

Article

Remediation of Per- and Polyfluoroalkyl Substances by Single-Step Foam Fractionation Enhanced Soil Washing: Concentration Profiles and Mass Balance

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Abstract

Per- and polyfluoroalkyl substances (PFASs) include thousands of fluorinated organic compounds of anthropogenic origin. Their extensive use, combined with their high stability, has led to the widespread contamination of water and soil resources. Here, single-step foam fractionation enhanced soil washing was carried out for the remediation of PFAS-contaminated soil. Concentrations of target Perfluoroalkyl Carboxylic Acids (PFCAs) and Perfluoroalkane Sulfonic Acids (PFSA) were monitored in foam and leachate along the duration of the treatment. Among PFCAs, only long-chain compounds peaked in foam at the beginning of the treatment. This was consistent with the increase in the sorption affinity to the air–water interface with chain length. The same behavior was observed also in PFSA by comparing PFHXs, PFHpS and PFOS. The fraction of PFCAs still in the leachate after 40 min of treatment was found to decrease with chain length, with PFSA showing a similar trend. PFAS removal significantly increased with soil particle size, ranging from $48.2 \pm 3.2\%$ (fraction $< 0.063 \mu\text{m}$) to $64.1 \pm 1.9\%$ (fraction $> 2 \text{ mm}$). Final mass balance analyses detail PFAS distribution among soil, leachate, and foam, providing valuable information for the additional treatment required to destroy the PFAS load extracted from the contaminated soil.

Keywords: PFAS; foam fractionation; soil washing; soil remediation

1. Introduction

PFASs are employed in a variety of industrial and consumer products worldwide [1]. These synthetic chemicals consist of a carbon backbone, fluorine atoms and a terminal functional group [2]. PFASs are thermally stable and unreactive due to the strength ($\approx 440\text{--}530 \text{ kJ/mol}$) and shortness ($\approx 1.3\text{--}1.4 \text{ \AA}$) of CF bonds and the electrostatic and steric shielding of the CC bonds by fluorine atoms. The non-fluorinated headgroups are often hydrophilic, while the perfluoro-chain is hydrophobic, conferring several PFAS surfactant-like properties. Differentiation in length, branching, fluorination and headgroup have enabled thousands of different PFAS structures to be developed, giving specificity for several applications, such as waterproofing, foaming agents, non-stick coatings, paper additives, metal plating aids, and many others [3,4].

The extensive use of PFASs, together with the high stability of carbon–fluorine bonds and the low removal attained in wastewater treatment facilities [4], have caused the widespread contamination of water and soil resources [5,6]. According to temporal trend



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studies on water, sediments, birds, fishes, marine mammals and humans, their exposure to PFASs has significantly increased over the last 20–30 years [7]. These fluorinated compounds have been linked to negative health effects like liver damage, hormone subjugation, thyroid illness, decreased fertility, and cancer [3].

The upcoming EU legislation is likely to become more stringent. The parameter “sum of PFAS” (sum of 24 named substances) has been proposed for addition to the Priority Substances list, as well as to Annex I, concerning, respectively, surface water and groundwater quality [8]. Both Perfluoroalkyl carboxylic acids (PFCAs) and Perfluoroalkane sulfonic acids (PFSAs) are included, with associated Relative Potency Factors (RPFs).

The scientific community is putting effort into adapting conventional treatment technologies, as well as into developing and advancing new methods. Concerning PFAS-contaminated soil, prompt remediation is fundamental to tackling the compounds before their spread to water resources. PFAS stabilization into concrete or adsorbents [9,10] offers the opportunity to face the contamination in situ, but PFASs will be released into the environment when the material used for stabilization decays. Chemical oxidation [11] can also be carried out in situ, while the cost of the strong oxidants required needs to be carefully evaluated, as well as the toxicity of the generated by-products, such as ultra-short-chain PFASs (e.g., C₂–C₃) or longer-chain fluorinated compounds. Thermal treatment vaporizes PFASs from soil [12] with associated high energy costs and CO₂ emissions. Microbial degradation and enzymatic treatment emerge as an environmentally friendly alternative, but there is still a myriad of challenges to be faced before realizing bioremediation as an effective tool for PFAS destruction at the environmental scale [13].

Soil washing relies on physical and chemical techniques to enhance PFAS transfer from soil to water [14]. Being the extent of PFAS solubilization based on soil–water partitioning coefficients, the efficiency of the treatment is expected to decrease with an increase in chain length. By providing additional air inflow, and adequate surfactant addition, bubbles can be formed in the solution. Given their amphiphilic nature, most of the PFASs solubilized into water tend to adsorb to the surface of the bubbles, with apolar tails inside the air bubble and polar parts into the water phase [15]. PFAS-enriched foam is formed on top of the water, collected and treated separately. This treatment option can also be applied for the remediation of contaminated soil and referred to as foam-fractionation-enhanced soil washing.

Notwithstanding foam fractionation, which has been studied by several authors in recent years for the removal of PFASs from aqueous streams [16], including the treatment of the leachate resulting from soil washing [17], the direct application of these two treatments—soil washing and foam fractionation—for the remediation of PFAS-contaminated soil has been barely explored. While a recent investigation assessed the potential of foam fractionation by using a pre-extraction reactor to facilitate the contact of gas bubbles with soil particles [18], here a single-step treatment was carried out. The removal efficiency of PFASs with the highest RPFs proposed for regulation in the upcoming EU legislation [8] was related to particle size and assessed on three different soil fractions. Concentrations of target PFCAs and PFSAs were monitored in foam and leachate throughout the treatment. Finally, mass balance analyses between soil, leachate and foam were carried out to evaluate the PFAS distribution, providing valuable information for the further treatment required to treat the PFAS load extracted from the contaminated soil.

