



Leaching potential of per- and polyfluoroalkyl substances from source zones with historic contamination of aqueous film forming foam - a surfactant mixture problem

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ABSTRACT

Per- and poly fluoroalkyl substances (PFAS) from aqueous film forming foam (AFFF) used at firefighting training facilities (FTF) contaminate waterbodies and pose a threat to human health and the environment worldwide. In this study, leaching of PFAS from historically AFFF contaminated field soil has been investigated under saturated conditions using up-flow columns for four soil samples with varying PFAS concentrations to quantify the long-term release potential of the source zone. PFOS was the most abundant PFAS present in the soils (84–98% of Σ PFAS₁₂), varying from 358 to 1097 $\mu\text{g}/\text{kg}$ and the total organic carbon (TOC) content varied from 0.73 to 2.0%. The experiment was run until a liquid to solid (L/S) ratio of 10 was reached (equivalent to 80 pore volumes or approximately 100 years of natural infiltration at the sampled field site). Results show a general trend of decreasing concentrations of short chain PFAS with increasing leaching volume. However, PFOS concentrations initially increased by 45–87% in three samples with relatively low TOC (0.7, 1.0 and 1.4%), before being reduced. In the 2.0% TOC soil PFOS concentrations continued to increase throughout the experiment. The residual PFOS content in the four soil samples showed no correlation with TOC content in the soil. Up to 50% of the initial PFOS content was retained in the soil with the lowest TOC content (0.7%), whereas all PFOS was removed in the soil with a TOC content of 1.4%. It is hypothesized that DOC present in the eluates originates from other non-fluorinated components present in AFFF that can facilitate PFAS leaching.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of extremely persistent chemicals used increasingly in industry and consumer products since the 1950s because of their useful properties like hydrophobicity, lipophilicity and thermal stability (Buck et al., 2011). Once present in the environment, PFAS require human intervention to remove them (Goldenman et al., 2019). In October 2020, EU's Chemicals Strategy for Sustainability Towards a Toxic-Free Environment was published, presenting the phase out of the use of PFAS, unless their use is essential (EU, 2020).

Introduction of PFAS in firefighting foams for hydrocarbon fuels, in the 1960's, resulted in aqueous film forming foams (AFFF) with superior firefighting capabilities due to surface tension lowering properties (Schaefer, 2008; Norden, 2013; Dauchy et al., 2017). However, the use

of AFFF at civil and military airports has resulted in PFAS contaminated soil, ground- and surface waters worldwide (Guelfo and Higgins, 2013; Houtz et al., 2013; Ahrens et al., 2015; Filipovic et al., 2015; Anderson et al., 2016; Nickerson et al., 2020). In Norway, AFFF impacted soil at civil and military airports has resulted in local PFAS contamination of groundwater, rivers and streams and elevated concentrations of PFAS in biota are detected at many of the investigated locations, such as Bodø and Svalbard airport (Langberg, et al., 2019; Ali et al., 2021; Avinor, 2021).

PFAS from an AFFF site will percolate through the vadose zone when water from precipitation or other sources infiltrates the soil. The percolation rate depends on several factors, for instance type and texture of soil, as well as the organic matter content, some of which have been thoroughly investigated (Lyu et al., 2018; Guelfo et al., 2020; Van Glubt et al., 2021). Sorption affinity to soil organic matter and different soil

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particles differs for individual PFAS (Higgins and Luthy, 2006; Hale et al., 2017; Høisæter et al., 2019; Zareitalabad et al., 2013; Schaefer et al., 2021). The desorption hysteresis and rate limited kinetics of the above-mentioned processes will also influence the transport and the weathering at the field sites. The time since the site was contaminated and the amount of water that infiltrates can substantially affect the transport. As a result, PFAS will be transported at different rates in the unsaturated soil profile due to variations in the sorption affinities to the soil matrix (Høisæter et al., 2019). The lipophobic/hydrophobic nature of the fluorocarbon tail of PFAS and the reduction in surface tension can contribute to PFAS adsorption at air-water interfaces in the soil pores, potentially retarding PFAS percolation in the vadose zone (Brusseau, 2018; Lyu et al., 2018; Brusseau et al., 2019). This air-water interfacial (AWI) sorption of PFAS has been further investigated by Schaefer and co-workers (Schaefer et al., 2019) and show that the transport of PFAS is not only determined by the chemical properties of the PFAS and the properties of the soil, but also by the varying degree of saturation of the soil which was investigated in our previous work (Høisæter et al., 2019). A clear chromatographic effect could be observed where PFOS was completely retained in the soil column, even after infiltration of an equivalent of 2 years of winter precipitation. However, short-chain PFAS were transported rapidly through the columns and were detected in the porewater two to three weeks after the start of the experiment. The dominating retention and sorption processes for PFAS in the vadose zone are complex and are still under investigation (Brusseau, 2020). Fully saturated transport of PFAS in AFFF contaminated soil has recently been investigated by Maizel et al. (2021). The experiment was performed columns under saturated conditions with artificial groundwater. The results suggested rate-limited desorption of anionic and zwitterionic PFAA precursors may result in these compounds being a large fraction of the remaining PFASs in AFFF-impacted surface soils.

The overall aim of the present study was to determine whether there could be a residual immobile fraction of PFAS in a historically AFFF contaminated sandy soil, with various degrees of weathering, after the soil has been exposed to decades of infiltration, while minimizing the contribution of AWI sorption. To this end, soil columns of the vadose zone at an AFFF contaminated field site were run under saturated flow conditions, representing worst-case percolation conditions for a surface soil. Soils with various PFAS contamination levels and organic carbon content were included. Quantification of the PFAS leaching potential of historically AFFF contaminated soils is an essential element to be able to perform a reliable risk assessment and design effective remedial measures to reduce risk at the large number of AFFF contaminated sites threatening our water quality.

