



Environmental occurrence and fate of semifluorinated *n*-alkanes and perfluorinated alkyl acids present in ski waxes

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Abstract

Highly fluorinated organic compounds are emerging environmental contaminants of concern, due to their persistence, ubiquitous distribution, bioaccumulation potential and toxicity. Ski waxes are sources of highly fluorinated chemicals to the environment that have not been investigated so far. Some contain fluorinated additives such as semifluorinated *n*-alkanes (SFAs). This thesis investigated the fate of SFAs after abrasion onto snow through skiing activities. Furthermore, perfluorinated alkyl acids (PFAAs) were found to be present in fluorinated ski waxes. A lot of attention has been paid to elucidating the environmental fate of PFAAs during the past decade. However, nothing was known so far about their release from melting snow packs.

Analytical methods for quantification of SFAs in different environmental matrices were developed. The methods were used to investigate the fate of SFAs during snow melt and to study their occurrence in ski areas. Laboratory snow melt experiments and model-based fate simulations suggested that SFAs will sorb to the snow grain surface and particles in the bulk snow and, after snowmelt, will end up on the underlying (soil) surface. SFAs were detected and quantified for the first time in snow and soil samples taken from a ski area in Sweden. Comparison of concentrations in snow and soil did not give any evidence for long-term accumulation of SFAs in surface soil, but suggested volatilization of shorter chain homologues during snow melt. Such a volatilization could also explain an observed SFA pattern difference between snow and soil samples.

Laboratory scale snow melt experiments were also used to investigate the behavior of PFAAs during snowmelt. PFAAs were released with the melt water from the snow pack in pulses. The pulses occurred early, late or with a so far unknown peak elution in the middle of the snowmelt, depending on the hydrophobicity of the PFAAs. These peak releases were further influenced by the age of the snow pack and thus the snow surface area and to a lesser extent by pH and ion concentrations.

Sammanfattning

Högfluorerade organiska ämnen är nya miljöföroreningar av stort intresse, på grund av deras persistens, bioackumuleringspotential, toxicitet samt global spridning. Skidvalla som möjlig källa till spridning av högfluorerade kemikalier till miljön har inte studerats tidigare. Skidvallor kan innehålla olika fluorerade additiv, som t.ex. semifluorerade *n*-alkaner (SFA). Syftet med denna avhandling har varit att studera vad som händer med dessa ämnen (ödet) efter att de nöts av från skidan till snön under skidåkning. Perfluorerade alkylsyror (PFAA) har även visats förekomma i skidvallor. Under det senaste årtiondet har mycket uppmärksamhet ägnats åt att studera denna ämnesgrupps öde i miljön, dock har inga kunskaper funnits om spridning av PFAA från smältande snö.

Analys-metoder för kvantifiering av SFA i olika miljömatriser har utvecklats. Dessa metoder har sedan använts för att studera ödet för SFA under snösmältning och för att kartlägga deras spridning i skidområden. Snösmältningsexperiment i laboratoriet och teoretiska uppskattningar visar att SFA adsorberar till snökornsytan samt till partiklar i snömassan och att de, efter snösmältningen, hamnar på den underliggande (jord)ytan. Förekomsten av SFA upptäcktes och kvantifierades för första gången i jord- och snöprover från skidområden i Sverige. Jämförelse mellan snö- och jordkoncentrationer visade ingen ackumulering av SFA i jordytan, men indikerar en volatilisering av kortkedjiga homologer under snösmältningen. En sådan volatilisering kunde också förklara skillnader i SFA-mönster mellan snö- och jordprover.

Snösmältningsexperiment i laboratoriet utfördes även för att studera beteendet av PFAA under snösmältning. Beroende på kedjelängd och därmed även på vattenlöslighet, uppträdde PFAA koncentrationerna i distinkta toppar under snösmältningsförloppet. Förloppet påverkades även av snöns ålder och därmed snöytans area, samt till en mindre grad av pH och jonkoncentration.

Zusammenfassung

Hochfluorierte organische Chemikalien sind relevante Umweltschadstoffe, die extrem persistent und weltweit verbreitet sind. Zudem reichern sie sich in Lebewesen an und führen zum Teil zu toxischen Effekten. Manche Skiwachse enthalten fluorierte Zusatzstoffe, wie beispielsweise semifluorierte *n*-Alkane (SFAs). Durch den Abrieb der Skiwachse vom Ski gelangen SFAs direkt in die Umwelt, was zu einer bis heute nicht untersuchten Umweltkontamination führen kann. In der vorliegenden Doktorarbeit wurden der Gehalt und das Umweltverhalten von SFAs im Schnee untersucht. Zusätzlich wurden auch perfluorierte Alkylsäuren (PFAAs) in den fluorierten Skiwachsen nachgewiesen. Das Umweltverhalten von PFAAs wurde im letzten Jahrzehnt gründlich untersucht. Allerdings war ihr Verhalten während der Schneeschmelze bis jetzt unbekannt.

Zu Beginn dieser Doktorarbeit wurden analytische Methoden zur Bestimmung von SFAs in verschiedenen Umweltmedien entwickelt. Diese Methoden wurden anschließend verwendet, um das Verhalten von SFAs während der Schneeschmelze und ihre Verbreitung in Skigebieten zu untersuchen. Laborexperimente zur Schneeschmelze und Abschätzungen von chemischen Eigenschaften haben gezeigt, daß SFAs bevorzugt an der Oberfläche von Schneekristallen und Partikeln im Schnee adsorbieren und somit nach der Schmelze auf dem darunterliegenden Boden verbleiben. SFAs wurden in Schnee- und Bodenproben von einem schwedischen Skigebiet nachgewiesen. Der Vergleich zwischen Konzentrationen im Schnee und im Boden ließ keinen Rückschluß auf Anreicherung über mehrere Jahre im Boden zu, wies jedoch auf eine Verflüchtigung von kurzkettigen SFAs während der Schneeschmelze hin. Eine solche Verflüchtigung konnte auch die beobachteten Unterschiede in der Zusammensetzung der SFAs zwischen Schnee- und Bodenproben erklären.

