



Cite this: *Environ. Sci.: Processes Impacts*, 2020, 22, 2142

Received 19th August 2020
Accepted 23rd September 2020

DOI: 10.1039/d0em00357c

rsc.li/espi

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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In the summer of 2019, eleven of the best-selling fluorinated ski wax products were purchased from one of Norway's largest sports stores and soon after analysed for a suite of 26 per- and polyfluoroalkyl substances (PFAS). The waxes were shown to contain a wide range of perfluoroalkyl acids, including perfluoroalkyl carboxylic acids with up to 25 carbons. Of particular concern was the finding that perfluorooctanoic acid (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 ski wax with the highest PFOA levels had a concentration that was 1215 times higher than the EU restrictions. Although some of the ski wax manufacturers have indicated that they have switched to formulations that contain chemistries based on shorter perfluoroalkyl chains, the analytical results show that this is not the case.

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 perfluoroalkyl carboxylic acids (PFCAs) 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^{1–12} and the public^{13,14} 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).¹⁵ 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 skis during skiing^{1–5} and (2) human exposure to PFAS during application of waxes to the skis.^{6–12} Unease regarding the use of fluorinated ski waxes in the ski-loving nation of Norway led to a series of prize-winning articles¹⁶ in the Norwegian daily newspaper *Dagbladet*. This analytical study

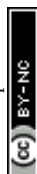
arose as a result of the journalistic detective work in which we collaborated.¹³

Ski waxes can be divided into hydrocarbon-based and fluorocarbon-based waxes.¹⁷ 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.¹⁷ 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.¹⁵ Powders mainly contain perfluorinated alkanes.¹⁸ 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.^{1,3,6} 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 PFCAs³ and SFAs¹ in snow and

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0em00357c



soil samples from ski areas in Sweden has been demonstrated and professional ski wax technicians have been shown to be highly exposed to PFCAs.^{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.¹⁹ Most commonly, the longer chain perfluoroalkyl chemistries have been replaced with shorter-chain perfluoroalkyl or perfluoroalkyl ether chemistries.^{15,20} For example, the manufacture and use of so-called “long-chain” perfluoroalkyl acids (PFAAs) has largely ceased (outside of Asia).²¹ Long-chain PFAAs are defined as including perfluoroalkane sulfonic acids (PFSAs) with perfluoroalkyl chains containing 6 carbons or more, and PFCAs with perfluoroalkyl chains containing 7 carbons or more.¹⁵ 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.^{21–23} The long-chain PFAAs include the well-studied perfluorooctanoic acid (PFOA), which has itself been the subject of recent regulation action in the European Union (EU).²⁴ From 4th 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).²⁴ Starting in the 2020–2021 winter season, fluorocarbon-based waxes have been banned in competition by the FIS (the International Ski Federation),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 journalists¹³ 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 PFSAs (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.*³ 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.*,¹ 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 μ L and 25 μ L recovery standard (M8PFOS and M8PFOA, both 20 μ g μ L^{−1}) and 200 μ L 4 mM NH₄OAc 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 μ m particles, 2.1 $\times$ 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^{−1}; cone gas flow at 150 L h^{−1}. The desolvation temperature was 350 °C. The *m/z* cone voltages and collision energies used for each PFAS are listed in Table S2.†

Quantification of all target analytes was performed using an internal standard calibration curve with nine points (0.008–150 ng mL^{−1}, *R*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 ¹³C₂-perfluorohexanoic acid (PFHxA), ¹³C₂-perfluorododecanoic acid (PFDoDA), ¹⁸O₂-perfluorohexane sulfonate acid (¹⁸O₂-PFHxS) and ¹³C₄-perfluorooctane sulfonate acid (¹³C₄-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 ¹³C₂-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^{−1}, with only PFOA (MDL = 2.5 ng g^{−1}) and PFOS (MDL = 0.1 ng g^{−1}) present in the blanks. The non-fluorinated wax only showed low levels of C12 (3 ng g^{−1}) and C14 (5.3 ng g^{−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.*³ is that the extraction procedure in the present study was more exhaustive, as the extraction was performed twice, while in Plassmann *et al.*³ 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.*³ 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 PFCAs 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 (Σ PFAS) 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, PFCAs 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.*³ and Freberg *et al.*⁶ The results indicate that PFCAs are impurities generated from the production process, whereas the presence of PFASs is more likely due to environmental contamination from production, contact with dust, *etc.*

Generally speaking, Σ PFAS 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 Σ PFAS 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.*⁶ who also observed higher concentrations of PFAS in powders compared to blocks.

