Cod: 8.6025

AIR SAMPLING FOR PER- AND POLYFLUORINATED CHEMICALS (PFCS) IN STORES SELLING 'OUTDOOR' EQUIPMENT

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Introduction

In previous reports, Greenpeace reported the presence of PFCs in waterproof outdoor gear including jackets and trousers, shoes, backpacks, tents, in leather gloves, and in swimwear (Greenpeace 2012, 2013a, 2013b, 2014, 2016). Among the PFCs found were perfluorocarbonic and perfluorosulfonic acids (ionic perfluorinated chemicals), as well as fluorotelomer alcohols and fluorotelomer acrylates (volatile polyfluorinated chemicals).

It is likely that volatile PFCs such as FTOH used in the production of textiles and which remain as residues in the clothes, are released into the surrounding air. In addition to the tests for PFC residues, in 2013 Greenpeace Germany showed with testchamber testings that PFCs are emitted from the items of clothing, and at what levels (Greenpeace 2013a).

So far, there have been only a few studies on the volatilization of PFCs from textiles (Langer 2010, Schlummer 2013). Some have already shown that there are higher concentrations of volatile PFCs in the air in stores selling outdoor clothing than in rooms without outdoor gear (Langer 2010, Fromme 2015).

In 2016 Greenpeace conducted air samplings in 30 indoor locations, among them 18 outdoor gear selling points, thirteen flagship stores from outdoor brands in Germany (Berlin, Wolfsburg, Hannover), Italy (Milan and Turin), Norway (Oslo), Sweden (Stockholm) and Switzerland (Zürich). In addition air sampling was done in 4 general 'outdoor' stores in Taipei/Taiwan, East Asia.

For comparison air samplings were conducted in office rooms at Greenpeace Headquarters in Hamburg/ Germany and Greenpeace East Asia office in Taipei /Taiwan, with additional testings in storage rooms for tools and outdoor gear at Greenpeace action unit warehouses in Hamburg and Taipei.

Materials and Methods

Method of airsampling for PFCs – longtime sampling

Samples were taken from 17 indoor locations in Germany, Switzerland, Norway and Taiwan.
Active air sampling was performed for 20-30 hours at a constant flow rate of about 9 L/min. Target analytes were enriched on ISOLUTE ENV+SPE cartridges, collection volume was between 11 and 19m³.
Field Blank were analysed for each sampling spot: sampling cartridges were transported to and opened at the sampling spot without collecting air. Concentrations of field blanks were always below the LOQ.
The sampler were placed – when possible - in the center of the rooms, height of air collection between 50cm and 1,5m.
The sampling in stores took place over weekend when the stores were closed
After sampling, the cartridges were tightly wrapped into aluminium foil.

Cartridges were extracted using ultrasonication with methyl tertiary butyl ether (MTBE). . Instrumental separation and detection of the target analytes was carried out by GC–MS in selected ion-monitoring mode using positive chemical ionization.

Method of airsampling for PFCs – shorttime sampling

Samples were taken from 13 indoor locations in Germany, Italy, Norway and Sweden.
Active air sampling was performed for 50 minutes at a flow rate of 0,2 L/min. Duplicate samples were taken and analysed. The total sampling volume was about 10 l. The sampler were placed and carried in a PFC-free linen bag, tube opening reaching out at least 10cm. The sampling was conducted by walking around in the store, by making sure that clothes of sampling persons and the equipment were free of PFCs. The height of air collection was between 50cm and 1m.
Target analytes were enriched on Tenax TA. Additionally field blanks were investigated for each sampling site and a break through experiment was performed. Concentrations of field blanks were always below the LOQ and a significant breakthrough was not observed.

For the analysis of semi-volatile neutral PFASs, the loaded tenax tubes were thermically desorbed (Gerstel TDS A2 / KAS 4). The quantitative analysis was effected by a capillary gas chromatography and mass spectrometer (GC-MS) according to DIN ISO 16000-6. The single substances were quantified with comparative standard solutions using the method of an external standard.

Results and Discussion: Findings of air sampling for PFCs

Samples in four outdoor-brand flagship stores in Europe were collected during closing hours over the weekend. Samples in four general, not brand specific 'outdoor' stores in Taipei/Taiwan were collected during closing and opening hours. Sampling time in all these cases was 20 to 30 hours, the target analytes were quantified after solvent extraction (MTBE) with GC-MS. The findings are given in Fig 1.

Concentrations for the sum of volatile polyfluorinated chemials FTOH and FTA were found in a range from 53ng/m³ to 197ng/m³. Highest concentrations were found in stores in Wolfsburg/ Germany and in Oslo/ Norway. The short chain polyfluorinated telomere alcohol 6:2 FTOH was predominant, in all cases accounting for at least 80% of the total PFCs concentration.
Significantly higher than in reference rooms were the concentrations found for C8-PFC 8:2 FTOH which can be degraded to PFOA which is a substance of very high concern (SVHC) under REACH.
Air samplings in 'outdoor' stores in Taipei / Taiwan show similar concentrations to those found in the samples in Europe, with the highest concentration found being148ng/m³, though with a different pattern; in these cases, long chain PFCs like 8:2 and 10:2FTOH contributed more than 50% to total PFCs.
For comparison, one indoor air sample taken in a 'non-outdoor' textile shop in Taipei showed a total PFC concentration of 2.1ng/m³.

