From emission sources to human tissues: modelling the exposure to per- and polyfluoroalkyl substances

Melissa Ines Gomis

Academic dissertation for the Degree of Doctor of Philosophy in Applied Environmental Science at Stockholm University to be publicly defended on Friday 12 May 2017 at 10.00 in Nordenskiöldsalen, Geovetenskapens hus, Svante Arrhenius väg 12.

Abstract

Produced since the 1950's, per- and polyfluoroalkyl (PFASs) substances are persistent, bioaccumulative and toxic compounds that are ubiquitous in the environment. Being proteinophilic with a tendency to partition to protein-rich tissues, PFASs have been found in human serum worldwide and in wildlife with a predominance of long-chain perfluoroalkyl carboxilic acids (C_7-C_{14} PFCAs) and perfluoroalkyl sulfonic acids (C_6-C_9 PFSAs). Due to rising concern regarding their hazardous properties, several regulatory actions and voluntary industrial phase-outs have been conducted since early 2000s, shifting the production towards other fluorinated alternatives. This thesis explores the human exposure to long-chain PFASs and their alternatives using different modelling methods and aims to 1) link comprehensively the past and current industrial production with the human body burden and 2) assess the potential hazardous properties of legacy PFASs replacements, on which information is very limited. In **Paper I**, the historical daily intakes in Australia and USA were reconstructed from cross-sectional biomonitoring data of perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA) andperfluorohexanesulfonic acid (PFHxS). The results indicate that humans experienced similar exposure levels and trends to PFOS and PFOA in both regions, suggesting a common historical exposure possibly dominated by consumer products. The model could not be fitted to PFHxS concentration in serum. In **Paper II**, the relative contribution of indirect (i.e. subsequent metabolism of precursors into legacy PFASs) versus direct exposure was evaluated on occupationally exposed ski wax technicians. The indirect exposure contributed by up to 45% to the total body burden of PFOA. In **Paper III**, the physicochemical properties, the persistence and the long-range transport of fluorinated alternatives were predicted using different *in silico* tools. Findings suggest that fluorinated alternatives are likely similar to their predecessors, in terms of physicochemical properties and environmental fate. Finally, **Paper IV** compares the toxic potency of PFOS, PFOA and their alternatives as a function of external and internal dose. While alternatives are less potent than their predecessors when considering the administered dose, they become similarly potent when the assessment is based on levels in the target tissue. This thesis demonstrates that pharmacokinetic models are effective tools to comprehensively reconnect the body burden to the exposure of phased-out chemicals. More importantly, the studies on fluorinated alternatives raise the necessity to provide more information and data on the potential hazard of these novel and emerging products.

Keywords: *PFAAs, PFOA, PFOS, fluorinated alternatives, human exposure, pharmacokinetic modelling, hazard assessment.*

Stockholm 2017
http://urn.kb.se/resolve?urn=urn:nbn:se:su:diva-141034

ISBN 978-91-7649-712-8
ISBN 978-91-7649-713-5

Department of Environmental Science and Analytical Chemistry

Stockholm University, 106 91 Stockholm