2. Materials and methods

2.1. Site description

The PFAS contaminated soil investigated in this study was sampled at a firefighting training facility (FTF) heavily impacted by several decades of AFFF use at Oslo Airport at Gardermoen north of Oslo. The site is described in detail in Høisæter et al. (2019). The amount of AFFF used at the site and the total amount of water infiltrated during fire training with fire engines varied across the various training platforms at the FTF. Legacy PFAS containing AFFF was used regularly according to training requirements at the site until the phasing out of PFOS started in 2001. At that time PFOS was replaced by fluorotelomer based AFFF until fluorine free foam was introduced at the site in 2011 (Avinor, 2021). Due to heavy restrictions on fuel contamination to protect the groundwater at the site, co-contamination from fuel is very limited. The area is flat and consists of glaciofluvial deposits dominated by sands. The sedimentology at the site is described in more detail in Høisæter et al. (2019). Earlier studies have determined a bulk density of 1.68 g/cm^3 , with a corresponding porosity of 0.37 for the sandy soil at the site (Klonowski et al., 2008). The hydraulic conductivity (Ks) at the site ranges from

10^{-3} to 10^{-5} m/s (French et al., 2009). Previous soil investigations have shown that PFOS accounts for an average of 96% of the total $\Sigma 12$ PFAS analyzed in the sandy soil at the AFFF impacted site, ranging from $<0.3 \text{ } \mu\text{g/kg}$ to $6500 \text{ } \mu\text{g/kg}$ (Høisæter et al., 2019). The average soil to water sorption coefficient (Kd) for PFOS was determined to be 10 L/kg using batch leaching tests with PFAS contaminated soil samples from the site (Hale et al., 2017).

2.2. Soil sampling

PFAS contaminated soil was sampled from four areas of the FTF, with various degrees of AFFF impact, TOC content and amount of water infiltrated historically into the soil. The soil samples are identified as sample A through D, where the sequence represents an increasing soil organic carbon content. Table 1 shows the soil characteristics and AFFF impact history of the four soil sampling areas.

The PFAS concentration in the soil samples were determined for 12 different PFAS to be able to evaluate the fate and transport behavior of different PFAS groups and chain lengths. The samples were collected using a small excavator to dig a trial pit in the sandy soil. Care was taken to prevent the presence of co-contaminants related to fuels used at the FTF. The soil was sampled down to 1.0 m depth, excluding the organic top layer, using a clean spade. Each trial pit was sampled vertically with a minimum of 10 subsamples evenly distributed over the soil depth to make the sample representative for the depth of the soil profile. The spade was cleaned with methanol between each sampling point. Soil was transferred into 1 L sampling bags (permeation resistant polyamide) and stored at $4 \text{ } ^\circ\text{C}$. The samples were homogenized, and triplicates subsamples of the soil were shipped to a commercial accredited laboratory for the analysis of the 12 selected PFAS, possible presence of fuel related hydrocarbons, as well as the total organic carbon content (TOC). Grain size distribution curves were determined for each soil sample as well.

2.3. Column set up

The four AFFF contaminated soil samples were packed in separate

Table 1

Description of the soil samples from the AFFF impacted site used in this study (see chapter 3.1 for details on characterisation results).

Sampling location	Sample A	Sample B	Sample C	Sample D
Surface cover	Grass	Grass	Grass	Grass/Forest bush
Organic top soil (m)*	0–0.2	0–0.1	0–0.05	0–0.02
Soil sampling depth (m)	0.2–1.0	0.1–1.0	0.05–1.0	0.02–1.0**
Mineral soil layer	Poorly graded medium sand	Poorly graded medium to fine sand	Poorly graded medium to fine sand	Poorly graded medium to fine sand
Cu (d60/d10) ***	2.7	3.3	3.4	3.7
TOC (%)	$0.7 \pm 0.1\%$	$1.0 \pm 0.1\%$	$1.4 \pm 0.1\%$	$2.0 \pm 0.1\%$
Historic AFFF use and impact	Extensive	Extensive	Limited	Limited
Historic use of water from fire engine	Extensive	Limited	Limited	Non-existing
PFOS ($\mu\text{g/kg}$ d.w.)	1097 ± 67	1030 ± 106	358 ± 20	803 ± 142
Σ PFAS ₁₂ ($\mu\text{g/kg}$ d.w.)	1123 ± 87	1103 ± 111	428 ± 30	958 ± 159

* The organic top layer was not included in the soil sampling **Some organic matter observed in the deeper profil *** Cu is the uniformity coefficient defined as the ratio of particle size where 60% pass (D60) to where 10% pass (D10).

columns with an inner diameter of 5 cm. The columns were packed in 6 cm increments to a total height of 29–30 cm, following the method described in EN 14405 (2017) (Characterization of waste - Leaching behavior test - Up-flow percolation test (under specified conditions)). The columns were weighed before and after packing. The columns were placed in a temperature-controlled room (8 °C) and operated in a vertical, up-flow mode to maintain saturated conditions. Each soil was run in triplicate columns. De-ionized water (milli-Q) was pumped through the columns with an average flow rate varying between 11.0 and 12.8 mL/h and eluate was collected at the top of the column in PE containers. The soil columns were initially saturated by pumping water until the water level reached the top of the columns. The water flow was halted for 3 days, to let the soil and porewater come into equilibrium. After 3 days, pumping was resumed at the defined constant rate until a liquid to solid ratio of 10 was reached after 30 days. The liquid to solid ratio of 10 represents 80 pore volumes or approximately 100 years of infiltration at this site, assuming that 50% of the annual precipitation will infiltrate.

2.4. Column eluate sampling

Water samples of the column eluate were sampled at given time intervals representing liquid to solid ratios (L/S) of 0.1, 2, and 10 as defined in standard (EN 14405 2017). pH and electrical conductivity and temperature were measured in all the eluate samples upon collection. The eluate samples were stored at 4°C before shipping to a commercial laboratory at the end of the experiment for chemical analysis. The eluate samples were analyzed for PFAS, macro and micro elements as well as anions and dissolved organic carbon (DOC).

2.5. Chemical analysis

The following 12 PFAS were analyzed in the soil samples: 6:2 fluorotelomer sulfonate (6:2 FTS) and 8:2 fluorotelomer sulfonate (8:2 FTS), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDeA) perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS). Basic properties are shown in SI Table S1.

The soil samples were also analyzed for total organic carbon content (TOC) and fuel related hydrocarbons to detect potential fuel residues from firefighting training activities.