2. Materials and Methods

2.1. Soil Sampling

Soil samples were collected at Boden, Sweden, where PFAS contamination was expected due to the extensive use of aqueous film-forming foams (AFFF) during firefighting

training. Approximately 1 m³ of soil was excavated and mixed, and 100 kg was sampled and dried at 45 °C to minimize any PFAS loss. Dried soil was then sieved into three fractions with diameters of >2 mm, between 2 and 0.063 mm, and <0.063 mm, corresponding to rocks and gravel, sand, and silt and clay, respectively, according to the World Reference Base for Soil Resources (WRB) [19].

2.2. Foam Fractionation Enhanced Soil Washing

The original soil texture was reconstituted by mixing the sieved fractions, with the exception of the fraction > 19 mm, corresponding to 1/10 of the diameter of the column, which was excluded from the treatment with the aim of obtaining data representative of the further scale up of the process. Moreover, the vast majority of the total PFAS contamination was expected to be concentrated into finer fractions. Experimental setup is summarized in Figure 1. Foam fractionation tests were conducted in a 50 L plexiglass column (19 cm × 175 cm); the elongated geometry of the column plays a fundamental role in the adsorption of PFASs at the air–liquid interfaces while the air bubbles are rising. Previous research recently compared L:S 4 and L:S 10; only a 14.8% enhancement in PFAS removal was reported, while the amount of liquid to be further treated dramatically increased [18]. Hence, we decided to run the test at L:S 7, i.e., the column was filled with 5.71 kg of soil and 40 L of water, to ensure the continuous collection of foam from the top. Air injection was provided from the bottom of the column at a constant flowrate of 50 L/min, selected on the basis of previous trials showing that this is the minimum air inflow capable of penetrating the bulk of the soil at the chosen L:S.

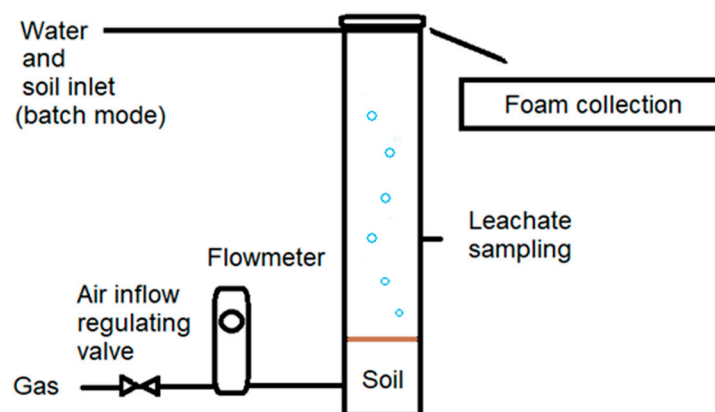


Figure 1. Experimental setup of single-step foam-fractionation-enhanced soil washing.

The soil under investigation had a very large fraction of particles with diameter > 2 mm, which would very likely damage a propeller if used to provide stirring into the mixture. Hence, no mechanical stirring of the mixture was applied during the treatment, to verify if airflow alone would be able to provide satisfactory treatment efficiency. Several amounts of surfactant were preliminary tested, as well as addition timing, in order to ensure constant foaming. Five milliliters of a diluted mixture of ionic (sodium lauryl sulfate), non-ionic (PEG-4 rapeseedamide), and amphoteric (cocamidopropyl betaine) surfactants (pH: 5.5) was selected for addition every ten minutes. Non-ionic and an anionic surfactant may exert a synergistic effect on the micellization process and the adsorption at liquid/air surfaces [20], while amphoteric surfactants contribute to enhancing foaming.

Foam was continuously collected above the liquid air interface. Foam and leachate samples were collected for analysis at min 1, 3, 5, 10, 20, 30, and 40, while the PFAS concentration in water at min 0 was used as the control. At the end of the test, soil was transferred to a clean container and rinsed from residual leachate and foam with water at L:S 1. Both samples of soil and water used for final soil rinsing were taken. Foam samples

were left overnight in open air (room temperature ~ 18 °C) to let bubbles fully collapse prior to analysis, while soil was dried at 45 °C prior to sieving into three fractions, extraction and analysis. The samples of foam, leachate and water used for rinsing the treated soil were diluted, filtered, and analyzed in duplicate. Soil samples were prepared as described in the Section: ‘Soil characterization’ and analyzed in triplicate.

2.3. PFAS Analyses and Data Processing

A schematic diagram of PFAS analysis and quantification is provided in Appendix A.6 (Figure A2).

