ATMOSPHERIC AND AQUATIC TRANSPORT, FATE AND SOURCE IDENTIFICATION OF FLUORINATED COMPOUNDS

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Atmospheric and Aquatic Transport, Fate and Source Identification of Fluorinated Compounds
含氟化合物在水與大氣環境中的歸趨，遷移及污染源識別

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ABSTRACT

Due to the unique properties of fluorine, millions of tonnes of fluorinated compounds have been synthesized and serve as key components in various domestic, industrial and commercial products. In terms of ecological and human risk, one group of these compounds, the polyfluorinated and perfluorinated chemicals (PFCs), are of particular importance. PFCs are a group of environmental contaminants of concern that have received worldwide attention in recent decades. They have been manufactured and used for more than 60 years, and are continuously released into the environment during their production, usage and disposal. Because of their persistence, they are globally distributed in various environmental and human matrices. Yet, the fate and transportation pathways of this class of contaminants are still not well understood.

To date, limited information is available on PFC concentrations in wet precipitation worldwide and their fate in the atmospheric environment. In addition, to address the issue of long-range atmospheric and oceanic transport of PFCs, there is an urgent need to examine PFC concentrations in abiotic environmental compartments in the circumpolar Arctic. The major aims of this PhD research study are to extend our knowledge on the geographical distribution of PFCs in worldwide atmospheric precipitates, such as rain, snow and ice cores, to identify their contamination sources, to examine the effectiveness of wet precipitation as a scavenger of PFCs, and to study their fate and transport to remote areas (e.g., the Norwegian Arctic). A mass balance approach involving the determination of total fluorine (TF), inorganic fluorine (IF) and extractable organic fluorine (EOF) was also adopted for understanding the fate and distribution of fluorinated compounds in wet precipitation. Furthermore, preliminary measurements of volatile PFC precursors in ambient air using GC-MS/MS were performed.

The first monitoring study of wet precipitation measured concentrations of 20 PFCs, including C3–C5 short chain PFCs, using LC/MS/MS in precipitation samples from Japan (n=31), USA (n=12), China (n=5), India (n=2) and France (n=2). Among the PFCs measured, perfluoropropanoic acid (PFPrA) was detected in all of the precipitation samples. Average total PFC concentrations ranged from 1.40–18.1 ng/L for the seven locations studied. The greatest total PFC concentrations were detected in Tsukuba, Japan, whereas the lowest concentrations were detected in Patna, India. PFPrA, perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) were found to be the dominant PFCs in Japanese and American precipitation samples. No observable seasonal trend was found in precipitation samples collected from two locations in Japan. Annual fluxes of PFCs were estimated for Japan and the USA and evidence for precipitation as an effective scavenger of PFCs in the atmosphere was reported.

The second monitoring study focused on quantification of 18 individual PFCs in snow (n=23), snow core (n=25) and drifting ice core samples (n=20) collected from five cities in Japan. A few snow samples from downtown Albany (n=6) and Slingerlands (n=4), New York, USA were also analyzed. For fresh snow samples, slightly higher concentrations of PFCs were detected in AIST, Tsukuba (urban area) than Mt. Tsukuba (rural area). When compared to rain samples collected from the same area (AIST, Tsukuba), similar PFC concentrations and composition profiles were observed, indicating that fresh snow may also reflect local atmospheric contamination. All deposited snow samples showed elevated PFC concentrations,

with the worst case found in deposited snow collected near a car park and hotel in Zao, which is a famous ski resort in north-eastern Japan. These results indicated that deposited snow is not indicative of recent PFC atmospheric pollution and that the timing of sampling of snow samples should be taken into account when interpreting PFC concentration patterns. Similar to Japanese precipitation, the dominant compounds found in Mt. Tateyama snow cores and Shiretoko drifting ice cores were PFOA and PFNA. *N*-ethyl perfluorooctanesulfonamidacetate (*N*-EtFOSAA), which is commonly used in local industries, was also detected in snow core samples, as Mt. Tateyama was situated in Toyama, which is an industrial area. Similar PFC composition patterns were found within layers of the upper drifting ice cores (above sea level), while each layer showed a unique composition profile, suggesting that the contamination sources of PFCs differ during the formation of drifting ice. PFC composition profiles of the bottom of the ice core (the layers below sea level) strongly reflected PFC contamination during drifting ice formation and its movement towards the coast.

