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An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples

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1 This article describes the optimisation and validation of an analytical method for the determination of
2 volatile polyfluorinated alkyl substances (PFAS) in environmental air samples. Airborne fluorinated
3 telomer alcohols (FTOHs) as well as fluorinated sulfonamides and sulfonamidoethanols (FOSAs /
4 FOSEs) were enriched on glass-fibre filters (GFFs), polyurethane foams (PUFs) and XAD-2 resin by
5 means of high-volume air samplers. Sensitive and selective determination was performed using gas

chromatography/chemical ionisation-mass spectrometry (GC/CI-MS). Five mass-labelled internal standard (IS) compounds were applied to ensure the accuracy of analytical results. No major blank problems were encountered. Recovery experiments were performed, showing losses of the most volatile compounds during extraction and extract concentration as well as strong signal enhancement for FOSEs due to matrix effects. Breakthrough experiments revealed losses for the most volatile FTOHs during sampling, while FOSAs / FOSEs were quantitatively retained. Both analyte losses and matrix effects could be remediated by application of adequate mass-labelled IS. Method quantification limits (MQLs) of the optimised method ranged from 0.2 to 2.5 pg/m³ for individual target compounds. As part of the method validation, an interlaboratory comparison of instrumental quantification methods was conducted. The applicability of the method was demonstrated by means of environmental air samples from an urban and a rural location in Northern Germany.

Keywords: Fluorotelomer alcohols, Fluorooctane sulfonamides / sulfonamidoethanols, High-volume air sampling, GC/PCI-MS, Isotope-labelled internal standards, Matrix effects

Introduction

The recent determination of per- and polyfluorinated alkyl substances (PFAS) in biota from remote regions and even in human blood from all over the world [1-3] initialised much research on possible adverse effects [4,5] and concentrations [6] in organisms. Among these ubiquitously found anthropogenic chemicals are perfluoroalkane sulfonates and perfluoro carboxylates (PFCAs) of four to fifteen carbon atoms chain length. The best investigated compounds of these groups are the C₈-chemicals perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). They have been produced in large amounts since the 1970s and 1950s, respectively. PFOS was applied in many industrial and consumer products while PFOA is used in the production of fluoropolymers such as polytetrafluoroethylene.

The main manufacturer of PFOS-based chemicals in the US, 3M, phased out the production of this product line in 2002 [7]. 3M used the electrochemical fluorination (ECF) process, yielding an isomer

31 mixture which is dominated by the linear isomer and additionally contains 15-30% branched isomers,
32 and was the only major company known to apply ECF [7]. N-alkylated fluorooctane sulfonamides and
33 sulfonamidoethanols (FOSAs / FOSEs) were produced by ECF. Other manufacturers of PFAS make use
34 of the telomerisation process, yielding exclusively linear compounds, which normally contain an even
35 number of fluorinated and two non-fluorinated carbon atoms adjacent to the functional group.
36 Telomerisation is also used to produce fluorotelomer alcohols (FTOHs) of the general structure $\text{CF}_3\text{-(CF}_2\text{)}_n\text{-CH}_2\text{-CH}_2\text{OH}$, where $n = 3, 5, 7, 9$. They are named based on the ratio of fluorinated to non-
37 fluorinated carbons (e.g. 8:2 FTOH for $n = 7$). Both production processes are described in detail by
38 *Schultz et al.* [8].

40 FOSAs / FOSEs were used in a variety of products for water- and dirt-proofing in carpets, leather,
41 upholstery and textiles, as paper protectors and performance chemicals (e.g. in aqueous film forming
42 fire-fighting foams [9]) or as an insecticide (N-ethyl fluorooctane sulfonamide (NEtFOSA):
43 Sulfluramid[®]). FTOHs are produced in large amounts and are used in similar applications as FOSAs /
44 FOSEs, such as precursor compounds in the production of fluorinated polymers used in paper and
45 carpet treatments, moreover in the production of paints, coatings, adhesives etc. [10,11].

46 The detection of ionic PFAS (PFOS and PFCAs) in organisms from remote locations [12-14] was
47 surprising at first, as these chemicals are non-volatile and only moderately water-soluble. Long-range
48 atmospheric transport seemed quite unlikely for these compounds. To explain the mentioned
49 observations, a theory arose that volatile PFAS precursors could be transported to remote regions via
50 the atmosphere and be degraded *in situ* (e.g. in polar regions) to form the persistent PFOS and PFCAs
51 [15]. This hypothesis was strongly supported by the detection of the potential precursors (FTOHs and
52 FOSAs / FOSEs) in air samples from North America [16,17], and by a number of smog chamber
53 degradation studies [10,18,19]. Furthermore, several studies showed the biodegradability of neutral,
54 volatile precursors to form persistent, ionic PFAS [11,20,21].

55 Analytical methods for volatile PFAS include gas chromatography/chemical ionisation-mass
56 spectrometry (GC/CIMS) as well as liquid chromatography/negative electrospray ionisation-(tandem)

57 mass spectrometry (LC/(-)ESI-MS(/MS)). GC methods have been published for both FTOHs and
58 FOSAs / FOSEs in environmental [16,17] and indoor [22] air with instrumental detection limits (IDLs)
59 of 0.2-20 pg [16], 0.3-5.0 pg [17] and 3.6-3.7 pg (FOSEs only) [22]. Regarding LC methods, MS/MS
60 was used on one occasion for FTOHs with IDLs of 1-20 pg [23], and on another for NEtFOSA and two
61 fluorinated alcohols (IDLs = 0.02-0.1 pg) [24]. LC-MS was applied for NEtFOSA and N-ethyl
62 fluorooctane sulfonamidoethanol (NEtFOSE) with IDLs of 0.02 pg [25]. Despite lower or comparable
63 IDLs using LC methods, possible co-analysis of non-ionic and ionic PFAS is impeded by ionisation
64 suppression of FTOHs caused by buffered mobile phases, which are necessary to separate ionic PFAS
65 [23]. The only application of an LC-MS method to air samples is described by *Boulangier et al.* [26]
66 without the specification of method detection or quantification limits (MDLs / MQLs), thus not
67 permitting comparison of method sensitivities.