The eluate samples were analyzed for the same 12 PFAS compounds as the soil samples. The aqueous samples were also analyzed for the content of macro and micro elements as well as major anions and DOC.

PFAS, fuel related hydrocarbons and TOC were analyzed at the accredited laboratory Eurofins GfA Lab Service GmbH (in Germany). For PFAS analysis of the soil samples method DIN 38414-S14 (2011) was used based on acetonitrile extraction followed by analysis using liquid chromatography coupled with mass spectrometry (LC/MS-MS). The eluate samples were extracted for PFAS following method DIN 38407-42 (2011), involving solid-phase extraction (SPE) followed by basic methanol elution, evaporation, and re-dissolving in methanol. Internal standards were used. Quantification was performed using LC/MS-MS for the eluate samples.

Macro and micro elements as well as anions and DOC were analyzed by the accredited laboratory ALS laboratory group, using the following methods; ICP-SFMS according to ISO 17294-1,2 and EPA 200.8. ICP-AES according to ISO 11885 and EPA 200.7. Hg according to ISO 17852. Chloride, fluoride, sulfate and DOC according to ISO 10304-1, EN16192, EN1484, EN 16192, SM 5310. EN1484.

2.6. Quality control and assurance

No materials that could influence PFAS sorption behavior (glass, metal) were used when handling samples from soil and the leaching

experiment. PE bottles were used to store samples until analysis. PFAS analysis were carried out at an accredited laboratory. Internal isotopically labeled standards were added to all soil and eluate samples prior to PFAS analysis. PFAS identification was based on retention time and molecule or fragment ions and quantification was carried out by using internal calibration by comparison with the internal isotopically labeled standards. Analytical detection limits were 0.2–1 µg/kg dry matter for PFAS in soil and 0.3–1 ng/l for PFAS in water and 0.1% for TOC in soil.

Analytical detection limits varied from 0.05 to 4 µg/l for macro and micro elements in water. Major anions had analytical detection limits for chloride 0.5 mg/l, fluoride 0.02 mg/l, sulfate 0.5 mg/l and for DOC 0.5 mg/l.

3. Results and discussion

3.1. Characterization of soil samples

3.1.1. Particle size distribution

The soil samples can be characterized as medium sand with a low silt content. The results from the grain size distribution curves are shown in SI Fig. S1 and indicate that there is an increase in the silt fraction (<0.065 mm), varying from 1.85 to 6.71% for sample A to D. Sample A is characterized as a poorly graded medium sand and has the lowest silt fraction. Sample B and C are both characterized as poorly graded medium to fine sand and have similar particle size distribution with a slightly lower silt content than sample D which is also characterized as a poorly graded medium to fine sand and has the highest silt fraction. The uniformity coefficient (Cu) is determined to be 2.7, 3.3, 3.4 and 3.7 for sample A, B C and D, respectively, indicating well sorted sands. Details are given in Table S2 in SI.

3.1.2. TOC concentration

The average TOC content in the four soil samples varied from 0.7 ± 0.1% in sample A, 1.0 ± 0.1% in B, 1.4 ± 0.1% in C to 2.0 ± 0.1% in sample D. Possible co-contaminants related to petroleum products were not detected in any of the soil samples (aliphatic hydrocarbons, C₅-C₃₅ were below the detection limit of 3–10 mg/kg d.w.).

3.1.3. PFAS concentration

The average PFAS concentrations from the three replicates of the four samples are graphically shown in Fig. 1. The most abundant PFAS in all soil samples is PFOS, accounting for 98% of the ∑12 PFAS in sample A and 93%, 84% and 84% in samples B, C and D, respectively. In sample C and D, the concentration of PFHxS is the second highest compound representing 6.8% and 8.8% of ∑12 PFAS, respectively. 6:2 FTS is the second most abundant PFAS in soil sample B accounting for 3.2% of the ∑12 PFAS in the sample. 6:2 FTS and 8:2 FTS contribute with 1.0% each to the ∑12 PFAS as the second most abundant PFAS in soil sample A. The complete overview of the average PFAS concentrations and the standard deviations for the four soil samples are given in Table S3 in SI, whereas the PFOS and ∑ 12 PFAS are shown in Table 1.

3.2. PFAS leaching behavior

3.2.1. Compound specific leaching

The PFAS concentration in eluates collected during the column experiment for L/S ratios of 0.1, 2 and 10 are shown in Figs. 2–4 for soil samples A to D. PFOS and other PFAS with relatively high concentrations are shown on a secondary axis for clarity due to large differences in eluate concentrations. Error bars in Figs. 2–4 are standard deviation of the triplicate water samples. Details for L/S 0.1, 2 and 10 eluate concentrations are given in Tables S4–S6.

The eluate concentrations show a general trend of decreasing PFAS concentrations with increasing amount of water flushed through the columns for all soil samples. PFAS concentrations decrease rapidly from L/S 0.1 to 2 for most PFAS and continue to decrease towards L/S 10.

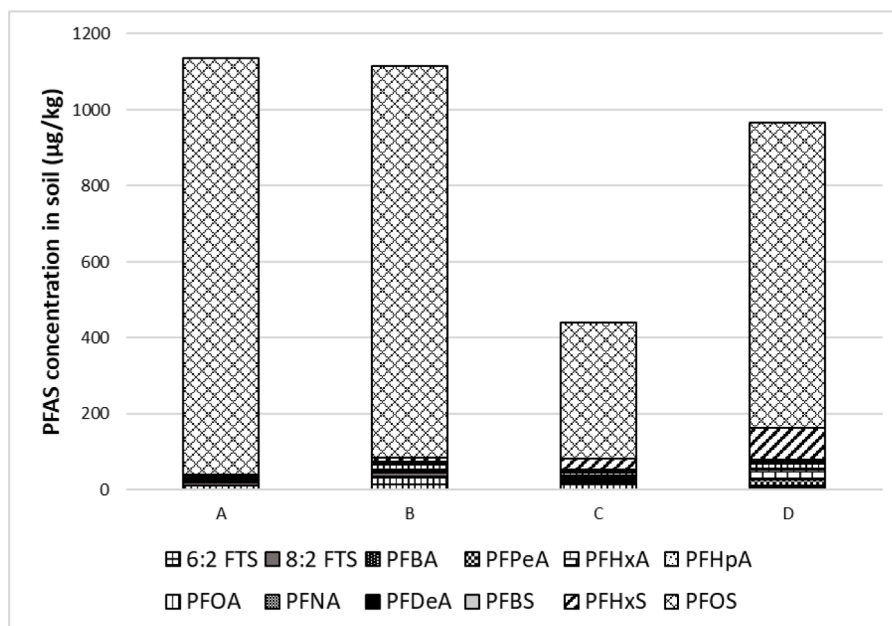


Fig. 1. . Average PFAS concentration in soil samples A, B, C and D (standard deviations for the three replicate samples are presented in Table S3).