Die Laborexperimente zur Schneeschmelze wurden auch zur Bestimmung des Verhaltens von PFAAs durchgeführt. Diese wurden abhängig von ihrer Kettenlänge und somit Wasserlöslichkeit in konzentrierten Pulsen aus dem schmelzenden Schnee abgegeben. Der Zeitpunkt dieser Abgabe wurde zum Teil vom Alter des Schnees und somit von der Größe der Schneekristalloberfläche sowie zu einem geringeren Teil vom pH Wert und der Ionenkonzentration beeinflusst.

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List of abbreviations

ECD	Electron capture detection
ECNI	Electron capture negative ionization
EI	Electron ionization
F _n H _m	F(CF ₂) _n (CH ₂) _m H (a SFA)
F _n H _m ene	F(CF ₂) _n CH=CH(CH ₂) _{m-2} H (a SFAene)
FTOHs	Fluorotelomer alcohols
K _{AW}	Partition coefficient between air and water
K _d	Partition coefficient between sediment and water
K _{IA}	Partition coefficient between snow and air
K _{IW}	Partition coefficient between snow and water
K _{OC}	Partition coefficient between organic carbon and water
LLE	Liquid liquid extraction
MS	Mass spectrometry
GC	Gas chromatography
PAHs	Polycyclic aromatic hydrocarbons
PFAAs	Perfluorinated alkyl acids
PFCAs	Perfluorinated carboxylic acids
PFCs	Perfluorocarbons
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFSAs	Perfluorinated sulfonates
POSF	Perfluorooctane sulfonyl fluoride
ppLFERs	Poly-parameter linear free energy relationships
SFAenes	Semifluorinated <i>n</i> -alkenes
SFAs	Semifluorinated <i>n</i> -alkanes
SPE	Solid phase extraction
SSA	Snow surface area
WC	Water content

List of papers and statements

Paper I: Plassmann, M.M.; Berger, U. (2010) Trace analytical methods for semifluorinated *n*-alkanes in snow, soil and air. *Analytical Chemistry*. 82. 4551-4557

Paper II: Plassmann, M.M.; Meyer, T.; Ying Duan, L.; Wania, F.; McLachlan, M.S.; Berger, U. (2010) Theoretical and experimental simulation of the fate of semifluorinated *n*-alkanes during snowmelt. *Environmental Science & Technology*. 44. 6692-6697

Paper III: Plassmann, M.M.; Meyer, T.; Ying Duan, L.; Wania, F.; McLachlan, M.S.; Berger, U. Laboratory studies on the fate of perfluoroalkyl carboxylates and sulfonates during snow melt. *Submitted to Environmental Science & Technology*

Paper IV: Plassmann, M.M.; Denninger, A.; Berger, U. Environmental occurrence and fate of semifluorinated *n*-alkanes in snow and soil samples from a ski area. *Submitted to Environment International*

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My contributions to the papers included in this thesis were:

Paper I: I performed all laboratory work, including development and validation of the methods, sampling and analysis, and took the lead in writing the paper.

Paper II: I was involved in conducting the experiments, performed the extraction and analysis of the samples and the model calculations, and I took the lead in writing the paper.

Paper III: I initiated the project, conducted the first experiment and was responsible for the analysis of all samples. I was involved in data interpretation and took the lead in writing the paper.

Paper IV: I was primarily responsible for the sampling campaigns, extraction and analysis of all samples, interpretation of data and for writing the paper.

Thesis objectives

The overall objective of this thesis was to investigate the environmental fate of highly fluorinated compounds used in ski waxes. The four studies included in this thesis aimed at

- determining the structures of semifluorinated *n*-alkanes present in ski waxes and developing trace analytical methods for the quantification of these compounds in environmental samples (**paper I**).
- studying the fate of fluorinated compounds from ski waxes after abrasion onto snow and subsequent snow melt (**papers II, III and IV**).
- measuring concentrations and patterns of semifluorinated *n*-alkanes in a ski area (**paper IV**).

1 Introduction

1.1 Why ski waxes?

Ski waxes consist of different chemicals, which are directly emitted into the environment through skiing activities. Ski waxes can be divided into hydrocarbon and fluorocarbon waxes. The latter are used due to two advantages over hydrocarbons; they are highly water repellent and thus result in a better glide compared to pure hydrocarbons, and they repel dirt. The electronegative fluorine repels dirt particles, as these tend to be negatively charged. A variety of highly fluorinated organic chemicals used today are of concern due to their environmental persistence, ubiquitous distribution, bioaccumulation potential and toxicity (see chapter 1.3 about perfluorinated alkyl acids). Therefore it was interesting to look further into these fluorinated additives used in ski waxes.

A patent on a solid lubricant consisting of a mixture of perfluorocarbons (PFCs) with chain lengths of 10 to 20 carbon atoms (*Gambaretto 1985*) led to the invention of fluorinated waxes, which were first sold in 1987 by SWIX as a product called Cera F (*Swix 2011*). PFCs do not mix well with hydrocarbons. They are mostly sold as 100 % PFC powders and applied as a last finish to the ski bases. A patent from 1991 by Enichem Synthesis S.p.A. introduced di-block semifluorinated *n*-alkanes (SFAs) in ski wax production (*Traverso and Rinaldi 1991*) (for a detailed description of SFAs see chapter 1.2). SFAs can easily be mixed with hydrocarbons; the non-fluorinated part mixes with the paraffins, while the fluorinated part sticks out of the wax layer towards the snow (*Rogowski et al. 2007*). Tests on how much fluorine content is needed for optimum water repellence of a wax showed 4 % fluorine content to be most effective, while a content above 10 % no longer showed any effect, due to the formation of micelles (*Rogowski et al. 2007, Mukerjee 1994*).

In addition to the SFAs investigated in this thesis, several other fluorinated additives are described in the literature for the use in ski waxes, for example tri-block SFAs with two fluorinated blocks in the molecule (*Conte et al. 2007*) or tetrakis(perfluoroalkyl)alkane (*Gambaretto et al. 2003*). A number of patents state even more fluorinated compounds as possible additives (*Grottenmueller et al. 2004, Grottenmueller et al. 2006, Werner 1993*). However, today di-block SFAs and PFCs are the predominant fluorinated substances applied in ski waxes (*Chardonnat 2001*).

