

Determination of Perfluoroalkyl Compounds in Aqueous Samples from Northern Vietnam

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Abstract—In this study, we investigated the occurrence of 17 perfluoroalkyl compounds (PFCs) in surface water collected from different areas in northern Vietnam in January 2011: a municipal dumping site (MD), a municipal wastewater discharge site (MW) in Hanoi, a lead battery recycling site (BR, Dong Mai), an e-waste recycling site (ER, Bui Dau) and a rural site (RU, Duong Quang) in Hung Yen province. Water sample was extracted with an OASIS-HLB and analyzed by UHPLC-MS/MS. Except for PFDS, PFDoDA, PFTeDA and PFOSA, all other thirteen PFCs were found at nanogram per liter levels in all water samples, indicating widespread contamination by PFCs in the aquatic environment of Vietnam. The highest mean PFCs concentrations were found in ER (56.5 ng/L), followed by MD (43.9 ng/L), BR (17.1 ng/L), MW (12.2 ng/L) and RU (9.40 ng/L). This may indicate that both e-waste and municipal waste are potential pollution sources of PFCs. Among target PFCs, PFOA and PFNA were the predominant compounds, except in MW.

Keywords: perfluoroalkyl compounds, aqueous samples, Vietnam

INTRODUCTION

As a result of extensive use in a wide variety of consumer products as surfactants and coatings, contamination by perfluoroalkyl compounds (PFCs) has been reported worldwide in human, wildlife, ambient water, and aquatic sediment (Konwick *et al.*, 2008; Murakami *et al.*, 2008; Ahrens *et al.*, 2009; Lin *et al.*, 2010). PFCs, such as perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), are water soluble and can easily be transported in the aquatic environment, while their neutral precursor compounds are transported via the atmosphere to remote regions. These compounds are of public concern because they are persistent in the environment, accumulate in human and wildlife, and potentially hazardous. The use of PFOS is now regulated under Annex B of the

Stockholm Convention on Persistent Organic Pollutants. However, only limited information exists on the occurrence and fate of PFOS and other PFCs in developing countries. On the other hand, leachate from open waste disposal sites could play an important role as the source of the anthropogenic contaminants. In the present study, we investigated the occurrence of 17 PFCs in aqueous samples from various locations with different characteristics in Vietnam.

MATERIALS AND METHODS

Samples

A total of 41 water samples was collected from various locations in northern Vietnam in January 2011; a municipal dumping site (MD; $n = 10$), an municipal wastewater site (MW; $n = 8$) in Hanoi, a lead battery recycling site (BR; $n = 7$) in Dong Mai, an e-waste recycling site (ER; $n = 10$) in Bui Dau, and a rural site (RU; $n = 6$) in Duong Quang in Hung Yen province. Duplicate water samples of 100 mL were kept in two polypropylene (PP) bottles. These bottles that were pre-rinsed with methanol were previously washed three times with water of the respective sampling point. The samples were stored in a cool box and frozen upon arrival at environmental specimen BANK (*es*-BANK) in Japan and stored at -25°C until analysis (Tanabe, 2006).

Chemical analysis

Quantification of the analytes was achieved using an internal standard method with calibration against absolute standard solutions. A 5-point calibration curve (1, 5, 10, 50, 100 $\mu\text{g/L}$) was constructed for each analyte. The coefficient of determination (R^2) was from 0.995 to 0.999. The recovery for the whole analytical procedure was checked through triplicate analysis of real water samples spiked with mixtures containing individual target compounds of 100 ng in 50 μL of methanol. Average recoveries of 17 PFCs ranged from 67.6 to 115% with relative standard deviation of $<13.7\%$. The limit of detection (LOD) of target analytes was evaluated for each sample, based on the blank concentration, the concentrations factors, the sample volume, and a signal-to-noise ratio of 3. The LODs of target chemicals were used in the analysis.

RESULTS AND DISCUSSION

Detection frequencies

Detection frequencies of targeted PFCs are summarized in Fig. 1. The most frequently detected PFCs in analyzed water samples were PFOA and PFUdA (68.3%) and PFNA (56.1%). On the other hand, PFDA (26.8%), PFBS (24.4%), PFPeA (19.5%), PFTrDA (19.5%), PFHpA (17.1%), PFOS (14.6%), PFHxS (4.88%) and PFHpS (2.44%) were detected with lower frequencies. Trace levels of PFDS, PFDoDA, PFTeDA and PFOSA were found in chromatograms of all the samples, but levels were below the detection limit of 0.8–1.5 ng/L. Higher

