Transport of perfluoroalkyl acids from the ocean to the atmosphere via sea spray aerosol

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Abstract
Perfluoroalkyl acids (PFAAs) are a subgroup of per- and polyfluoroalkyl substances (PFASs) that have been widely used in commercial and industrial applications. PFAAs are very persistent in the environment and some can bioaccumulate and have adverse health effects on human health. They have been detected ubiquitous in the abiotic environment, in biota and in humans. Long-range atmospheric transport (LRAT) is considered an important pathway to their global distribution. PFAAs are detected in the global oceans and they can be enriched in sea spray aerosol (SSA) due to their high surface activity. Thus, ocean-to-atmosphere transfer via sea spray aerosol (SSA) emission is suggested to be one of the major sources of PFAAs to the atmosphere, yet the contribution of this source to PFAAs in air is not well-understood. The aim of this thesis is to improve the knowledge regarding the importance of SSA as a global source of PFAAs in the atmosphere. In Paper I, PFAA enrichment on SSA particles of different sizes was investigated via a series of laboratory experiments. A sea spray simulation chamber filled with sodium chloride solution (~35 g L⁻¹) was used to generate SSA. The results showed that variation in PFAA water concentrations had little impact on the SSA enrichment factors (EFs). Furthermore, the results suggested that SSA production mechanisms result in different enrichment behaviors of PFAAs on <1 μm and >1μm SSA particles. Paper II provided clear field evidence that SSA is an important source of PFAAs in the atmosphere. Significant positive correlations (p<0.05) were identified between the concentrations of PFAAs and SSA tracer ion (i.e. Na⁺) in aerosol samples collected at two Norwegian coastal sites during long-term air monitoring. Such correlations suggested that PFAAs transported via SSA can have significant influence on their air concentrations in coastal areas. Aiming at bridging the gap between the lab and the field, in Paper III, a series of field experiments were conducted along a transect from ~50°N to ~50°S on the Atlantic Ocean. Changes in surface seawater temperature, salinity, conductivity and fluorescence during the field experiments revealed minor influences on EFs. However, the EFs derived from the field experiments were higher than the lab experiments in Paper I, which may be due to the different composition and properties of the chamber water in the two studies. It was concluded, however, that the variation of PFAA concentrations in the global oceans is the major contributor to the uncertainty in the estimation of PFAA ocean-to-air flux via SSA emission. Paper IV investigated mass-size distributions of PFAAs in aerosol samples collected near an industrial source and the associated LRAT potential of the PFAAs emitted. The results suggested that industrial sources can have regional influence on PFAA concentration in air. The information in Paper IV will help evaluate the relative importance of atmospheric sources of PFAAs at certain locations. This thesis contributes to a better understanding on the transport of PFAAs via SSA emission and on the sources of PFAAs to air in general.

Keywords: Perfluoroalkyl acids, PFAAs, Per- and polyfluoroalkyl substances, PFAS, atmospheric transport, sea spray aerosol, industrial sources.

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