

Supplementary material

Modelling the sorption behaviour of perfluoroalkyl carboxylates and perfluoroalkane sulfonates in soils

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Table S1. Main physicochemical properties of target PFASs.

Name	PFAS acronym	Chemical form	CAS number	Molecular Weight (g/mol)	Number of CF ₂	log K _{ow}	pK _a
Perfluorobutanoic acid	PFBA	C ₄ HF ₇ O ₂	375-22-4	214.0	3	2.3 ^a	0.4 ^a
Perfluorobutane sulfonic acid	PFBS	C ₄ HF ₉ O ₃ S	375-73-5	300.1	4	2.7 ^a	0.14 ^a
Perfluoropentanoic acid	PFPeA	C ₅ HF ₉ O ₂	2706-90-3	264.1	4	2.9 ^c	n.a.
Perfluorohexanoic acid	PFHxA	C ₆ HF ₁₁ O ₂	307-24-4	314.1	5	3.1 ^a	-0.16 ^a
Perfluoroheptanoic acid	PFHpA	C ₇ HF ₁₃ O ₂	375-85-9	364.1	6	3.8 ^b	n.a.
Perfluorohexane sulfonic acid	PFHxS	C ₆ HF ₁₃ O ₃ S	355-46-4	400.1	6	4.3 ^a	0.14 ^a
Perfluorooctanoic acid	PFOA	C ₈ HF ₁₅ O ₂	335-67-1	414.1	7	4.6 ^{a, b}	-0.2 ^a
Perfluorononanoic acid	PFNA	C ₉ HF ₁₇ O ₂	375-95-1	464.1	8	5.5 ^b	n.a.
Perfluorooctane sulfonic acid	PFOS	C ₈ HF ₁₇ O ₃ S	1763-23-1	500.1	8	5.3 ^{a, b}	-3.27 ^a
Perfluorodecanoic acid	PFDA	C ₁₀ HF ₁₉ O ₂	335-76-2	514.1	9	6.4 ^b	n.a.
Perfluoroundecanoic acid	PFUnA	C ₁₁ HF ₂₁ O ₂	2058-94-8	564.1	10	7.4 ^b	n.a.
Perfluorodecane sulfonic acid	PFDS	C ₁₀ HF ₂₁ O ₃ S	335-77-3	600.1	10	6.4 ^c	n.a.
Perfluorododecanoic acid	PFDoA	C ₁₂ HF ₂₃ O ₂	307-55-1	614.1	11	8.1 ^c	n.a.

n.a. = not available; ^a Deng et al., 2012; ^b Kelly et al., 2009; ^c Pubchem database

Table S2. Initial concentrations of spiked PFASs (ng mL⁻¹) in each soil for the sorption experiments.

Soil	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFNA	PFOS	PFDoA
ALM	30	30	35	50	50	60	170	330
DELTA2	30	30	35	50	50	170	170	500
OVI01	30	30	35	50	50	170	170	500
UIAR	30	50	50	140	150	570	670	1000
BRA	30	50	50	140	150	570	670	1000
DUBLIN	30	50	50	140	150	570	670	1000
KOM	30	50	50	140	150	570	670	1000

Section S1. PFAS determination in the supernatants by LC-MS/MS.

PFASs concentrations in the supernatants were analysed by HPLC equipped with an auto-sampler (Agilent 1100 Wellplate) thermostated at 10 °C and a pump and solvent system (Agilent 1100 LC). A Luna C₁₈ (2)-HST reverse phase column (2.5 µm, 100 x 2.00 mm, Phenomenex) thermostated at 45°C was used for the chromatographic separation. The chromatographic separation conditions were adapted from (Gómez-Canela et al., 2012) and briefly consisted in an injection volume of 10 µL (full loop) with a mobile phase A composed of 10 mmol L⁻¹ ammonium acetate and a mobile phase B composed of acetonitrile. The flow rate was set at 300 µL min⁻¹ while the elution gradient was set at 75% A during one minute and then reached until 85% B during 5 minutes. After, mobile phase reach 100% B during the next 30 seconds and this percentage was set during 30 seconds more until decrease at 25% B during the next minute. This elution grade of 25 % B was held during the next 7 minutes to condition the column for the next analysis.

