Supporting Information:

Taking a Look at the Surface: μ-XRF Mapping and Fluorine K-edge μ-XANES Spectroscopy of Organofluorinated Compounds in Environmental Samples and Consumer Products

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<u>Total SI-Figures:</u> 24

<u>Total SI-Tables:</u> 6

<u>Total SI-Pages:</u> 39

Table of Contents

Instrumental Methods

Fluorine K-edge XANES spectroscopy.

Fluorine K-edge XANES spectra (bulk and µ-XANES) were collected on the PHOENIX II beamline of the Swiss Light Source (SLS, Villigen, Switzerland). All soil and sewage sludge samples were pressed into small pellets for easier sample preparation prior to the measurements and the experiments were conducted at room temperature under a high vacuum (10^{-6} mbar). The incoming intensity, I_0, was measured from the total electron yield signal taken from a nickel coated, 0.5 mm thick polyester foil. Bulk-XANES spectra were collected from an area of approx. 2×3 mm² at the sample over the range 660–780 eV in fluorescence mode, using a silicon drift diode (SDD, manufacturer: Ketek). For µ-XANES, the beam spot size was reduced to 8×15 µm^2 by elliptically bend Kirkpatrick-Baez mirrors. Two-dimensional micro-X-ray fluorescence (µ-XRF) elemental maps of 300 x 300 µm^2 were first collected at 695 eV (above the F K-edge) by raster scanning the sample with respect to the X-ray beam and a step size of 10.0 µm. Some of the maps were repeated after some hours see if a thermal shift of the beam take place. However, no shift was observed. To optimize the discrimination of the various µ-XRF line contributions (C, O and F), the µ-XRF spectra were batch fitted at each map pixel using the PyMca software.[1] Areas with varying levels of fluorine fluorescence were then targeted for micro-XANES analysis. To determine the XANES point spectra, from the X-ray fluorescence point spectra, the integrated count rate of the fluorine peak was used without further background subtraction or peak fitting. The collected spectra were normalized, and background corrected using the Athena software from the Demeter 0.9.26 package.[2]

Additionally, the fluorine K-edge micro-XANES spectra of each spot were analyzed with linear combination (LC) fitting of the fluorine reference compounds with the Demeter Athena software.[3] Therefore, twelve reference data sets of the following fluorine K-edge XANES spectra were preselected and then processed via linear combination: CaF_2, $FeF_3 \cdot 3H_2O$, $AlF_3 \cdot 3H_2O$, Fluoroapatite, Na_2SiF_6, NH_4F, PFPrA, PFOA, PFOS, K-PFBS, Na-TFMS, PFPD, HFPO-DA, 6:2-FTOH, 6:2-FTAc, PTFE, PFA, fluoxetine, tolylfluanid, 4-fluorobenzoic acid. The spectral fitting range was set from -5 to +13 eV of the fluorine K-edge at 690 eV. The maximum number of compounds in the final LC fit was limited to four and the sum of the compounds was forced to add up to 100 %. From the resulting LC fits the one with the lowest R-values were chosen (see also Table S1).

LC-MS/MS Analysis

Analyses for soil and sewage sludge samples were performed using an Agilent 1260 HPLC and an AB SCIEX TSQ 6500 as mass selective detector. 7 µL of the samples was injected and separated on a Nucleodur C 18 Pyramid pre-column (8 mm × 3 mm, 3 µm) and a Nucleodur C18 Pyramid column (125 mm × 2 mm; 3 µm) (both Macherey- Nagel, Düren, Germany) at 35 °C and a flow rate of 0.3 ml/min using the following gradient program using water with 10 mM ammonium acetate solution (eluent A) and methanol (eluent B): the eluent composition of 75 % A and 25 % B at the beginning changed after 9 min to 25 % A and 75 % B. The ion source was operated at 425 °C and with an ion spray voltage of 1200 V and all measurements were executed in the multireaction mode (MRM).

All samples were analysed as triplicates. Recovery rates were determined by spiking soil/sludge samples with appropriate concentration of all PFAS targets. All LOQs for individual PFAS were determined by applying the respective regulations according to DIN 38402-51: 2017-05 (see also Table S2).4

For textile and paper samples, chromatographic separation was achieved using an Agilent ZORBAX RRHD Eclipse Plus C18 (100 mm × 3 mm, 1.8 µm) column installed on an Agilent 1290 Infinity II UHPLC system consisting of the following modules: Agilent 1290 Infinity II High Speed Pump (G7120A), Agilent 1290 Infinity II Multisampler with Multiwash Option (G7167B) and Agilent 1290 Infinity II Multicolumn Thermostat (G7116B).

A gradient elution was performed with 5 mM ammonium acetate in water (mobile phase A) and methanol (mobile phase B) at 0.4 mL/min with a total run time of 17 minutes. To minimize background PFAS contamination, the Agilent PFC-Free HPLC Conversion Kit (part number 5004 0006) and a PFC delay column (part number 5062 8100) for delaying potential per- or polyfluorochemical impurities from the mobile phases was installed on the UHPLC system.

Dynamic MRM (dMRM) analysis was performed using a 6495C LC/TQ with an Agilent Jet Stream (AJS) ion source operated in negative ionization mode. Data acquisition and processing were performed using Agilent MassHunter Data LC/MS Acquisition software version 10.0 and Quantitative Analysis software version 10.2, respectively.

Again, all samples were analysed as triplicates. PFAS target recovery rates were determined by spiking samples with known PFAS concentrations. LOQs for individual PFAS were determined by applying DIN 32645 (see also Table S3).5

Reference compound calibration was done by applying the isotope dilution calibration method. Linear calibration curves contained up to eight calibration points and ranged from 0.07 – 48.55 ng/g per analyte. The overall weight factor was required to yield R2 > 0.99. Exceeding the range of the specified calibration curves was not tolerated and samples had to be diluted and remeasured if necessary. All measured blank values were below the limit of detection.

Fluorine µ-XANES spectra

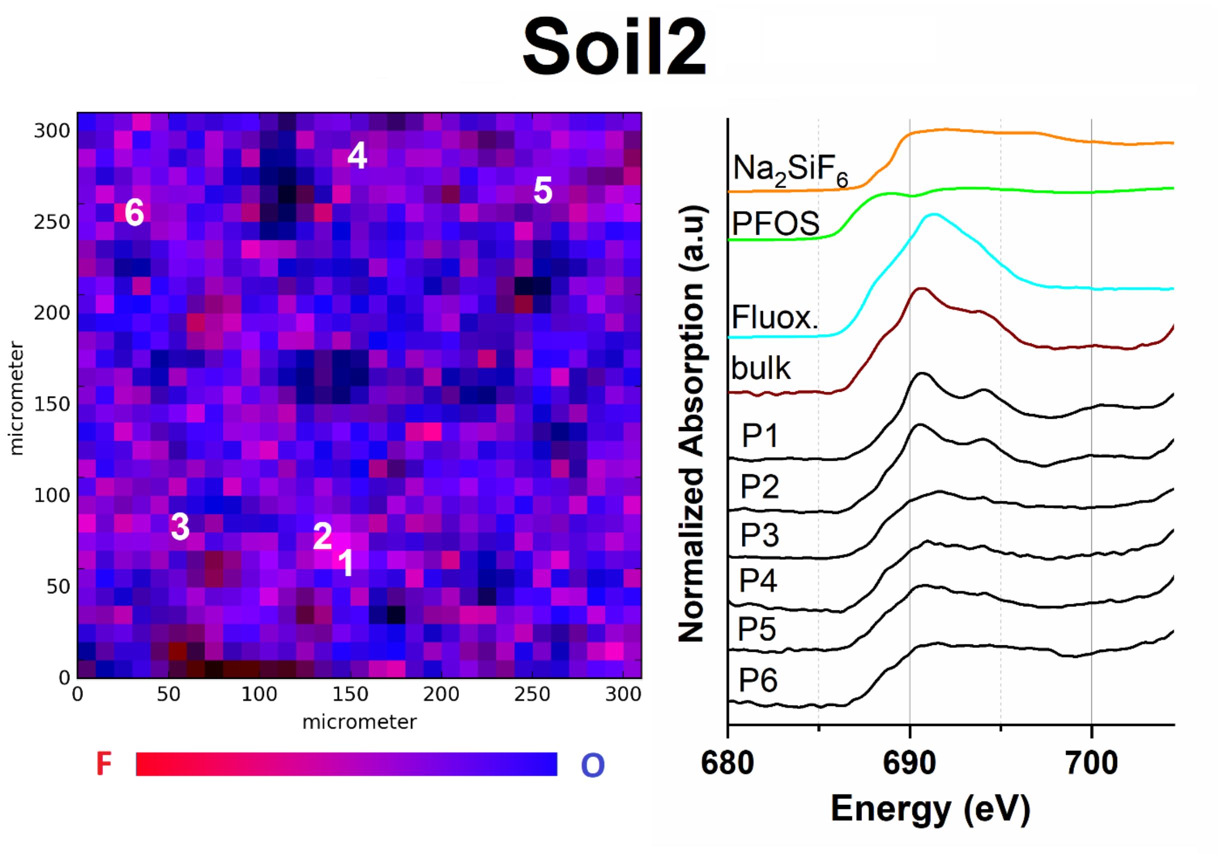


Figure S1: µ-XRF map of fluorine (red) and oxygen (blue) (left; 300 × 300 µm^2, 10 µm step, color scale is arbitrary) and corresponding F K-edge micro-XANES spectra of **Soil2** (right). All black spots in µ-XRF map are low in intensity; PFOS = perfluorooctanesulfonic acid; Fluox. = fluoxetine.

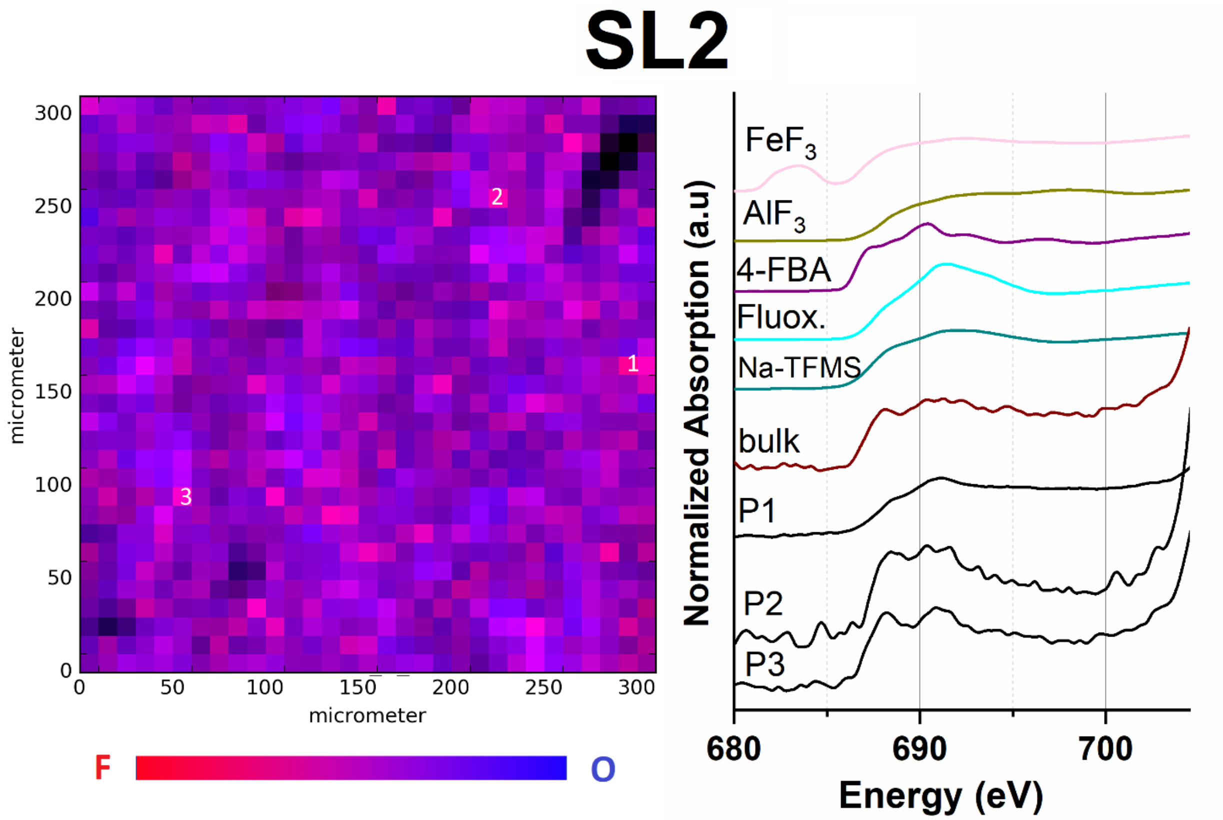


Figure S2: μ-XRF map of fluorine (red) and oxygen (blue) (left; 300 × 300 μm^2, 10 μm step, color scale is arbitrary) and corresponding F K-edge micro-XANES spectra of **SL2** (right). All black spots in μ-XRF map are low in intensity; Na-TFMS = sodium trifluormethyl sulfonate; Fluox. = fluoxetine; 4-FBA = 4-flurobenzoic acid.