Several methods were evaluated to determine the PFAS content in soil [21–24]. Methanolic extraction with or without acetic acid was associated with the highest recovery, if compared with methanolic NaOH digestion and ion-pair extraction [21]. Samples of the dried soil were weighed, placed in 15mL PP tubes, and spiked with 50 μ L of 1 μ g/L of PFAS internal standard. Extraction was performed by adding methanol (3:1 *v/w*), vortexing, shaking, sonication (10 min), and centrifugation (4000 rpm, 15 min). The supernatant was then transferred into a new PP tube. Methanol addition and the following steps were conducted three times, increasing the soil–methanol contact time by shaking 10, 20, and 30 min. The total amount of supernatant collected was then evaporated until dryness at 40 °C by a centrifugal vacuum concentrator (Labconco Corporation, Kansas City, MO, USA); then 400 μ L of methanol was added to each PP tube to redissolve PFASs. To achieve this, samples were sonicated for 5 min and gently shaken for ten minutes. Then, 600 μ L of a diluent solution (60:30:10:0.01; water: acetonitrile: methanol: formic acid) was added to the extract, and the resulting mixture was filtered using a hydrophilic non-sterile 0.2 μ m Syringe Filter (Sartorius, Göttingen, Germany) before instrumental analysis.

The PFAS content in the extracts of pure and treated soil was assessed by Ultra-High-Performance Liquid Chromatography–Mass Spectrometry (UPLC-MS/MS), with a Waters Acquity Ultra-performance Liquid chromatograph coupled to a triple quadrupole mass spectrometer XEVO-TQS (Waters corp., Milford, MA, USA) equipped with a 100 mm \times 2.1 mm C18 BEH column. A gradient mobile phase of (A) 2 mM ammonium acetate (95:5, methanol: Milli-Q water) and (B) 2 mM ammonium acetate in MeOH was flowed at 0.30 mL/min. The MS/MS worked in Unispray ionization mode (Waters corp.) and a multiple reaction monitoring mode quantified the PFASs. The Unispray conditions were as follows: 1.0Kv impact voltage, 600 °C desolvation temperature, 1000 L/h desolvation gas flow, 150 L/h cone gas flow, and 130 °C source temperature. Internal calibration using mass-labeled standard was used for quantification.

The target compounds and associated RPFs are listed in Table 1. The aim of this investigation was to focus on the seven Perfluoroalkyl Carboxylic Acids (PFCAs) and the four Perfluoroalkane Sulfonic Acids (PFASs) with RPF > 0.5 included in the EU PFAS-24 group [8].

Table 1. PFASs with RPFs > 0.5 according to the EU-PFAS24 group [8].

PFCAs	Perfluoroalkyl Carboxylic Acids		RPF
PFHpA	Perfluoroheptanoic acid	C ₆ F ₁₃ COOH	0.5
PFOA	Perfluorooctanoic acid	C ₇ F ₁₅ COOH	1
PFNA	Perfluorononanoic acid	C ₈ F ₁₇ COOH	10
PFDeA	Perfluorodecanoic acid	C ₉ F ₁₉ COOH	7
PFUnA	Perfluoroundecanoic acid	C ₁₀ F ₂₁ COOH	4
PFDoA	Perfluorododecanoic Acid	C ₁₁ F ₂₃ COOH	3
PFTrDA	Perfluorotridecanoic acid	C ₁₂ F ₂₅ COOH	1.65

Table 1. *Cont.*

PFSAs	Perfluoroalkane Sulfonic Acids		RPF
PFHxS	Perfluorohexanesulfonic acid	C ₆ F ₁₃ SO ₃ H	0.6
PFHpS	Perfluoroheptanesulfonic acid	C ₇ F ₁₅ SO ₃ H	1.3
PFOS	Perfluorooctanesulfonic acid	C ₈ F ₁₇ SO ₃ H	2
PFDS	Perfluorodecane sulfonic acid	C ₁₀ F ₂₁ SO ₃ H	2

Mass Spectrometry information was acquired and analyzed through MassLynx™ Software V4.2 (Waters™, Milford, MA, USA). Data related to compound identification and quantification were re-processed and adjusted manually when needed. The limit of quantification (LOQ) was defined as the lowest measured standard for which a signal to noise (S/N) ratio > 10 was found (effluents: 4–10 ng/L; soil: 20 ng/kg).

2.4. Chemicals

Analytical native PFAS standards and mass-labeled PFAS internal standards were purchased from Wellington Laboratories. The purity of analytical standards was above 98%. Ammonium acetate (>99%) and LC-grade methanol (99.9%) were purchased from Fluka (Steinheim, Germany) and Fisher Scientific (Leicestershire, UK), respectively. Acetonitrile (>99.9%) was supplied by Fisher Scientific, Hampton, NH, USA). Pure water (Mill-Q) was purchased from Honeywell, Charlotte, NC, USA.

3. Results and Discussion

3.1. Soil Composition and Contamination

Particle size analyses show the coarse fraction accounting for 70.27% of the total soil to be remediated. The remaining 28.54% and 1.19% of the soil particles were included between 2–0.063 μm, and below 0.063 μm, respectively. The main PFAS content of the untreated soil distributed among the three fractions is shown in Figure 2, while the PFAS concentration of each single fraction and related standard deviations are shown in Table A1. All the target compounds have been detected, except for PFTrdA. PFNA and PFDeA have been found at a concentration above the LOQ in the soil fraction < 0.063 mm, and below the LOQ in the two fractions > 0.063 mm. Soil contamination is dominated by PFOS (79.1 ± 0.2 μg/kg), followed by the target PFSAs, PFHpA and PFOA. The fine fraction is the richest in PFASs (410.6 ± 15 μg/kg, compared to 95.7 ± 1.4 μg/kg and 74.2 ± 0.9 μg/kg of fractions between 0.063 and 2 mm and >2 mm, respectively).

