Supporting Information:

Levels of Per- and Polyfluoroalkyl Substances (PFAS) in various Wastewater-derived Fertilizers - Analytical investigations from different perspectives

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Total SI-Tables: 4

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Additional Materials and Methods

Sample extraction and preparation for quantitative EOF analysis by Roesch et al. 2022[1]

Dried solid samples (1 g) were weighed directly in 50 ml centrifugal polypropylene (PP) tubes, followed by addition of 10 ml of a NH_3 in MeOH (0.1 M) solution. After that, an established extraction process including sonication (15 min), followed by 30 min of vortexing (1500 min^{-1}) and subsequent centrifugation (5 min, 4000 min^{-1}) was applied to the samples. In the next step the supernatant liquid was carefully decanted. Subsequently, the remaining residues were extracted in a second run using 10 ml of pure MeOH. After decanting the eluates, the combined solutions were carefully concentrated (~2 ml) using a gentle constant flow of N_2. For SPE preparation, all samples were pH adjusted (pH = 4-5) using 0.5 % formic acid and afterwards diluted to 15 ml with ultra-pure water and eventually centrifuged. All SPE cartridges were primed applying first 4 ml basic MeOH (0.3 % NH_3), then 4 ml pure MeOH, followed by two subsequent 4 ml steps of ultra-pure water. After that, diluted samples were loaded on the solid phases maintaining a constant dripping rate of approx. 1 drop/s. Two washing steps were applied afterwards using 2 x 10 ml of aqueous ammonia solution (0.01 %) and 10 ml of deionized water. Subsequent application of a constant vacuum (~40 mbar) for approx. 30 min, lead to cautious drying of the loaded SPE cartridges. After that, all cartridges were firstly eluted upon slow addition of 2 x 2 ml pure MeOH, followed by three-time addition of 2 ml basic MeOH (0.3 % NH_3) into 15 ml PP vials. Eventually, all SPE cartridges were eluted with 4 ml hexanes, followed by 4 ml of acetone and collected in fresh 15 ml PP vials. Both separated eluates were slowly evaporated to dryness by N_2 gas and subsequently reconstituted in 2 mL of fresh MeOH. Finally, both eluates were analyzed by CIC and the values summed up.

LC-MS/MS QA/QC

The isotopically labelled internal standard species were obtained from Wellington Laboratories as a prepared solution with a concentration of 50 µg mL^{-1} with an uncertainty of ±2.5 %. For quality assurance and control an independent certified reference material (Chiron) containing all target PFAS with a concentration of 5 µg mL^{-1} with an uncertainty of ±5 % was used. All organic solvents, reagents, and modifier used for extraction and for LC-MS/MS analysis were tested with respect to a possible blank value. All dilution and spiking steps were gravimetrically controlled.

Table S1: EOF values of various sewage sludge and wastewater-based fertilizer samples; * taken from (Roesch et al. 2022); From SSA4 and SS5 two samples out of the triplicate were negative after blank correction and hence, values were omitted.

	EOF (µg/kg)
SL1*	7209.4 ± 1748.6
SL2	537.6 ± 125.3
SL3	429.7 ± 19.3
SL4*	421.2 ± 76.6
SL5*	357.4 ± 81.6
SL6*	256.1 ± 16.9
SL7	243.7 ± 44.1
SL8*	173.1 ± 12.7
SL9	162.1 ± 101.8
SL10*	154.3 ± 21.7
SSA1	121.6 ± 37.6
SSA2	92.9 ± 58.3
SSA3	89.9 ± 30.4
SSA4	87.3
SSA5	84.6
SSA6	<LOQ
TT1	88.8 ± 2.4
TT2	82.1 ± 37.5
TT3	77.8 ± 21.4
TT4	<LOQ
TT5	<LOQ
TT6	<LOQ
LTC1	<LOQ
LTC2	<LOQ
Struvite1	112.1 ± 8.7
Struvite2	96.2 ± 14.4

Table S2: Comparison EOF vs. PFAS DGT. From SL2, SL8 and SSA1 one sample each (DGT) was negative after blank correction, hence, values were omitted

	EOF (µg/kg)	DGT PFAS-F (ng)
SL1	7209.4 ± 1748.6	2.25 ± 0.30
SL2	537.6 ± 125.3	0.42
SL3	429.7 ± 19.3	0.09 ± 0.02
SL5	357.4 ± 81.6	0.15 ± 0.05
SL7	243.7 ± 44.1	0.15 ± 0.00
SL8	173.1 ± 12.7	0.22
SSA1	121.6 ± 37.6	0.22
SSA2	92.9 ± 58.3	<LOQ
TT3	77.8 ± 21.4	0.07 ± 0.00
Struvite1	112.1 ± 8.7	<LOQ
Struvite2	96.2 ± 14.4	0.08 ± 0.01

Table S3: Targeted analysis by LC-MS/MS of selected PFAS (in µg/kg); n. d. (not detected)

