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Method Article

A serial PFASs sorption technique coupled with adapted high volume direct aqueous injection LCMS method

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are ubiquitous global environmental contaminants, environmentally persistent, mobile, can bioaccumulate and are toxic. Increasing emphasis is placed on the immobilisation and removal of PFAS from contaminated environmental matrices such as: potable water, surface water, groundwater, wastewater, sediments and soils (Dauchy et al., 2017; Cao et al., 2019; Hepburn et al., 2019). To achieve this, development of PFAS sorbents is increasingly undertaken (Du et al., 2014). Sorption studies are used to observe the interaction of sorbent and sorbate, but have two key limitations when undertaking sorption experiments for PFAS (1) the experimental protocol and (2) analytical techniques. The current batch sorption methods approached recommended by OECD Guideline 106 (OECD, 2000) are problematic, firstly, due to large sample numbers and PFAS specific laboratory difficulties, including near ubiquitous background PFAS contamination. Secondly, PFAS analytical techniques currently require solid-phase extraction (SPE) to be employed, which is slow and expensive, prior to instrumental analysis with liquid chromatography-mass spectrometry (LC-MS). A suitable alternative approach is needed to mitigate the drawbacks of current methodologies whilst catering for the high sample throughput required by benchtop trials characterising the sorption behaviour of PFAS - sorbent pairings.

- A suitable method for PFAS measurement, overcoming shortcomings of current batch sorption methodologies is presented
- The method can be applied to a wide range of sorbents and sorption environment conditions associated with PFAS immobilisation or removal in the environment
- The presented method is novel through its high sample throughput, simple approach and minimisation of cross contamination sources

Specifications table

Subject Area:	*EnvironmentalScience*
More specific subject area:	*Soil Science*
Method name:	*N/A*
Name and reference of original method:	*N/A*
Resource availability:	*N/A*

Method

The method outlined addresses the testing of sorbents capacity for PFAS sorption in an aqueous matrix, adaptable to several potential experimental conditions or sorbent types, in a fast and cost-effective manner. This was achieved by modifying commonly applied sorption and analytical methods [1–5] and coupling these approaches with a high throughput LC-MS direct aqueous injection method. The current work was not designed to detail the performance of the sorbents used in method validation. Instead the work aims to demonstrate method performance towards application as a screening tool for multiple candidate PFAS sorbents under variable environmental conditions.

Chemicals and Reagents

EMD Millipore Hyper-grade LiChrosolv methanol (MeOH) was used as the mobile phase in LC-MS analysis, for the reconstitution of all samples in 10% MeOH and for washing pipette tips when preparing calibration standards. EMD Millipore LC-MS grade MeOH was employed in sample preparation and triplicate wash of all polypropylene bottles or equipment used in experiments. All solvents were tested for PFAS content by LC-MS prior to use. Additionally, Milli-Q water (Ultrapure Millipore Synergy UV Milli-Q water system) was utilised and confirmed to be PFAS-free.

Native PFAS standards (purity ≥98.0 %) were acquired from Sigma Aldrich (Australia). These included Perflurorbutanoic acid (PFBA), Perfluorohexanoic acid (PFHxA), Perfluorooctanoic acid (PFOA), Perfluorobutanesulfonic acid (PFBS), Perfluorohexanesulfonic acid (PFHxS), and Perfluorooctanesulfonic acid (PFOS). PFBA, PFBS and PFHxA were liquid at standard laboratory temperature, while the remaining compounds were provided as solid potassium salts. ^{13}C labelled standards for the above PFAS were obtained from Wellington Laboratories Inc. at a concentration of 50 μg/mL and ≥99 % purity , and were labelled as follows: PFBA (M3), PFHxA (M2), PFOA (M2), PFOA (M8), PFBS (M3), PFHxS (M3), PFOS (M4), PFOS (M8), where M denotes the labelled carbon number.

"PFAS Clean" Preparation of Solvents, Stocks and Standards

Pipette Tip Wash
Pipette tips were a known source of PFAS contamination in previous laboratory experiments. Therefore, all pipette tips were tested and confirmed to be PFAS-free prior to commencing experimental work. Furthermore, pipette tips used in experiments were washed using a two step-sequence to prevent the carryover of PFAS, or leaching of PFAS impregnated within the pipette material, into samples. Pipette tips were rinsed with MeOH three times followed by a further rinse with 10% MeOH Milli-Q water solution.

