

Supporting information

Independent mode sorption of perfluoroalkyl acids by single and multiple adsorbents

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I. Mass transitions applied in the MS/MS

Compound	Q1 mass	Q3 mass	Transition
PFBA	213	169	1
PFPA	263	219	1
PFH _x A	313	269	1
	313	119	2
PFHpA	363	319	1
	363	169	2
PFOA	413	369	1
	413	169	2
PFNA	463	419	1

Table SI.1 Mass transitions of the PFAAs for the tandem mass spectrometer

II. Dead volume measurements

The dead volumes were obtained with different compounds which would not be expected to have interaction with the sorbent. The apex of the chromatograms were taken as the dead volume (t_0). In this table the different sorbents with the corresponding dead volumes and testing compounds are showed.

	Dead volume (t_0 , min)	Test compound
C18	2.8	acetone/thiourea
WAX	0.24	metformin
MAX	0.257	metformin
HLB	0.434	metformin/thiourea
Al ₂ O ₃	0.26	metformin

Table SI.2 Dead volume of the columns used with corresponding test compounds.

III Peaks and graphs of $\ln K_D$ vs different methanol fractions for the columns and observed R^2 for each adsorbent

Figure SI.3.1 shows the peak shapes at different ϕ_{MeOH} in the vials on the sorbent: C18.

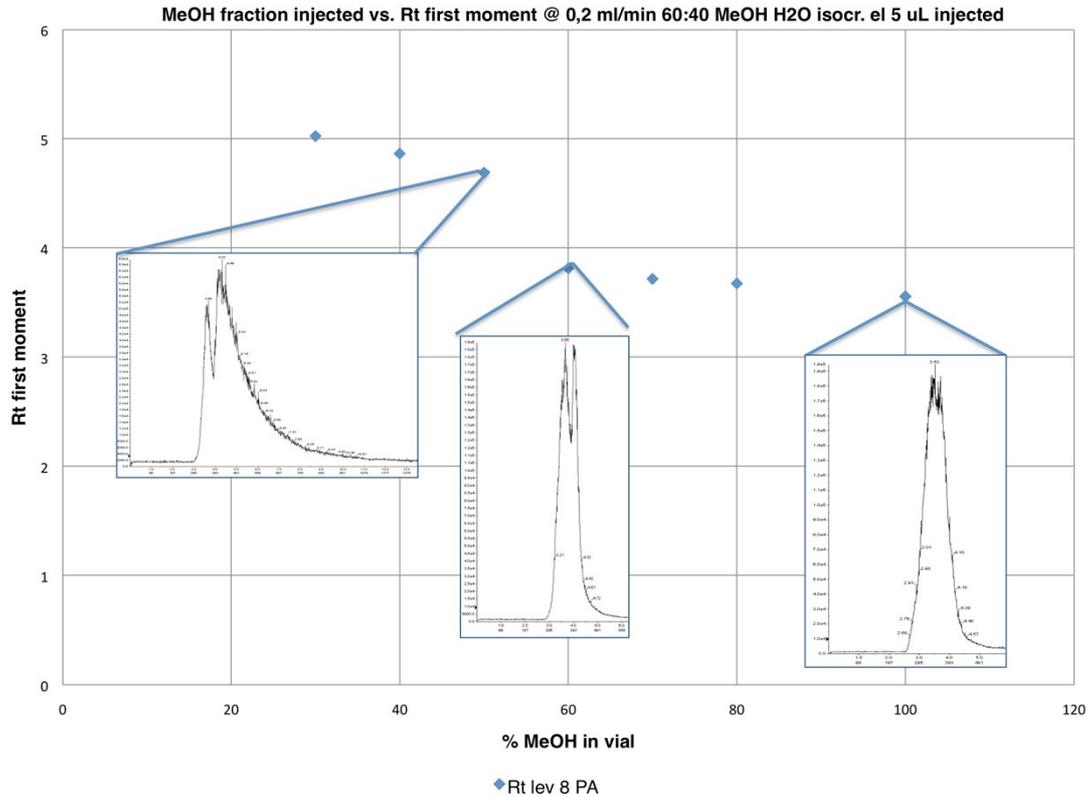


Fig. SI.3.1: Graph of retention time vs ϕ_{MeOH} in vial for C18, PFPA, with some peak shapes.

