

MASS BALANCE ANALYSIS OF PERSISTENT PERFLUORINATED COMPOUNDS AFTER THE EXTENSIVE USE OF FIREFIGHTING FOAMS IN JAPAN

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Abstract

In this study, two cases of accidental petrochemical fires in Japan (Tomakomai and Kashima) that involved the use of aqueous film-forming foam (AFFF) were investigated as potential sources of perfluorinated compounds (PFCs). Surface water samples were collected from the coastal and inland areas of Tomakomai, Lake Utonai, Hakodate, and Oshamanbe (remote areas of Hokkaido), and seawater and pond water samples were collected near the area that was affected by the fire in Kashima. A huge amount of PFOS was found in the surface water samples as a result of the use of AFFF. However, there was no clear profile of perfluorinated chemical pollution in the Kashima case. We measured the total fluorine (TF), extractable organic fluorine (EOF), and inorganic fluorine (IF) content using combustion ion chromatography for fluorine (CIC-F), which is a newly developed method for the trace analysis of fluorinated chemicals. The results show multi-diversity pollution by known and unknown perfluorinated chemicals in the water samples, and clarify that mass balance analysis using CIC-F is a novel tool for surveying complex fluorinated chemicals in the environment.

Introduction

Perfluorinated compounds (PFCs) have been used in certain types of aqueous film forming foam (AFFF) since the early 1960s. Perfluorocarboxylic acids (PFCA) are the major PFCs in AFFF, which is used in military, oil and gas production, and petroleum refineries. In this study, two cases of accidental petrochemical fires in Japan that involved the use of AFFF were investigated as potential sources of PFCs. The first case occurred near Tomakomai City, on the Pacific coast of southern Hokkaido, and was caused by the damaging of 45 of the 105 oil storage tanks at the Tomakomai oil refinery after an earthquake that occurred in Hokkaido on 26 September 2003. The damaged tanks released petroleum naphtha, which ignited accidentally. Detailed information regarding the type of FFF that was used was not available, but it is known that AFFF is widely used in the control of fuel-related fires. The second accident happened near Kashima city on the eastern Pacific coast of Honshu island at the Kashima oil refinery, which has the capacity to manufacture 30,000 barrels per day of low sulfur fuel oil.

Materials and Methods

Surface water samples were collected from coastal and inland areas of Tomakomai, Lake Utonai, Hakodate, and Oshamanbe in Hokkaido. Snow and runoff samples were also collected from several locations in Tomakomai (Figure 1). The samples from Lake Utonai, Hakodate, and Oshamanbe were used as reference samples for comparison. Seawater and pond water were collected near the area that was affected by the fire in Kashima in Ibaraki prefecture. A total of 31 samples were analyzed. All of the samples were collected using a stainless steel bucket that was pre-cleaned by rinsing with methanol, Milli-Q water, and then the water from the specific locations. The samples were then stored in 1-L narrow-mouth polypropylene bottles with screw caps. The snow samples were placed in clean, blank-checked polypropylene bags and after melting at room temperature were stored in 1-L polypropylene bottles.

The analytical procedure that was used for the extraction of the water samples was similar to that described in earlier work.¹ Before extraction, Oasis® WAX cartridges were preconditioned by eluting with 4 mL of 0.1% NH₄OH/MeOH followed by 4 mL of MeOH and 4 mL of Milli-Q water. The water samples were then passed through the preconditioned cartridges at a rate of 1 drop/sec. The cartridges were washed and the target analytes

eluted. We also analyzed the total fluorine in the samples. The removal of inorganic fluoride from the organic fraction is an important step in the analysis of total organic fluorine, and was achieved by the additional washing of the cartridge with a mixture of $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ before the elution of the target analytes. The analytical procedure for the determination of total fluorine, organic fluorine, and inorganic fluoride is described in detail elsewhere.²

The PFCs in the water samples were identified, and their concentrations determined through high-performance liquid chromatography with electrospray tandem mass spectrometry (HPLC-MS/MS) using the parameters that are described in detail elsewhere (Taniyasu et al., 2005). A mixture of perfluorinated compounds (PFCmix) that contained perfluorooctanesulphonate (PFOS), perfluorohexanesulphonate (PFHxS), perfluorobutanesulphonate (PFBS), perfluorooctanesulfonamide (PFOSA), perfluorodecanoate (PFDA), perfluorononanoate (PFNA), perfluorooctanoic acid (PFOA), perfluoroheptanoate (PFHpA), perfluorodecanoate (PFUnDA), and perfluorohexanoate (PFHxA) were used for quantification. Analyses of the total fluorine (TF) and extractable organic fluorine (EOF) content were performed by combustion ion chromatography for fluorine (CIC-F). This is a newly developed method for the analysis of total fluorine and extractable organic fluorine that involves the modification of conventional CIC through the combination of an automated combustion unit (AQF – 100 type AIST; DIA Instruments Co., Ltd.) and an IC system (ICS – 3000 type AIST; Dionex Corp., Sunnyvale, CA), which enables the fluoride content at sub ppb ($\mu\text{g-F/L}$) levels to be determined.²