Calibration Standard and Spiking Solution Preparation
Calibration standards were prepared in Agilent Technologies 1 mL Polypropylene snap lid GC vial by serial dilution using all six native PFAS standards in a 10% by volume MeOH milli-Q water solution.

Calibration standards ranged from 0.01 to 10 µg/L and included a constant concentration of 1 µg/L carbon labelled standards as PFBA (M3), PFHxA (M2), PFOA (M2), PFBS (M3), PFHxS (M3), and PFOS (M4).

A 10 µg/L Carbon labelled PFAS solution was prepared in a 50 mL polypropylene centrifuge tube using hypergrade MeOH and PFBA (M3), PFHxA (M2), PFOA (M2), PFBS (M3), PFHxS (M3), and PFOS (M4) carbon labelled standards. This solution was used for addition of surrogates to samples during sample preparation.

PFOA (M8) and PFOS (M8) were prepared in a 10% by volume MeOH milli-Q water solution to achieve a 1 µg/L concentration for injection standard.

Each target PFAS congener had a spiking solution prepared in ACS grade methanol washed 1 L polypropylene screw cap bottles using milli-Q water to achieve desired concentration. PFAS standards were dissolved in 10 mL MeOH in a polypropylene centrifuge tube before addition to a polypropylene bottle with 990 mL of milli-Q water. This bulk spiking solution was placed on a shaker for an hour before it was divided out into relevant serial experiments. 1 mL of each spiking solutions was prepared for sampling as per Section 2.3.2 and analysed by LCMS to determine exact concentration as starting concentration for experiments (C_0).

In all cases, pipette tip washing mentioned in 2.2.1 was adhered to, and solutions were retained for no longer than 24 hours if not exhausted in experiments.

Sample Preparation and Sorption Experiments

Equilibrium Experimental Protocol

Equilibrium experiments were designed to determine the contact time required to reach a steady state (equilibrium) in a sorption system. This time value is applied to subsequent sorption/desorption experiments. In triplicate, 200 mg of sorbent (selected mass dependant on projected sorbent strength) and 5 mL of 5 µg/L PFAS spiking solution were added to pre-weighed 15 mL polypropylene centrifuge tubes. Seven (7) triplicate sets were created to be destructively sampled at their relevant timepoint, resulting in 21 samples. The samples were re-weighed and the exact mass of sorbent and PFAS spiking solution could then be determined by difference. The sample was vigorously shaken to ensure wetting of all sorbent with PFAS solution. The above was undertaken for testing the equilibrium times of each individual target PFAS – sorbent pairing resulting in the following factorial, n= (21 samples)*(number target compounds)*(number of sorbents requiring testing). Samples were placed on large orbital shakers in centrifuge tube racks which were collectively secured in batches by large rubber bands and removed at time intervals of 0, 1, 2, 3, 8, 24, 48 hours for sample preparation (see section 2.3.2) and subsequent analysis (see section 2.4). Equilibrium time was determined by statistically interrogating the data using Microsoft's Excel package to determine the time point at which no statistically significant change in solution concentration was observed compared to the timepoint sampled before and after it.

Sorption Experimental Protocol

Sorption experiments were conducted to determine the capacity of a sorbent for a given sorbate under specific environmental conditions when the system is at equilibrium. In triplicate, various amounts of sorbent (10, 50, 75, 100, 200, 300, 400, 500 and 1000 mg – in the case of this particular experiment) were each added to individual pre-weighed 15 mL polypropylene centrifuge tubes with 5 mL of 5 µg/L PFAS spiked solution (spiked concentration experiment specific). The samples were reweighed and, by difference, the exact mass of sorbent and PFAS spiked solution was determined. The sample was vigorously shaken to ensure wetting of all sorbent with PFAS solution. Samples were placed on large orbital shakers in centrifuge tube racks, collectively secured in batches by large rubber bands, for their relevant equilibrium times as determined in Section 2.3.1. Hereafter, samples underwent sample preparation (see section 2.3.2) before analysis by LC-MS (see section 2.4). Sorption samples in centrifuge tubes were retained, weighed, and this value used to calculate the volume of water remaining in the tube for upcoming desorption testing. The above was undertaken for each sorbent - sorbate pairing to be tested.

