Footprints in the snow
Hazardous PFCs in remote locations around the globe
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Searching for Clues

Outdoor brands and their suppliers rely upon stunning natural images of lonely, pristine mountain lakes and remote snowy mountain ranges climbed by famous out-door adventurers’ for their advertising. Yet the chemicals used to make their products weatherproof are leaving an indelible footprint in the remote mountainous regions so loved by outdoor enthusiasts.

To search for clues about the extent that these chemicals are contaminating these pristine environments, Greenpeace undertook eight expeditions to remote mountainous areas on three continents. Snow, and

PFC in an outdoor-jacket
How a jacket is put together – and where the PFCs are

in some places water samples, were taken at a total of 10 locations and analysed for the presence of environmentally hazardous per- and polyfluorinated chemicals (PFCs). An array of scientific studies suggests that the PFC problem is nowhere near to being solved.1 Greenpeace now wants to raise awareness among outdoor enthusiasts and the wider public with this unique, globally organized study tour.

PFCs are used in many industrial processes and consumer products, and are well known for their use by the outdoor apparel industry in waterproof and dirt-repellent finishes. They are used for their unique chemical properties, especially their stability and their ability to repel both water and oil.

However, PFCs are environmentally hazardous substances, which are persistent in the environment.1 Once released into the environment they break down very slowly; they can remain in the environment for many years after their release and are dispersed over the entire globe. These pollutants are found in seeped mountain lakes and snow from remote locations, they accumulate in living organisms such as the livers of polar bears in the Arctic and also in human blood.2 For some PFCs there is evidence that they cause harm to reproduction, promote the growth of tumors and affect the hormone system.3 Previous Greenpeace research found PFCs in the wastewater of Chinese textile factories,4 in wild fish that are caught for consumption in China5 and in eels from eleven European countries.6 In other studies PFCs were even detected in drinking water.4 In reports from 2012 and 2013,7 8...

9  OECD (2013), op.cit.
Greenpeace found that PFCs are routinely present in outdoor clothing and shoes and showed that volatile PFCs can evaporate from these products into the air.

1 "Long-chain perfluorinated compounds" refers to Perfluorocarboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA); Perfluoralkyl sulfonates (PFAS) with carbon chain lengths C8 and higher, including perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic sulfonic (PFOS).


4 German Federal Environment Agency (Umweltbundesamt), 2009. op.cit.


6 German Federal Environment Agency (Umweltbundesamt), 2006. op.cit. The development of cell tumours has been observed in animal tests. When products containing PFCs are disposed of, the products that contain them. They can be present in wastewater from factories but also from domestic washing machines, not all PFCs can be removed from wastewater in sewage treatment plants. Some PFCs have the potential to evaporate during production and to a lesser extent from the finished products. When products containing PFCs are disposed of PFCs can enter into groundwater and surface water when such products are landfilled.

1.2 The expeditions

Greenpeace organized these expeditions to some of the most beautiful and unspoilt regions on three continents to draw attention to a long standing, but little known and certainly unsolved problem. In May and June 2015, eight Greenpeace teams were equipped with PFC-free clothing and undertook expeditions to remote mountainous areas on three continents: to take snow, and in most cases water, samples for laboratory analysis.

For the selection of sampling sites remote but accessible locations were chosen. One key criterion for snow to be sampled was that the snow had been recently deposited (this winter). Another key criterion was for the snow to have been untouched since it fell. The snow must not have had the potential to be influenced by local sources of PFC, such as settlements, skiing activities, hiking paths, cattle, industry, traffic etc. For water sampling, lakes were selected that were not influenced by local sources of PFCs, as far as could be determined.

1.3 Key findings

All results and comparison with previous studies are given in tables in Annex. The eight Greenpeace expeditions in 10 countries took place in May and June 2015. They show clearly that PFC chemicals are widely detected in remote locations across the globe and that inputs to these remote locations have occurred even as recently as the winter of 2015. PFCs do not occur naturally and should therefore not be found in remote wilderness regions. Nevertheless, they can travel around the world in the atmosphere, either as gas or bound to dust particles, until they are washed out in rain or snow. It is noteworthy that PFCs were detected in snow samples from all the sites. The highest concentrations were in the samples from the High Tatras in Slovakia, the Sibillini Mountains near Lago Pilato in the Italian Apenines and the Alps (Macun Lakes in the Swiss National Park).
The substances with the highest concentrations in snow were the long chain PFCAs PFNA (C9-PFC), with values up to 0.725 ng/l and PFHpA (C7-PFC) which was detectable in significant concentrations of up to 0.319 ng/l in the snow.

The levels found (0.034 – 0.219 ng/l of PFHpA, and up to 0.775 ng/l for PFNA) are comparable to other studies which analysed surface snow in the Tibetan mountains (PFHA: 0.241 – 0.924 ng/l) and Antarctica (PFNA: 0.204 – 1.14 ng/l).

Comparable studies of snow in European remote areas in Europe show that levels in snow from Sweden were 0.0021 ng/l for PFHpA, 0.0169 ng/l for PFNA, and 0.0659 ng/l for PFOA while snow from the Alps contained up to 0.20 ng/l for PFNA and 0.23 – 0.65 ng/l for PFOA.

1 Wang et al (2014); op. cit.
2 Cai et Al (2012); op. cit.
6 Kevis et al (2013); op. cit.
7 Kirchgeorg et al (2013); op. cit.
8 Cordingley O (2014); op. cit.
9 Kirchgeorg T (2013); op. cit.

In this current study PFOA was detected in samples from Slovakia (0.107 and 0.348 ng/l), Switzerland (0.087 ng/l) and Italy (0.209 ng/l). PFOS was detected in samples from Italy (0.024 ng/l). The snow sampled at an altitude of over 5000m in the Haba Snow Mountains in China contained the lowest concentrations, with only the sulfonic 8.2 TS faintly detectable. This compound has not been reported in previous studies.

The concentrations of short chain PFCs were found in snow samples from six of the locations. For example, the fluorosulfonic acid (C4) was detected in the snow samples from Trento, Greece (Wiborg et al, 2011). PFHxA was detected in samples from Treriksrød and Alp (Kirchgeorg et al, 2013). These concentrations of short chain PFCs were detectable in similar studies. However, in studies from Switzerland, Shortchain PFBA and the Alp’s short chain PFBA (C4) was found. This compound was not detected in the samples from Greenpeace’s expeditions in Europe.