68 The aim of this study was to optimise and validate a highly selective and sensitive analytical method
69 for the simultaneous analysis of FTOHs and FOSAs / FOSEs in outdoor air samples. The analytical
70 protocol developed by *Martin et al.* [16] using GC/CI-MS was adapted, further optimised and validated.
71 Five mass-labelled internal standards (IS) were used to ensure the accuracy of analytical results. The
72 instrumental method performance was evaluated by comparison to a similar method developed at the
73 Norwegian Institute for Air Research (NILU) in Tromsø. Finally, the applicability of the method was
74 shown by means of environmental air samples from an urban and a rural site in Northern Germany.

75 **Experimental**

76 **Chemicals and standards.** 4:2 FTOH (of 97% purity) and 1H,1H,2H,2H-perfluorooctyl acrylate (6:2
77 PFOAc, 97%) were purchased from Aldrich (Steinheim, Germany). 6:2 FTOH (97%), 8:2 FTOH (97%),
78 10:2 FTOH (97%), 1H,1H-perfluoro-1-octanol (7:1 fluorinated alcohol (FA), 98%) and 1H,1H-
79 perfluoro-1-dodecanol (11:1 FA, 90%) were from Lancaster Synthesis (Frankfurt a.M., Germany).
80 NEtFOSA (95%) and perfluorooctane sulfonamide (PFOSA, 97%) were from ABCR (Karlsruhe,
81 Germany). Mass-labelled compounds of >98% purity used as IS were purchased from Wellington
82 Laboratories Inc. (Guelph, Ontario, Canada): 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4],

83 N-methyl fluorooctane sulfonamide (NMeFOSA [M+3]) and NEtFOSA [M+5]. Native NMeFOSA and
84 N-methyl fluorooctane sulfonamidoethanol (NMeFOSE) were donated by 3M, while NEtFOSE was
85 obtained from the Mabury group at the University of Toronto, Canada. All native FOSAs / FOSEs were
86 a mixture of linear and branched isomers at a ratio of approximately 70:30 as determined by
87 GC/electron impact (EI)-MS analyses and also described in [27], while mass-labelled FOSAs only
88 contained the linear isomer. Independent FTOH reference compounds (named “R-X”) were purchased
89 from Fluorochem (Old Glossop, UK): R-4:2 FTOH (97%), R-6:2 FTOH (97%), R-8:2 FTOH (97%), R-
90 10:2 FTOH (97%). Mass-labelled IS were spiked before sampling (gaseous phase) or before sample
91 extraction (particulate phase), respectively, to correct for analyte losses during sampling and / or
92 extraction as well as for signal suppression / enhancement during determination. Recovery internal
93 standards (RIS: 7:1 FA, 11:1 FA) were added to sample extracts just before analyses to determine
94 recoveries of the IS. Structures of all compounds included in this study are depicted in Table 1.

95 Ethyl acetate (EtOAc) and methanol of SupraSolv[®] quality as well as sodium sulfate for organic trace
96 analysis were obtained from Merck (Darmstadt, Germany). All standards and solvents were used as
97 received. Nitrogen of $\geq 99,9995\%$ purity was purchased from Messer Griesheim / Air Liquide
98 (Wittenberg, Germany).

99 **Preparation of sampling media.** For the enrichment of airborne PFAS, glass columns with a glass
100 frit, a slice of polyurethane foam (PUF, 6.5 cm diameter / 5 cm height, Klaus Ziemer GmbH,
101 Langerwehe, Germany), 25 g of Amberlite XAD-2 resin (Supelco, Munich, Germany) and another slice
102 of PUF were used. The PUF/XAD-2/PUF columns were prepared in a clean lab (class 10.000) at GKSS
103 and extensively cleaned by Soxhlet extraction using 500 mL of methanol (2 d) and 500 mL of EtOAc (2
104 d). The sampling columns were dried using high-purity nitrogen at a pressure of ~ 1.5 bar and sealed in
105 alumina coated polypropylene (PP) bags. GF8 glass-fibre filters (GFF) of 15 cm diameter were
106 purchased from Schleicher & Schuell / Whatman (Dassel, Germany), rinsed with EtOAc and heated
107 overnight at 250°C. GFFs were individually wrapped in aluminum foil and sealed in alumina coated PP
108 bags.

109 **Sampling.** High-volume air samples were taken after spiking of 40 ng of the IS 6:2 FTOH [M+4], 8:2
110 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3] and NEtFOSA [M+5] (10 µL of a 4 ng/µL
111 solution in EtOAc) onto the upper PUF slice. Sampling was started immediately using SV 5.130/2-05
112 pumps purchased from ISAP (Asendorf, Germany) at a flow rate of approximately 12-15 m³/h. The
113 described method was used to analyse environmental air samples taken in spring, 2005 at two locations
114 in Northern Germany (Hamburg / urban - Waldhof / rural). Waldhof is a background monitoring site of
115 the German Federal Environmental Agency (UBA) and European Monitoring and Evaluation Program
116 (EMEP) station, located around 100 km south-east of Hamburg. A comprehensive sampling campaign
117 at both locations is described in detail elsewhere [28].

118 Collection of environmental air samples was done for ~3.5 days, leading to average sample volumes
119 of 1160 m³. After sampling, GFFs were sealed into test tubes, stored in alumina coated PP bags together
120 with the respective PUF/XAD columns and stored at -18°C until extraction within several days. To
121 control possible background contamination, field blanks were taken by attaching open PUF/XAD
122 columns close to the sampling sites during sampling. They were stored, extracted and analysed along
123 with the samples.

124 **Sample extraction.** PUF/XAD columns were extracted using cold column elution with 300 mL
125 EtOAc (infusion time: 1 h) and another 200 mL-aliquot EtOAc (30 min), and the extracts were
126 combined. GFFs were extracted in round-bottomed flasks after spiking of 40 ng of the IS (i.e. 6:2 FTOH
127 [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3] and NEtFOSA [M+5], 10 µL of a 4
128 ng/µL solution in EtOAc) directly onto the filter using solvent soak with 50 mL EtOAc. The flask was
129 placed on a mechanical shaker for 1 min. Subsequently, the extract was transferred to another flask and
130 the procedure was repeated three more times (resulting in 200 mL EtOAc extract). Both PUF/XAD and
131 GFF extracts were concentrated to approximately 1 mL using a Rotavapor R-200 (Büchi, Flawil,
132 Switzerland), dried over sodium sulfate, filtered over pre-cleaned cotton wool and transferred to
133 graduated Wheaton vials. The extracts were finally concentrated to 200 µL under a gentle stream of

high-purity nitrogen. Before GC/CI-MS determination, 40 ng of the RIS 7:1 FA and 11:1 FA (10 μ L of a 4 ng/ μ L solution in EtOAc) were spiked to sample extracts as well as to calibration solutions.