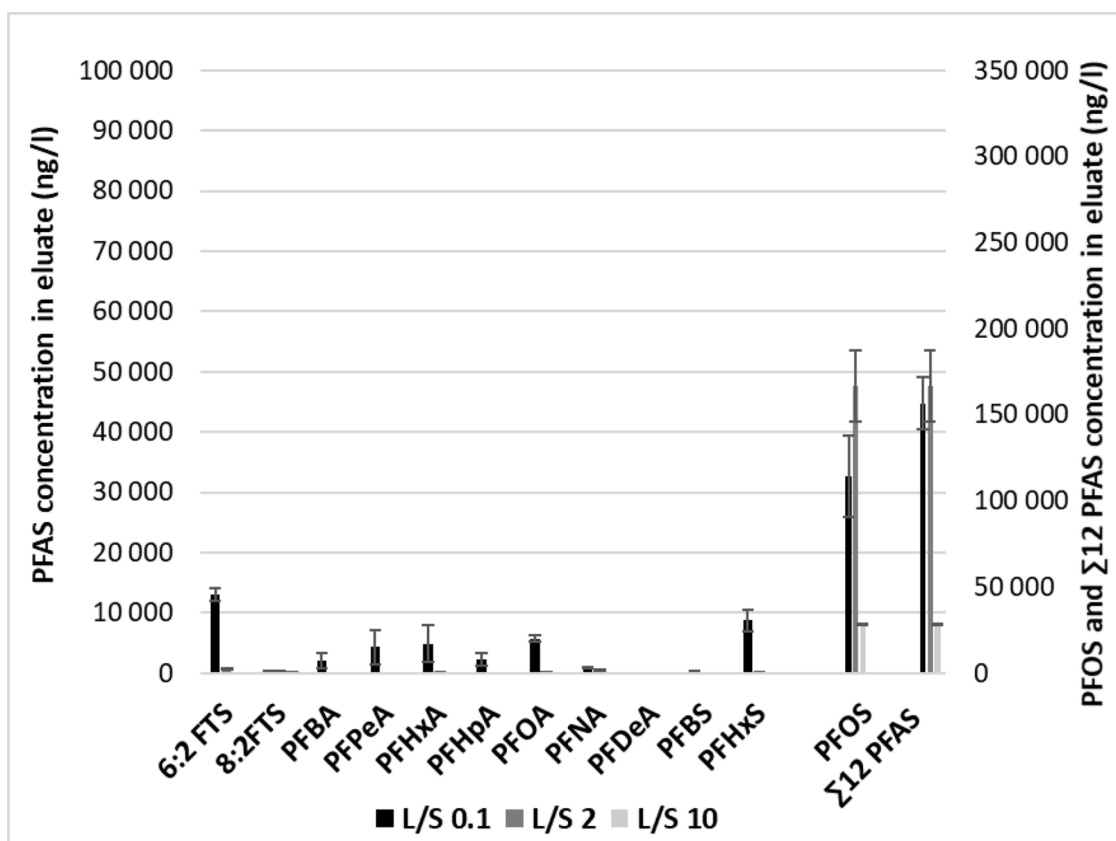


Fig. 2. . PFAS eluate concentration (ng/l) for sample A at L/S 0.1, 2.0 and 10. Eluate concentrations for PFOS and Σ_{12} PFAS are shown on the secondary axis. (detailed concentrations can be found in SI. Tables S4–S6).

However, in sample A, B and C, the PFOS concentration increases from L/S 0.1 to 2 and subsequently decreases towards L/S 10. Due to the limited number of observation points in time, it is not possible to know exactly when PFOS achieves its maximum concentration.

In sample A, PFOS accounts for 73% of the aqueous Σ_{12} PFAS concentration in the eluate at L/S 0.1 but reaches 100% and 99% of the

Σ_{12} PFAS concentration in eluate at L/S 2 and 10, respectively. The aqueous concentration of all PFAS decreases in sample A from L/S 0.1 to 10, with the exception of PFOS, 8:2 FTS and PFDeA, which increases from L/S 0.1 to L/S 2.

In sample B, PFOS accounts for 44% of the aqueous Σ_{12} PFAS at L/S 0.1 and 92% and 97% in L/S 2 and 10, respectively. No increase in the

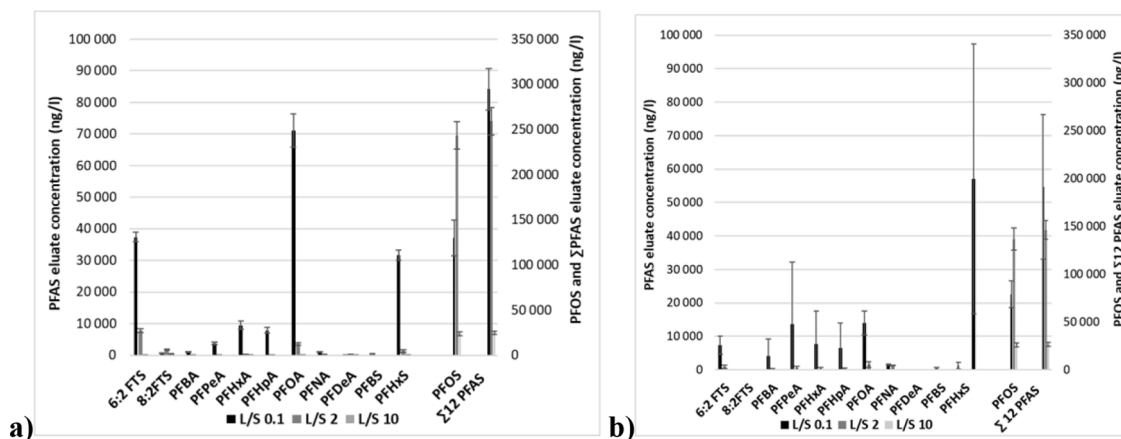


Fig. 3. . PFAS eluate concentration (ng/l) for (a) sample B and (b) sample Cat L/S 0.1, 2.0 and 10. Eluate concentrations for PFOS and Σ 12 PFAS are shown on the secondary axis. (detailed concentrations can be found in SI. Tables S4–S6).

