Contents lists available at ScienceDirect

Analytica Chimica Acta

A multi-platform approach for the comprehensive analysis of per- and polyfluoroalkyl substances (PFAS) and fluorine mass balance in commercial ski wax products

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HIGHLIGHTS

- PFAS profile among the ski wax products varies between manufacturers.
- Analysis of EOF and TF by CIC aid to estimate the total PFAS burden.
- Complementary techniques such as ICP-MS or ^{19}F NMR have shown potential for the determination of F.
- Pyrolysis GC-MS was used to study the nature of the non-extractable fluorine present in the ski wax products.
- The developed multi-platform approach provides a more holistic perspective on the PFAS and F content in ski wax products.

GRAPHICAL ABSTRACT
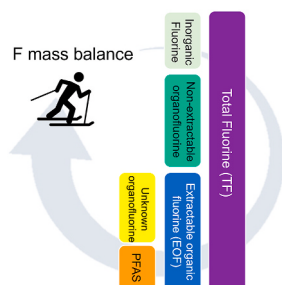
ARTICLE INFO

ABSTRACT

The unique properties of per- and polyfluoroalkyl substances (PFAS) have led to their extensive use in consumer products, including ski wax. Based on the risks associated with PFAS, and to align with PFAS regulations, the international ski federation (FIS) implemented a ban on products containing "C$_8$ fluorocarbons/per-fluorooctanoate (PFOA)" at all FIS events from the 2021/2022 season, leading manufactures to shift their formulations towards short-chain PFAS chemistries. To date, most studies characterising PFAS in ski waxes have measured a suite of individual substances using targeted analytical approaches. However, the fraction of total fluorine (TF) in the wax accounted for by these substances remains unclear. In this study, we sought to address this question by applying a multi-platform, fluorine mass balance approach to a total of 10 commercially available ski wax products. Analysis of TF by combustion ion chromatography (CIC) revealed concentrations of 1040–51700 μg F g^{-1} for the different fluorinated waxes. In comparison, extractable organic fluorine (EOF) determined in methanol extracts by CIC (and later confirmed by inductively-coupled plasma-mass spectrometry and ^{19}F- nuclear magnetic resonance spectroscopy) ranged from 92 to 3160 μg g^{-1}, accounting for only 3–8.8 %

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of total fluorine (TF). Further characterisation of extracts by cyclic ion mobility-mass spectrometry (IMS) revealed 15 individual PFAS with perfluoroalkyl carboxylic acid concentrations up to 33 µg F g^{-1}, and 3 products exceeding the regulatory limit for PFOA (0.025 µg g^{-1}) by a factor of up to 100. The sum of all PFAS accounted for only 0.01–1.0 % of EOF, implying a high percentage of unidentified PFAS, thus, pyrolysis gas chromatography-mass spectrometry was used to provide evidence of the nature of the non-extractable fluorine present in the ski wax products.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic chemicals comprised of several thousand species [1]. These chemicals exhibit unique physical and chemical properties which are useful for various industrial and consumer applications [2]. However, due to their extensive application in society and extreme persistence, PFAS occur throughout the global environment. This is particularly concerning given the links between exposure to certain PFAS and health effects in humans and wildlife [3].

Among the many applications of PFAS is their use in ski waxes for increasing hydrophobicity and lowering friction. The length of the hydrocarbon chain determines hardness in gliding waxes while fluoroalkyl chains increase water-repellence [4]. Historically, the main PFAS used in ski waxes were perfluoroalkanes and semi-fluorinated alkanes [5]. Fluoropolymers are also used in some waxes [6] and perfluoroalkyl carboxylic acids (PFCAs) of varying carbon chain lengths (6–22 carbons) have been found as residual impurities in commercially available fluorinated ski waxes [7–9]. It has been demonstrated that skiing performance improves by an average of 4 % directly after the application of highly fluorinated waxes [10]. Consequently, PFAS-based-ski waxes have continued to be used until recently, despite the risks to the health of ski wax appliers and contamination of the environment [9,11–14]. In response to the introduction of EU Regulation 2020/1021 (POPs-regulation) and EC Regulation 1907/2006 (REACH-regulation)[15], the international ski federation (FIS) prohibited any products containing "C$_8$ fluorocarbons/PFOA" at all FIS events from season 2021/2022 onwards, which was followed by a total fluorine ban in competitive skiing at the start of the 2023/2024 season [16]. This later ban affects to the addition of all kind of fluorinated compounds/additives in the ski waxes.

The presence of fluorinated compounds in ski wax products has already been reported in several studies. Plassman et al. focused on the determination of semi fluorinated n-alkanes [17] and PFCAs in commercially available ski waxes, reporting C$_6$–C$_{22}$ chemistries in the latter [18]. Certain manufacturers of fluorocarbon-based ski waxes indicated a shift to short-chain PFAS chemistries, after the implementation of the PFOA-regulation in 2019 [13]. However, analysis of commercial ski waxes in 2019 revealed PFOA levels above the EU limit (25 ng g^{-1}) in nine of the eleven ski wax products analysed, casting doubts on whether changes to the formulation of fluorinated ski waxes were being made [8].