Desorption Experimental Protocol

Desorption experiments were conducted to determine the extent at which the sorbed fraction is reversible sorbed as a percentage of total sorbed fraction. This experiment employed triplicate 10, 50, 75, 100, 200, 300, 400, 500, and 1000 mg sorbent treatment samples retained from prior sorption experiments, to which 5 mL of milli-Q water were added to each tube. The samples were vigorously shaken to ensure the resuspension and adequate mixing of sorbent with milli-Q water. Samples were placed on large orbital shakers in centrifuge tube racks, collectively secured in batches by large rubber bands, for their relevant equilibrium times as determined in Section 1.3.1. The samples were reweighed, and the exact mass of milli-Q water could be determined by difference. Sample expected PFAS solution concentration could then be calculated using known PFAS concentration and remaining volume of water in tube, and exact dilution by 5 mL unspiked milli-Q addition. The difference between expected solution concentration and measured solution concentration was considered the desorbed fraction. Samples were prepared using the previously described technique (see section 1.3.2) and analysed by LC-MS (see section 2.4). Desorption was calculated as the percentage represented by the difference between expected and analytically determined solution concentration, as a factor of total sorbed fraction determined in sorption experiments (section 1.3.3).

Sample Preparation

All samples underwent the following preparation technique prior to LC-MS analysis. Samples for the equilibrium, sorption and desorption protocols were prepared in new Nunc™ 15 mL screw top sterile polypropylene centrifuge tubes. Samples were centrifuged at 15,000 rpm for 30 minutes and 900 μL of the supernatants decanted from each sample by washed pipette into individual pre-weighed 15 mL centrifuge tube. One hundred μL of MeOH containing 10 μg/L carbon labelled surrogates were added to the sample to result in a the 10% MeOH solution by volume with carbon labelled surrogates at a concentration of 1 μg/L. Samples were then vortexed before filtering with Terumo™ 5 mL Luer Lock polypropylene stopperless syringes and Corning™ polypropylene housed 15 mm diameter 0.2 μm cellulose syringe filters. The filtrate was delivered into a labelled polypropylene GC vial with polypropylene snap top lid and placed in a fridge at 4°C until analysis by LC-MS. Sample tubes could then be disposed of, in the case of equilibrium and desorption experiments, or retained for desorption experiments, in the case of sorption experiments.

LCMS Direct Aqueous Injection Method

Calibration and Mobile Phases

Calibration stock solutions were prepared in 10% MeOH milli-Q water solution at the following concentrations by serial dilution: 0.01, 0.03, 0.06, 0.09, 0.15, 0.20, 0.30, 0.50, 0.75, 1.00, 2.00, 3.00, 4.00, 6.50, 10.00 μg L^{-1}. One μg L^{-1} carbon labelled injection standards (PFOA (M8) and PFOS (M8)) were used for "sandwich injections" to monitor instrumental method performance and replaced every 12 hours of LC-MS sampling or every 209 samples. Quantitation was achieved through isotope dilution; wherein a calibration curve was included in every new set of 209 samples.

All mobile phases were tested for PFAS contamination prior to use. Solvents were prepared in isopropyl alcohol (IPA) and MeOH washed 1 L glass Schott bottles with Teflon™ liners removed, as these were a known source of PFAS contamination.

Sample analysis

Samples were analysed on an Agilent 1290 Infinity II™ Liquid Chromatograph coupled to an Agilent 6495B Triple Quadrupole Mass Spectrometer. Instrument operational conditions are outlined in Table 1 and transitions for target compounds in Table 2. All target analytes were analysed in negative polarity mode and with a cell accelerator voltage of 2V. Sample analysis employed a "sandwich injection" in which injection standards were added to sample. This entailed the drawing of 5 μL of sample followed by 1 μL of 1 μg/L ^{13}C injection standard, and then a further 5 μL of sample. A needle washing program was employed to prevent carry over.

Data processing and quantitation was undertaken using the Agilent Mass Hunter Suites Quantitative analysis package (Version 8). Measured PFAS concentrations were corrected in software

Table 1
LC-MS Operational Conditions.