As shown in Fig. S1 in the ESI,† C12–C25 PFOA 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 PFCAs present in these samples have been previously identified in ski waxes.³ Their continued presence indicates that for these products there has not been a shift in formulations to short-chain PFAS chemistries. PFOA concentrations in ski waxes 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%) PFCAs, while long-chain PFCAs were the predominant PFAS in the other ski wax samples (>74%). It could be that the low levels of long-chain PFCAs observed in SWIX's HF MARATHON block is an indication of a shift in formulation

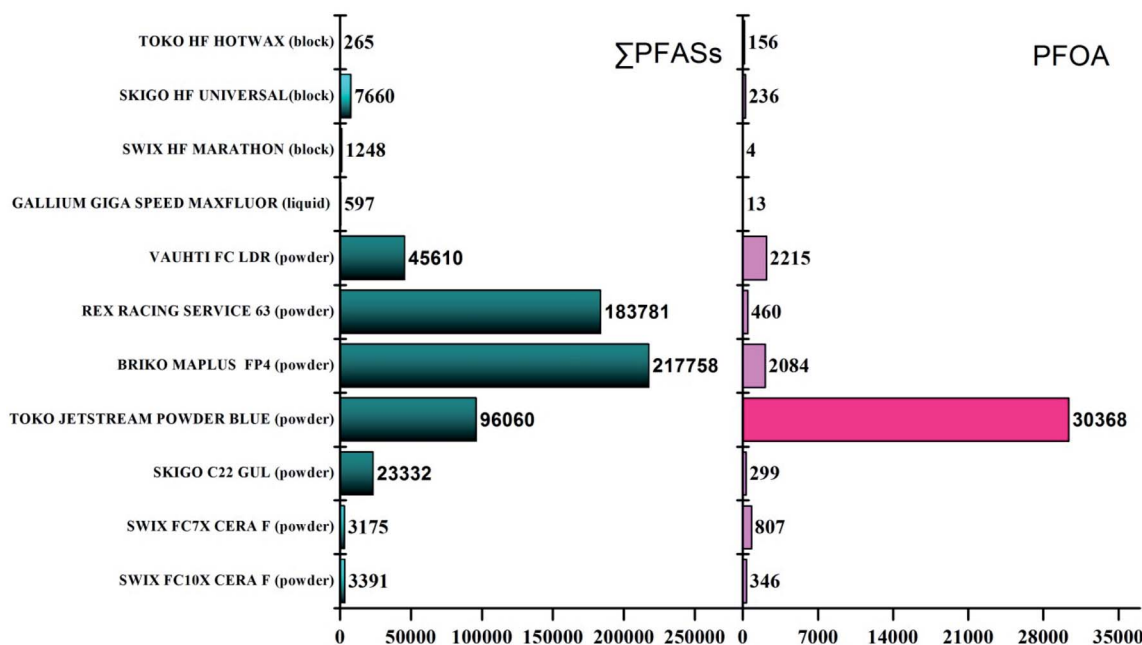


Fig. 1 Σ PFAS and PFOA concentrations (ng g^{−1}) in the eleven commercial ski wax products purchased from a Norwegian retailer in 2019. Concentrations exceeding the highest calibration point are marked with darker colours.



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 ($3.5\text{--}30\,368\text{ ng g}^{-1}$) were higher than in waxes analysed in 2010 by Plassmann *et al.* ($29\text{--}12\,000\text{ ng g}^{-1}$)³ and Freberg *et al.* ($7.0\text{--}6420\text{ ng g}^{-1}$)⁶ and in 2015 by Blom and Hanssen ($0.97\text{--}92\text{ ng g}^{-1}$).²⁶

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.²⁵ A recent paper noted that the country of origin of the ski waxes in this study, Norway,²⁷ was indeed international leaders in terms of protecting the environment and human health from potential harmful exposures from fluorinated ski waxes. The Norwegian ski wax manufacturer, SWIX, was also commended in the article²⁷ 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”²⁸ 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 2020.²⁴ 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 several years ago indicating no changes in formulations in recent years.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

SU would like to thank the Norwegian daily newspaper, Dagbladet (*via* their owners; Aller Media), for paying for the consumable costs (solvents, standards, *etc.*) of the chemical analyses. We also like to point out that the results were previously published and discussed in Dagbladet¹³ (in Norwegian) as part of series of articles focused on fluorinated ski waxes on 20th November 2019.

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