Until now, product characterisation has focused primarily on targeted analysis, thereby underestimating PFAS concentrations. To address this problem, techniques such as combustion ion chromatography (CIC) have been employed to determine total and extractable organic fluorine (TF and EOF, respectively) and thereby estimate the total PFAS burden [19]. There is also need for the comparison of total fluorine methods, and a recent direction towards the analysis of F is the application of atomic spectroscopy. Relevant techniques include high-resolution continuum source – graphite furnace molecular absorption spectroscopy (HR-GFMAS) [20,21] and inductively-coupled plasma - mass spectrometry (ICP-MS) [22,23]. The latter has become the method of choice for elemental analysis. High sensitivity paired with isotopic selectivity and a vast dynamic range endorsed ICP-MS for the interrogation of metals in the context of biomedical and environmental questions and new advances targeted non-metal entities such as halogens, S or P atoms [24]. Moreover, ICP-MS is an element-specific hard

ionisation technique with low matrix effects, showing the same response of a certain element regardless of the matrix [23]. Independent of the ionisability of different compounds is the use of ^{19}F nuclear magnetic resonance spectroscopy (^{19}F NMR) for EOF analysis. ^{19}F NMR can capture organofluorine compounds, including non-PFAS related chemicals, and has already been proposed as a suitable tool for total PFAS analysis for industrial products [25], as the LODs for NMR are not suitable for the analysis of background concentration of environmental samples. In the past, some interlaboratory comparison for the analysis of TF have involved the join use of CIC, particle-induced γ-ray emission spectroscopy (PIGE) and instrumental neutron activation analysis (INAA) [26], but to date, no studies have compared CIC with ^{19}F^{-}NMR, or ICP-MS.

While it is necessary to know the total amount of F exposure, the sum parameters can be somewhat insufficient when information on the identity and concentrations of individual fluorinated species are required. Current analytical methods to investigate PFAS typically target between twenty to forty compounds via gas or liquid chromatography coupled to tandem mass spectrometry (MS/MS) reaching LODs within the ng g^{-1} range [27–29]. Analysis based on liquid chromatography (LC) coupled to high-resolution (HR) and/or tandem mass spectrometry (MS/MS) to identify and quantify specific PFAS based on retention time, specific fragments and exact mass is considered to be the method of choice for PFAS identification. Data filters using the Kendrick mass defect [30] and fragment ion flagging support the identification of PFAS [31,32] and recent technologies such as ion mobility mass spectrometry (IMS) improve the differentiation between different isomers [33–35]. Although neutral PFAS can still be ionised using electrospray ionisation (ESI), atmospheric pressure chemical ionisation (APCI) and/or atmospheric pressure photoionisation (APPI), high limits of detection are usually achieved and a hard ionisation source such as electron impact (EI) is required for highly sensitive detection, which can only be used after gas chromatography. Determination of PFAS by gas chromatography (GC) is not as well established as LC-based methods. Nevertheless, GC can be considered as a complementary method, and particularly, pyrolysis-GC has been recently used to characterise the nature of fluorine in consumer products [36]. This new perspective can help to gain information for volatile and difficult-to-ionise PFAS, and to complement the LC analysis.

In this work we present a comprehensive characterisation of PFAS and F in commercial ski wax products. LC-IMS was used for the determination of target PFAS. EOF and TF were determined to assess the fraction of identifiable PFAS as well as the fractions of not-yet-identify or non-extractable PFAS. Additionally, the comparison of fluorine analysis by CIC, ICP-MS and ^{19}F NMR was assessed along with the use of pyrolysis GC-MS and GC-atomic emission detection (AED) for a more holistic investigation of PFAS and TF in ski wax products.

2. Experimental

2.1. Chemicals and consumables

Native and isotopically-labelled standards were purchased from Wellington Laboratories. Target PFAS included C$_4$–C$_{16}$ and C$_{18}$ PFCAs, C$_4$–C$_{10}$ perfluoroalkyl sulfonic acids (PFSAs), perfluorooctane sulfonamide (FOSA), perfluorooctane sulfonamidoacetic acid (FOSAA), N-methylperfluorooctanesulfonamido acetic acid (N-MeFOSAA), N-ethyl-perfluorooctanesulfonamido acetic acid (N-EtFOSAA) and 4:2, 6:2 and

8:2 fluorotelomer sulfonates.

Methanol (99.8 %, LiChrosolv®) and ammonium acetate (98 %) were purchased from Merck (Darmstadt, Germany). Acetonitrile (≥99.9 %, Chromasolv™) was obtained from Honeywell (France). Water was purified by a Millipore water purification system and had a resistance <18 MΩ cm (Milli-Q water). Fluoride standard (1000 mg L^{-1}) was obtained from Thermo Scientific. The certified reference material (CRM) clay (BCR-461) and 1000 mg L^{-1} ICP-MS elemental Ba standard (TraceCERT®) were purchased from Sigma Aldrich (St Louis, MO, USA).

2.2. Sample collection

A total of 10 commercially available ski wax products were purchased in Graz, Austria in February–March 2022 and in Stockholm, Sweden before 2020 when the PFOA-regulation entered into force. However, unfortunately no production date or lot number was found on the label. The ski wax products in this study included 8 blocks, 1 powder and 1 grip wax (see Table S1), ranging from fluorine-free to high fluorine content.