Item	Parameters
Sample Injection	10 μL (5 μL sample, 1 μL ^{13}C, 5 μL sample)
	Draw speed 400 μL min^{-1}
	Ejected at 200 μL min^{-1}
	Offset of 0.2 mm
^{13}C Addition	1 μL
Separation Column	Agilent EclipsePlusC18 - RRHD 1.8 um (2.1 $\times$ 50 mm)
Delay Column	Agilent EclipsePlusC18, 3.5 um (4.6 $\times$ 50mm)
Column environment	40°C
Multi-wash	1 - Needle (10 s – 90 % MeOH)
	2 - Seat Backflush (10 s 50/50 MeOH)
	3 - Needle and Seat Backflush (10 s start conditions)
Injection programme	1 - Needle wash (5 s)
	2 - Sample draw
	3 - Needle wash (5 s),
	4 - ^{13}C draw,
	5 - Needle wash (5 s),
	6 - Sample draw,
	7 - Needle wash (5 s),
	8 – Inject
	Time: 55 seconds
Solvents	Organic: Hypergrade MeOH
	Aqueous: H$_2$O with 5 mM NH$_4$ acetate
Gradient	0 - 0.5 mins start condition (40 % MeOH)
	0.5 - 3 mins ramp to 100 % MeOH
	3 – 5.5 mins system at 100 % MeOH
	5.5 mins end run
Source conditions	Gas temp: 250°C
	Flow: 11 l/min
	Nebulizer: 25 psi
Ionisation	Negative electrospray ionization
Sheath	Sheath gas 375°C
	Sheath gas flow 11 L/min
Capillary	Capillary pos 3500V neg
	2500V chamber current 0.18 uA
iFunnel	High Pressure RF (negative) 90V
	Low Pressure RF (negative)100V
Detection mode	Dynamic Multiple Reaction Monitoring
Total run time:	6.5 mins per sample

for ^{13}C recovery, and concentrations of branched and linear isotherms quantified as a total for any PFAS congener.

Method QA/QC

Sample batches of ~200 samples included 15 QA/QC samples (method blanks (3), laboratory control samples (3), milli-Q solvent blank (3), MeOH solvent blank (3), and 1 µg/L QC (3). The instrument was flushed between consecutive runs, followed by a suite of three no inject samples and two levels (high and low) of confirmatory calibration standard injections before the commencement of the following run. No inject samples exhibiting peaks for target PFAS resulted in an hour-long LCMS system flush using 50:50 MeOH to water. This process was repeated until no injects were demonstrated to be non-detect for target PFAS.. If either calibration standard deviated by 20 % of its previous PFAS concentration the run was stopped, and new calibration standards prepared while the system was flushed with 50:50 MeOH to water for an hour.

Method blanks were created by adding 5 mL of milli-Q water to a centrifuge tube. Laboratory control samples (LCS) were prepared in triplicate by adding 5 mL of 5 µg/L PFAS spiking solution to a centrifuge tube and processing this alongside experimental samples. These allowed the determination

Table 2
LC-MS Target PFAS Transitions and retention times.

Compound Name	Precursor Ion	Product Ion	Ret Time (min)	Delta Ret Time	Fragmentor	Collision Energy
PFBA	213	169	0.9	1.03	380	6
PFBA-13C3	216	172	2	0.5	380	8
PFBS	299	99	2.36	0.97	380	36
PFBS	299	80	2.36	0.97	380	44
PFBS-13C2	302	99	2.28	0.5	380	36
PFHxA	313	269	2.93	0.97	380	6
PFHxA	313	119	2.93	0.97	380	22
PFHxA-13C2	314.9	269.9	2.93	0.88	380	8
PFHxS	399	119	3.32	1.02	380	44
PFHxS	399	99	3.32	1.02	380	44
PFHxS	399	80	3.32	1.02	380	48
PFHxS-1C3	402	99	2.73	0.5	380	44
PFOA	413	368.9	3.55	1.07	380	6
PFOA	413	169	3.55	1.07	380	18
PFOA-13C8	421	376	3	0.5	380	6
PFOS	498.9	99	3.73	1.12	380	56
PFOS	498.9	80	3.73	1.12	380	56
PFOS - 13C4	503	99	3.27	0.5	380	48

Table 3
Method Performance Data.

	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
MDL (ng L^{-1})	66	31	19	70	25	72
LOQ (ng L^{-1})	207	99	59	221	79	228
Trueness (%)	99.3	89.6	97.5	100.4	107.5	107.7
Accuracy (%)	1.3	0.8	0.6	2.6	0.7	2.2

of any fraction of PFAS lost during storage or preparation of samples. Solvent blanks consisted of either 1 mL milli-Q water or 1 mL hyper grade methanol used in sample preparation added directly to 1 mL polypropylene GC vials with clip on polypropylene caps.

In addition, each LC-MS run included five 1 μg/L QC samples interspersed between experimental samples. A 10% RSD was allowed for 1 μg/L QC samples. Exceedance of the RSD saw the preparation and validation of a new set of calibration standards after the instrument had been flushed with 50:50 MeOH to water solution for an hour. QC samples ensured consistency in sampling and were also used to ensure no significant impact went unnoticed between solvent changes, preparation of samples and instrument running conditions for different batches.

