Supplementary material

Closing the gap - inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol

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1. Chemicals and Materials

In this chapter the chemicals, materials, and equipment used in this study are presented. Unless otherwise stated, the suppliers of chemicals, materials and equipment were located in Germany.

1.1 Chemicals

Native and mass-labelled per- and polyfluoroalkyl substances used and their suppliers are summarized in Table S 1.

Table S 1: Suppliers, abbreviations and concentrations of PFAS standards used in this study. All solutions were in methanol.

Chemical (purity)	Abbreviation	Concentration
Supplier: Neochema (Mainz)		
Sodium trifluoroacetate (≥99%)	NaTFA	(neat)
Sodium perfluoropropanoate (98%)		(neat)
Mixture of perfluroalkylcarboxylic acids (*n*-isomers of C_4–C_{14})	PFCAs	10 µg/mL each
Perfluorooctane sulfonamide	FOSA	50 µg/mL
Supplier: Campro Scientific (Berlin)		
Sodium bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2 diPAP	50 µg/mL
Sodium bis(1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorooctyl)phosphate	6:2 diPAP-M4	50 µg/mL
Sodium (1H,1H,2H,2H-perfluorooctyl-1H,1H,2H,2H-perfluorodecyl)phosphate	6:2/8:2 diPAP	50 µg/mL
Sodium bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2 diPAP	50 µg/mL
Sodium bis(1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorodecyl)phosphate	8:2 diPAP-M4	50 µg/mL
Sodium bis[2-(*N*-ethylperfluorooctane-1-sulfonamido)ethyl]phosphate	diSAmPAP	50 µg/mL
Mixture of perfluoroalkyl sulfonates (*n*-isomers of C_4, C_6, C_7, C_8, and C_{10})	PFSAs	2.0 µg/mL each
Perfluoropentane sulfonic acid	PFPeS	50 µg/mL
Perfluoro-*n*-[$^{13}C_4$]butanoic acid	PFBA-M4	50 µg/mL
Perfluoro-*n*-[$^{13}C_5$]pentanoic acid	PFPeA-M5	50 µg/mL
Perfluoro-*n*-[1,2-$^{13}C_2$]hexanoic acid	PFHxA-M2	50 µg/mL
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$]heptanoic acid	PFHpA-M4	50 µg/mL
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$]octanoic acid	PFOA-M4	50 µg/mL
Perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	PFNA-M5	50 µg/mL
Perfluoro-*n*-[1,2-$^{13}C_2$]decanoic acid	PFDA-M2	50 µg/mL
Perfluoro-*n*-[1,2-$^{13}C_2$]undecanoic acid	PFUnDA-M2	50 µg/mL
Perfluoro-*n*-[1,2-$^{13}C_2$]dodecanoic acid	PFDoDA-M2	50 µg/mL
Perfluoro-*n*-[1,2-$^{13}C_2$]tetradecanoic acid	PFTeDA-M2	50 µg/mL
Sodium perfluoro-[2,3,4-$^{13}C_3$]-butanesulfonate	PFBS-M3	50 µg/mL
Sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate	PFHxS-M2	50 µg/mL
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]-octanesulfonate	PFOS-M4	50 µg/mL
Supplier: Chiron (Trondheim, Norway)		
Sodium (1H,1H,2H,2H-perfluorododecyl)phosphate	10:2 monoPAP	50 µg/mL
Supplier: Toronto Research Chemicals (Toronto, Canada)		
Sodium trifluoroacetate-$^{13}C_2$	NaTFA-M2	(neat)
Supplier: TCI (Eschborn)		
Perfluoroethane sulfonamide (>98%)	FEtSA	(neat)
Supplier: Apollo Scientific (Stockport, United Kingdom)		
Perfluorobutane sulfonamide (>97%)	FBSA	(neat)
Supplier: ABCR (Karlsruhe)		
Perfluorohexane sulfonamide (>97%)	FHxSA	(neat)