The concentrations of short chain PFCs in the water of most remote lakes are higher than those of long chain PFCs, in water samples from Patagonia, Russia and Switzerland, the short chain C4, C5 and C6 compounds are particularly clearly dominated with concentrations of up to 1.1 ng/l.

These findings are within the range of concentrations reported in previous studies from lake water analysis in the USA** or in Austria/Alps.** However, in these studies the concentrations found are predominantly higher than those in the samples collected by Greenpeace.

Box 1 PFCs in remote areas

The long range transport of some PFCs to remote areas has been studied scientifically for several years. Particularly those PFCs known to have toxic properties such as the long chained perfluorinated alkyl acid PFOA or sulfonate PFOS are commonly found in snow and water. Studies discuss three possible ways that PFCs are distributed in the environment. Some PFCs can bind to suspended particulate matter which is transported through the atmosphere and washed out and deposited in rain and snow. Volatile compounds such as polyfluorinated fluorotelomer alcohol (PFHxA) and sulfonate can be transported in the atmosphere over long distances. They are called precursor substances, as their transport is subject to atmospheric oxidation, transforming them into accumulatively perfluorinated alkyl acids or sulfonates which can then be deposited in high mountains. For example, finally, ocean currents may play an important role by transporting PFCs globally, for example to the Arctic and Antarctic.


1.4 The ‘great outdoors’ a growth industry

Positive images of beautiful mountain landscapes, majestic forests, freshly fallen snow and clean rivers, are heavily promoted by manufacturers of all weather clothing to market their products. The growing interest in nature and outdoor activities means that outdoor clothing is the fastest growing segment of the global sports apparel market, with the global market estimated at US$ 35 billion in 2012.

While PFCs are used in many industrial processes and consumer products, a major use is in protective treatments for textiles, used throughout the outdoor industry.* Outdoor clothing companies are also aware of the inherent contradiction of this practice and are worried about their image. The manufacturers claim to have made an appropriate response to the problem by phased out particularly harmful substances such as the long-chain PFCs (C8 and longer, including PFOA and PFOS) and replacing them with short-chain C4 to C6 PFCs. However, these chemicals are also persistent and may exacerbate the problem of PFC pollution; they need to be used in larger quantities than the equivalent C8 compounds to achieve comparable performance. Many of them are more volatile and mobile and therefore have the potential to disperse rapidly in water and air across the globe. The limited steps taken by the outdoor industry so far are nowhere near sufficient to protect the remote natural areas and water bodies which are heavily promoted as positive images of beautiful mountain landscapes, majestic forests, freshly fallen snow and clean rivers.
As this report demonstrates, volatile PFCs have a small selection of PFC-free products in their collections. Meanwhile, Jack Wolfskin and Vaude have published credible Detox Commitments with Greenpeace. This corresponds to about 15 percent of global textile production revenue.

Some other outdoor companies such as Paramo, Pyua, Rotauf, Patagonia, Salewa and Mammut have also made significant commitments to eliminate hazardous chemicals from their production and products by 2020. More than 30 international fashion brands, sportswear brands and outdoor brands such as Lidl and Penny have published credible Detox Commitments with Greenpeace. This corresponds to about 15 percent of global textile production revenue.

Their way, some are transformed into more dangerous and persistent PFCs, which will contaminate the environment for many years. Once released, it is impossible to control PFCs. Volatile PFCs are being used by outdoor brands today to make their products weather resistant. These brands use images of pristine nature in their advertising and promote their “sustainable” products. At the same time, they are contributing to the distribution of hazardous chemicals such as PFCs to the farthest corners of the planet.

Both the outdoor industry and political decision makers urgently need to ensure that the well-known and controversial long chain PFC chemicals are not substituted with larger quantities of the lesser known volatile or short chain PFCs. There is no need to risk greater contamination of the environment with PFC chemicals as alternatives that completely avoid the use of any PFCs are already available for many applications in outdoor clothing, as demonstrated by their use in these expeditions.

Outdoor brands must make a genuine and credible Detox commitment to stop using hazardous chemicals – with ambitious schedules and concrete measures that match the urgency of the situation and short-term deadlines for completely phasing out the use of all PFCs in products and production processes. This will send an important signal to the chemical industry to increase its efforts on the further development of non-hazardous alternatives.

To be credible, the commitment to eliminate PFCs must include transparency, to ensure that data on the discharge of hazardous chemicals into waterways by suppliers is published on a global online platform and to demonstrate the progressive reduction of their use. This kind of data is being published by other companies so there is no excuse for outdoor brands not to make sure that their suppliers disclose this kind of data and allow everyone, including local populations, the right to find out which chemicals are being released.

Political decision makers must also take action. In view of the hazardous properties of many PFCs, including the potential for volatile substitutes to transform into persistent PFCs, it is no longer enough to only regulate a small number of individual substances such as PFOA and PFOS. The precautionary principle must involve an examination of the full range of alternatives, including, where necessary, substitution through the development of sustainable alternatives where they do not already exist.

Greenpeace calls on policy makers to fully implement the Precautionary Principle by restricting the entire group of PFCs. To make this happen, pressure from the public is vital – from nature lovers, outdoor and wilderness enthusiasts such as climbers, skiers and walkers, to city dwellers and families – anyone who cares about the future of our wild places and our own health and environment. If we do not act now to stop the spread of PFCs across the planet, contamination could build up to much greater levels, adding to the pollution that will need to be dealt with in the decades to come. The outdoor industry and the politicians need to hear your voices, to urge them to take action on the elimination of ALL PFCs.

Environment

PFCs are released into the environment during the manufacturing of textiles, as well as during the use and disposal of products containing PFCs. These substances can reach our bodies when we breathe air containing PFCs or when we ingest food, drink water, or through exposure to house dust.

Industries

PFCs are used in several industries, and are released to the environment during manufacturing processes and during the use and disposal of products containing PFCs. Once in the environment, PFCs spread globally.

Outdoors-gear

Apart from textile and outdoor products, PFCs are used in a variety of other products. But for volatile PFCs (FTOHs), information summarized by the Danish Ministry of Environment shows that about 50% of the production (5,000 t) goes to the impregnation of textile consumer products.

