SEMIFLUORINATED *N*-ALKANES AND PERFLUOROALKYL CARBOXYLIC ACIDS IN SNOW AND SOIL SAMPLES FROM A SKI AREA IN SWEDEN

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Introduction

Semifluorinated *n*-alkanes (SFAs) with the formula $F(CF_2)_n(CH_2)_mH$ (or, short, F_nH_m) exist with a wide variety of chain lengths. Short chain SFAs with up to 14 carbons are used in medical applications, while long chain compounds with 22 carbons and more (mostly F_nH_{16}, n=6-16) are used in fluorinated ski waxes, mixed with normal paraffins [1,2]. Next to SFAs the corresponding semifluorinated *n*-alkenes (SFAenes) were detected in ski waxes. Recently, also perfluoroalkyl carboxylic acids (PFCAs) have been found to be present in ski waxes in up to µg/g concentrations [2,3].

The environmental fate of SFAs present in ski waxes after abrasion onto the snow surface has been studied in snow chamber experiments [4]. It was demonstrated that SFAs, which are water insoluble chemicals with low volatility, end up on the soil surface after snow melt. Only a few environmental samples from ski areas have so far been analyzed for levels of SFAs and PFCAs [2,5]. Levels of SFAs were in the high ng/L range in snow samples, while soil samples showed pg/g levels. PFCAs have been analyzed in 4 snow samples from different ski tracks in Norway, compared to a control site [5]. C6 to C9 PFCAs and perfluorooctane sulfonate (PFOS) have been found to be present in the range of 1-50 ng/L in all four samples, though not in the control sample.

These few analyses showed that ski wax usage leads to locally high concentrations of SFAs and PFCAs that might affect local ecosystems. The goal of this study was thus to gain more information about levels, patterns and yearly inputs of SFAs and PFCAs in skiing areas.

Materials and methods

Sampling

Snow and soil samples were taken on the route of the Vasaloppet in Dalarna, Sweden in 2010. The Vasaloppet is a 90 km cross-country ski competition, taking place every year in March. Snow sampling took place the day after the main competition. Samples were taken from different sites along the route, either out of the prepared ski tracks or from packed snow between these. Additionally samples were taken from undisturbed deep snow close to the path. The top 5 cm surface snow were sampled and the surface area that each sample represented was recorded. At two places also the underlying snow was sampled. Soil samples from the same sites were taken in May, just after all snow had melted. At two of the sites where snow samples were taken it was not possible to obtain any soil samples. This was for one site due to moss growing on the soil (a moss sample was taken and analyzed for SFAs), and for the other site due to too muddy conditions (no samples were taken here). Soil samples were taken from the top 1 cm of surface soil. The samples were air dried for two days and sieved through a 2 mm sieve. The dry weight was determined for each sample by heating a 1 g aliquot at 105°C for 24 hours.

Analysis of SFAs

Snow and soil samples were extracted using methods developed previously [2]. Snow samples (about 500 to 800 mL melt water) and a method blank (500 mL tap water) were extracted via liquid-liquid extraction using twice 30 mL cyclohexane. The combined extracts were evaporated to 0.5 mL. Soil samples (about 5 g) and a method blank (5 g standard soil 2.3 from Lufa, Speyer, Germany) were extracted by solid-liquid extraction using twice 10 mL of cyclohexane. The samples were sonicated for 20 min, centrifuged and the combined supernatants were evaporated to 0.5 mL. Both the snow and soil sample extracts were cleaned-up over silica solid phase extraction (SPE) cartridges (1 g, 6 mL, Biotage, Uppsala, Sweden). The target SFAs were eluted from the cartridges using 5 mL cyclohexane, which was then evaporated to 0.5 mL. F_8H_{10} (5 µL of a 0.5 mg/mL solution in cyclohexane) was added as volumetric standard prior to instrumental analysis. A gas chromatograph coupled

to a mass spectrometer (Trace GC Ultra, Thermo Scientific, Waltham, MA) using electrochemical negative ionization (ECNI) was used for the analysis of SFAs.

