Evaluation of the Current Contamination Status of PFASs and OPFRs in South Korean Tap Water Associated with its Origin

Park H[1], Choo G[1], Kim H[1], Oh JE[1]

[1]Department of Civil and Environmental Engineering, Pusan National University, Busan, South Korea, 46241, heejeongpark@pusan.ac.kr

Introduction

Among the emerging contaminants in drinking water, perfluoroalkyl substances (PFASs) and organophosphate flame retardants (OPFRs) have attracted particular attention. In 2009, perfluorooctane sulfonate (PFOS) and its salts were listed as persistent organic pollutants (POPs) under the Stockholm Convention, and the use of tris(2-chloroethyl) phosphate (TCEP) and/or tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) in products for children have been banned due to their various toxic (i.e. carcinogenic and neurotoxic) effects[1–3]. PFASs and OPFRs have been ubiquitously detected in water systems[4,5]. Accordingly, there has been increasing concern about potential human exposure via drinking water consumption[4,6–8]. In South Korea, a major source of tap water is surface water, for example from rivers and lakes/reservoirs in the four representative watersheds of the Han River (HR), the Geum River (GR), the Yeongsan Seomjin River (YSR), and the Nakdong River (NR). Within these watersheds, tap water originates from regions where river surface water can be highly contaminated by various chemicals emanating from industrial facilities along the river basin. In addition, purified water may also be contaminated by various pollution paths to the faucet via the water distribution system, such as polluted water storage tanks, corroded parts, and pipe leakages[9]. However, until now, no previous study has investigated PFAS or OPFR contamination in tap water according to tap water origin, and there remains a need to investigate the overall tap water quality of the four key watersheds in South Korea. Therefore, this study aimed to evaluate the current PFAS and OPFR contamination status of tap water according to its origin, river water or lake/reservoir water, in each key watershed. We also assessed the presence and distribution of PFASs and OPFRs in tap water samples collected from major Korean cities. In addition, we estimated the daily intake of these contaminants via tap water consumption in the general Korean population, and describe regional intake differences.

Materials and methods

Sample collection

44 tap water samples were collected in 2017 from eight major cities including Seoul (n = 10), Incheon (n = 4), Suwon (n = 4), Daejeon (n = 7), Gwangju (n = 7), Daegu (n = 3), Andong (n = 1) and Busan (n = 8). These cities all have populations over 1,000,000, with the exception of Andong, and were selected to cover four representative watersheds in Korea: HR, GR, YSR, and the NR. Samples were distinguished by origin: river water (n = 20) or lakes/reservoirs (n = 24). Lake/reservoir water is usually managed within a protected area and is known to have no direct input of wastewater; meanwhile, withdrawing river water for tap water production often raises concerns about pollution due to nearby sources of pollution, particularly industrial facilities located midstream of the NR basin.

Sample preparation and instrumental analysis

Samples were prepared according to the methods described in previous studies with minor modification (Kim et al., 2016; Cristale et al., 2013). Each sample was devided into two sets for the determination of OPFRs and PFASs, and sample extraction and clean-up were conducted by solid phase extraction (SPE) by using Oasis WAX cartridges for PFASs, or Oasis HLB cartridges for OPFRs. PFASs were analyzed by HPLC-MS/MS (Agilent 1200/6460QQQMSD, Agilent), and OPFRs were analyzed by GC-MS/MS (Agilent 7890B/7000C, Agilent).

Results and discussion:

Evaluation of current contamination status of tap water by region and origin

PFASs

Some degree of variability was found in the levels and distribution patterns of PFASs among the different cities (Fig. 1a). Among eight cities, Daegu and Busan City showed the highest PFAS levels in tap water, where these cities are located in the NR basin. The average concentrations of $\sum_{14}$PFASs increased dramatically as the source water flowed from upstream to downstream locations in the NR basin; upstream (4.98 ng/L in Andong) < midstream (78.1 ng/L in Daegu) < downstream (109 ng/L in Busan). River water was mostly used for tap water production in those cities, and poor elimination of PFASs in drinking water treatment processes have been reported[5,12]. Therefore, the presence of industrial facilities (i.e., electronics, textile, and chemical industries) midstream of the NR basin may strongly affect tap water contamination.

