The Environmental Group Limited
Engineering a Sustainable Future

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Extracting 99% of PFAS from Water & Soil

Research Paper

Engineering a Sustainable Future

PFAS PATENTED SEPARATION TECHNOLOGY WATER AND SOIL

A patent technology that will remove 99% of PFAS from water and soil.

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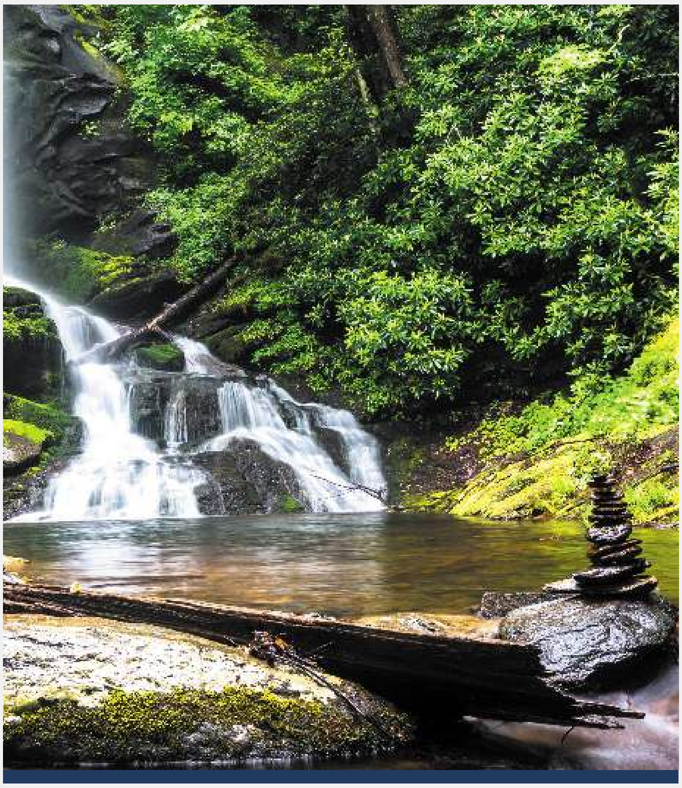


EXPLORE

Our study investigated a gas fractionation enhanced soil washing method for poly-and perfluoroalkyl substances (PFAS) removal from contaminated soil. With the assistance of gas fractionation, PFAS removal was increased by a factor of 9, compared to the conventional soil washing method. Pre-extraction (pre-treatment) of the soil with water before gas fractionation enhanced PFAS removal from soil. The optimum extraction time varied based on the soil particle size, since it will change the swelling time of the soil. The influence of various operational conditions such as water to soil mass ratio (W:S ratio), gas type in fractionation, gas flowrate, fractionation time and soil pre-treatment condition have been studied to identify the critical influencing factors. Among various W:S ratios (2, 4, 5, 6, 8, and 10) studied, higher W:S ratio resulted in better PFAS removals, but PFAS removal began to plateau as the W:S ratio increased. PFAS removal could be improved by repeated treatment with low water consumption. Air, oxygen, and ozone generated by air and oxygen were used, in which ozone generated by oxygen achieved the highest PFAS removals of 55.9%. Among different fractionation times (10 min, 20 min and 30 min), a fractionation time of 20 min achieved better total PFAS removal for studied soil, because PFOS was the dominant species in the total PFAS. However, the removal of some PFAS species, such as PFHxS, would be increased with extended fractionation time. With constant fractionation time (10 min), PFAS removal performance improved with the increasing gas flowrate.

THE EXPERIMENT

PFAS contaminated soil was provided by EGL, Australia. Large particles, such as gravel, in the soil were removed using a plastic sieve (sieve size = 5 × 5 mm, Icon Plastics, Australia). All the sieved wet soil was mixed thoroughly and dried at 105oC for 72 hours in a ventilated oven (Memmert UFB500, Germany), where there should have been no significant loss of the analysed PFAS, and especially regulated PFAS components, based on study from Kim et al. (Kim et al., 2015). The moisture in the sieved soil was calculated by measuring the soil mass prior and after the drying.