Instrumental analysis. Quantitative analytical determination was performed using positive chemical ionisation (PCI) GC-MS operating in the single ion monitoring (SIM) mode. For this study, an Agilent (Böblingen, Germany) 6890 N gas chromatograph coupled to an HP 5973 mass-selective detector (MSD) was used.

For separation of the analytes, a polar Varian CP-Wax 57 CB capillary column for glycols and alcohols (25 m x 0.25 mm x 0.2 μ m) and an Agilent HP-INNOWax polyethylene glycol precolumn (~5 m x 0.25 mm x 0.2 μ m) were used. Helium was employed as carrier gas at a constant flow of 1.1 mL/min. The GC-oven was programmed as follows: 50°C (1 min)/50°C > 70°C (3°C/min, 0 min)/70°C > 130°C (10°C/min, 0 min)/130°C > 225°C (20°C/min, 11.4 min)/225°C > 50°C (80°C/min, 0 min), resulting in a run time of 32 min. Retention times (RT) of all compounds are given in Table 1. Injection volumes were 1 μ L. The PTV inlet was programmed at 200°C (2 min)/200°C > 250°C (500°C/min, 3 min)/250°C > 200°C (100°C/min, 10 min) with a pulsed splitless injection mode. The GC-MS interface was set to 250°C.

EI was only used for determination of standard purities, because of the low intensity of the molecular ions and the lack of specific fragments. PCI was chosen due to the simple yet definite mass spectra compared to negative chemical ionisation (NCI) [29]. The reagent gas (methane) was set to 20% in PCI mode and to 40% in NCI mode, respectively. For most analytes, at least two m/z were monitored, except for PFOSA, NEtFOSA, NMeFOSA and the respective mass-labelled analogues, where only one m/z could be detected (Table 1). For FOSAs, qualitative confirmation in NCI mode was performed (i.e. the determination of FOSAs was confirmed if the ions in NCI mode, as given in Table 1, were detected). Quantification was based on the most intensive ion (quantifier), while the other ions were used as qualifiers. Identification of the compounds was ensured (a) by monitoring several characteristic ions for each analyte, (b) by considering a specific time window of elution (mean RT of standards $\pm$ 0.5 s), and (c) by specific ratios of quantifier and qualifier ions ($\pm$ 20% of the ratio determined in calibration

solutions). For some analytes at very low concentrations, a reasonable confirmation by qualifier ratios was not possible as peak areas were close to the noise in the chromatogram.

Internal standard compounds. Quantification was done by normalisation of the analyte areas to those of the corresponding IS followed by quantification using the external two point calibration curve. In the optimised method, several compounds were used as IS to be spiked before sampling in order to control the whole process from sampling and extraction to determination. RIS were spiked just before GC/PCI-MS analysis to determine recoveries of the IS. For analytes where mass-labelled IS were available (i.e. 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3], NEtFOSA [M+5]), those were applied. Due to the non-availability of further mass-labelled IS at the time of the study, 6:2 FTOH [M+4] was also used as IS for 4:2 FTOH and 6:2 PFOAc due to similar RTs, while NEtFOSA [M+5] was also assigned to the later eluting NMeFOSE, NEtFOSE and PFOSA. Moreover, 7:1 FA and 11:1 FA were employed as RIS because of their chemical and structural similarity to the analytes of interest. The RIS had been shown to be not detected (n.d.) in environmental air samples. 11:1 FA was used to calculate recoveries of 10:2 FTOH [M+4] due to similar behaviour in the sample matrix, while 7:1 FA was used as RIS for all other IS.

Method validation

Blank experiments. *Solvent blanks* ($n = 4$) were determined using 500 mL EtOAc spiked with 40 ng of the IS mixture (10 μ L of 4 ng/ μ L in EtOAc). *Column blanks* ($n = 4$) were evaluated by spiking of the IS onto the upper PUF slice of sampling columns and subsequent drawing of 10 m³ air through the material in order to preclude evaporative loss of the IS. Extraction, concentration and determination were done as described above.

Recovery experiments. The first recovery experiment was to test how many elution steps were necessary for quantitative recovery of the analytes. For this purpose, all analytes were spiked at high concentrations (400 ng) to the glass columns containing the sampling media. Immediately afterwards, the columns were soaked with 300 mL of EtOAc and allowed to infuse for 1 h. The solvent was eluted and replaced by 200 mL of EtOAc (30 min infusion, 3 additional repeats). All five fractions were

186 concentrated separately to 200 μ L and determined by GC/PCI-MS. The first two fractions contained
187 together >96% of the analytes, so that in the following, elution was done with 300 mL EtOAc (1 h) and
188 another 200 mL aliquot (30 min).

189 Several spiking experiments at two concentration levels were performed to determine the general
190 recovery rates of the analytes in the gaseous and particulate phase. *Solvent recoveries* were evaluated by
191 spiking of 40 ng of the IS mixture (10 μ L of 4 ng/ μ L in EtOAc) as well as 20 or 80 ng absolute ($n =$
192 3+3) of a standard mixture containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 PFOAc,
193 NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA at a concentration of 2 ng/ μ L in EtOAc (10
194 or 40 μ L, respectively) into 500 mL EtOAc and subsequent concentration to 200 μ L as described above.
195 For determination of *column recoveries*, 40 ng IS and 20 or 80 ng absolute ($n = 3+3$) of the analytes
196 were spiked onto the upper PUF slice of a sampling column. 10 m³ of air were drawn through the
197 material to ensure there was no evaporative loss and the spiked columns were subsequently treated like
198 real samples. Furthermore, *GFF recoveries* were investigated by spiking of 40 ng of the IS and 20 or 80
199 ng absolute ($n = 4+4$) of the analytes onto pre-cleaned GFFs and subsequent extraction as described
200 above.