To verify the impact of the type of source water on PFAS contamination in tap water, PFAS concentrations and distributions were compared according to the origin of the tap water: river water or lakes/reservoirs. The higher PFAS concentrations were observed in tap water originating from river water rather than lake/reservoir water (Fig. 1c): the difference was significant in HR (15.0 ng/L vs. 11.1 ng/L, respectively, $p < 0.01$) and NR (120 ng/L vs. 5.063 ng/L, respectively, $p < 0.05$). The tap water originating from the main stream in NR showed 10–40 fold higher PFAS concentrations than that originating from lake/reservoir water. These results indicate that tap water originating from river water could be adversely affected by PFAS contamination from nearby sources, such as industrial facilities in the midstream of the NR basin. This increase of PFAS contamination downstream seems to be related to the replacement of short-chained PFASs, and particularly PFHxS, due to a ban on PFOS implemented in 2012; this is supported by the higher proportion of PFHxS in the main stream of NR water than in lake/reservoir water. There were also increased PFAS levels midstream, where many industries are located. In agreement with this, the proportions of short-chained PFASs were higher compared with a previous study conducted in Korea [6], and the proportions of PFHxS and PFPeA rapidly increased from 1.9 to 33%, and from 4.4 to 12%, while those of PFOS and PFOA decreased from 6.3 to 0.42%, and from 31 to 20%, respectively. These findings were similar to previous studies done in other countries[5,13–15].

OPFRs

Unlike PFASs, regions located in the NR basin showed comparably lower OPFR levels; OPFR levels were also lower in Seoul City, which has the highest population density among all cities in South Korea, whereas other regions (Incheon, Suwon, Daejeon, and Gwangju City) showed comparably high OPFR levels (Fig. 1b). In addition, OPFR concentrations are a little bit higher in tap water with lake/reservoir origins than river origins (Fig. 1d). These results may indicate another source of OPFR contamination in tap water, considering the relatively higher OPFR levels in Incheon, Suwon, Daejeon, and Gwangju City.

Pipe materials are known to promote the formation of disinfection byproducts and/or biofilm in water flowing through distribution systems[16–19]. There have also been previously suggested probable sources of OPFR contamination in drinking water due to leaked from intact media in the pipeline network[20,21]. For those reasons, OPFR concentrations, and distances from the water intake stations to the sampling sites, were measured to examine their impact on OPFR contamination of tap water. There was a significant positive Spearman correlation (r = 0.358, $p < 0.05$) between the sum of the lineal distance and total OPFR concentration, although it is possible that multiple factors in addition to the water source, including the water treatment process (i.e. formation of chlorinated OPFRs from precursor compounds or via chlorination process), could also contribute to OPFR contamination[22–25]. A longer distance to the tap from each water intake station would engender increased contact with pipe materials, and therefore increase the possibility of contamination. In addition, an impact of pipelines on OPFR contamination may be supported by the relatively higher OPFR concentrations seen in tap water samples from Incheon, Suwon, Daejeon, and Gwangju City, although in these regions lakes and reservoirs are the water sources; these do not have point sources, unlike river water. This result may be related to two factors: first, tap water sources in Incheon and Suwon City are farther away from the water intake station (median = 38 km) relative to the other sampling sites (median = 20 km); second, the amount of PVC usage in water pipe network was at least 7–60-fold higher in Incheon, Daejeon, and Gwangju City than in other cities[26]. One recent study done in Pakistan also suggested an influence of pipelines on potable water with respect to OPFR content[20], which is consistent with our findings.

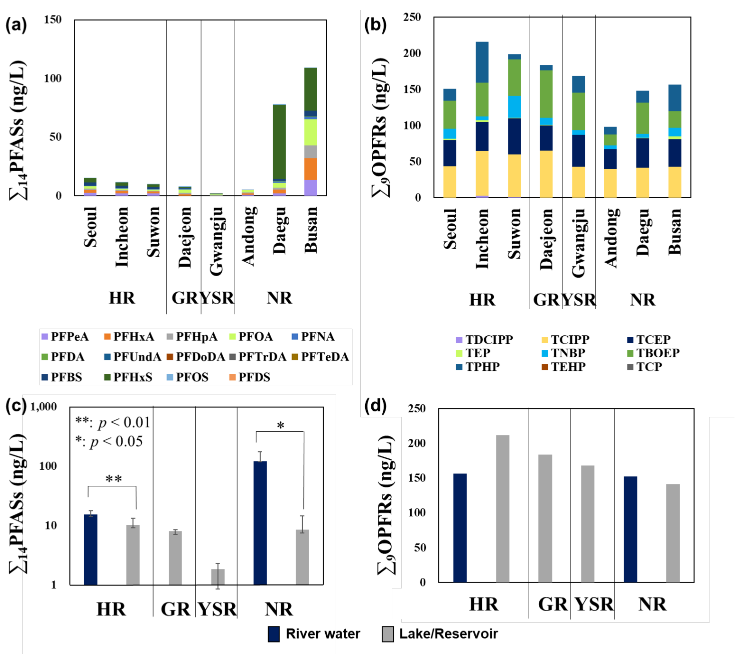

Fig. 1. Total concentrations by region of PFASs (a), of OPFRs (b), or by tap water origin of PFASs (c), of OPFRs (d)