Due to logistical reasons it was not possible to use the long time sampling in all 'outdoor' store locations. Therefore additional a second methodology was tested in 13 stores in Europe. Samples were collected during store opening hours with a sampling time of 50 minutes, using thermodesorption for extraction of the analytes, identification and quantification by GC-MS. The findings are given in Fig 2.

Air samplings in outdoor brand stores in Germany, Switzerland, Italy, Sweden and Norway yielded total PFC concentrations between 15ng/m³ and 297ng/m³, again 6:2FTOH dominates..
For comparison: Total PFCs concentration in indoor air sample taken in a 'non-outdoor' textile shop in Hamburg was below limit of quantification (LOQ = 5ng/m³ for each PFC).

With one exception (297ng/m³), the samples from short time sampling during opening hours show lower concentrations of PFCs than in long time sampling during closing hours. Most likely this is caused by different ventilation conditions, but another reason could be different product portfolios in different brand stores.
Due to logistical reasons it was not possible to sample 'outdoor' stores with both methods at the same time. But two of the investigated stores were sampled with both methods on different days. Total PFCs were detected for longtime sampling the store in Wolfsburg with 197ng/m³ and with 116ng/m³ for short time sampling. In Hannover the longtime sampling gave 176ng/m³, the shorttime sampling 71ng/m³.

Our findings are in a comparable range of concentrations to those that have been reported in previous studies from 'outdoor' stores in Germany (Langer et al 2010: 177ng/m³ - 460,ng/m³; Schlummer et al. 2013: 120ng/m³ - 380ng/m³). However, the Greenpeace study shows a shift from C8-PFCs dominating

to C6-PFCs which are mainly found in samples from Europe. As mentioned above, samples collected in Taipei stores showed different patterns, with C8 substances still dominating.

The concentrations of PFC in stores selling outdoor-gear are 5 to 10 times higher than in office and storage rooms. Six rooms were tested, the concentrations for total PFCs are between LOQ and 10ng/m³, with one exception in an office room in Taipei 28.2ng/m³ were found.

Comparable studies from Fromme et al (2015), Schlummer et al (2013) and Jahnke et al (2007) investigating rooms in residences, offices and schools show similar concentrations mostly in a range from LOQ to values below 10ng/m³.

Outdoor air concentrations are reported to be around 1000times lower in a range from <0.1ng/m³ in air from Atlantic to Southern Ocean (Wang et al: 2015) to <1ng/m³ in German urban outdoor air (Jahnke et al 2007).

Studies on ski waxers exposure to PFCs show that when exposed to per- but also polyfluorinated substances like 6:2FTOH and 8:2FTOH degradation products from these substances can be detected in blood of the ski waxers. However, the concentrations of PFCs in the breathing air at such working places are much higher. than the values found in outdoor stores like shown in this study. Nevertheless it cannot be excluded that customers and especially employees from outdoor stores are exposed not only to volatile FTOH in breathing air but also exposed to their degradation products like corresponding perfluorinated carboxylic acids, among them the toxic PFOA, degraded from 8:2FTOH.

In 2011 Greenpeace started the detox campaign, urging textile brands to eliminate all hazardous chemicals from their supply chain until 2020. Some of the most difficult to substitute chemicals in textile manufacturing are PFCs, used for durable water repellent (DWR) functionality in outdoor gear. The investigations in stores selling outdoor clothing and gear give reason to intensify scientific research on the impact on indoor air quality due to volatalization of PFCs from textiles. To protect employees and clients from unwanted persistent chemicals in breathing air efforts to eliminate PFCs from the production of textiles have to be enhanced.

Acknowledgement: David Santillo (Greenpeace Research Laboratories), Dieter Marchl (Analyse Labor Berlin)