Detection was performed using a triple quadrupole mass spectrometer (API3000 Perkin-Elmer Sciex Instruments) provided with a ionization chamber (Turblon SprayTM) located at 10 mm from the analyser and working in the negative mode, ESI(-). The most significant m/z transition of each PFAS was used for quantification while the second one was used for confirmation. The dwell time for each transition was established at 30 ms, and the software used for the determination was Absciex Analyst. Experimental parameters of the mass spectrometer were set as:

PFAS	Transition (m/z)	Declustering Potential (V)	Focusing Potential (V)	Collision Energy (V)
PFBA	213 > 169	-17	-91	-18
PFH _x A	313 > 269, 119	-20	-104	-21
PFOA	413 > 369, 169	-23	-122	-20
PFNA	463 > 419, 169	-27	-123	-21
PFD _o A	613 > 569, 319	-32	-110	-24
PFBS	299 > 80, 99	-40	-121	-45
PFH _x S	399 > 80, 119	-43	-133	-58
PFOS	499 > 80, 130	-44	-131	-68
MPFOA	417 > 372, 172	-23	-122	-20
MPFOS	503 > 80, 99	-44	-131	-68

Quantification was performed using 1/x weighted calibration curves using calibration standards of 0; 0.5; 2; 5; 10; 20; 50; 100 and 200 ng mL⁻¹ for each PFAS, together with the inner standards MPFOS and MPFOA. The Pearson coefficients of the resulting calibration lines were up to 0.999. The limit of detection (LOD) and the limit of quantification (LOQ) were determined as a signal-to-noise ratio set at 1:3 and 1:10 respectively, and were similar to other LODs and LOQs reported elsewhere (Habibullah-Al-Mamun et al., 2016; Liu et al., 2015). Repeatability was determined after ten analysis at a concentration of 20 ng mL⁻¹.

The quality figures of the method were:

PFAS	Repeatability at 20 ng mL ⁻¹ (%RSD)	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	Pearson coefficient of calibration curves	Recovery of controls (%)
PFBA	4	0.10	0.30	0.999	> 98
PFHxA	5	0.04	0.10	0.991	> 98
PFOA	3	0.02	0.08	0.997	> 95
PFNA	4	0.01	0.05	0.998	> 95
PFDoA	4	0.01	0.04	0.995	40
PFBS	5	0.03	0.10	0.997	> 98
PFHxS	5	0.03	0.10	0.998	> 98
PFOS	5	0.06	0.20	0.999	> 95

Table S3. List of references including information about which PFASs were used to construct the dataset of PFAS sorption parameters.

Reference	Number of samples (total entries)	OC range (%)	PFBA	PFBS	PFPeA	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFUnA	PFDS	PFDoA
Hong Chen et al., 2012	5 (5)	0.42 – 1.43									X				
Mejia-Avendaño et al., 2020	5 (15)	1.7 – 7.3							X		X	X			
Chen et al., 2013	5 (10)	0.52 – 16							X		X				
Enevoldsen & Juhler, 2010	2 (12)	0.42 – 1.0		X			X		X	X	X	X			
Guelfo & Higgins, 2013	3 (30)	0.8 – 4.5	X	X	X	X	X	X	X	X	X	X	X		
Higgins & Luthy, 2006	5 (24)	0.56 – 9.66							X	X	X	X	X	X	
Higgins & Luthy, 2007	1 (1)	4.34													X
Internal report, 3M, 2000	4 (4)	1.3 – 2.8									X				
Internal report, Dupont, 2003	4 (4)	0.8 – 5.76							X						
Jeon et al., 2011	3 (6)	0.21 – 0.55							X		X				
Johnson et al., 2007	1 (1)	2.5									X				
Milinic et al., 2015	2 (6)	0.2 – 3.9		X					X		X				
Knight et al., 2019	100 (100)	0.1 – 3.5							X						
You et al., 2010	15 (15)	0.16 – 1.49									X				
Kwadijk et al., 2013	1 (1)	2.6									X				
Martz et al., 2019	5 (5)	0.05 – 11.7							X						
Miao et al., 2017	10 (10)	0.52 – 5.76							X						
Ahrens et al., 2011	3 (5)	0.03 – 1.6							X		X				
Oliver, et al., 2020	19 (57)	0.1 – 11						X	X		X				
Wei et al., 2017	6 (6)	0.87 – 2.71									X				
Gredelj et al., 2020	1 (9)	1.43	X	X	X	X	X		X	X	X	X			
Pan et al., 2009	1 (1)	0.75									X				
Hong Chen et al., 2009	1 (1)	0.91									X				
Brusseau et al., 2019	2 (2)	0.10 – 0.38									X				
Xiao et al., 2019	5 (5)	0.10 – 5.3							X						
Huiting Chen et al., 2016	1 (5)	2.52						X	X	X	X	X			
McLachlan et al., 2019	2 (24)	0.40 – 0.93	X	X	X	X	X	X	X	X	X	X	X		X
Aly et al., 2019	1 (6)	1.44		X			X	X	X	X	X				
Campos Pereira et al., 2018	1 (6)	45	X	X	X	X	X		X						
Xiang et al., 2018	1 (1)	0.69							X						
Zhi & Liu, 2018	1 (2)	47							X		X				
This study	7 (56)	1.6 – 41	X	X		X		X	X	X	X				X

Table S4. Sorption percentages (%S) resulting from the batch experiments.