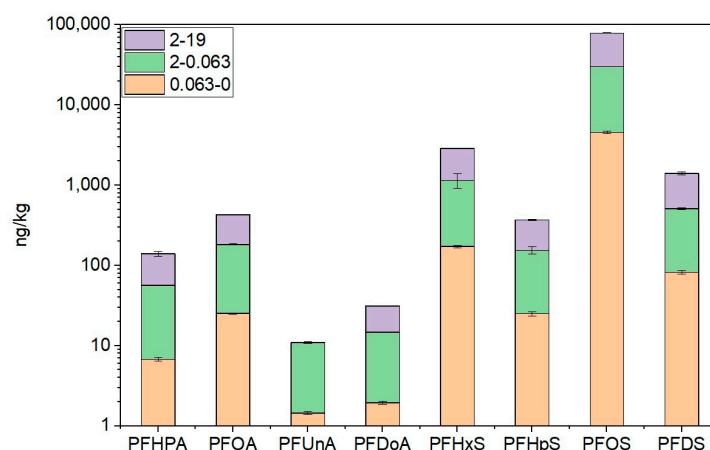


Figure 2. PFAS concentration of each single fraction and related standard deviation are presented in Table A1.

3.2. Concentration Profiles

PFAS-enriched foam continuously formed on top of the water due to repeated surfactant addition and was periodically collected. Being most PFAS amphiphilic, they adsorb to the surface of the air bubbles, with their polar parts remaining in the water phase and their apolar tails inside the air bubble [15]. Profiles of the concentration of PFCAs and PFSA in foam over time are presented in Figure 3. All the PFASs detected above the LOQ in the untreated soil were tracked, except for PFDoA and PFDS, due to peak overlap and noise in the UPLC-MS/MS signal.

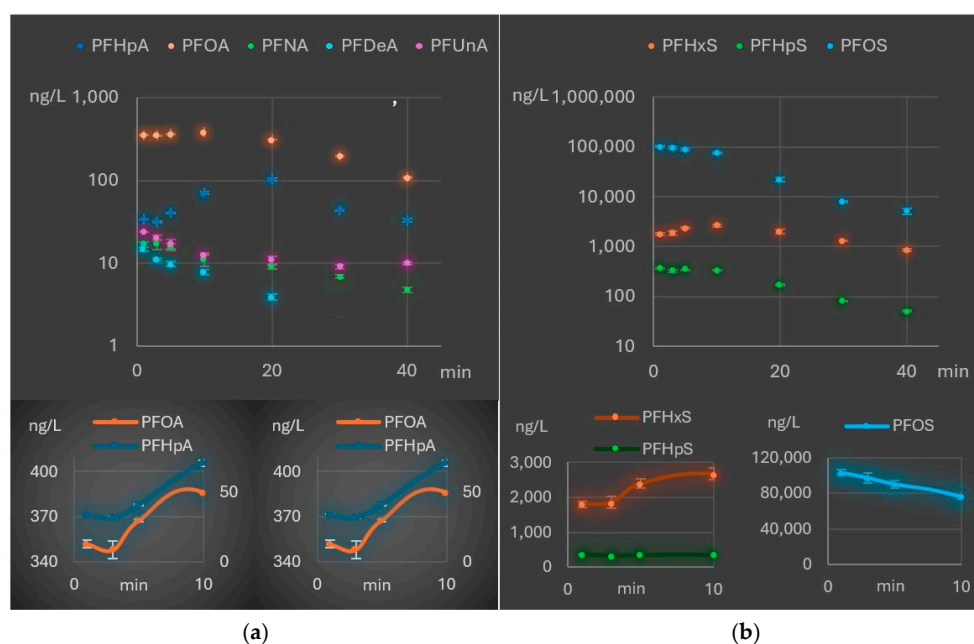


Figure 3. PFAS concentration in foam: PFCAs (a) and PFSA (b). Values provided in Table A2.

The removal of PFAS by foam fractionation is linked to their surface-active properties, related to the hydrophobic fluorinated alkyl moieties and hydrophilic functional groups of their chemical structures. Differences in chemical structures here resulted in different removal behaviors over time. Maximum concentrations of PFHpA and PFOA were observed after 20 and 10 min, respectively, while concentrations of longer chain PFCAs in foam peaked at the beginning of the treatment (Figure 3a). A similar behavior was also observed in PFSA: PFHXs peaked only at minute ten, the concentration of PFHpS was stable in the first ten minutes before decreasing, while PFOS peaked at the beginning of the treatment (Figure 3b). Concentration profiles are in agreement with the increase in the sorption affinity to the air–water interface with the chain length [15], as opposed to the soil–water partition coefficient of these compounds (K_d), which increase with increasing chain length [25–31].

The PFAS concentrations observed in the leachate were significantly lower than those found in foam, confirming the effectiveness of foam fractionation. However, the soil contamination of PFHpA, PFOA, PFHxS, PFHpS, and PFOS was high enough to allow the reliable detection of these compounds along all the duration of the treatment. The results are shown in Figure 4. The concentrations of PFCAs and PFSA over time in the leachate showed profiles analogous to those observed in foam; an increase was observed during the first 10 min, followed by a gradual decrease until the end of the treatment, with the exception of PFHpA, which peaked at min 20.