The retention time first moment (t_R) takes into account the peak shape because the centre of mass of the peak is used instead of the time that corresponds to the highest signal (apex). The %MeOH of the flow varied between 0.4-0.8.

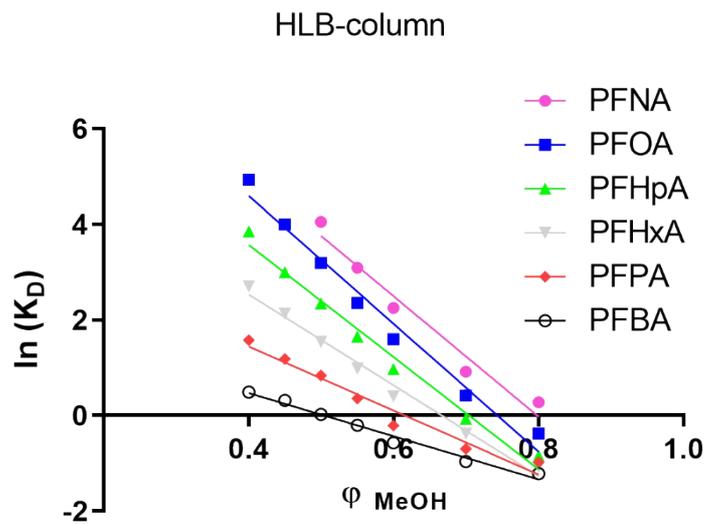


Fig. SI.3.2 Plots of the linear relationship between $\ln K_D$ and ϕ_{MeOH} for the HLB sorbent.

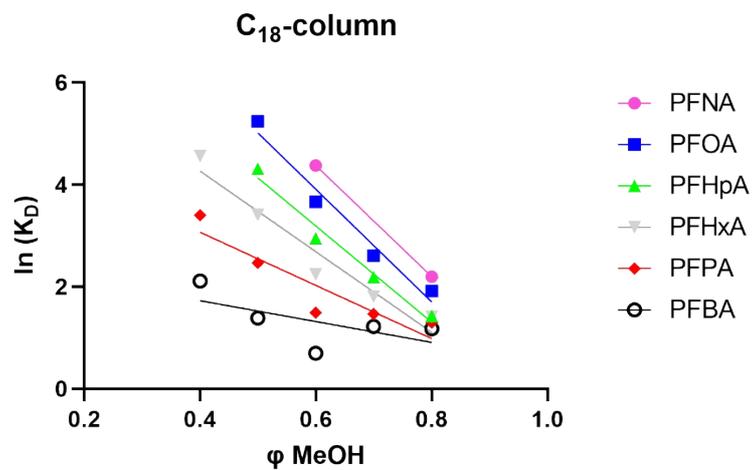


Fig. SI.3.3 Plots of the linear relationship between $\ln K_D$ and ϕ_{MeOH} for the C18-column

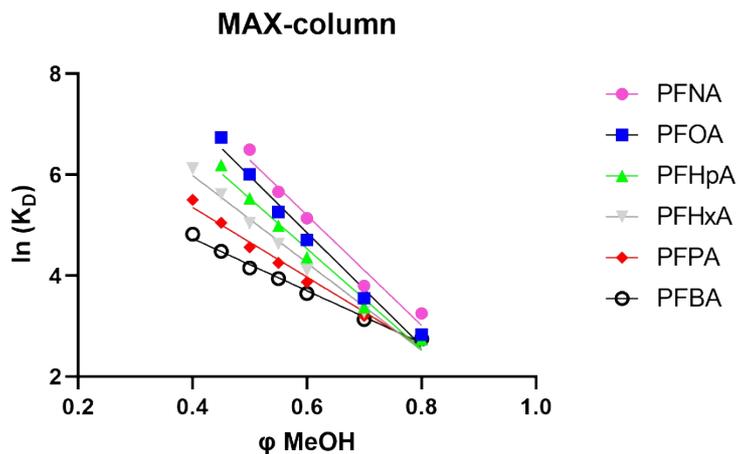


Fig. SI.3.4 Plots of the linear relationship between $\ln K_D$ and ϕ_{MeOH} for the MAX-sorbent

