Levels of per- and polyfluoroalkyl substances (PFAS) in ski wax products on the market in 2019 indicate no changes in formulation

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Environmental significance

Starting in 2000, per- and polyfluoroalkyl substances (PFAS) containing “long” (defined below) perfluoroalkyl chains have been under regulatory scrutiny. The reason for the regulatory focus on PFAS containing “long” perfluoroalkyl chains is because there is a clear relationship between the length of the perfluoroalkyl chain and the bioaccumulation potential of the substance in humans and wildlife. Nearly a decade ago, it was revealed that fluorinated ski waxes contained perfluorooctanoic acids (PFOAs) with greater than 20 carbons and contained relatively high levels of PFOA, a substance listed on the Stockholm Convention and recently restricted under the European REACH regulation. The present study reveals that despite the increasing regulatory scrutiny of PFAS in recent years, the chemical formulations of fluorinated ski waxes appears to have remained unchanged, which has negative consequences for both environmental and human health.

Introduction

Concerns have arisen among scientists and the public regarding the use of fluorinated ski waxes by professional as well as amateur skiers. The concerns have been raised because the fluorinated organic substances present in fluorinated ski waxes include hazardous substances that belong to the chemical class known as per- and polyfluoroalkyl substances (PFAS). The presence of PFAS in ski waxes has been shown to lead to: (1) potential contamination of pristine environments when waxes are lost from the skies during skiing and (2) human exposure to PFAS during application of waxes to the skies. Unease regarding the use of fluorinated ski waxes in the ski-loving nation of Norway led to a series of prize-winning articles in the Norwegian daily newspaper Dagbladet. This analytical study arose as a result of the journalistic detective work in which we collaborated.

Ski waxes can be divided into hydrocarbon-based and fluorocarbon-based waxes. Whereas most recreational skiers use hydrocarbon-based glide waxes, fluorocarbon-based waxes are also available, though much more expensive. The fluorocarbon-based waxes, which are typically sold as blocks or powders, are favoured by competitive skiers or serious amateurs because they have high water repellency and result in better performance (i.e. improved glide) compared to hydrocarbon-based waxes. The PFAS that are the main ingredients in fluorocarbon-based ski waxes are di-block and tri-block semi-fluorinated n-alkanes (SFAs), which are mixed with normal paraffins in the formulations. Powders mainly contain perfluorinated alkanes. In addition to these main fluorinated ingredients, perfluoroalkyl carboxylic acids (PFCAs) of varying carbon chain lengths (4–22 carbons) have been shown to be present in commercially available fluorinated ski waxes. It is not thought that the PFCAs have a technical function in the ski waxes given their relative low levels compared to the SFAs. Instead, PFCAs are expected to be residual impurities from manufacture. The presence of PFCAs and SFAs in snow and
soil samples from ski areas in Sweden has been demonstrated and professional ski wax technicians have been shown to be highly exposed to PFCAs.\textsuperscript{7,9,12}

Since 2000 there have been a number of voluntary industry phase-outs and regulatory actions to cease the manufacture and use of certain PFAS.\textsuperscript{7} Most commonly, the longer chain perfluoroalkyl chemistries have been replaced with shorter-chain perfluoroalkyl or perfluoroalkyl ether chemistries.\textsuperscript{15-20} For example, the manufacture and use of so-called "long-chain" perfluoroalkyl acids (PFAAs) has largely ceased (outside of Asia).\textsuperscript{21} Long-chain PFAAs are defined as including perfluoroalkane sulfonic acids (PFSA)s with perfluoroalkyl chains containing 6 carbons or more, and PFCAs with perfluoroalkyl chains containing 7 carbons or more.\textsuperscript{25} The so-called "precursors" to long-chain PFAAs have also been voluntarily phased-out and/or regulated given that they can transform in the environment or within organisms to long-chain PFAAs.\textsuperscript{21-23} The longchain PFAAs include the well-studied perfluorooctanoic acid (PFOA), which has itself been the subject of recent regulation action in the European Union (EU).\textsuperscript{24} From 4\textsuperscript{th} July 2020 onwards, PFOA and related substances (e.g. substances which might form PFOA in the environment) were banned in all products sold in the EU, including ski waxes, due to its recent addition to the REACH Annex XVII list of restricted substances (entry 68).\textsuperscript{24} Starting in the 2020–2021 winter season, fluorocarbon-based waxes have been banned in competition by the FIS (the International Ski Federation),\textsuperscript{25} although there are concerns about how this regulation will be enforced.

The objective of this study was to determine if there had been a recent change in the formulations, and thus PFAS content, of fluorocarbon-based ski waxes commonly available on the market. Certain manufacturers of fluorocarbon-based ski waxes had indicated to Norwegian journalists\textsuperscript{13} that they had shifted to using chemistries based on shorter perfluoroalkyl chains compared to those used in older products.