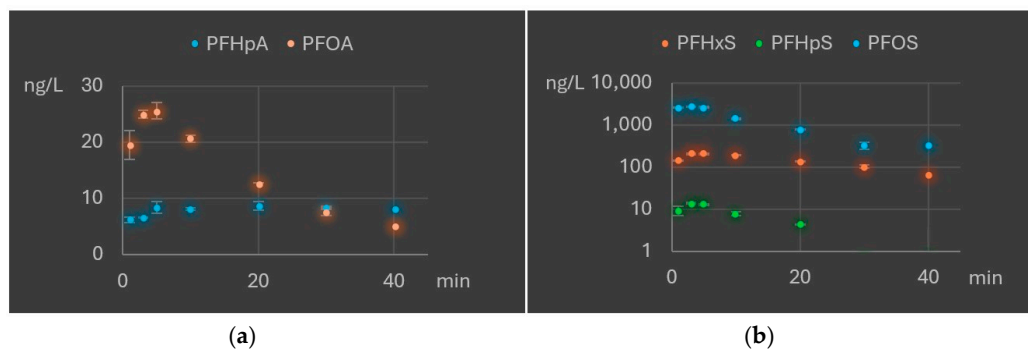


Figure 4. Concentration of detected PFCAs (a) and PFSA (b) in leachate. Values provided in Table A3.

3.3. Removal Efficiency

The removal of PFCAs and PFASs in soil at the end of the treatment (40 min) is presented in Figure 5. No significant differences can be observed among PFCAs and PFSA, or among compounds with different chain lengths. The removal efficiency of previous studies on landfill leachate was found to increase as the carbon number in the alkyl chain of both PFCAs and PFSA increased [32–36]. However, significant differences were observed among C3–C7 PFAS, while this investigation focuses mainly on longer chain compounds. Here, the duration of the treatment may also have allowed compounds with a low sorption affinity to the air–water interface (i.e., PFCAs if compared with PFSA, and short chain PFAS if compared with long chain) to be both captured and removed efficiently.

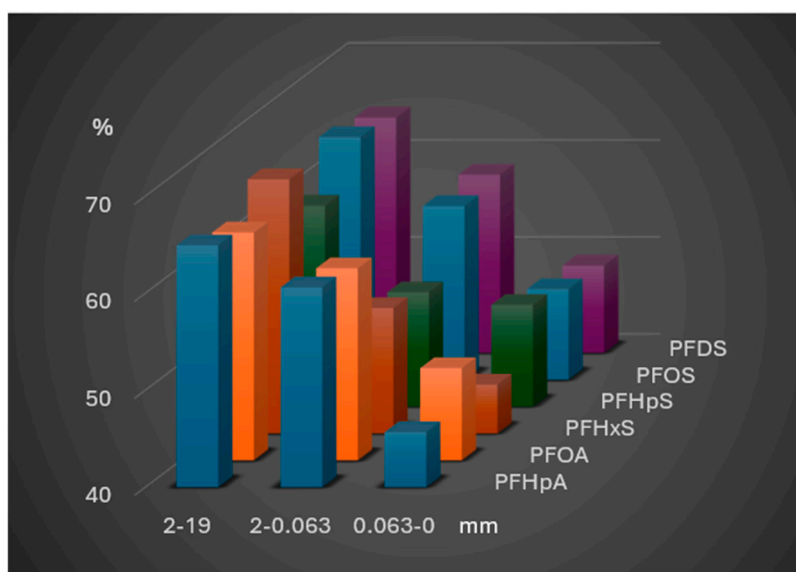


Figure 5. Removal of main PFCAs and PFSA in different soil fractions (<0.063 mm; 2–0.063 mm; >2 mm) at 40 min. Values, including the removal of C9–12 PFCAs, are reported in Table A4.

Concerning the influence of soil texture, the removal efficiency of each compound significantly increased with particle size, ranging from $48.2 \pm 3.2\%$ (fraction < 0.063 μm) to $64.1 \pm 1.9\%$ (fraction > 2 mm, excluding C9–C13 PFCAs which were below LOQ in the treated soil). These results highlight the relevance of sieving and analyzing separate soil fractions in order to avoid a significant overestimation of the treatment efficiency due to the loss of the fine fraction dispersed into the leachate at the end of the treatment. Indeed, the finest fraction was here the richest in PFASs (Figure 2), as well as that with the lowest removal efficiency (Figure 5). Analogous behavior was also recently observed in soil washing trials carried out individually on different soil fractions [17,18].

Our previous 24 h batch test where no bubbling was provided showed ~40% PFOS release from the finest fraction at L/S 10 [17], while here more than 50% removal from the analogue fraction was achieved in 40 min and at L/S 7. In this regard, the equilibrium of PFASs among three phases needs to be discussed. When soil washing is carried out and foam fractionation is later applied to the resulting leachate, the equilibrium between PFASs at the air–water interface and PFASs in solution is continuously displaced by air bubbles leaving the system through the removal of the foam. However, the overall removal efficiency is limited by the equilibrium achieved during the initial soil washing step, which is defined by the soil–water partition coefficient of PFASs. Conversely, by applying foam fractionation directly to the soil, the overall equilibrium of the entire soil–water–air system is continuously displaced, with the resulting enhancement of removal efficiencies.