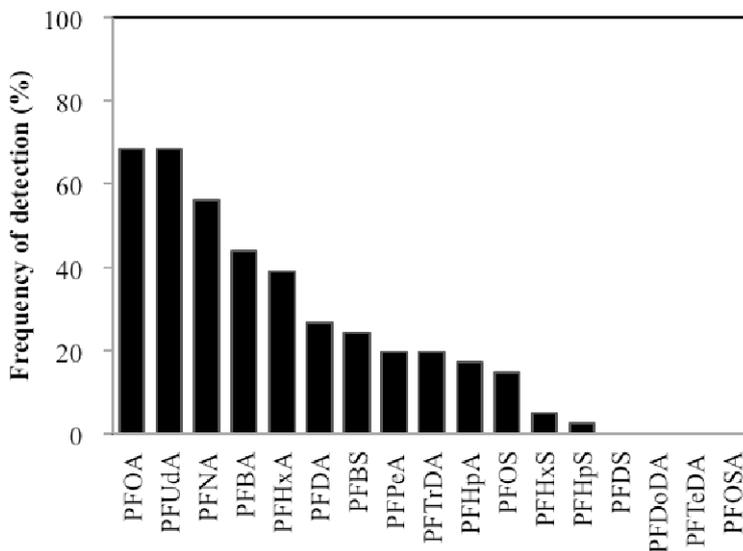


Fig. 1. Detection frequency of 17 PFCs in water samples.

detection frequencies of PFOA, PFUDa and PFNA in water indicate that the ubiquitous contamination of Vietnamese aquatic environments by these compounds and their extensive usage compared to other PFCs, although the usage and production volumes in Vietnam are currently unknown. Only one study reported the levels of PFOA and PFOS in surface waters and tap waters from Vietnam (Tanaka *et al.*, 2006). To our knowledge, this is the first study reporting a wide range of PFCs (17 compounds) in the aquatic environment of Vietnam.

Detection levels

Among the PFCs analyzed, PFOA (average 8.54 ng/L) and PFNA (average 5.76 ng/L) were the predominant compounds in water samples (Fig. 2). Similarly, PFNA and PFOA were detected at relatively high concentrations (median 20.1 ng/L and 6.7 ng/L, respectively) in river waters from Tokyo (Zushi *et al.*, 2011). One obvious reason for the predominance of PFOA and PFNA is that the domestic and industrial discharge at the study locations contained high concentrations of these compounds at this time. Secondly, it is also possible that large quantities of PFOA and PFNA-contained products were imported to Vietnam from Japan. Zushi *et al.*, (2011) reported that after the regulation of PFOS by Stockholm Convention, PFNA has been extensively used in industrial products in Japan. In addition, the Vietnamese import of second-hand commodities such as TVs, computers, household products, etc., from Japan has increased rapidly. Number of imported CRT TV units increased from 60,371 units in 2006 to 838,168 units in 2007 (NIES, 2008).

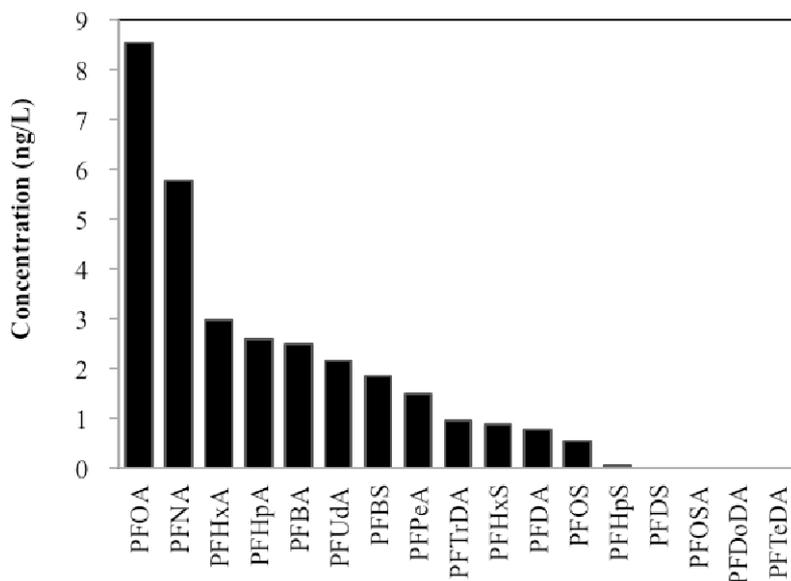


Fig. 2. Mean concentrations of each PFC in water samples collected from Vietnam.

