# A TEMPORAL TREND STUDY OF HUMAN EXPOSURE TO FLUORINATED SKI WAX

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**Abstract**

Only a limited number of studies on human accumulation and elimination of perfluorinated compounds (PFCs) are available. In a previous study we observed elevated levels of PFOA in an individual who reported frequent use of fluorinated ski wax.

The objective of the study was to assess the temporal accumulation and elimination of PFCs in blood. We aimed to compare the levels in ski wax technicians exposed to fluorinated ski waxes to those of the general population.

Individual levels of 11 PFCs were measured in monthly blood samples collected before, during and after the ski season from eight technicians exposed to fluorinated ski wax. The perfluorocarboxylates PFOA (4.80-534 ng/mL), PFNA (0.76-163 ng/mL), PFDA (0.87-23.7 ng/mL) and PFUnDA (0.11-2.84 ng/mL) were present in all samples. PFHxA was found in blood collected during the ski season but not in the unexposed period. Blood levels of carboxylates were inversely correlated to the chain length, C8>C9>C10>C11. The perfluorosulfonate PFOS (0.28-26.7 ng/mL) was found at background levels in all samples and individual concentrations were unaffected by the ski wax exposure. Notably PFOA, PFNA, PFDA and PFHpA have high bioaccumulation potential and upon continued exposure reach levels far above current background levels for the general population.

**Introduction**

In general, two types of ski wax are used by both professional and amateur cross country skiers; grip- and glide wax. Glide waxes are applied to prevent adhesion of snow, ice, dirt and moisture that slow down the skis' movement. Fluoropolymer based ski waxes are a blend between a wax matrix, for example paraffin, and carbon fluoride. For optimum performance they are heated to 150-190 $^{o}$C [1-4] when applied to the ski's sole, leading to emission of airborne particles and fumes containing a blend of gaseous organofluorine compounds. Inhalation of thermal degradation products could cause pulmonary edema and polymer fume fever, informally called the Teflon flu [5, 6].

The typical wax cabin for professional service technicians is a small room with poor ventilation where several persons are working generating large amounts of airborne dust particles and fluoroorganic vapors.

Our study focused on cross country skiing wax technicians' exposure to PFCs before, during and after the ski season, and how the blood levels of perfluorochemicals were affected. The blood levels were used to establish the relation between exposure to fluorinated ski waxes and their temporal trends in blood throughout the skiing season and during the unexposed period.

**Materials and Methods**

We collected individual monthly blood samples before, during and after exposed period of World Cup competitioning season in 2007/2008. Sampling during the unexposed period took place in the participants' local hospital at regular monthly intervals during 5 months. Samples were stored in blood tubes containing EDTA at -20 $^{o}$C prior to analysis.

Ammonium acetate was purchased from Fluka (Steinheim, Germany), formic acid from Scharlau (Barcelona, Spain), and methanol from Labscan (Dublin, Ireland). All water used was laboratory produced ultra pure water. Ammonium hydroxide was purchased from Merck (Darmstadt, Germany). PFBS, tetrabutylammonium salt, PFOS, potassium salt, PFDA and PFHxA were purchased from Fluka. PFHpA, PFNA, PFOA and PFUnDA were purchased from Aldrich (Steinheim, Germany and Milwaukee, WI). PFHxS was purchased from Interchim (Montlucon, France). PFBA, PFPeA and $^{13}C_4$-labeled PFOA, $^{13}C_4$-labeled PFOS and $^{13}C_5$-labeled PFNA were from Wellington Laboratories (Guelph, Ontario, Canada).

Sulfonates C4-C8 and carboxylates C4-C11 were analyzed using weak anion exchange, solid phase extraction (Waters Oasis® WAX) and ultra-performance chromatography coupled to a tandem mass spectrometer. Detailed information about the sample extraction is described elsewhere[7]. Briefly, internal standards ($^{13}C_4$-PFOA and $^{13}C_4$-PFOS) and 2 mL formic acid/water (1:1v/v) were added to 0.5 mL whole blood. After sonication and centrifugation, the supernatant was extracted using Oasis WAX and the perfluorinated compounds were eluted with 1 mL 2% ammonium hydroxide in methanol. The volume of the blood extract was adjusted to 200 µl using nitrogen. Performance standard $^{13}C_5$-PFNA and 300 µl 2 mM ammonium acetate in water were added prior to analysis.