Ammonium acetate (NH_4Ac, UHPLC-MS Optigrade) was purchased from LGC Standards (Wesel). Formic acid (HCOOH, LC-MS grade, ≥98.0 %), ammonium formate (NH_4Form, ≥99.0%), sodium hydroxide (NaOH, p. a., ≥98.0%), ammonium hydroxide solution (NH_4OH, ≥25%, puriss.), ammonium bicarbonate (≥99.5%) and acetonitrile (ACN, Honeywell, Chromasolv™ LC-MS, ≥99.9%) were purchased from Sigma Aldrich (Steinheim). Methanol (MeOH, Rotisolv®, ≥99.95%, LC-MS grade) and hydrochloric acid (HCl, ≥32%, p.a.) were purchased from Carl Roth (Karlsruhe). Acetone (Pestinorm, ≥99.9%) was obtained from VWR (Darmstadt). Potassium peroxodisulfate (p. a., ≥99.0%) and ethyl acetate (EtOAc, SupraSolv®, ≥99.8%) were purchased from Merck (Darmstadt). Unbuffered QuEChERS salt kits (4 g $MgSO_4$ and 1 g NaCl) were bought from Bekolut (Hauptstuhl).

Ultrapure water (H_2O_{mQ}, 18 MΩ·cm) was produced using an "Arium 611 UV" water purification system from Sartorius (Göttingen). The nitrogen (N_2) used for sample preparation had a purity of 5.0 (≥99.999%) and was applied using a heatable sample concentrator (Techne DB3, Cole Parmer, Staffordshire, United Kingdom).

1.2 Materials

Polypropylene copolymer (PPCO) vessels (Nalgene™, 10-mL nominal volume) were purchased from Thermo Fisher Scientific (Darmstadt), 50-mL and 15-mL centrifuge tubes (PP) were bought from Carl Roth (Karlsruhe). PP vials and screw caps (*ultra clean*) were purchased from Ziemer (Langerwehe). Glasbeads (⌀ = 3 mm) were from Scherf-Präzision Europa (Meiningen). Polyethylene (PE) Pasteur pipettes were purchased from Brand (Wertheim).

Glassware used during sample preparation (glass beads, test tubes) were cleaned prior to use by successively rinsing with 5% acetic acid, H_2O_{mQ}, MeOH, and H_2O_{mQ}, followed by pyrolysis at 550 °C (Carbolite LHT 6/120, Hope, United Kingdom) to avoid contamination.

1.3 Laboratory instrumentation

Quick homogenization or extraction was done with a vortex shaker (IKA MS3, Staufen). For longer extractions, an ultrasonic bath (Sonorex RK 510, Bandelin, Berlin) and a vortexer with multiple places (Multireax, Heidolph Instruments, Schwabach) were used. For centrifugation either an 8KS (Sigma, Osterode) or a Microstar 17R (VWR, Darmstadt) centrifuge was used. TOP assay mixtures were brought to reaction by heating them in an oven (Genlab Ltd, Widnes, UK). Before clean-up, the cooled TOP assay mixtures were dried using an RVC 2-33 IR rotary vacuum concentrator equipped with a CT 04-50 SR cooling trap (both: Christ, Osterode).

1.4 Working solutions

Individual stock solutions of TFAA, PFPrA, perfluoroethyl sulfonamide (FEtSA), perfluorobutyl sulfonamide (FBSA), and perfluorohexyl sulfonamide (FHxSA) with 1.0 mg/mL each were prepared in acetonitrile (ACN). A combined working solution containing native PFCAs (C_2–C_{14}) and PFSAs (C_4–C_8, C_{10}), each of 1.0 µg/mL, was prepared in ACN. This solution was used for the preparation of

calibration samples and in spike recovery experiments. A separate working solution (FASA-mix) of 1.0 µg/mL each in ACN was prepared from four perfluorinated sulfonamides (FASA): perfluoroethyl, -butyl, -hexyl, and -octyl sulfonamide. The FASA-mix was used for the preparation of calibration samples and in spiking experiments. An internal standard working solution (IS-mix) containing all isotopically labelled PFAS (0.1 µg/mL each) was prepared in ACN. Individual solutions of sodium hydroxide (NaOH; 10 N) and potassium peroxodisulfate ($K_2S_2O_8$; 20 g/L) were prepared in ultrapure water (H_2O_{mQ}) and renewed on a weekly basis.