Nothing is known about the fate and concentrations of SFAs in skiing areas after abrasion onto snow. Therefore, their release from melting snow packs (**paper II**) and concentrations and distribution in a ski area (**paper IV**) were explored. In addition to SFAs, perfluorinated alkyl ac-

ids (PFAAs) were also studied, as they were found to be present in fluorinated ski waxes (**paper I**) (Freberg *et al.* 2010) and have been found in snow samples from different countries (Kim and Kannan 2007, Liu *et al.* 2009a, Liu *et al.* 2009b, Young *et al.* 2007). Their release from melting snow packs (**paper III**) was investigated with a similar experimental setup as for SFAs in **paper II**.

1.2 Semifluorinated *n*-alkanes

SFAs are a group of highly fluorinated chemicals with the general formula $F(CF_2)_n(CH_2)_mH$ or, short, F_nH_m . They are made up of a straight and even-numbered carbon chain, of which one part is totally fluorinated and the other is totally hydrogenated, see Figure 1. Short-chain SFAs (for example F_6H_8 and F_8H_2) are being tested for medical applications like oxygen carriers in blood substitutes (Riess 2001) and tamponades in ophthalmology (Kirchhof *et al.* 2002). Long-chain SFAs (chains of 22 carbons and more) are applied in fluorinated ski waxes to enhance the glide.

SFAs are synthesized through the addition of a perfluoroalkyl iodide to a 1-alkene applying a free-radical catalyst, followed by dehalogenation using zinc powder and aqueous hydrochloric acid (Napoli *et al.* 1993, Traverso and Rinaldi 1991). During these reactions byproducts like semifluorinated *n*-alkenes (SFAenes) with the general formula $F(CF_2)_nCH=CH(CH_2)_{m-2}H$ (short form F_nH_m ene, Figure 1) are produced (Coe and Milner 1972). In this thesis SFAs is often used as a generic term including both SFAs and SFAenes.

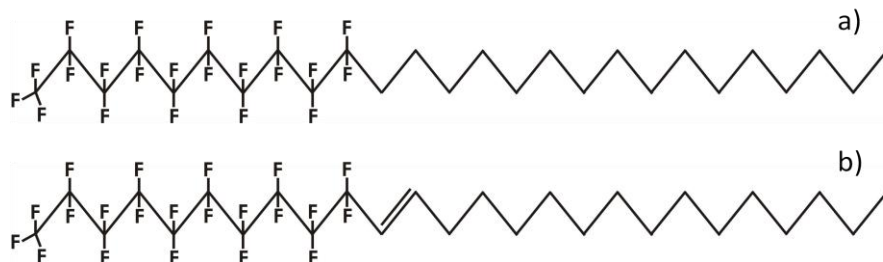


Figure 1: Structure of a) $F_{10}H_{16}$ and b) $F_{10}H_{16}$ ene

Very little is known about the physico chemical properties of SFAs. In contrast to PFAAs, SFAs do not possess a functional group. Due to the incompatibility of their two segments and thus their amphiphilic character, they are referred to as a new class of surfactants (Turberg and Brady 1988). The CF_2-CH_2 linkage provides SFAs with a higher polarity compared to hydrocarbons or PFCs. SFAs have been shown to be more so-

luble in fluorocarbon or hydrocarbon solvents than PFCs or hydrocarbons in the respective other solvent (*Twieg et al. 1985*). The formation of micelles in perfluorocarbon and hydrocarbon solvents has been observed, with F_8H_{12} having a critical micelle concentration of 5.8 wt % in perfluorotributylamine (*Turberg and Brady 1988*). In addition SFAs form Langmuir monolayers at the water/air interface (*Gaines 1991*).

Despite the potentially fragile CF_2-CH_2 linkage, electron ionization (EI) mass spectrometric (MS) studies have shown SFAs to be chemically very stable (*Napoli et al. 1993*). No metabolites of F_6H_{12} ene have been detected in a biodistribution study in rats (*Zarif et al. 1994*), but metabolism studies using rat liver microsomes *in vitro* showed F_2H_4 to be metabolized to the 5-hydroxy derivative (*Baker et al. 1984*). Thus SFAs could possibly be prone to biotransformation with PFCAs as probable end products. However, this hypothesis remains to be tested.

In **paper I** analytical methods for the quantification of SFAs in different environmental matrices were developed. The methods were used in the studies on the fate of SFAs during snow melt in **paper II** and on the presence of SFAs in a highly frequented cross-country ski area in Sweden in **paper IV**.

1.3 Perfluorinated alkyl acids

PFAAs include perfluorinated surfactants with a variety of acidic functional groups. The main focus of research has so far been on the perfluorinated

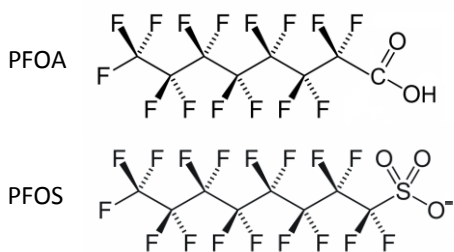


Figure 2: Structure of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS)

carboxylates (PFCAs) and sulfonates (PFSAs). The structures of the most frequently studied homologues with eight carbon atoms can be seen in Figure 2.

PFAAs are used in a range of different applications, due to their hydrophobic and lipophobic properties and low surface tension (*Kissa 2001*). They are present in surface coatings applied to textiles, carpets and paper, in fire-fighting foams, cosmetics and lubricants (*Paul et al. 2009, Prevedouros et al. 2006*).