2.3. Fluorine mass balance analysis

The analysis of EOF and PFAS in the ski waxes was performed following a procedure previously described by Plassmann et al. [17] with a few modifications. Briefly, 0.1 g of sample (accurately weighted) was extracted with 5 mL of MeOH. The wax/MeOH mixture was vortexed and placed in an ultrasonic bath for 1 h and then stored at room temperature overnight. The samples were sonicated again the next day for 1 h, centrifuged at 4000 rpm for 5 min, and the supernatant was collected into 15 mL polypropylene tubes. The entire procedure was repeated a second time, the extracts combined and evaporated to dryness with N$_2$ gas. After reconstituting with 0.5 mL of MeOH, 100 μL of the extract were mixed with 10 μL of recovery standard (M8PFOS and M8PFOA, both at 20 pg μL^{-1}) and 90 μL of 4 mM NH$_4$OAC in water for targeted analysis. The rest was collected into HPLC vials for EOF determination by CIC. All final extracts were stored at 4 °C until analysis.

For TF determination by CIC, 2.5 mg of solid product were weighed directly into the ceramic boats. For EOF analysis, 100 μL of ski wax extract was injected into a ceramic sample boat containing glass wool. The samples (TF and EOF) were combusted slowly following a procedure previously described by Schultes et al. [37]. Quantification was carried out using a linear six-point calibration curve of NaF ranging from 0.1 to 50 μg mL^{-1} (r^2 = 0.9991). LOD and LOQ were calculated as 3 × and 10 × the standard deviation of the blank divided by the slope of the calibration curve and were 0.03 and 0.11 μg g^{-1}, respectively. Quality controls consisting of a known concentration of PFOA/PFOS standard for EOF and a certified reference material (CRM, BCR®-461, fluorine in clay) for TF were measured periodically. Measurements for TF showed good agreement with the reference value with an average recovery of 103 % (n = 4). While EOF analysis produced recoveries of 105 % (n = 4).

Target PFAS was performed on a Waters ACQUITY UPLC I-Class system coupled to a Selected Series Cyclic IMS-quadrupole time of flight mass spectrometer (QTOF-MS) with high definition MS^E data acquisition using the Waters UNIFI software (Waters Corporation, Milford, MA, USA). An ACQUITY UPLC BEH C18 (100 × 2.1 mm; 1.7 μm particle size) column (Waters) was used for chromatographic separation. Mobile phase *A* consisted of 99 % ultrapure water and 1 % ACN and *B* of 90 % ACN and 10 % ultrapure water, each containing 2 mM ammonium acetate. The initial conditions of 20 % B were held for 1 min, followed by a linear increase to 100 % B at 10 min. This was maintained for 3 min before returning to the starting conditions and equilibrating for 2 min. The flow rate was set at 0.4 mL min^{-1}, the column temperature at 40 °C, and the injection volume was 5 μL. Internal lock mass (Leucine enkephalin C$_{28}$H$_{37}$N$_5$O$_7$, [M − H]$^-$ *m/z* 554.2620) was acquired periodically during each injection to compensate for potential drift and to maintain high mass accuracy. The electrospray ionisation (ESI) source was operated in negative ionisation mode and the optimised instrumental parameters are listed in Table S2.

A standard mix containing 24 PFAS (including isotopically enriched M8PFOS and M8PFOA) was used to set up a targeted screening method with compounds identified using a scientific library. This library contained the exact masses of a set of known PFAS for identification from a data-independent acquisition (DIA) file. After optimisation of the cyclic-IMS-QTOF-MS method, the observed exact *m/z* and retention times were placed into this library for targeted analysis of the known PFAS standards. Calibration was performed with a six-point calibration curve with a concentration range of 0.06–35 ng g^{-1}, with R^2 values greater than 0.9967 for all compounds. The instrument limits of detection (LOD) and quantification (LOQ) were calculated as 3 × and 10 × the standard deviation of y-intercept divided by the slope of the calibration curve, and were between 0.05 and 2.2 μg L^{-1} and 0.2 and 7.2 μg L^{-1}, respectively. The analytical figures of merit are presented in Table S3.

Individual PFAS concentrations obtained by target analysis (IMS-QTOF-MS) were converted into the corresponding fluoride concentration (C$_{F\_PFAS}$; ng F/g) using the following formula:

$$C_{F\_PFAS} = n_F \text{ x } A_F/MW_{PFAS} \text{ x } C_{PFAS}$$

Where n$_F$ corresponds to the number of fluorine atoms in the formula, A$_F$ is the atomic mass of fluorine, MW$_{PFAS}$ the molecular weight of the corresponding PFAS and C$_{PFAS}$ is the obtained PFAS concentration.

2.4. Inter-method comparison

EOF concentrations determined by CIC were confirmed by two additional techniques (ICP-MS and ^{19}F NMR) according to the following approaches. A second aliquot of ski wax was prepared simultaneously as described above, and after reducing to dryness with N$_2$ gas, the samples were reconstituted with 2 mL of MeOH and divided for EOF analysis by ICP-MS and ^{19}F NMR.

Inductively-coupled plasma-mass spectrometry (ICP-MS) - Determination of F levels present in the ski wax extracts (i.e. EOF) was carried out by ICP-MS. An 8900 series ICP-MS/MS system (Agilent Technologies, Santa Clara, CA, USA) was equipped with platinum cones, s-lenses and operated with MassHunter software (Agilent Technologies). A Scott-type double-pass spray chamber was cooled to 2 °C and a MicroMist™ concentric nebuliser (Elemental Scientific Inc., Omaha, NE, US) was used for sample nebulisation. The instrument was operated in MS/MS mode. The performance of the ICP-MS was tuned daily with a solution containing 1 ng mL^{-1} Li, Y, Tl, Ce and Ba to monitor the instrument's performance and a multi-elemental standard was used to set the P/A factor. The plasma was operated at 1.6 kW, oxygen was used as cell gas (65 %) and the typical nebulizer flow rate was 1.07 L min^{-1}. S-lenses were used to employ hard extraction conditions by inverting the polarity of the first and second extraction lenses with values of −200 V and 0 V, respectively.