201 **Breakthrough experiments.** In order to check the quantitative collection of the analytes in the
202 gaseous phase, breakthrough experiments were conducted. Two sampling columns were operated in
203 series ($n = 2$). The upper column was spiked with 40 ng of IS as well as with 80 ng (40 μ L of 2 ng/ μ L in
204 EtOAc) of the analyte mixture, while the lower column was not spiked at all in order to investigate
205 breakthrough of the analytes as well as the IS from the upper column. Subsequently, approximately
206 1000 m³ of air were drawn through the tandem column. Quantification was done using the internal
207 standard method for the upper column, while the lower column was quantified externally.

208 **Interlaboratory comparison.** As part of the method validation, an interlaboratory comparison of
209 instrumental quantification was conducted at GKSS Research Centre Geesthacht and the Norwegian
210 Institute for Air Research (NILU) in Tromsø. Two unknown standard mixtures were exchanged and
211 analysed, containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA,

212 NMeFOSE, NEtFOSE and PFOSA in a lower (20-250 pg/ μ L, prepared at GKSS) or an upper
213 concentration range (100-900 pg/ μ L, prepared at NILU), respectively.

214 **Results and discussion**

215 **Instrumental linear range.** The calibration procedure was adapted from the draft of ISO 22032 for
216 the determination of polybrominated diphenyl ethers [30] and was applied to PFAS analysis for the first
217 time. Calibration solutions for the quantification of the analytes were prepared to cover the range of 10
218 to 800 pg/ μ L. This range was sub-divided into a lower and an upper calibration range: 10-200 and 200-
219 800 pg/ μ L. Each range had been shown to be linear by analysis of individual calibration solutions at 10,
220 25, 50, 100, 200, 400 and 800 pg/ μ L. In the following, two point calibrations for each sub-range were
221 carried out. Triplicate analyses at each level (10 and 200 or 200 and 800 pg/ μ L, respectively) were used
222 for further calculations. In addition, two independent standard solutions containing the reference
223 compounds (R-4:2 FTOH, R-6:2 FTOH, R-8:2 FTOH, R-10:2 FTOH) and 6:2 PFOAc, NMeFOSA,
224 NEtFOSA, NMeFOSE, NEtFOSE and PFOSA in the middle of the lower and upper calibration range
225 (at 100 and 400 pg/ μ L, respectively) were also analysed in triplicate to check for accuracy and stability
226 of the GC-MS system.

227 **Blank experiments.** *Solvent* and *column blanks* are given in Table 2. Regarding *solvent blanks*, only
228 NEtFOSA, NMeFOSE (<instrumental quantification limit, IQL as discussed below) and NEtFOSE
229 could be detected, corresponding to absolute amounts in whole extracts of 0.02 ng (NEtFOSA) or 0.01
230 ng (NEtFOSE), respectively. In *column blanks*, only 8:2 FTOH (0.51-0.74 ng), 10:2 FTOH (0.23-0.41
231 ng), NEtFOSA (<IQL-0.09 ng) and NMeFOSE (n.d.-0.01 ng) could be quantified, while 6:2 FTOH and
232 NEtFOSE were additionally detected below the IQL. Related to average sample volumes of 1160 m³,
233 these results imply a maximum blank contamination of 0.64 pg/m³ (8:2 FTOH). In view of the high
234 concentrations of FTOHs in environmental air samples (Table 3), column blanks could also be
235 influenced by the air volume (10 m³) drawn through the sampling columns to avoid evaporative loss of
236 the IS. Given the low blank levels, analyte concentrations in real samples were not blank-corrected.

237 **Limits of detection and quantification.** IDLs, IQLs and MQLs as given in Table 2 were determined
238 using different methods. The blank method was mostly not applicable due to the absence of several
239 analytes in solvent and column blanks. The calibration method (following the German DIN 32645,
240 which is the national equivalent to ISO) was applied using standard mixtures at very low concentrations
241 (2.5, 5.0, 7.5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 pg/ μ L). However, the procedure most often used in
242 chromatography is the evaluation of the signal-to-noise (S/N) ratio of standard solutions at very low
243 concentration levels. In this study, an extrapolated concentration at a S/N of 3 was taken as the IDL.
244 Correspondingly, a S/N of 10 was related to the IQL.

245 While IDLs and IQLs only depend on the instrumental sensitivity, MQLs include the whole procedure
246 starting from sampling, sample extraction, extract concentration to determination. Furthermore, blank
247 levels have to be considered to obviate false-positive results. Given the very low method blanks, MQLs
248 for most analytes were estimated using means of six real samples with lowest analyte concentrations
249 and extrapolation to a S/N of 10 (Table 2). Only for 8:2 FTOH and 10:2 FTOH, where column blank
250 contamination was found, the MQL was dominated by blank levels. Concerning these two analytes,
251 MQLs were determined as ten times the standard deviation of column blanks ($n = 4$).

252 Compared to previously reported methods, MQLs determined in our study were very low as they
253 ranged from 0.2 pg/ m^3 (NMeFOSA) to 2.5 pg/ m^3 (6:2 PFOAc). These levels correspond to MDLs
254 between 0.06 and 0.75 pg/ m^3 . The original analytical protocol developed by *Martin et al.* showed
255 MDLs of 0.15 (10:2 FTOH) up to 6.2 pg/ m^3 (NEtFOSE) [16]. *Stock et al.* reported MDLs between 2
256 (FOSEs) and 14 pg/ m^3 (6:2 FTOH) [17], while the method of *Shoeib et al.* (not including FTOHs)
257 showed MDLs of 0.01 (NEtFOSA) up to 7.1 pg/ m^3 (NMeFOSE) [31].

258 **Recovery experiments.** All recovery experiments were performed in triplicate at two concentration
259 levels each by spiking of analyte mixtures at 20 and 80 ng absolute, respectively. Due to comparable
260 findings at both spiking levels, results given in Figure 1 were combined (PUF/XAD, $n = 6$ / GFF, $n = 8$).
261 Absolute recoveries were calculated by normalisation of the analyte areas to those of the corresponding
262 *RIS* (7:1 and 11:1, respectively) and quantification using the external two point calibration curve (Figure

263 1 A). In this case, the RIS were used to correct for the injection volumes of the autosampler. Recovery
264 experiments at two concentration levels showed absolute *solvent recoveries* between 33% (PFOSA) and
265 153% (NMeFOSE), while absolute *column recoveries* were 29% (4:2 FTOH) up to 266% (NEtFOSE).
266 *GFF recoveries* ranged from 49% (4:2 FTOH) to 125% (NEtFOSA and NEtFOSE).

