OCCURRENCE AND DISTRIBUTION OF PERFLUOROALKYL ACIDS IN SNOW AND RAIN IN SHENYANG AND DALIAN, CHINA

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Abstract
Wet deposition is an important matrix while comparatively limited information is available on perfluoroalkyl acids concentrations in precipitation. Snow and rain samples collected from Shenyang and Dalian were analyzed for perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) to investigate the occurrence and distribution of these compounds in the atmosphere. The compounds of interest for the PFSAs and PFCAs were homologues with varying fluorinated chain lengths. Among the homologues, perfluorooctane sulfonate (PFOS) concentrations were the highest, ranged from 2.0 to 145 ng/L. Followed were perfluorooctanoate (PFOA) concentrations in the range of 2.0-40.8 ng/L. Perfluorodecane sulfonate (PFDS) and PFCAs with shorter than 6 or longer than 9 carbon chain were not detected in any samples. Concentrations of perfluoroalkyl acids in several precipitation events in Dalian were significantly higher than those in Shenyang. This may be partly due to the geophysical and meteorological characteristics of Dalian. The results of the present study indicate that wet deposition may be a potential transport mechanism of perfluoroalkyl acids in the environment.

Introduction
Perfluoroalkyl acids constitute a diverse class of compounds used in a variety of consumer and industrial applications. The physiological properties of perfluoroalkyl acids, notably the chemical and thermal stability, that make these compounds so desirable appear to preclude any degradation or metabolism, resulting in the bioaccumulation and persistence in the environment. Perfluoroalkyl acids have been reported in a large number of environmental matrices and spurred monitoring efforts and regulatory concerns regarding these emerging contaminants.

Wet deposition is the principal process governing the transfer of toxic chemicals from the atmosphere on to surfaces. A number of investigators has sampled precipitation and analyzed the organic pollutants constituent, which were important for understanding the behavior of these compounds in the environment. Wet deposition of perfluoroalkyl acids is likely to be highly efficient due to their low vapor pressures and relatively high water
solubility. However, comparatively limited information is available on perfluorooalkyl acids concentrations in precipitation.

Shenyang and Dalian are the first two largest cities of Liaoning Province, located in the north eastern region of China. Shenyang is the capital of Liaoning Province, and Dalian is a typical coastal city. Both cities have been subjected to rapid economic development involving commerce and industrialization. This study aimed to investigate the occurrence and distribution of perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) in the Chinese precipitation and to compare the difference in perfluorooalkyl acids presence between the two cities.

Materials and Methods

Standards and Reagents

The target analytes list was composed of four PFSAs (C4, C6, C8, C10) and seven PFCAs (C6-12). Perfluorobutane sulfonate (PFBS) and perfluorohexanoate (PFHxA) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnA) were obtained from Sigma-Aldrich (St. Louis, MO). Perfluorododecanoate (PFDoA) was purchased from Acros Organics (Morris Plains, NJ, USA). Ultrapure water (Millipore Milli-Q) was used as working water after passage through a Presep-C Agri cartridge (Wako Pure Chemical Industries, Japan) and an Oasis plus HLB cartridge (Waters, USA) to remove perfluorooalkyl acids, called PFAS-free water.

Sample Collection and Pretreatment

Sampling sites located at Shenyang and Dalian, representing areas of distinct land use and human activities. Snow samples were collected after the snowfalls at individual site by sweeping the fresh snow and packed in polyethylene bags. Rainfall was sampled by a home-made collector made of polyvinyl chloride (PVC) and was collected in polyethylene bottles. Snow samples were melted at room temperature after transporting to laboratory. The snowmelt and the rainwater were filtered through glass fiber filters (pore size: 1.0 µm, Advantec GA 200, Toyo Roshi Kaisha, Japan). The filtrate was passed through a Presep-C Agri cartridge and an Oasis plus HLB cartridge at a flow rate of 10 mL/min using a Waters Concentrator System (Concentrator Plus, Waters, Japan). Cartridges were then eluted with 2 mL methanol and concentrated under nitrogen gas flow to 1 mL for the LC/MS analysis.

Analytical Procedure

Chromatographic separation for PFSAs and PFCAs was performed following the same procedure. The methanol extracts (10 µL injection volume) were chromatographically separated using an Agilent 1100 series HPLC/MSD system at a flow rate of 0.2 mL/min. The total runtime was 55 min. The mobile phase consisted of acetonitrile (A) and 10 mM ammonium acetate buffer (B) starting at 20% A, increasing to 25% in 5 min, to 35% in next 5 min, to 55% in 20 min, to 90% in 3 min, being held for 8 min, decreasing to 20% in 3 min and being held for 12 min. Thereafter the mobile phase composition returned to the starting condition in 3 min. Mass spectra were taken on an LC/MS system equipped with an orthogonal spray interface, employing electrospray ionization in the negative mode. The nebulizer pressure was 50 psig and the drying N₂ gas flow rate
was 10.0 L/min. The selected ion monitoring (SIM) mode was employed for quantification of analytes.