Atmospheric oxidation of volatile precursor compounds like fluorotelomer alcohols (FTOHs) (*Ellis et al. 2004, Hurley et al. 2004*), perfluoroalkyl sulfonamides, sulfonamide alcohols (*D'eon et al. 2006, Martin et al.*

2006), and iodides (Young *et al.* 2008) has been shown to result in formation of PFCAs and PFSAs. Biotransformation of FTOHs (Dinglasan *et al.* 2004, Hagen *et al.* 1981, Liu *et al.* 2010, Martin *et al.* 2005, Nabb *et al.* 2007), perfluoroalkyl sulfonamides (Tomy *et al.* 2004) and phosphates (D'eon and Mabury 2007) in rats, liver microsomes and microbial cultures has also been found to form PFCAs and PFSAs. Thus, the above hypothesized biotransformation of SFAs/SFAenes could lead to the formation of FTOHs and subsequent transformation to PFAAs.

The global historical emissions (direct and indirect) of PFCAs up until 2004 have been estimated to be 3200-7300 t (Prevedouros *et al.* 2006). The worldwide production from 1970 to 2002 of perfluorooctane sulfonyl fluoride (POSF), the common building block of all perfluorooctane sulfonate (PFOS) related chemicals, has been estimated to be 96,000 t (Paul *et al.* 2009). The major manufacturer of POSF based products and of perfluorooctanoic acid (PFOA) phased out its production of the eight carbon chain chemistry by the end of 2002 (3M Company 2000a, 3M Company 2000b) but production has been shifted to shorter chain homologues of POSF and PFOA (UNEP 2009) and has also been taken up by other manufacturers (UNEP 2008).

There are two main transport routes leading to a ubiquitous distribution of PFAAs in the environment, namely direct transport via ocean currents (Prevedouros *et al.* 2006, Armitage *et al.* 2006, Armitage *et al.* 2009) and atmospheric long range transport via volatile precursors (Ellis *et al.* 2004, Tomy *et al.* 2004). PFAA precursors have been found in Arctic air samples at pg/m³ concentrations (Shoeib *et al.* 2006) and PFAAs themselves have been detected in ice and snow from the Russian and Canadian Arctic (Saez *et al.* 2008, Young *et al.* 2007) and in water from all big oceans in tens of pg/L concentrations (Caliebe *et al.* 2005, Ahrens *et al.* 2009, Wei *et al.* 2007, Yamashita *et al.* 2005, Yamashita *et al.* 2008).

PFAAs are not only present in abiotic samples like water, but also in blood samples from wildlife and humans. Levels in human blood from the general Swedish population are in the ng/mL range, with PFOS having the highest median whole blood concentration of 17.1 ng/mL (n=66), followed by PFOA and perfluorononanoic acid (PFNA) at 2.5 and 0.3 ng/mL, respectively (Kärroman *et al.* 2006). Many studies of animal toxicity of PFOA and PFOS have been published, but the findings are difficult to extrapolate to humans. Several studies found PFAAs to show liver and immunotoxicity, as well as developmental and hormonal effects in rodents (Lau *et al.* 2007). A few studies on humans that had been occupationally exposed to high levels of PFOA and PFOS exist. However, no statistically significant associations between different cancer forms

and PFOA/PFOS exposure was found (Alexander and Olsen 2007, DuPont 2006).

PFCAs showed elevated levels in whole blood from professional ski wax technicians compared to the general Swedish population, with 112 ng/mL for PFOA (45 times higher than in the general Swedish population) and 14.7 ng/mL for PFNA (49 times higher), whereas PFOS concentrations were not elevated (Nilsson *et al.* 2010a). A similar study also showed elevated levels in blood samples from ski wax technicians, including the detection of C14 PFCA for the first time in human serum (Freberg *et al.* 2010). Additionally, Freberg and colleagues found C4 to C14 PFCAs to be present in air samples taken at the work places of these technicians. Another study revealed high concentrations of FTOHs in personal air samples taken while the ski wax technicians were at work (Nilsson *et al.* 2010b). Concentrations of PFCAs in these air samples were up to 800 times lower than 8:2 FTOH. Both the PFCAs and the high FTOH levels could be the reason for the elevated PFCA concentrations found in blood samples, as FTOHs have been shown to biodegrade to PFCAs (see above). The analysis of PFAAs in ski waxes and in fluorinated raw materials for ski waxes revealed up to $\mu\text{g/g}$ concentrations of C6 to C14 PFCAs (**paper I** and Freberg *et al.* 2010). These findings suggest that PFCAs present in ski waxes might not only lead to occupational exposure of ski wax technicians, but also to emissions to the environment. Thus the behavior of PFAAs during snow melt was investigated in a snow chamber experiment in **paper III**.

2 Analytical method development

At the start of this project analytical methods for SFAs in environmental matrices had not been described and thus had to be developed. Method development and validation are described in **paper I**. These methods were a prerequisite for the further studies about the fate and environmental distribution of SFAs in **papers II** and **IV**.

The fact that SFAs are used in ski waxes was known prior to this work; however, nothing was publicly known about their chain lengths and composition. Therefore, the first task was to identify the SFAs present in fluorinated glide waxes and to develop a sensitive instrumental method for their detection. For this purpose four different fluorinated ski waxes from three manufacturers were purchased and different organic solvents were tested to dissolve the waxes. The solutions were subsequently analyzed by gas chromatography (GC) coupled to mass spectrometry (MS). The MS was operated in different ionization modes. Electron ionization (EI) and electron capture negative ionization (ECNI) resulted in fragments and molecular ions of, amongst others, SFAs. The EI spectra were comparable to another EI-MS study on short-chain SFAs (*Napoli et al. 1993*). Overall ECNI proved to be more sensitive and is commonly preferred to EI for the analysis of environmental samples due to better selectivity. Thus it was chosen as the ionization method for further method development.

Apart from the GC-ECNI-MS method, a method using GC coupled to electron capture detection (ECD) was also developed. This worked well, although for environmental snow and soil sample extracts it sometimes resulted in interfering peaks and high baseline noise and was thus not used for environmental samples. However, GC-ECD was applied in **paper II** for the analysis of samples from the laboratory based snowmelt experiments.

The most abundant SFAs found in the ski waxes tested were F_nH_{16} with $n=6-16$ carbon atoms (only even numbers). Next to these all corresponding SFAenes were detected. F_8H_{16} was found at lower concentrations as the other F_nH_{16} SFAs. Only one of the SFAs found in ski waxes was commercially available as a pure chemical standard, namely F_8H_{16} , and thus four SFAs and one SFAene (Table 1) were custom synthesized for quantitative analysis.