Soil	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFNA	PFOS	PFDoA
	(3)	(4)	(5)	(6)	(7)	(8)	(8)	(11)
ALM	5.2	5.7	23	19	21	52	76	98
DELTA2	8.2	14	20	29	28	78	88	98
OVI01	3.2	12	11	35	42	80	92	99
UIAR	8.3	13	21	64	72	91	94	> 99
BRA	11	23	35	63	73	92	95	> 99
DUBLIN	15	41	34	68	79	92	97	> 99
KOM	11	23	39	64	79	93	95	> 99

Table S5. Desorption $K_{d,des}$ ($L\ kg^{-1}$) values derived from the batch experiments.

Soil	PFHxA (5)	PFHxS (6)	PFOA (7)	PFNA (8)	PFOS (8)	PFDoA (11)
ALM	N.Q.	4.4	18	35	43	761
DELTA2	N.Q.	16	11	43	83	6591
OVI01	9.1	7.7	12	57	107	7117
UIAR	25	18	38	177	437	9376
BRA	29	29	41	226	560	12705
DUBLIN	32	41	61	262	760	13148
KOM	23	37	48	297	749	17888

N.Q.: Not quantifiable

Section S2. Evaluation of the predictive accuracy of the model

To evaluate the predictive accuracy of the model, the root square mean error (RMSE) and the residual predictive deviation (RPD) were calculated as:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (m_i - p_i)^2}{N}}$$

where m are the measured values, p are the predicted values, i is the entry being tested and N is the total number of entries included in the model. The RPD was calculated as:

$$\text{RPD} = \frac{\text{SD}}{\text{RMSE}}$$

where SD is the standard deviation of the original data. RPD values indicate the quality of the model: RPD values < 1.5 are considered poor; RPD values from 1.5 to 2.0 are acceptable; RPD values between 2.0 and 3.0 are good; and RPD values > 3.0 are excellent (Knight et al., 2019).