Method Performance

LCMS and Sample Preparation

All recoveries were found to be within a 90 – 110% range, falling within the allowable 80 – 120% predetermined criteria. Table 3 demonstrates method MDLs and LOQs, where LOQs in method validation constituted a maximum of 5% of error as a fraction of 5 ppb solution concentration in experiments. Experimental replication was evident with high accuracy between samples. The method was found to be precise with quantitation demonstrating near 89.6 – 107.7% trueness as a factor of actual value. RSD, for the average of 1 ppb QC samples included in a single LC-MS run was found to have a maximum value of 4.5% for any of the 6 studied compounds, well below the selected sample RSD acceptance criteria of 10%. Performance data are tabulated for each compound in Table 3.

Establishment of Isotherms and Sorbed Fractions

The data collected from analysis were input into Freundlich and Langmuir isotherms for sorption modelling. Using the appropriate isotherm or equilibrium model, R^2 values of 95 - >99 % were readily achieved for compounds that adequately sorbed to tested sorbents; demonstrating that the method was fit for purpose. It was noted that PFAS-sorbent pairings with less than 40 % removal of PFAS from solution did not achieve desirable R^2. While suitability for isotherm input was namely determined by extent of sorption for sorbent-PFAS pairing, RSDs of <5 % were readily achieved for sorbent-sorbate pairings that resulted in high sorption. Formulae applied in validation study are outlined below. Sips isotherm was found to be the most effective modelling complex PFAS sorption behaviour (often sigmoidal).

Equilibrium Calculations

Sorbed fraction at any measured timepoint was represented as Q_t (Eq. 2.1), and input into experimental models used in the exploration of kinetic behaviour as described below. Q_t was calculated from experimental data, where C_0 was the starting concentration of PFAS in solution (µg/L) and C_t represented the remaining PFAS in solution (µg/L) at timepoint t (hours) for a given mass of sorbent m (g).

$$Q_t = \frac{(c_0 - c_t)V}{m} \tag{2.1}$$

First Order Kinetic Model

Eq. 2.2 represented the First Order kinetic model which proposes a system where sorption is directly proportional to the concentration of PFAS in solution (linear). Where K_1 is the first order rate constant (h), C_t is the concentration of PFAS (µg/L) remaining in solution at t (hours) and C_0 is the initial concentration (µg/L) of PFAS in solution at t = 0. Q_t is the µg/g PFAS sorbed at time t (hours) and Q_e is the mass PFAS sorbed per unit sorbent (µg/g) at equilibrium (Eq. 2.1).

$$Q_t = Q_e\left(1 - e^{k_1 t}\right) \tag{2.2}$$

Pseudo-Second Order Kinetic Model

The Pseudo-Second Order model, an indicator of chemisorption in place of physisorption was fitted to equilibrium data using Eq. 2.3. Here the rate is said to be exponentially related to the concentration of PFAS in solution, where fitting suggests an excess of one reactant in solution (sorption sites). Where K_2 is the sorption rate constant (g/(µg h)) for the second-order sorption model.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} = \frac{t}{Q_e} \tag{2.3}$$

Sorption Calculations

Sorbed fraction at equilibrium was represented as Q_e, and input into isotherms used in the exploration of sorption capacity as described below. Q_e is defined as sorbed mass of sorbate, per mass of sorbent vat equilibrium (Eq. 2.4), where C_0 and C_e were determined by averaging the triplicate results for each sampling point. Q_e is calculated from experimental data, where C_0 is starting concentration of PFAS in solution (µg/L) and C_e is the remaining PFAS in solution (µg/L) at equilibrium for a given mass of sorbent m (g). The collected data is input into the following models. Models are employed in this manner to establish a relation between the solute sorbed on the surface of the sorbent (per unit mass sorbent) to the concentration of the solute remaining in solution.