267 By normalisation of the analyte areas to those of the corresponding *IS*, losses during extraction and
268 extract concentration can be corrected, leading to enhanced accuracy and lower standard deviations.
269 This is demonstrated by the IS-corrected relative recoveries given in Figure 1 B. Relative *solvent*
270 *recoveries* were found between 44% (PFOSA) and 164% (NMeFOSE), while relative *column*
271 *recoveries* ranged from 56% (4:2 FTOH) to 151% (NMeFOSA) for most compounds (Figure 1 B). Only
272 for NMeFOSE and NEtFOSE where mass-labelled analogues were not available at the time of the
273 study, the *column recoveries* (311-319%) were very high, pointing out the importance of appropriate
274 mass-labelled IS for each individual analyte. Such signal enhancements of FOSEs have also been
275 observed elsewhere [32] and probably lead to overestimation of those compounds in real samples.

276 Erney *et al.* characterised matrix enhancement effects concerning the analysis of pesticide residues in
277 food by GC-MS [33]. The authors described the blocking of active sites in the GC system, especially in
278 the injection liner, by matrix constituents as the main reason for the mentioned effect. Following this
279 theory, the co-extracted sample matrix increases analyte signals in comparison with solvent-only
280 standard injections where the analytes themselves interact with the active sites. In our study, improved
281 peak shapes in sample analyses compared with standard injections gave an indication that blocking of
282 active sites by matrix constituents might have occurred. This is exemplified for NMeFOSE in Figure 2.
283 Among several ways to overcome or reduce the matrix enhancement effect of up to >200%, Schenck *et*
284 *al.* described the usage of matrix-matched standards, the application of an appropriate clean-up or the
285 use of similarly affected mass-labelled IS [34].

286 The matrix effects observed for FOSEs could be remediated by IS-correction using NMeFOSE [M+7]
287 and NEtFOSE [M+9] now available from Wellington Laboratories Inc. (Guelph, Ontario, Canada). The
288 same applies for the most volatile compounds 4:2 FTOH and 6:2 PFOAc, where results had to be IS-

289 corrected using the less volatile 6:2 FTOH [M+4], so that losses during extraction and concentration
290 were not fully accounted for (relative recoveries <100%, Figure 1 B). Thus, air concentrations of 4:2
291 FTOH were probably underestimated. Relative recoveries for those five analytes where mass-labelled
292 analogues could be applied were around 100%, ensuring highly accurate results in air measurements.
293 Regarding relative *GFF recoveries*, values between 61% (PFOSA) and 115% (NMeFOSA) were
294 determined. No signal enhancement for FOSEs was found in GFFs, leading to the conclusion that the
295 specific matrix resulting from extraction of PUF/XAD columns with EtOAc was mainly responsible for
296 matrix effects. Recoveries of the IS in real samples are given in Table 3.

297 **Breakthrough experiments.** Figure 3 shows the results of the breakthrough experiments. Relatively
298 high losses for the most volatile compounds were revealed. This holds especially for 4:2 FTOH, where a
299 higher percentage of spiked analytes was found on the non-spiked lower ‘breakthrough’ column. By
300 correction using 6:2 FTOH [M+4], the 4:2 FTOH concentrations are thus underestimated (see also
301 discussion of recovery experiments above), underlining the importance of the application of the mass-
302 labelled IS 4:2 FTOH [M+4], as soon as available.

303 Furthermore, moderate breakthrough could be found for the other FTOHs. In accordance with the
304 trend of decreasing volatility with increasing chain length, breakthrough of 6:2 FTOH was much lower
305 than that of 4:2 FTOH, but higher than breakthrough of 8:2 FTOH. Surprisingly, for 10:2 FTOH a
306 breakthrough similar to that of 6:2 FTOH was determined. For this phenomenon, no explanation has
307 been found yet. The breakthrough of 6:2 PFOAc is comparable to that of 8:2 FTOH. Regarding FOSEs,
308 breakthrough was minimal (2-3%), while PFOSA and both FOSAs could not be detected at all on the
309 lower column.

310 The relatively high breakthrough of 4:2 FTOH leads to the assumption that a certain percentage of the
311 spiked analyte is also lost from the lower column as confirmed by the low absolute recoveries of 22 ng
312 (spiking level 80 ng). Recoveries in the breakthrough experiments are directly linked to relative
313 recoveries described above, but also influenced by the environmental air concentrations sampled during
314 the experiment. This especially holds for 8:2 FTOH and 6:2 FTOH with highest air concentrations

315 (Table 3). Moreover, matrix effects resulting in signal enhancement of FOSEs as described above could
316 also be seen in the breakthrough experiments as absolute recoveries of NMeFOSE and NEtFOSE were
317 very high: 206 and 193 ng (spiking level 80 ng, results not shown), respectively, despite relatively low
318 environmental air concentrations (Table 3).

319 Referring to breakthrough of the IS, relative proportions of 18%, 9.1% and 11% of 6:2 FTOH [M+4],
320 8:2 FTOH [M+4], and 10:2 FTOH [M+4] respectively, were found on the non-spiked lower column.
321 Corresponding to the results for native FOSAs, breakthrough of the isotopically labelled FOSAs was
322 very low as only 1.3% NEtFOSA [M+5] and 0.9% NMeFOSA [M+3] were detected on the lower
323 column.

324 **Selectivity.** High method selectivity was ensured by monitoring several characteristic ions for each
325 analyte. For FOSAs, where only one m/z could be monitored, qualitative confirmation was done in NCI
326 mode as discussed above. Furthermore, a specific time window of elution (mean RT of standards $\pm$ 0.5
327 s) and specific ratios of quantifier and qualifier ions (ratios determined in standard solutions $\pm$ 20%)
328 were considered. In addition, extensive QA/QC measures including blank experiments precluded false-
329 positive and false-negative results.

330 **Precision.** In order to evaluate *instrumental precision*, within-day precision was tested by tenfold
331 injection of the same calibration solution at 100 pg/ μ L and ranged from 4.2% (4:2 FTOH) to 7.4% (10:2
332 FTOH). Between-day precision at 200 pg/ μ L was shown to be between 5.5% (NMeFOSE) and 9.7%
333 (PFOSA). For the evaluation of *method precision*, environmental air samples were always taken in
334 parallel. Despite the complexity of the analytical procedure, the gaseous phase concentration data (see
335 Table 3) obtained from parallel samples usually deviated by less than 30%, demonstrating the excellent
336 repeatability of the presented method.