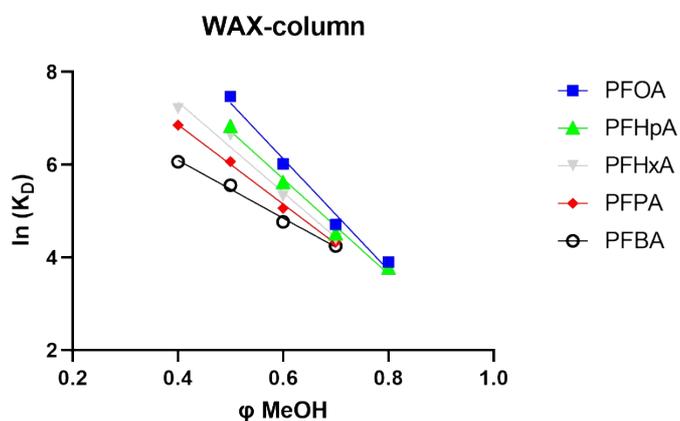


Fig. SI.3.5 Plots of the linear relationship between $\ln K_D$ and ϕ_{MeOH} for the WAX-sorbent

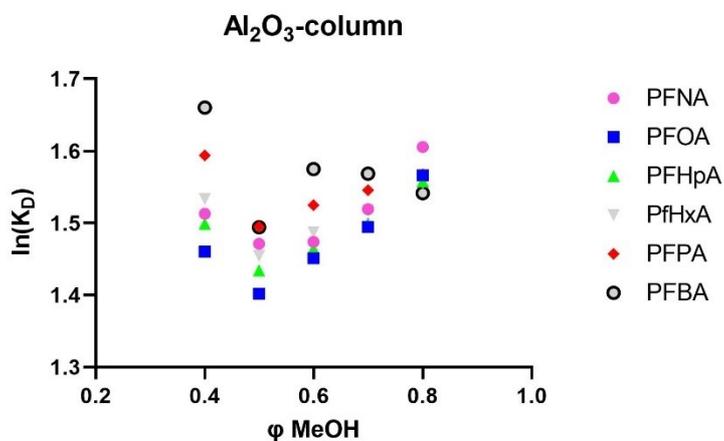


Fig. SI.3.6 Data plots between $\ln K_D$ and ϕ_{MeOH} for the Al₂O₃-sorbent

	R^2				
	C18	HLB	WAX	MAX	Al ₂ O ₃
PFBA	0.396	0.982	0.991	0.9712	0.180
PFPA	0.844	0.961	0.996	0.9846	6*10 ⁻⁵
PFHxA	0.940	0.986	0.980	0.9856	0.184
PFHpA	0.975	0.984	0.998	0.9891	0.393
PFOA	0.9683	0.979	0.984	0.9865	0.622
PFNA		0.964		0.9923	0.460

Table SI.3.1 R^2 values for the extrapolation to 100% water for all adsorbents.

PFAA	$\Delta_s G^0$ (kJ/mol)				
	C ₁₈	HLB	WAX	MAX	Al ₂ O ₃
PFBA	-6.1±3.8	-5.4±2.8	-20±1.0	-16±0.31	-4.0±0.35
PFPeA	-13±2.7	-9.8±1.3	-25±0.88	-19±0.54	-3.7±0.34
PFHxA	-18±2.2	-15±1.0	-27±2.3	-23±0.61	-3.4±0.32
PFHpA	-21±3.4	-20±0.76	-28±2.2	-25±1.0	-3.3±0.32
PFOA	-25±3.8	-24±0.91	-32±3.0	-28±1.2	-3.1±0.34
PFNA		-24±0.41		-28±2.2	-3.3±0.48

Table SI.3.2. Absolute values of $\Delta_s G^0$ (kJ/mol) for the different PFAAs and adsorbents tested