1.5 Preliminary clean-up tests

In the TOP assay, potassium peroxodisulfate ($K_2S_2O_8$) and sodium hydroxide (NaOH) are reacted to produce hydroxyl radicals. In the course of this reaction, large quantities of sulfate are formed and unreacted hydroxide also remains in solution. In addition to the extraction of the analytes, an important requirement for the clean-up step to be developed was, therefore, the effective removal of inorganic anions from the analytes, in order to avoid interferences in chromatography (especially IC) and mass spectrometric detection.

Four approaches were tested: Liquid-liquid extraction (LLE) using an unbuffered QuEChERS salt mix protocol and either (i) ACN or (ii) EtOAc with an acidified TOP assay solution or solid-liquid extraction (SLE) with (iii) acetone and (iv) ACN, respectively, using dried residues (vacuum concentration) of a TOP assay solution. For each approach, triplicates of matrix free (except H_2O_{mQ}, $K_2S_2O_8$, and NaOH) were prepared, reacted and cooled down, as described in the main article (section 2.3) without adding IS.

For LLE, a 10-mL aliquot of the cooled solution was given into a 50-mL PP centrifuge tube and 250 µL of HCl (≥32 %) were added, resulting in a pH of 0-1. Then, 10 mL of either ACN or EtOAc were added, the mixture was shaken for 1-2 min using a vortex shaker, a QuEChERS salt mix was added and the resulting mixture was shaken again for 15 min at 1800 rpm. After 5 min centrifugation at 3000 rpm (2968 × *g*), the organic phase was transferred into a 15 mL PP tube and dried in a gentle N_2 stream. The dry residue was redissolved in 1,0 mL H_2O_{mQ} and the solution was transferred to a glass vial for sulfate analysis.

For SLE, a 10 mL aliquot of the cooled solution was dried as described (main article, section 2.3). The sample preparation was performed as described in the main article (section 2.4), with the difference that 1,0 mL of solvent (either acetone or ACN) was used for extraction in each step and the final extract for sulfate analysis was made up with 1,0 mL H_2O_{mQ}.

2. Instrumental analysis

2.1 Liquid chromatography-mass spectrometry of PFAA and FASA

A liquid chromatography-mass spectrometry (LC-MS) system consisting of an Infinity 1260 HPLC system (Agilent Technologies, Waldbronn), an API 5000 triple quadrupole mass spectrometer (Sciex, Darmstadt) equipped with a Turbo V-ESI source, and a two-position valve was used for instrumental analysis. Measurement was performed with two separate methods based on ion chromatography (IC) and reversed phase (RP) chromatography.

For **IC-MS/MS** a Dionex IonPac AS17-C column (2 mm × 250 mm, Thermo Fisher) with a pre-column (2 mm × 50 mm) filled with the same material was used. Eluent A was 50 mM ammonium bicarbonate, eluent B was MeOH. The gradient for IC started with 20% eluent A, increased to 50% eluent A within 10 min, and decreased to 20% eluent A within 1 min. The system was then equilibrated for 6 min using the initial conditions. The applied flow rate was 0.3 mL/min, the column was thermostated at 30 °C, and 100 µL sample extract were injected. The MS was operated in MRM mode using a dwell time of 200 ms and a curtain gas pressure of 30 psi was applied.

