

Sources, transport and fate of perfluoroalkyl acids in the atmosphere

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Abstract

Perfluoroalkyl acids (PFAAs) are man-made chemicals which have been observed in the global environment, even in locations far away from where they are emitted. These persistent substances are taken up in humans and biota and may have toxic effects. Knowledge about how PFAAs are dispersed in the environment is needed to discern strategies to manage their sources and to evaluate the efficacy of adopted legislation. This thesis aimed to increase our understanding of the sources of PFAAs to the atmosphere and how PFAAs are transported in air. The results of **Paper I** demonstrated that gaseous perfluorooctanoic acid (PFOA) sorbs to typical glass fibre filters (GFFs) used in high-volume air sampling of PFAAs. As a consequence, the fraction of gaseous PFOAs present in sampled air is underestimated, while the fraction of PFOA associated with aerosols is overestimated. Replacing GFFs with filters deactivated through silanisation and siliconisation did not eliminate this sampling artefact and is therefore not recommended as a means to determine the gas-particle partitioning of PFAAs. In **Paper II**, monitoring of the mass of PFOA transferred from water solutions of pH 0.2-5.5 demonstrated that the acid dissociation constant of linear PFOA and the four most ubiquitous branched PFOA isomers is around or below 1. Furthermore, the results demonstrated that the presence of counter ions and organic matter in water retarded, rather than enhanced, the volatilisation of PFOA. Therefore, volatilisation of all isomers of PFOA from environmental waters is expected to be negligible. To further study the transfer of PFAAs from environmental waters to air, **Paper III** simulated the process of sea spray generation in the laboratory. Strong enrichment of PFAAs was observed from bulk water to the surface microlayer and to aerosols. The enrichment increased with PFAA chain length, indicating that this process is of greater importance for more surface active substances. The highest enrichment was observed in aerosols < 1.6 µm, which can travel over long distances if not rained out. Based on the measured aerosol enrichment factors we estimated that approximately 70 metric tonnes of PFAAs are aerosolised from the global oceans yearly and that 3% of this mass is deposited in terrestrial environments. **Paper IV** reported the occurrence of branched PFOA isomers in deposition sampled in five geographical locations. The presence of these isomers demonstrated that atmospheric transformation of fluorotelomer alcohols is not the only ongoing source of PFAAs to air. We hypothesised that, additionally, both sea spray aerosols and direct emissions from manufacturing sources contributed to the contamination of the precipitation on different spatial scales. Although further research is required to determine the relative importance of different sources to the atmosphere locally and globally, this thesis has substantially advanced the state-of-the-science by i) demonstrating the significance of an air sampling artefact discussed as an uncertainty in the scientific literature over the past decade, ii) definitively ruling out volatilisation from environmental waters as a source of PFOA to air, iii) demonstrating transfer of PFAAs from seawater to air via sea spray aerosols and thus quantifying the environmental importance of this process, and iv) ultimately demonstrating that several types of sources of PFAAs impact the global atmosphere and thus PFAA contamination patterns in precipitation.

Keywords: *Perfluorinated alkyl acids, PFOS, PFOA, Isomers, Sources, Atmospheric transport, Sea spray, Gas-particle partitioning, Volatilisation.*

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