We here achieved an overall 63% PFOS removal at L/S in 40 min. A preliminary cost–benefit comparison with alternative process layouts may consider at least L/S, time and the eventual addition of chemicals required to achieve a similar target. In our previous investigation on soil washing followed by foam fractionation, approximately the same removal in soil was reached at L/S 4, but this required severe pH adjustment (to reach an initial pH of 11.5), two washing cycles, and 400 min [17]. The removal achieved within this investigation was obtained by a single reactor, without a pre-mixing container or any mechanical devices providing stirring of the soil–water mixture and without any pH adjustment. Enhanced removal is expected by mixing water and soil via pre-extraction, increasing the PFAS in the water phase prior to gas fractionation [18]. Indeed, compared with single-step fractionation, pre-extraction or providing direct mixing into the fractionation column would facilitate the contact of gas bubbles with soil particles, fractionating more PFASs in the water phase to the foam. However, this option is hindered by the expected damage of the propeller when the soil is very rich in coarse fractions (as the soil under investigation), while replacing air with ozonated oxygen may be evaluated when increased removal is required. Indeed, the dissolved gas, being hydrophobic, accumulates to the hydrophobic surfaces (interface between the gas bubbles and water), increasing the affinity of the surfaces to hydrophobic components. Moreover, dissolved gas in water significantly prolongs the lifetime of gas bubbles. Hence, the bubbles formed by gas that has a higher solubility than air would possess interfaces with more affinity to hydrophobic components and a prolonged lifetime, resulting in enhanced PFAS removal [18].

Based on our preliminary test, the scaling up of the technique will require the development of a closed system that allows the continuous collection of the foam to avoid foam collapsing and the re-dissolution of PFASs, while preventing any dispersion in the atmosphere. When optimizing the process by tuning the size of the bubbles injected into the media, the position and the number of injectors may also be considered. Modifying the properties of the added surfactant to increase the affinity to a specific compound may also be a viable option where the compound accounts for the vast majority of the contamination, as applies for PFOSs in the present investigation. The addition of chemical co-surfactants will also be needed to achieve a significant removal of short-chain PFAS ($C < 7$) [16].

3.4. Mass Balance

To the best of our knowledge, mass balance attempts have barely been carried out on foam fractionation processes focused on PFAS removal and only concern the remediation of liquid streams [15]. Here, mass balance analysis shows the distribution of each main PFAS detected in leachate, foam, and the water used for the final rinsing compared with the amount removed from soil (Figure 6). Moreover, the total PFAS mass balance including soil is presented in Figure A1 (Appendix A.5).

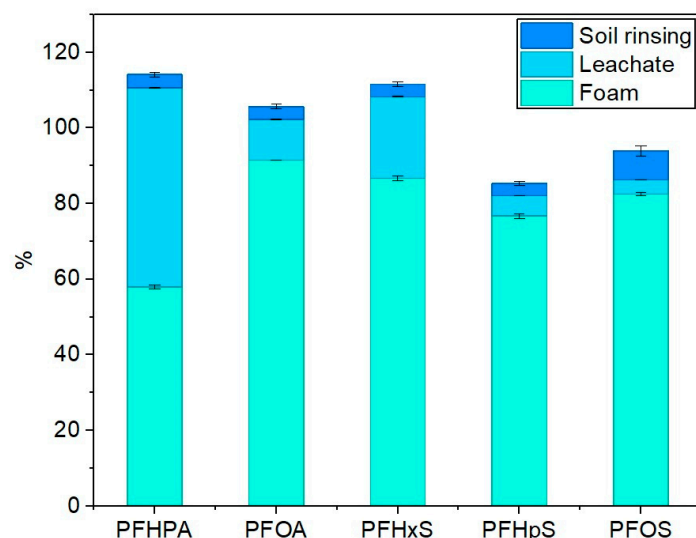


Figure 6. Mass balance. Distribution of main PFAS among leachate, foam, and water used for final soil rinsing. Total amount of PFAS removed from soil accounting for 100%.

According to the sorption affinity to the air–water interface, the fraction of PFCAs still in the leachate after 40 min of treatment decreases with chain length. PFSAs show similar behavior. The same applies if comparing PFHpA and PFOA with PFSAs analogues in terms of chain length.

As can be seen from the standard deviation bars (Figure 6), the failure of mass balance closure cannot be attributed only to measurement uncertainties. The mean mass balance closures were above 100% for PFHpA, PFOA and PFHxS, i.e., the shortest chain compounds among the PFCAs and PFSAs screened here. The excess of short-chain PFASs could possibly be explained by the oxidative transformation of precursors not included in the analyses [15]. Concerning long-chain compounds, low mass balance closures were also observed by Smith et al. during a pilot-scale continuous foam fractionation of landfill leachate [34], and later attributed to sorption to reactor components, as well as to PFAS loss through adsorption to particulate or suspended matter [16]. However, experimental evidence is still needed to support assumptions concerning both mass balance closure >100% for short-chain PFASs and <100% for long-chain analogues. Recently, foam fractionation trials on industrial water confirmed that PFAS volatilize at an appreciable extent during the process; mean Σ PFAS concentrations of 98 ng m^{-3} were measured in the air surrounding the reactor. However, based on the influent concentration of the water during each corresponding run, the highest loss of PFAS recorded in aerosols corresponded to only 0.3% of the entire aqueous Σ PFAS mass treated during the operation of the foam fractionation system (20–60 min, reactor diameter 49.4 cm, water level at 108.5 cm) [15]. Hence, only minor refining of the mass balance is expected by accounting air emissions from the foam fractionation reactor, while appropriate monitoring would be required for the assessment of the operator exposure in fully operational treatment facilities.

