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KJ2900 – PFAS release from ski wax and methods of determination for use in sports

Bachelor's project in Chemistry

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Abstract

PFAS are a group of pollutants that can be released into the environment from their use in ski waxes. PFAS can potentially bioaccumulate and can possibly also biomagnify. It has been shown that they can have adverse effects on animals and humans. Due to this, the use of these substances will be banned from skiing competitions. It is important to have analytical techniques that can detect potential competitors who attempt to avoid the ban. Multiple techniques have been proposed. There is still need for further testing to be able to enforce the ban.

Introduction

In recent years there has been an increased focus on the use of per- and polyfluoroalkyl substances (PFAS)^[1]. PFAS are recognized as persistent organic pollutants (POPs) and certain PFAS, like perfluorooctane sulfonic acid (PFOS) and others, are recognized under the Stockholm Convention to be eliminated from use^[1]. Concerns about PFAS are that they can persist in the environment over many years^[2] and that they can bioaccumulate in organisms and remain with long half-lives^[3]. This is potentially dangerous because a number of PFAS, like PFOS, are linked with a number of health conditions in humans^[3]. Further studies on wildlife have shown that PFAS substances bioaccumulate in the environment^[4], and that the effect of this could lead to behavioral changes and hormonal imbalances in affected animals^[5]. It seems likely that the release of these substances into the environment can have negative consequences for wildlife and for people.

One of the uses of PFAS in consumer products are in the use of ski waxes^[6]. The hydrophobic properties of the fluorinated alkyls are excellent at improving the glide of the skis in wet snow^[6]. It has been found however that abrasive friction between skis and snow may be a leading cause for loss of ski wax during a ski race^[7], and that this is a possible reason for the release of PFAS into the environment^[2]. Further the application of ski wax onto skis can release PFAS as aerosols, and this can be an important factor in human intake both for hobby skiers and professional ski waxers^[8].

Due to the concerns described above the international ski federation (FIS), implemented a ban on fluorinated ski waxes from the season 2019/2020^[9]. However as there were delays in implementing proper methods for qualitatively analyzing fluorine content in the ski wax, it was decided to delay the implementation of the ban until the season 2020/2021^[10]. With the implementation of the ban approaching, as of the writing of this, there are still questions about how the implementation of the ban is going to be carried out. Some results coming back from the testing of the analytical equipment have been reported to have mixed results^[11].

For the sport it is important to have proper methods of analysis to enforce this ban. Because of the excellent gliding properties of fluorinated ski waxes^[6], it is possible that competitors might attempt to cheat in competition by using them despite of the ban. For the sport there is a desire to be able to detect and disqualify competitors who attempt to use banned substances prior to the start of the race^[12].

This project will try to show that the use of fluorinated ski wax is a source of PFAS pollution in the environment, is a source of exposure to humans, that this has potentially harmful consequences, and compare and evaluate different methods that have been discussed as analytical methods for the enforcement of the fluorine ban.

Theory

PFAS are widely used in a number of commercial products. One important application is in ski waxes^[13]. Due to the high stability of carbon-fluorine bonds, PFAS can persist in the environment^[14]. Studies of the composition of ski wax has found that even with increasing focus on these substances there has still not been much change in the levels found in ski waxes^[15]. Some background on why PFAS have favorable properties in ski wax will be given, and why this is concerning from an environmental standpoint before explaining proposed methods of analysis.

PFAS in ski waxes

PFAS are widely used in ski waxes. When gliding, friction creates a layer of water under the skis^[7]. When attempting to improve glide the surface interface between the skis and the snow or water is important. It is therefore a challenge to be able to get ski wax that can bind effectively to the surface of the skis that also is able to effectively repel water and snow^[7]. The advantage of fluorinated carbon in ski wax is that it can attach to the ski while it is highly hydrophobic. This is then used to decrease surface tension under the skis^[7] and therefore reduce drag as the energy to break the surface decreases^[16]. Studies aimed at measuring the hydrophobic properties of ski wax have found that the hydrophobic properties do not increase linearly with the fluorine content, but that a maximum can be found at somewhat lower concentration^[7]. The studies also found that the hardness of the wax increased with increasing chain length and with increasing fluorine content^[7]. The cause of the increases in hardness, but not the hydrophobicity is that the surface may be saturated and the formation of micelles occur^[7].