1 Precautionary Principle: This means taking preventive action before waiting for conclusive scientific proof regarding cause and effect between the substance (or activity) and the damage. It is based on the assumption that some hazardous substances cannot be rendered harmless by the receiving environment (i.e. there are no ‘environmentally acceptable’ or ‘safe’ use or discharge levels) and that prevention of potentially serious or irreversible damage is required, even in the absence of full scientific certainty. The process of applying the Precautionary Principle must involve an examination of the full range of alternatives, including, where necessary, substitution through the development of sustainable alternatives where they do not already exist.
2. PFCs – pollutants in weather-proof clothing

PFCs are all man-made; there are no natural background levels of PFCs. Yet PFCs have been found throughout the natural environment, from industrial areas to the remote wildernesses of the Arctic and Antarctic, and in the air, water and living beings of these ecosystems. PFCs do not stay in manufacturing facilities or in the products that contain them. They are released into the air and water from manufacturing sites, from the clothing that we wear and wash, from the fire-fighting foams that are used to train firefighters and combat fires, from carpets, electronics and a vast number of other sources. They can then travel via air and water currents to all parts of the earth.

The very strong chemical bond between carbon and fluorine in the PFC molecule ensures that natural processes can only degrade these substances extremely slowly. They may stay in their original form or they may transform into other types of PFCs, but ultimately they take a very long time, some of them an extremely long time, to break down. This means that what we release into nature today will stay there for the foreseeable future.

In 2012 and 2013 Greenpeace Germany conducted investigations which showed that most of the outdoor sector relies on per- and polyfluorinated chemicals (PFCs) to make outdoor gear waterproof and that they are present in a range of outdoor products, for example rain jackets and trousers, leather gloves, shoes and finally also in swimwear. Other studies have also found PFCs in water proofing sprays, ski wax and sleeping bags. The second Greenpeace study also found that long chained PFCs – such as PFOS and PFHxA which are now regulated in some countries – are increasingly being replaced with short chained PFCs which are more volatile. The report demonstrated, using test chamber experiments, that these short chain PFCs do not remain in the clothes, but evaporate into the air. In addition, as they are less effective waterproofing agents, they are used in larger volumes than long chain PFCs. It has been shown that there are higher concentrations of volatile PFCs in the air in stores selling outdoor clothing than those without outdoor gear.

PFCs have been detected in the environment around the globe – in animals, in human blood and in breast milk. Some accumulate in food, in drinking water and in the air we breathe, and thus can pass into the body. In earlier research, Greenpeace found certain PFCs in wastewater from Chinese textile factories and in wild fish which are also caught for consumption in China. PFOS, PFHxS and several other PFCs have also been detected in drinking water and in food from Chinese textile factories.

References:
Footprints in the snow — PFCs in the snow and water of remote regions

The snow and water of remote mountainous regions should be pristine and untouched; however, recent scientific studies that examined snow and water samples show that PFCs have left a chemical footprint that reflects the changing patterns of their use. Studies of the Canadian Arctic show PFCs in high ice caps where the only possible source is atmospheric deposition, and that degradation of the volatile PFCs FTOHs and FSAs into the more persistent PFCs NEFOSA and PFOSA is occurring in the Arctic enviroment.

However, there are currently no limits set for the use of any PFCs by any industry, despite concerns about their hazardous nature and the fact that they can commonly be found at far higher concentrations in textiles.

2.1. PFCs — global travelers

An array of scientific studies suggests that the PFC problem is nowhere near to being solved. Greenpeace does not consider short-chained PFCs as a safe alternative to the less volatile PFCs and FSAs, due to their potential to transform into persistent PFCs, as well as the lack of information about the direct hazards of some volatile PFCs.

Only one PFC, PFOA, has so far been classed as a persistent organic pollutant (POP) under the Stockholm Convention, a global treaty that requires contracting parties to take measures to restrict the production and use of POPs.

The marketing and use of PFOA within the EU has been prohibited for certain uses since 2008, with a proposed ban on all use of PFOS within the EU has been proposed by the European Commission under the Sixth Amendment to the Stockholm Convention.

Norway is the first country where the sale of textiles containing PFOA is prohibited, with a limit of 1 μg/m² from June 2014, and further regulations and administrative provisions of the European Commission under the Sixth Amendment to the Stockholm Convention.


Box 3 Footprints in the snow — PFCs in the snow and water of remote regions

Water and snow contamination in remote mountainous regions should be pristine and untouched; however, recent scientific studies that examined snow and water samples show that PFCs have left a chemical footprint that reflects the changing patterns of their use. Studies of the Canadian Arctic show PFCs in high ice caps where the only possible source is atmospheric deposition, and that degradation of the volatile PFCs FTOHs and FSAs into the more persistent PFCs NEFOSA and PFOSA is occurring in the Arctic enviroment.

However, there are currently no limits set for the use of any PFCs by any industry, despite concerns about their hazardous nature and the fact that they can commonly be found at far higher concentrations in textiles. In Europe, the transformation of recently deposited volatile PFCs into more persistent PFCs is also apparent in the melting snow of a boreal forest in Scandinavia and in the European Alps, where volatile PFCs have been shown to accumulate in the atmosphere over the winter months and be washed out with spring snow.

This study also provides evidence of the changing composition of PFCs in snow (from PFOAs to compositions to PFOA-dominated compositions). The levels of PFCs in Tibetan mountain snow are lower than in European Alps, but still reflect the changing patterns of PFC production and use in the Northern Hemisphere; notably, samples from Lake Namco (‘Heavenly Lake’) show a recent accumulation of short chain PFCs from sources in India. Interestingly, Gore-Tex, the leading manufacturer of membranes for outdoor wear, currently using PFC technology, sponsored a 2014 expedition led by a Chinese philanthropist to ‘clean up Heavenly Lake.’

Winding the future of PFCs

The majority of outdoor products such as clothing, tents and backpacks are made in China, but the bulk of them produced for export to Europe, Canada, the United States and other countries such as Russia, Turkey, Taiwan, Korea, Chile and Argentina. All these products will eventually reach the end of their useful lives and end up either in incinerators or in landfills. During their lifetime and on disposal, depending on the method of waste treatment, large quantities of PFCs could be released from these products collectively into the air or washed into surface waters or groundwater. It is predicted that the maximum levels of PFOA in the environment will be reached by 2040, even though this chemical is becoming subject to some restrictions.

