HUMAN EXPOSURE TO FLUORINATED SKI WAX

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Introduction

Taves et al discovered in 1968[1] that blood of the general population contained organic fluorinated compounds and in 2001 one of those chemicals was confirmed as perfluorooctanoic acid (PFOA)[2]. Since then perfluorinated carboxylic acids (PFCAs) have been found in humans, biota and diverse environmental compartments all over the globe[3-7] and it is of great interest to reveal the sources of human exposure to PFCAs. In recent years the debate is increasingly focusing on precursor compounds known to degrade to PFOA[8-9]. One class of compounds who has shown to transform to PFCAs through OH radical oxidation in atmosphere and electrophilic biotransformation in biota are fluorotelomer alcohols (FTOHs)[10-11].

Mainly two different types of ski waxes are used; kick and glide wax. Kick wax is used to allow the skier to kick in a forward motion whereas the glide wax increases the speed of the skis by lowering the friction towards the surface and preventing adhesion of snow, ice crystals, dirt and moisture. Cross-country skis, downhill skis and snowboards are all optimized for maximum speed using glide waxes. The exact contents of the waxes are seldom revealed by the manufacturers but it has been shown that most of the gliders available on the market contain semifluorinated *n*-alkanes (SFAs) and PFCAs[12]. SFAs are a group of highly fluorinated chemicals with the general formula $F(CF_2)_n(CH_2)_mH$. Application of glide waxes to snowboards, downhill- and cross country skis is performed in a similar way using an iron of 300-375 F/150-190 ^oC to melt the wax onto the base of the ski[13]. This procedure causes a lot of smoke and fumes containing a blend of gaseous organofluorine compounds which are easily inhaled by the worker[14-15]. Inhalation of organofluorine breakdown products are known to induce pulmonary edema and polymer fume fever, informally called Teflon flu[16-17]. Reduced fecundity have been observed at levels of PFOA found in the general population [18] as well as developmental toxicity[19-20] and hormonal disruption[21]. In addition, fluorotelomer alcohols demonstrate estrogen-like properties[22].

Materials and Methods

The ski wax technicians (*n=8*) are employed by the Swedish and US national cross-country ski teams. During the exposed skiing season from December through to March the technicians apply fluorinated ski wax for approximately 30 hours a week. Personal sampling in the respiratory zone was performed for all the technicians in the study (n=8) using ISOLUTE® ENV+ cartridges (Biotage, Uppsala, Sweden) connected to air pumps (SKC AirCheck 2000, Neuss, Germany) operating at an airflow rate of 2.0 L min^{-1}. Samples were collected during World Cup events in Kuusamo, Finland (December-07) followed by Val di Fiemme, Italy (January-08), Otepaa, Estonia (February-08), and finally in Holmenkollen, Norway (March-08). Mass labeled internal standards were spiked prior to the extraction using. 20 mL 100% methanol followed by evaporation to 0.5 mL under nitrogen. Performance standards for PFCs and FTOHs were added. Levels of PFCAs C5-C11 and PFSAs C4, C6, C8 and C10 were analyzed using an UPLC-MS/MS and 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were analyzed using GC-MS/MS. The mean extraction recoveries for internal standards in all samples were 56% for PFHxA, 43% for PFOA, 65% for PFNA and 67% for 6:2 FTOH. The recovery of sampling spike 13C-8:2 FTOH was 80-90%.

Table 1. Ranges of perfluorinated carboxylates (C8 and C9) and telomer alcohol 8:2 FTOH in air (ng/m^3) from wax cabin

	PFOA	PFNA	8:2 FTOH
Kuusamo Finland Dec-07	2 700-4 900	9-35	10 000-220 000
Val di Fiemme Italy Jan-08	86-530	27-42	830-5 200
Otepaa Estonia Feb-08	9.1-140	9.1-140	2 300-250 000
Holmenkollen Norway Mar-08	4.1-24	4.1-24	2 000-230 000

Results and Discussion

Blood. We detected PFOA (4.8-535 ng mL^{-1}), PFNA (0.8-163 ng mL^{-1}), PFDA (0.9-24 ng mL^{-1}), PFUnDA (0.1-2.8 ng mL^{-1}) and PFOS (0.3-27 ng mL^{-1}) in all blood samples. PFHxS (0.3-4.3 ng mL^{-1}) was found in 93% of the samples, i.e. in all except the first four monthly samples from technician 1. Three technicians showed initial levels of PFOA <10 ng mL^{-1} but five technicians had levels >99 ng mL^{-1} in the pre-seasonal sample from September 2007. The highest and median PFOA levels in our study (535 ng mL^{-1} and 112 ng mL^{-1}) are 43 and 45 times higher than the maximum and median levels found in a study by Kärrman et al [23]. The PFOA levels in technicians 1, 2 and 5 who have low initial levels of PFOA (<10.0 ng mL^{-1} in sample from Sep -07) increased by 254, 134 and 120% whereas the five technicians with higher initial levels (>100 ng mL^{-1}) increased by 6-29% from September 2007 to March 2008, i.e. during the course of skiing season as shown in Figure 1.