References

- Ahrens, L., Yeung, L. W. Y., Taniyasu, S., Lam, P. K. S., Yamashita, N., 2011. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. *Chemosphere* 85 (5), 731–737. <https://doi.org/10.1016/j.chemosphere.2011.06.046>
- Aly, Y. H., McInnis, D. P., Lombardo, S. M., Arnold, W. A., Pennell, K. D., Hatton, J., Simcik, M. F., 2019. Enhanced adsorption of perfluoroalkyl substances for in situ remediation. *Environ. Sci-Wat Res.* 5 (11), 1867–1875. <https://doi.org/10.1039/c9ew00426b>
- Brusseau, M. L., Khan, N., Wang, Y., Yan, N., Van Glubt, S., Carroll, K. C., 2019. Nonideal Transport and Extended Elution Tailing of PFOS in Soil. *Environ. Sci. Technol.* 53 (18), 10654–10664. <https://doi.org/10.1021/acs.est.9b02343>
- Campos Pereira, H., Ullberg, M., Kleja, D. B., Gustafsson, J. P., Ahrens, L., 2018. Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon – Effect of cation composition and pH. *Chemosphere* 207, 183–191. <https://doi.org/10.1016/j.chemosphere.2018.05.012>
- Chen, Hong, Chen, S., Quan, X., Zhao, Y., Zhao, H., 2009. Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: Influence of solution pH and [Ca²⁺]. *Chemosphere* 77 (10), 1406–1411. <https://doi.org/10.1016/j.chemosphere.2009.09.008>
- Chen, Hong, Zhang, C., Yu, Y., Han, J., 2012. Sorption of perfluorooctane sulfonate (PFOS) on marine sediments. *Mar. Pollut. Bull.* 64 (5), 902–906. <https://doi.org/10.1016/j.marpolbul.2012.03.012>
- Chen, Huiting, Reinhard, M., Tung, V., Gin, K. Y., 2016. Reversible and irreversible sorption of perfluorinated compounds (PFCs) by sediments of an urban reservoir. *Chemosphere* 144, 1747–1753. <https://doi.org/10.1016/j.chemosphere.2015.10.055>
- Chen, Y. C., Lo, S. L., Li, N. H., Lee, Y. C., Kuo, J., 2013. Sorption of perfluoroalkyl substances (PFASs) onto wetland soils. *Desalin. Water Treat.* 51 (40–42), 7469–7475. <https://doi.org/10.1080/19443994.2013.792145>
- Deng, S., Zhang, Q., Nie, Y., Wei, H., Wang, B., Huang, J., Yu, G., Xing, B., 2012. Sorption mechanisms of perfluorinated compounds on carbon nanotubes. *Environ. Pollut.* 168, 138–144. <https://doi.org/10.1016/j.envpol.2012.03.048>
- du Pont, 2003. Adsorption /Desorption of ammonium Perfluorooctane to Soil (OECD, 106), E.I. du Pont de Nemours and Company EMSE report no. 17-03, U.S. Environmental Protection Agency docket OPPt-2003-0012-0401
- Ellefson, M., 2001. Soil adsorption/desorption study of potassium perfluorooctane sulfonate (PFOS); EPA Docket AR226-1030a030; 3M Company; Maplewood, MN.
- Enevoldsen, R., Juhler, R. K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: Using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. *Anal. Bioanal. Chem.* 398 (3), 1161–1172. <https://doi.org/10.1007/s00216-010-4066-0>
- Gómez-Canela, C., Barth, J. A. C., Lacorte, S., 2012. Occurrence and fate of perfluorinated compounds in sewage sludge from Spain and Germany. *Environ. Sci. Pollut. R.* 19 (9), 4109–4119. <https://doi.org/10.1007/s11356-012-1078-7>
- Gredelj, A., Nicoletto, C., Valsecchi, S., Ferrario, C., Polesello, S., Lava, R., Zanon, F., Barausse, A., Palmeri, L., Guidolin, L., Bonato, M., 2020. Uptake and translocation of perfluoroalkyl acids (PFAA) in red chicory (*Cichorium intybus* L.) under various treatments with pre-contaminated soil and irrigation water. *Sci. Tot. Environ.* 708, 134766. <https://doi.org/10.1016/j.scitotenv.2019.134766>
- Guelfo, J. L., Higgins, C. P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.* 47 (9), 4164–4171. <https://doi.org/10.1021/es3048043>
- Habibullah-Al-Mamun, M., Ahmed, M. K., Raknuzzaman, M., Islam, M. S., Negishi, J., Nakamichi, S., Sekine, M., Tokumura, M., Masunaga, S., 2016. Occurrence and distribution of perfluoroalkyl acids (PFAAs) in surface water and sediment of a tropical coastal area (Bay of Bengal coast, Bangladesh). *Sci. Tot. Environ.* 571, 1089–1104. <https://doi.org/10.1016/j.scitotenv.2016.07.104>
- Higgins, C.P., Luthy, R.G., 2006. Sorption of Perfluorinated Surfactants on Sediments. *Environ. Sci. Technol.* 40, 7251–7256. <https://doi.org/10.1021/es061000n>
- Higgins, C.P., Luthy, R.G., 2007. Modeling Sorption of Anionic Surfactants onto Sediment Materials: An a priori Approach for Perfluoroalkyl Surfactants and Linear Alkylbenzene Sulfonates. *Environ. Sci. Technol.* 41 (9), 3254–3261. <https://doi.org/10.1021/es062449j>