The temperature has a large impact on the wax. As temperature falls the snow becomes much harder^[17]. To decrease the abrasive friction between snow and ski wax it becomes necessary to use a harder wax for lower temperature^[17]. Studies have found that this correlates with waxes in commercial use, that waxes for colder environments are harder, and that waxes with longer alkenes are harder^[6]. It has also been found that because in a colder environment less water is formed between the skis and the snow, the hydrophobic properties of fluorocarbons

are less important, and hardness dominates^[7]. This means that the fluorine content may be lower, or not included, in harder ski waxes^[7]. For warmer, wetter, and therefore less hard snow however, fluorinated wax may be useful^[7].

PFAS and abrasive friction

The wear on skis are determined by the abrasive friction on the skis^[17]. When skiing this is an effect of the different hardness between the snow and ski-wax^[17]. This has the effect of wearing down the layer of wax and depositing it on the snow^[2]. After a while it can be seen that the concentration of wax on the ski has decreased, and on certain areas of the ski surface the presence of wax is not detectable^[17]. Studies in skiing areas have found that the concentration of PFAS in the track is greatest near the starting line and that this gradually decreases with distance^[2-3]. This can be correlated with the loss of fluorinated ski wax that was observed in the study of ski wax wear.

Spread of PFAS in nature

There have only been a few studies examining the ski sports role in spreading PFAS in the environment that have been conducted near ski resorts and ski races to the authors knowledge. One study found that the concentration of the longer chain PFAS were detected mostly at the surface snow and soil, and at the start of the race^[3]. Similar results were found in a study of per-fluorinated carboxylic acids (PFCA)^[2]. Shorter chained PFAS were found in soil samples taken deeper into the ground^[2]. In general, the water solubility is lower for longer chained fluorocarbons. This is maybe a reason why the longer chains were found on the surface, while shorter chains were removed through meltwater^[3]. A sample taken from shallow groundwater indicated concentrations of PFAS, possibly because it was carried by meltwater^[3]. It was observed that the levels of PFCA contamination possibly indicate that they do not degrade over a season, and that this could contribute to higher levels^[2]. Another study found that PFAS levels in air near a skiing resort were comparable between the active- and off-season, but that the composition of the air changed drastically between the seasons and that the predominant PFAS in the active season corresponded with the predominant PFAS found in a number of common ski waxes^[18]. This indicated that skiing activity could be related to some release in the active season, but that there is some other emission in the off-season^[18].

Bioaccumulation

Studies have been conducted to identify the biological effect of PFAS, but only one study by Grønnestad et al.^[4] has been conducted in a skiing area to the authors knowledge. The

presence of PFAS on the surface or in the upper levels of soil in skiing areas have potential implications for wildlife and for human populations. The concern that PFAS contamination can persist over many years^[2] have led to a study of the potential for biomagnification^[4]. Bioaccumulation is a substance's ability to accumulate in an individual organism, while biomagnification is the increase of a pollutant in individuals going higher up in the food chain^[19]. To find signs of bioaccumulation the concentration of PFAS was measured in the soil near a ski center. Then a number of earthworms and bank voles were collected, euthanized and the levels of PFAS were measured^[4]. This was done because if the PFAS are biomagnifying, the diet of the earthworms should expose them to higher concentrations of PFAS than the reference soil, and the bank voles who eat earthworms should have higher concentrations. It was found that there was a larger concentration of PFAS in the earthworms than in the soil samples, and there was a larger concentration for certain PFAS in the bank voles than in the earthworms^[4]. This could indicate a degree of biomagnification^[4]. It was also noted that it was found a very large mixture of different PFAS, who all were under any toxic limit, but who as a mixture could have adverse effects on the voles. Much of the bank voles' diet is however roots and plants, and this could have lowered the number of worms eaten, thus hiding some of the effect. Further studies of animals higher up in the food-chain are needed^[4].