It is conceivable that the use of short-chain PFCs in much larger quantities could create greater pollution of the global environment for decades into the foreseeable future.

References

1 OECD (2013), op.cit.
Who hasn’t dreamt of visiting the untouched wilderness of the Himalayas, the Andes or the Altai Mountains, to hike or climb in these incredible natural landscapes. In few places in the world the snow is purer than at more than 5000 metres above sea level in China, or the water cleaner than in a clear mountain lake far from civilization in the Altai Mountains. Very few nature lovers would expect persistent and hazardous chemicals to be found in such places. Greenpeace organized these expeditions to some of the most beautiful and unspoilt regions on three continents to draw attention to a long-standing, but little-known and certainly unsolved problem.

In May and June 2015, eight Greenpeace teams on three continents took water and snow samples to be tested for PFCs. Some of the expeditions were very demanding, with extreme weather conditions and climbing challenges. Others were pleasant walks, with breathtaking scenery and wildlife.
Leonel Mingo (Greenpeace campaigner) and Roberto Roa (Greenpeace Chile logistics team) walked more than 64 kilometers in the Torres del Paine National Park in Patagonia to collect snow and water samples from the mountains and lakes. At night the temperature dropped to minus 13 degrees centigrade and wind speeds reached more than 80 kilometers per hour.

“We completed the sampling successfully but then we had to get out quickly because a snowstorm was approaching fast and it was totally dark,” says Leonel Mingo. “We began a six-hour descent from the mountain in extreme weather in the middle of the night. We could not break to rest because we risked freezing every time we stopped. We could see only a few meters ahead of us with our head-lamps."

When Mingo and Roa finally reached their tents after the twenty-hour trek, they fell asleep right away, still fully clothed. “Apart from the wind and cold, it was a great experience,” said Mingo.

In the Chinese Naxi language “Golden Flower” is the highest of the Haba Mountains. It lies on the banks of the “Golden Sand” river; rare animal and plant species thrive on its slopes and in its gorges. The main peak of the mountain is 5396 m high, where it is freezing cold and the air is thin. In 1999 Zhong Yu became the first woman to climb the mountain, together with her mountain guide Haosi. Sixteen years later the two of them returned to the summit of “Golden Flower” — this time with a Greenpeace team.

Some things have changed. China leads the world for producing the most perfluorocarbons for all kinds of applications. The smog in China’s cities has become denser and the pollution of air and water has increased. Tourism in the Haba Mountains has become professional and an increasing number of mountain climbers have left their tracks.

Another change is in the clothing worn by the two pioneers. For her first climb, Zhong Yu wore a cotton jacket with a broken zipper. Haosi wore sneakers — without socks. This time, they wore warmer and drier PFC-free outdoor clothing and were accompanied by Lei Yutung, head of research at Greenpeace Asia. From their base camp at 4,000 metres, they set out at dawn to climb a further 1,000 up the mountain, to collect the samples and return to camp by sundown.
The Altai is a high mountain region in Central Asia with peaks of up to 4,506 metres, in the borderlands of Kazakhstan, Russia, Mongolia and China. It extends from taiga (swampy coniferous forest) and alpine meadows to glacier zones, high mountain tundra and steppes. The Greenpeace team climbed to Lake Verhnemultinskoe in the Katunskiy biosphere reserve. The Golden Mountains of Altai are a UNESCO World Heritage Site because they are home to rare and endemic flora and fauna. “People told me that if I ran into a bear, I should start to sing,” said Nina Lesikhina, Greenpeace Russia’s expert on chemicals. But the Greenpeace team only came across the fresh tracks of bears, as well as foxes, rabbits, and squirrels. The people who live in the area were very friendly and interested, and concerned about the quality of water in their mountain lakes.

In the Slovak Carpathians Greenpeace colleagues Branislav Blascak and Matej Hlinican visited the remote High Tatras Mountains. They trekked up the Zabia Bielovodská valley (also known as the “Whitewater Valley of Frogs”) to a height of 1722 metres. The High Tatras national park is closed to all tourist activities during the winter season. The valley is situated within a protected area (classified as 5th degree, which is the highest level of protection) and so is permanently closed to all tourists.

Blascak said: “It was a unique feeling to visit this place (with permission from the National Park) and do sampling work. It was also not easy as there were no trails and we had lot of equipment. On top of that it rained all day long. In the valley there was still lot of snow; we had to cross the snow fields very carefully because the lakes are right underneath. Any mistake would have meant big trouble and a fall into the cold 4 degree water. Still, it was a pleasure for us to do this trip.”
"I’m back from a spectacular trek to one of the most beautiful and remote places in the Alps," said Manfred Santen, Greenpeace Germany’s expert on chemicals. Together with Mirjam Kopp, project leader of the current Detox campaign, and Thom Mueller, Santen collected samples of snow and water at the Lakes of Macun in the Swiss National Park.

“It is a paradox that the outdoor industry claims to love nature, yet leaves traces of persistent chemicals in pristine natural areas,” said Santen. “We want to show how widespread these hazardous chemicals are - even in areas far away from civilization and dirty industries.”

This Greenpeace team also made it home warm and dry in outdoor clothes that are PFC-free – despite encountering almost every kind of weather, from sunshine to rain, snow and sleet.

Switzerland
Swiss National Park Macun Lakes
Snow and water samples taken at 2,600 meters

Italy
Monti Sibillini National Park Umbria (Apennines)
Samples (snow, water) taken at 1,950 meters

Lago di Pilato (Pilate’s Lake) at the foot of the Pizzo di Diavolo (Devil’s Peak) rock formation is of great interest to biologists. The shimmering turquoise lake, only 500 meters long, is the habitat for an endemic crustacean called Chirocephalus marchesoni, a freshwater shrimp about 10 mm long. It is found nowhere else in the world. Giuseppe Ungherese (toxics campaigner) and Luca Nicolini (volunteer) from Greenpeace Italy were concerned about disturbing these creatures during sampling. However, the park authorities assured them that at this time of year, Chirocephalus marchesoni only dwells at the bottom of the lake.
The Kackar Mountains near the Black Sea are known among enthusiasts for lonely high-altitude hikes between lakes, streams and springs. A four-person Greenpeace team collected samples of water and snow from four pristine places – from lakes to a glacier summit. On the way they saw a wolf pack and came across bear tracks.