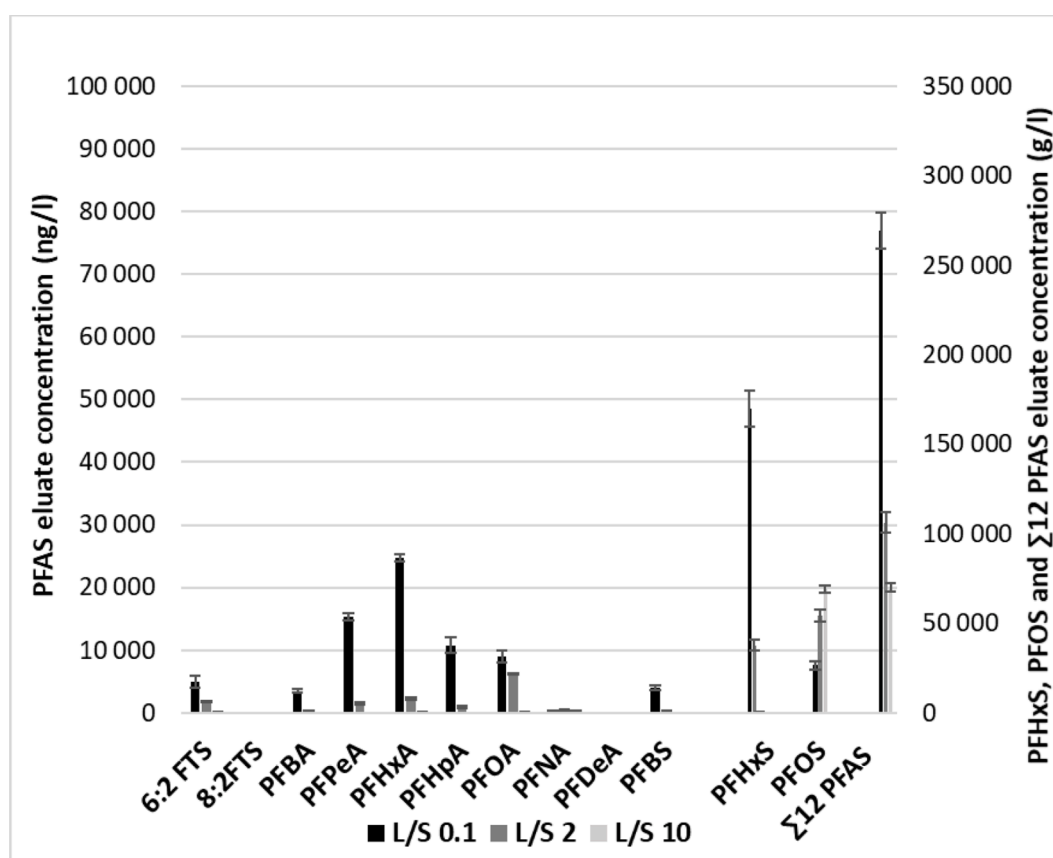


Fig. 4. . PFAS eluate concentration (ng/l) for sample D for L/S 0.1, 2.0 and 10. Eluate concentrations for PFHxS, PFOS and Σ 12 PFAS are shown on the secondary axis. (detailed concentrations can be found in SI. Tables S4–S6).

eluate concentration of Σ 12 PFAS from L/S 0.1 to 2 was observed in sample B due to the high contribution of other PFAS than PFOS in the eluate at L/S 0.1.

The same can be observed in sample C, where PFOS accounts for 40% of the Σ 12 PFAS concentration in eluate at L/S 0.1 and 91% and 99% at L/S 2 and 10. In the eluates for L/S 10, PFBA, PFBS are not detected or have concentrations below 20 ng/L in all 4 samples.

In sample D, the PFOS eluate concentration at L/S 0.1 only account for 10% of the Σ 12 PFAS concentration but the concentration increases to 51% and 98% of the Σ 12 PFAS for L/S 2 and 10. The Σ 12 PFAS eluate concentration shows a strong decrease from L/S 0.1 to 2 and is

almost completely composed of PFOS at L/S 10 in sample D. Unlike the other three samples, there is a continuing increase in the eluate concentrations for 8:2 FTS and PFDeA until L/S 10 is reached concomitant to the PFOS, although at much lower concentrations (see Tables S4–S6 for details). In all the samples a small increase in eluate concentrations of 8:2 FTS and PFDeA is observed from L/S 0.1 to 2 with exception of sample C, in which 8:2 FTS is not detected in L/S 0.1 or 2 (see Tables S4–S6 for details). In sample D, PFOS accounts for 84% of the total Σ 12 PFAS soil concentration. There is also a relatively high eluate concentration of PFHxS of 170 000 ng/L in sample D at L/S 0.1, which could be explained by the relatively high PFHxS concentration (84 μ g/

kg) in the soil compared to the other 3 soil samples. The eluate concentration of PFOS increases in sample D from L/S 0.1 to 2. However, the PFOS concentration continues to increase until L/S 10, unlike the other soil samples. Sample D is the least weathered soil sample, in terms of AFFF exposure and infiltration and also has the highest TOC content (2%) and the highest silt amount (6.7%) of the four soil samples.