For the extraction of snow samples (analyzed as melt water), liquid liquid extraction (LLE) was chosen, which allowed for simultaneous extraction of SFAs that adsorbed to the sample bottle walls. After LLE a clean-up step was necessary, due to co-extracted material that caused

interferences during GC-MS analysis. Silica solid phase extraction (SPE) cartridges were chosen as they remove particles and at the same time retain co-extracted polar compounds. For the enrichment of SFAs from air, Isolute ENV+ cartridges showed good performance. Soil samples were extracted by solid liquid extraction using cyclohexane and the extracts were treated with the silica clean-up developed for snow samples.

Instrumental limits of detection and quantification varied depending on the degree of fluorination of the analytes, decreasing with increasing fluorinated carbon chain length. The same was true for the method detection and quantification limits determined for each environmental matrix. No blank contamination during extraction and clean-up was detected. The accuracy and precision of the methods were determined through replicate recovery experiments. Recoveries for all individual analytes were determined for the extraction of the three matrices snow, soil and air at three different concentration levels, see Table 1. Both recoveries and standard deviations were very good, making quantification using external calibration possible. These methods could then be used for all further studies on the environmental fate of SFAs.

Table 1: Recoveries for SFAs from different environmental matrices

	F ₆ H ₁₆	F ₈ H ₁₆ *	F ₁₀ H ₁₆	F ₁₂ H ₁₄	F ₁₂ H ₁₆	F ₁₂ H ₁₆ ene
Air method recoveries (standard deviation), n = 4 [%]						
High spike concentration	93 (6.3)	88 (6.3)	90 (5.6)	92 (5.3)	92 (4.9)	97 (4.2)
Medium spike concentration	93 (4)	97 (2.9)	110 (3.5)	114 (4.1)	126 (4.8)	135 (5.6)
Low spike concentration	87 (2.6)	105 (5.1)	113 (5.4)	112 (2.9)	122 (2.2)	115 (5.4)
Water method recoveries (standard deviation), n = 4 [%]						
High spike concentration	88 (8.3)	82 (9.6)	82 (12)	83 (9.5)	84 (12)	86 (12)
Medium spike concentration	74 (11.4)	78 (13)	82 (12)	79 (13)	88 (14)	90 (12)
Low spike concentration	67 (22)	76 (18)	83 (18)	89 (31)	91 (23)	87 (20)
Soil method recoveries (standard deviation), n = 4 [%]						
High spike concentration	110 (6.3)	74 (3.1)	74 (3.2)	76 (4.2)	70 (4.7)	74 (6.6)
Medium spike concentration	124 (22.5)	78 (6.6)	95 (8.3)	112 (10.3)	111 (11.7)	107 (13.3)
Low spike concentration	113 (22.9)	88 (4.2)	125 (5.2)	137 (5.7)	141 (5)	119 (9.1)

*Standard impure

3 Fate of highly fluorinated chemicals during snow melt

3.1 Properties and fate estimation for semifluorinated *n*-alkanes

Chemical calculators and poly-parameter linear free energy relationships (ppLFERs) were used to gain first information about physico chemical properties of SFAs and to predict their fate after abrasion from skis onto snow (**paper II**). Chemical calculators estimate properties and distribution coefficients of chemicals based on a large set of compounds with known properties. In the same way ppLFERs estimate different distribution coefficients. The calculator SPARC was used in this study because it gave reasonable results for other highly fluorinated chemicals compared to other calculators tested (*Arp et al. 2006*). PpLFERs developed by Niederer et al. (*Niederer et al. 2006*) and Roth et al. (*Roth et al. 2002, Roth et al. 2004*) were used to calculate properties like water solubility, vapor pressure, Henry's law constant, and partition coefficients (supporting information of **paper II**). The results showed that SFAs exhibit extremely low water solubility and low vapor pressures.

The distribution of SFAs in snow was estimated in order to predict the fate of SFAs after abrasion from ski waxes. The equilibrium distribution of chemicals in a snow pack generally depends on the snow pack characteristics and the chemical's partition coefficients. The snow pack characteristics in this case were the particle content, specific snow surface area (SSA), melt water content, and snow pack density, which were all adjusted to match the conditions of the snow experiments conducted in **paper II** (see section 3.2.1). Using the estimated partition coefficients, SFAs were plotted on a chemical space plot which displayed the equilibrium distribution between snow surface, particles and air. Melt water was neglected in the space plot due to the predicted extremely low water solubility of SFAs.

The SFAs used in ski waxes were predominantly present in the chemical space regions representing chemicals that are associated with the snow surface and the particles. Thus they are predicted to sorb to either of these surfaces and not to volatilize. When snow melts, the area of the snow surface diminishes while the particles are largely retained in the snowpack. This results in a shift in the equilibrium distribution of the SFAs from the snow surface to the particle surface. After snow melt the SFAs would thus be deposited with the particles on the (soil) surface underneath the snow. These predictions were compared to laboratory snowmelt experiments as described in the next section.

3.2 Snow chamber experiments

The release of chemicals from snow packs depends on the physico chemical properties of these chemicals, which determine their behavior during snowmelt. Measurements of chemical concentrations in snow and ice samples exist for a multitude of compounds, but only a few studies have dealt with the release of these compounds during snow melt.

The release of ions from snow packs has been studied both in laboratory experiments and in field studies. Ions have been shown to be released with the first melt water as a so-called "ionic pulse" (*Colbeck 1981, Williams and Melack 1991*). Additionally, a preferential elution has been demonstrated for sulfate and nitrate compared to chloride, influenced by ion exclusion and snow grain growth during melt-freeze cycles (*Tranter et al. 1986, Cragin et al. 1996*).

Studies of organic chemicals have so far mostly concentrated on determining concentrations in bulk snow. A few field measurements of levels in melt water showed a late release of poorly water soluble organic chemicals, which depended on particle transport in the snow pack (*Daub et al. 1994, Simmleit et al. 1986, Simmleit and Herrmann 1987*). However, these field studies are difficult to reproduce and thus it is problematic to identify the parameters governing the release of organic contaminants.