337 **Accuracy.** Due to the lack of certified reference materials, the accuracy of the method was
338 investigated by the relative recovery experiments discussed above. Additionally, we performed an
339 interlaboratory comparison of the quantification method between GKSS Research Centre Geesthacht
340 and the Norwegian Institute for Air Research (NILU) in Tromsø [32].

341 **Interlaboratory comparison.** Two unknown standard mixtures were exchanged between GKSS and
342 NILU. Concentrations of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA,
343 NMeFOSE, NEtFOSE and PFOSA ranged from 20-250 pg/ μ L (low concentration mix, prepared at
344 GKSS) and 100-900 pg/ μ L (high concentration mix, prepared at NILU), respectively. The solutions
345 were analysed and quantified at both laboratories using their particular analytical methods.

346 Both laboratories used GC/PCI-MS approaches, but different instrumentation (NILU: Varian CP-
347 3800 gas chromatograph / 1200 triple quadrupole mass spectrometer, Varian, Palo Alto, CA, US),
348 analytical methods and calibration models (NILU: 10, 25, 50, 100, 250, 500, 1000 and 2000 pg/ μ L,
349 quadratic regression). Results of the interlaboratory comparison are given in Table 4. Of all reported
350 values of the interlab study, 82% were within $\pm 30\%$ of the theoretical values. However, some results
351 revealed deviations from theoretical values of up to $+180\%$ (4:2 FTOH in the high concentration mix
352 determined at GKSS). These discrepancies can be explained by the analytical challenges posed by
353 volatile PFAS and the low concentrations in the test mixtures. The results from the interlaboratory
354 comparison emphasise the need for further method improvement.

355 **Environmental air samples.** Environmental air concentrations obtained from two sets of parallel
356 samples from Northern Germany (Hamburg / urban - Waldhof / rural) are given in Table 3 together with
357 field blanks of the respective sampling periods. Most analytes except for 6:2 PFOAc and PFOSA could
358 be quantified in the gaseous phase of ambient air samples from both locations. The method thus proved
359 applicable for the trace-analytical determination of FTOHs and FOSAs / FOSEs at an urban as well as a
360 rural site in Northern Germany. A comprehensive sampling campaign at both locations is described in
361 detail elsewhere [28], representing the first airborne PFAS data available for Europe.

362 **Conclusions**

363 The method originally developed by *Martin et al.* [16] for the determination of volatile PFAS in high-
364 volume environmental air samples was further developed and validated. An additional analyte was
365 included: NMeFOSA. Moreover, the method was further optimised for quantitative determination of 4:2

366 FTOH as well as 10:2 FTOH at environmental levels. By means of recovery and breakthrough
367 experiments, the imperative need to use adequate mass-labelled internal standard compounds in order to
368 generate accurate concentration data was demonstrated. Further studies should include the mass-
369 labelled IS 4:2 FTOH [M+4] (as soon as available), NMeFOSE [M+7] and NEtFOSE [M+9] in order to
370 avoid significant under- or overestimation of results. Moreover, by optimisation of the ratio of final
371 extract volume (200 μ L) to injection volume (1 μ L), a shortening of sampling times could be achieved.
372 Additionally, a clean-up should be considered to diminish matrix effects and to avoid early deterioration
373 of GC injection liners and capillary columns encountered in relation with PUF/XAD extracts. In
374 particular, FTOHs require further investigations as they continue to be produced in rising amounts and
375 have recently been shown to possess estrogen-like properties by promoting MCF-7 breast cancer cell
376 proliferation [35].

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References

1. Kannan K, Corsolini S, Falandysz J, Fillmann G, Kumar KS, Loganathan BG, Mohd MA, Olivero J, van Wouwe N, Yang JH, Aldous KM (2004) *Environ Sci Technol* 38:4489-4495
2. Kärrman A, van Bavel B, Järnberg U, Hardell L, Lindström G (2005) *Anal Chem* 77:864-870
3. De Silva A, Mabury SA (2006) *Environ Sci Technol* 40:2903-2909
4. Inoue K, Okada F, Kator S, Sasaki S, Nakajima S, Uno A, Saijo Y, Sata F, Yoshimura Y, Kishi R, Nakazawa H (2004) *Environ Health Persp* 112:1204-1207
5. Austin ME, Kasturi BS, Barber M, Kannan K, MohanKumar PS, MohanKumar SMJ (2003) *Environ Health Persp* 111:1485-1489
6. Holmström KE, Järnberg U, Bignert A (2005) *Environ Sci Technol* 39:80-84
7. Renner R (2001) *Environ Sci Technol* 35:154A-160A
8. Schultz MM, Barofsky DF, Field JA (2003) *Environ Eng Sci* 20:487-501
9. De Voogt P, Saez M (2006) *Trac-Trends Anal Chem* 25:326-342
10. Ellis DA, Martin JW, Mabury SA, Hurley MD, Sulbaek Andersen MP, Wallington TJ (2003) *Environ Sci Technol* 37:3816-3820
11. Dinglasan MJA, Ye Y, Edwards EA, Mabury SA (2004) *Environ Sci Technol* 38:2857-2864
12. Smithwick M, Mabury SA, Solomon KR, Sonne C, Martin JW, Born EW, Dietz R, Derocher AE, Letcher RJ, Evans TJ, Gabrielsen GW, Nagy J, Stirling I, Taylor MK, Muir DCG (2005) *Environ Sci Technol* 39:5517-5523
13. Kannan K, Franson JC, Bowerman WW, Hansen KJ, Jones PD, Giesy JP (2001) *Environ Sci Technol* 35:3065-3070