Effects on humans

Concerns have been raised about human exposure to PFAS. People who are especially at risk are those who work with the application of ski wax^[8]. During the application of ski wax, hot irons are used for melting the ski wax or ski powder. This has the ability of vaporizing volatile components of the wax and forming aerosols^[8]. Blood tests were taken at the end of and before the start of two successive seasons. This showed that PFAS levels dropped between seasons. The same PFAS were found in the ski wax, samples of aerosols in the air of waxing cabin, and blood samples from the professional ski waxers^[8]. It found that the levels of PFAS in the blood samples were lower at the beginning of the second season were lower than at the end of the first. Further it was found that certain PFAS concentrations were higher in older ski waxers than younger and this could indicate bioaccumulation^[8]. This is concerning because exposure might be correlated with health conditions like diabetes and obesity^[20].

Effects on animals

Several studies have been carried out on the possible effects of PFAS on organisms. A follow up study by Grønnestad et al. in the same area as the research into bioaccumulation^[4] investigated the effect of the PFAS concentration on the animals^[5]. A number of substances in the brain regulate important body functions. One notable substance is dopamine. Dopamine is important for controlling many functions in the brain, like fear or anger responses. When the voles from the earlier study was tested for levels of PFAS and dopamine a correlation was found between PFAS and higher levels of dopamine. Longer chain length seemed to have a stronger relation than shorter. It was also found that the ratio of dopamine to its metabolites, that break down the substance, was higher. Further dopamine is important for regulating hormones in the body and it was found that testosterone levels were lower^[5]. Another study on male lab rats that were fed perfluorooctane sulfonic acid PFOS observed a similar increase in dopamine, and a decrease in the ratio to its metabolites^[21]. Another study on frogs did not show the same results, indicating that the effect is species specific^[5].

Analytical methods for determination

Several analytical methods have been proposed for the determination of fluorine in ski waxes. However, not many sources are available explicitly about analysis of ski waxes in a sports context.

The most common method of PFAS determination is the use of chromatography coupled to a mass spectrometer^[22]. Commonly high pressure liquid chromatography (HPLC) is used for the analysis of ionic non-volatile components, while gas chromatography (GC) is used for more volatile uncharged components^[22]. There are a large number of identified PFAS substances and approximately 5000 have been identified^[22]. With PFAS being spread in the environment it can be found in a large number of different matrices. With proper sample collection and preparation chromatography can be used to determine PFAS concentration even in very dilute amounts^[23]. This has made the technique very useful in environmental studies where concentrations are often low.

A challenge of chromatographic detection is that a large number of precursor PFAS have unknown structures, and the wide category of PFAS leads to difficulty in developing a method for all analytes in a sample^[24], many times only selected analytes are determined^[22, 25]. Some methods have been developed to gain more information on PFAS samples. It has been proposed that a coupled ICP-MS for elemental analysis, with an ESI-MS for compound

specific analysis can be used for the determination of unknown substances in PFAS mixtures^[25]. An alternative method has been proposed where ion mobility spectroscopy (IMS) separation can be used to help identification of PFAS^[26]. Here the particles are ionized and vaporized, then under an electric field the particles migrate through an inert gas and are separated based on their cross sectional area^[26]. This can also be fed into MS with very little additional time, allowing more information on the size of the particle and potentially separating two substances with very similar retention times under chromatography^[26].