Analysis of PFCAs

Snow samples (analyzed as melt water) were extracted using a method described by McLachlan et al. [6]. Ammonium acetate, formic acid and internal standards (IS) were added to the samples followed by extraction over Oasis HLB Plus SPE cartridges (Waters, Milford, MA). The cartridges were washed with 2 mL methanol/water (40/60) and the PFCAs were subsequently eluted with 8 mL methanol. A method blank was performed by spiking the IS into the washing solution. The eluent was concentrated and applied to a further SPE clean-up using a C8+quaternatry amine cartridge (UTC, Bristol, PA). After washing with 2 mL of 2% formic acid in a methanol/methyl-*tert*butylether mixture (95/5) followed by 1 mL methanol, the analytes were eluted from the column with 8 mL of 2% N-methyl-piperidine in a methanol/acetonitrile mixture (60/40). The extract was concentrated to 450 µL, and 50 µL C^{13}_8-mass labeled perfluorooctane sulfonate (M8PFOS, 200 pg/µL in methanol) as volumetric standard and 500 µL 4 mM aqueous ammonium acetate were added prior to instrumental analysis.

Soil samples were extracted by solid-liquid extraction. About 1 g of sample was spiked with IS. A method blank was extracted without using any soil. For extraction twice 5 mL methanol were added and the mixture was sonicated for 20 min and centrifuged. The combined supernatants were evaporated to about 1 mL and subjected to a clean-up step, using the same SPE clean-up (C8+quaternary amine) as described for the snow samples. The resulting eluent was evaporated to about 950 µL, and 50 µL M8PFOS were added as volumetric standard prior to instrumental analysis. A liquid chromatograph coupled to a triple quadrupole mass spectrometer (Xevo TQ-S UPLC-MS/MS from Waters) was used in negative electrospray ionization (ESI-) mode for the analysis of PFCAs.

Results and discussion

SFAs

The ∑SFA concentrations in snow from within or between the ski tracks ranged from 0.37 to 17 µg/L, except for the sample taken at the start field (km 0 of the competition), which contained 858 µg/L. These concentrations were generally slightly higher than the only previously published results for SFAs in snow from ski tracks in a smaller ski area in Sweden [2]. For better comparability with levels in soil, the concentrations are also reported per m^2 surface area. This additionally gives a better picture of the total amount of SFAs present in the ski area, as compounds from ski waxes are abraded on the snow surface and are thus not homogenously distributed in the snow pack. ∑SFA concentrations in snow ranged from 4.5 to 200 µg/m^2, with the exception of the sample from the start field which contained 3240 µg/m^2. Concentrations in samples taken in the prepared tracks were not in all cases higher than in samples taken between the tracks at the same site. This could be due to the skiing style (classical in tracks versus skating uphill) or due to the fact that at some sites the tracks had already been renewed after the Vasaloppet by the time of sampling. In samples taken from the snow adjacent to the trail only a few analytes were detected at low concentrations. This showed that the contamination of snow with SFAs in skiing areas is locally confined. Depth profile samples taken from deeper snow layers at two locations contained much lower levels of SFAs than the surface snow samples. This confirmed that sampling of the top 5 cm surface snow was sufficient to capture the bulk of SFAs present in the snow. The ∑SFA concentrations in surface snow sampled from the tracks showed a significant (with a Spearman's rank correlation coefficient of 0.643) decrease with increasing distance from the start of the Vasaloppet course (Figure 1). However, a steep decrease found between km 0 and km 3 might have been biased by two factors. First, only one sample has been taken at km 0 (the start field), and thus the concentration might not be representative for the whole site. Second, the tracks at km 3 had already been renewed after the Vasaloppet by the time of sampling. Therefore, the concentrations determined at km 3 probably underestimated the concentrations present in the original tracks. An indication for this is that higher concentrations were found in the samples taken between the tracks compared to within the tracks at km 3. On the other hand, it is also possible that the majority of the wax had already abraded from the ski bases by the time the skiers reached the km 3 site. The further decrease of ∑SFA concentrations from km 3 to km 26 by a factor 3 was much less steep than between km 0 and km 3.