14. Giesy JP, Kannan K (2001) *Environ Sci Technol* 35:1339-1342
15. Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD, Sulbaek Andersen MP, Wallington TJ (2004) *Environ Sci Technol* 38:3316-3321
16. Martin JW, Muir DCG, Moody CA, Ellis DA, Kwan WC, Solomon KR, Mabury SA (2002) *Anal Chem* 74:584-590
17. Stock NL, Lau FK, Ellis DA, Martin JW, Muir DCG, Mabury SA (2004) *Environ Sci Technol* 38:991-996
18. D'Eon J, Hurley MD, Wallington TJ, Mabury SA (2006) *Environ Sci Technol* 40:1862-1868
19. Martin JW, Ellis DA, Mabury SA, Hurley MD, Wallington TJ (2006) *Environ Sci Technol* 40:864-872
20. Wang N, Szostek B, Folsom PW, Sulecki LM, Capka V, Buck RC, Berti WR, Gannon JT (2005) *Environ Sci Technol* 39:531-538
21. Tomy GT, Tittlemier SA, Palace VP, Budakowski WR, Braekevelt E, Brinkworth L, Friesen K (2004) *Environ Sci Technol* 38:758-762
22. Shoeib M, Harner T, Ikonomou M, Kannan K (2004) *Environ Sci Technol* 38:1313-1320
23. Berger U, Langlois I, Oehme M, Kallenborn R (2004) *Eur J Mass Spectrom* 10:579-588
24. Taniyasu S, Kannan K, So MK, Gulkowska A, Sinclair E, Okazawa T, Yamashita N (2005) *J Chromatogr A* 1093:89-97
25. Boulanger B, Vargo J, Schnoor JL, Hornbuckle KC (2004) *Environ Sci Technol* 38:4064-4070
26. Boulanger B, Peck AM, Schnoor JL, Hornbuckle KC (2005) *Environ Sci Technol* 39:74-79
27. Giesy JP, Kannan K (2002) *Environ Sci Technol* 36:146A-152A

28. Jahnke A, Ahrens L, Ebinghaus R, Temme C (2006) *Environ Sci Technol*, in press
29. Ellis DA, Mabury SA (2003) *J Am Soc Mass Spectr* 14:1177-1191
30. Draft International Standard ISO/DIS 22032 2004, Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and gas chromatography/mass spectrometry. ISO/TC 147/SC 2.
31. Shoeib M, Harner T, Wilford BH, Jones KC, Zhu J (2005) *Environ Sci Technol* 39:6599-6606
32. Berger U, Barber JL, Jahnke A, Temme C, Jones KC (2005) Poster at the International Symposium on Fluorinated Alkyl Organics in the Environment, Toronto, Canada, 18-20 August 2005 <http://www.chem.utoronto.ca/symposium/fluoros/pdfs/ANA015Berger.pdf>.
33. Erney DR, Gillespie AM, Gilvydis DM, Poole CF (1993) *J Chromatogr A* 638:57-63
34. Schenck FJ, Lehotay SJ (2000) *J Chromatogr A* 868:51-61
35. Maras M, Vanparys C, Muylle F, Robbens J, Berger U, Barber JL, Blust R, De Coen W (2006) *Environ Health Persp* 114:100-105

Table 1. Analytes, acronyms, retention times (RT, for chromatographic conditions see Experimental part), structures and ions detected in PCI and NCI mode.

Analyte	Acronym, molecular weight (u)	RT (min)	Structure	Ions in PCI (m/z) (% rel. abundance)	Ions in NCI (m/z)
1H,1H,2H,2H-perfluoro-1-hexanol	4:2 FTOH, 264	6.52		265.0 (100), 227.0 (46), 293.1 (7)	-
1H,1H,2H,2H-perfluorooctyl acrylate	6:2 PFOAc, 418	7.77		419.0 (100), 447.0 (15), 399.0 (10)	-
1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH, 364	9.33		365.1 (100), 327.0 (56), 393.1 (13)	-
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH, 464	11.38		465.1 (100), 427.0 (46), 493.1 (14)	-
1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH, 564	13.01		565.1 (100), 527.1 (36), 593.2 (13)	-
N-ethyl fluorooctane sulfonamide	NEtFOSA, 527	16.50 ^a		528.2 ^b	483.0, 400.1, 526.1
N-methyl fluorooctane sulfonamide	NMeFOSA, 513	16.84 ^a		514.1 ^b	483.0, 512.0, 400.1
N-methyl fluorooctane sulfonamido-ethanol	NMeFOSE, 557	17.68 ^a		540.1 (100), 558.1 (99)	400.1, 483.0, 494.0
N-ethyl fluorooctane sulfonamido-ethanol	NEtFOSE, 571	17.75 ^a		554.1 (100), 572.1 (98)	483.0, 400.1, 508.1
Perfluorooctane sulfonamide	PFOSA, 499	20.41 ^a		500.0	483.0, 400.1
1H,1H,2D,2D-perfluoro-1-octanol	6:2 FTOH [M+4] (IS), 368	9.29		369.0 (100), 331.1 (33), 397.1 (11)	-
1H,1H,2D,2D-perfluoro-1-decanol	8:2 FTOH [M+4] (IS), 468	11.35		469.0 (100), 431.0 (33), 497.1 (13)	-
1H,1H,2D,2D-perfluoro-1-dodecanol	10:2 FTOH [M+4] (IS), 568	12.99		569.1 (100), 531.1 (32), 597.2 (14)	-
D5-N-ethyl fluorooctane sulfonamide	NEtFOSA [M+5] (IS), 532	16.48		533.1	483.0, 531.1
D3-N-methyl fluorooctane sulfonamide	NMeFOSA [M+3] (IS), 516	16.82		517.0	483.0, 515.1
1H,1H-perfluoro-1-octanol	7:1 FA (RIS), 400	10.59		401.0 (100), 381.0 (45), 345.0 (5)	-
1H,1H-perfluoro-1-dodecanol	11:1 FA (RIS), 600	13.75		601.1 (100), 581.1 (42), 545.1 (5)	-

^a The mentioned RT is that of the main peak of several isomers.

^b Qualitative confirmation was performed in NCI mode.

Table 2. Solvent and column blanks, typical instrumental limits of detection and quantification (IDLs / IQLs) using the signal-to-noise (S/N) approach as well as the calibration method and method quantification limits (MQLs) extrapolated from S/N ratios of real samples with lowest analyte concentrations. Details for the calculation of IDLs, IQLs and MQLs are given in the text.