Geographical distribution

The average of the total concentrations of PFCs were significantly different among locations (Fig. 3). PFCs concentrations ($p < 0.05$, Mann-Whitney U test) were higher in ER (56.5 ng/L) and MD (43.9 ng/L), compared to BR (16.1 ng/L), MW (12.1 ng/L) and RU (9.40 ng/L). The highest PFCs concentrations observed in e-waste recycling site could be attributed to recycling activities of end-of-life electrical and electronic appliances, such as computers, TVs, stereo systems, printers and cell phones. Samples from MD also showed high levels of PFCs, which could be originated from the municipal waste materials including personal care and household products (Thanh *et al.*, 2011). These results indicate that current contamination sources of PFCs could be both electrical and electronic appliances recycled in e-waste recycling facilities and household products used in urban areas. The levels of total PFCs in BR were 3 times lower than those in ER and MD, although the differences were not statistically significant. This may be because PFCs are not used in lead batteries.

The highest concentration (363 ng/L) of total PFCs was detected in MD-7, which is located on leachate from the municipal dumping site. The second highest concentration (169 ng/L) was in ER-1, which was the downstream of the e-waste recycling facilities. These results also suggest that municipal dumping site and e-waste recycling facilities could be the point sources of PFCs contamination. The PFCs concentrations varied substantially among the sampling locations, indicating that the PFCs contamination is probably derived from local discharges.

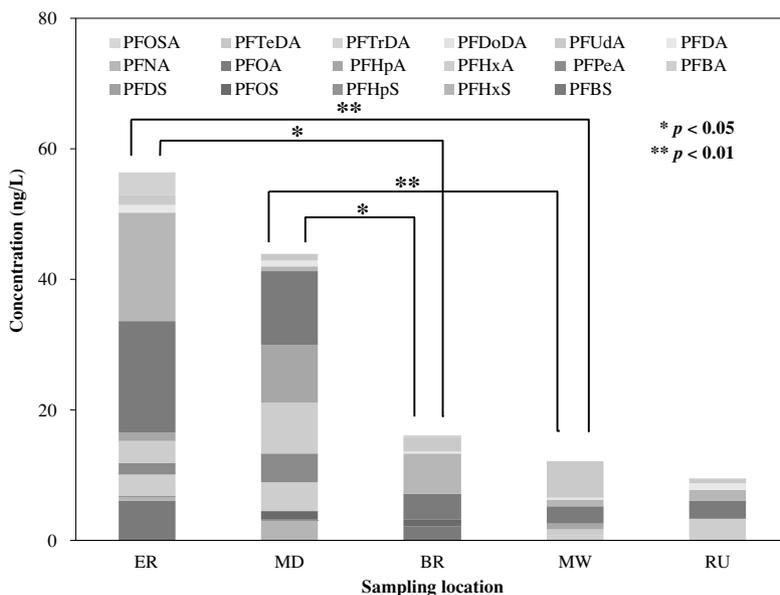


Fig. 3. Total concentrations of PFCs in water samples from different sampling location in Vietnam.

The levels of PFCs in river, effluent of wastewater and other water samples (pond, lake, etc.) were compared with available data in literatures. The levels of PFOS in water samples in the present study were lower than those in other countries. Absence of PFOS may imply a smaller extent of consumption of this compound in Vietnam. In addition, the levels of PFOA, PFNA and PFDA observed in water samples are comparable or lower than those measured in Vietnam, China, Japan and USA. Interestingly, concentrations of PFNA in effluents of wastewater were higher than those in Germany and Taiwan, whose sources may be e-waste and/or municipal wastewaters.

Correlations among PFCs

The correlations among the concentrations of PFCs in water samples were examined using Spearman's rank correlations. Correlations were found between the concentrations of PFBS and those of PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFTrDA ($p < 0.05$). Significantly positive correlations were also observed for most of the PFCs. The strong correlations among PFCs in water samples imply that they may share similar environmental behavior or pollution sources. Similarly, So *et al.*, (2007) also found positive correlations between PFOS and PFNA, PFOS and PFHpA, PFHxS and PFDA, PFBS and PFNA, and PFBS and PFHxA in Pearl River and Yangtze River of China.

CONCLUSIONS

PFCs detected in most of water samples up to hundreds ng/L, suggesting their ubiquitous contamination in Vietnam. PFOA and PFNA were abundant among analytes, with an average concentration of 8.54 ng/L (<1.2–102 ng/L) and 5.76 ng/L (<1.5–100 ng/L), respectively. Significantly higher concentrations of PFCs were found in water samples from e-waste recycling site (56.6 ng/L) and municipal dumping site (43.9 ng/L), indicating that a wide range of industrial and consumer products could be the potential sources. Correlations were found among concentrations of PFCs, implying that they may share the environmental behavior or contamination source. Therefore, continuous monitoring is necessary to understand the temporal/spatial trends of contamination and human exposure levels in Vietnam.

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