The dried and sieved soils were used for characterisations and PFAS removal tests. PFAS in the soil was analysed with LC/MS-MS (EP231X, 28 analytes) by ALS Water, Australia. The pH of soil was measured with a standard method (Thomas, 2018) using a Hach pH meter (HQ11d Portable pH/ORP Meter, Hach, Australia).

The procedures of a standard method (Telliard, 2001) were followed to measure the organic matter of the soil by using a ventilated oven at 105 ^{0}C (Memmert UFB500, Germany) for 24 hours and a muffle furnace at 550 ^{0}C (Vulcan Model 3-550 PD Burn Out Oven, USA) for 2-3 hours.

The soil was classified by a hand sieving method (Smith, 2014)and the size distribution of the soil was measured by a Mastersizer (Mastersizer 3000, Malvern Panalytical Ltd, United Kingdom) instrumental method. The soil texture was determined by jar test.

A Brunauer- Emmett-Teller (BET) instrument (Micrometritics TriStar 3000, USA) was used to measure the specific surface area of soil samples by following a BET theory-based analytical method (Kuila and Prasad, 2013).

To determine the influence of the particle size on PFAS removal, 100 g soil was ground using a pestle and mortar and the size distribution of the ground soil was also measured by a Mastersizer (Mastersizer 3000, Malvern Panalytical Ltd, United Kingdom) instrumental method.

PFAS REMOVAL TESTS
SOIL WASHING

To determine the influence of the particle size on PFAS removal, 100 g soil was ground using a pestle and mortar and the size distribution of the ground soil was also measured by a Mastersizer (Mastersizer 3000, Malvern Panalytical Ltd, United Kingdom) instrumental method.

PFAS REMOVAL BY SOIL WASHING

The soil washing trials were conducted by varying mass ratios of soil to water, extraction times and soil particle sizes. Soil of 100 g was used for each test and the experimental conditions are listed in Table 1.

The soil-water slurry post extraction was filtered by a 0.45 μm filter to remove the free water from soil. The water filtrate and filtered soil were collected separately. The water retained by the soil was estimated by measuring the initial and final water volumes respectively.

Table 1. Extraction conditions of the soil washing tests

Sample	Water: Soil mass ratio	Extraction time
Sieved dry soil	1	20 min
	1.5	
	2	
	2.5	
	2	5 min
		10 min
		20 min
		4 days
Ground soil	2	10 min

PFAS REMOVAL BY GAS FRACTIONATION ENHANCED SOIL WASHING

A schematic of the experimental setup is shown in Figure 1. In each test, 100 g soil sample was premixed/pre-extracted with a set amount of water in a premixing/extraction container for 10 min, and then transferred into a gas fractionation column, where the soil sample was extracted with gas fractionation for a given time. The foam generated from the gas fractionation overflowed into a reject concentrate tank.

After fractionation, the supernatant and soil were separated and filtered through a 0.45 μm filter respectively. The filtrate, the soil that was dried at 105°C for 24 hours and the collected foam were sent to ALS for PFAS analysis.

Fine bubbles were generated from a stainless-steel bubbler with pore size of 0.5 μm. Air and oxygen were supplied from a compressor and a cylinder respectively and were ozonated by an ozone generator (MP-3000, O2Z Inc., USA) to produce ozonated air and ozonated oxygen. The gas flowrate was monitored by a gas flowmeter (MF5706 digital electronic gas flowmeter, Taiwan) and adjusted by both a gas bypass valve and flowrate regulating valve. The tests were conducted at room temperature (25°C) under different operational conditions as shown in Table 2.

Additionally, a double fractionation test was undertaken to explore the PFAS removal performance. The operational conditions are shown in Table 2. It should be noted that for the second-round gas fractionation test, the first-time treated soil was dried at 105 ℃ for 72 hours before it was used again, and the same W:S ratio was applied by using the same freshwater feed.