	SL1	SL4	SL5	SL6	SL8	SL10
PFBA	3.8 ± 0.3	1.8 ± 0.1	1.9 ± 0.0	5.7 ± 0.3	0.6 ± 0.1	1.3 ± 0.2
PFPeA	45.4 ± 1.9	n.d.	n.d.	1.8 ± 0.5	0.3	0.6
PFHxA	34.6 ± 0.3	5.9 ± 0.2	4.5 ± 0.8	18.6 ± 1.5	5.1 ± 2.4	6.4 ± 1.0
PFHpA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	3.3 ± 0.4	3.6 ± 1.1	4.1 ± 1.0	5.7 ± 0.2	2.8 ± 0.6	3.3 ± 0.5
PFNA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	1.8 ± 0.1	0.2 ± 0.2	3.8 ± 0.7	1.1 ± 0.2	0.5 ± 0.0	1.3 ± 0.3
PFBS	5.9 ± 0.3	4.9 ± 0.1	5.9 ± 0.3	5.2 ± 0.1	6.1 ± 0.2	4.5 ± 0.3
PFHxS	1.8 ± 0.0	1.4 ± 0.0	2.3 ± 0.4	1.4 ± 0.1	1.6 ± 0.1	1.6 ± 0.2
PFOS	7.7 ± 0.5	4.1 ± 0.1	6.1 ± 0.1	18.5 ± 0.2	2.4 ± 0.1	3.4 ± 0.4
Sum Target	104.3 ± 2.1	21.8 ± 1.1	28.5 ± 1.5	58.0 ± 1.6	19.6 ± 2.5	22.3 ± 1.3
EOF	7209 ± 1748	421.2 ± 76.6	357.4 ± 81.6	256.1 ± 16.9	173.1 ± 12.7	154.3 ± 21.7

Table S4: Results from suspect screening of the EOF extract from SL1

Group	Name	Formula	Retention time	Observed m/z	Intensity
PFCA (C4-C7)	2,3,3,4,4,4-Hexafluorobutanoic acid	C4H2F6O2	1.477	194.99352	81
PFCA (C4-C7)	Perfluorobutanoic acid	C4HF7O2	1.803	212.98203	9
PFCA (C4-C7)	PFCA-H; C5H2F8O2	C5H2F8O2	1.994	244.99001	315
PFCA (C4-C7)	PFCA-H; C6H5F7O3	C6H5F7O3	3.241	257.00537	184
PFCA (C4-C7)	PFCA-diether_Hsubstituted; C5H2F8O4	C5H2F8O4	2.024	276.97424	1952
PFCA (C4-C7)	3-(Perfluorobutyl)propanoic acid	C7H5F9O2	4.286	291.00787	366
PFCA (C4-C7)	PFCA-H; C6H2F10O2	C6H2F10O2	2.316	294.98871	55
PFCA (C4-C7)	Perfluorohexanoic acid	C6HF11O2	2.74	312.97717	151
PFCA (C4-C7)	PFCA-H; C7H3F9O4	C7H3F9O4	4.662	320.98083	220
PFCA (C4-C7)	PFCA-H; C7H2F12O2	C7H2F12O2	2.485	344.98318	56
PFCA (C4-C7)	PFCA-perfluoroalkyl_branched; C7HF13O2	C7HF13O2	3.192	362.97394	19
PFCA (C8-C10)	53FTA	C8H5F11O2	3.234	341.00659	504
PFCA (C8-C10)	PFCA-H; C8H5F11O3	C8H5F11O3	2.896	357.00262	276
PFCA (C8-C10)	Perfluorooctanoic acid	C8HF15O2	3.607	412.97229	252
PFCA (C8-C10)	PFCA-H; C9H2F16O2	C9H2F16O2	3.266	444.97824	77
PFCA (C8-C10)	PFCA-H; C10H2F18O2	C10H2F18O2	0.121	494.97598	25
PFCA (C8-C10)	Perfluorodecanoic acid	C10HF19O2	4.404	512.96625	53
PFSA	FT-PFSA; C5H5F7O3S	C5H5F7O3S	2.129	276.9765	400
PFSA	PFSA-H; C5H2F8O4S	C5H2F8O4S	2.306	308.94522	532
PFSA	Perfluorooctanesulfonic acid	C8HF17O3S	4.009	498.94046	1780
PAPs	PFAP-FT_PAP; C4H6F5O3P	C4H6F5O3P	2.813	226.99152	292
PAPs	PFAP-diPAP; C2HF6O4P	C2HF6O4P	2.397	232.94884	665
PAPs	PFAP-FT_diPAP; C6H9F6O4P	C6H9F6O4P	4.286	289.01077	1747
Pesticide	Fludioxonil	C12H6F2N2O2	3.267	247.03737	493
Pesticide	Flufenacet ESA	C11H14FNO4S	2.863	274.05988	156
Pharmaceuticals	Flufenamic acid	C14H10F3NO2	3.442	280.06329	661