Materials and methods

A total of 11 separate commercially available and best-selling ski wax products were purchased from one of Norway’s largest sports stores in the summer of 2019. The ski wax products were stored at room temperature, transported from Norway to Sweden and analysed in the laboratory at Stockholm University. The ski wax products comprised: 3 wax blocks, 1 liquid wax and 7 powders (see Table S1 in the (ESI) for more information including product pictures). Ski waxes were analysed for a suite of 26 PFAS, namely; 22 (C4–C25) PFCAs and 4 PFSA s (see Table S2 in the ESI for a full list of analytes and abbreviations). Additionally one non-fluorinated ski wax (provided from home by a colleague) and two old waxes which had been analysed in 2013 by Plassmann et al.\textsuperscript{7} were analysed as part of the quality control measures. Three empty tubes were extracted together with the samples to serve as method blanks.

The analysis of PFAS in the ski waxes was performed following the procedure described by Plassmann et al.,\textsuperscript{7} with a few modifications. Briefly, ~10 mg (accurately weighed) of ski wax spiked with 0.5 ng of internal standards was extracted with 5 mL methanol. The wax/methanol mixture was vortexed and extracted in an ultrasonic bath for 20 min and then stored at room temperature overnight. The mixture was placed in an ultrasonic bath for 20 min again the next day and then centrifuged (3000 rpm, 10 min) to facilitate sedimentation of the extracted solids. A 4 mL aliquot of the supernatant was transferred to a 13 mL polypropylene tube. The extraction of ski wax was repeated and the supernatant solutions combined. Following extraction, the 8 mL of supernatant was evaporated to approximately 200 µL and 25 µL recovery standard (M8PFOS and M8PFOA, both 20 pg µL\textsuperscript{-1}) and 200 µL 4 mM NH\textsubscript{4}OH in water were added. The extracts were then transferred to a polypropylene (PP) centrifuge tube with a nylon membrane filter and centrifuged at 13 000 rpm for 5 min. The filtered extract was transferred to an autosampler vial and stored at 4 °C until analysis.

PFAS were quantified using an ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS) instrument (Waters, ACQUITY-UPLC/XEVO-TQS) fitted with a BEH C18 column (1.7 µm particles, 2.1 x 50 mm; waters). The mass spectrometer (MS) was operated in negative electrospray ionization multiple reaction monitoring (MRM) mode with the following MS parameters: capillary voltage 1100 V; nebulizer gas flow at 7 bars; desolvation gas flow at 600 L h\textsuperscript{-1}; cone gas flow at 150 L h\textsuperscript{-1}. The desolvation temperature was 350 °C. The m/z cone voltages and collision energies used for each PFAS are listed in Table S2.\textsuperscript{†}

Quantification of all target analytes was performed using an internal standard calibration curve with nine points (0.008–150 ng mL\textsuperscript{-1}, \textit{R}\textsuperscript{2} > 0.99). Stable isotope mass labelled internal standards were available for C4–C6 and C8–C12 PFCAs, as well as for PFHxS and PFOS. C7 and C13–25 PFCAs, PFBS and PFDS were quantified using \textsuperscript{13}C\textsubscript{x}-perfluorohexanoic acid (PFHxA), \textsuperscript{13}C\textsubscript{2}-perfluorododecanoic acid (PFDoDA), \textsuperscript{18}O\textsubscript{2}-perfluorohexane sulfonate acid (\textsuperscript{18}OS-PFHxS) and \textsuperscript{13}C\textsubscript{4}-perfluorooctane sulfonate acid (\textsuperscript{13}C\textsubscript{4}-PFOS) as internal standards, respectively. Reference standards for native C15, C17 and C19-25 PFCAs were not available. Therefore, for quantification of C15, C17 and C19–25 PFCAs the relative response factors (relative to \textsuperscript{13}C\textsubscript{2}-PFDoDA) were calculated from the calibration curves of C14, C16 and C18 PFCAs, respectively. All reported concentrations for C15, C17 and C19–25 PFCAs should thus be considered as semi-quantitative estimates due to the lack of authentic native standards for these compounds. The method detection limit (MDL) was defined as the lowest calibration point concentration resulting in a signal-to-noise ratio of three, if the specific PFAS were not detected in the blanks. For the analytes which were detected in the blanks, MDLs were defined as the mean blank concentration plus three times the standard deviation of the blank.

Results

The MDL range was 0.1–2.5 ng g\textsuperscript{-1}, with only PFOA (MDL = 2.5 ng g\textsuperscript{-1}) and PFOS (MDL = 0.1 ng g\textsuperscript{-1}) present in the blanks. The non-fluorinated wax only showed low levels of C12 (3 ng g\textsuperscript{-1}) and C14 (5.3 ng g\textsuperscript{-1}), which might have come from a previous
contamination, as this wax was not newly bought but had been in use for waxing of skis. The two waxes that had been analysed previously in 2013 were >50% higher than in the original analyses (see Fig. S1 in the ESI†). Some of the high concentrations detected in the 11 ski waxes exceeded the highest calibration point and thus should be seen as estimates. These concentrations are marked with a darker colour in the figures.