Table 2. Experimental conditions of the soil gas fractionation tests

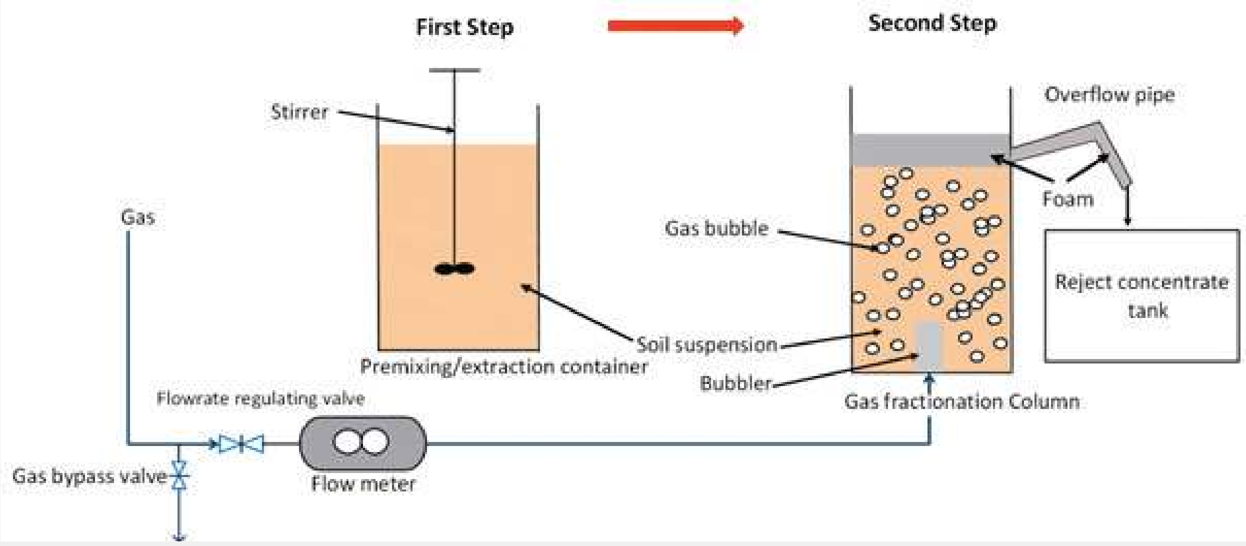
SINGLE GAS FRACTIONATION TESTS

SAMPLE	WATER: SOIL MASS RATIO	EXTRACTION TIME (MIN)	GAS FLOWRATE (L/MIN)	GAS FRACTIONATION TIME (MIN)	GAS TYPE
Sieved dry Soil	2	10	0.2	10	Oxygen
	2	10	0.4 0.6 0.8 1	10	Ozonated oxygen
	4	0 10	0.4	10	Ozonated oxygen
	4 10		1	30	Air Oxygen Ozonated air Ozonated oxygen
	4 5 6 8 10	10	1	30	Ozonated oxygen
	4	10	1	10 20 30	Ozonated oxygen

Double gas fractionation test

Sample	Water: Soil	Extraction mass ratio	Gas flowrate time (min)	Gas fractionation (L/min)	Gas type time (min)
First-time Sieved dry soil	4	10	1	30	Ozonated oxygen
Second-time Dry soil	4	10	1	30	Ozonated oxygen

Figure 1. Experimental setup of the gas fractionation enhanced soil washing



All the experiments were repeated at least three times and mean values were reported. A sample with known PFOS loading was sent with the other testing samples for PFAS analysis to verify the accuracy of the PFAS analysis, which varied in range of ±5% of known values.

RESULTS AND DISCUSSION

CHARACTERISTICS OF THE SOIL

The analysed characteristics of the soil sample are listed in Table 3. It can be found the soil is classified as clay based on its sieving size (Blott and Pye, 2012) and being slightly alkaline. More than 90% of the soil particles were smaller than 103 µm.