An alternative method of determination of fluorine is its absorption in the infrared (IR) spectrum. One method is Attenuated Total Reflectance Fourier-Transform Infrared Spectrophotometry (ATR-FTIR)^[27]. Here as the sample is radiated by a beam of light, there occurs absorption from functional groups of the sample and this is recorded^[28]. This allows for determination by observing absorbance in wavenumbers between 1400-1100 cm^{-1} ^[14]. In this region C-F bonding can absorb and a clear peak can be observed. It is also possible to develop instruments that are light enough to be field portable^[29]. This method has been used to verify the presence of C-F bonds in ski wax and showed clear difference between fluorinated and non-fluorinated ski-waxes and ski-powders^[27]. This method has also been used for tracking the amount of fluorine with distance^[17]. A study on aqueous pollutants found that ATR-FTIR had detection limits on an order of millimolar concentrations, while coating the ATR crystal with a layer of adsorbent substance that absorbed to a target analyte could lower the detection limit to micromolar concentrations^[29].

X-ray fluorescence (XRF) has been proposed as a method of surface determination of fluorine^[30]. XRF functions by radiating X-rays onto a sample analyte. This ionizes the inner shell electrons of a target atom which will then become unstable. As an outer shell electron enters a lower energy orbital it will emit X-ray radiation and this can be recorded^[31]. When analyzing lighter elements, the emitted X-rays might be absorbed in air. This causes problems for analysis of fluorine because vacuum is needed for analysis^[31]. Heavier elements may also absorb emitted X-rays from fluorine but lighter elements did not have large effect^[32]. Lab based XRFs have been used for the determination of fluorine in different soil matrixes^[33]. Traditionally XRF has been a lab based technique, but field portable alternatives are available and used in the environmental analysis of heavy metals^[34]. Developments of field portable XRF devices have detection limits close to those of larger lab based XRFs^[35]. Development of portable XRFs for the study of light elements seem to be difficult and these devices are not available^[36]. Laser induced breakdown spectroscopy (LIBS) has the ability to screen for the

lighter elements and handheld portable versions have been developed ^[36]. However, fluorine releases light in the vacuum UV range which might require a vacuum to create a good signal^[37]. LIBS has not been discussed in the context of ski wax fluorine determination to the authors knowledge.

The FIS has asked for the development of a fluorine tracker to be the primary fluorine test device ^[10]. This is still in development and very little information is available on its current status at the time of writing this thesis was written. To the authors knowledge only one article discusses the working principle of the testing device. It functions on the basis of “Selective Broadband Reflection and Adsorption Spectroscopy”^[27] SBRAS^[27, 38]. Here the sample is radiated by a wide range of light waves in the UV, visible, and infrared spectra. The device then uses a number of sensors to determine the reflected and absorbed light. A computer learning algorithm then uses the information from the sensors to determine the surface concentration of fluorine compounds ^[38].

XPS has been used for determination of fluorine on ski wax surfaces ^[7]. For calibration of the fluorine tracker it is also used as a standard ^[38]. XPS also has been used to determine fluorine on other consumer product surfaces ^[20]. XPS has a penetration depth of only 0.01 µm and therefore gives very little information of the composition of the whole sample except the surface ^[20]. XPS also uses a vacuum during analysis ^[20]. To the authors knowledge XPS has not been discussed in relation to fluorine analysis in ski waxes.

Discussion

The use of fluorinated ski wax has been very common. It is therefore important to determine if this plays a detrimental role in the environment. The ski sport has decided to ban fluorine from use in competitions. Because fluorinated waxes are effective it is possible that competitors will want to cheat by using the banned substances. For this it is important to have effective analytical techniques that can detect and disqualify cheating athletes. It is preferable to be able to detect potential cheaters already before the start of a race. Therefore, the techniques are evaluated also on their ability to return quick results in field conditions.

PFAS in nature from ski wax

Several studies have found that PFAS have excellent properties for gliding on wet snow ^[6], and that the fluorine content is very important for some of the properties of the ski ^[7]. However it has been found that friction between wax and snow causes loss of wax with the

distance traveled ^[17]. This together with studies near ski tracks and resorts has found that PFAS in the environment is also correlated with the distance into a track ^[2-3]. Another study found that the composition of PFAS pollutants in air was correlated with the activity of skiing ^[18]. It is therefore reasonable to believe that skiing is a source of contamination in these areas as wax wears off the ski with contact to the snow. When the same skiing areas as in previous studies were examined after melting of the snow it was found to be elevated levels of PFAS were found in the environment ^[2-3]. This could then indicate that the PFAS contaminants are carried with meltwater into other environmental matrixes.