Air. The most dominating compound in the air samples was the 8:2 FTOH with individual levels 8 to 32 times higher than PFHxA and 10 to 800 times higher than PFOA. The sum of all PFCAs reported here is 7% of the total amount of 8:2 FTOHs. Average concentrations of telomer alcohols 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were 280 ng/m^3, 92 800 ng/m^3 and 370 ng/m^3 in the air respectively. Mean levels of bioaccumulative perfluorocarboxylates PFOA and PFNA [24] were 1200 ng/m^3 and 30 ng/m^3 compared to 4900 ng/m^3 for the less persistent [25] PFHxA which was found at highest level of all the perfluorocarboxylates. Average levels and ranges of PFCAs and FTOHs in air are shown in Figure 3.

Results from our first study shows that there seems to be a metabolic lag time for PFOA in blood, since the World Cup ends in March and we noticed that the levels of PFOA in blood continued to rise to April or even May when the technicians are unexposed to ski waxes [24]. This information indicates that the PFOA exposure is

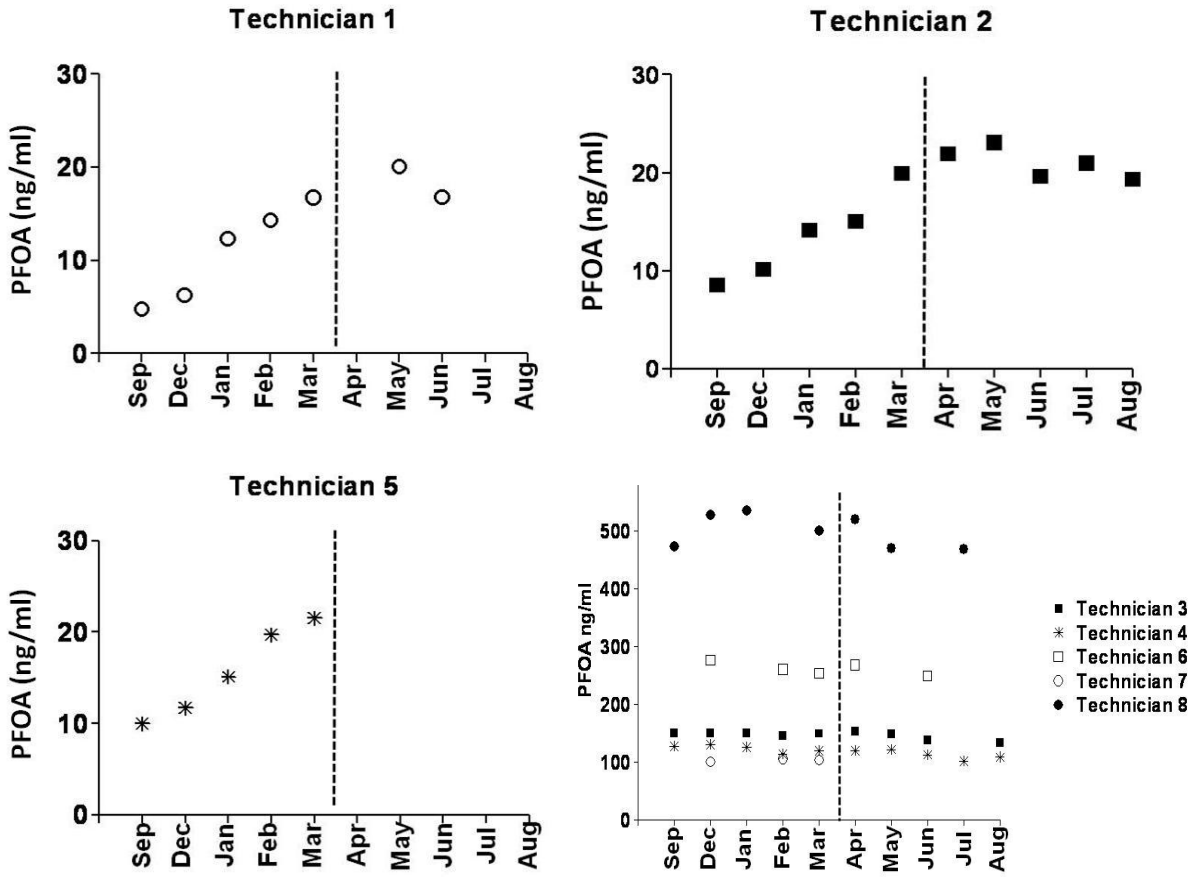

Figure 1. Temporal trend of whole blood levels (ng mL^{-1}) of PFOA in a) technician 1, b) technician 2, c) technician 5 and d) technicians 3, 4, 6, 7 and 8. Dotted line marks end of World Cup season. Unexposed period (Sep-07), exposed period (Dec-07-Mar-08), unexposed period (Apr – Aug-08).

in fact indirect and that metabolic biological systems are active for some time after the exposure.

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