Analysis was performed using an Acquity UPLC coupled to an Quattro Premier XE (Waters Corporation, Milford) with an atmospheric electrospray interface operating in negative ion mode (ES-MS/MS). Separation was performed on an Acquity BEH C18 2.1 x 50mm, 1.7 µm kept at 50 °C. Injection volume was 10 µl and the flow rate was set to 400 µl/min. A gradient program delivering mobile phases consisted of 2 mM ammonium acetate in water (A) and 2 mM ammonium acetate in methanol (B) was prepared. The gradient sets off with 60% A for 0.3 minutes followed by 5 minutes ramp up to 94% B followed by 1 minute wash sequence of 100% mobile phase B before the program reverts to initial conditions of 100% for three minutes allowing the system to equilibrate. We used multiple reaction monitoring of molecular anion $[M^-]$ for sulfonates and $[M\text{-}H]^-$ for carboxylates and measuring the product ions $[FSO_3]^-$ and $[M\text{-}COOH]^-$ for sulfonates and carboxylates respectively.

Quantification was performed using the internal standard method with non-extracted standards dissolved in 35% methanol in water containing 2 mM ammonium acetate. $^{13}C_4$-PFOS was used as internal standard for the sulfonates and $^{13}C_4$-PFOA was used for the carboxylates. The mean recoveries for internal standards in all samples were 70% for PFOS and 80% for PFOA.

**Results**

PFOS (0.28-26.7 ng/mL), PFOA (4.80-534 ng/mL), PFNA (0.76-163 ng/mL), PFDA (0.87-23.7 ng/mL) and PFUnDA (0.11-2.84 ng/mL) were detected in all samples. PFHxS (0.30-4.29 ng/mL) was found in 93% of the samples, i.e. in all except the first four monthly samples from technician 1. Generally, PFHxA (<0.07-12.2 ng/mL) was only observed in samples collected during the exposed period from December 2007 to March 2008, and was not found over the detection limit 0.07 ng/mL in samples collected during the unexposed period of June, July or August 2008. Concentrations of PFHpA varied between <0.37 and 19.8 ng/mL, but was detected in all samples except in five from technician 2 and one from technician 5. PFBS, PFBA and PFPeA were detected in 7, 35 and 10 samples respectively.

*Perfluorinated carboxylates.* A large variation was seen in PFOA levels on inter-individual basis (4.8-535 ng/mL). Three technicians showed initial levels of PFOA less than 10 ng/mL but five technicians showed levels larger than 99 ng/mL in the pre-seasonal sample from September 2007. Generally, levels of carboxylates increased inversely to the chain lengths of 8-11 carbons in the samples collected during the exposed period. The technicians with low initial levels (4.8-10.0 ng/mL) increased by 116- 319% whereas the five technicians with higher initial levels increased by 6-29% from September 2007 to March 2008, i.e. during the course of skiing season. We found that PFOA concentrations continued to increase for 1-2 months after the ski season ended and then the levels abated (Figure 2). For the technicians with high initial levels of PFOA the concentration stayed relatively constant throughout the sampling campaign.

We found PFNA (10.1-163 ng/mL) to be the second highest PFC for technicians 3, 4, 6 and 8; 10-31% of corresponding PFOA levels. Initially technicians 2 and 5 showed higher PFOS levels than PFOA levels. However, PFOA exceeded PFOS after 3 months for technician 5 and by the end of the season technician 2 had a PFOA level similar to his PFOS level. The concentration of PFHpA was found to be second highest level for technician 1 with 31-39% of corresponding PFOA concentration. Clearly elevated levels of PFHxA compared to the whole sampling campaign were seen in the December -08 samples, especially for technicians 1-5 (Figure 3). PFHxA concentration in the samples collected in December ranged between 0.65-0.80 ng/mL respectively 2.23-12.20 ng/mL in samples from US and Swedish teams' technicians.