The first laboratory study on the behavior of organic chemicals during snowmelt was conducted by Schöndorf and Herrmann (1987). They studied the release of ions and polyaromatic hydrocarbons (PAHs) from artificial snow cores. All ions were released from the cores with the first melt water, while PAHs, due to their hydrophobicity, sorbed to particles and were released with the last melt water fractions. These results were later confirmed by the work of Meyer et al. (2006, 2009a). In these studies bigger snow packs were produced in order to avoid capillary wall effects that might have been present in the cores and to achieve a better time resolution by taking more melt water samples over the melt period. Snow packs differing in depth, age (melt-freeze cycles were applied, changing the SSA) and particle content, with and without bottom melt as well as layered snow packs were investigated to simulate different natural conditions (*Meyer et al. 2009b*). The release of PAHs and pesticides was tested and found to depend on the chemical's hydrophobicity. The releases were additionally influenced to a certain extent by the depth and age of the snow pack, by the presence of bottom melt and by the layering of the snow packs.

Due to the hydrophobicity and lipophobicity of the perfluorinated moiety, both SFAs and PFAAs possess very different physico chemical prop-

erties compared to the chemicals which had been investigated in snow melt experiments prior to this work. Therefore, the release of these compound classes from snow was investigated in **papers II** and **III** using the snow chamber developed by Meyer and coworkers (*Meyer et al. 2006*). Snow was produced from tap water using a snow gun in a cold room at -26°C. The snow was collected in a snow melt vessel and aged for different time periods. Melting was induced with infrared lights directed to the snow from the top for the PFAAs. For the SFAs a lid was placed on top of the vessel to allow for air sampling, and thus in this experiment the lights were directed to the side of the vessel. The results of these experiments together with the properties and fate estimations (section 3.1) were important for the design of the sampling campaign (e.g., the choice of matrices) in **paper IV**.

3.2.1 Semifluorinated n-alkanes

SFAs were spiked on top of the produced snow, simulating the environmental situation where SFAs are abraded from skis onto the snow surface. During the snowmelt, air was sampled in addition to melt water and particles. A lid was put on top of the vessel and air was drawn through a SPE cartridge connected to a hole in the lid. A small fraction of the SFAs used in ski waxes was present in the last melt water sample (including particles eluting therein), but the dominant fraction sorbed either to the particles that remained in the vessel after snow melt or to the snow melt vessel itself. In air samples only short chain SFAs that are not used in ski waxes were detected.

These results were in agreement with the predicted distribution based on estimated physico chemical properties (section 3.1). In **paper II** it was thus concluded that SFAs used in ski waxes would end up on the (soil) surface underneath the snow after melting. **Paper II** also showed that calculations can help predict the environmental distribution and fate of chemicals, even if only very limited property data are available.

3.2.2 Perfluorinated alkyl acids

PFAAs were directly spiked into the tap water used for snow production. In this way a homogenous distribution of analytes in the snow was achieved. The elution of PFAAs with different chain lengths was investigated in three different experiments to gain an understanding of the influence of snow pack properties on PFAA release. During the first experiment the snow was melted directly one day after production, while during the second and third experiment six melt-freeze cycles were

conducted to age the snow, resulting in a lower SSA. The third experiment additionally had a higher calcium ion concentration and a lower pH compared to the second experiment. Examples of chain length dependent release patterns from the first experiment are shown in Figure 3. Three types of releases were observed. The short chain compounds, i.e. the ones that were most hydrophilic, eluted very early with the first melt water. The long chain compounds, i.e. the more hydrophobic ones, stayed in the snow pack until the end of the melt. They were released in the last melt water fractions or sorbed to the particles remaining in the vessel. The compounds with intermediate chain lengths showed a peak release in the middle of the snow melt period. This type of release had not been observed for any other compounds reported in the literature. It is probably due to the amphiphilic character of the surface active PFAAs, leading to different sorption behavior to the snow surface and particles compared to neutral compounds like PAHs or inorganic ions.

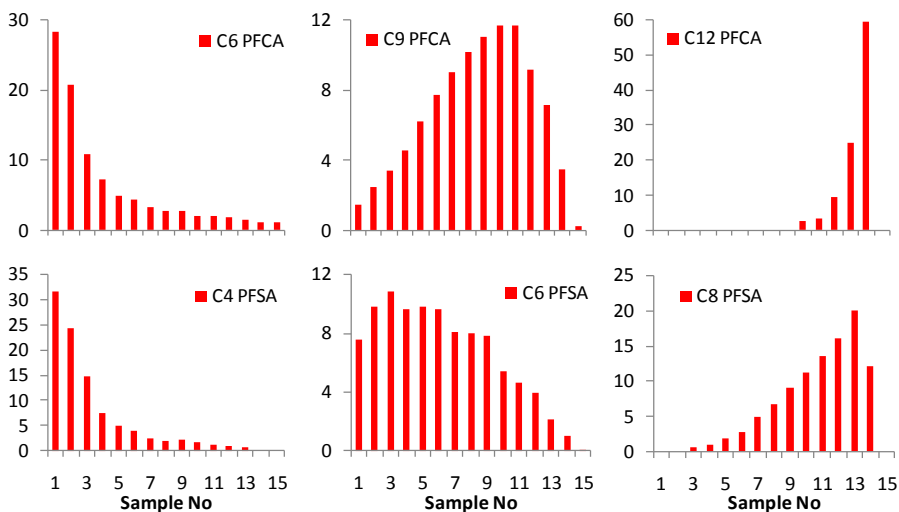


Figure 3: Elution pattern of some PFAAs in snow melt samples during the first snow melt experiment. For results for other PFAAs and additional experiments, see paper III. The y-axis shows the percentage of the totally recovered amount in each individual melt water fraction.

In the second experiment the SSA was identified as a major snow pack property influencing the time point of the peak release. The PFAAs eluted earlier with a lower SSA, due to a smaller snow surface area to sorb to. The third experiment showed only a minor influence of ion concentrations on the release pattern. There was a somewhat greater elution of medium chain compounds in the first melt water fractions, while the lower pH might have resulted in a slightly higher sorption to snow and thus later peak releases of C9 and C10 PFCA.