For **RP-LC-MS/MS** a Kinetex C18-column (100 × 3 mm, 2.6 µm, 100 Å; Phenomenex, Aschaffenburg) coupled to a SecurityGuard Ultra pre-column (3 mm, Phenomenex, Aschaffenburg) was used with a binary gradient. Eluent A was 2 mM NH_4Form and 0.2% HCOOH in H_2OmQ/MeOH (4:1, v/v), eluent B was MeOH. The gradient started with 87.5% eluent A, which was held for 2 min before decreasing to 25% eluent A within 3 min and further decreasing to 2.5% eluent A within 6 min. This condition was held for 4 min before switching back to the starting conditions and equilibrating for 5 min. The flow rate was 0.25 mL/min, and the column temperature was set to 35 °C. The MS operated in scheduled MRM mode with measurement windows of 60 s and curtain gas set to 25 psi. Instrumental parameters, which were constant for both methods, are listed in Table S 2.

Table S 2: Constant instrumental parameters used in IC-MS/MS and RP-LC-MS/MS measurements.

Parameter	Value
Heater temperature / °C	500
IonSpray Voltage / V	−4500
CAD gas / psi	5
Nebulizer gas (GS1) / psi	60
Heater gas (GS2) / psi	75

2.2 Compound-specific MS parameters

Compound-specific parameters used in the MS methods were optimized by infusion of methanolic solutions containing single substances into the MS. The optimized values for each compound in scope of this study are listed in Table S 3.

Table S 3: Analytical parameters for mass transitions observed during instrumental analysis of analytes' quantifiers (Qn) and qualifiers (Ql). TFAA, PFPrA and isotopically labelled standards were analyzed with one mass transition.

Substance	Mass transitions (Qn, Ql) / Da	DP /V	CE (Qn, Ql) /V	CXP (Qn, Ql) /V
Analytes				
TFAA	113 → 69	−35	−18	−8
PFPrA	163 → 119	−30	−15	−6
PFBA	213 → 169, 213 → 147	−35	−13, −10	−10,−6
PFPeA	263 → 219, 263 → 197	−30	−12, −12	−12, −12
PFHxA	313 → 269, 313 → 119	−50	−13, −30	−10, −6
PFHpA	363 → 319, 363 → 169	−40	−14, −24	−16, −7
PFOA	413 → 369, 413 → 169	−35	−13, −25	−12, −10
PFNA	463 → 419, 463 → 219	−40	−15, −24	−15, −13
PFDA	513 → 469, 513 → 219	−40	−16, −25	−25, −5
PFUnDA	563 → 519, 563 → 269	−45	−18, −26	−16, −19
PFDoDA	613 → 569, 613 → 169	−70	−19, −38	−20, −10
PFTrDA	663 → 619, 663 → 169	−70	−19, −40	−20, −10
PFTeDA	713 → 669, 713 → 169	−85	−20, −40	−20, −15
PFBS	299 → 80, 299 → 99	−50	−50, −45	−10, −10
PFPeS	349 → 80, 349 → 99	−120	−60, −50	−10, −13
PFHxS	399 → 80, 399 → 99	−60	−75, −52	−12, −12
PFHpS	449 → 80, 449 → 99	−120	−85, −55	−10, −10
PFOS	499 → 80, 499 → 99	−180	−90, −60	−10, −10
PFDS	599 → 80, 599 → 99	−45	−110, −75	−10, −13
FEtSA	198 → 78, 198 → 48	−60	−30, −80	−11, −3
FBSA	298 → 64, 298 → 78	−80	−114 ,−38	−9, −11
FHxSA	398 → 78, 398 → 48	−90	−46, −130	−11, −5
FOSA	498 → 48, 498 → 78	−150	−125, −80	−10, −10
6:2 diPAP*	789 → 443, 789 → 97	−170	−28, −58	−19, −10
8:2 diPAP*	989 → 543, 989 → 97	−210	−36, −100	−17, −15
Internal Standards				
TFAA-M2	115 → 70	−35	−18	−8
PFBA-M4	217 → 172	−40	−14	−20
PFPeA-M5	268 → 223	−25	−12	−20
PFHxA-M2	315 → 270	−40	−14	−18
PFHpA-M4	367 → 322	−40	−13	−18
PFOA-M4	417 → 372	−40	−13	−13
PFNA-M5	468 → 423	−40	−16	−25
PFDA-M2	515 → 470	−75	−17	−22
PFUnDA-M2	565 → 520	−40	−17	−14
PFDoDA-M2	615 → 570	−60	−18	−16
PFTeDA-M2	715 → 670	−85	−20	−21
PFBS-M3	302 → 80	−50	−50	−10
PFHxS-M2	403 → 84	−70	−60	−10
PFOS-M4	503 → 80	−30	−80	−13
FOSA-M8	506 → 78	−25	−70	−7
6:2 diPAP-M4*	793 → 445	−170	−28	−19
8:2 diPAP-M4*	993 → 545	−210	−36	−17