Analyte	Solvent blanks (pg/m ³) ^a	Column blanks (pg/m ³) ^a	IDL (pg injected)		IQL (pg injected)		MQL (pg/m ³)
			S/N = 3	calibration method	S/N = 10	calibration method	
4:2 FTOH	n.d.	n.d.	1.1	1.1	3.6	3.7	1.8
6:2 FTOH	n.d.	n.d.-<IQL	1.0	1.3	3.4	4.4	1.4
8:2 FTOH	n.d.	0.44-0.64	0.6	1.7	2.0	5.7	1.0 ^b
10:2 FTOH	n.d.	0.20-0.35	0.4	2.2	1.4	7.2	0.7 ^b
6:2 PFOAc	n.d.	n.d.	0.3	0.9	0.9	2.9	2.5 ^{c,d}
NEtFOSA	n.d.-0.02	<IQL-0.08	0.2	1.4	0.7	4.7	0.3
NMeFOSA	n.d.	n.d.	0.2	1.3	0.7	4.5	0.2
NMeFOSE	n.d.-<IQL	n.d.-0.01	0.8	2.6	2.6	8.5	0.4
NEtFOSE	n.d.-0.01	n.d.-<IQL	0.7	2.5	2.2	8.3	0.3
PFOSA	n.d.	n.d.	0.2	n.l.	0.8	n.l.	0.6 ^d

n.d., not detected n.l., not linear

^a Blanks were related to an average sample volume of 1160 m³.

^b Due to detectable method blanks, MQLs were defined as ten times the standard deviation of *column blanks* ($n = 4$).

^c As 6:2 PFOAc could not be determined in any sample, the corresponding blank signal was integrated and quantified. The result times ten was considered as MQL.

^d Due to very small analyte peak areas, the calibration was forced through the origin.

Table 3. Airborne PFAS concentrations (pg/m³) and recoveries of the IS (%) determined in the gaseous and particulate phase of two sets of parallel air samples from an urban (Hamburg) and a rural (Waldhof) location in Northern Germany. Field blanks of the respective sampling periods are listed. Analyte concentrations are given in brackets if peak areas were smaller than those of the lowest calibration solution.

		Hamburg (25.-28.04.2005)			Waldhof (23.-26.05.2005)		
		Concentration (pg/m ³)	Recovery of IS (%)	Blank (pg/m ³)	Concentration (pg/m ³)	Recovery of IS (%)	Blank (pg/m ³)
4:2 FTOH	gaseous phase	32, 29		n.d.	7.2, 11		n.d.
	particulate phase	n.d.			n.d.		
6:2 FTOH	gaseous phase	55, 56	57, 55	n.d.	29, 29	52, 42	n.d.
	particulate phase	n.d.	40, 48		n.d.	71, 71	
8:2 FTOH	gaseous phase	106, 110	91, 86	1.3	81, 88	77, 54	<1.0
	particulate phase	<1.0	56, 63		<1.0	108, 108	
10:2 FTOH	gaseous phase	29, 28	141, 154	1.1	27, 29	128, 80	<0.7
	particulate phase	<0.7, (0.8)	62, 67		<0.7	110, 112	
6:2 PFOAc	gaseous phase	n.d.		n.d.	n.d.		n.d.
	particulate phase	n.d.			n.d.		
NEtFOSA	gaseous phase	2.5, 2.6	84, 84	<0.3	(2.6), 3.2	86, 59	<0.3
	particulate phase	n.d.	113, 120		n.d.	139, 132	
NMeFOSA	gaseous phase	6.8, 7.2	63, 62	<0.2	5.1, 9.7	69, 32	<0.2
	particulate phase	<0.2	116, 126		<0.2	150, 144	
NMeFOSE	gaseous phase	22, 14		<0.4	4.2, 7.8		n.d.
	particulate phase	7.6, 15			4.7, 3.5		
NEtFOSE	gaseous phase	4.5, 2.6		0.3	5.8, 11		n.d.
	particulate phase	4.8, 8.5			15, 13		
PFOSA	gaseous phase	n.d.		n.d.	n.d.		n.d.
	particulate phase	n.d.			n.d.		

Table 4. Results of the interlaboratory comparison between GKSS, Geesthacht and NILU, Tromsø.

Two unknown standard mixtures were exchanged and analysed.

	low concentration mix (20-250 pg/ μ L)					high concentration mix (100-900 pg/ μ L)				
	Theoretical conc. (pg/ μ L)	GKSS (pg/ μ L)	Dev. (%)	NILU (pg/ μ L)	Dev. (%)	Theoretical conc. (pg/ μ L)	GKSS (pg/ μ L)	Dev. (%)	NILU (pg/ μ L)	Dev. (%)
4:2 FTOH	66.7	67.2	+1	69.9	+5	682	1900	+180	1226	+80
6:2 FTOH	-	<IDL		4.6		455	578	+27	365	-20
8:2 FTOH	100	85.8	-14	96.0	-4	227	235	+3	233	+2
10:2 FTOH	20.0	19.6	-2	32.7	+63	636	1529	+140	766	+20
NEtFOSA	167	142	-15	66.5	-60	227	285	+25	176	-23
NMeFOSA	233	205	-12	288	+23	409	424	+4	797	+95
NMeFOSE	33.3	28.6	-14	32.9	-1	909	1059	+16	710	-22
NEtFOSE	-	<IDL		26.9		455	421	-7	371	-18
PFOSA	40.0	34.7	-13	-	-	682	597	-12	-	-

Figure 1. Absolute (A) as well as IS-corrected relative analyte recoveries (B) determined at two concentration levels: 20 ng and 80 ng ($n = 3+3$) by spiking into EtOAc (*solvent recoveries*) or onto PUF/XAD columns (*column recoveries*). *GFF recoveries* were determined at 20 ng or 80 ng ($n = 4+4$). Details are given in the text.

Figure 2. Chromatograms of NMeFOSE (m/z 558.1) in a standard solution (black) as well as sample extracts from Hamburg (blue) and Waldhof (grey). The improved resolution of isomers in real samples can be attributed to the blocking of active sites in the chromatographic system by matrix constituents.

Figure 3. Evaluation of the quantitative collection of the analytes in the gaseous phase by breakthrough experiments ($n = 2$). Relative recoveries based on ‘upper column’ + ‘lower column’ = 100% are given. The upper column (spiked with 40 ng of IS and 80 ng of a standard mixture) showed considerable breakthrough for FTOHs. The lower column (non-spiked) was quantified externally.

Figure 1.

Figure 2.

Figure 3.