3.3 Model simulations for perfluorinated alkyl acids

In **paper III** a snowmelt model developed by Meyer and Wania (2011) was applied and further refined to simulate the distribution and release of PFAAs during snowmelt (section 3.2.2). The model is a simple mechanistic model, which stepwise calculates the equilibrium distribution between the different bulk snow phases (as discussed in section 3.1) in different layers of a snow pack, depicted in Figure 4.

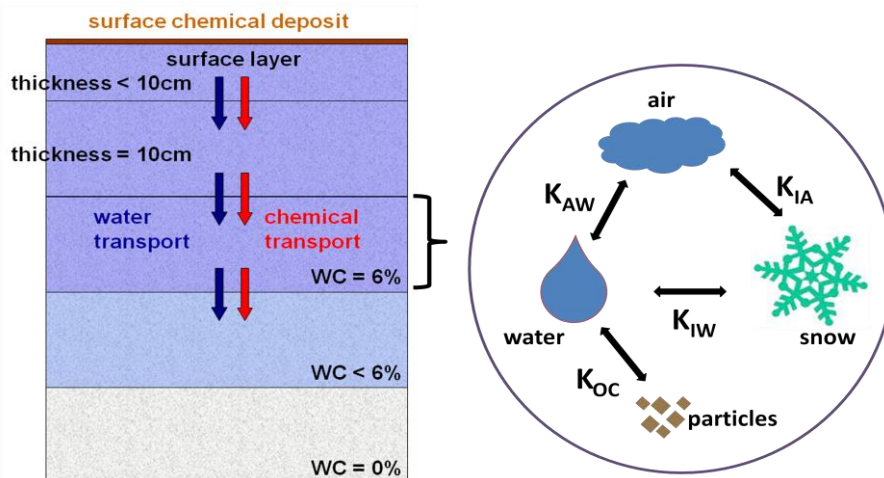


Figure 4: Diagram of the snowmelt model at an early stage of melting (left side, WC means water content), taken from Meyer and Wania (2011), combined with a scheme of the equilibrium distribution including the different phases in the bulk snow (right side)

The snow pack is divided into layers of 10 cm depth. The thickness of the surface layer decreases during the melt, until it has melted away and the next deeper layer becomes the surface layer. Particles above a certain size are not transported downwards with the melt water but instead accumulate in the surface layer. As soon as the melt water content of a layer reaches 6 %, the melt water starts filling up the underlying layer. In this way, chemicals that are dissolved in the melt water are transported downwards. The equilibrium distribution in each layer is calculated for each time step. As described before, this distribution of chemicals in a snow pack depends on the snow pack characteristics and the partition coefficients of the chemicals. In the model used in **paper III** the snow pack characteristics were adjusted to match the conditions during the snow experiments with PFAAs described in section 3.2.2. Apart from the characteristics mentioned above (particle content, SSA, melt water content and snow pack density), the snow permeability towards particles (percentage of particles that accumulate on top of the surface layer) was also defined.

The decrease in SSA during melting was shown to be very important for the elution profile of PFAAs in the experiments (section 3.2.2). This was not considered in the original model by Meyer and Wania (2011) and thus needed to be included to correctly simulate the release of PFAAs.

The partition coefficients of PFAAs between the different bulk snow phases were important input parameters for the model and needed to be defined. Values for the partition coefficient between particles (as organic matter) and water (K_{OC}) were taken from Higgins and Luthy (2006), who measured the sorption of PFAAs to sediments. Values for the partition coefficient between air and water (K_{AW}) were taken from Arp et al. (2006), who calculated these values using chemical calculators. However, no values for the other two partition coefficients K_{IW} (partitioning between snow surface and water) and K_{IA} (between snow surface and air) were available. It was not possible to use ppLFERs for their determination, because these are not applicable to ionic substances.

Thus the model needed to be calibrated against the experimental results. This was done in two steps. First, after including the snow bulk properties, the decrease in SSA over the melt period, and the known partition coefficients taken from the literature, it was determined that the model was not able to simulate the peak release found for the medium chain PFAAs. Thus, the K_{IW} needed to be adjusted over the melt period. This change in K_{IW} was calibrated to fit the release for one compound, i.e. PFNA. The best fit between model and experiment for PFNA was found when $\log K_{IW}$ decreased exponentially by 0.7 log units over the course of melting from an initial value of -3.7. The same change of 0.7 log units was used for all other compounds. However, the change was different in experiment three, where higher ion concentrations were present. Here, an exponential decrease of 0.35 log units from an initial value of -3.9 best fitted the experimental findings for PFNA. Second, initial K_{IW} values for the other PFAAs were fitted against the experimental results. In this way K_{IW} and K_{IA} values (K_{IA} can be calculated using the thermodynamic triangle $\log K_{IW} = \log K_{IA} + \log K_{AW}$) were obtained as output parameters of the model simulations. K_{IW} increased by 0.5-0.6 log units for each additional CF_2 moiety. These are of course relatively rough estimates. However, similar incremental changes between different perfluorinated chain lengths have also been found for the sorption of PFAAs to freshwater sediments (K_d) (Higgins and Luthy 2006).