IV. Structure and possible interaction locations between the adsorbents investigated and a PFAA moiety

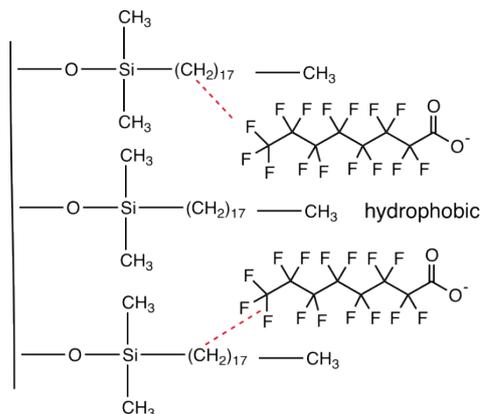


Figure SI.4.1 C₁₈ material

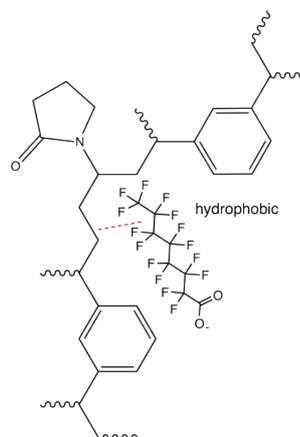


Figure SI.4.2 HLB structure

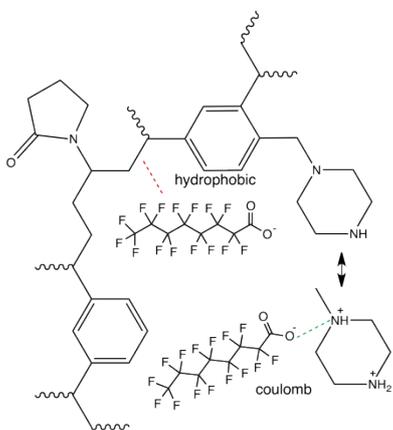


Figure SI.4.3 WAX material.

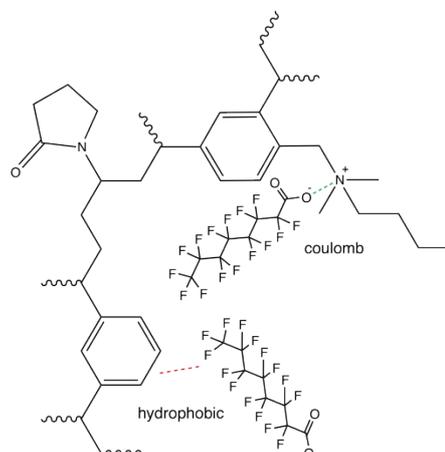


Figure SI.4.4 OASIS MAX structure

V. Derivation of relative contribution of PFAAs adsorbed on WAX and HLB when mixed together

For a system with two adsorbents present in a liquid the total mass of single adsorbate, m_{tot} (nmol), and total volume, V_{tot} , are defined as follows:

$$m_{tot} = m_{A1} + m_{A2} + m_{aq} \quad (A1)$$

where m_A is the mass of the adsorbate sorbed to the specific sediment and m_{aq} is the mass dissolved in the liquid at equilibrium and

$$V_{tot} = V_w + \rho_{S1} * m_{S1} + \rho_{S2} * m_{S2} \quad (A2)$$

where ρ_s is the specific volume of the mass (L/kg), m_s the mass of the sediment applied (e.g. g) and V_w the volume of the liquid applied (L).

Multiplying m_A in eq A1 by m_s/m_s where m_s is the mass of the sediment (g) for each specific adsorbent leads to Eq A3.

$$m_{tot} = \frac{m_{A1}}{m_{S1}} * m_{S1} + \frac{m_{A1}}{m_{S2}} * m_{S2} + m_{aq} \quad (A3)$$

We consider the mass applied in the experimentally defined system as a fraction, f_s , multiplied by the mass normalization factor, M_s (eq A4)

$$m_s = f_s * M_s \quad (A4)$$

Using eq A3 and eq A4 for each specific adsorbent leads to Eq A5

$$m_{tot} = \frac{m_{A1}}{M_{S1}} * M_{S1} + \frac{m_{A1}}{M_{S2}} * M_{S2} + m_{aq} \quad (A5)$$

