HUMAN EXPOSURE TO PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN GAS- AND PARTICLE PHASE VIA SKI WAX

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Introduction

Per- and polyfluorinated compounds (PFAS) is a group of emerging environmental pollutants that are ubiquitous, bioaccumulative and persistent. They have wide commercial applications because of the chemical and thermal stability and are often used when a dirt- and water repelling surface is desired.[1] The perfluorinated compounds comprise the perfluoroalkyl carboxylic acids (PFCAs) and the polyfluorinated compounds include fluorotelomer alcohols (FTOHs), saturated and unsaturated fluorotelomer acids (FTCAs and FTUCAs). Many different PFASs have been found in humans, biota, air and water from all over the world. [2-4]

Ski wax is one product where PFAS are used as additives since they reduce the friction between the snow and the ski and subsequently generating a higher speed. The ski wax is applied to the ski by using heat of approximately 130-220 ^{o}C. This process releases particles and vapors containing a blend of organofluorine compounds. [5] Inhalation of thermal degradation products from fluoropolymers can cause severe pulmonary distress.[6; 7]

Scientific reports are clearly showing that airborne particulate matter (PM) affects human health and predominantly the cardio vascular (CV) system adversely.[8; 9] Depending on the size of the particle, when PM is inhaled it may reach the alveoli of the lungs where it is transmitted to the blood stream and subsequently causing oxidative stress, pulmonary response and inflammation.[10] Therefore it is essential to closely monitor the dust levels is certain occupational groups.[11] The occupational exposure limit (OEL), threshold limit value (TLV) and time weighted average (TVA) for organic dust and paraffin wax fume is set to 2 mg/m^3. Previous reports show that the partitioning of perfluoroalkyl acids (PFAAs) in gas and particulate phases differ between PFCAs and PFSAs. They showed that PFSAs were mostly associated in the particulate phase whereas the PFCAs were more frequently detected in the gas phase. [12]

In our previous study of wax technicians´ PFAS exposure we report very high levels of FTOHs in the air of wax cabins during work and elevated blood levels of PFOA and presence of metabolic intermediates FTCAs and FTUCAs.[13; 14]

Materials and Methods

We collected three size fractions of dust samples (n=243) (inhalable, respirable and total aerosol) and air samples (n=84) by using portable pumps in stationary and personal sampling in the breathing zone of the wax technicians (n=11) during work as shown in Figure 1. Concentrations of C_4-C_{18} PFCAs were determined using UPLC-MS/MS, and 6:2, 8:2 and 10:2 FTOH with GC-MS/MS in air and dust.

Mass labeled internal standards (IS) were spiked to the particle membrane filters and air filters (SPE ENV+ cartridges).

Membrane filters: The analytes were extracted with 100% methanol. The filters were sonicated for 15 minutes and filtered prior to analysis.

SPE cartridges: The extraction procedure is described in detail elsewhere.[13]

The extracts were split to a GC-fraction in 100% methanol and an LC fraction to which 2 mM ammonium acetate in water was added (60/40 water/methanol). Recovery standards (RS) for PFCAs and FTOHs were added. Levels of C_4-C_{14}, C_{16} and C_{18} PFCAs were analyzed on an UPLC- MS/MS and 6:2, 8:2 and 10:2 FTOHs were monitored on a GC- MS/MS as previously described.[13; 14] Dust levels were gravimetrically determined according to standardized methods.

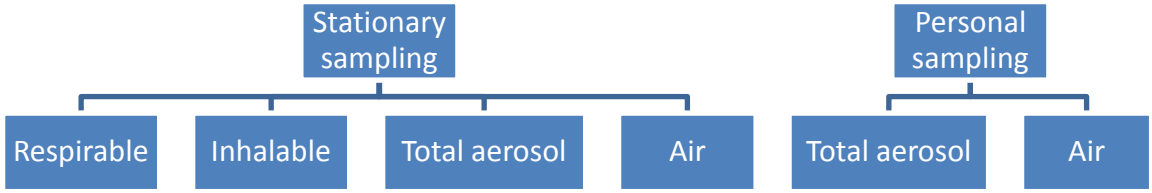

Figure 1 shows the particulate (respirable, inhalable and total aerosol) and air fractions collected in stationary and personal sampling.