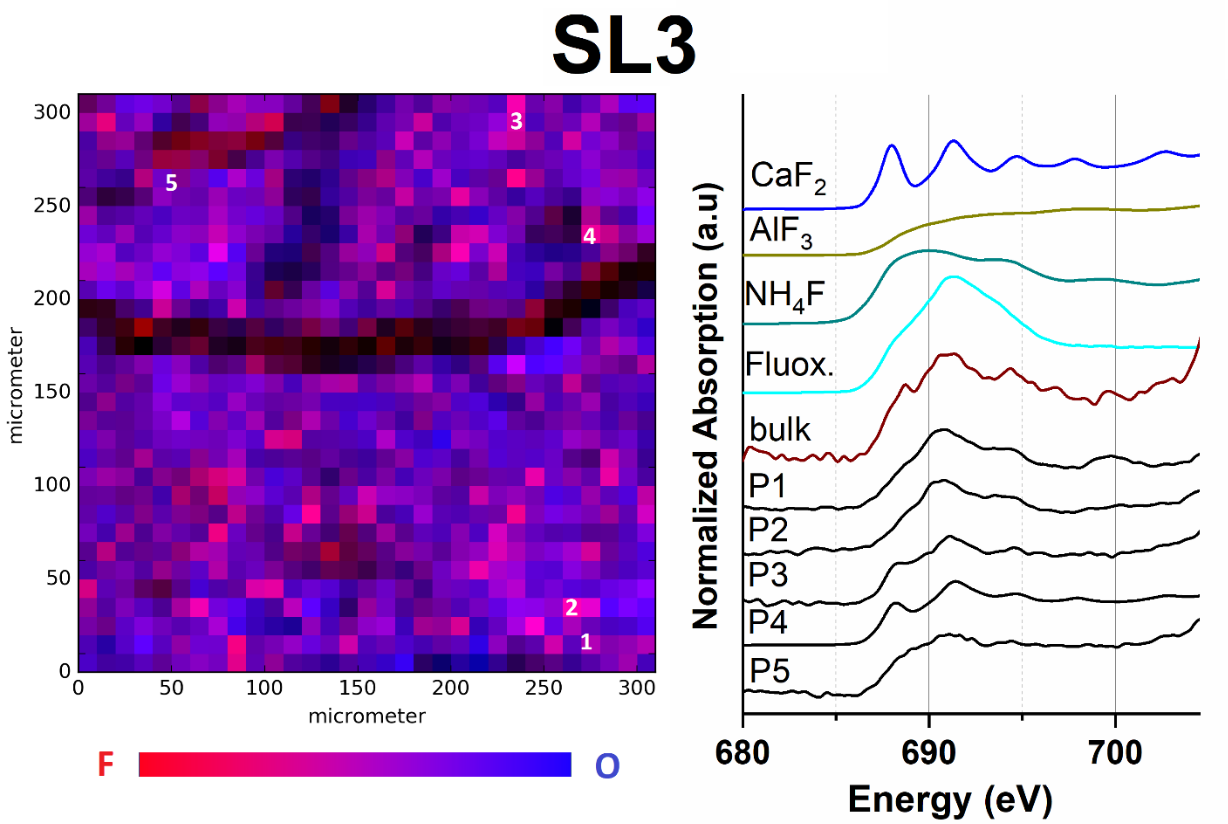


Figure S3: μ-XRF map of fluorine (red) and oxygen (blue) (left; 300 × 300 μm^2, 10 μm step, color scale is arbitrary) and corresponding F K-edge micro-XANES spectra of **SL3** (right). All black spots in μ-XRF map are low in intensity; Fluox. = fluoxetine.

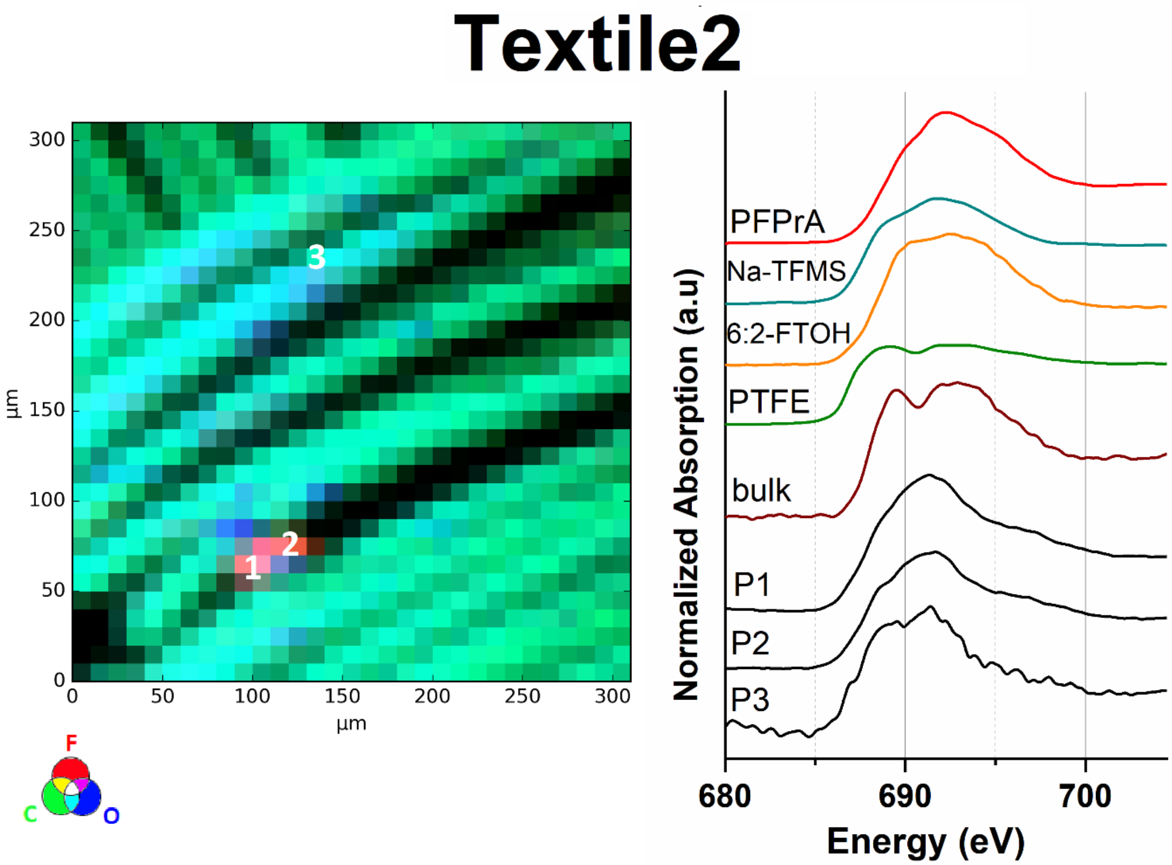


Figure S4: µ-XRF map of fluorine (red), carbon (green) and oxygen (blue) (left) and corresponding F K-edge micro-XANES spectra of **Textile2** (right). All µ-XRF maps 300 × 300 µm^2, 10 µm step, color scale is arbitrary**.** All black spots in µ-XRF map are low in intensity; Na-TFMS = sodium trifluormethyl sulfonate; 4-FBA = 4-fluorobenzoic acid; HFPO-DA = hexafluoropropylene oxide dimer acid.

Element specific X-ray fluorescence maps of investigated samples

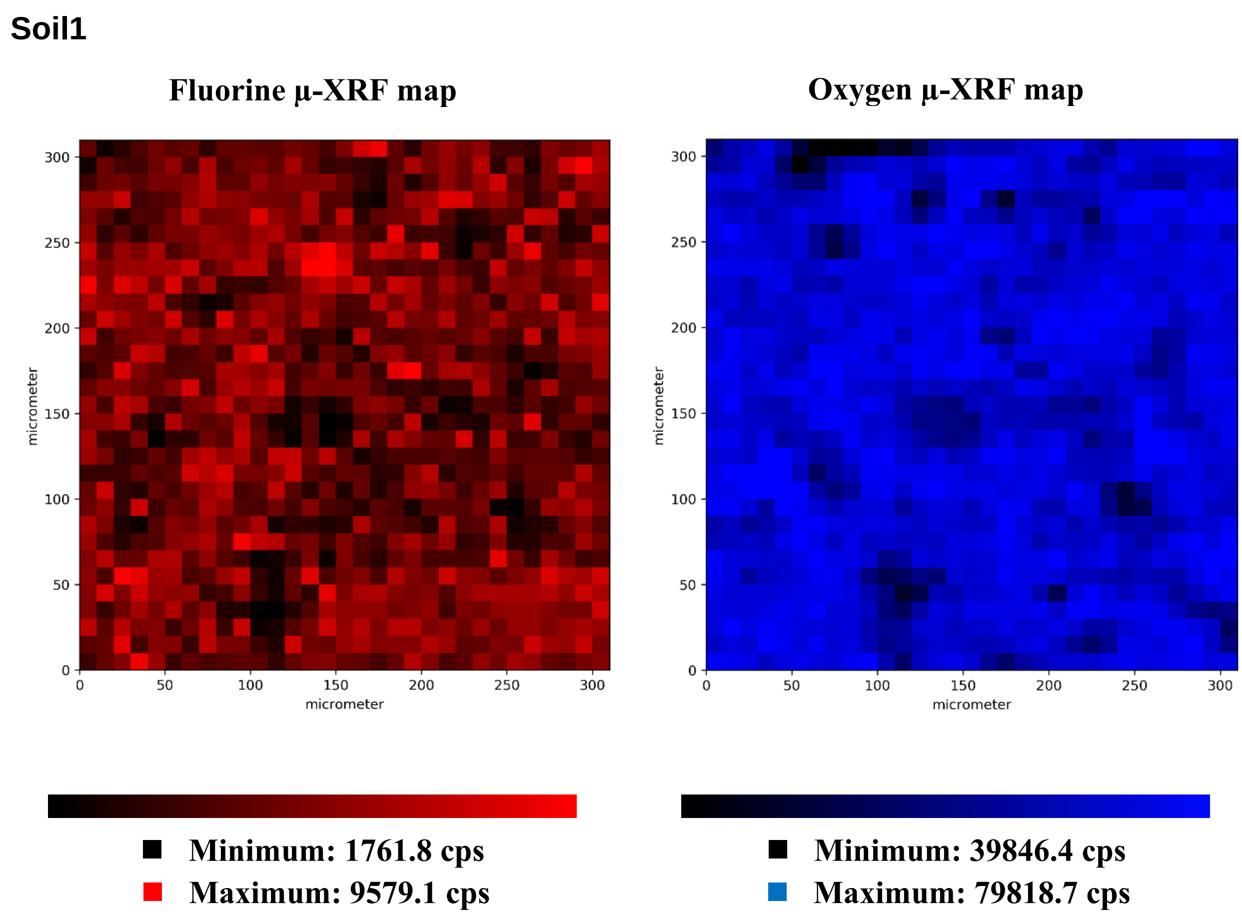


Figure S5: Separated µ-XRF maps of recorded fluorine (left, red) and oxygen atoms (right, blue) at the surface of **Soil1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 µm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

Soil2

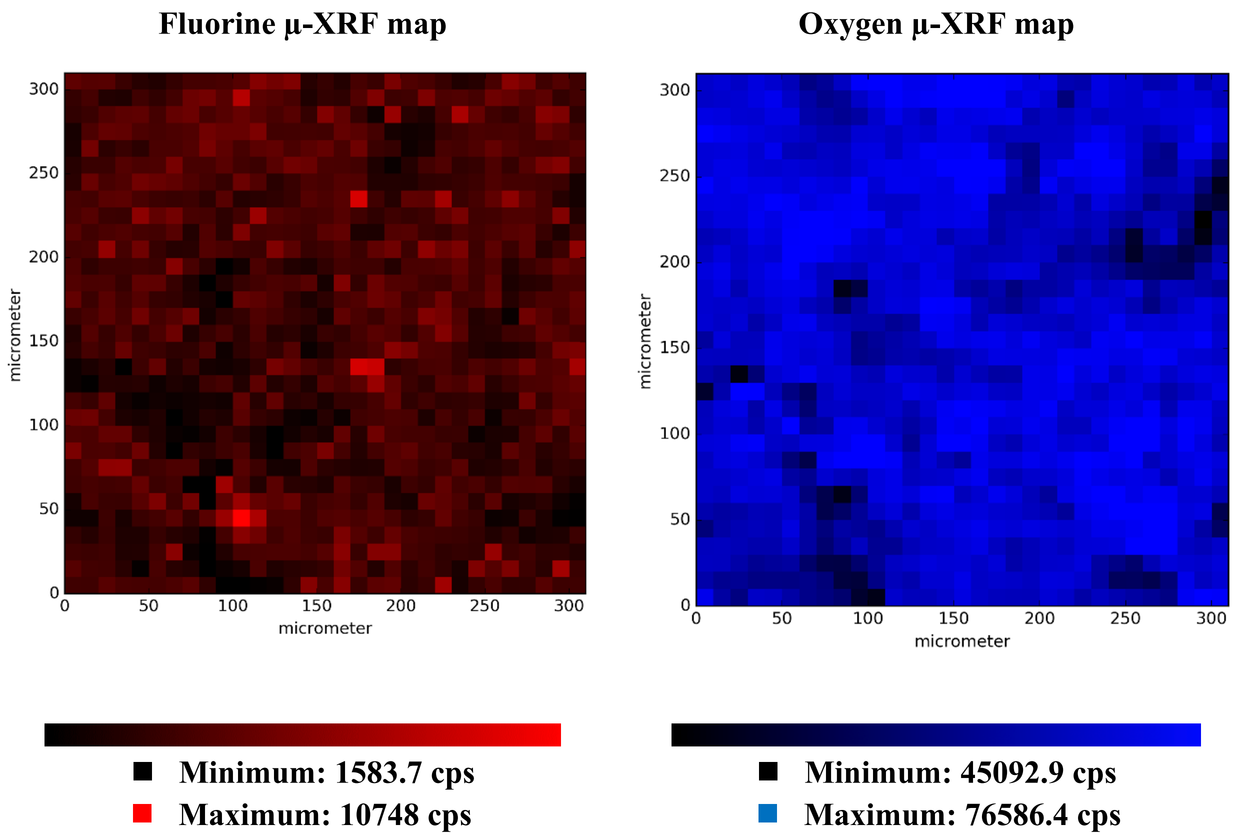


Figure S6: Separated µ-XRF maps of recorded fluorine (left, red) and oxygen atoms (right, blue) at the surface of **Soil2**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 μm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