After investigation of regional atmospheric contamination by PFCs in wet precipitation, the global transportation and fate of PFCs were studied. The third monitoring study reported the concentrations of 17 PFCs in two ice cores (n=26), surface snow (n=9) and surface water samples (n=14) collected along a spatial gradient in Svalbard, Norway, in the European Arctic. Concentrations of selected ions (Na^+, SO_4^{2-}, etc) were also determined for tracing the origins and sources of PFCs. Perfluorobutanoic acid (PFBA), PFOA and PFNA were the dominant compounds found in ice core samples. Higher concentrations of PFOA, PFNA and perfluorooctane sulfonate (PFOS) were detected in the middle layers of the ice cores representing the period of 1997–2000. Lower concentrations of C8–C12 perfluorocarboxylates (PFCAs) were detected in comparison with concentrations measured previously in an ice core from the Canadian Arctic, indicating less PFC contamination in the European Arctic. Average PFC concentrations were found to be lower in surface snow and melted glacier water samples, while increased concentrations were observed in downstream river water collected near the coast. Perfluorohexanesulfonate (PFHxS) was detected in the downstream locations, but not in the glacier, suggesting local sources of this compound. Long-range atmospheric transport of PFCs was the major deposition pathway for the glaciers, while local sources (e.g., skiing activities) were identified in the downstream locations.

In order to assess the risk of fluorinated compounds in wet precipitation, mass balance analysis were performed using combustion ion chromatography for fluorine (CIC-F). Concentrations of TF and IF were measured in rain (n=50) and snow samples (n=14). EOF was extracted from several rain (n=10) and snow samples (n=6) using specific solid phase extraction (SPE) procedures for removal of inorganic fluorides. Concentrations of 19 known individual PFCs were also determined. The geographical distribution of TF and IF in precipitation among several locations was compared. The highest concentrations of TF (arithmetic mean: 919,000 ng-F/L) and IF (6520 ng-F/L) were found in Kawaguchi (industrial area), whereas the lowest concentrations (TF: 384,000 ng-F/L; IF: 2530 ng-F/L) were found in Tsukuba (science city with no industry). These results suggested that precipitation can reflect primarily local contamination sources of both total and inorganic fluoride ions. The contributions of EOF and IF to TF for different kinds of wet precipitation samples were also further investigated. A high percentage of non-extractable organic fluorine (OF-to-TF ratio: 99%) was found in precipitation samples, in contrast to what was observed in seawater (<20%). This difference may be due to the forms of fluoride present in the atmosphere and water – fluoride tends to bind to particulates in the atmosphere and exist as organic fluoride, while it dissolves in water and ionizes. Known PFCs were found to contribute around 0.0001–0.001% to EOF, suggesting the need to identify the unknown fluorinated chemicals present in the precipitation samples.

Volatile environmental pollutants undergo long-range transportation through the atmosphere, and atmospheric processes such as wind and chemical reactions can determine atmospheric concentrations in particular region. Therefore, in the last part of my PhD study, preliminary measurements of volatile polyfluorinated precursors in Japanese ambient air using GC-MS/MS were performed. Concentrations of seven volatile polyfluorinated precursors, including fluorotelomer alcohols (FTOHs), sulfonamides (FOSAs), and sulfonamidoethanols (FOSEs), were determined in ambient air samples collected at both ground level (n=5) and an altitude of 450 m (n=2) in Japan during August 2009. A helicopter was used to collect air samples from Tsukuba to Kamakura (inland air), and from Kamakura to Hachijyo Island (oceanic air) at a height of 450 m. At the same time, ground air samples were also collected from the heliport and AIST in Tsukuba, as well as Kawaguchi, Kamakura (urban areas) and Hachijyo Island (rural area) to study the transport of these volatile precursors. Similar to PFCs, higher concentrations of total FTOHs and were detected in urban areas (404 $\mu g/m^3$) than in rural areas (349 $\mu g/m^3$). Taking 8:2 FTOH and *N*-EtFOSA as examples, around 80–90% of the measured concentrations were detected at a higher level in the atmosphere, while only 10–20% remained near the ground. These results indicated that FTOH and FOSA/SE contamination is largely regional, although the potential for long range transportation of the compounds cannot be neglected.

In the present study, wet precipitation was found to reflect local PFC contamination in the atmospheric environment, and to be an effective scavenger of PFCs. Although the production and use of PFOS and it derivatives were phased-out starting from 2002 by 3M, this compound can still be found in worldwide atmospheric precipitates even in the glacial ice cores from the European Arctic. Long-range atmospheric transport of PFC precursors is the most feasible pathway through which these compounds reach the remote areas. Therefore, in addition to detection of PFCAs and PFASs, efforts should be made on developing analytical methods for several new classes of perfluorinated surfactants (e.g., perfluoroalkylphosphonic acid (PFPAs), perfluoroalkylphosphinites (PFPiAs), etc.), which are considered to be PFCA precursors, and volatile precursors of PFCs (i.e., FTOHs and FOSA/SEs), not only in air samples, but in different kinds of environmental matrices (e.g. water and sediment). Tracing these chemicals can help to identify the major PFC contamination sources and to understand the degradation pathways of these compounds into PFCs in the environment. Regionally, PFC contamination in Chinese estuaries is a major concern, and the fate, transport and degradation pathways of PFCs should be examined in both atmospheric and aquatic systems in China.

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