Pharmaceuticals	Pitavastatin	C25H24FNO4	4.334	420.16705	234
FCA	4,4'-Difluorobenzophenone	C13H8F2O	3.899	217.04753	1801
FCA	1-cyclopropyl-6,7-difluoro-1,4-dihydro-8-hydroxy-4-oxo-3-Quinoline-3-carboxylic acid	C13H9F2NO4	1.825	280.03494	501
PFPA	2-(Perfluorohexyl)ethylphosphonic acid	C8H6F13O3P	3.58	426.97366	338
Other	FT-thioether; C6H7F5O2S	C6H7F5O2S	3.234	237.00038	273
Other	3,3,4,4,5,5,6,6,6-Nonafluorohexene	C6H3F9	1.739	245.00185	290
Other	Perfluorovaleraldehyde	C5HF9O	2.733	246.98608	137
Other	HFPO-DA, 2,3,3,3-Tetrafluoro-2-(pentafluoroethoxy)propanoic acid	C5HF9O3	2.031	278.96927	366
Other	Perfluoroheptanal; 1,1,2,2,3,3,4,4,5,5-Decafluoro-1-((trifluoro vinyl)oxy)pentane	C7HF13O	3.607	346.97931	442
Other	(Perfluorododecyl)ethylene	C14H3F25	4.63	644.97241	763

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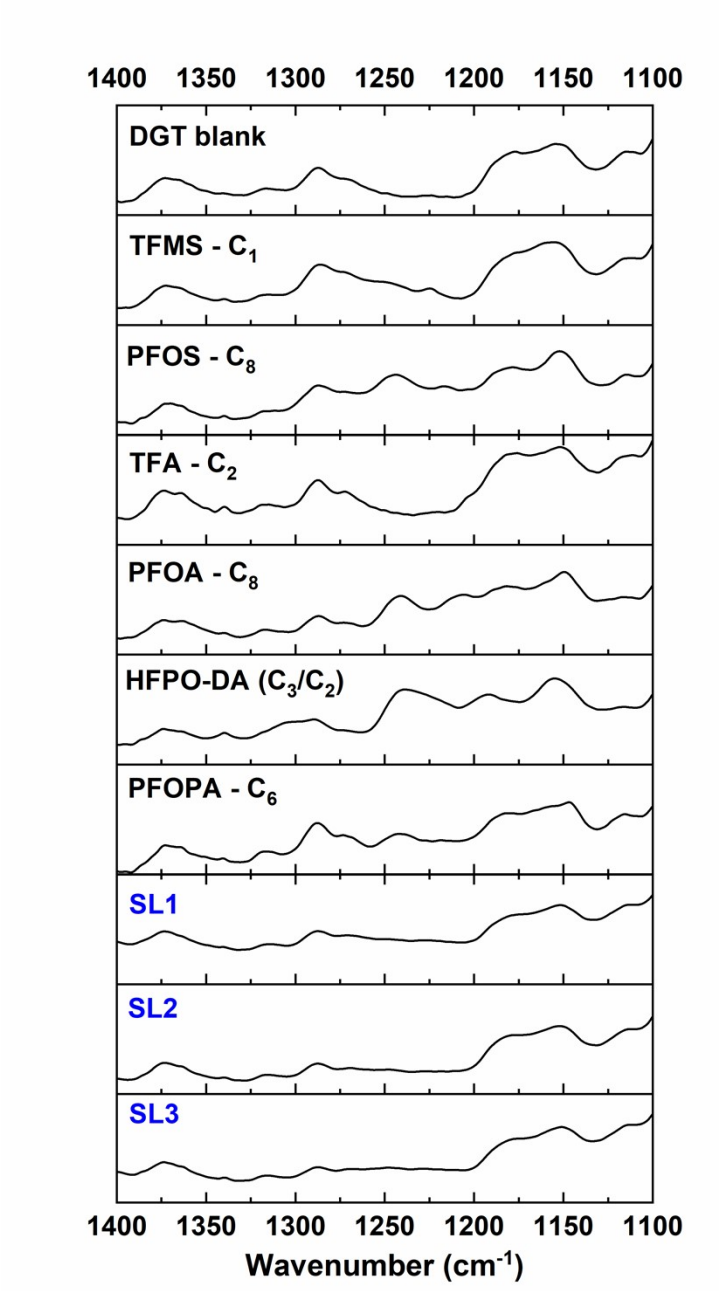

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74 **Figure S1:** Raw FT-IR spectra of the applied DGT binding layers.

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References:

1. P. Roesch, C. Vogel, T. Huthwelker, P. Wittwer and F.-G. Simon,Investigation of per- and polyfluoroalkyl substances (PFAS) in soils and sewage sludges by fluorine K-edge XANES spectroscopy and combustion ion chromatography *Environmental Science and Pollution Research*, 2022, **29**, 26889-26899, https://doi.org/10.1007/s11356-021-17838-z.