Turkey
Rize-Çamlıhemşin and Erzurum Moryay-la-Yedigöller area Kackar Mountains
Samples of snow and water taken between 2,980 and 3,400 meters

The Kackar Mountains near the Black Sea are known among enthusiasts for lonely high-altitude hikes between lakes, streams and springs. A four-person Greenpeace team collected samples of water and snow from four pristine places – from lakes to a glacier summit. On the way they saw a wolf pack and came across bear tracks.

Sweden/Finland/Norway
Treriksroset (Three-Country Cairn) in Scandinavia
Samples taken at 511 metres at Kiruna Övre Soppero in Sweden, at 616 metres at Skibotndalen Troms fylke in Norway, and at 742 metres at Kilpisjärvi Enontekiö in Finland.

The Detox expedition team hiked to the summits of three mountains (one in Sweden, one in Norway, and one in Finland) near the Treriksroset monument (Three-Country Cairn) marking the point where the borders of these three countries meet. “The beauty of the remote Scandinavian mountains is breathtaking. For three stunning and adventurous days our small but determined Detox expedition team hiked to the top of three mountains in the area of the Three Country Cairn. Under the midnight sun and with the curious company of reindeers, we crossed rivers and walked on snowshoes to collect the snow samples we needed,” said Therese Jacobson, leader of the Scandinavian expedition.
4. Samples and Results

Eight Greenpeace teams were equipped with PFC-free clothing and backpacks and sent on expeditions to the most pristine places in their respective regions, which took place in May and June 2015. The teams collected snow and water samples.

4.1. Methodology in brief

Specially pre-cleaned glass bottles were used for the sampling, which were previously cleaned and heated in the investigation laboratory (for details see Annex). The bottles were wrapped individually and transported in PFC-free polyethylene bags. All auxiliary items required for sampling were also pre-cleaned, individually wrapped in aluminum foil and transported in PFC-free polyethylene bags.

On arrival at the sampling point, the first step was to ascertain that the existing snow was untouched. The sample of snow was taken near the surface with pre-cleaned small stainless steel blades. Two wide mouth 2.5 litre bottles were filled with snow, while attempts were made to compress the snow to achieve the highest possible sample volume. The water samples were filled directly from the lake shore in 1 litre glass bottles. Again, two bottles were filled.

Four snow samples (duplicates) were collected from the expeditions in the Haba Snow Mountains (China), the High Tatras (Slovakia) and the Alps (Switzerland) and each duplicate was analysed separately. Two duplicate water samples were collected from the expeditions in the Haba Snow Mountains (China), the Altai Mountains (Russia) and Patagonia (Chile) respectively, to improve the detection limit the two samples were combined into one for each location. Only one water sample was collected from each of the expedition in Turkey and Italy.

For all the snow and water samples, in all locations apart from Turkey, field blanks were taken in order to determine if any contamination had occurred during the sampling, or as a result of the equipment used. In each case one 2.5 litre (for snow) or a 1 litre (for water) glass bottle, identical to that used to collect the samples, was transported to and opened at the sampling site and resealed. In the laboratory the bottles were rinsed with purified water which was subsequently analysed in an identical way to the samples.

The closures of all sample bottles were sealed at the sampling site, firstly with a layer of pre-cleaned aluminum foil, a screw cap, and then externally sealed with self-sealing thermoplastic film (parafilm), with one exception: all the bottles from the expedition in China were finally sealed at 4000 metres, because the bottles had to be opened briefly and reclosed twice on the way down to equalize pressure. Samples were sent to an independent accredited laboratory for analysis. Further details of the methodology are in Annex. PFCs were found in several remote areas visited by these expeditions. Short chain PFCs such as the PFBS (C4 PFC) are particularly apparent in the snow samples from Treriksroset in Scandinavia, while the short chain PFCs found in the samples from the Swiss Alps and the High Tatras in Slovakia were dominated by PFHxA (see chart in Annex).

The highest concentrations of individual PFCs were detected in the samples from the Swiss Alps, the High Tatras in Slovakia and the Italian Alpennines, with the highest concentration (0.775 ng/l) in snow found for the long chain PFNA (C9 PFC). The lowest concentrations were found in snow sampled at an altitude of over 5000m in the Haba Snow Mountains in China.

4.2 Results and their interpretation

All results of the snow and water sampling are listed in Annex, where a comparison with previous studies on snow and water sampling is also provided.

The following are selected highlights from the data. Concentrations are given without subtraction from field blank data; these are provided in the tables in Annex. Sample concentrations that are below field blank concentrations are not reported. In cases where the PFC concentrations are close to the detection limit or to the levels in the field blanks, these are mentioned below.

PFCs were detected in samples from all sites, from the 5000m peaks of the Shangri-La region in China to Tierra del Fuego in southern Chile, clearly showing that PFC chemicals are widely detected across the globe and that contamination of these remote locations has occurred even as recently as the winter of 2015. Short chain PFCs were found in several remote areas visited by these expeditions. Short chain PFCs such as the PFBS (C4 PFC) are particularly apparent in the snow samples from Treriksroset in Scandinavia, while the short chain PFCs found in the samples from the Swiss Alps and the High Tatras in Slovakia were dominated by PFHxA (see chart in Annex).

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The highest concentrations of individual PFCs were detected in the samples from the Swiss Alps, the High Tatras in Slovakia and the Italian Alpennines, with the highest concentration (0.775 ng/l) in snow found for the long chain PFNA (C9 PFC). The lowest concentrations were found in snow sampled at an altitude of over 5000m in the Haba Snow Mountains in China.
The lake water samples show persistent PFC chemicals that have accumulated over the years, resulting in concentrations that are significantly higher than the snow samples, with concentrations of short chain PFCs in the water of most remote lakes higher than that of long chain PFCs.

The aim of this investigation was to provide a snapshot of PFC contamination in these remote areas. Because only single samples have been analysed (with some exceptions where duplicates were conducted), a statistical analysis would not be meaningful.