3.5. Considerations on Foam and Leachate Management

Several technologies have been tested for the management of PFAS-contaminated streams. Ion exchange resins and adsorption methods have shown the high removal of long-chain PFASs but are less effective for short-chain analogues. Moreover, these techniques need to be coupled with additional treatments to destroy the contaminants removed from the treated media. Reverse osmosis and nanofiltration are also viable options, but pre-treatment to prevent excessive fouling of the membranes is required [37].

Electrochemical oxidation may be a promising technology to treat the foam produced here. It has been proven to be more effective than Fenton-based processes, photochemical oxidation, the addition of hydrogen peroxide, and ozonation [38]. This technique has an extremely low requirement for external chemicals [39], and a minimal amount of waste generation [40]. Boron-doped diamond (BDD) electrodes offer excellent mechanical, chemical, and thermal stability, as well as high electron transfer abilities. A recent pilot-scale study reported ~65% of Σ PFAS degradation in foam fractionate by EO-BDD [41]. Both the obtained rate and percentage of degradation were lower for PFASs compared to PFCAs due to the slower electron transfer from PFASs to BDD than from PFCAs, given the higher electrophilicity and standard reduction potential of a sulfonic group compared to a carboxyl group [42,43]. Our preliminary test on the electrochemical treatment of the foam collapsed after fractionation revealed the fundamental need to avoid re-foaming due to both the electric current and the turbulence applied. Otherwise, contact among PFASs in the foam at the top layer of the reactor and the electrode is not ensured, reducing the efficiency of the treatment. Concerning the leachate collected at the end of the treatment, it may be entirely or partially recirculated, sent to a dedicated treatment, or treated together with the foam, depending on the associated PFAS load. The same applies to the liquid used for rinsing the treated soil.

4. Conclusions

This study presents the application of foam-fractionation-enhanced soil washing for the remediation of PFAS-contaminated soil, focusing on the compounds with the highest relative potency factors among those proposed for the upcoming EU legislation. The treatment was applied as a single step, without the use of a pre-extraction reactor to facilitate the contact of gas bubbles with soil particles. Moreover, the soil under investigation was extremely rich in coarse fractions, demanding the assessment of the process without any mechanical device providing stirring into the soil–water mixture.

According to the sorption affinity to the air–water interface, the highest concentration of shorter chain PFCAs ($C < 9$) in foam was reached after ten minutes of treatment, while the concentrations of long-chain PFCAs in foam peaked at the beginning of the treatment. PFASs showed similar behavior. The removal of all the screened compounds significantly increased with particle size. As observed from mass balance analyses, the remaining fraction of PFCAs and PFASs still in the leachate after 40 min of treatment decreased with chain length. The same applies if comparing PFHpA and PFOA with PFSA analogues in terms of chain length. The process may be further improved by developing surfactants with specific affinity to compounds dominating the contamination (i.e., cationic/anionic/zwitterionic PFAS), as well as by process optimization and tuning the size of the bubbles injected into the media, the position and the number of injectors.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Appendix A.1

Table A1. Average (Av.) PFAS content of the soil to be remediated (ng/kg dw) and related standard deviations.

Soil Fraction (mm)		PFHPA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFHxS	PFHpS	PFOS	PFDS
0.063–0	Av.	569	2116	51	48	121	163	14,467	2104	384,002	6932
	Stdev	25	47	5	4	5	7	456	133	14,409	347
2–0.063	Av.	174	553	<LOQ	<LOQ	33	45	3430	452	89,511	1506
	Stdev	2	11	-	-	1	0	822	55	452	48
2–19	Av.	118	349	<LOQ	<LOQ	<LOQ	23	2473	305	69,677	1277
	Stdev	14	10	-	-	-	0	50	10	714	96

LOQ: 20 ng/kg.

Appendix A.2

Table A2. Concentration profiles, foam (ng/L). Sample name: F, x (minute), A/B.

Sample	PFHPA	PFOA	PFNA	PFDeA	PFUnA	PFHxS	PFHpS	PFOS
F1A	34	354	16	14	24	1865	373	100,746
F1B	34	350	18	16	24	1743	370	105,778
Av	34	352	17	15	24	1804	371	103,262
Stdev	0	3	1	1	0	87	2	3558
F3A	31	344	15	11	22	1977	311	101,388
F3B	32	352	19	12	19	1728	333	93,187
Av	32	348	17	11	20	1852	322	97,287
Stdev	0	6	2	0	2	176	16	5799
F5A	40	368	17	9	19	2295	340	87,201
F5B	41	367	15	10	16	2483	344	93,066
Av	41	368	16	10	17	2389	342	90,134
Stdev	1	1	1	1	2	133	3	4147
F10A	69		10	7	13	2542	341	73,958
F10B	72	386	13	8	13	2783	335	77,570
Av	71	386	11	8	13	2663	338	75,764
Stdev	2		2	1	0	170	4	2554
F20A	100	310	9	4	12	2134	168	20,884
F20B	106	310	10	4	10	1863	174	23,620
Av	103	310	9	4	11	1998	171	22,252
Stdev	4	0	1	0	1	191	5	1935
F30A	44	197	7	<LOQ	9	1358	81	7785
F30B	44	199	7	<LOQ	10	1355	81	8228
Av	44	198	7	-	9	1357	81	8007
Stdev	0	1	0	-	1	3	0	313
F40A	32	107	5	<LOQ	10	819	52	4604
F40B	34	111	5	<LOQ	10	890	50	5655
Av	33	109	5	-	10	854	51	5129
Stdev	1	3	0	-	0	50	2	743
FTotA	39	175	4	4	8	1152	123	30,079
FTotB	35	176	4		9	1068	112	28,725
Av	37	175	4	4	9	1110	118	29,402
Stdev	2	1	0		1	59	8	957

Appendix A.3

Table A3. Concentration profiles, leachate (ng/L). Sample name: L, x (minute), A/B.