Due to the high first ionisation potential of F (17.42 eV), the F$^+$ ion yield in the plasma is insignificant. To make F analysis via ICP-MS feasible, Ba^{2+} can be added to the plasma as modifier to form BaF$^+$, which can be targeted instead of F$^+$. In this work we have exploited the capabilities of the above method previously described by Jamari et al. [38] to quantify the F levels present in the EOF fraction of the ski wax products. To follow this strategy 100 μg mL^{-1} Ba solution was added continuously through a T-piece. Quantification was carried out using a linear six-point calibration curve of NaF ranging from 10 to 500 μg mL^{-1} (r^2 = 0.9997). The instrument limits of detection (LOD) and quantification (LOQ) were calculated as 3 × and 10 × the standard deviation of the blank divided by the slope of the calibration curve, and were 2.9 and 9.7 μg g^{-1}, respectively.

Fluorine-19 nuclear magnetic resonance spectroscopy (^{19}F NMR) – For quantitative ^{19}F NMR analysis 300 mg of each extract were mixed with

around 80 mg of an internal standard consisting of 20 mg 2,2,2,-trifluoroethanol in 1 mL deuterated methanol. All ^{19}F NMR spectra were recorded at 298 K on a Bruker Advance Neo 500 MHz NMR spectrometer, equipped with a 5 mm direct F19-detection probe with z-axis gradients. Sixty-four scans with a relaxation delay of 20 s were recorded for each inverse gated proton-decoupled ^{19}F spectrum and exponential window functions with a line broadening of 3 Hz were applied prior to Fourier transformation using TopSpin 3.1.

2.5. Characterisation of unidentified fluorine

Pyrolysis gas chromatography-mass spectrometry (GC-MS) – Identification of non-extractable fluorinated compounds which may occur in the ski waxes was carried out by Pyr-GC-MS using a method previously developed for quantitative analysis of fluorinated polymers [36]. No sample preparation is needed before pyrolysis. About 0.5 mg of ski wax was removed using a scalpel. The scalpel was cleaned in between samples using ethanol and by burning to avoid carry over. Pyrolysis was performed using a filament pulse pyrolyser (PYROLA 2000, Pyrol AB, Lund, Sweden) mounted on an Agilent 8900 (GC), and equipped with an Agilent HP-5MS UI capillary column (30 m × 0.25 mm i.d 0.25 μm.) (Chrompack) and an Agilent 5977B MSD mass spectrometer (+EI at 70eV). The pyrolysis chamber was held at 165 °C and purged with helium. Pyrolysis of the sample was carried out at 600 °C. For chromatographic separation, the oven was held at 50 °C (2 min), increasing at 21 °C min^{-1} to 325 °C and hold for 12 min, using He as carrier gas (1.2 ml min^{-1}). To avoid memory effects blanks were run in between samples. PFAS fragments were identified using the NIST (National Institute of Standard Technology) mass spectral library.

For PFAS, electron impact ionisation produces extensive fragmentation where two series of ions are commonly observed, one starting at m/z 69 $[CF_3]^+$ and the other at m/z 131 $[C_3F_5]^+$. Each series increases in increments of 50 Da $[CF_2]$, i.e. m/z 69, 119, 169, 219, and m/z 131, 181, 231, and 281, respectively [39]. According to Skedung et al. [36] m/z 131 is relatively sensitive and specific for PFAS, making it useful as a marker for identifying pyrolysis products containing perfluoroalkyl chains.

Gas chromatography-atomic emission spectroscopy (GC-AES) – MeOH and hexane EOF extracts were measured for volatile PFAS, which cannot be determined by LC-MS/MS. The analysis was carried out on an Agilent 7890A GC system, equipped with an Agilent HP-5MS capillary column (30 m × 0.25 mm i.d 0.25 μm), a CombiPAL autosampler system (CTC

Analytics, Zwingen, Switzerland) and a JAS G2350A atomic emission detector (Joint Analytical Systems, Moers, Germany). 1 μL of extract was injected in splitless mode with an inlet temperature of 280 °C. For chromatographic separation, the oven was held at 45 °C (2 min), increasing at 20 °C min^{-1} to 260 °C and hold for 7 min, using He as carrier gas (2 mL min^{-1}). Semi quantification was performed using a 50 μg g^{-1} 8:2 FTOH standard, based on the compound-independent element (F) specific rather than molecule-specific response of the atomic emission detector (AED). For element specific detection, 2 wavelengths were monitored corresponding to C and F (496 nm and 690 nm nominal emission wavelength, respectively).