* details on diPAP-analysis are presented in section 2.4.

2.3 Sulfate analysis

The extracts were analyzed for concentrations of sulfate by an in-house facility applying a validated method with an IC system (Dionex ICS-1000) equipped with an AS22 column and a conductivity detector. The chromatography was performed in isocratic mode with an eluent of 1.4 mM sodium bicarbonate and 4.5 mM sodium carbonate, the injection volume was 25 µL, and the samples were quantified using an external calibration prepared in ultrapure water.

2.4 Analysis of 6:2 diPAP and 8:2 diPAP

For both diPAPs the limit of quantification was 5 µg/kg DW each. The concentrations in the soil samples were determined as follows:

Sample preparation: 1 g (DW) of soil was spiked with the internal standards 6:2 diPAP-M4 and 8:2 diPAP-M4 (25 µg/kg DW each) and extracted (15 min sonication and 1 h vortexing) twice by 10 mL of MeOH. After centrifugation at 3000 rpm (2968 × *g*) the MeOH of the combined extract was evaporated to dryness using a gentle stream of N_2. The residues were reconstituted in 1 mL MeOH containing 0.1% NH_4OH.

RP-LC-MS/MS: For chromatographic separation, the Aquity UPLC BEH C18 (100×2.1 mm, 1.7 µm) column from Waters (Eschborn) was used. Eluent A was ultrapure water containing 0.1% NH_4OH and eluent B was MeOH containing 0.1% NH_4OH. The gradient was as follows: The elution started isocratically for 2 min with 90% A followed by a linear gradient for 6.4 min to 0% A. This was held for 5 min. It was followed by a 0.1-min linear gradient to 90% A, which was maintained for 6.5 min to equilibrate the system. The flow was 200 µl/min, the separation was carried out at 40 °C, and the injection volume was set to 10 µl. Mass transitions of the native diPAPs and the internal standards are presented in Table S 3.

3. Results

3.1 Separation of sulfate in clean-up

To assess the separation efficiency, the sulfate concentrations in the extracts were compared with the sulfate concentration of the reacted TOP assay solution. The concentration factors of the methods applied were also taken into account. The results are compiled in Table S 4.

Table S 4: Sulfate concentrations determined in the extracts and the removal efficiency derived therefrom, based on the level present in an aliquot of 10 mL.

Technique	Solvent	c / (mg/L)	Removal / %
SLE	acetone	< 1	> 99.99
SLE	ACN	< 1	> 99.99
LLE	ACN	480	99.80
LLE	EtOAc	< 1	> 99.99

Both SLE methods and LLE with EtOAc were capable to efficiently separate sulfate. In contrast, LLE with ACN still led to substantial sulfate concentrations in the final extracts and was not further considered. In spiking experiments (data not shown) LLE with EtOAc showed insufficient extraction recoveries (<10 %) for the isolation of TFAA. In SLE with acetone, side-reactions occurred, which led to interferences in solvent-exchange. Therefore, ACN was used as extractant for the final method.