Results and Discussion

Individual PFCs analysis

The PFCs were identified and quantified in selected seawater, lake water, snow, and runoff samples. The main criterion for selection was the distance from the fire accident. Samples from the source locations, remote locations, and control locations outside of Tomakomai and Kashima were chosen. Relatively high concentrations of individual PFCs were detected in the snow samples (40 – 152 ng/L), which suggests that a significant amount of the PFCs in the AFFF were released into the air and deposited onto the land through a wet deposition process. The PFCs that were released from the AFFF were at the highest concentrations in the coastal waters right after accident at the Tomakomai oil refinery, but decreased significantly through dilution and the exchange between coastal and offshore waters. The greatest concentrations of individual PFCs were observed in the runoff water samples that were collected in December (1984 ng/L). The PFC concentrations in the seawater samples from Kashima ranged from 0.9 ng/L to 6.9 ng/L. The highest concentration of 45 ng/L was observed in the pond water sample, which suggests that the amount of AFFF that was used during the fire was several times less than that used in the Tomakomai incident. Increased concentrations of individual PFCs in the pond water sample also suggest a local source of constant PFC pollution in that area, possibly a fluorochemical industry facility that is located near Kashima.

The ratio of PFOS to PFOA in the Kashima samples was below 1 in all of the sample extracts except for the KSW1 sample, which suggests a greater proportion of PFOA in these samples. The proportions of individual PFCs in each sample (seawater, snow, and runoff) from the contaminated site at Tomakomai were similar, but the composition of the PFC concentration in the seawater from the remote sites was different. The proportions of individual PFCs in the samples from Kashima were different from those collected at Tomakomai, which further supports the hypothesis that the AFFF that was used in the fire incident in Kashima was not the main source of the individual PFCs in the environment, and that industrial sources should be considered instead.

Mass balance analysis

The TF, EOF, and inorganic fluoride contents were analyzed in selected samples from the area around Tomakomai and remote areas of Hokkaido, and in the samples from Kashima. The contribution of individual PFCs to the measured EOF was less than 2% for the samples from the remote and control sites of Hokkaido (1.52 and 1.79%, respectively), 27 to 48% in the snow samples from the contaminated site, and 0.5% in the seawater samples and 23.5% in the pond water sample from Kashima (Figure 2). This suggests the occurrence of significant levels of unknown organic fluorine compounds in all of the water samples. PFOS, PFOA, PFHxS, and PFNA were the dominant PFCs among the known EOF compounds that were detected in the samples from Tomakomai. In the Kashima samples (except for the KSW1 sample) this order was switched to PFOA, PFOS, and PFHpA. Several other fluorinated acids are expected to have contributed to the EOF in the analyzed water

samples.

Inorganic forms of fluorine constituted the major part of the TF in the analyzed samples. However, the major portion of the organofluorine fraction remains unknown, which suggests the presence of unknown fluorinated compounds in addition to the known PFCs such as PFOS, PFOA, and PFNA. The Organization for Economic Cooperation and Development (OECD) has published a 150-page list of compounds that can degrade to perfluorocarboxylic acids and that contribute to the TF in water samples. The composition and profiles of the fluorinated compounds were different at the two accident sites in Tomakomai and Kashima, which intimates that there were different sources of organic fluorine in these environments. In the case of Tomakomai, the release of AFFF is the most likely source of PFCs, whereas in the Kashima case it is suspected that the use of AFFF is insignificant, and that a fluorochemical industry facility is the main source of PFCs in this location. Further studies to investigate the unknown components of the EOF are necessary.