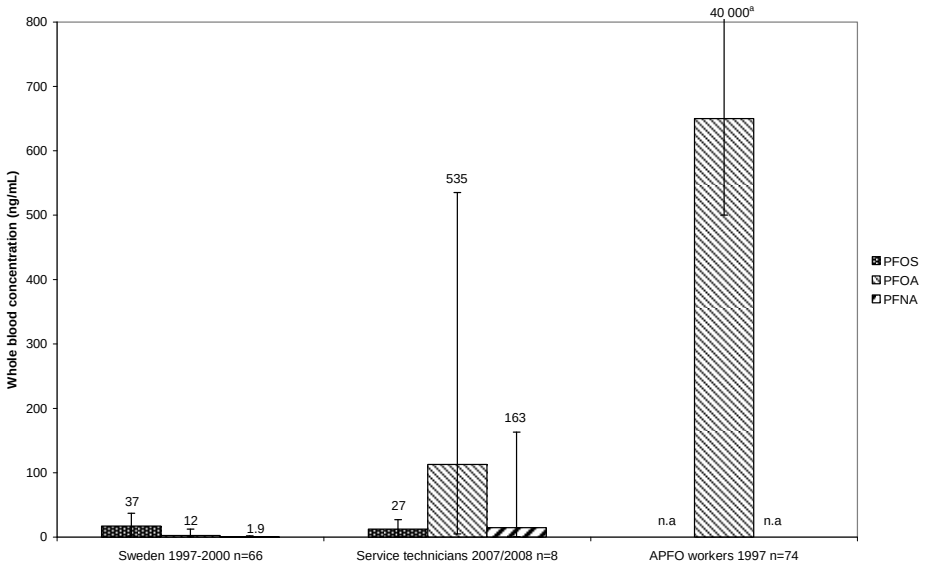


**Figure 1.** Median levels and range of PFOA, PFNA and PFOS in the service technicians compared to the general Swedish population and occupationally exposed 3M workers. [a] Serum concentrations was divided by 2 to give the approx. whole blood concentration. [b] n.a. not analyzed

*Perfluorinated sulfonates.* Levels of the sulfonates showed no temporal trends for any of the eight participants. The sulfonates PFBS, PFHxS and PFOS ranged between <0.02-0.04, <0.06-4.29 and 0.28-26.7 ng/mL respectively for all technicians.

**Discussion**

Our results show that ski wax technicians have distinctly elevated levels of perfluorocarboxylates compared to the US data in the CDC study [8] and a previous study representing a general Swedish population [9] with a mean of 140 ng/ml for PFOA, 29 ng/mL for PFNA and 7.9 ng/mL for PFDA. Especially PFOA is elevated up to 250-fold compared to a general population, increasing with proceeding ski season for persons with intial levels less than 10 ng/mL and abating during unexposed period. Occupationally exposed workers in a 3M plant showed PFOA levels ranging between 50*-40 650* ng/mL whole blood [10] as shown in Figure 1.

In the discussion we have compared whole blood levels to serum levels. The serum levels are divided by 2 when converting it to the whole blood level assuming equal distributions, which is indicated by an asterisk (*)[11].

The bioaccumulation potential of the compound and the number of years in the profession explain the wide ranges of carboxylate levels in this study [12]. Notably PFOA, but also other chain lengths of 7 to 11 carbons, are present in samples from the unexposed period indicating long half-lives. The technicians with more than 6 years in the profession had initial levels of PFOA between 99 and 474 ng/mL and PFNA 10-145 ng/mL. The technicians with less than 7 years showed levels of PFOA and PFNA between 5-10 ng/mL and 0.9- 4 ng/mL

respectively, except for technician 3 who has worked for 6 years and showed initial levels of PFOA and PFNA at 150 ng/mL and 15 ng/mL.

