Chemosphere 122 (2015) 115–124

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence of perfluoroalkyl acids in environmental waters in Vietnam

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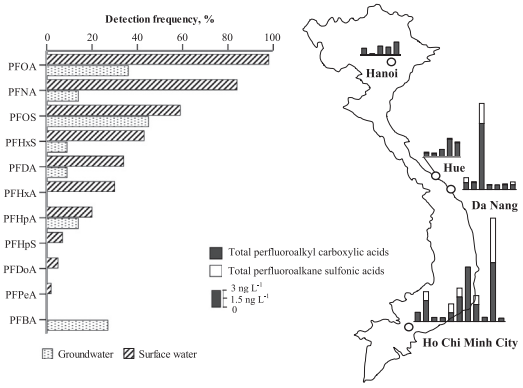
HIGHLIGHTS

- This is the first comprehensive study on PFAAs in environmental waters in Vietnam.
- PFOS, PFOA and PFNA were the most prevalent PFAAs detected.
- PFAA concentrations were much lower than those in developed countries.
- None of PFAA exceeded health-based values and advisory guideline for drinking water.
- Imported industrial products containing PFAAs might be one of the sources of PFAAs.

GRAPHICAL ABSTRACT

Detection and concentrations of perfluoroalkyl acids in Vietnamese waters.



ARTICLE INFO

Article history:
Received 14 July 2014
Received in revised form 21 October 2014
Accepted 10 November 2014
Available online 12 December 2014

Handling Editor: I. Cousins

Keywords:
Perfluoroalkyl acids
PFOS
PFOA
Environmental water
Vietnam

ABSTRACT

This is the first nationwide study of perfluoroalkyl acids (PFAAs) in environmental waters in Vietnam. Twenty-eight river water and 22 groundwater samples collected in four major cities and 14 river water samples from the Red River were screened to investigate the occurrence and sources of 16 PFAAs. Perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA) were the most prevalent of 11 detected PFAAs with maximum concentrations in urban river water of 5.3, 18 and 0.93 ng L^{-1}, respectively, and in groundwater of 8.2, 4.5 and 0.45 ng L^{-1}, respectively. PFAAs in the Red River water were detected at low levels. PFAA concentrations in river water were higher in the rainy season than in the dry season, possibly due to storm water runoff, a common phenomenon in Southeast Asian countries. The highest concentrations of PFAAs in river water were observed in samples from highly populated and industrialized areas, perhaps sourced from sewage. The PFAA concentrations observed were similar to those in other Southeast Asian countries, but lower than in developed nations. From the composition profiles of PFAAs, industrial products containing PFAAs imported from China and Japan might be one of the major sources of PFAAs in the Vietnamese aquatic environment. According to the health-based values and advisory issued by the United States Environmental Protection Agency (USEPA), the concentrations of detected PFAAs in this study do not pose an immediate health risk to humans and aquatic organisms.

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http://dx.doi.org/10.1016/j.chemosphere.2014.11.023
0045-6535/

1. Introduction

Perfluoroalkyl acids (PFAAs) includes perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids, which are highly persistent substances that have been directly emitted to the environment or are formed indirectly from the environmental degradation or metabolism of precursor substances, and because they (or their salts) are or have been used in a wide variety of industrial and consumer applications (Buck et al., 2011). Since 2000 long-chain perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \geqslant 7$), perfluoroalkane sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$, $n \geqslant 6$) and their potential precursors (Buck et al., 2011), have attracted attention as global contaminants. Long-chain PFCAs and PFSAs are problematic because they are highly persistent (Parsons et al., 2008; Frömel and Knepper, 2010), bioaccumulative (Conder et al., 2008) and have been detected ubiquitously in the abiotic environment (Rayne and Forest, 2009), biota (Giesy and Kannan, 2001), food items (Clarke and Smith, 2011) and humans (Vestergren and Cousins, 2009).

Of the PFAAs, PFOS and PFOA are the most intensively studied compounds and were the first PFAAs recognized as global pollutants (Giesy and Kannan, 2001). These two compounds have been frequently detected in environmental samples, very often occur at the highest concentrations (So et al., 2007; Post et al., 2013), and can be found in the tissues of aquatic and terrestrial living organisms including humans (Suja et al., 2009). PFOS is the stable end product of the degradation of perfluorooctane sulfonyl fluoride (POSF) and POSF-based polymers (Giesy and Kannan, 2002). The production of PFOA from 8:2 fluorinated telomer alcohols in a biotic system has been first observed by Hagen et al. (1981), and more recently, Dinglasan et al. (2004) reported that the PFOA was also formed from biodegradation of precursor fluorotelomer alcohols. Chronic exposure to PFOA and PFOS causes tumors in experimental animals, but there are no chronic toxicology data for other PFAAs (Lau, 2012). PFOA has been described as a likely human carcinogen by USEPA Science Advisory Board (USEPA, 2006) and has been linked to two types of cancer in communities with drinking water exposure (Vieira et al., 2013). PFOA may also increase the risk of prostate cancer (Gilliland and Mandel, 1993).