3. Results and discussion

3.1. Target PFAS analysis by LC-cyclic-IMS

A total of 15 PFAS (C$_6$–C$_{18}$ PFCAs and C$_4$–C$_{10}$ PFSA) were detected among the analysed ski waxes , with profiles varying considerably between individual products (Fig. 1, Table S4). PFAS were detected in all 7 of the waxes which contained fluorine according to their labelling, while the remaining 3 ski waxes (Toko FF, Swix CH8 and Red Creek FF) showed no detectable PFAS, consistent with their labels. PFCAs were found in all fluorinated ski waxes while PFSA were only observed in 4 and at relatively low concentrations. ΣPFAS concentrations in the fluorinated ski waxes ranged from 12 ng g^{-1} up to 46300 ng g^{-1} and was remarkably higher in the powder (46300 ng g^{-1}) compared to the blocks (53–506 ng g^{-1}). These findings are consistent with Freberg et al. [12] and Fang et al. [8] who also observed higher concentration of PFAS in powder compared to blocks. The most abundant PFAS were PFDoDA, PFTeDA, PFHxDA and PFOcDA in the powder with values higher than 6000 ng g^{-1} while PFHxA, PFHpA and PFOA were the most abundant in the blocks. In fact, PFOA was found above the regulatory limit (25 ng g^{-1}) in 3 of the 10 analysed samples with levels up to 206, 271 and 2820 ng g^{-1} for Toko HF, Red Creek HF and LDR, respectively. Red Creek HF and LDR powder were purchased before 2020, while for Toko HF no information about the manufacturing date was provided.

A comparison of "low-fluorine" and "high-fluorine" waxes from the same manufacturer revealed some differences in PFAS profiles. For example, while for the high fluorinated ski wax (HF8) 12 PFAS are found, with the most abundant species being PFHxA and PFHpA, in the low fluorinated one (LF8) only 7 PFAS are present with PFHpA as the most abundant. Interestingly, Moly F, which is produced by the same
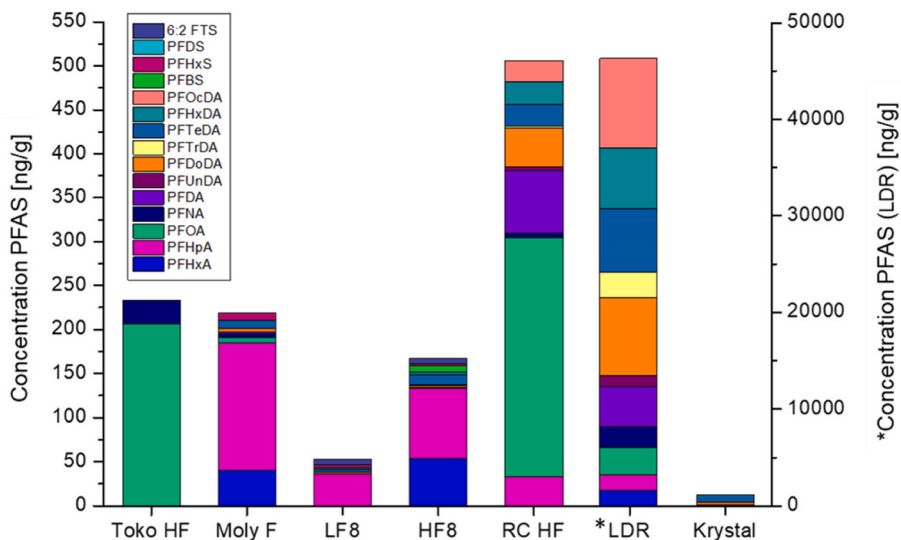

Fig. 1. Concentration (ng/g) of the 15 individual PFAS analytes found in the 7 fluorinated commercial ski products. The 3 non-fluorinated waxes (Toko FF, Swix CH8 and Red Creek FF) did not contain PFAS and therefore not shown here. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

manufacturer as LF8 and HF8, also displayed a profile dominated by PFHxA and PFHpA. One possible explanation for this is that the same PFAS formulation was used in all 3 products but diluted in different amounts.

For the ski wax Red Creek HF, 10 PFAS were found, among which PFOA was the dominant substance. Similarly, for Toko HF only two fluorinated compounds were found, PFHxA and in higher abundance PFOA. The analysis of the fluorinated powder (LDR, 100 % fluoro-carbon) revealed C_6–C_{18} PFAS all above 1100 ng g^{-1} with higher con-centrations towards the long-chain PFAS (see Table S4) aligning with what is expected since the product was purchased before 2020.

3.2. Fluorine mass balance

Among the 7 fluorinated waxes, TF concentrations ranged from 1040 µg g^{-1} (Krystal) up to more than 53000 µg g^{-1} (LDR). Fluorine content in the ski waxes appears to be stipulated by the manufacturer: while for Toko HF the concentration of F was 5820 µg g^{-1}, the amount of F found in Swix LF8 was 8740 µg g^{-1} (see Fig. 2 and Table S5), meaning that the label "high" or "low" fluorine content does not depend only on the TF amount but the manufacturer guidelines. A recent study by Müller et al. [40] determined TF in ski waxes by microwave induced combustion followed by IC detection, reporting values between 4300 up to 31200 µg g^{-1}, which are in line with the ranges obtained in this study. TF concentrations in the 3 non-fluorinated ski waxes (Toko FF, Swix CH8 and Red Creek FF) were negligible and comparable with the blank responses. Concentrations of EOF in the MeOH extracts ranged from 92 µg g^{-1} (Krystal) to 3165 µg g^{-1} (LDR) (see Table S6 and Fig. 2).