In Eq 5 m_A/M_S is the thermodynamic adsorbed fraction, C_s^{therm} . Multiplying the right side of A5 with V_{tot}/V_{tot} leads to Eq A6

$$m_{tot} = \left[\frac{C_{S1}^{therm} * M_{S1}}{V_{tot}} + \frac{C_{S2}^{therm} * M_{S2}}{V_{tot}} + \frac{m_{aq}}{V_{tot}} \right] * V_{tot} \quad (A6)$$

The following assumption are introduced; $C_s^{therm} = K_{p,0}^S * C_w^{therm}$ which is related to the linear part of the Langmuir sorption isotherm where the number of adsorbed moieties is still small compared to the overall number of sorption locations, and $V_w \gg \rho_{S1} * m_{S1}$ and $V_w \gg \rho_{S2} * m_{S2} \rightarrow V_{tot} \approx V_w$ meaning that the volume of the water is very large compared to the volumes of the adsorbents in the system. It leads to Eq (A7)

$$m_{tot} = \left[\frac{K_{p,0}^{S1} * C_w^{therm} * M_{S1}}{V_w} + \frac{K_{p,0}^{S2} * C_w^{therm} * M_{S2}}{V_w} + \frac{m_{aq}}{V_w} \right] * V_w \quad (A7)$$

In Eq A7 m_{aq}/V_w is equivalent to C_w^{therm} and rearranging C_w^{therm} leads to Eq (A8)

$$m_{tot} = C_w^{therm} \left[\frac{K_{p,0}^{S1} * M_{S1}}{V_w} + \frac{K_{p,0}^{S2} * M_{S2}}{V_w} + 1 \right] * V_w \quad (A8)$$

If we normalize M_S on 1 kg and V_w on 1L as is normally done in sorption experiments Eq A9 is derived.

$$C_w^{therm} = \frac{m_{tot}/1L}{\left[K_{p,0}^{S1} * \frac{1kg}{1L} + K_{p,0}^{S2} * \frac{1kg}{1L} + 1 \right]} = \frac{m_{tot}}{\left[K_{p,0}^{S1} + K_{p,0}^{S2} + 1 \right]} \quad (A9)$$

If Eq A4 is not applied then the experiment is conducted with specific masses of the sediment and volume of the liquid but the same assumptions are still valid (linear sorption isotherm and $V_w \gg \rho_{S1} * m_{s1}$ and $V_w \gg \rho_{S2} * m_{s2}$) the following equation for C_w^{therm} is obtained (Eq A10).

$$C_w^{therm} = \frac{m_{tot}}{\left[\frac{K_{p,0}^{S1} * m_{S1}}{V_w} + \frac{K_{p,0}^{S2} * m_{S2}}{V_w} + 1 \right] * V_w} \quad (A10)$$

In this case m_s/V_w is equivalent to the sediment concentration in the liquid, S_{aq} leading to Eq A11. If $K_{p,0}^S$ is expressed in L/kg then S_{aq} must be expressed in kg/L.

$$C_w^{therm} = \frac{m_{tot}}{\left[K_{p,0}^{S1} * S_{aq}^{S1} + K_{p,0}^{S2} * S_{aq}^{S2} + 1 \right] * V_w} \quad (A11)$$

This equation is useful for sorption experiments conducted in the lab. If it is assumed that S_{aq} is normalised to 1 kg/L and V_w to 1L, Eq A9 returns.

VI. Fraction of PFAA adsorbed in a *batch* experiment with a mixture of HLB and WAX adsorbents

Using the values $\Delta_s G^0(0)$ and $\Delta\Delta_L G^0$ from Table 2 in the main text for HLB and WAX respectively and the relationship $\Delta_s G^0 = -RT \ln K_{p,0}$ the individual $K_{p,0}$ values of WAX and HLB can be established. According to the IM model in an experimental system where both adsorbents are present the overall $K_{p,0}^{elec+hydr}$ can be established as follows $K_{p,0}^{elec+hydr} = K_{p,0}^{elec} + K_{p,0}^{hydr}$. Table SI.6.1 shows the results.