Potential for human exposure to PFASs and OPFRs via tap water consumption

Total PFAS and OPFR intakes for an adult via tap water consumption have been estimated at 46.8 and 254 ng/person/d, respectively, by reference to the observed PFAS and OPFR concentrations in tap water (C, ng/L), the daily consumption rate of tap water (R, L/d), and average body weight (BW, kg). Tap water consumption was found to be significantly more influential with respect to PFAS exposure versus bottled water consumption, whereas the contributions of tap and bottled water to human exposure to OPFRs were not different. Although PFAS and OPFR DI values in this study were lower than the TDIs and RfDs, the DIs were nevertheless not negligible. The DI via tap water was approximately 70 times higher than that via bottled water, based on total PFAS concentrations (bottled water: 0.721 ng/person/d; tap water: 48.6 ng/person/d), and up to 140 times higher for PFOA in Busan City (bottled water: 0.237 ng/person/d; tap water: 33.3 ng/person/d). Furthermore, PFASs were expected to show distinct human exposure patterns by sampling location, due to regional differences in concentrations (which were not seen for OPFRs). As expected, in locations with higher PFAS concentrations, the human exposure risk due to tap water consumption was estimated to be 10 times higher (Daegu: PFHxS; Busan: PFOA) relative to other regions. This suggests that withdrawing water from river basins could expose local populations to high levels of PFASs in certain regions.

Acknowledgements:
This work was supported by a 2-Year Research Grant of Pusan National University.

References:
1. Alexander BH, Olsen GW, Burris JM, et al. (2003); *Occupational and Environmental Medicine* 60(10): 722-29
2. Lau C, Anitole K, Hodes C, et al. (2007); *Toxicol Sci* 99(2); 366-94
3. Stahl T, Mattern D, Brunn H. (2011); *Environ Sci Eur* 23(1), 38
4. Lee S, Jeong W, Kannan K, et al. (2016); *Water Research* 103: 182-88
5. Rahman MF, Peldszus S, Anderson WB. (2014); *Water Research* 50: 318-40
6. Heo JJ, Lee JW, Kim SK, et al. (2014); *Journal of Hazardous Materials* 279: 402-09
7. Noorlander CW, van Leeuwen SPJ, te Biesebeek JD, et al. (2011); *J. Agric. Food Chem.* 59(13): 7496–505
8. Thompson J, Eaglesham G, Mueller J. (2011); *Chemosphere* 83(10): 1320-25
9. Lee EJ, Schwab KJ. (2005); *Journal of Water and Health* 3(2): 109-27
10. Kim HY, Seok HW, Kwon HO, et al. (2016); *Science of The Total Environment* 563-64: 530-37
11. Cristale J, Katsoyiannis A, Sweetman AJ, et al. (2013); *Environmental Pollution* 79: 194–200
12. Appleman TD, Higgins CP, Quinones O, et al. (2014); *Water Research* 51: 246-55
13. Eschauzier C, Beerendonk E, Scholte-Veenendaal P, et al. (2012); *Environ. Sci. Technol.* 46(3): 1708-15
14. Renner R (2006); *Environ. Sci. Technol.* 40(1): 12-13
15. Ullah S, Alsberg T, Berger U. (2011); *Journal of Chromatography A* 1218(37): 6388-95
16. Garcia-Villanova RJ, Garcia C, Gomez JA, et al. (1997); *Water Research* 31(6): 1405-13
17. Hu CY, Jing Z, Bin Z, et al. (2016); *Desalination and Water Treatment* 57(2): 553-61
18. Schwartz T, Hoffmann S, Obst U. (2003); *Journal of Applied Microbiology* 95(3): 591-601
19. Wang JJ, Liu X, Ng T, et al. (2013); *Water Research* 47(8): 2701-709
20. Khan MU, Li J, Zhang G, et al. (2016); *Science of The Total Environment* 565: 346-59
21. Rodil, R. Quintana J, Concha-Grana, E, et al. (2012); *Chemosphere* 86(10): 1040–49
22. Kim UJ, Oh JK, Kannan K. (2017); *Environ. Sci. Technol.* 51(14): 7872-880
23. Liang K, Liu J. (2016); *Science of The Total Environment* 544: 262-70
24. Marklund A, Andersson B, Haglund P. (2005); *Environ. Sci. Technol.* 39(19): 7423-29
25. Schreder ED, La Guardia MJ. (2014); *Environ. Sci. Technol.* 48: 11575-83
26. MOE. Statics of Waterworks. (2016); Available at: http://www.me.go.kr/home/web/index.do?menuId=129. (Accessed: 14th January 2018)