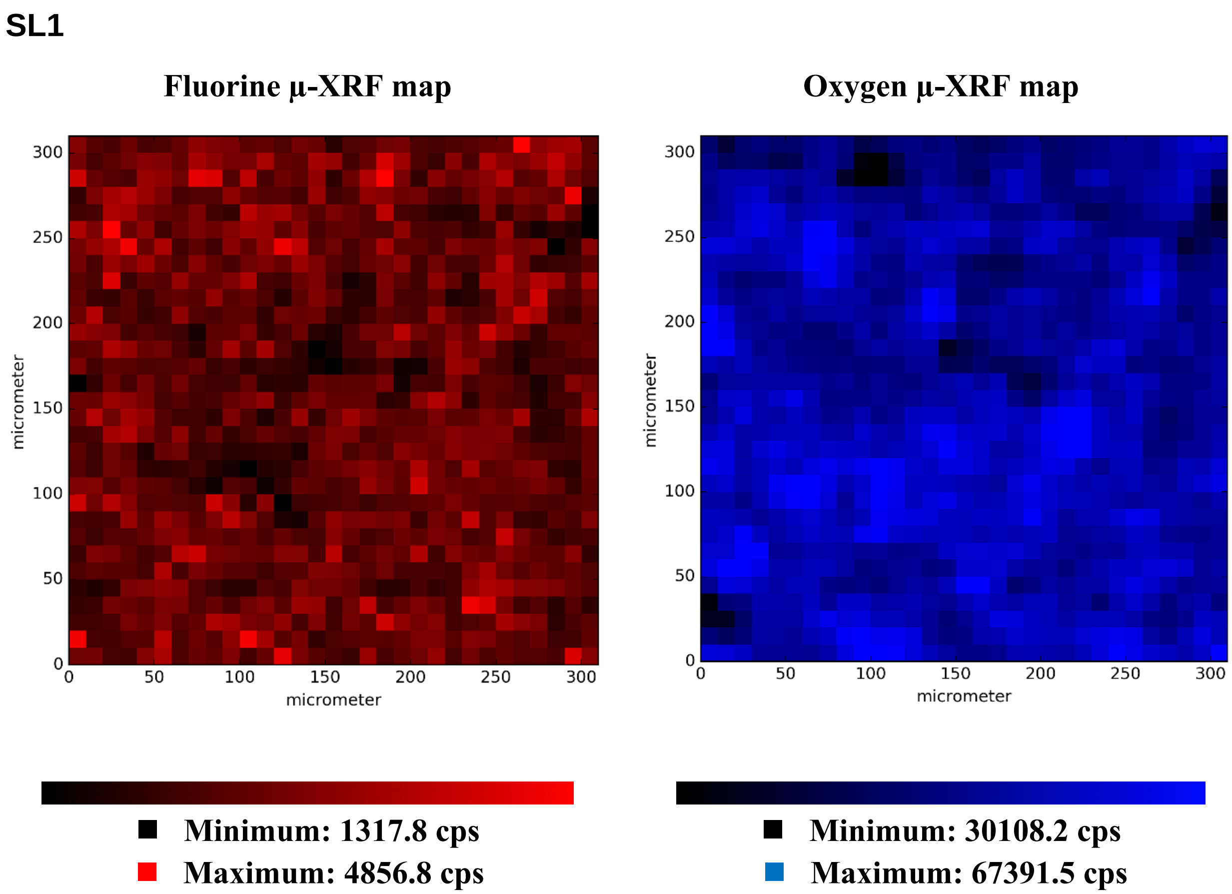


Figure S7: Separated µ-XRF maps of recorded fluorine (left, red) and oxygen atoms (right, blue) at the surface of **SL1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 µm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

SL2

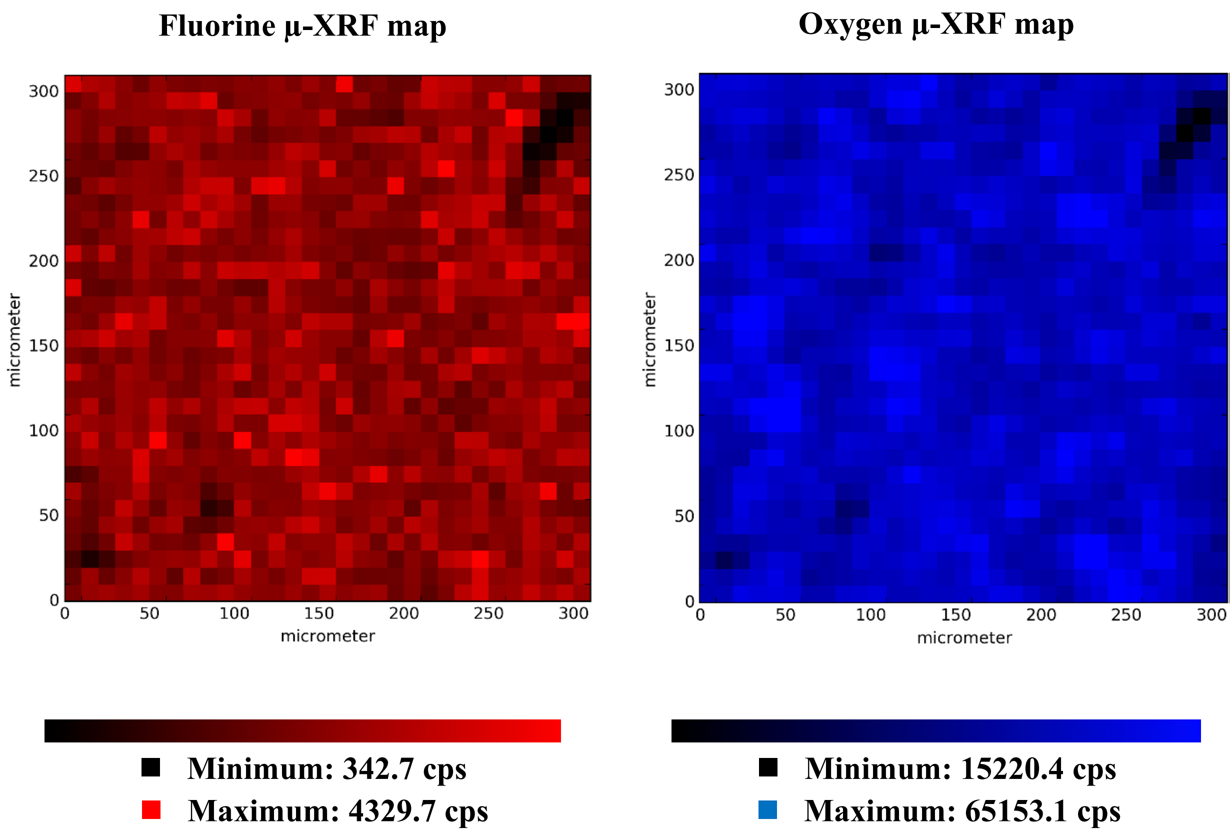


Figure S8: Separated μ-XRF maps of recorded fluorine (left, red) and oxygen atoms (right, blue) at the surface of **SL2**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All μ-XRF maps span 300 × 300 μm^2, 10 μm step, color scale is arbitrary. All black spots in μ-XRF map are considered low in intensity.

SL3

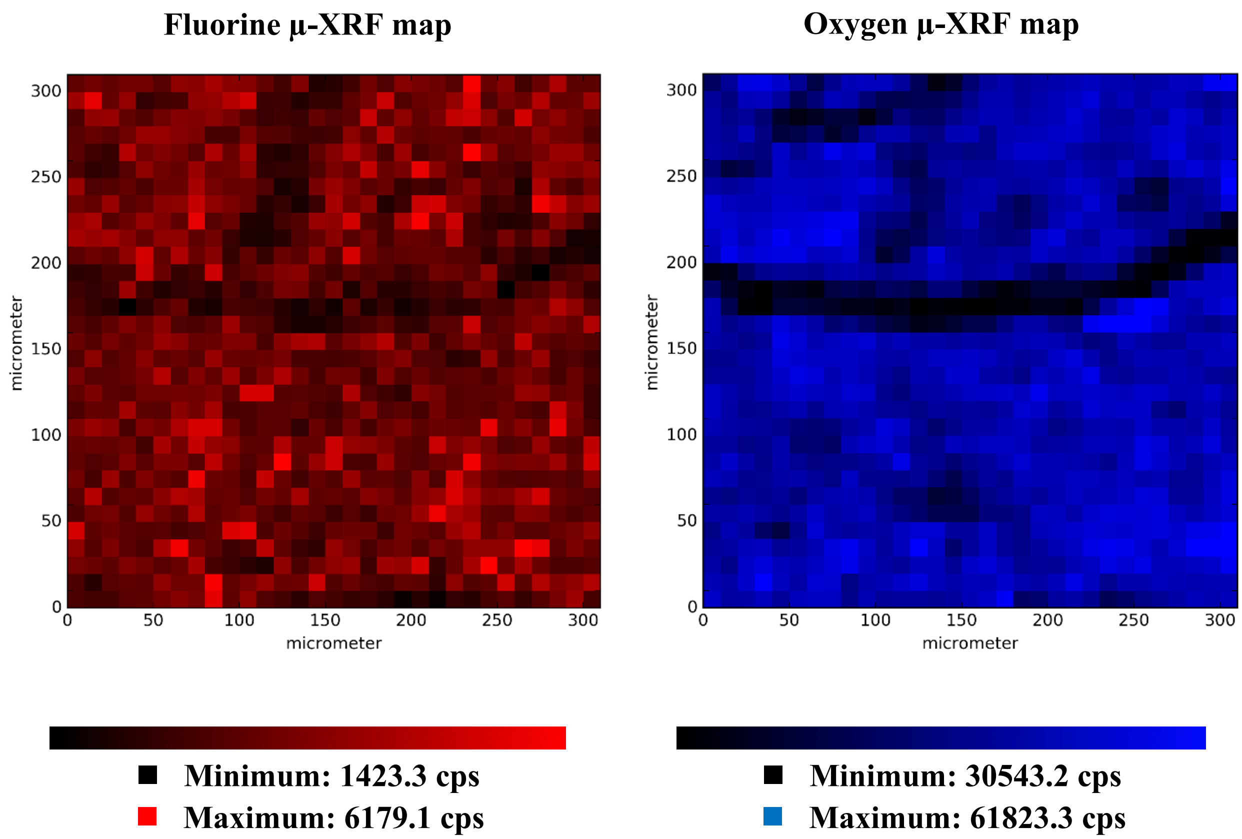


Figure S9: Separated µ-XRF maps of recorded fluorine (left, red) and oxygen atoms (right, blue) at the surface of **SL3**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 µm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

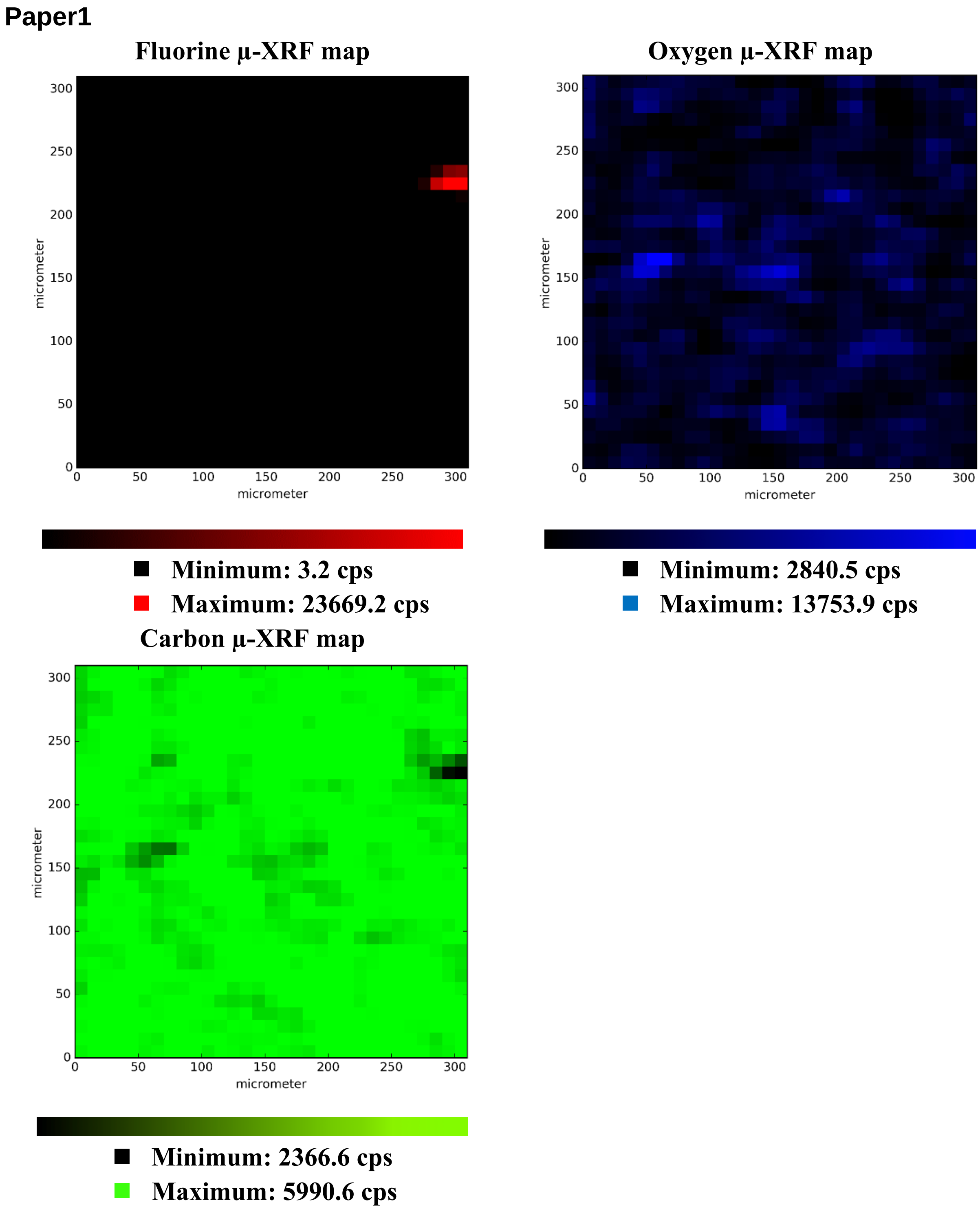
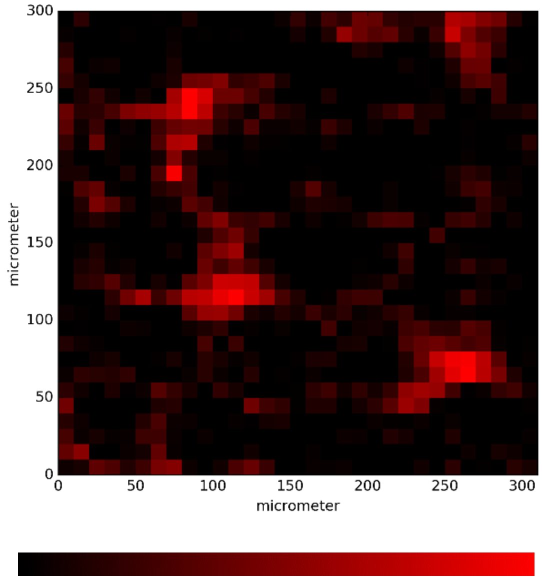