Individual PFAS concentrations obtained by targeted analysis were converted into fluorine equivalents (i.e. ng F g^{-1}) to facilitate compar-isons to EOF and TF values (see Fig. 2 and Table S5). The sum of all PFAS accounted for between 0.01 and 1.04 % of EOF, and the EOF in turn accounted for the 3–8.8 % of the TF, indicating that targeted PFAS in this work accounts for only a tiny fraction of the fluorine in wax, and con-firming the presence of PFAS only as impurities from the manufacturing process.

3.3. Inter-method comparison for EOF

EOF concentrations obtained by CIC were in general highly consis-tent with EOF determined by ICP-MS and ^{19}F NMR (see Fig. 3 and Table S6). The only exceptions were for LDR, which displayed higher concentrations by ICP-MS compared to ^{19}F NMR and CIC, and Krystal,
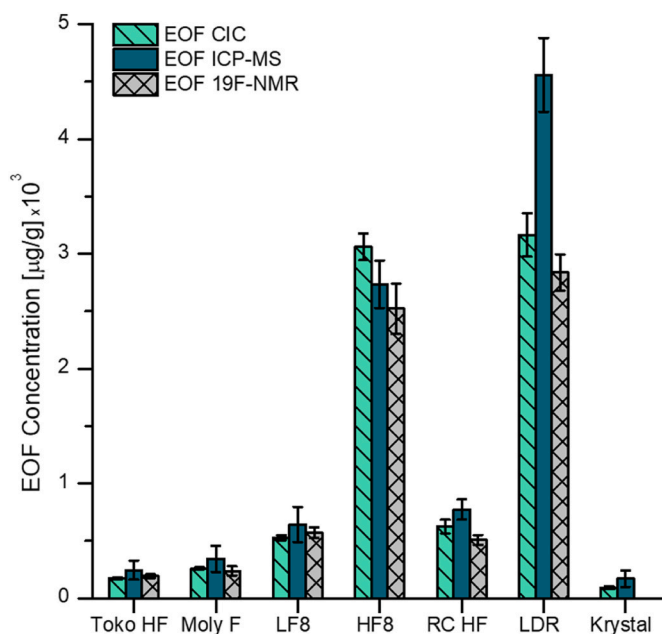

Fig. 3. Comparison of the EOF concentration (µg/g $\pm$ SD) determined in the 7 fluorinated waxes by CIC, ICP-MS and ^{19}F NMR. Krystal wax product was analysed by the 3 techniques although not signal was observed using ^{19}F NMR.

which was measurable by CIC and ICP-MS, but non-detected by ^{19}F NMR. All three methods showed a similar level of precision (RSD-10 %) being comparable for EOF determination. While CIC appeared to have lower detection limits (30 ng g^{-1}) and offers the possibility for TF determination, ^{19}F NMR offers the potential of combining total fluorine measurements with measurement of individual structures, albeit with higher detection limits.

3.4. Determination of fluorinated species in ski wax by gas chromatography

Based on the discrepancy between EOF$_{MeOH}$ and TF concentrations, it was clear that the majority of organofluorine substances were not extracted. To address this problem, the waxes were re-analysed directly (i.e. without sample extraction) by pyrolysis-GC-MS. Pyrolysis-GC-MS has been used successfully to identify both fluoropolymers and side-
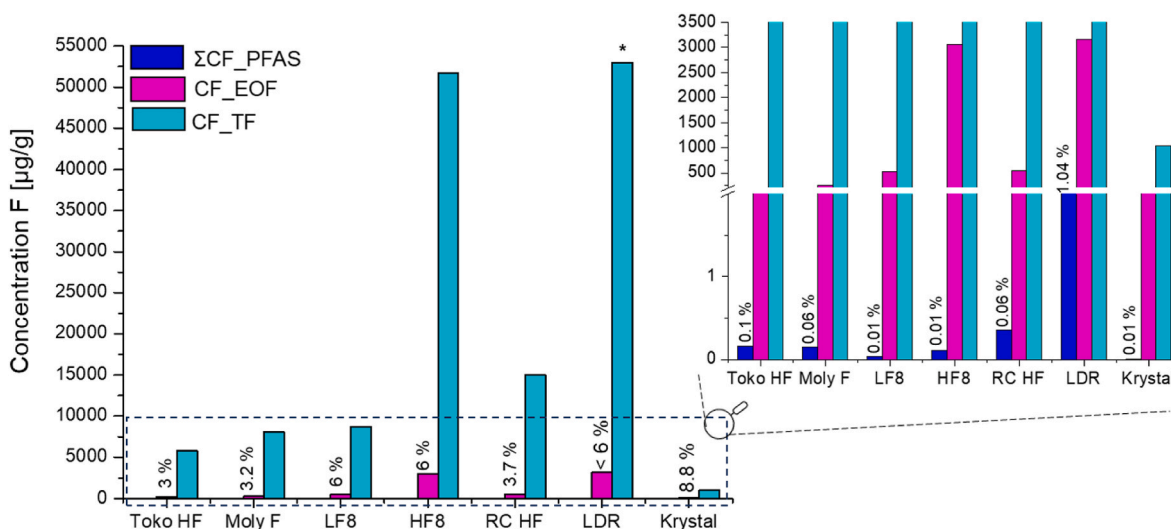

Fig. 2. Comparison of F concentration found in the ΣPFAS, EOF, and TF. The analysis of TF for the LDR powder was not possible due to its high concentration overloading the IC detector (>53000 µg g^{-1}) even when using the least possible amount of sample.