As shown in Table 4, there were 23 different types of PFAS detected in the initial dried soil (Australian regulated PFAS contaminants in bold red), for which the concentration of PFOS was 21.95 mg/kg and constituted 90.6% of the total PFAS (24.23 mg/kg).

Table 3. Analysed characteristics of the soil sample

Soil characteristic	Result
Moisture	18 wt%
pH (20 ℃)	7.95
Organic matter	3.69 wt%
Soil texture	Sand 20%, silt 40%, clay 40%
Particle size (µm)	10% ≤ 7.21 µm, 50% ≤45.8 µm, 90% ≤103 µm
Soil classification	Clay
Specific surface area	19.48 m²/g

Table 4. Detected PFAS compounds in the initial dried and sieved soil (error = ±5% based on PFOS standard)

PFAS Compound	**Concentration (mg/kg)**	**Percentage (wt%)**
Perfluorobutane sulfonic acid (PFBS)	0.030	0.13
Perfluoropentane sulfonic acid (PFPeS)	0.046	0.19
Perfluorohexane sulfonic acid (PFHxS)	0.70	2.87
Perfluoroheptane sulfonic acid (PFHpS)	0.078	0.32
Perfluorooctane sulfonic acid (PFOS)	21.95	90.60
Perfluorodecane sulfonic acid (PFDS)	0.34	1.41
Perfluorobutanoic acid (PFBA)	0.056	0.23
Perfluoropentanoic acid (PFPeA)	0.091	0.38
Perfluorohexanoic acid (PFHxA)	0.20	0.81
Perfluoroheptanoic acid (PFHpA)	0.067	0.28
Perfluorooctanoic acid (PFOA)	0.121	0.50
Perfluorononanoic acid (PFNA)	0.022	0.09
Perfluorodecanoic acid (PFDA)	0.029	0.12
Perfluoroundecanoic acid (PFUnDA)	0.032	0.13
Perfluorododecanoic acid (PFDoDA)	0.027	0.11
Perfluorotridecanoic acid (PFTrDA)	0.091	0.38
Perfluorotetradecanoic acid (PFTeDA)	0.0062	0.03
Perfluorooctane sulfonamide (FOSA)	0.21	0.86
N-Methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA)	0.0112	0.05
N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA)	0.0046	0.02
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	0.026	0.11
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	0.18	0.75
10:2 Fluorotelomer sulfonic acid (10:2 FTS)	0.0060	0.02
Total PFAS	**24.23**	**100**

SOIL WASHING

INFLUENCE OF WATER TO SOIL MASS RATIO (W:S RATIO) ON PFAS REMOVAL

The influence of water to soil mass ratio on PFAS removal is shown in Figure 2. As shown in Figure 2a, except for PFOA, all PFAS concentration in the water phase increased initially when more water was added. For the regulated PFAS compounds, more water was required to reach the maximum concentration in the water, as the solubilities of PFAS becomes lower (PFOS<PFHxS<PFOA) as shown in Table 5. This phenomenon could be due to the combination of insufficient mixing and the short extraction time. The extraction rate is determined by both the solubility (driving force) and agitation (Freudig et al., 1999). When less water is added to the soil, the viscosity of the slurry increases and will supress the agitation (Fradette et al., 2007), which will reduce the extraction rate. For substances with lower solubility, a longer time is required to reach an equilibrium state at higher viscosity. Since the partition coefficient (Kd) between the soil and water is constant under the equilibrium state (Franco and Trapp, 2008; Seth et al., 1999), when more water is added, both concentrations in the water and soil phases will decrease based on Equation (1). Hence, based on Figure 2a, it can be estimated that to reach the equilibrium state in 20 min, the W:S ratios for PFOA, PFHxS and PFOS are respectively 1, 1.5 and 2, where their highest concentrations in water phase are reached.