The most probable reason for the approximately >50% higher concentrations in this study compared to Plassmann et al. is that the extraction procedure in the present study was more exhaustive, as the extraction was performed twice, while in Plassmann et al. the extraction was only performed once. Other, but in our opinion less plausible, explanations for the discrepancies are as follows. First, the previously analysed waxes had been stored for 10 years in a cupboard in a laboratory, where many PFAS are handled and extracted, and may have been contaminated during storage over the years. Second, the instrumental analysis was done on two different instruments; Plassmann et al. was done on an older triple quadrupole instrument than the one used in the present study, which might explain some differences in the long-chain PFASs that have different response factors and are only semi-quantitative.

PFAS were detected in all of the commercial 11 ski wax samples, but the 26 analytes were not equally prevalent in the different products. Concentrations for the sum of 26 PFAS (ΣPFAS) and PFOA are provided in Fig. 1, while concentrations for all analytes are provided in Fig. S2 of the ESI†. In summary, C5–C10, C12–C14 and C16–C17, PFCA were found in all of the eleven ski wax samples, while PFBS, PFHxS and PFOS were only quantified in three of eleven samples, and PFDS in one of eleven. In addition, concentrations of PFASs in ski wax products were much lower than PFCAs (as shown in Fig. S2†), which is consistent with previous studies reported by Plassmann et al. and Freberg et al. The results indicate that PFCA concentrations in ski wax powders (3175–217,758 ng g⁻¹) were higher than in the blocks (265–7660 ng g⁻¹) (see Fig. 1). The highest ΣPFAS concentration was found in Maplus’s BRIKO FP4 powder (217 758 ng g⁻¹), while the lowest was in TOKO’s HF HOTWAX solid blocks (265 ng g⁻¹). This finding is consistent with Freberg et al. who also observed higher concentrations of PFAS in powders compared to blocks.

As shown in Fig. S1 in the ESI, C12–C25 PFCA concentrations in Maplus’s BRIKO FP4 powder and REX’s RACING SERVICE 63 powder were higher than in other ski wax samples. The ultra long-chain PFCA present in these samples have been previously identified in ski waxes. Their continued presence indicates that for these products there has not been a shift in formulations to short-chain PFASA chemistries. PFOA concentrations in ski wax sold in 2019 ranged from 3.5–30 368 ng g⁻¹ (Fig. 1), and nine of the ski wax products exceed the EU limit value of 25 ng g⁻¹ which came into force on 4th July 2020. The ski wax with the highest PFOA levels, had levels approximately 1215 times higher than the EU limit value. The lowest concentrations of PFOA were observed in SWIX’s HF MARATHON block (3.5 ng g⁻¹), in which the main PFAS observed were C7 (59%) and C6 (32%) PFCA, while long-chain PFCA were the predominant PFAS in the other ski wax samples (>74%). It could be that the low levels of long-chain PFCA observed in SWIX’s HF MARATHON block is an indication of a shift in formulation.

![Fig. 1 ΣPFAS and PFOA concentrations (ng g⁻¹) in the eleven commercial ski wax products purchased from a Norwegian retailer in 2019. Concentrations exceeding the highest calibration point are marked with darker colours.](image-url)

**Fig. 1** ΣPFAS and PFOA concentrations (ng g⁻¹) in the eleven commercial ski wax products purchased from a Norwegian retailer in 2019. Concentrations exceeding the highest calibration point are marked with darker colours.
for a few products, but the results on the whole indicate that there has not been a shift in chemical formulations for the majority of commercial fluorinated ski wax products sold in Norway in 2019. Indeed, PFOA concentrations in some ski waxes sold in 2019 (3.5–30 368 ng g⁻¹) were higher than in waxes analysed in 2010 by Plassmann et al. (29–12 000 ng g⁻¹) and Freberg et al. (7.0–6420 ng g⁻¹) and in 2015 by Blom and Hansen (0.97–92 ng g⁻¹).

It is possible that ski wax manufacturers are more interested in developing fluorinated-free waxes than changing their fluorinated ski wax formulations given the recent ban by FIS on fluorinated ski waxes in international competitions. A recent paper noted that the country of origin of the ski waxes in this study, Norway, was indeed international leaders in terms of protecting the environment and human health from potential harmful exposures from fluorinated ski waxes. The Norwegian wax manufacturer, SWIX, was also commended in the article for its research into the development of novel high-performance fluorinated-free ski waxes. The original development of fluorinated ski waxes was driven by their exceptional technical performance and a market opportunity. However, fluorinated waxes were recently considered to be “non-essential” given that functioning hydrocarbon-based ski waxes were in use before the fluorinated waxes were introduced to the market.

Conclusions

Although the manufacturers of ski waxes have indicated to journalists that they have switched their formulations to chemistries based on shorter perfluoroalkyl chains, the analytical results from this present study indicate that this has not occurred. It is possible that the 11 ski waxes analysed are not representative of the market but this seems unlikely. PFOA levels in nine of the eleven ski lubrication products analysed were above the EU limit values of 25 ng g⁻¹, which came into force on 4th July 2020. The analytical results obtained for ski waxes purchased in 2019 recorded broadly similar contamination patterns and slightly higher concentrations for PFCAs compared to those analyses performed some years ago indicating no changes in formulations in recent years.

Conflicts of interest

There are no conflicts to declare.

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References