chain fluorinated polymers in a range of consumer products, but until now has never been applied to characterising PFAS in ski wax [36]. Chromatograms and mass spectra obtained from the analysis of 4 fluorinated ski waxes (LDR, Red Creek HF, HF8 and Moly F) are provided in Fig. 4. The LDR fluorocarbon racing powder displayed high intensity fluorinated fragments over the entire chromatogram, characterised by typical PFAS ions such as 69, 100, 119, 131, 169, 181, 219 and 231

(Fig. 4A and B). The Red Creek HF paraffin block wax which contained a lower PFAS concentration than LDR also displayed PFAS fragments at several retention times. At 1.95 min and 4.28 min (data not shown) the fragment m/z 77 occured at the highest intensity whereas m/z 69 was highest at 3.02 min, 3.33 min, 4.94 min, 6.18 min and 7.24 min. This may indicate that the product contains different chain lengths with shorter fluorinated chains (C_6 and C_8 chemistries) eluting faster as
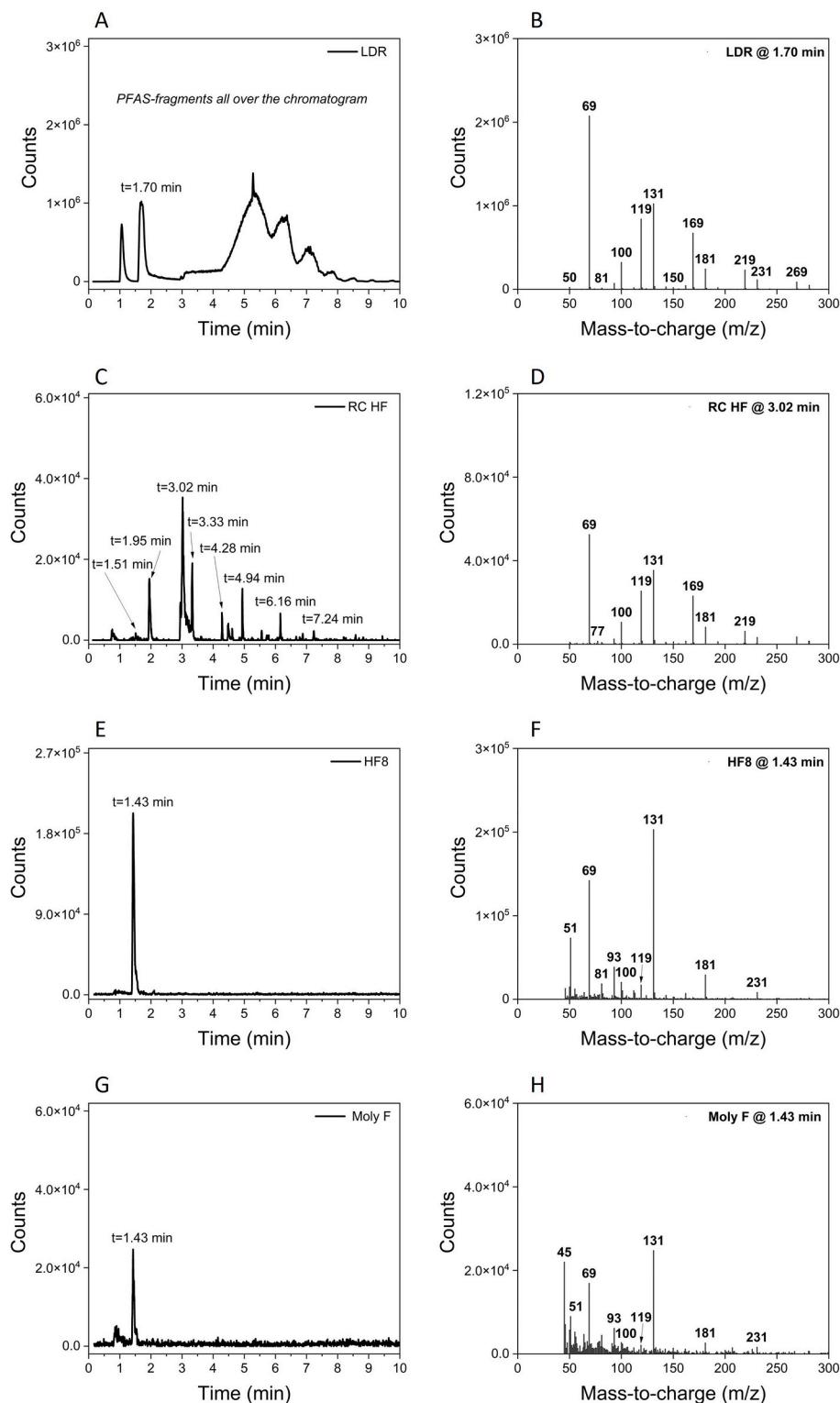

Fig. 4. Extracted ion chromatograms (m/z 131) for four different F waxes, i.e. Vauti LDR powder (A), RF HF (C) Swix HF8 (E) and Moly F (G), with one mass spectrum per sample (B, D, F and H). Note difference in the y-axis scale.

recently reported by Skedung et al. [36] for textile treatments.