3.2 Analytical performance parameters

Table S 5: Instrumental methods and internal standards (IS) associated with the analytes and the analytical performance characteristics determined for PFAAs and FASAs: Linearity for the working range (0.1–25 µg/L, expressed as R^2), retention times (t_R), and limits of quantification of the instrument (LOQ_{Inst}) and referring to a soil sample (LOQ_{Sam}). LOQs were derived according to DIN 32645, the marked (*) value was derived from a signal-to-noise ratio of ≥10.

Analyte	Assigned IS	Instrumental method	t_R / min	R^2	LOQ_{Inst} / (µg/L)	LOQ_{Sam} / (µg/kg)
TFAA	TFAA-M2	IC-MS/MS	4.5	0.994	0.061	0.6
PFPrA	PFBA-M4	IC-MS/MS	4.0	0.993	0.034	0.3
PFBA	PFBA-M4	IC-MS/MS	3.2	0.995	0.052	0.5
PFPeA	PFPeA-M5	RP-LC-MS/MS	8.3	1.000	0.075*	0.8
PFHxA	PFHxA-M2	RP-LC-MS/MS	9.0	0.996	0.084	0.8
PFHpA	PFHpA-M4	RP-LC-MS/MS	9.5	0.994	0.095	1.0
PFOA	PFOA-M4	RP-LC-MS/MS	10.0	0.996	0.110	1.1
PFNA	PFNA-M5	RP-LC-MS/MS	10.5	0.992	0.069	0.7
PFDA	PFDA-M2	RP-LC-MS/MS	11.1	0.996	0.066	0.8
PFUnDA	PFUnDA-M2	RP-LC-MS/MS	11.6	0.998	0.082	0.6
PFDoDA	PFDoDA-M2	RP-LC-MS/MS	12.1	0.996	0.060	0.2
PFTrDA	PFDoDA-M2	RP-LC-MS/MS	12.6	0.998	0.029	0.3
PFTeDA	PFTeDA-M2	RP-LC-MS/MS	13.1	0.991	0.032	0.6
PFBS	PFBS-M3	RP-LC-MS/MS	8.4	0.995	0.063	0.4
PFPeS	PFBS-M3	RP-LC-MS/MS	9.0	0.991	0.043	0.4
PFHxS	PFHxS-M2	RP-LC-MS/MS	9.5	0.996	0.031	0.3
PFHpS	PFHxS-M2	RP-LC-MS/MS	9.9	0.995	0.057	0.6
PFOS	PFOS-M4	RP-LC-MS/MS	10.5	0.992	0.058	0.6
PFDS	PFOS-M4	RP-LC-MS/MS	11.5	0.998	0.042	0.4
FEtSA	PFBS-M3	RP-LC-MS/MS	7.4	0.998	0.052	0.5
FBSA	PFBS-M3	RP-LC-MS/MS	9.1	0.998	0.048	0.5
FHxSA	PFHxS-M2	RP-LC-MS/MS	10.1	0.996	0.061	0.6
FOSA	FOSA-M8	RP-LC-MS/MS	11.1	0.998	0.047	0.5

3.3 Procedural recoveries

Table S 6: Mean procedural recoveries ($\bar{x}_{Rec}$) and corresponding relative standard deviations (RSD) for PFCAs and PFSAs in this study obtained from spiking experiments in triplicate.

Analyte	($\bar{x}_{Rec}$ ± RSD) / %
TFAA	87 ± 5.8
PFPrA	68 ± 8.6
PFBA	95 ± 4.1
PFPeA	106 ± 10
PFHxA	95 ± 3.1
PFHpA	91 ± 2.1
PFOA	97 ± 0.2
PFNA	114 ± 2.7
PFDA	104 ± 3.1
PFUnDA	113 ± 2.9
PFDoDA	111 ± 1.6
PFTrDA	105 ± 25
PFTeDA	123 ± 21
PFBS	111 ± 0.9
PFPeS	119 ± 2.0
PFHxS	110 ± 0.8
PFHpS	110 ± 1.4
PFOS	122 ± 0.8
PFDS	104 ± 0.9

3.4 Concentrations in soil core segments

Table S 7: Mean concentrations ($\bar{x}$), standard deviations (s) and relative standard deviations (RSD) of analyte concentrations in four segments (SEG) of a soil core after oxidative treatment. Samples were analyzed in triplicates; n. d.: not detected.