Figure S10: Separated µ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Paper1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 µm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

Textile1

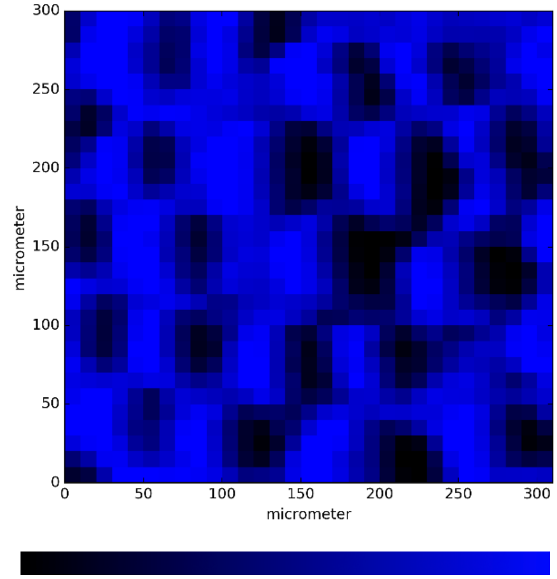
Fluorine μ-XRF map



■ **Minimum: 0.262761 cps**

■ **Maximum: 2422.83 cps**

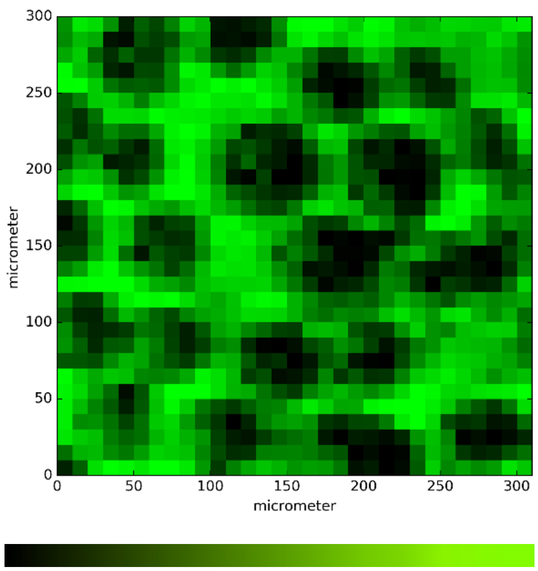
Oxygen μ-XRF map



■ **Minimum: 3343.07 cps**

■ **Maximum: 27668.2 cps**

Carbon μ-XRF map



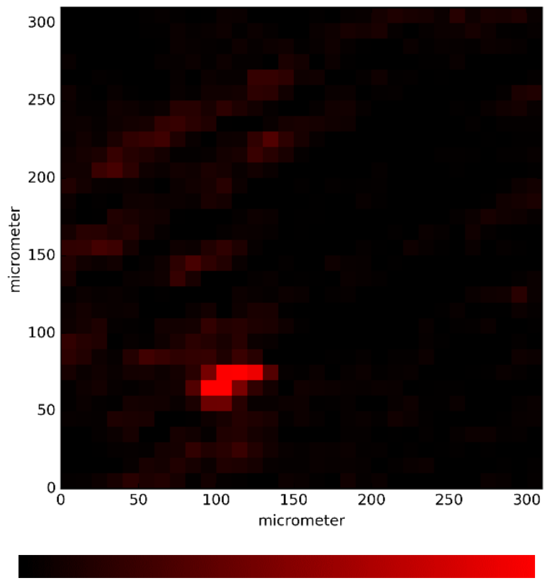
■ **Minimum: 237.362 cps**

■ **Maximum: 3352.37 cps**

Figure S11: Separated μ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Textile1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All μ-XRF maps span 300 × 300 μm^2, 10 μm step, color scale is arbitrary. All black spots in μ-XRF map are considered low in intensity.

Textile2

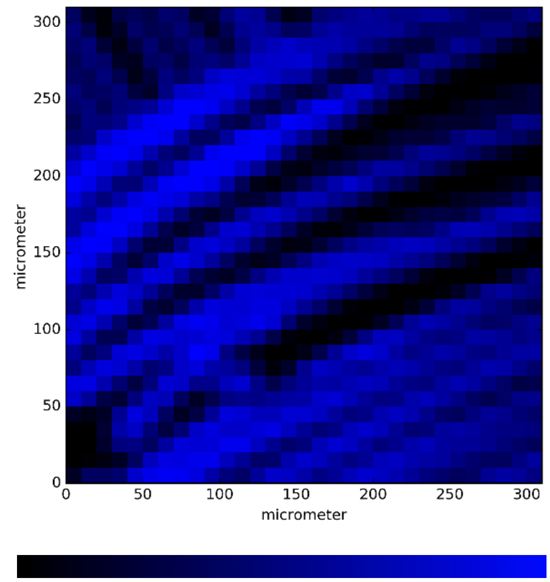
Fluorine μ-XRF map



■ **Minimum: 33.7 cps**

■ **Maximum: 7479.4 cps**

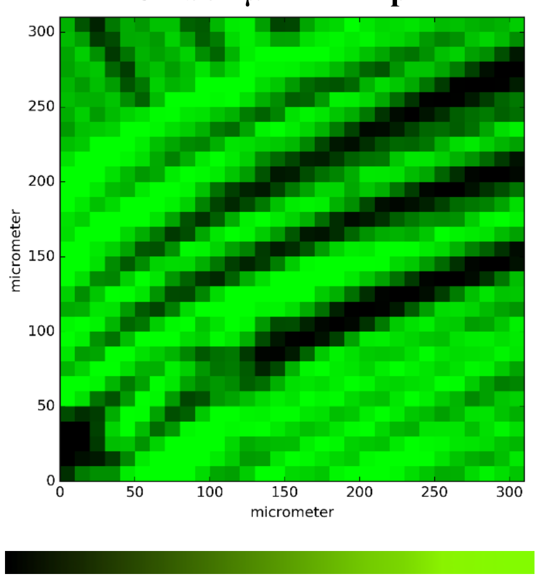
Oxygen μ-XRF map



■ **Minimum: 1330.1 cps**

■ **Maximum: 19214.9 cps**

Carbon μ-XRF map



■ **Minimum: 437.6 cps**

■ **Maximum: 4251.2 cps**

Figure S12: Separated μ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Textile2**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All μ-XRF maps span 300×300 μm^2, 10 μm step, color scale is arbitrary. All black spots in μ-XRF map are considered low in intensity.

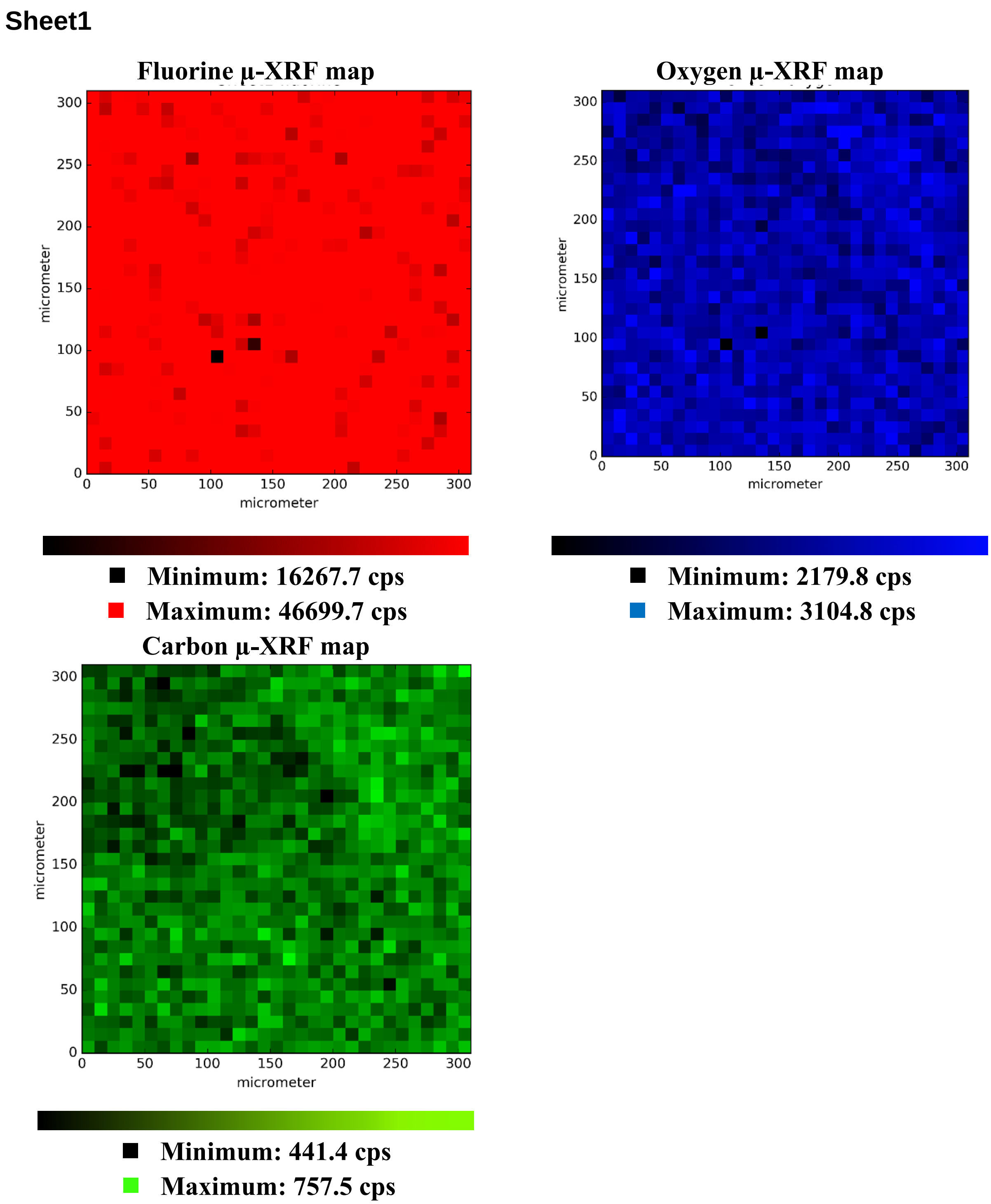


Figure S13: Separated µ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Sheet1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 μm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

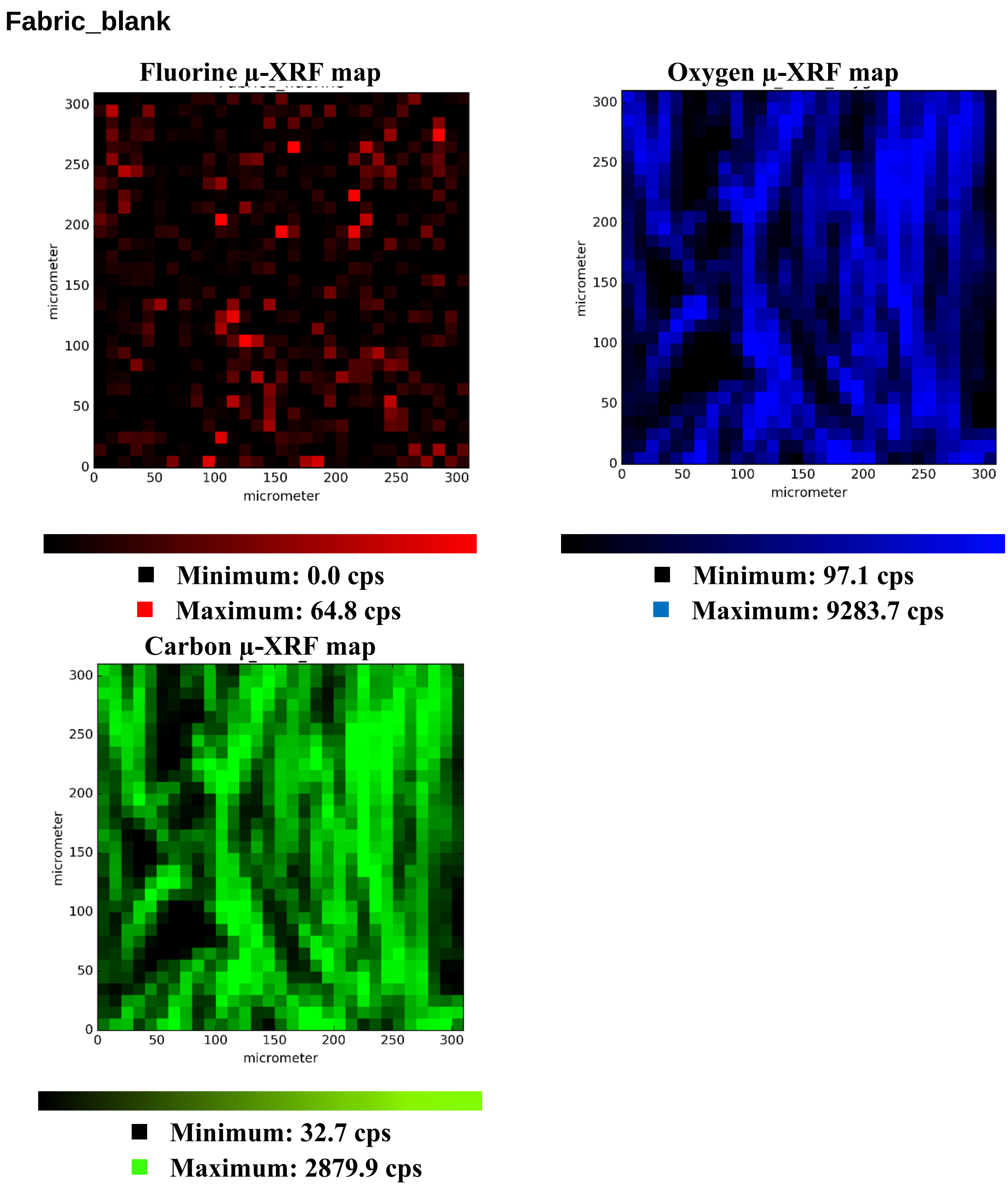


Figure S14: Separated µ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Fabric_blank**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300 × 300 μm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