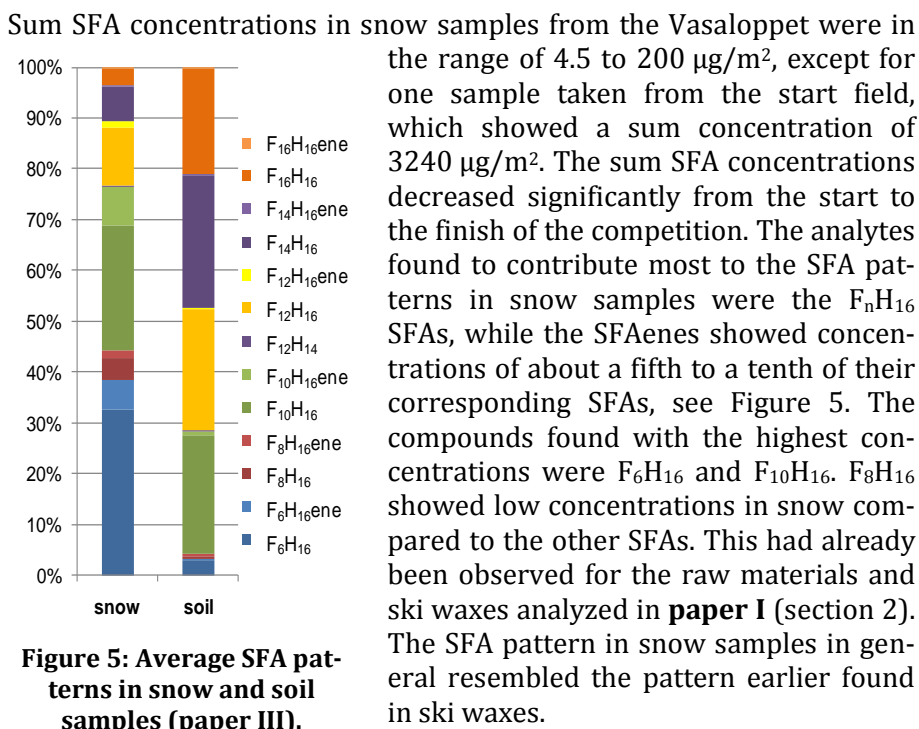
The previously existing model was refined to also be able to describe the fate of surface active compounds. Further evaluation (e.g. by comparing the model output for other surfactant groups with experimental measurements) is necessary to show if the refined model can be used as a predictive tool.

4 Occurrence and patterns of semifluorinated *n*-alkanes in skiing areas

In **paper IV** SFAs were analyzed in samples collected after an important cross-country skiing competition in Sweden, the Vasaloppet, to gain knowledge about their concentrations and patterns in the environment. SFAs had been found to sorb to particles and were thus expected to be transferred to soil after snowmelt in **paper II**. Therefore, snow and soil samples were taken and analyzed using the methods developed in **paper I**.

SFAs from ski waxes had been abraded onto the snow surface during the competition and were therefore expected to be predominantly present in the top layer of the snow rather than being homogenously distributed in the snow pack. Thus all concentrations for SFAs in both snow and soil samples in **paper IV** were converted to $\mu\text{g}/\text{m}^2$ units.

4.1 Semifluorinated *n*-alkanes in snow



4.2 Semifluorinated *n*-alkanes in soil and pattern comparison with snow

Sum SFA concentrations in soil samples were in the range of 1.2 to 296 $\mu\text{g}/\text{m}^2$. No decreasing trend of SFA concentrations in soil from the start to the finish of the competition was found. The pattern of individual analytes in soil samples revealed that the longer chain SFAs dominated (Figure 5). F_6H_{16} could only be detected at very low concentrations in a few samples.

An estimated input onto the soil surface derived from the snow concentrations for each analyte was compared to the concentrations found in the soil samples. The estimated and measured concentrations for the longer chain SFAs agreed well, suggesting that these compounds did not accumulate over several years. However, for the short chain SFAs and for SFAenes the estimated input exceeded the soil inventory, suggesting that these compounds may volatilize during snowmelt.

The average analyte patterns in snow and soil samples were significantly different from each other (Figure 5). The shorter chain compounds were much less prominent in the soil samples compared to snow. On the other hand, the proportion of longer chain SFAs in the snow samples decreased with increasing fluorinated chain length, while in the soil samples they made up similar fractions.

This general pattern shift towards higher percentages of long chain SFAs in soil could be explained by the volatilization of the shorter chain compounds suggested above, or, alternatively, the shorter chain SFAs could have been washed away with the melt water. The latter is unrealistic, due to the extremely low water solubility of SFAs (**paper II**). Volatilization of SFAs during snow melt was not found in **paper II**. However, the conditions were different in the laboratory, where no environmental factors like direct sunlight, elevated temperatures, and wind were included and snowmelt was achieved during only one day. Thus, when including these environmental factors, volatilization seems the most plausible explanation for the observed pattern shift.

Another interesting pattern change between snow and soil samples was observed for the ratio between SFAs and their corresponding SFAenes. In snow samples the ratio SFAene/SFA is significantly higher than in soil samples for all detected SFAene/SFA pairs. This suggests that the SFAenes might volatilize to a larger extent than their corresponding SFAs. The estimated vapor pressures of SFAenes are indeed about one order of magnitude higher than for the corresponding SFAs (**paper II**). Another possible explanation is that SFAenes might be more readily transformed than SFAs due to the presence of the double bond.

5 Conclusions and outlook

Sensitive and fully validated analytical methods were developed for the analysis of SFAs in different environmental matrices. These methods made the determination of concentrations and patterns of SFAs in snow and soil possible and allowed hypotheses about their environmental fate. The methods open the possibility for further process based field or laboratory studies on SFAs, such as degradation studies in soil.

SFAs and PFAAs showed different distribution behavior in snow, depending on their properties and partition coefficients. For both groups, the individual compounds were released as pulses during snowmelt, which may lead to temporally high environmental concentrations. As many species and ecosystems are in a vulnerable phase of their development during spring, these peak releases might have negative effects on certain organisms. The investigation of possible ecotoxicological effects of highly fluorinated compounds warrants further research. For this purpose, the snowmelt model, which was refined for PFAAs (and therewith possibly for other surface active compounds), could be used together with known concentrations in bulk snow to predict peak concentrations in runoff at certain times during snowmelt.

Analysis of SFA levels and patterns in snow and soil samples from a ski area revealed high local concentrations of these compounds, which may be a problem for local ecosystems (see above). Furthermore, the results suggested volatilization of shorter chain SFAs and SFAenes during snowmelt. This was not predicted using either calculations based on estimated partition coefficients or snow chamber experiments.

Overall, this thesis presents the first investigation of the environmental occurrence and fate of SFAs used in ski waxes. It is a major contribution to the understanding of the fate of highly fluorinated chemicals in snow. At the same time it also raises questions regarding e.g. the ecotoxicity and transformation potential of SFAs in the environment, thus opening for future research.

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