Analyte	SEG1: 0-10 cm		SEG2: 20-30 cm		SEG3: 40-50 cm		SEG4: 60-70 cm	
	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)
TFAA	15	0.07	16	0.51	2.8	0.68	3.3	1
PFPrA	17	1.5	20	0.28	n. d.	-	n. d.	-
PFBA	45	12	47	0.9	6.4	0.71	5.7	0.52
PFPeA	100	9.7	130	16	3.6	0.76	3.1	0.2
PFHxA	110	6.7	150	23	4.1	1.3	3.7	0.17
PFHpA	190	39	210	50	2.8	2.4	2.6	3.2
PFOA	590	150	520	110	8.5	1	6.2	0.32
PFNA	130	27	140	13	3.1	0.59	2.8	0.37
PFDA	230	36	330	50	21	3.3	18	3
PFUnDA	120	19	140	51	1.1	0.58	n. d.	-
PFDoDA	120	6.7	120	17	2.2	0.63	n. d.	-
PFTrDA	35	3.2	43	8.5	n. d.	-	n. d.	-
PFTeDA	42	2.8	53	4.8	n. d.	-	n. d.	-
PFBS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFPeS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFHxS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFHpS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFOS	320	6.3	520	26	52	1.2	40	0.33
PFDS	n. d.	-	n. d.	-	n. d.	-	n. d.	-

Table S 8: Native mean concentrations ($\bar{x}$), standard deviations (s) and relative standard deviations (RSD) of analyte concentrations in four segments (SEG) of a soil core. Samples were analyzed in triplicates; n. d.: not detected.

Analyte	SEG1: 0-10 cm		SEG2: 20-30 cm		SEG3: 40-50 cm		SEG4: 60-70 cm	
	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)	$\bar{x}$ / (µg/kg dw)	s / (µg/kg dw)
TFAA	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFPrA	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFBA	1.5	0.036	3.3	0.056	1.6	0.088	1.5	0.045
PFPeA	n. d.	-	5.5	0.1	n. d.	-	n. d.	-
PFHxA	1.1	0.089	3.4	0.31	1.0	0.15	1.1	0.06
PFHpA	1.3	0.43	2.5	0.36	n. d.	-	n. d.	-
PFOA	9.3	0.11	19	1.4	3.1	0.35	2.1	0.57
PFNA	5.4	0.44	13	2.9	2.9	0.21	2.8	0.33
PFDA	84	9	150	29	20	0.95	15	3.4
PFUnDA	22	2.1	28	4.7	n. d.	-	n. d.	-
PFDoDA	64	2.1	59	4.2	n. d.	-	n. d.	-
PFTrDA	6	2.7	7.1	0.21	n. d.	-	n. d.	-
PFTeDA	7.1	0.27	6.3	1.3	n. d.	-	n. d.	-
PFBS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFPeS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFHxS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFHpS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
PFOS	320	1.7	520	27	51	0.57	38	1.1
PFDS	n. d.	-	n. d.	-	n. d.	-	n. d.	-
FEtSA	n. d.	-	n. d.	-	n. d.	-	n. d.	-
FBSA	n. d.	-	n. d.	-	n. d.	-	n. d.	-
FHxSA	n. d.	-	n. d.	-	n. d.	-	n. d.	-
FOSA	98	3.9	130	0.22	5.8	0.34	3.1	0.23
6:2 diPAP*	53	-	56	-	n. d.	-	n. d.	-
8:2 diPAP*	150	-	180	-	n. d.	-	n. d.	-

*** diPAP analyses were performed as single determination.**