**Quality Assurance/Quality Control** Data quality assurance and quality control protocols included matrix spikes, laboratory blanks, and continuing calibration verification. Recoveries of analytes ranged from 68 to 110% with CV less than 5%. The limit of detection (LOD), defined as the lowest concentration that the analytical process can reliably differentiate from background levels, was considered to be three-fold larger than the signal to noise (S/N) ratio. The limit of detection (LOD) for the analytes varied from 0.19 to 0.38 ng/L and the lowest limit of quantification (LOQ) varied from 0.50 to 0.98 ng/L.

**Results and Discussion**

Detectable concentrations of PFBS, PFHxS, PFOS, PFHpA, and PFOA were found in some of the precipitation samples. PFDS and PFCAs with shorter than 6 or longer than 9 carbon chain were not detected in any samples. The concentrations of the quantifiable analytes in the samples were shown in Table 1. PFOS was the dominant compound measured in the samples followed by PFOA. Concentrations of PFBS, PFHxS and PFHpA were more than two orders of magnitude lower than that of PFOS.

<table>
<thead>
<tr>
<th>Date</th>
<th>Type of Precipitation</th>
<th>n</th>
<th>PFBS (ng/L)</th>
<th>PFHxS (ng/L)</th>
<th>PFOS (ng/L)</th>
<th>PFHpA (ng/L)</th>
<th>PFOA (ng/L)</th>
</tr>
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<tbody>
<tr>
<td>Shenyang</td>
<td>Snow</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>2007-03-03</td>
<td>Snow</td>
<td>34</td>
<td>&lt;0.58</td>
<td>0.19</td>
<td>5.4</td>
<td>2.9</td>
<td>3.3</td>
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<tr>
<td>Dalian</td>
<td>Rain</td>
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<td>&lt;0.58</td>
<td>&lt;0.49</td>
<td>9.92</td>
<td>4.80</td>
<td>32.9</td>
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<tr>
<td></td>
<td>Snow</td>
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<td>2.75</td>
<td>2.08</td>
<td>138</td>
<td>5.12</td>
<td>16.7</td>
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<tr>
<td></td>
<td>Snow</td>
<td>21</td>
<td>0.34</td>
<td>0.90</td>
<td>145</td>
<td>2.50</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>Rain</td>
<td>1</td>
<td>2.08</td>
<td>&lt;0.49</td>
<td>113</td>
<td>23.5</td>
<td>40.8</td>
</tr>
</tbody>
</table>

*Not analyzed; b Concentration is below the limit of quantification.

It is notable that concentrations of perfluoroalkyl acids in several precipitation events in Dalian were significantly higher than those in Shenyang. This may be partly due to the geophysical and meteorological characteristics of Dalian. The evolution of local and regional sea-breeze circulation is believed to be responsible for forming meteorological conditions for high air-pollution episodes in the coastal area. Moreover, PFCs might be transported to the atmosphere from the seawater at the air-sea interface. Many persistent organic pollutants are known to enrich significantly in the seawater microlayer (SML) by factors of up to 100 in coastal areas, relative to underlying subsurface waters. In our previous study, the enrichment of PFCs in SML was observed. Many factors can promote sea-to-air exchange of compounds with a low volatility, for example, bursting process of the bubbles generated by breaking waves. Recently, Mcmurdo et al. found significantly higher concentrations of PFOA in aerosols than in the water body, illustrating the transportation of PFOA from
water into the atmosphere. Thus transportation of PFCs to air from SML could possibly contribute in part to the high concentration in the atmosphere around Dalian city.

Measurable amounts of perfluoroalkyl acids were found in precipitation samples collected from Shenyang and Dalian demonstrating that wet deposition is one possible pathway for the removing of selected perfluoroalkyl acids chemicals from atmosphere. Thus, selected perfluoroalkyl acids related contaminants should be evaluated with regard to long-range transport potential. Moreover, the presence of perfluoroalkyl acids in the precipitation suggests that human exposure to these contaminants through inhalation accounts for part of the whole exposure. Results of this study indicate that air-borne perfluoroalkyl acids are discernible sources of contamination for the ecological system and should be addressed.

Acknowledgements
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References