Fabric1

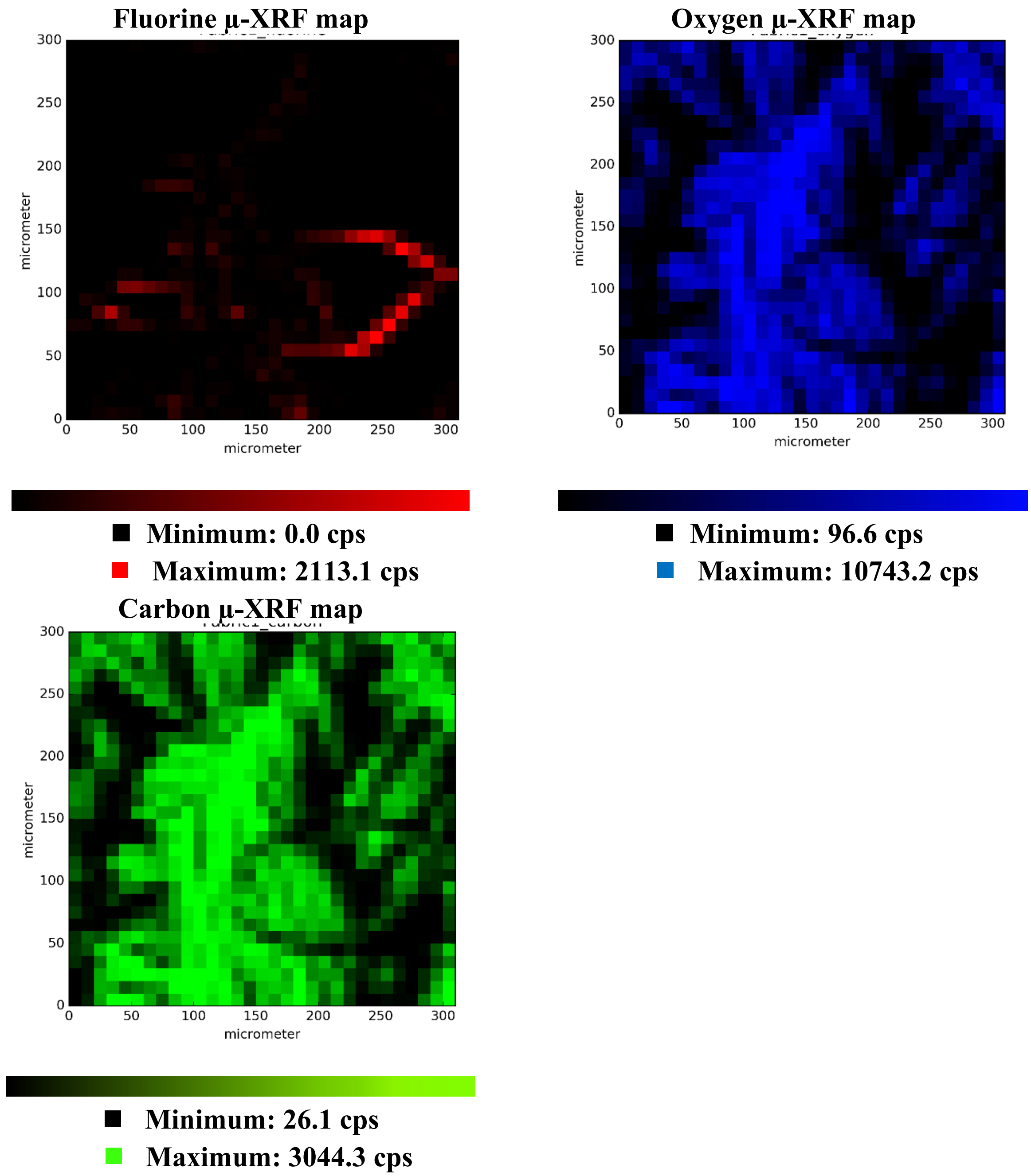


Figure S15: Separated μ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Fabric1**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All μ-XRF maps span 300 × 300 μm^2, 10 μm step, color scale is arbitrary. All black spots in μ-XRF map are considered low in intensity.

Fabric2

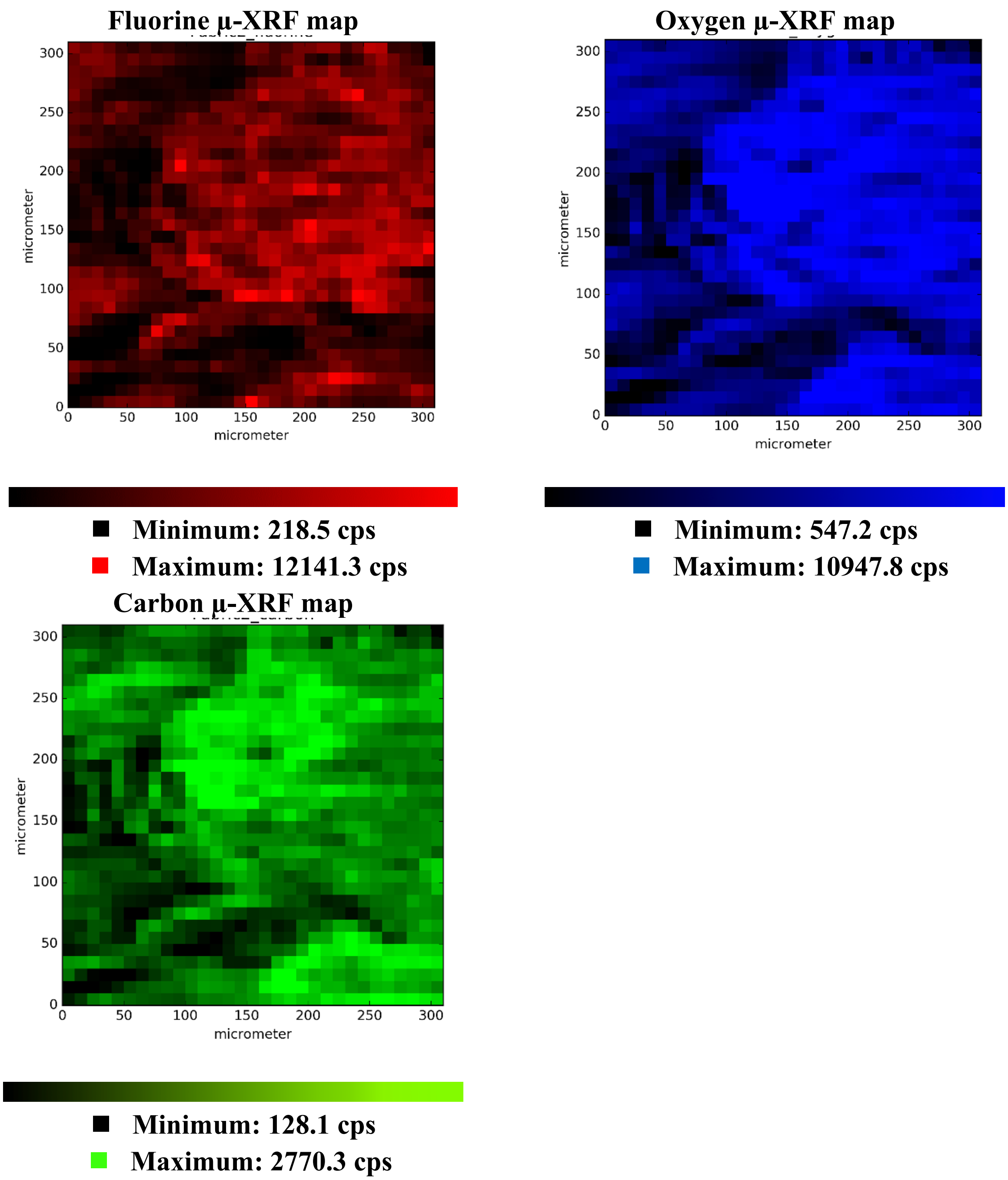


Figure S16: Separated µ-XRF maps of recorded fluorine (upper left, red), carbon (lower left, green) and oxygen atoms (right, blue) at the surface of **Fabric2**. Respective maxima and minima recorded counts per second (cps) are shown by color gradients. All µ-XRF maps span 300×300 µm^2, 10 µm step, color scale is arbitrary. All black spots in µ-XRF map are considered low in intensity.

Limitation of detection: Dilution series of PFOS in sand samples

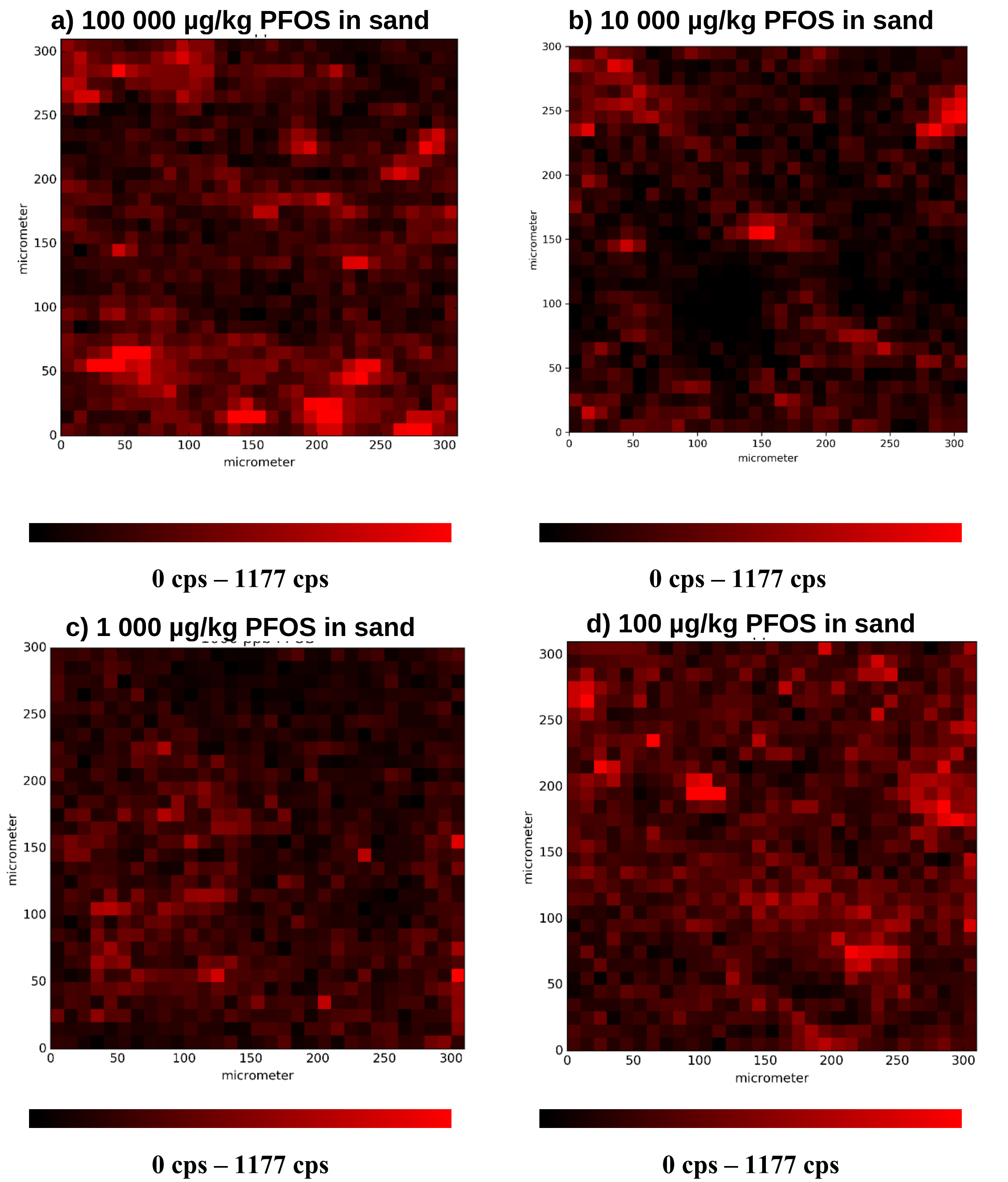


Figure S17: Normalized fluorine specific µ-XRF maps of a) 100000 µg/kg based on fluorine amount of PFOS in quartz sand, b) 10000 µg/kg F of PFOS in quartz sand, c) 1000 µg/kg F of PFOS in quartz sand and d) 100 µg/kg F of PFOS in quartz sand. All µ-XRF maps were recorded by 10 µm step and span 300 × 300 µm^2. The color scale for all maps is normalized from 0.3 cps (minimum, black) to 1177 counts per second (maximum, red).