Results and Discussion

The detection frequency of PFHxA, PFHpA, PFOA, PFNA, PFDA and PFDoDA were 100% and for PFUnDA it was 97% in all analyzed dust samples. FTOH was not detected in any of the dust samples but in 100% of the analyzed air fraction. 6:2 FTOH, 10:2 FTOH, PFHxA, PFHpA, PFOA, PFNA and PFDA were detected in 99% of the air samples and PFUnDA in 95%. Average concentrations of 8:2 FTOH and PFOA in air from personal sampling was 114 000 ng/m^3 (range=830 - 997 000 ng/m^3) and 530 ng/m^3 (range=2 - 4 900 ng/m^3) respectively. Average PFOA concentrations in dust were 47 000 ng/g dust (range=2 500 – 332 000 ng/g).

8:2 FTOH represent 94% of the ∑PFAS in air as shown in Figure 2. Second highest average level was determined for PFHxA at 3%. PFDoDA dominate the dust fraction with 61% of ∑PFCA in dust. PFOA was approximately 1% of ∑PFAS in air and 10% in dust samples from personal sampling.

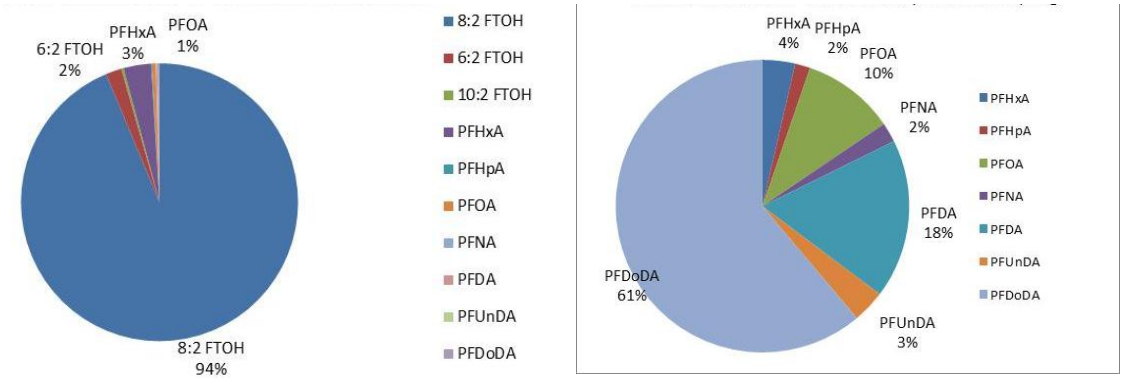

Figure 2 show distribution of PFAS in air (A) and particle phase (B) from personal sampling of wax technicians during work.

Both air and dust samples are dominated by the even numbered homologues suggesting that ski wax is produced using the telomerization method.

Average total aerosol concentrations from stationary samplings were gravimetrically determined to 1.3 mg/m^3 (range=0.1-4.0 mg/m^3) and 2.8 mg/m^3 (range=0.2-15 mg/m^3) for personal sampling. Inhalable and respirable fractions were sampled stationary and showed averages of 2.0 mg/m^3 (range=0.5-4.6 mg/m^3) and 0.7 mg/m^3 (range=0.1-2.2 mg/m^3) respectively.

29% of the dust samples have concentrations exceeding the occupational exposure limit (OEL) of 2 mg/m^3. Not only are the workers exposed to high dust levels which is associated with elevated risk for cardio vascular disease but the PFCA concentrations in air and dust are also very high.

Acknowledgements

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