- Jeon, J., Kannan, K., Lim, B. J., An, K. G., Kim, S. D., 2011. Effects of salinity and organic matter on the partitioning of perfluoroalkyl acid (PFAs) to clay particles. *J. Environ. Monitor.* 13 (6), 1803–1810. <https://doi.org/10.1039/c0em00791a>
- Johnson, R. L., Anschutz, A. J., Smolen, J. M., Simcik, M. F., Lee Penn, R., 2007. The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces. *J. Chem. Eng. Data*, 52 (4), 1165–1170. <https://doi.org/10.1021/je060285g>
- Kelly, B. C., Ikonomou, M. G., Blair, J. D., Hoover, D., Grace, R., Gobas, F. a P. C., Surridge, B., 2009. Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure. *Environ. Sci. Technol.* 43, 4037–4043.
- Knight, E. R., Janik, L. J., Navarro, D. A., Kookana, R. S., McLaughlin, M. J., 2019. Predicting partitioning of radiolabelled ^{14}C -PFOA in a range of soils using diffuse reflectance infrared spectroscopy. *Sci. Tot. Environ.* 686, 505–513. <https://doi.org/10.1016/j.scitotenv.2019.05.339>
- Kwadijk, C. J. A. F., Velzeboer, I., Koelmans, A. A., 2013. Sorption of perfluorooctane sulfonate to carbon nanotubes in aquatic sediments. *Chemosphere* 90 (5), 1631–1636. <https://doi.org/10.1016/j.chemosphere.2012.08.041>
- Liu, B., Zhang, H., Xie, L., Li, J., Wang, X., Zhao, L., Wang, Y., Yang, B., 2015. Spatial distribution and partition of perfluoroalkyl acids (PFAAs) in rivers of the Pearl River Delta, southern China. *Sci. Tot. Environ.* 524–525, 1–7. <https://doi.org/10.1016/j.scitotenv.2015.04.004>
- Martz, M., Heil, J., Marschner, B., Stumpe, B., 2019. Effects of soil organic carbon (SOC) content and accessibility in subsoils on the sorption processes of the model pollutants nonylphenol (4-n-NP) and perfluorooctanoic acid (PFOA). *Sci. Tot. Environ.* 672, 162–173. <https://doi.org/10.1016/j.scitotenv.2019.03.369>
- McLachlan, M. S., Felizeter, S., Klein, M., Kotthoff, M., De Voogt, P., 2019. Fate of a perfluoroalkyl acid mixture in an agricultural soil studied in lysimeters. *Chemosphere* 223, 180–187. <https://doi.org/10.1016/j.chemosphere.2019.02.012>
- Mejia-Avendaño, S., Zhi, Y., Yan, B., Liu, J., 2020. Sorption of Polyfluoroalkyl Surfactants on Surface Soils: Effect of Molecular Structures, Soil Properties, and Solution Chemistry. *Environ. Sci. Technol.* 54 (3), 1513–1521. <https://doi.org/10.1021/acs.est.9b04989>
- Miao, Y., Guo, X., Dan Peng, Fan, T., Yang, C., 2017. Rates and equilibria of perfluorooctanoate (PFOA) sorption on soils from different regions of China. *Ecotox. Environ. Safe.* 139, 102–108. <https://doi.org/10.1016/j.ecoenv.2017.01.022>
- Milinic, J., Lacorte, S., Vidal, M., Rigol, A., 2015. Sorption behaviour of perfluoroalkyl substances in soils. *Sci. Tot. Environ.* 511, 63–71. <https://doi.org/10.1016/j.scitotenv.2014.12.017>
- Oliver, D. P., Navarro, D. A., Baldock, J., Simpson, S. L., Kookana, R. S., 2020. Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) as affected by the properties of coastal estuarine sediments. *Sci. Tot. Environ.* 720, 137263. <https://doi.org/10.1016/j.scitotenv.2020.137263>
- Pan, G., Jia, C., Zhao, D., You, C., Chen, H., Jiang, G., 2009. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. *Environ. Pollut.* 157 (1), 325–330. <https://doi.org/10.1016/j.envpol.2008.06.035>
- Wei, C., Song, X., Wang, Q., Hu, Z., 2017. Sorption kinetics, isotherms and mechanisms of PFOS on soils with different physicochemical properties. *Ecotox. Environ. Safe.* 142, 40–50. <https://doi.org/10.1016/j.ecoenv.2017.03.040>
- Xiang, L., Xiao, T., Yu, P. F., Zhao, H. M., Mo, C. H., Li, Y. W., Li, H., Cai, Q. Y., Zhou, D. M., Wong, M. H., 2018. Mechanism and Implication of the Sorption of Perfluorooctanoic Acid by Varying Soil Size Fractions. *J. Agr. Food Chem.* 66 (44), 11569–11579. <https://doi.org/10.1021/acs.jafc.8b03492>
- Xiao, F., Jin, B., Golovko, S. A., Golovko, M. Y., Xing, B., 2019. Sorption and Desorption Mechanisms of Cationic and Zwitterionic Per- And Polyfluoroalkyl Substances in Natural Soils: Thermodynamics and Hysteresis. *Environ. Sci. Technol.* 53 (20), 11818–11827. <https://doi.org/10.1021/acs.est.9b05379>
- You, C., Jia, C., Pan, G., 2010. Effect of salinity and sediment characteristics on the sorption and desorption of perfluorooctane sulfonate at sediment-water interface. *Environ. Pollut.* 158 (5), 1343–1347. <https://doi.org/10.1016/j.envpol.2010.01.009>
- Zhi, Y., Liu, J., 2018. Sorption and desorption of anionic, cationic and zwitterionic polyfluoroalkyl substances by soil organic matter and pyrogenic carbonaceous materials. *Chem. Eng. J.* 346, 682–691.