In contrast to LDR and Red Creek HF, both Swix HF8 and Moly F only show one peak in the extracted ion chromatogram (EIC) at 1.43 min (Fig. 4E and G). The mass spectra at 1.43 min reveals m/z fragments typical for PFAS (Fig. 4F&H). In addition, Swix LF8 displayed a chromatogram resembling HF8 with one PFAS-fragment at 1.43 min (data not shown). When the acquired mass spectra were compared to those in the NIST database, compounds with fluorinated segments of less than 7 fluorinated carbons are suggested. These results align with the targeted analysis (Table S4) where PFHxA (C_6) and PFHpA (C_7) occured in the highest concentrations in both Swix HF8 and Moly F. Red Creek HF contained concentrations of different PFCAs over 25 ng g^{-1}, i.e. PFHpA, PFOA, PFDA, PFDoDA, PFTeDA and PFHxDA, with PFOA showing the highest concentration (270 ng g^{-1}). The pyrolysis-GC-MS results from the LDR powder (which displayed PFAS fragments throughout the chromatogram) are also in agreement with the target analysis where PFCAs from C_4–C_{18} were quantified in concentrations over 1000 ng g^{-1} with PFOcDA (C_{18}) showing the highest concentration up to 9200 ng g^{-1}. It should be noted that both Red Creek HF and LDR powder were purchased before the PFOA-restriction entered into force. The total ion and extracted ion (m/z 131) chromatograms for the Toko HF product are shown in Figure S1. The intensity of the peaks is very low, but the observed ions confirm the presence of PFAS. According to the TF-concentration, the amount of PFAS should be lower in this product compared to all the other fluorine containing ski waxes, including the low fluorine product Swix LF8. For the 3 fluorine-free waxes analysed, no representative PFAS fragments were found by pyrolysis GC-MS (Figure S2).

The aforementioned methods provided information on the EOF and TF content of the samples, along with identities of both extractable and non-extractable fluorinated species which offer clues as to the PFAS-chemistry used in the products. The results showed that some companies were proactive in removing PFOA from products before 2020. Nevertheless, this fraction of PFAS in the ski wax products is low and not representative of the EOF fraction, thus, other methods might be needed to identify whether the EOF fraction contains polymers or volatile fluoroalkanes. Since GC-MS may be problematic due to the hydrocarbon matrix, a more selective technique is required. Here we employed GC coupled to a microwave-induced He plasma atomic emission detector (GC-AED). The analysis of the EOF_{MeOH} fraction revealed that various volatile neutral PFAS can be detected, albeit in low amounts (Figure S3A). Thus, in order to obtain more information about the nature of the compounds present in the ski wax products another solvent more compatible with GC analysis was evaluated. Two representative fluorinated ski wax products were selected (Swix Moly F and Toko HF), extracted with hexane and analysed by GC-AED. Figure S3 shows a comparison of the chromatograms obtained for MeOH and Hexane extracts of Swix Moly F, and a direct comparison of the F lines obtained for both extracts is represented in Figure S3C. While the Hexane extract contained 2 main F-species at 13 min and 14 min, the MeOH extract only shows a major peak at 13 min, whereas several smaller peaks (>10) are observed along the chromatogram.

Although the structure of these species is unknown at this stage, taking into account that the majority of F (>90 %) is not detectable by target IMS, PFCAs would not be expected. Secondly, it is apparent that the industrial product is a mixture of several PFAS as impurities (neutral volatile PFAS in addition to the ionic PFCAs). F levels (ng g^{-1}) found in the MeOH and hexane extracts obtained by GC-AED after integration of the chromatographic peaks (Table S7) shows that hexane extract yields higher amount of F (between 4 and 12 times) although this amount is not drastically increased. These findings corroborate that most of the fluorinated species present in the EOF are neither volatile nor ionic, suggesting an extractable polymer or extractable F such as nano or microparticles.

4. Conclusions

In this work we applied a multi-platform approach for the comprehensive determination of PFAS and F mass balance in commercial ski wax products. Analysis of TF by CIC revealed concentrations of 1040–51700 µg F g^{-1} for the different fluorinated waxes. In comparison, EOF determined in MeOH extracts by CIC, and further confirmed by ICP-MS and ^{19}F NMR, ranged from 92 to 3165 µg g^{-1}, accounting for only 3–8.8 % of TF. Target analysis of EOF extracts revealed the presence of 15 PFAS within the 7 fluorinated ski wax products, with 3 of them exceeding the limit for PFOA (25 ng g^{-1}) by factors between 8 and 100 times depending on the ski wax product. This was expected for two of the ski waxes that were purchased before 2020 when the PFOA-regulation entered into force. Pyr-GC-MS experiments showed the presence of fluorinated compounds in the studied products while elucidating the possible C chemistry. The carbon chemistry found was corroborated by target analysis of the EOF extracts. Furthermore, the presence of volatile fluorinated species was confirmed by GC-AED, which however do not explain the unidentified fraction of the EOF. This study reveals the need for the use of complementary analytical techniques to provide a more holistic insight into the PFAS and F content in ski wax products.

CRediT authorship contribution statement

Raquel Gonzalez de Vega: Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Merle Plassmann:** Writing – review & editing, Investigation. **David Clases:** Writing – review & editing, Methodology, Investigation. **Klaus Zangger:** Writing – review & editing, Investigation. **Viktoria Müller:** Writing – review & editing, Investigation. **Erwin Rosenberg:** Writing – review & editing, Investigation. **Anders Reimann:** Writing – review & editing, Investigation. **Lisa Skedung:** Writing – review & editing, Methodology, Investigation. **Jonathan P. Benskin:** Writing – review & editing, Resources, Conceptualization. **Jörg Feldmann:** Writing – review & editing, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2024.342754.

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