Fluorine K-edge XANES Reference spectra

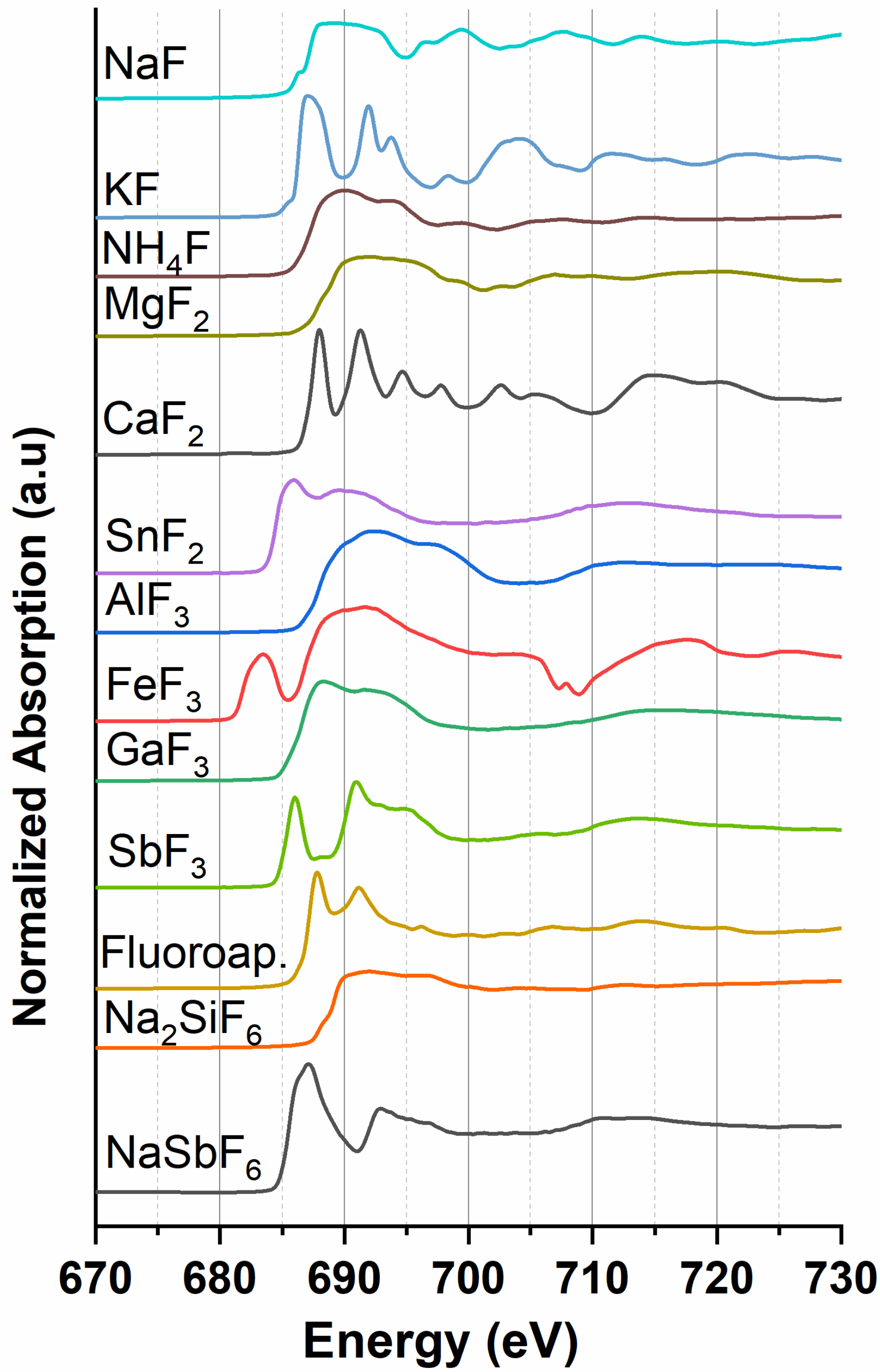


Figure S18: Fluorine K-edge XANES spectra of various inorganic compounds.

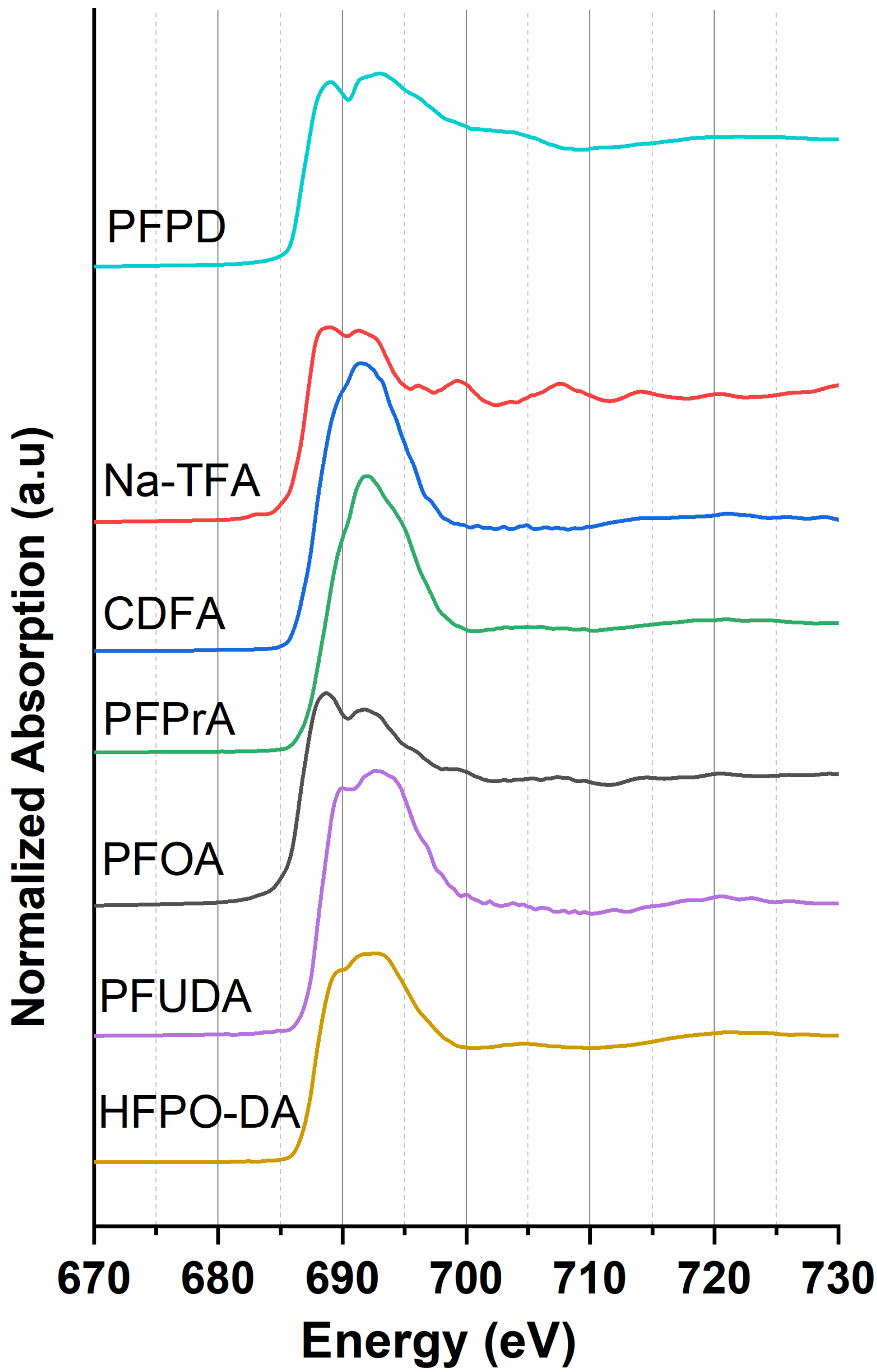


Figure S19: Fluorine K-edge XANES spectra of Perfluoropentadecane (PFPD) and various PFCAs.

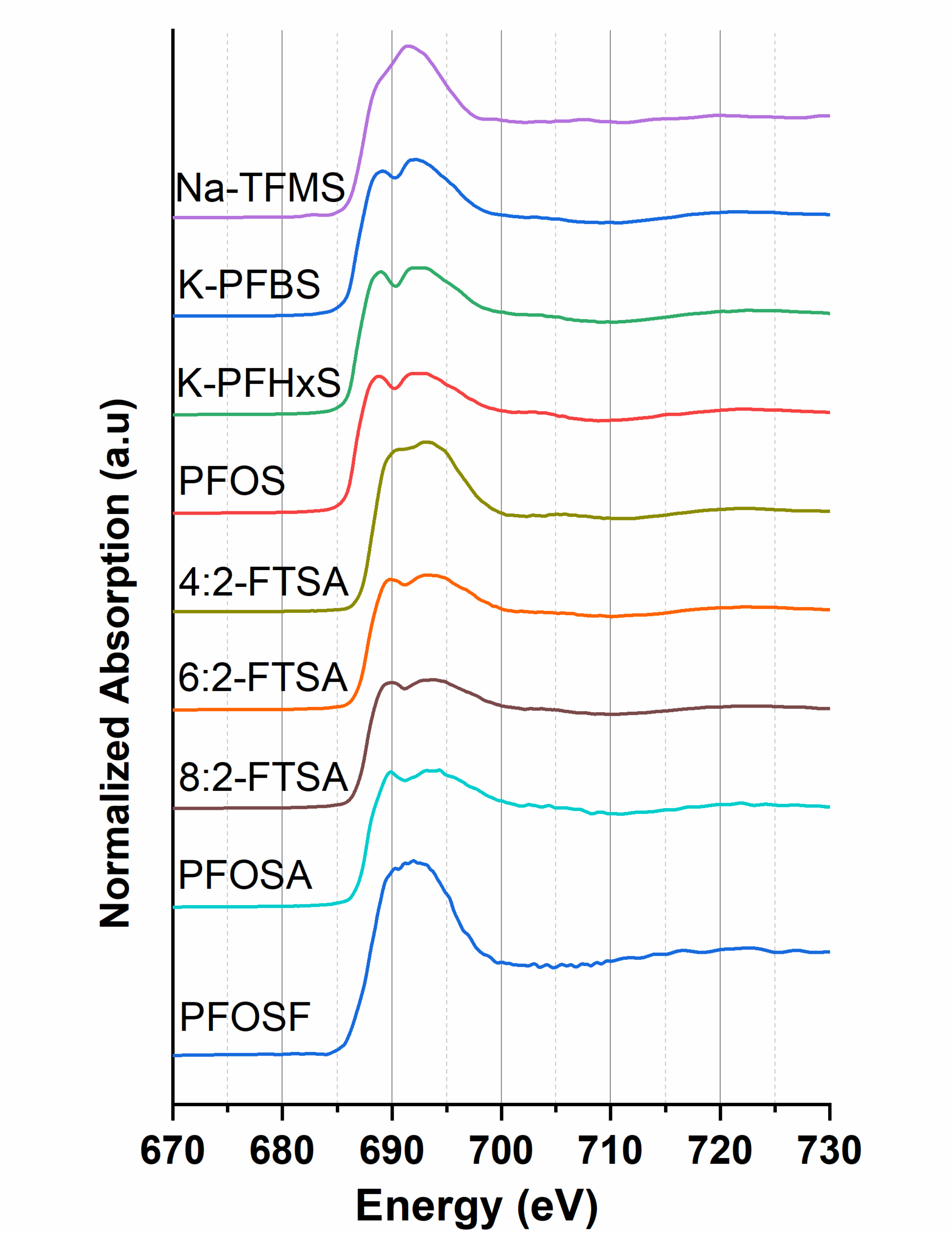


Figure S20: Fluorine K-edge XANES spectra of various PFSAs.

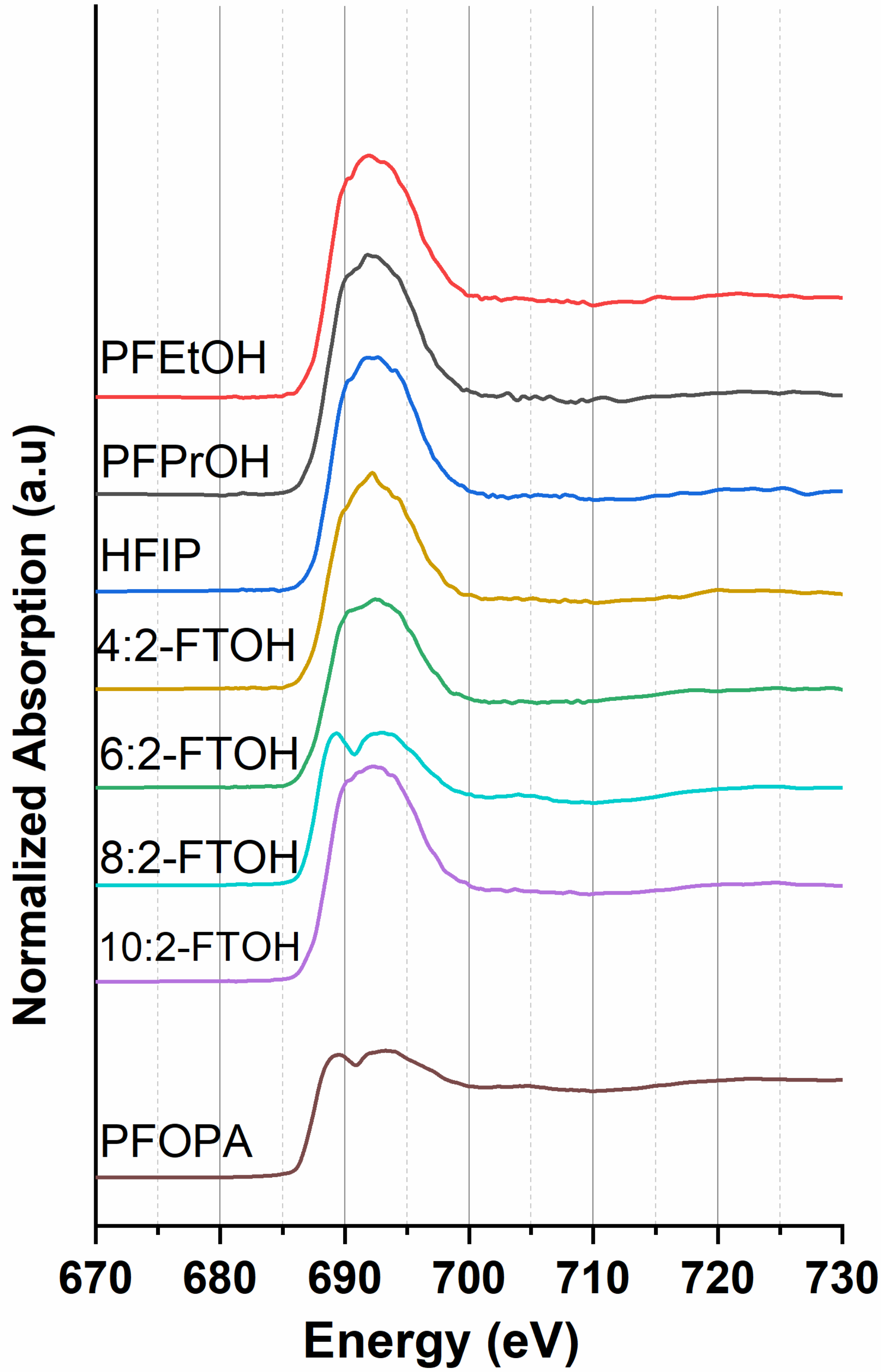


Figure S21: Fluorine K-edge XANES spectra of various fluorinated alcohols, FTOHs and PFOPA.