3.2.2. Increased concentrations of PFOS

The observed increase in aqueous concentration of PFOS, from L/S 0.1 to 2 in three samples and until L/S 10 in the fourth sample, is counter intuitive given the assumption of local equilibrium between soil and porewater in the first leachate fraction (L/S 0.1). The same trend is observed for other long-chain PFAS with relatively low water solubilities like 8:2 FTS, PFNA (only in sample D) and PFDeA, although a much lower eluate concentration. Similar observations have recently been reported by Maizel et al. (2021) and Kabiri et al. (2022). One hypothesis put forward is kinetic constraints that might explain that equilibrium is not attained for PFOS and other PFAS with low aqueous solubility. However, this does not explain our observations that once the percolation starts concentration of these compounds increase, since the residence time of water in the soil column will decrease by approximately a factor 3 once the leaching is started. Schaefer et al. (2021) observed the opposite, in soils sampled 22 years after the last PFAS application. Equilibrium was attained for long-chain PFAS and not for short-chain. They proposed a two-domain desorption model including a rapid equilibrium domain and a more persistent kinetically controlled domain. This is an interesting point put forward by the authors, drawing attention to the variation in the site of sorption or retention of PFAS depending on age of the legacy site and pertaining weathering/leaching conditions.

Here we would like to draw the attention to the complex composition of AFFF as a potential factor in the reported observations. PFAS only constitutes approximately 5% of legacy AFFF applied at our study site. In addition, hydrocarbon-based surfactants (20–40%), organic solvents (10–40%) as well as polymers (0–10%) are present as well as salts, buffers, preservatives and other additives (5–10%) (Stevenson, 2012). The exact composition is of a proprietary nature and will vary between supplier. We hypothesize that the non-fluorinated compounds in AFFF influence the leaching behavior of PFAS in source zones.

The solubility of non-polar compounds has previously been shown to

be predictable following Raoult's law (Hildebrand, 1916; Hildebrand, 1919). For complex mixtures like mineral oil products this theory has been successfully applied (Cline et al. 1991; Lane and Loehr 1992). The main observation is that the mole fraction of the compound in the non-aqueous phase mixture determines the aqueous solubility. Changes in composition of the mixture will directly influence the solubility in the aqueous phase, which might result in poorly soluble compounds expressing higher aqueous concentrations than compounds with a higher pure compound solubility. AFFF contains many surfactants with both polar and non-polar properties which might comprise as much as 90% of the mixture composition. Even though we have no proof of the existence of a separate surfactant phase in the source zone, we hypothesize that rapid leaching of some of the bulk constituents might increase the relative molar fraction of PFOS resulting in increased aqueous solubility. This process is illustrated in Fig. 5, showing leaching for a hypothetical ternary system composed of three compounds (5, 5 and 90% by weight) with increasing relative solubility 1, 10 and 2000 mmol/L, respectively. The behavior of compound B shows similarity to the observations for PFOS in this column study for soils A, B and C. Reducing the solubility of the bulk compound C by one order of magnitude will result in continued increase of the solubility of compound B like observed for PFOS in soil D (data not shown). For pesticide formulations the presence of surfactants has been shown to have the potential to both accelerate as well as retard leaching depending on the applied surfactants properties (Hua et al. 2009). Although being readily degradable, these surfactants can persist in the soil environment (Cirelli et al. 2009)

3.3. Apparent PFAS sorption

The eluate concentrations at L/S 0.1 are assumed to represent the theoretical equilibrium concentrations between the solid (soil) and liquid (porewater) phase in the columns since the water has been stagnant in the columns for 3 days. This allows for calculation of an assumed partitioning coefficient between soil and porewater (K_d) (L/kg). The calculated K_d values are presented in Table 2 together with the organic carbon normalized partitioning coefficient ($\log K_{oc}$) (L/kg), using the TOC content determined in the soil samples. PFDeA has the highest K_d values observed in this study ranging from 21 to 184 L/kg, while PFOS has the second highest K_d values in the range of 4.5 to 30 L/kg. The K_d

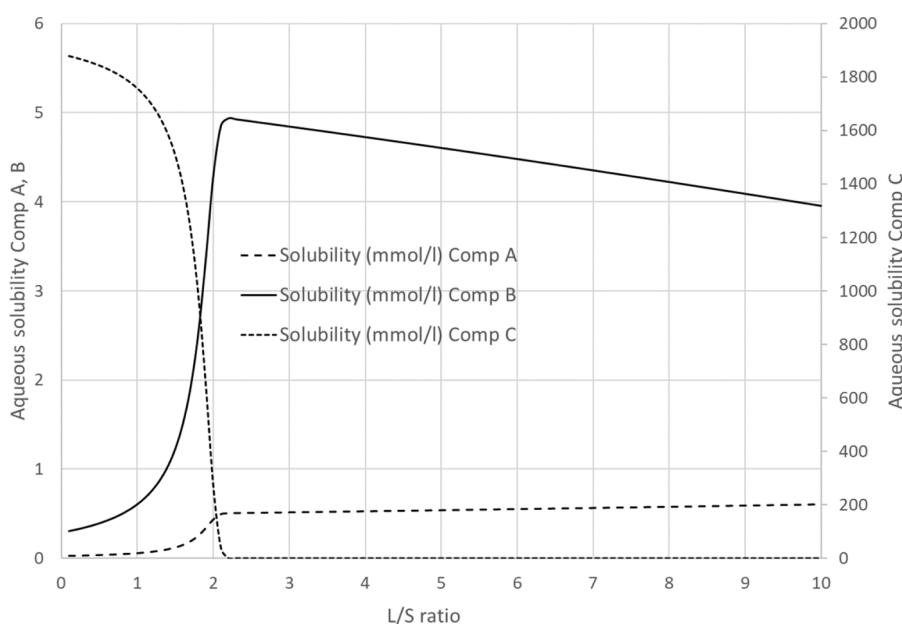


Fig. 5. . Aqueous concentrations in leachate from a hypothetical ternary system composed of three compounds (5%, 5% and 90% by weight) with increasing solubility of 1, 10 and 2000 mmol/L, respectively.

Table 2

Soil water partitioning coefficients Kd (L/kg) at assumed equilibrium at L/S 0.1 and log Koc (L/kg) for the four samples.

