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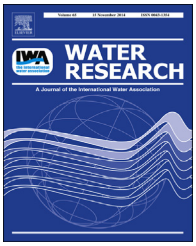

Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent – Case study of Tama River, Japan

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ABSTRACT

Production and use of perfluorooctane sulfonate (PFOS) is regulated worldwide. However, numerous 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. Therefore, knowledge about the levels and sources of the precursors is essential. We investigated the total concentration of potential PFAA precursors in the Tama River, which is one of the major rivers flowing into the Tokyo Bay, by converting all the perfluorinated carboxylic acid (PFCA) and perfluoroalkyl sulfonic acid (PFSA) precursors into PFCAs by chemical oxidation. The importance of controlling PFAA precursors was determined by calculating the ratios of PFCAs formed by oxidation to the PFAAs originally present ($\Sigma\Delta[\mathrm{PFCA}_{\mathrm{C4-C12}}]/\Sigma[\mathrm{PFAAs}]_{\text{before oxidation}}$) (average = 0.28 and 0.69 for main and tributary branch rivers, respectively). Higher total concentrations of Δ[PFCAs] were found in sewage treatment plant (STP) effluents. However, the ratios found in the effluents were lower (average = 0.21) than those found in the river water samples, which implies the decomposition of some precursors into PFAAs during the treatment process. On the other hand, higher ratios were observed in the upstream water samples and the existence of emission sources other than the STP effluents was indicated. 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. To reduce the levels of PFAAs in the aquatic environment, it is necessary to reduce the emission of the PFAA precursors as well.

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1. Introduction

Perfluorooctane sulfonate (PFOS), the production of which was voluntarily phased out by its primary manufacturer in 2001/2002, was added to the list of persistent organic pollutants in the Stockholm Convention in 2009. Eight major manufacturers agreed to a PFOA stewardship program in conjunction with the US EPA to regulate PFCAs that are greater than C7, and that of their precursors. On the other hand, their production by other manufacturers might continue. According to Butt et al. (2007), Hart et al. (2009), and Olsen et al. (2012), the PFOS concentration in tissues has decreased rapidly in human and wildlife species over the past decade; however, samples from some parts of the world have shown an increase in the levels of PFOS even after the 2002 phase–out (Long et al. (2012) and Reiner et al. (2011)). Moreover, Zushi et al. (2011) conducted a study on several major rivers in Tokyo and showed that significant changes in the PFOS and perfluorodecanoate (PFDA) concentration were not observed between 2005 and 2009 in some of the rivers, which suggests that the regulations on the use/production/emission of perfluoroalkyl acids (PFAAs) have not mitigated contamination of PFAAs in river water. In addition, a study by Gewurtz et al. (2013) on multimedia assessment including air, water, sediment, fish, and birds across Canada showed that the recent temporal trends varied depending on media and locations, and phase-outs and regulations were not consistently reflected in the temporal trends.

Some studies have focused on the PFAA precursors that eventually decompose into PFAAs such as PFOS and PFOA. In addition to being emitted during synthesis and use, PFAAs are produced from abiotic or biotic degradation of their precursors. Rhoads et al. (2008) and Xu et al. (2004) reported that the biotransformation of PFAA precursors is the potential source of PFAAs, e.g., the decomposition of perfluorooctane sulfonamide (FOSA) into PFOS. Butt et al. reviewed fluorotelomer-based polyfluoroalkyl substances, which ultimately degrade into PFCAs; numerous studies have shown that the metabolism of 8:2 FTOH results in the formation of PFOA (Butt et al., 2014). According to Murakami et al. (2009), Shivakoti et al. (2010), and Sun et al. (2012), the increase in the PFOA and other PFAA concentrations during the sewage treatment process is due to the biodegradation of their precursors. However, according to Benskin et al. (2012), Motegi et al. (2013), and Zushi et al. (2011), the total concentrations of a limited number of routinely monitored PFAA precursors in the river water were much lower than the concentration of the PFAAs. Martin et al. (2010) showed that only a small number of the numerous precursors available have been monitored, and hence, only limited information on these is available.

Buck et al. (2011) defined all the polyfluorinated alkyl substances by classifying them into various families and recommended a pragmatic set of common names and acronyms for the families as well as their individual members. Trier et al. (2011) 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. The occurrence of some precursors, namely polyfluoroalkyl phosphoric acid diesters in house dust and biosolid-applied soil were studied by De Silva et al. (2012) and Lee et al. (2014), respectively. Ahrens et al. (2011) reported that fluorotelomer alcohols, FOSAs, and perfluorooctane sulfonamidoethanols, which may be degraded to PFCAs or PFSAs in the atmosphere or under aerobic conditions, were emitted to the atmosphere from STPs and landfills. Since there are no routine analytical methods for most precursors, limited information regarding the occurrence of many individual precursors and the overall behaviors of the precursors is available.

Recently, 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 (•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. The concentrations of the total PFAA precursors could be inferred by comparing the PFCA concentrations before and after oxidation. It was reported that the total concentrations of PFCAs with 5–12 carbon chains increased owing to oxidation in the range from 2.8 to 56 ng L^{-1} (a 69% increase in the median compared to the concentration

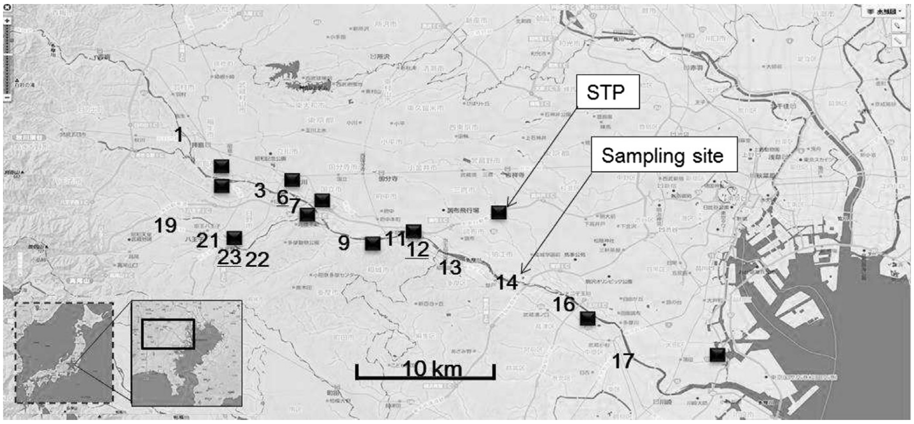

Fig. 1 – Map of the Tama River and sampling locations. Squares represent sewage treatment plants (STPs). The underlined numbers represent STP effluent sampling sites, and non-underlined numbers represent river water sampling sites.