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{2.4}$$

Freundlich

The Freundlich isotherm was applied to data in the form seen in Eq. 2.5, this model can be used to model sorption to non-heterogeneous surfaces as well as multilayered sorption. Where Q_e is the mass of solute sorped per mass sorbent (µg/g). C_e is the mass of solute remaining in solution per litre

(μg/L), K_f is the Freundlich constant related to sorption affinity, and $1/n$ a sorption intensity constant. $1/n$ values between 0 and 1 are linked to a chemisorption process, whereas values over 1 suggest cooperative sorption.

$$Q_e = K_f C_e^{1/n} \qquad (2.5)$$

Langmuir

The Langmuir isotherm models data under the assumption that the adsorption of a single sorbate was on to sites upon a flat surface, where all sites are homogenous. It assumes only one molecule is sorbed per site, in a permanent manner and without further interaction with the solution or the surface. The model is described by Eq. 2.6, where Q_m was the maximum amount of sorbate that can be sorbed per unit of sorbent (μg/g). K_L represents the Langmuir energy of adsorption (L/μg).

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (2.6)$$

Sigmoidal Langmuir Modification

A modified sigmoidal Langmuir models sorption to non-heterogenous surfaces with a sigmoidal point of inflection (Eq. 2.7). The point of inflection denoting two opposing forces or mechanisms of sorption that are acting against each other and are solute concentration dependant. K_L is the Langmuir adsorption energy constant which describes the strength of the sorption energy (L/g). S is a dimensionless reflection of sigmoidal behaviour. The model was applied in the form seen in equation 2.7.

$$Q_e = Q_{\max} \frac{(K_L C_e)}{1 + (K_L C_e) + \left(\frac{S}{C_e}\right)} \qquad (2.7)$$

Sips

The Sips model combines Langmuir and the Freundlich models to model sorption to heterogenous surfaces at both high and low concentrations. This occurs as the model is adaptive and performs similarly to Langmuir in higher concentration ranges and closely to the Freundlich model at lower concentrations of solute. The model is expressed in Eq. 2.8, where K_L is the Sips isotherm constant (L/g), maximum adsorption capacity is reflected by Qmax (μg/g), and n is dimensionless reflection of sigmoidal behaviour.

$$Q_e = \frac{Q_m (K_L C_e)^{1/n}}{1 + (K_L C_e)^{1/n}} \qquad (2.8)$$

Desorption

Desorption was represented by Eq. 2.9, where desorption was calculated as a percentage (%) which represented the desorbed fraction in terms of the sorbed fraction Q_e. Where $C_{e\,[sorp]}$ is the concentration of PFAS in solution at equilibrium after sorption experiments (μg/L) and $C_{e\,[desorp]}$ is the concentration of PFAS in solution, at equilibrium, after desorption experiment (μg/L). Q_e is the sorbed fraction of PFAS from sorption experiments (μg/g).

$$Desorption = \frac{Ce[sorp] - Ce[desorp]}{Q_e} \times 100 \qquad (2.9)$$

Limitations of Method

Due to the low MDL and LOQ of this method, it is sensitive to PFAS contamination. This means, the highest level of PFAS clean technique needs to be applied alongside a sound QA/QC program. While this is well addressed in the sample preparation technique, the method is reliant on operator adherence to PFAS clean techniques. In addition, experimentally determined MDLs and LOQs imply an alternative method would be required to measure behaviours wherein most sample points fall in the concentration bracket 0 - 0.25 μg/L. As, such this method was not designed to measure sorption behaviour at ultra-trace (< 0.25 μg/L) concentrations. The use of a serial method as opposed to batch

method generates greater control of contamination risk and identification; however it does produce a large volume of waste in the form of centrifuge tubes, filters, syringes and pipettes. Due to the gradient and short run time employed in this high throughput method, the separation of branched and linear isomers was not possible.

Benefits of Improved Method

The novelty of the outlined method lies in the delivery of a high sample throughput (~182 samples in 24-hours), excluding instrument preparation and determination of equilibrium time. This represents a low cost analytical technique directed at managing the large experimental factorials intrinsic to trailing a variety of candidate PFAS sorbents under a variety of sorption environment conditions. These include variable PFAS concentration, congener types (including mixtures thereof), sorbent type, sorbent application rate, matrix conditions (i.e. pH, solution ionic strength, co-contaminants, dissolved organic matter, electrical conductivity and temperature) and scale.

Materials and reagents employed in the experimental method were demonstrated to be PFAS free or suitably controlled, with blank samples returned as non-detect for target PFAS, in turn reducing the incidence of overestimation through contamination. Further, the application of this serial method removes the accumulative encumbrance of batch samples to cross contamination where in the serial method each triplicate sample is a true standalone triplicate, meaning statistical analysis is not subject to deviations of a single source, as in the case for traditional batch experiments.

Declaration of Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mex.2020.100886.

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