Substance	Kd (L/kg)				Log Koc (L/kg)			
	Sample A	Sample B	Sample C	Sample D	Sample A	Sample B	Sample C	Sample D
6:2 FTS	0.92	0.94	2.5	0.69	2.1	2.0	2.2	1.5
8:2 FTS	28	13	-	-	3.6	3.1	-	-
PFBA	0.95	2.3	0.56	0.96	2.1	2.4	1.6	1.7
PFPeA	0.46	0.59	0.33	1.1	1.8	1.8	1.4	1.7
PFHxA	0.40	0.24	0.46	1.0	1.7	1.4	1.5	1.7
PFHpA	0.85	0.3	0.59	0.35	2.1	1.5	1.6	1.2
PFOA	0.38	0.16	0.58	1.2	1.7	1.2	1.6	1.8
PFNA	2.1	2.2	1.8	8.6	2.5	2.3	2.1	2.6
PFDeA	38	21	184	-	3.7	3.3	4.1	-
PFBS	11	7.2	11	1.7	3.2	2.8	2.9	1.9
PFHxS	0.34	0.34	0.51	0.49	1.7	1.5	1.6	1.4
PFOS	9.6	7.9	4.5	30	3.1	2.9	2.5	3.2

value for PFHxS is much lower than both PFOS and PFBS even though PFBS has a shorter chain length than PFHxS. The log Koc values for PFOS found in this study are in the same range as previous published results, (Higgins and Luthy, 2006; Johnson et al., 2007; Milinovic et al., 2015; Ahrens et al., 2011; Kwadijk et al., 2010; Guelfo and Higgins, 2013).

3.4. Estimation of residual PFAS content

The extractable amount of PFAS leached out of the columns is determined using Eq. (1).

$$Mass\ leached = Average\ concentration\ eluate * Volume\ eluate \quad (1)$$

The residual PFOS in each sample was determined by Eq. (2) and shown in Fig. 6 as percent of total amount of PFOS in the original soil.

$$Residual\ PFOS\ in\ soil = Initial\ mass\ PFOS\ in\ soil - PFOS\ mass\ leached \quad (2)$$

The estimated results of residual amounts of other PFAS in the soil at L/S 10 are presented in SI Table S7. Some short-chain PFAS are only detected in small concentrations in the initial soil samples and one would expect complete leaching by L/S 10. However, most of these compounds do not achieve 100% removal which indicates that there could be a residual PFAS fraction in the soil for most PFAS. The results

indicate that at the end of the experiment up to 50% of the PFOS is still left in soil A which has the lowest TOC content. While 35% and 18% PFOS is left in sample B and D with higher TOC content in the soil. However, in sample C, over 100% of the total extractable PFOS was leached out indicating that there is theoretically no PFOS left in the soil. Initial extractable concentrations for the PFAS measured in the soil and the relative amount removed for each sample after L/S 10 as a% of the total extractable soil concentrations are given in Table S8. It can be observed that in sample A there are lower amounts of each PFAS eluted that in the other samples with PFOA and PFNA being eluted in the highest relative amount of 57 and 60%. For the other samples up to 100% is removed for some PFAS. Sample D has a much higher initial soil content of PFHxS than the other samples, indicating a lower historic infiltration at this site. However, the removal efficiency in the column study is 100% for PFHxS in this sample.

3.5. Observed DOC concentrations in the eluates

To explore the observation of variation in the calculated retention of PFAS and especially PFOS between the four soil samples, PFOS concentrations at L/S 2 and 10 are plotted against the DOC concentration in the collected eluates showing no direct correlation (Fig. 7). The DOC concentrations in the eluates at the end of the experiment (L/S 10) are

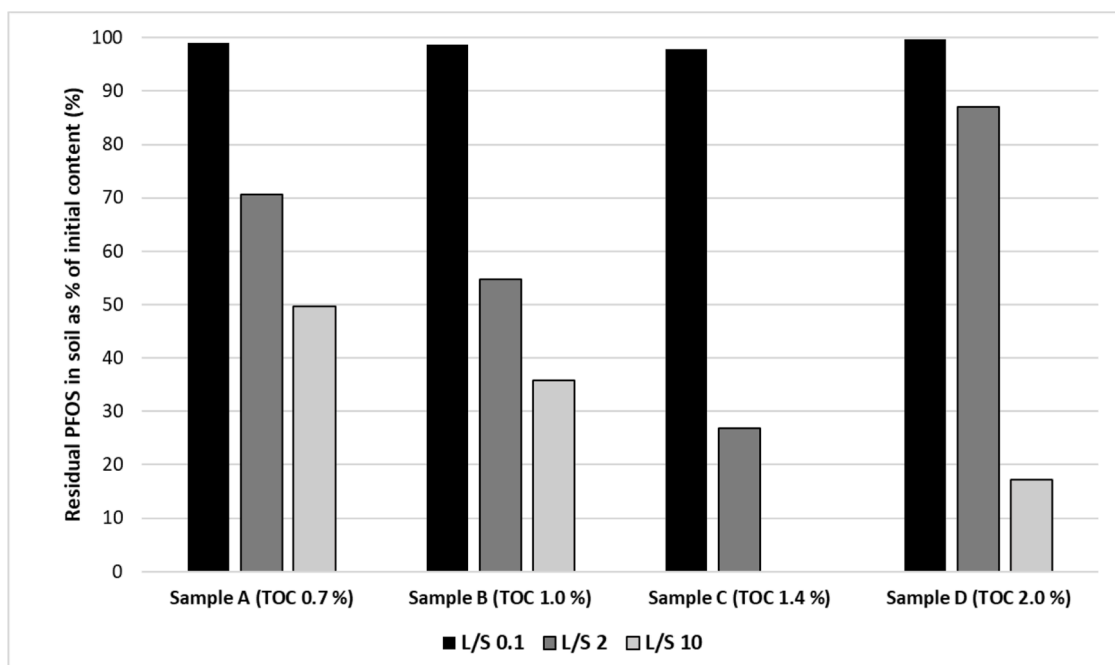


Fig. 6. . Residual PFOS in soil as percent of total amount of PFOS in the original soil.