Several sampling conditions could have influenced the data presented in this report, which is important to keep in mind when making comparisons of PFC levels between sites and with previous studies from the scientific literature. Conditions such as the weather, season, altitude and distance from point sources can all affect the levels and composition of PFCs in samples. However, we are confident that the overall data set in this study confirms the presence of short and long chained PFCs in snow and lake water samples from remote areas across the world.

Snow samples PFCs were detected in snow samples from all sites. The highest concentrations of individual PFCs were found in samples from the High Tatras (Slovakia), the Apennines (Italy) and the Alps (Switzerland), all of which were dominated by the long chained PFC (C9) PFNA (Perfluorononanoic Acid).

The substance PFHpA (Perfluorohexanoic acid) was found in samples from all locations, apart from China. The levels found (0.034 – 0.319 ng/l of PFHpA, and between limit of quantification and 0.755 ng/l for PFNA) are comparable to other studies which analysed surface snow in the Tibetan mountains (PFHpA: 0.241 – 0.982 ng/l) and Antarctica (PFNA: 0.0188 – 1.142 ng/l).

Long chain PFCs in snow samples
- In Patagonia, Chile, three long chain PFCs - PFUnA (C11, 0.090 ng/l), PFTrA (C13, 0.305 ng/l) and PFTeA (C14, 0.021 ng/l) – were found in snow from the Altai Mountains, Russia.
- The samples from the High Tatras (Slovakia) were dominated by the long chained PFC (C9) PFNA at concentra-
Findings of this study show the relative amounts of different PFCs in the snow samples. The concentrations found are lower than in a comparable study.\(^1\) In one of the two snow samples from the Alps in Switzerland, PFPeA (C\(_5\)-PFC) was detected in the reference sample (field blank). The concentration of PFPeA was 0.07 ng/l and PFHxA (C\(_6\)-PFC) was detected in the sample present. However, the levels of PFPA (C\(_5\)-PFC, 0.04 ng/l) and PFHxS (C\(_6\)-PFC, 0.07 ng/l) that were found are comparable to the findings from the other Greenpeace expeditions.

**Water samples**

Seven out of the eight expeditions took samples of lake water from remote mountain areas, from the Haba Snow Mountains in China; the Altai Mountains in Russia; the Kackar Mountains in Turkey; the High Tatras in Slovakia; the Macuner lakes in the Swiss Alps and Lake Pilato in Apennines (Monti Sibillini Italy). Unlike the snow samples collected in this investigation, which predominantly contain PFAS that were deposited in the months prior to sampling, lake water samples will have accumulated concentrations of PFCS over years. Two duplicate samples from each location were analysed from the Macun lakes in the Swiss Alps and from the mountain lake in the High Tatras in Slovakia. The samples of lake water from China could not be evaluated, as higher concentrations of the target substances were found in the field blank sample.

**Long chain PFCs in water samples**

The only location where PFOS (C\(_6\)-PFC) was clearly detected in the samples was the Macun lakes in the Swiss Alps, with concentrations of 0.561 ng/l and 0.335 ng/l in the two samples collected from this site. However, PFOS was also present in the corresponding reference sample (field blank) at 0.248 ng/l. In the two samples from this site, the very per-sistent and toxic PFOS was also found at 0.035 ng/l and 0.089 ng/l, PFNA (C\(_5\)-PFC) at 0.140 ng/l and 0.233 ng/l, and PFDA (C\(_6\)-PFC) at 0.041 ng/l and 0.051 ng/l.

Lake water from the High Tatras (Slovakia) also contained PFOS at 0.030 ng/l in both samples collected at this site. PFNA (C\(_5\)-PFC) was also found at 0.117 ng/l and 0.118 ng/l, together with PFDA (C\(_7\)-PFC, 0.047 ng/l and 0.048 ng/l), PFPeA (C\(_5\)-PFC, 0.021 ng/l and 0.022 ng/l), and PFNA (C\(_6\)-PFC, 0.031 ng/l).

The sample of lake water from China could not be evaluated, as higher concentrations of the target substances were found in the field blank sample.
These findings are within the range of concentrations reported in previous studies from lake water analysis in the USA or in Austria/Alps. However, in these studies the concentrations that were found are predominantly higher than in the samples collected by Greenpeace; one reason could be that these expeditions sampled in more remote areas. The results of the water sample from the Kackar Mountains in Turkey should be interpreted with caution, as no reference sample was taken. However, the PFCs which were detected above the lowest quantification limit (PFHxA, PFHpA, PFOA, PFDA and PFBS) are in line with the concentrations measured in samples from the other expeditions.

Figure 3 short chain PFCs in water (ng/l)

Figure 4 short chain PFCs in water (ng/l)

Short chain PFCs in water samples
With the exception of China and Chile the C7-PFC PFHpA was detected in samples from all sites in a concentration range from 0.084 to 0.319 ng/l (Switzerland). The results for the sample of lake water from China could not be evaluated, as higher concentrations of the target substances were found in the field blank sample.

- The C4-PFC PFBA was found in the sample from Patagonia (Chile) at concentrations of 1.118 ng/l.
- The lake sample from the Altai Mountains in Russia also contained PFBA at 0.605 ng/l.
- There was also clear evidence of PFBA in one of the two samples from Macun Lakes in the Swiss Alps, which contained 0.773 ng/l. Another C4-PFC, PFBS was also found, with levels of 0.056 or 0.075 ng/l and the C6-PFC PFHxA was found at concentrations of 0.127 and 0.156 ng/l respectively, in the two samples from this site.

- PFBS was also found in the sample from Lago Pilato in the Italian Alps (at 0.121 ng/l or 0.216 ng/l) and the C6-PFC PFHxA was found at concentrations of 0.083 and 0.087 ng/l.
- PFBA was also found in the sample from Lago Pilato in the Italian Alps (at 0.121 ng/l or 0.216 ng/l) and the C6-PFC PFHxA was found at concentrations of 0.083 and 0.087 ng/l.

These findings are within the range of concentrations reported in previous studies from lake water analysis in USA or in Austria/Alps. However, in these studies the concentrations that were found are predominantly higher than in the samples collected by Greenpeace; one reason could be that these expeditions sampled in more remote areas.