Grønnestad et al. studied potential biomagnification of PFAS near a skiing area. It was found that as there was PFAS in the soil, there was also higher concentrations in animals, increasing higher up the food chain ^[4]. This could indicate that the breakdown of PFAS are slow, and that as animals eat each other the levels build up. It was found that there was a mixture of different PFAS in the collected animals ^[4]. This could indicate that many PFAS substances have substantial half-lives and could explain why many PFAS were seen, and not just the a few of the most stable. However more research could be needed in this ^[4].

This large amount of different PFAS could have a detrimental effect on animals. It has been found that PFOS in male rats causes hormone disturbances ^[21]. Further it was shown by Grønnestad et al. that in the animals collected in the biomagnification study ^[4], the hormones in the brains of the animals also were disturbed ^[5]. This means could mean that potentially harmful effects on wild animals can result from release of PFAS in nature.

PFAS exposure has also been shown on people associated with application of ski wax professionally^[8]. It is believed that PFAS may enter the body via breathing if there are aerosol particles in the air, this might be formed during ski wax application ^[8]. Due to this there is a health risk associated with ski waxing. Many studies have linked PFAS with detrimental health effects ^[20]. It is therefore possibly beneficial for the ski waxers if fluorinated compounds are banned from competition and phased out from amateur use as this could help reduce levels of PFAS in their blood.

It seems likely that PFASs application in ski wax could explain the elevated levels in areas near ski resorts. By applying PFAS waxes to skis it is possible this makes its way into the environment after separating off the skis due to friction. The compounds could also have potentially harmful effects on animals in the wild while remaining with long half-lives. Further during waxing of the skis, it is possible for the person applying the wax to inhale

PFAS aerosols, and this is thought to be detrimental to a person's health. The decision to ban fluorine from ski waxes can therefore be seen as an attempt to limit these substances from humans and to try and keep them out of the environment. Fluorocarbons very good gliding properties therefore could potentially induce someone to cheat by applying wax that is not allowed. There is therefore a need for testing to prevent people from using fluorine in ski waxes.

Comparison of analytical methods

Several analytical methods have been considered. Chromatography is the most commonly applied method of determination of PFAS [22]. It is very versatile and therefore it is commonly used [23]. Some challenges are associated with the use of chromatography as a method. It is not desirable to wait a long time for sample analysis but the methods developed by Plassmann and Berger [23] had retention times up to near 9 minutes. With large international competitions if this method is required before start this could mean that many competitors would have to queue waiting for analysis, or that there would have to be many parallel chromatographs increasing equipment cost. Another problem with chromatography for determination is that a sample has to be taken from the ski. This is problematic as it is likely that competitors would object to let a sample their newly waxed skis as it might ruin the glide on the snow. The preparation of the sample might also need to be conducted in a laboratory, meaning that it is not fit to be used for field tests. This means that chromatography might not be preferable as a means of determining fluorine before a competition, but it might be a supplemental technique to test skis after a race. Using ICP-MS elemental analysis is possible [25], this can then be used to find fluorine content if it is present.

FTIR is a potential analytical method as it is commonly used in many laboratories, and transportable versions exist [27]. ATR-FTIR suffers from some problems as a method of determination. While FTIR is a non-destructive, surface active technique that does not disturb the wax layer, it is also not very selective towards fluorine [27]. While fluorine can be determined by the absorption specter it is also possible for other functional groups to have similar absorption to the one from fluorine. This means that it is difficult to say if the absorption in this area is due to fluorine or from another substance in the wax. If the method is to be used to disqualify potential cheaters it must be used together with an alternative method to guarantee that the competitor is not wrongfully disqualified. If another method can be used to give a less ambiguous result it would be preferred to use this instead of ATR-FTIR if they are similarly quick.