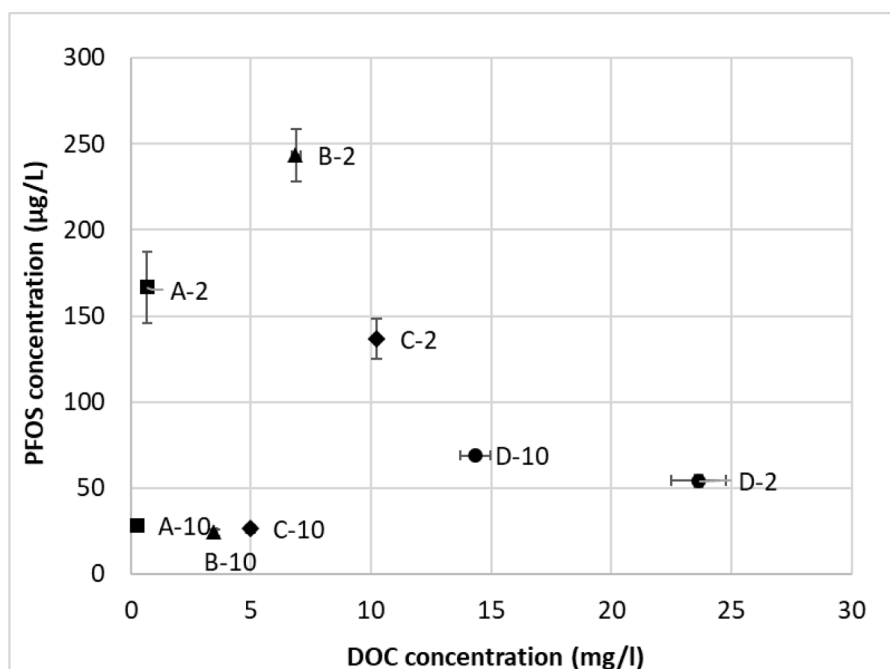


Fig. 7. . Observed PFOS ($\mu\text{g/L}$) and DOC concentration (mg/L) in the eluates.

<0.5 mg/L for sample A and 3.49, 4.98 and 14.33 mg/L, respectively, for samples B, C and D. Soil sample A, with the highest PFOS retention of 50% of total content at L/S 10, has no detectable DOC concentration in the eluates (<0.5 mg/L) while the soil sample C had no PFOS left in the soil. Soil sample D with the highest TOC levels and lowest historic water infiltration has the highest DOC values in the eluate at L/S 10 as well as increased PFOS concentrations.

3.6. Relevance for field scale contamination

The amount of water infiltrated during the column study equals 80 pore volumes, representing approximately 100 years of natural infiltration at the studied field site (Jørgensen and Østmo, 1990). Assuming idealized and homogeneous conditions, as used in our experiment, the fully saturated conditions during the experiment indicate that there might be an average PFOS concentration in the porewater leaching to the underlying groundwater in the range of 54 000 to 243 000 ng/l after 20 years and 24 000 to 69 000 ng/l for several subsequent decades. Even after such a long-time perspective, our data indicate that a residual amount of PFAS, mainly PFOS, will remain in the soil at this source zone area, indicating an urgency to find appropriate remedial measures. The different AFFF application and water infiltration/weathering history at each soil sampling site shows different leaching amounts and rates for different PFAS compounds indicating that the history of AFFF applied at the source zone and the amount and rate of water infiltrated at the site will determine the amount of leaching from the source zone for each PFAS. In a source zone where there has been extensive use of AFFF as well as extensive use of water during fire training, the most water soluble PFAS and DOC in the source zone could have been eluted while less water soluble PFAS like PFOS for instance remains as a residual fraction. This scenario is similar to what we observed in sample A. However, for sample D there has historically not been added water other than natural precipitation, the initial content of PFHxS in soil is higher than in the other samples. It is observed that the DOC level in the eluates is higher throughout the experiment for sample D and the percent PFOS eluted is higher than in sample A and B. It is hypothesized that this can be due to a higher amount of the AFFF related dissolvable organic carbon being present in the initial soil sample. In addition, sample D has a higher TOC level than the other samples. There is an indication that the dissolved

organic carbon (DOC) in the soil water could influence the amount of PFOS being leached from the soil. It is important to note that the amount of DOC in the soil solution at an AFFF site is not limited to the contribution of soil organic matter at the site but also will include the contribution from non-fluorinated compounds present in the complex AFFF mixture in the source zone. Strong historic flushing as seen in sample A in this study, where extensive use of water has been documented, resulted in low DOC levels and a high residual PFAS content, dominated by PFOS.

4. Conclusion

The use of AFFF at the studied FTF has resulted in soil contamination by PFAS dominated by PFOS, however relatively high concentrations of 6:2 FTS, PFHxS and some PFCAs are also found indicating the historic change from PFOS containing AFFF to 6:2 FTS and shorter chain PFAS containing AFFF. The site ceased all use of PFAS containing firefighting foams in 2011. Our results show a clear variation in the leaching behavior of the remaining PFAS at the four sampled sites. Even under fully saturated flow conditions some residual PFOS remained in the soil and result in high concentrations in the eluate for a long period of time given that the amount of water applied is equivalent to 100 years of natural infiltration. Up to 50% of the PFOS remained in some of the sandy soils studied here. The relative leaching potential was not directly correlated to the TOC content of the soils. Despite the fact that the leaching potential is considerably higher under saturated conditions than previously found for a similar soil under unsaturated conditions, leaching cannot be predicted based on pure compound solubility or soil properties measured in this study. The potential contribution of other non-fluorinated compounds in the complex AFFF mixture to the observed retention behavior, hypothesized in this study, warrants further exploration. Our results confirm the risk associated with PFAS in soil as a long-term source of groundwater contamination. Better insight in the retention processes in the vadose zone is essential to achieve a more accurate prediction of leaching rates and improve risk assessment and remediation design at PFAS contaminated sites.

CRedit authorship contribution statement

Åse Høisæter: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Project administration, Funding acquisition. Gijs D. Breedveld: Validation, Writing – review & editing, Supervision.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2022.100222.

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