	PFBA	PFHxA	PFOA	PFDA	PFDoDA	PFTeDA	PFHxDA
N_{CF_2}	3	5	7	9	11	13	15
$\Delta G_s^0(N_{CF_2})$ (HLB) kJ/mol	-6.5	-14.5	-22.5	-30.5	-38.5	-46.5	-54.5
$\Delta G_s^0(N_{CF_2})$ (WAX) kJ/mol	-20.5	-25.5	-30.5	-35.5	-40.5	-45.5	-50.5
$K_{p,0}^{hydr}$ (HLB) (L/kg)	1.4E+01	3.6E+02	9.4E+03	2.4E+05	6.3E+06	1.6E+08	4.2E+09
$K_{p,0}^{elec}$ (WAX) (L/kg)	4.2E+03	3.2E+04	2.4E+05	1.9E+06	1.4E+07	1.1E+08	8.2E+08
$K_{p,0}^{hydr+anionic}$ (L/kg)	4.2E+03	3.2E+04	2.5E+05	2.1E+06	2.0E+07	2.7E+08	5.0E+09

Table SI.6.1: Individual $K_{p,0}$ value of HLB and WAX and the overall $K_{p,0}^{anionic+hydr}$ value for several PFAA in the range from C_4 to C_{16} . $K_{p,0}$ -values with $N_{CF_2} > 8$ are estimated by assuming that the linearity for each adsorbent as shown in Fig 3 still holds.

Based on the $K_{p,0}$ values from the individual adsorbents HLB and WAX from table SI.6.1 one can calculate the adsorbed fraction on HLB and WAX individually in a batch experiment with e.g. a starting mass of each PFCA of 100 nmol, volume of the water of 1 L and sediment masses of 0.010 kg each. As a first step the equilibrium concentration of the PFAA in water, $C_w(t=t_{eq})$, is calculated according to Eq A12 in section V of this SI. It is assumed that the assumptions in the derivation of Eq A12 are valid in the selected experimental setup. On using the data of Table 1, the 10 g of WAX and HLB in this 1 L can adsorb a maximum of 5.3 mmol and 2.6 mmol PFAA which is far above the applied mass of 100 nmol and therefore easily fulfilling the linear assumption. The relative fractions of each PFAA adsorbed on WAX and HLB,

	PFBA	PFHxA	PFOA	PFDA	PFDoDA	PFTetraDA	PFHexaDA
N_{CF_2}	3	5	7	9	11	13	15
C_w^{eq} (nmol/L)	2.3E+00	3.1E-01	4.0E-02	4.8E-03	4.9E-04	3.7E-05	2.0E-06
C_s^{hydr} (HLB) (nmol/kg)	3.29E-01	1.13E+00	3.72E+00	1.16E+01	3.07E+01	6.00E+01	8.36E+01
$C_s^{anionic}$ (WAX) (nmol/kg)	9.73E+01	9.86E+01	9.62E+01	8.84E+01	6.93E+01	4.00E+01	1.64E+01
C_s^{total} (nmol/kg)	9.77E+01	9.97E+01	1.00E+02	1.00E+02	1.00E+02	1.00E+02	1.00E+02
C_s^{hydr} HLB (%)	0.32859454	1.12654127	3.72391303	11.58250213	30.72483452	60.02491012	83.56231586
$C_s^{anionic}$ WAX (%)	97.3239732	98.8699514	96.2746080	88.4169444	69.2750148	39.9750676	16.4376825
C_s^{total} (%)	97.6604395	99.6896289	99.9602997	99.9952219	99.9995095	99.9999629	99.9999980

respectively, are presented Table SI.6.2.

Table SI.6.2: Expected adsorbed fractions of several PFCA to WAX and HLB in a *batch* experiment with starting mass of 100 nmol of each PFAA in 1 L of water and 10 g of HLB and WAX each. C_s (%) values above $N_{CF_2} > 8$ are estimated by assuming that the linearity for each adsorbent as shown in Fig 3 still holds.