Sample	PFHPA	PFOA	PFHxS	PFHpS	PFOS
L1A	6	18	140	8	2598
L1B	7	21	144	11	2649
Av	6	20	142	9	2624
Stdev	0	3	3	2	36
L2A	7	25	213	14	2810
L2B	7	26	202	13	2757
Av	7	25	207	14	2783
Stdev	0	1	8	1	37
L5A	9	27	212	13	2794
L5B	8	25	202	13	2575
Av	8	26	207	13	2685
Stdev	1	1	7	0	155
L10A	9	21	200	7	1345
L10B	7	21	193	8	1496
Av	8	21	197	8	1421
Stdev	1	0	5	1	107
L20A	9	12	139	4	813
L20B	9	13	137	5	757
Av	9	13	138	4	785
Stdev	0	1	1	1	40
L30A	9	8	100	<LOQ	346
L30B	8	8	106	<LOQ	323
Av	8	8	103	-	334
Stdev	1	0	5	-	16
L40A	8	6	73	<LOQ	374
L40B	8	5	61	<LOQ	281
Av	8	5	67	-	328
Stdev	0	1	9	-	66

Appendix A.4

Table A4. Average removal efficiency, soil (%).

Soil Fraction	PFHPA	PFOA	PFNA	PFDeA	PFUnDA	PFDoA	PFHxS	PFHpS	PFOS	PFDS
0.063–0	45.67	49.50	52.72	50.47	48.35	41.89	45.03	50.47	49.32	48.99
2–0.063	60.59	59.78	-	-	*	54.35	52.91	51.77	57.90	58.35
2–19 mm	64.92	63.47	-	-	-	*	66.19	60.69	65.00	64.22

- initial concentration < LOQ * concentration in treated soil < LOQ. LOQ: 20 ng/kg.

Appendix A.5

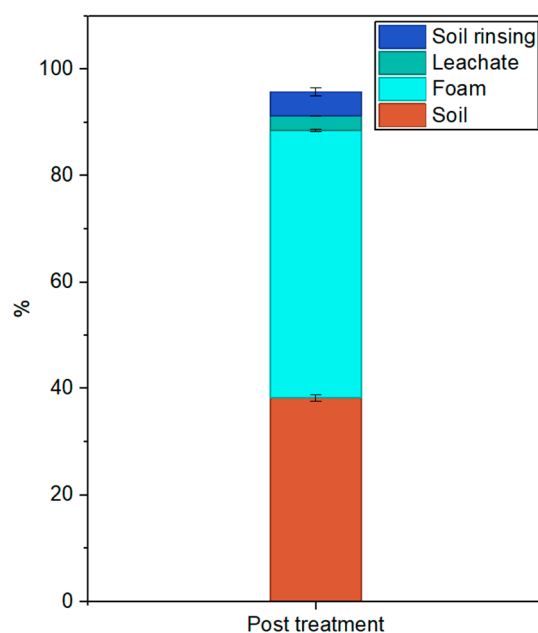


Figure A1. PFAS mass balance post-treatment. Total PFAS distribution among treated soil, leachate, foam, and water used for final soil rinsing. Total PFAS content in the untreated soil accounting for 100%.

Appendix A.6

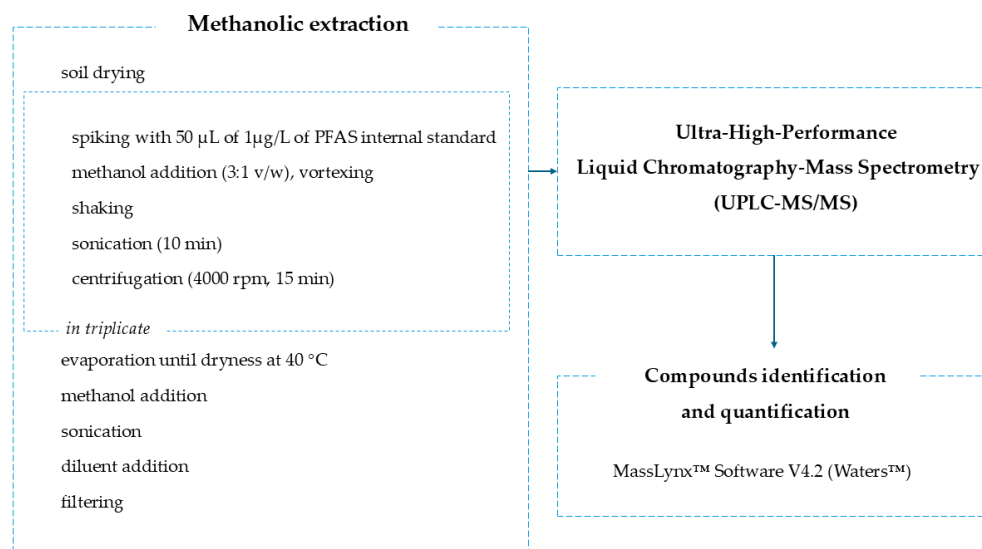


Figure A2. PFAS analysis and quantification: main steps.

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