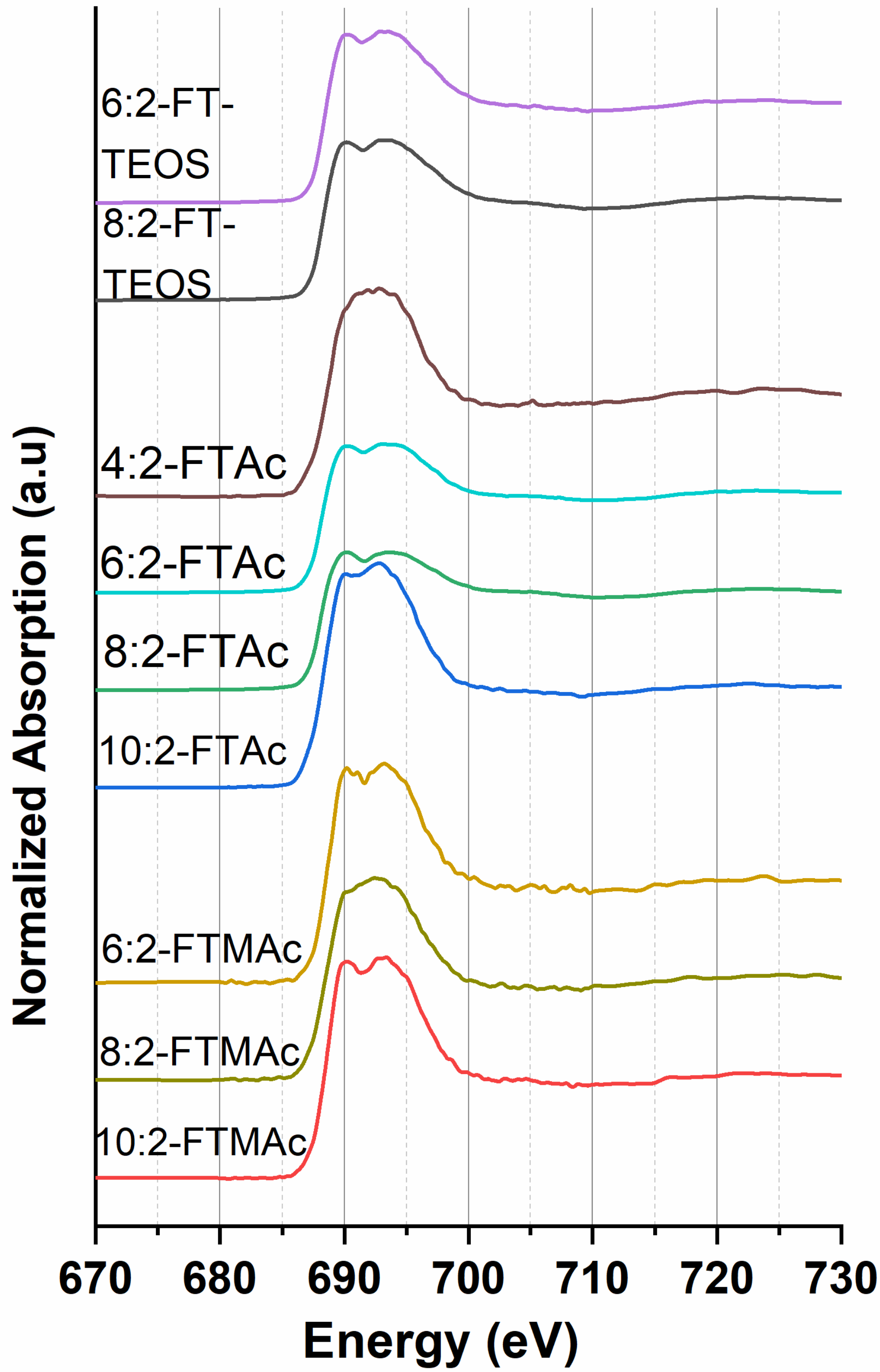


Figure S22: Fluorine K-edge XANES spectra of various fluorotelomersilanes (FT-TEOS), fluorotelomeracrylates (FTAc) and fluorotelomermethacrylates (FTMAc).

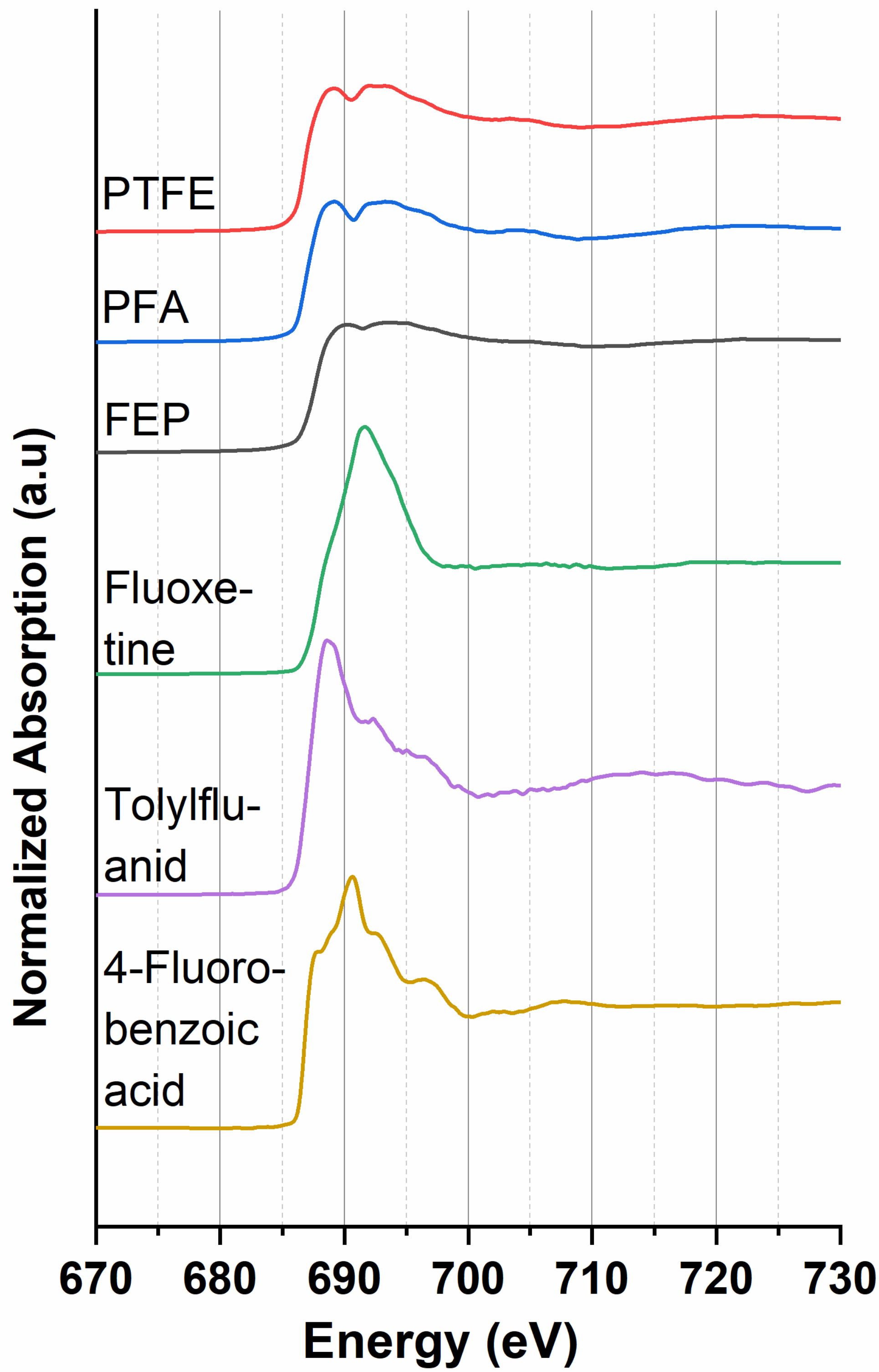


Figure S23: Fluorine K-edge XANES spectra of various fluoropolymers (top) and low fluorinated compounds (bottom).

Linear combination fitting analysis

Table S1: Best linear combination (LC) fits of the collected fluorine K-edge micro-XANES spectra**.**

sample	best LCF-fit	R-factor	reduced χ2
Soil1-P1	53% CaF2 + 40% AlF3 + 7% TFMS	0.016	0.004
Soil1-P2	38% CaF2 + 40% AlF3 + 22% Fluoxetine	0.024	0.009
Soil1-P3	31% FeF3 + 25% AlF3 + 44% Fluoxetine	0.025	0.007
Soil1-P4	64% AlF3 + 36% Fluoxetine	0.050	0.018
Soil1-P5	46% AlF3 + 43% Fluoxetine + 11% FeF3	0.009	0.003
Soil1-P6	46% TFMS + 32% AlF3 + 22% FeF3	0.017	0.004
Soil2-P1	72 % Na2SiF6 + 1,8 % PFOS + 26,3 % Fluoxetin	0.039	0.017
Soil2-P2	77,6 % Na2SiF6 + 0,4 % MgF2 + 22 % Fluoxetin	0.035	0.017
Soil2-P3	83,9 % Na2SiF6 + 16 % PFOS + 0,1 % TFMS	0.023	0.008
Soil2-P4	86,5 % Na2SiF6 + 13,5 % PFOS	0.052	0.019
Soil2-P5	57,1 % Na2SiF6 + 33,6 % PFOS + 9,3 % Fluoxetin	0.019	0.006
Soil2-P6	100 % Na2SiF6	0.055	0.017
SL1-P1	42% Fluorapatit + 41% AlF3 +17% Fluoxetin	0.006	0.002
SL1-P2	50% Fluoxetin + 47% AlF3 + 3% 4-FB	0.013	0.004
SL1-P3	69% Fluoxetin +29% AlF3+ 3% 4-FB	0.038	0.018
SL1-P4	68% AlF3 + 23% Fluoxetin + 9% Tolylfluanid	0.006	0.001
SL1-P5	40% Fluoxetin + 25% AlF3 + 25% Fluoroapatite	0.032	0.012
SL2-P1	45% AlF3 + 45,5% TFMS + 9,5% FeF3	0.012	0.003
SL2-P2	40% Fluoroapatite + 32 % AlF3 + 28% TFMS	0.053	0.014
SL2-P3	55% Fluorapatite + 40% AlF3 + 5% 4FB	0.022	0.006
SL3-P1	3,1 % 4-FBA + 43% Fluoxetin + 53,9 % AlF3	0.025	0.011
SL3-P2	37,9 % Fluoxetin + 54,8 % AlF3 + 7,3 % FeF3	0.031	0.010
SL3-P3	20,9% + Fluoxetin + 7,6 % NH4F + 71,5 %AlF3	0.035	0.011
SL3-P4	39,6 % AlF3+ 18,9 % Fluoexetin + 40,5 % CaF2 + 0,9 % NaTFMS	0.023	0.007
SL3-P5	73,3 % AlF3+ 18,3 % Fluoexetin + 4,5 % CaF2 + 3,9 % 4-FBA	0.030	0.008
Paper1-P1	74.0 % PTFE + 26.0 % 6:2FTOH	0.029	0.010
Textile1-P1	58.4 % PFPrA + 30.5 % NaTFMS + 11.1 PTFE	0.020	0.010
Textile1-P2	91.3 % PFPrA + 8.7 % NaTFMS	0.035	0.025
Textile1-P3	65.0 % NaTFMS + 27.9 % PFPrA + 7.1 % PTFE	0.019	0.008
Textile2-P1	82.0 % PFPrA + 10.5 % PTFE + 7.5 % 6:2-FTOH	0.021	0.012
Textile2-P2	48.9 % PFPrA + 34.5 % PTFE + 16.6 % NaTFMS	0.028	0.011
Textile2-P3	53,6 % PTFE + 46.4 % 6:2-FTOH	0.155	0.068
Sheet1-P1	100.0 % PTFE	0.089	0.017
Sheet1-P2	95.7 % PTFE + 4.3 % 6:2FTOH	0.035	0.024
Sheet1-P3	96.3 % PTFE + 3.7 % 6:2FTOH	0.042	0.009
Sheet1-P4	99.5 % PTFE + 0.5 % 6:2FTOH	0.045	0.009

Fabric1_P1	100.0 % 6:2FTOH	0.245	0.399
Fabric1_P2	97.0 % 6:2FTOH + 3.0 % PTFE	0.071	0.042
Fabric1_P3	100.0 % 6:2FTOH	0.074	0.053
Fabric2_P1	62.0 % PFPrA + 26.3 % PFPD + 11.6 % NaTFMS	0.104	0.025
Fabric2_P2	92.7 % PFPrA + 7.3 % PTFE	0.106	0.030
Fabric2_P3	83.3 % 6:2FTOH + 16.7 % PFPrA	0.024	0.013

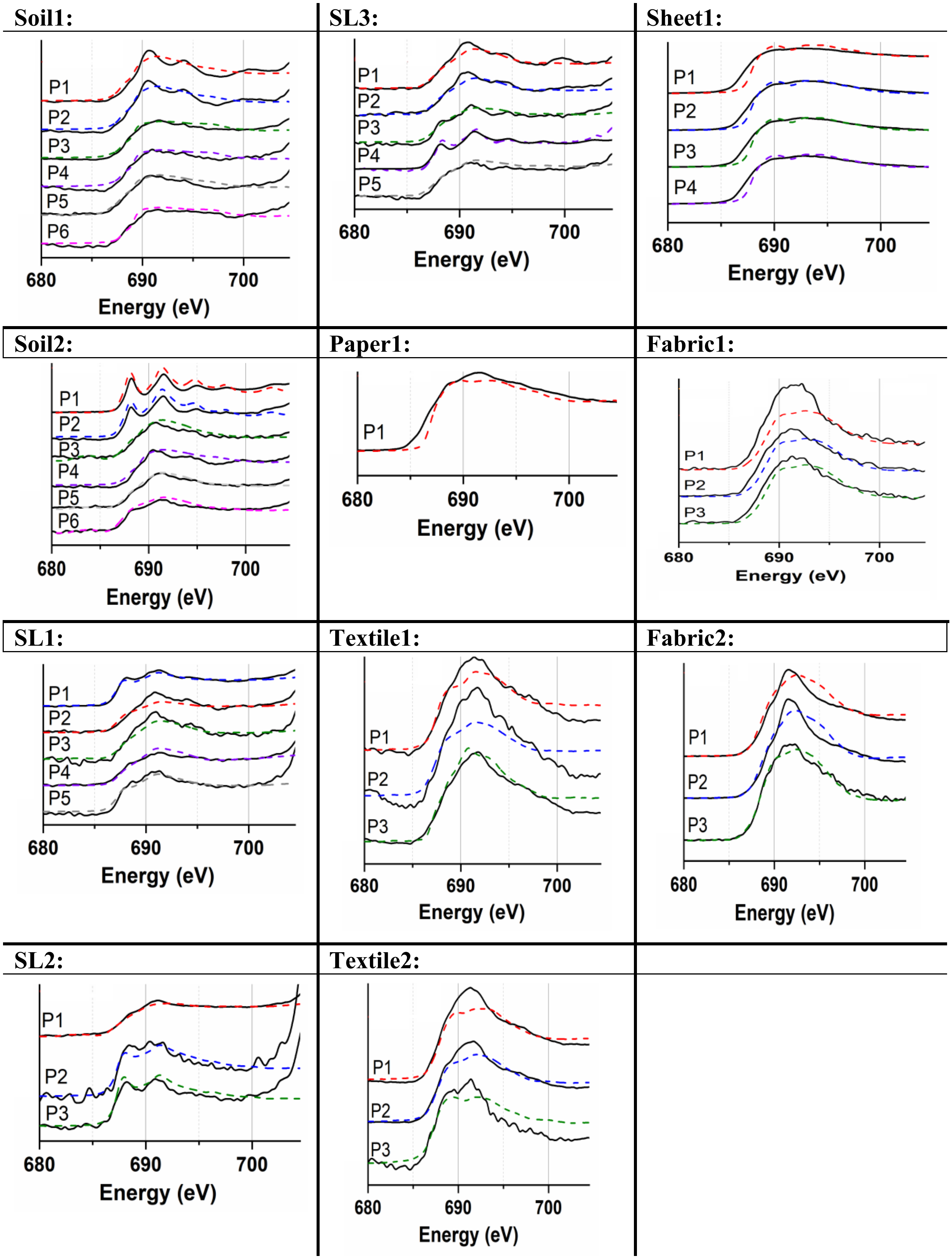


Figure S24: Raw point specific μ-XANES data and respective best LC fits in dashed lines.