References

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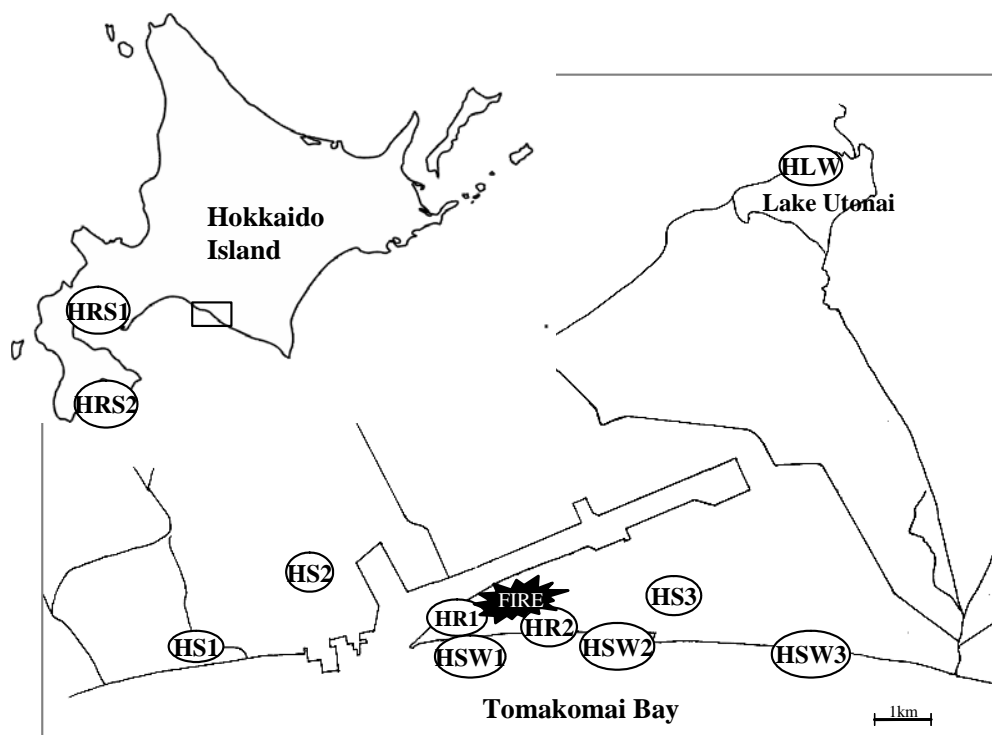


Figure 1. Sampling locations on Hokkaido Island.

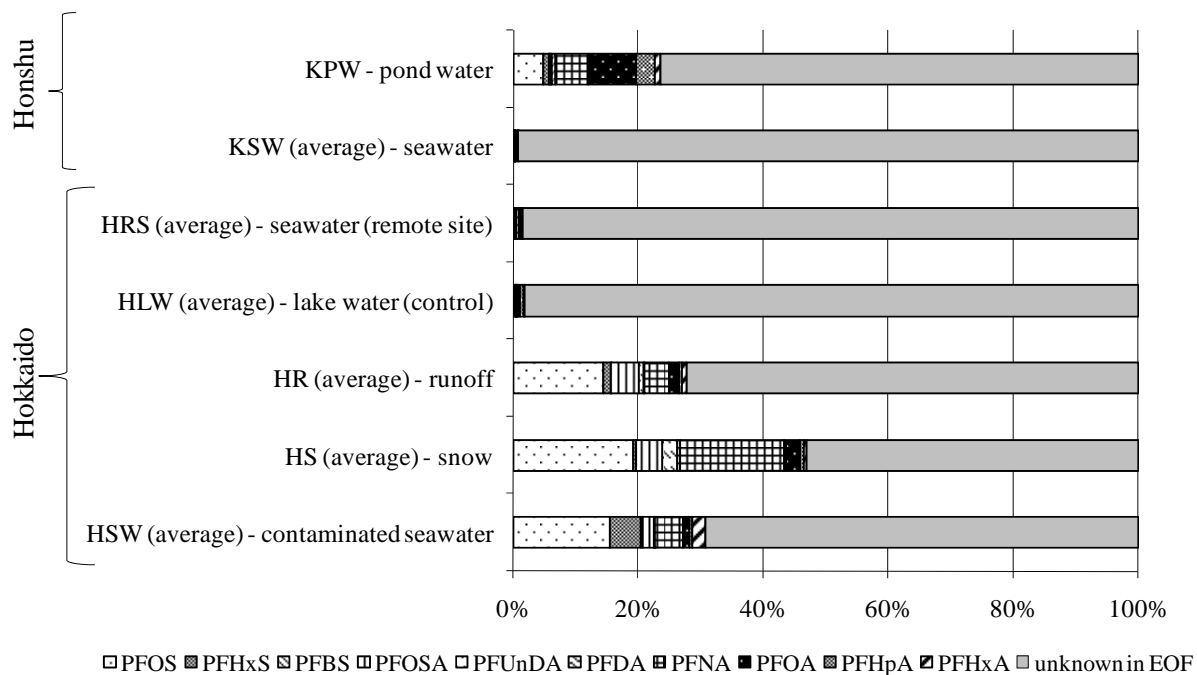


Figure 2. Contribution of individual PFCs to the EOF in the samples from Tomakomai, remote areas of Hokkaido, and Kashima.