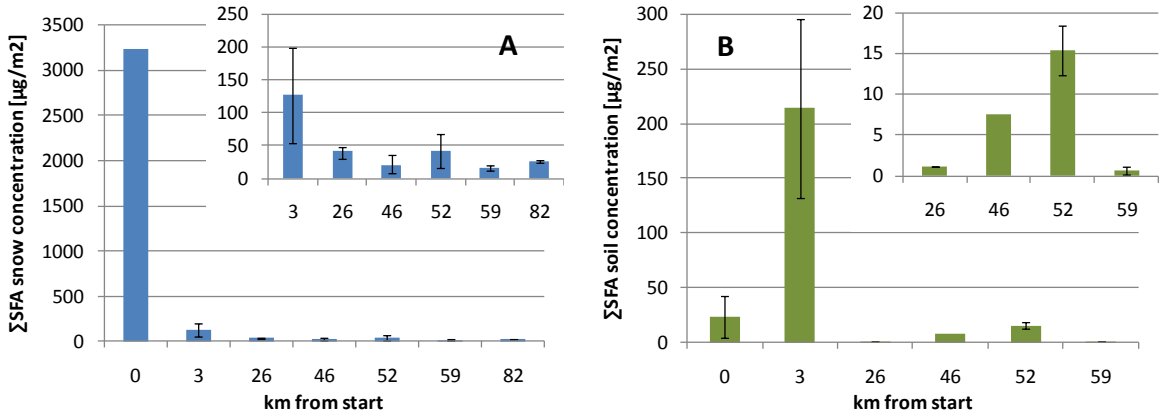

Figure 1: Average ∑SFA concentrations in (A) snow and (B) soil samples at different sites along the route of the Vasaloppet. Whiskers represent the minimum and maximum values.

The ∑SFA concentrations found in the soil samples ranged from 0.25 to 33 ng/g dry weight. Single analyte concentrations were typically about one order of magnitude higher than the few previously published values from a smaller ski area in Sweden [2]. Normalized to surface area, ∑SFA levels in soil ranged from 1.2 to 296 µg/m^2. The control samples taken from soil distant from or adjacent to the trail did not show any detectable SFAs, again demonstrating that the environmental contamination of SFAs from ski waxes is locally confined. A decreasing trend of ∑SFA concentrations in surface soils along the Vasaloppet was not observed (Figure 1). The samples taken at km 3 were markedly more contaminated than the samples from all other sites. The observation of lower concentrations in soil at km 0 compared to km 3 seems to be contradictory to the results from the snow samples, which showed the reverse. However, as discussed above, the snow samples from the start field and from km 3 might not have been fully representative for these two sites. Also, SFA concentrations in soil are a result of input from the whole skiing season (or even accumulation from several seasons). The site at km 0 is only used for skiing as the start field of the Vasaloppet, while km 3 is also a public ski trail during the rest of the season.

Individual SFA soil inventories were compared to calculated input concentrations derived from the quantified concentrations in snow. In general the calculated inputs were higher or of similar magnitude than the median soil inventories (the ratio of average median input to soil inventory being over or close to 1 for all SFAs), suggesting that the SFAs found in the snow after the Vasaloppet accounted for a large portion of the SFAs in the surface soil two months later. Hence, no evidence for long-term accumulation of SFAs in surface soil from skiing activities over several seasons was found. In contrast, for all SFAenes and for the shorter chain SFAs F_6H_{16}, F_8H_{16} and $F_{10}H_{16}$ the average median calculated input was higher than the median soil inventories, while for the longer chain SFAs the medians (and minimum and maximum) fitted fairly well.