- The results of the water sample from the Kackar Mountains in Turkey should be interpreted with caution, as no reference sample was taken. However, the PFCs which were detected above the lowest quantification limit (PFHxA, PFHpA, PFOA, PFDA and PFBS) are in line with the concentrations measured in samples from the other expeditions.

The outdoor industry stands for freedom and love of nature, the ‘great outdoors’. It uses images of beautiful mountain landscapes, majestic forests, freshly fallen snow and clean rivers, to market its products. These positive images are heavily promoted by manufacturers of all-weather clothing and have brought strong double-digit growth in recent years. The global market was estimated in 2012 at US$ 25 billion in 2012, with the European market estimated at around 4.8 billion euros in 2014.\(^1\) Within Europe, Germany has the biggest market, with a turnover of over one billion euros, followed by Great Britain, Ireland and France. The most popular products are jackets and trousers (50 percent) followed by shoes (25 percent) and backpacks (6 percent). Consumers are often prepared to pay hundreds of euros for an extra warm Supranxt, unlike the trend for cheaper ‘fast fashion’.

The VF Corporation, owner of the world’s largest outdoor apparel company The North Face reported revenues of US$ 1.9 billion in 2012.\(^2\) Brands such as The North Face, Patagonia, Vaude or Jack Wolfskin are no longer only aimed at mountain climbers or skiers. The industry has evolved from a specialist supplier to manufacturers of trendy everyday clothes, with their stores now a part of every city. Jack Wolfskin has 200 of its own stores between the North Sea and the Alps, while in China it distributes its products in more than 300 shops.

The outdoor industry: still at base camp on corporate responsibility for PFC pollution

Outdoor products are promoted with images of deep snow skiers or fearless climbers – despite the fact that most customers are not exceptional athletes, but city dwellers who simply want to stay warm and dry on a bike ride or an autumn hike. Children’s clothing is also sold with “high performance” finishes – although it is more often used in the rain and mud, in the sandpit or in the playground. Nevertheless, the industry has started a veritable arms race to ensure that its clothing can always resist the most extreme weather conditions found in the ‘great outdoors’ that represents the brand’s biggest selling point. This unfortunately results in an increasing chemical burden, especially with the controversial PFCs.

The global spread of toxic chemicals in the textile industry is the focus of the Greenpeace’s Detox My Fashion campaign. Clothing companies that commit to Detox, undertake to eliminate hazardous chemicals – including PFCs – from their production and products by 2020. More than 30 international fashion brands, sportswear brands and discounters such as Lidl and Penny have subsequently made Detox Commitments with Greenpeace (see Box 4 for details) This corresponds to about 15 percent of global textile production by revenue.

Box 4: Examples show PFC elimination is possible

The outdoor sector lags behind other textile companies in acting on PFCs and other hazardous chemicals. The feasibility of eliminating all PFCs is about the actions of fashion brands and budget retailers that have made Detox commitments to eliminate the discharge of all hazardous chemicals by 2020 which they are now implementing.\(^3\) Some fashion brands have already eliminated PFCs from their products and supply chains; H&M was the first brand to deliver on its commitment to eliminate PFCs, reporting that as from January 2013 all PFCs have been eliminated from their products, and Mango delivered on its commitment to eliminate PFCs in all products produced and sold by July 2013. Some sportswear companies – which also make outdoor products – have also made Detox commitments. Puma commits to eliminate all PFCs by the end of December 2017 and the adidas Group will ensure that all of its products will be at least 99 % PFC-free by no later than 31 December 2017. Of the sportswear companies, only Nike has failed to make a credible Detox Commitment to eliminate all PFCs. Retailers such as Lidl, Aldi and Rewe have already phased out PFCs from the production of rainwear especially for children and have recently committed to the elimination of 100 % of all PFCs. Despite the lack of credible action from outdoor brands, there are signs that some brands are already working on PFC-free products – for example, in 2013 Jack Wolfskin published a case study on Subsport demonstrating the successful use of an alternative product that does not use PFCs.\(^4\)

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6. Greenpeace conclusions and recommendations

Both the outdoor industry and political decision makers urgently need to ensure that the well-known and controversial long chain PFC chemicals are not substituted with the lesser known volatile or short chain PFCs, used in even larger quantities to ensure similar functionality to long chain PFCs. There is no need to risk greater contamination of the environment with any PFC chemicals since alternatives that completely avoid the use of PFCs are already available for many applications in outdoor clothing, as demonstrated by their use in these expeditions.

Since 2011, Greenpeace’s Detox My Fashion campaign has been working to ensure that hazardous chemicals are removed from the entire manufacturing supply chain of the textiles industry. The outcome of this investigation underlines the need for all PFCs to be eliminated by all sectors, not only textiles; in particular, the outdoor clothing industry urgently needs to take action to eliminate the entire group of PFC compounds. Regrettably, there is not one outdoor brand among the 16 companies that have committed to zero discharges of all hazardous chemicals by 2020 and are acknowledged Detox Leaders.¹

As global players, outdoor companies such as The North Face, Jack Wolfskin, Patagonia and other companies have an opportunity and the responsibility to improve manufacturing practices in their supply chains. Brands must make a genuine and credible commitment to stop using hazardous chemicals – with ambitious schedules and concrete measures that match the urgency of the situation. In particular, outdoor clothing brands must set short-term deadlines for completely phasing out the use of all PFCs in production processes. As prominent users of PFCs, these brands need to take the lead on the elimination of all PFCs; this will send an important signal to the chemical industry and other innovators to increase their efforts on the further development of non-hazardous alternatives. Phasing out PFCs by 2020, as some outdoor clothing brands aspire to do, is not ambitious enough. PFC-free materials are already available today that are suitable for most applications and other companies, some of which also produce outdoor clothing, such as Puma and adidas, have adopted much more ambitious elimination targets for PFCs; others, such as H&M and Mango have already eliminated PFCs in their products.²

Transparency

On the road to clean production, outdoor clothing brands must commit to greater transparency. For every product in which hazardous chemicals are found there is a factory releasing unknown quantities of these substances into the surrounding environment. Where are these factories? Which hazardous chemicals are being used by suppliers and emitted at their sites? What volume of chemicals does this involve? Greenpeace is calling on all businesses in the industry to publish precise information on the hazardous chemicals released in wastewater from all production facilities, factory by factory, and chemical by chemical. This kind of disclosure is not an unrealistic expectation, as some in the industry would claim; several fashion brands e.g. Mango, G-Star, Inditex, Puma, Levi’s and Fast Retailing/Uniqlo have already ensured the publication of data from their suppliers on the discharge of hazardous chemicals into waterways, on a global online platform.³ There is no excuse for outdoor brands not to ensure that their suppliers disclose this kind of data. As long as the textile industry continues to use water-based chemicals instead of using alternatives, including, where necessary, substitution through the development of sustainable alternatives where they do not already exist.