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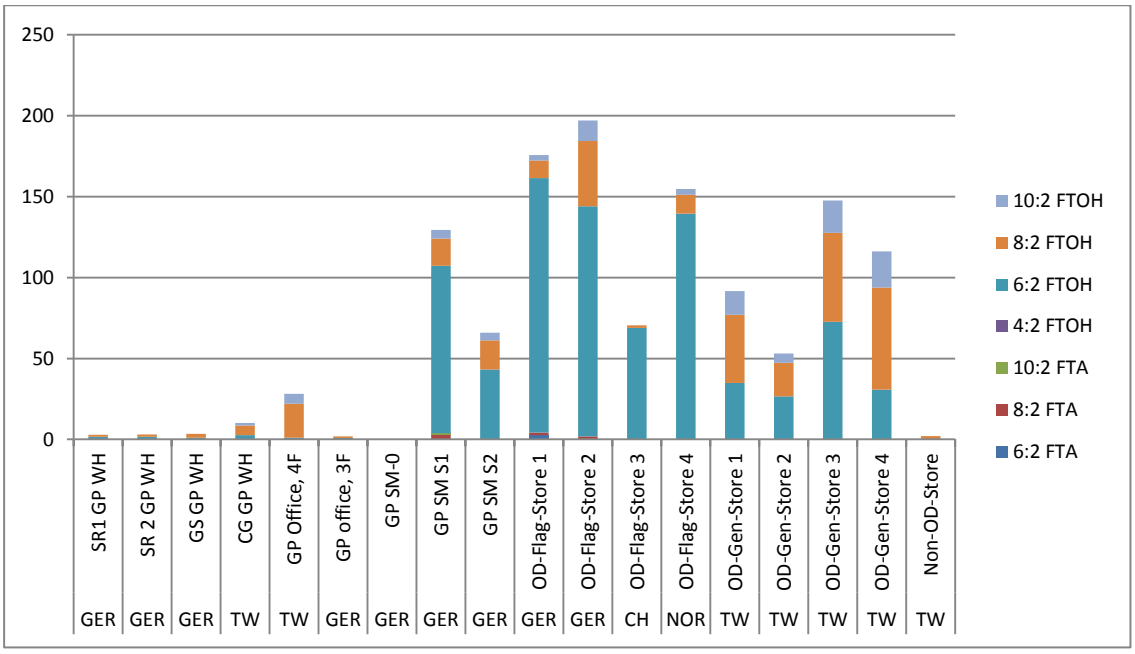
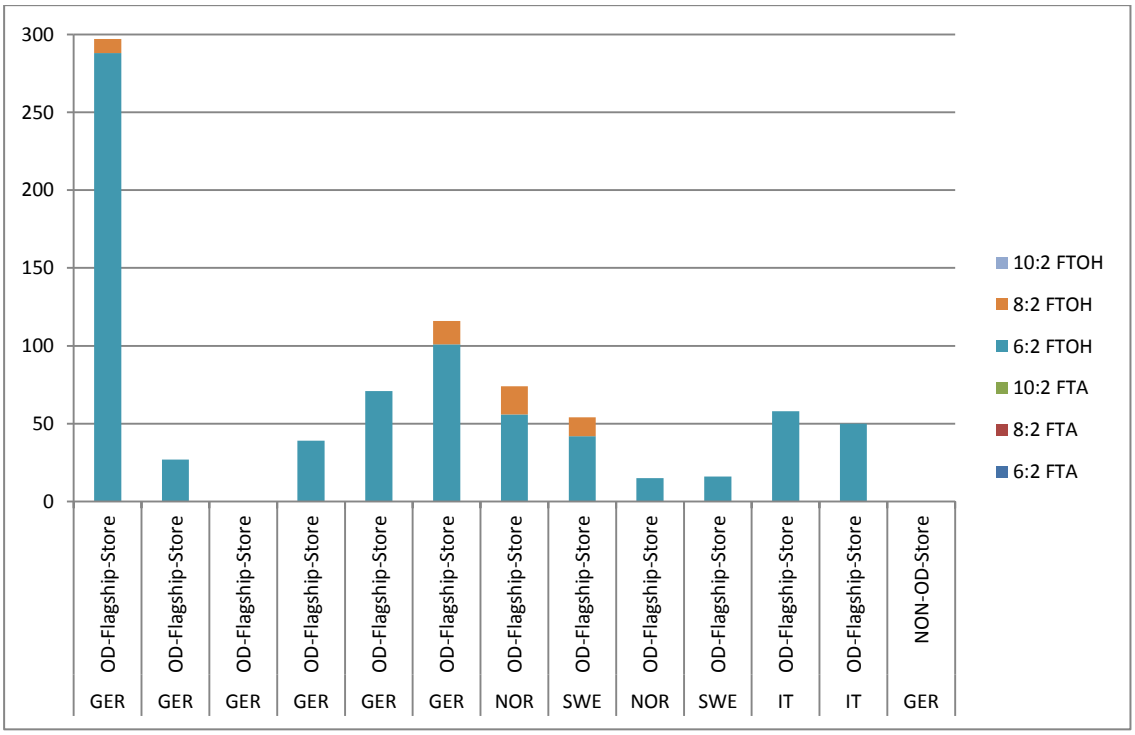
Fig 1: Air sampling Results: Concentration of PFCs in indoor air from 'Outdoor' Stores in Europe and Taiwan (in ng/m³), compared to rooms in Greenpeace offices, long sampling time (20-30 hours)



Legend: SR: Seminar Room, GS: Gear Store, GP WH: Greenpeace Warehouse, GP office: Greenpeace office room, GP SM S1: Small Room at Greenpeace office, GP SM S1 and S2: Small Room at Greenpeace office equipped with 40 samples from product testing 'Leaving Traces 2016', OD Flagship store: brand specific store, OD-General-store: selling point for clothes and gear from several brands, Non-OD-Store: textile store without outdoor gear

Fig 2: Concentrations of PFCs in indoor air from 'Outdoor' Stores in Europe (in ng/m³), short sampling time (50 minutes)



Legend: SR: OD Flagship store: brand specific store, selling point for clothes and gear, Non-OD-Store: textile store without outdoor gear