Concerns about the potential environmental and toxicological impact of long-chain PFSAs and PFCAs have led to the phasing out the production of PFOS, its precursors and POSF by 2003 (3M General Offices, 2000). As a result, PFOS and related substances based on POSF were listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009 (UNEP, 2009). In 2006, eight major fluoropolymer and telomer manufacturers and the USEPA jointly launched the 2010/2015 PFOA Stewardship Program with two goals: (1) to commit to achieve, no later than 2010, a 95% reduction, measured from a year 2000 baseline, in both facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and product content levels of these chemicals and (2) to commit to working toward the elimination of these chemicals from emissions and products by 2015 (USEPA, 2011). The five-year agreement (2010–2015) between Environment Canada, Health Canada and four companies from the perfluorinated products industry was signed on March 30, 2010, and is in effect until December 31, 2015. The agreement was negotiated in support of industry's commitment to significantly reduce residual perfluorinated carboxylic acids (PFCAs) and their precursors (Environment Canada, 2010). In addition, C_{11}–C_{14} PFCAs were included in the Candidate List of Substances of Very High Concern under the European chemicals regulation in 2012, REACH (ECHA, 2014). In 2013, also PFOA and ammonium perfluorooctanoate (APFO) were listed in the Candidate List of Substances of Very High Concern ECHA (2014). EPA has promulgated Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) to limit any future manufacture (including import) of 271 perfluoroalkyl sulfonates (USEPA, 2013). In addition, on September 30, 2013, EPA published a final SNUR for perfluoroalkyl sulfonate and long-chain perfluoroalkyl carboxylate chemicals that designates manufacturing (including importing) and processing for use as part of carpets or for treating carpet (USEPA, 2013). A European Union Marketing and Use Directive have been restricted the use of "perfluorooctane sulfonates" in the European Union (European Parliament, 2006). Several water guidelines on PFOS and PFOA have been introduced such as: (1) guidance on the water supply (water quality) regulations 2000/01 specific to PFOS and PFOA concentrations in drinking water (Drinking Water Inspectorate, 2007, 2009) and (2) guidance for PFOA in drinking water at Pennsgrove Water Supply Company (NJDEP, 2007).

Although the occurrence of PFAAs in various environmental media has been vigorously investigated in other parts of the world, there is only limited information on the number and levels of PFAAs as it is in the Vietnamese environment. To the best of our knowledge, there are only 4 reports of PFAAs in environmental waters in Vietnam (Lien et al., 2006a, 2006b; Isobe et al., 2012; Kim et al., 2013) which were focused on limited study areas, but no extensive study throughout Vietnam. In addition, there is no study on PFAAs in groundwater, even though it is well known that groundwater is easily polluted with PFAAs due to their high water solubility. In order to address this knowledge gap, we undertook a comprehensive survey of 16 PFAAs, which included 11 PFCAs and 5 PFSAs in surface and groundwater of four major cities in Vietnam and the biggest river of northern Vietnam in order: (1) to give an overview on the occurrence of PFAAs in the environmental waters throughout Vietnam; (2) to provide a nationwide profile of the PFAAs concentration; (3) to find potential sources of PFAAs; (4) to compare the determined concentrations of PFAAs pollution with the ones found in other countries; and (5) to assess the potential risk of PFAAs on human and aquatic organisms.

2. Materials and methods

2.1. Chemicals and standards

Eleven PFCAs: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA); five PFSAs: perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), PFOS, perfluorodecane sulfonic acid (PFDS) (Table S1); eight surrogate compounds: perfluoro-n-[^{13}C5]-pentanoic acid (M5PFPeA), perfluoro-n-[1,2,3,4,6-^{13}C5]-hexanoic acid (M5PFHxA), perfluoro-n-[1,2,3,4-^{13}C4]-heptanoic acid (M4PFHpA), perfluoro-n-[^{13}C8]-octanoic aicd (M8PFOA), perfluoro-n-[^{13}C9]-nonanoic acid (M9PFNA), perfluoro-n-[1,2,3,4,5,6-^{13}C6]-decanoic acid (M6PFDA), perfluoro-n-[1,2,3,4,5,6,7-^{13}C7]-undecanoic acid (M7PFUdA), sodium perfluoro-1-[1,2,3-^{13}C3]-hexanesulfonate (M3PFHxS) (Table S2); nine internal standards (ISs): perfluoro-n-[1,2,3,4-^{13}C4]-butanoic acid (^{13}C4PFBA), perfluoro-n-[1,2-^{13}C2]-hexanoic acid (^{13}C2PFHxA), perfluoro-n-[1,2,3,4,-^{13}C4]-octanoic acid (^{13}C4PFOA), perfluoro-n-[1,2,3,4,5-^{13}C5]-nonanoic acid (^{13}C5PFNA), perfluoro-n-[1,2-^{13}C2]-decanoic acid (^{13}C2PFDA), perfluoro-n-[1,2-^{13}C2]-undecanoic acid (^{13}C2-PFUdA), perfluoro-n-[1,2,^{13}C2]-dodecanoic acid (^{13}C2PFDoA), sodium perfluoro-1-hexane-[^{18}O2]-sulfonate (^{18}O2-PFHxS), sodium perfluoro-1-