal on perfluorinated chemicals, 2011;
http://www.oecd.org/site/0,3407,en_21571361_44787844_1_1_1_1_1_1,00.html
- Olsen GW, Chang S-C, Noker PE, Gorman GS, Ehresman DJ, Lieder PH, et al. A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans. *Toxicology* 2009; 256: 65–74.
- Plumlee MH, Larabee J, Reinhard M. Perfluorochemicals in water reuse. *Chemosphere* 2008; 72: 1541–1547.
- Post GB, Louis JB, Cooper KR, Boros-Russo BJ, Lippincott RL. Occurrence and potential significance of perfluorooctanoic acid (PFOA) detected in New Jersey public drinking water systems. *Environ. Sci. Technol.* 2009; 43: 4547–4554.
- Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* 2005; 40: 32–44.
- Quiñones O, Snyder SA. Occurrence of perfluoroalkyl carboxylates and sulfonates in drinking water utilities and related waters from the United States. *Environ. Sci. Technol.* 2009; 43: 9089–9095.
- Rostkowski P, Yamashita N, So IMK, Taniyasu S, Lam PKS, Falandysz J, et al. Perfluorinated compounds in streams of the Shihwa industrial zone and Lake Shihwa, South Korea. *Environ. Toxicol. Chem.* 2006; 25: 2374–2380.
- Sakurai T, Serizawa S, Isobe T, Kobayashi J, Kodama K, Kume G, et al. Spatial, phase, and temporal distributions of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in Tokyo Bay, Japan. *Environ. Sci. Technol.* 2010; 44: 4110–4115.
- Schultz MM, Barofsky DF, Field JA. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. *Environ. Sci. Technol.* 2004; 38: 1828–1835.
- Schultz MM, Higgins CP, Huset CA, Luthy RG, Barofsky DF, Field JA. Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ. Sci. Technol.* 2006; 40: 7350–7357.
- Scott BF, Spencer C, Mabury SA, Muir DCG. Poly and perfluorinated carboxylates in North American precipitation. *Environ. Sci. Technol.* 2006; 40: 7167–7174.
- Shinohara H, Murakami M, Managaki S, Kojima S, Takada H, Sato N, et al. Removal of water-soluble organic micro-pollutants by soil infiltration. *J. Environ. Sci. (in Japanese with English abstract and figure captions)* 2006; 19,: 435–444.

- Simcik MF, Dorweiler KJ. Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. *Environ. Sci. Technol.* 2005; 39: 8678–8683.
- Sinclair E, Kannan K. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environ. Sci. Technol.* 2006; 40: 1408–1414.
- Skutlarek DE, M.; Färber, H. . Perfluorinated surfactants in surface and drinking waters. *Environ. Sci. Pollut. Res.* 2006; 13: 299–307.
- Takagi S, Adachi F, Miyano K, Koizumi Y, Tanaka H, Watanabe I, et al. Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes. *Water Res.* 2011; 45: 3925–3932.
- Thurston GD, Spengler JD. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmos. Environ.* 1985; 19: 9–25.
- Tokyo Institute of Civil Engineering and Technology Research, Geological map of Tokyo. In *Geology of Tokyo* (1), 1977 (in Japanese).
- Tokyo Institute of Civil Engineering and Technology Research, Map of deep underground of Tokyo. In *Geological Map of Tokyo* (6), 1996 (in Japanese).
- Tokyo Metropolitan Government. Basic survey of land, 2001 (in Japanese).
- Tokyo Metropolitan Government. Report on land subsidence and groundwater in Tokyo, 2006 (Website in Japanese);
<http://www.kankyo.metro.tokyo.jp/water/groundwater/index.html>
- USEPA, Long-chain perfluorinated chemicals (PFCs) action plan, Washington DC, 2009;
http://www.epa.gov/opptintr/existingchemicals/pubs/pfcs_action_plan1230_09.pdf.
- Watanabe H, Murakami M, Komura T, Moroizumi T, Furumai H. Evaluation of water balance and water use stress in principal cities in Japan. *J. Water Waste* (in Japanese with English abstract) 2009; 51: 137–148.
- Weiß O, Wiesmüller GA, Bunte A, Göen T, Schmidt CK, Wilhelm M, et al. Perfluorinated compounds in the vicinity of a fire training area – human biomonitoring among 10 persons drinking water from contaminated private wells in Cologne, Germany. *Int. J. Hyg. Environ. Health* 2012; 215: 212–215.
- Xiao F, Simcik MF, Gulliver JS. Perfluoroalkyl acids in urban stormwater runoff: Influence of land use. *Water Res.* 2012; 46: 6601–6608.
- Zushi Y, Masunaga S. First-flush loads of perfluorinated compounds in stormwater runoff from Hayabuchi River basin, Japan served by separated sewerage system. *Chemosphere* 2009; 76: 833–840.
- Zushi Y, Takeda T, Masunaga S. Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan. *Chemosphere* 2008; 71: 1566–1573.
- Zushi Y, Tamada M, Kanai Y, Masunaga S. Time trends of perfluorinated compounds from the sediment core of Tokyo Bay, Japan (1950s–2004). *Environ. Pollut.* 2010; 158: 756–763.
- Zushi Y, Ye F, Motegi M, Nojiri K, Hosono S, Suzuki T, et al. Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo Bay basin of Japan. *Environ. Sci. Technol.* 2011; 45: 2887–2893.