LC-MS/MS data

Table S2: Qualifier and quantifier ions in the multireaction mode MS method part for soil and sewage sludge samples

Compound	Abbreviation	PFAS group	Molecular ion [Da]	Quantifier [Da]	Qualifier [Da]	LOQ [ng/ml]	LOD [ng/ml]
Heptafluorobutyric acid	PFBA	PFCA	213	168.9	-	2,31	0,77
Nonafluoropentaonic acid	PFPeA	PFCA	263	219	-	1,11	0,37
Undecafluorohexanoic acid	PFHxA	PFCA	313	269	119	0,72	0,24
Tridecafluoroheptanoic acid	PFHpA	PFCA	363	319	169	0,41	0,14
Pentadecafluorooctanoic acid	PFOA	PFCA	413	369	169	0,31	0,10
Heptadecafluorononanoic acid	PFNA	PFCA	463	419	219	0,22	0,07
Nonadecafluorodecanoic acid	PFDA	PFCA	513	469	219	0,43	0,14
Nonafluorobutane-1-sulfonic acid	PFBS	PFSA	299	80	99	0,76	0,25
Tridecafluorohexane-1-sulfonic acid	PFHxS	PFSA	399	80	99	0,31	0,10
Heptadecafluoro-1-octanesulfonic acid	PFOS	PFSA	499	80	99	0,13	0,04

Table S3: Qualifier and quantifier ions in the multireaction mode MS method part for food contact material and fabric samples

Compound	Abbreviation	PFAS group	Molecular Ion [Da]	Quantifier [Da]	Qualifier [Da]	LOQ [ng/ml]	LOD [ng/ml]
Heptafluorobutyric acid	PFBA	PFCA	213	168.9	-	0,1	0,02
Nonafluoropentaonic acid	PFPeA	PFCA	263	219	-	0,07	0,02
Undecafluorohexanoic acid	PFHxA	PFCA	313	269	119	0,11	0,03
Tridecafluoroheptanoic acid	PFHpA	PFCA	363	319	169	0,08	0,02
Pentadecafluorooctanoic acid	PFOA	PFCA	413	369	219	0,12	0,03
Heptadecafluorononanoic acid	PFNA	PFCA	463	419	219	0,13	0,03
Nonadecafluorodecanoic acid	PFDA	PFCA	513	469	269	0,25	0,07
Perfluoroundecanoic acid	PFUnDA	PFCA	563	519	319	0,06	0,01
Perfluorododecanoic acid	PFDoDA	PFCA	613	569	319	0,014	0,003
Nonafluorobutane-1-sulfonic acid	PFBS	PFSA	298.9	80	99	0,17	0,04
Perfluoropentanesulfonic acid	PFPeS	PFSA	348.9	80	99	0,03	0,01
Tridecafluorohexane-1-sulfonic acid	PFHxS	PFSA	398.9	80	99	0,1	0,02
Perfluoroheptanesulfonic acid	PFHpS	PFSA	448.9	80	99	0,09	0,02
Heptadecafluoro-1-octanesulfonic acid	PFOS	PFSA	498.9	80	99	0,12	0,03

Table S4: Isotopically labelled internal standards used for the quantification of PFAS of interest for soil and sewage sludge samples.

Target PFAS species	Abbre-viation	Internal standards	Surrogate
Heptafluorobutyric acid	PFBA	[$^{13}C_4$] Heptafluorobutyric acid	$^{13}C_4$-PFBA
Nonafluoropentaonic acid	PFPeA	[1,2-$^{13}C_2$] Undecafluorohexanoic acid	$^{13}C_2$-PFHxA
Undecafluorohexanoic acid	PFHxA	[1,2-$^{13}C_2$] Undecafluorohexanoic acid	$^{13}C_2$-PFHxA
Dodecafluoroheptanoic acid	PFHpA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_4$-PFOA
Pentadecafluorooctanoic acid	PFOA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_4$-PFOA
Heptadecafluorononanoic acid	PFNA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_4$-PFOA
Nonadecafluorodecanoic acid	PFDA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_4$-PFOA
Perfluorobutanesulfonic acid	PFBS	[1, 2, 3, 4-$^{13}C_4$] Heptadecafluoro-1-octanesulfonic acid	$^{13}C_4$-PFOS
Tridecafluorohexane-1-sulfonic acid	PFHxS	[1, 2, 3, 4-$^{13}C_4$] Heptadecafluoro-1-octanesulfonic acid	$^{13}C_4$-PFOS
Heptadecafluoro-1-octanesulfonic acid	PFOS	[1, 2, 3, 4-$^{13}C_4$] Heptadecafluoro-1-octanesulfonic acid	$^{13}C_4$-PFOS

Table S5: Isotopically labelled internal standards used for the quantification of PFAS of interest for food contact material and fabric samples.

Target PFAS species	Abbreviation	Internal standards	Surrogate
Heptafluorobutyric acid	PFBA	$[^{13}C_4]$ Heptafluorobutyric acid	$^{13}C_4$-PFBA
Nonafluoropentaonic acid	PFPeA	$[^{13}C_5]$ Nonafluoropentanoic acid	$^{13}C_5$-PFPeA
Undecafluorohexanoic acid	PFHxA	[1, 2, 3, 4, 5-$^{13}C_5$] Undecafluorohexanoic acid	$^{13}C_5$-PFHxA
Dodecafluoroheptanoic acid	PFHpA	[1, 2, 3, 4-$^{13}C_4$] Dodecafluoroheptanoic acid	$^{13}C_4$-PFHpA
Pentadecafluorooctanoic acid	PFOA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_8$-PFOA
Heptadecafluorononanoic acid	PFNA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_9$-PFNA
Nonadecafluorodecanoic acid	PFDA	[1, 2, 3, 4-$^{13}C_4$] Pentadecafluorooctanoic acid	$^{13}C_6$-PFDA
Perfluoroundecanoic acid	PFUnDA	[1, 2, 3, 4, 5, 6, 7-$^{13}C_7$] Perfluoroundecanoic acid	$^{13}C_7$-PFUnDA
Perfluorododecanoic acid	PFDoDA	[1, 2-$^{13}C_2$] Perfluorododecanoic acid	$^{13}C_2$-PFDoDA
Perfluorobutanesulfonic acid	PFBS	[1, 2, 3-$^{13}C_3$] Heptafluorobutylsulfonic acid	$^{13}C_3$-PFBS
Perfluoropentanesulfonic acid	PFPeS	[1, 2, 3-$^{13}C_3$] Heptafluorobutylsulfonic acid	$^{13}C_3$-PFHxS
Tridecafluorohexane-1-sulfonic acid	PFHxS	[1, 2, 3, 4-$^{13}C_4$] Tridecafluorohexane-1-sulfonic acid	$^{13}C_3$-PFHxS
Perfluoroheptanesulfonic acid	PFHpS	$[^{13}C_8]$ Heptadecafluoro-1-octanesulfonic acid	$^{13}C_8$-PFOS
Heptadecafluoro-1-octanesulfonic acid	PFOS	$[^{13}C_8]$ Heptadecafluoro-1-octanesulfonic acid	$^{13}C_8$-PFOS

Table S6: Mean values of all samples investigated by LC-MS/MS (target) analysis (per PFAS molecule in µg/kg). No conversion to fluorine equivalent concentrations were conducted. Standard deviations were calculated from duplicate sample measurements. * Half of the data points were below the detection limit and not considered. # The analyte was not tested for this sample.

µg/kg	Soil1	Soil2	SL1	SL2	SL3	Textile1	Textile2	Paper1	Sheet1	Fabric1	Fabric2
PFBA	9.69 ± 0.95	2.99 ± 0.30	3.76 ± 0.31	0.64 ± 0.11	1.86 ± 0.01	2.56 ± 0.37	47.08 ± 3.62	6.45 ± 1.82	<LOQ	<LOQ	17.16 ± 0.71
RSD	9.8 %	10.1 %	8.1 %	17.7 %	0.3 %	14.4 %	7.7 %	28.2 %	-	-	4.0 %
PFPeA	29.18 ± 1.09	1.04 ± 0.32	45.43 ± 1.91	0.33*	<LOQ	<LOQ	3.56 ± 0.11	<LOQ	<LOQ	<LOQ	<LOQ
RSD	3.7 %	30.3 %	4.2 %	-	-	-	3.0 %	-	-	-	-
PFHxA	25.35 ± 0.29	7.54 ± 0.16	34.59 ± 0.28	5.10 ± 2.42	4.53 ± 0.80	3.91 ± 0.78	26.72 ± 0.22	<LOQ	<LOQ	3.6 ± 0.69	6.21 ± 0.04
RSD	1.2 %	2.1 %	0.8 %	47.5 %	17.6 %	19.9 %	0.8 %	-	-	19.0 %	1.0 %
PFHpA	26.91 ± 0.36	0.89 ± 0.49	<LOQ	<LOQ	<LOQ	<LOQ	12.06 ± 1.02	<LOQ	<LOQ	<LOQ	<LOQ
RSD	1.4 %	54.9 %	-	-	-	-	8.5 %	-	-	-	-
PFOA	73.72 ± 4.89	29.96 ± 4.28	3.28 ± 0.38	2.84 ± 0.61	4.09 ± 1.04	4.66 ± 1.17	27.98 ± 1.58	<LOQ	<LOQ	<LOQ	<LOQ
RSD	6.6 %	14.3 %	11.4 %	21.5 %	25.5 %	25.0 %	5.7 %	-	-	-	-
PFNA	34.05 ± 0.62	23.42 ± 5.43	<LOQ	<LOQ	<LOQ	6.65 ± 4.76	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
RSD	1.8 %	23.2 %	-	-	-	71.6 %	-	-	-	-	-
PFDA	351.86 ± 5.28	240.01 ± 16.76	1.85 ± 0.13	0.48 ± 0.01	3.76 ± 0.67	2.19 ± 1.25	2.91 ± 0.21	<LOQ	<LOQ	<LOQ	<LOQ
RSD	1.5 %	7.0 %	6.8 %	1.9 %	17.7 %	57.0 %	7.1 %	-	-	-	-
PFUDA	#	#	#	#	#	3.65 ± 2.96	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
RSD	-	-	-	-	-	81.1 %	-	-	-	-	-
PFDoDA	#	#	#	#	#	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
RSD	-	-	-	-	-	-	-	-	-	-	-
HFPO-DA	#	#	#	#	#	<LOQ	<LOQ	<LOQ	<LOQ	87.38±75.71	<LOQ
RSD	-	-	-	-	-	-	-	-	-	70 %	-
PFBS	3.95 ± 0.24	4.12 ± 0.11	5.91 ± 0.35	6.15 ± 0.21	5.90 ± 0.29	7.64 ± 3.26	14.09 ± 0.11	9.67 ± 1.50	6.03 ± 1.31	17.18 ± 7.65	37.72 ± 5.53
RSD	6.0 %	2.8 %	5.9 %	3.5 %	5.0 %	42.6 %	0.8 %	15.5 %	22.0 %	45.0 %	15.0 %
PFPeS	#	#	#	#	#	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ
RSD	-	-	-	-	-	-	-	-	-	-	-
PFHxS	1.34 ± 0.07	1.25 ± 0.05	1.76 ± 0.02	1.63 ± 0.14	2.26 ± 0.44	<LOQ	<LOD	<LOQ	<LOQ	<LOQ	<LOQ
RSD	5.0 %	4.3 %	1.2 %	8.7 %	19.3 %	-	-	-	-	-	-

PFHpS	#	#	#	#	#	<LOQ	<LOD	<LOQ	<LOQ	0.23*	<LOQ
RSD	-	-	-	-	-	-	-	-	-	-	-
PFOS	579.96 ± 4.16	2.16 ± 0.22	7.70 ± 0.50	2.42 ± 0.10	6.06 ± 0.14	1.99 ± 0.27	10.62 ± 3.12	4.09 ± 1.65	<LOQ	<LOQ	<LOQ
RSD		10.2 %	6.5 %	4.1 %	2.3 %	13.6 %	29.4 %	40.4 %	-	-	-
Sum amount 14 PFAS	**1136.01 ± 8.47**	**313.38 ± 18.14**	**104.28 ± 2.09**	**19.59 ± 2.51**	**28.46 ± 1.57**	**33.25 ± 6.77**	**145.02 ± 5.15**	**20.21 ± 2.88**	**6.04 ± 1.32**	**108.16 ± 76.10**	**61.31 ± 5.57**

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