The temporal trend for PFOA concentrations is presented in Figure 2 which shows that the highest PFOA levels are found in samples from April or May although the exposure ended in March. This suggests a toxicokinetic lag time or metabolization following the exposure of fluoroorganic compounds released during waxing. Also, the relation between a technicians PFOA level and the number of years in the profession is evident in Figure 2 with the three least experienced technicians showing the lowest levels of PFOA. During the unexposed period, from June through to August, the PFOA concentrations for all technicians remained constant. For technicians 1, 2 and 5, with initial low concentrations, the range of PFOA in the samples from the exposed period was 4.8-17, 8.5-20 and 10-22 ng/mL which is an increase of 254, 134 and 120%. It seems like the PFOA levels have reached a steady state for technicians 3, 4, 6, 7 and 8 with initial levels exceeding 100 ng/mL, since their perfluorocarboxylate concentrations do not increase over time despite a considerable exposure to wax fumes. Considering that the half-life for PFOA in humans is 5.4 years [13], and if usage of ski wax would elevate the concentrations of PFOA by 10-15 ng/mL blood per year (as for technicians 1, 2 and 4 who increase by 15.2, 14.5 and 11.5 ng/mL respectively), the level at steady state is 80-120 ng/mL at the current exposure conditions.

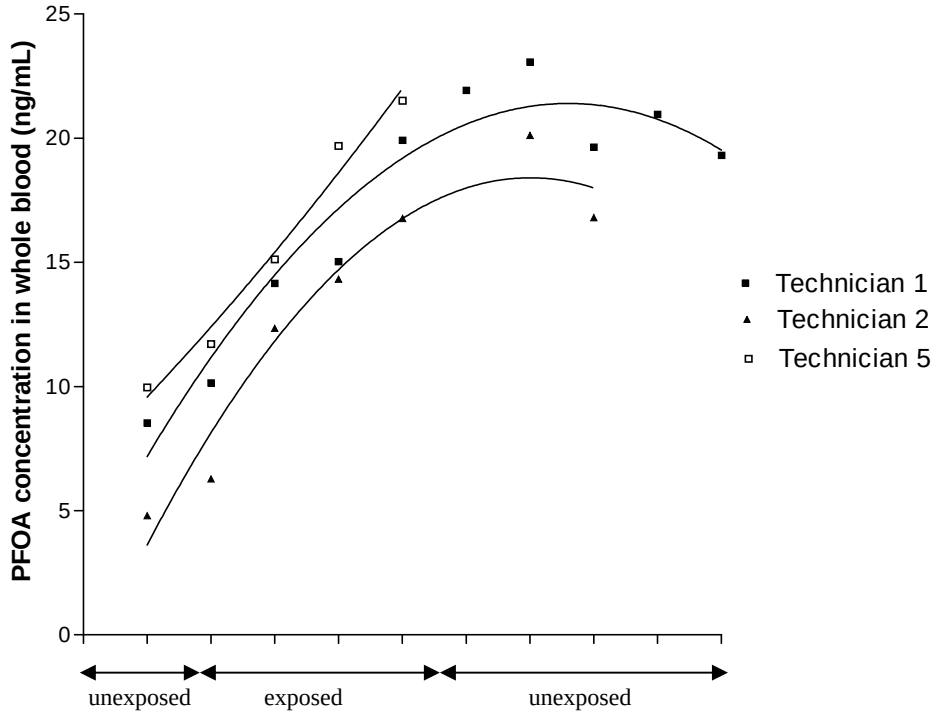


**Figure 2.** Temporal trend of blood concentrations (ng/mL) of PFOA for service technicians (1,2 and 5) with initial levels of PFOA <10 ng/mL sampled September 2007 and December 2007- August 2008. [a] Unexposed period (Sep-07), exposed period (Dec-07-Mar-08), unexposed period (Apr – Aug-08)

The compound that showed the second highest level in the majority of technicians was PFNA (10.1-163 ng/mL); between 10-31% of corresponding PFOA levels for all technicians (Figure 2). Hence, we observed PFNA levels 15-270 times higher than in representative populations from North America, Sweden and China who show PFNA levels of 0.3-0.8 ng/mL (35-37). A clear increase over time is seen for technicians 1 and 5. A

slight increase of PFNA can be seen for the technicians with initially low levels of PFOA (<10 ng/mL). Levels of PFNA did not significantly decrease during the unexposed period indicating a long half-life also for PFNA.

The mean level of PFDA in this study is 7.9 ng/mL (range 0.9-24 ng/mL) which constitutes of 0-8% and 6-25% of the corresponding PFOA concentration for the US and Swedish teams respectively. This is an elevation of up to 80 times compared to a representative population as reported by Ericson et al [14].