The average SFA patterns were distinctively different between snow and soil samples (Figure 2). In general, the pattern in snow samples was similar to the pattern found in ski waxes. Multivariate statistical comparison of the average SFA patterns in snow and soil samples revealed that they were significantly different from each other. The SFAs with shorter chain lengths up to $F_{10}H_{16}$ exhibited a lower fraction in soil compared to snow samples, while the longer chain SFAs $F_{12}H_{16}$, $F_{14}H_{16}$ and $F_{16}H_{16}$ showed larger fractions in soil compared to snow samples. An overall pattern shift towards a higher proportion of longer chain SFAs during the period of snowmelt was thus observed. An

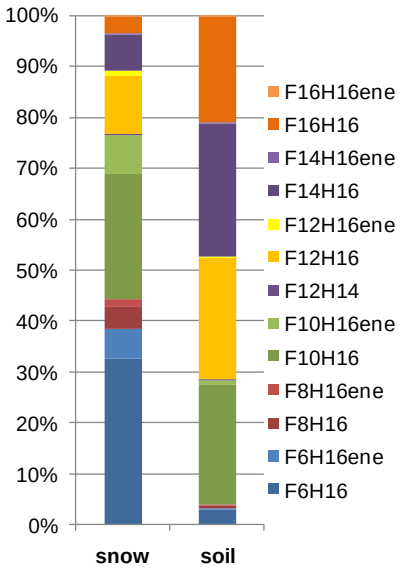

Figure 2: Comparison of average SFA patterns in snow and soil samples. Half the respective method detection limit was used in calculation of averages for non-detects.

explanation for this pattern change and the difference of calculated and analyzed soil inventories for shorter chain SFAs could be volatilization of the shorter chain SFAs and SFAenes (or transformation of SFAenes) during the snowmelt period. Laboratory snow chamber experiments suggested earlier that SFAs used in ski waxes would end up unchanged on the soil after snowmelt [4]. However, in the snow chamber experiments the snow was melted one day after spiking with SFAs. The input calculations and pattern change in the present study showed that a longer experimental period and/or environmental factors not accounted for in the laboratory experiments such as direct sunlight, elevated temperatures and wind might lead to volatilization of shorter chain SFAs and SFAenes present in ski waxes.

The average concentration ratios of SFAs to their respective SFAenes in snow samples were significantly (p-values <0.05) lower than in soil, indicating a different fate of SFAs and SFAenes during snowmelt. Earlier property estimations resulted in calculated vapor pressures for SFAenes that were one order of magnitude higher than for the corresponding SFAs [4]. Thus, SFAenes probably volatilize to a larger extent than their corresponding SFAs. This would explain the observed changes in concentration ratios. Furthermore, SFAenes may be prone to transformation due to the relative lability of the double bond. Reaction of fluorotelomer olefins ($C_4F_9CH=CH_2$ and $C_6F_{13}CH=CH_2$) with hydroxyl radicals in a photoreactor has for example been shown to lead to the formation of perfluorinated aldehydes [7].

PFCAs

PFCAs were analyzed in ski waxes and two raw materials used in ski wax production. Quantified concentrations of PFCAs with chain lengths of C6-C14 have been published previously [2,3]. In the present study also PFCAs with chain lengths from C15 to C23 were detected. To the best of our knowledge this is the first report on PFCAs with chain lengths up to C23. However, due to the lack of reference standards for quantification of the long-chain PFCAs, no concentrations can be given here and the PFCAs will only be discussed qualitatively. C6 to C22 PFCAs were detected in snow samples, with C15-C22 only present in samples from the first 46 km of the competition. C6 to C23 PFCAs were also detected in soil samples, with C15-C23 only present in soil samples from the first 26 km of the competition. Two soil samples taken further away from the trail contained C6-C13 PFCAs with concentrations about one order of magnitude lower than the ones taken on the trail. These samples represent a background contamination, which is not or only slightly influenced by the Vasaloppet and other skiing activity. The concentrations found at the site of the Vasaloppet were thus elevated compared to background levels. The ski waxes were a direct input source for all PFCA homologues.

Acknowledgements

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