XRF has also been proposed as a method of analysis. For on-site determination, a handheld or portable XRF would be preferable. While XRF offers a good way to measure for fluorine ^[33], it can be limited by other factors. One important factor is the atmosphere. Since fluorine is a light substance in terms of atomic weight it gives low signal ^[32], this is complicated further by elements in air that can absorb X-rays emitted from fluorine to give an even worse signal ^[31]. It is therefore necessary to keep the samples in a vacuum during analysis. This is problematic because it is costly and hard to create, especially for handheld devices. A proposal has been to take a sample from the ski and analyze later ^[30] but this creates the same problem as for chromatography and skiers will likely not risk ruining the applied wax. The difficulty of creating a vacuum in field is problematic and might also be a reason XPS and LIBS have not been discussed as potential analytical methods.

Due to the limited knowledge of the fluorine tracker that is being developed it is difficult to say how effective it might be. More information is needed from the producer before a judgement can be made. Some tests that have been conducted have shown mixed results ^[11]. This shows that there are still problems with development, but it is not possible to say why these mistakes were made. The fluorine tracker still promises to be a cost effective, non-destructive, handheld, and sensitive method of analysis. If this is achieved, it would be a very good analytical tool.

For this bachelor thesis, several proposed analytical methods have been shown and compared. The different proposed solutions came with different drawbacks. For chromatography, a sample had to be taken from the skis. This might not be acceptable for competitive skiers due to possibly interfering with the ski wax. If the sample also has to be prepared prior to analysis this method is perhaps not applicable in the field analysis before start but can be a supplemental method after goal. XRF has been shown to be able to detect fluorine in lab-based equipment, but the handheld devices are not good enough to be able to detect fluorine in normal atmosphere. If samples must be taken to be able to analyze under vacuum it is possible that athletes will object. It is also possible the samples cannot be analyzed in the field before start and must be taken to a lab for analysis. FTIR and the fluorine tracker are both portable, applied directly to the surface without disturbing the wax layer, and quickly returns a result. All these traits are desirable for the testing of ski wax prior to the start of the race. The problem with FTIR comes with a potential lack of selectivity. If FTIR identifies too many false positives this might limit its usefulness. Too little is known about the fluorine tracker to make a proper assessment of its potential as an applied analytical method in this case.

Conclusion

PFAS are a group of substances with good gliding properties when used in ski wax. However, during skiing the wax will wear off and be deposited in the environment, which could be detrimental to animals. People who work with applying these waxes as a job or as part of their hobby are also especially at risk. By banning the substances these effects can be stopped but the gliding properties of PFAS can create incentives to cheat.

To stop cheating several methods of analysis have been proposed. It is desirable to be able to detect and disqualify cheating athletes prior to the start of a race. Chromatography is the major method used for determining PFAS in environmental samples due to its high sensitivity, and its ability to separate complex mixtures. If a chromatographic technique is used it is possible its use in the field is limited by the need to prepare the samples prior to injection increasing testing time, and possibly not being possible in a field setting. There could also be objections due to the need to take a sample from the applied wax. XRF is also proposed but suffers from problems related to fluorine being a low mass atom. This makes it difficult to determine fluorine without controlling the atmosphere the target analyte is placed in, this is however difficult to do in the field and sending a sample to be tested in a lab is maybe not sufficient for disqualifying cheaters before the start of a race. FTIR is proposed as a possible alternative because it is a portable and widely used technique already, however it is possible that it is not selective enough towards fluorine that it is applicable as a technique here. Lastly the fluorine tracker is being developed for the purpose of being a fast method for stopping cheating. There is however not very much information available around it, and this makes any judgement difficult at the present moment.

If a method of analysis that is fast, does not need a sample of the applied wax and is relatively inexpensive this is the preferred option.

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