Further, clearly elevated levels of PFHxA compared to the whole sampling campaign were seen in the December -08 samples, particularly for technicians 1-5 as shown in Figure 3. Ranges for the US and Swedish teams respectively are 0.65 to 0.80 ng/mL and 2.23-12.20 ng/mL. The analyte PFHxA was found in 96% of the samples collected during the exposed period in contrast to 19% from the unexposed period, and in none of the pre-seasonal samples. These findings confirm a fast elimination and excretion which is supported by Gannon and colleagues [15] who suggest PFHxA to eliminate rapidly, within 24 hours, and almost entirely in its unmetabolized form when excreted in the urine of rats.

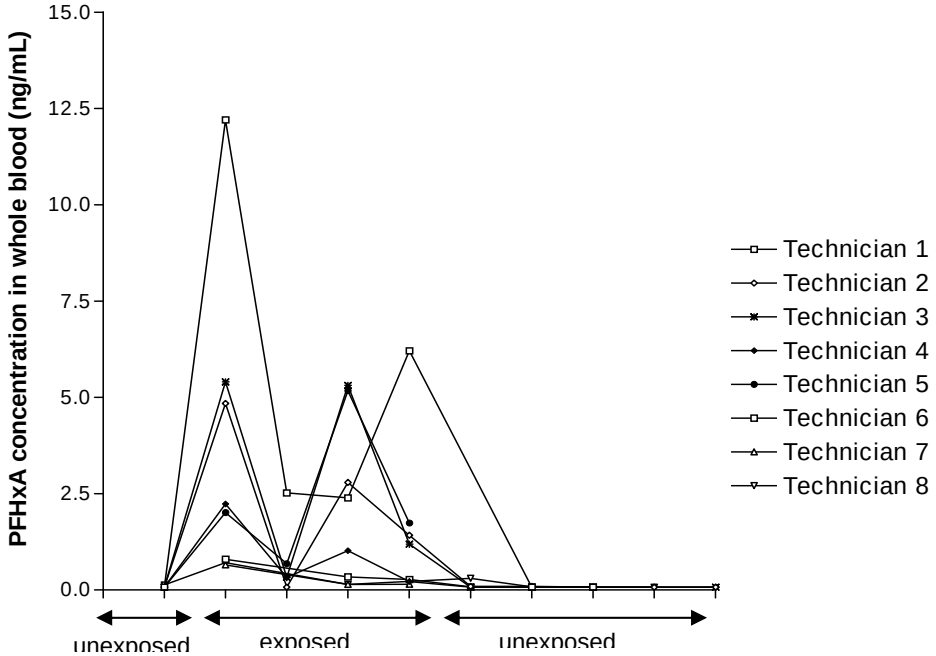


**Figure 3.** Temporal trend of blood concentrations (ng/mL) of PFHxA for service technicians (1-8) sampled September 2007 and December 2007- August 2008. [a] Unexposed period (Sep-07), exposed period (Dec-07-Mar-08), unexposed period (Apr – Aug-08)

The concentrations of perfluorinated sulfonates in the blood of the technicians remain stable all through the sampling campaign. They are also within the range of several representative populations (PFOS range <0.5*-328* ng/mL and PFHxS range <0.2*-356* ng/mL) [9, 14, 16-18].

Our study confirms the long half-lives of several carboxylates in humans. We show that notably PFOA, PFNA, PFDA and PFHpA have high bioaccumulation potential and upon continued exposure reach levels far above current background levels for the general population. The bioaccumulation potential of perfluorocarboxylates depends on the chain length. PFHxA showed fast elimination and excretion compared to the hepta, octa, nona and deca carboxylates. There is a potential risk for increasing human body burdens for

these carboxylates upon continued environmental exposures, life-style exposures as well as occupational exposures.

Perfluorosulfonates levels of PFOS, PFHxS and PFBS in this study are all within ranges of the general population. Hence, the concentrations are not affected under these PFC exposure conditions. Their stability further confirms that a background level of perfluorosulfonates in blood from the same person does not undergo rapid alterations.

Long term studies are necessary to determine whether perfluorocarboxylates are associated with future health effects in this exposed group. We also need to asses to what extent the great number of amateur skiers worldwide face increased health risks if exposed to fluorinated ski waxes. The contribution of ski wax degradation products to the environmental pollution should also be considered.

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