2 See Box 4, Examples show PFC elimination is possible
3 IPE – Chinese Institute for Environmental Affairs; which is the only credible global chemical discharge disclosure platform
4 Precautionary Principle: This means taking preventive action before waiting for conclusive scientific proof regarding causes and effect between the substance (or activity) and the damage. It is based on the assumption that some hazardous substances cannot be rendered harmless by the receiving environment (i.e. there are no “environmentally acceptable”/safe use or discharge levels) and that prevention of potentially serious or irreversible damage is required, even in the absence of full scientific certainty. The process of applying the Precautionary Principle must involve an examination of the full range of alternatives, including, where necessary, substitution through the development of sustainable alternatives where they do not already exist.

1 It’s time to act. It’s time to Detox! www.greenpeace.de/detox
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**Table 1 Results PFCs (ng/l) in snow samples from Greenpeace expeditions into remote areas**
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Table 4 PFCs in water – literature overview for comparison

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References for tables 3 and 4

Method of investigation
Snow and lake water samples were taken by Greenpeace teams at sites classified as remote. Water samples were taken using pre-cleaned 1 litre amber glass bottles. Snow samples were taken using pre-cleaned stainless steel or aluminum shovels and transferred to 2.5 litre pre-cleaned amber glass bottles. The snow inside of the glass bottle was compacted by a pre-cleaned glass in order to maximize the water volume which would result from melting snow later on. With the exception of Turkey, at each site two snow and two lake water samples and one field blank for each matrix were taken. After sampling, glass bottles were covered with aluminum foil and closed carefully by a screw cap and sealed with Parafilm. All samples were transported and stored refrigerated.

Samples were extracted applying an analytical method optimized for larger water volumes of up to 2 litres. The optimized method based on the accredited routine method for the analysis of PFAS in water samples which is routinely applied for rather small water volumes. The optimization mainly referred to the selection of suited solid phase extraction (SPE) adsorbents and suited materials and equipment for filtration as large sample volumes may result in SPE cartridge clogging. Furthermore, PFC analyses were accompanied with an elevated number of laboratory blanks.

Prior to the analysis, samples within the amber glass bottles were weighed. The bottle contents (water) were transferred to pre-cleaned polyethylene beakers. Bottles were rinsed with ultrapure water which was added to the corresponding sample water. Empty glass bottles were weighed again to determine the sample volume on the basis of the mass difference. If the volume of a snow sample was below 1.5 litres, both snow samples of one site were combined in order to enhance the probability of PFAS quantification (snow samples from Chile, Italy, Russia, Finland, Sweden, and Turkey). If snow samples volumes were above 1.5 litres, parallel samples were analyzed separately. With the exception of samples from Russia, China and Chile, parallel lake water samples were always analyzed separately. Taken the results of snow samples, it was decided to combine parallel lake water samples from Russia, China and Chile to enhance the probability of PFAS quantification. Overall, 23 snow and 15 water samples were analyzed (including field blanks).

Prior to the extraction, mass-labelled internal standards (13C4-PFOA, 13C2-PFHxA, 13C8-PFOA, 13C3-PFNA, 13C7-PFDA, 13C3-PFUnA, 13C2-Da, 18O2-PFHxS, 13C4-PFOS) were added to each sample. Samples were left for equilibration for about half an hour and then filtered using pre-cleaned cellulose wool. The wool was slightly dried and then extracted twice by ultrasonication using methanol. The methanol was concentrated to about 1 ml and added to the water phase. Filtered water samples were extracted by SPE. The weak anion exchange SPE was first rinsed with methanol and ultrapure water. After application of the water sample and a washing step with an ammonia acetate buffer, PFASs were eluted using 0.1 % ammonia in methanol. Identification of the individual substances was based on retention times, precursor-to-product ion ratios and peak areas. Quantification was conducted according to the isotope dilution method.

QA/QC
Sample equipment was rinsed with water, methanol, and acetone and then heated to 250°C overnight. Equipment which could not be heated was intensively washed with high purity solvents prior to use. With the exception of Turkey, one field blank per matrix was taken at each site. Separate analytical steps were investigated for their contribution to cause blank contamination.

With each batch of extracted samples, one laboratory blank was analyzed (i.e. overall eight lab blanks). Method quantification limits (MQLs) were calculated on the basis of lab blanks. All results were corrected by the average lab blank.

Instruments were regularly checked. Calibrations were performed using at least 10 calibration points. Calibration was reassessed with each sequence using individual calibration standards. At significant differences, calibration was repeated. Several mass labelled internal PFAS standards were added to each sample to determine individual recovery rates and identify potential retention time shifts. All results were checked for plausibility.

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Abbreviation</th>
<th>Compound</th>
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<tbody>
<tr>
<td>Perfluorocarboxylates (PFCAs)</td>
<td>PFBA</td>
<td>Perfluorobutanoate</td>
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<td></td>
<td>PFBA</td>
<td>Perfluorocarboxylates</td>
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<td>PFHxA</td>
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<td>PFHpA</td>
<td>Perfluorohexane-2-sulfonate</td>
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<td>PFOA</td>
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<td></td>
<td>PFNA</td>
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<td>other polyfluorinated substances</td>
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<td>8:2 FTS</td>
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<tr>
<td></td>
<td>8:2 FTS</td>
<td>1H,1H,2H,2H-perfluorocarboxylate sulfonate</td>
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</table>

PFASs (Table 1) were measured by HPLC/MS/MS (mobile phase methanol/water + HCOOH/ammonia acetate buffer, gradient elution). Identification of the individual substances was based on retention times, precursor-to-product ion ratios and peak areas. Quantification was conducted according to the isotope dilution method.