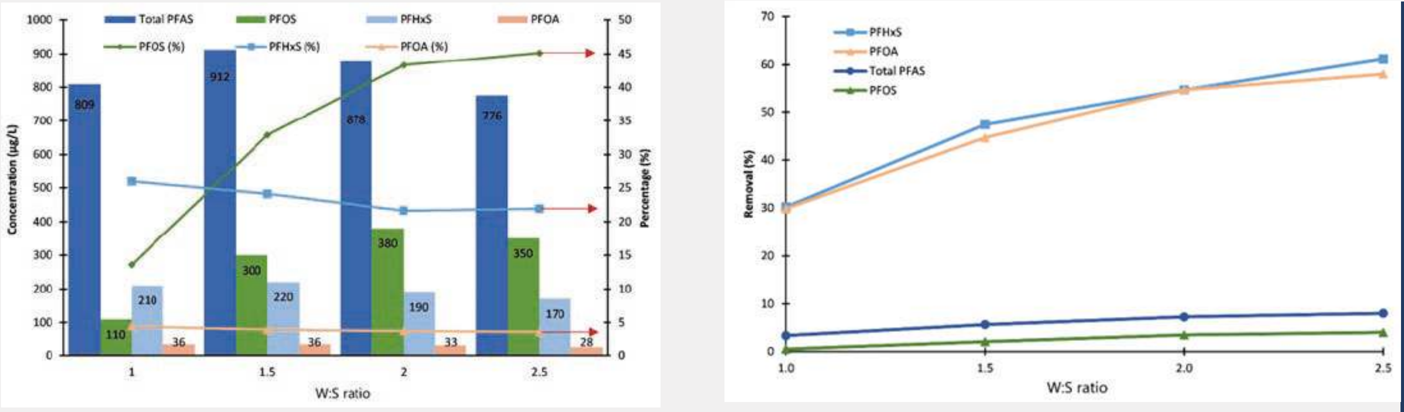
$$K_d = \frac{C_{soil}}{C_{water}}$$

where Csoil and Cwater are the concentrations of substances in the soil and water respectively.

Although PFOS constituted 90% of the total PFAS in the soil, it only composed of 14 - 45% of the total PFOS in the water phase. Hence, PFOS demonstrates a higher affinity to soil compared to other PFAS species. From Figure 2b, it can be found that all the PFAS removal increased as more water was added into the soil. The maximum removal of total PFAS, PFOS, PFHxS and PFOA were 8.0%, 4.0%, 61.1% and 58.0% respectively at the highest W:S ratio of 2.5. However, the trend plateaued at the W:S ratio of 2, which could be considered as the optimum W:S ratio in the following soil washing tests.

The low removal efficiency of PFOS could be attributed to the highest organic carbon-water partitioning coefficient (log(KOC)) value in Table 5, since all the regulated PFAS should have been extracted into the water phase based on their solubility at the lowest W:S. Organic matter tends to be hydrophobic (Capriel, 1997) and are generally considered as the main active components for promotion of sorption of PFAS onto soils (Li et al., 2019; Sima and Jaffé, 2021). The Log(KOC) of PFOS, PFHxS and PFOA are 2.57, 2.4 and 2.06 respectively, which suggests the bonding forces of the regulated PFAS to the hydrophobic organic matter in the soil are in the order of PFOS>PFHxS>PFOA. Hence, the percentage of PFAS comprised of dissolved PFOS in the water phase (≤45.2%) was much lower than that in the dry raw soil phase (90%), due to its greater affinity to organic matter compared to other PFAS compounds.

Figure 2. Influence of mass ratio of water to soil (W:S) on PFAS removal from soil (extraction time = 20 min, error = ± 5%)


a. Total PFAS and regulated PFAS in water phase

b. Total PFAS and regulated PFAS removal from soil

DATA

Table 5. Properties of PFOS, PFOA and PFHxS (Mahinroosta and Senevirathna, 2020)

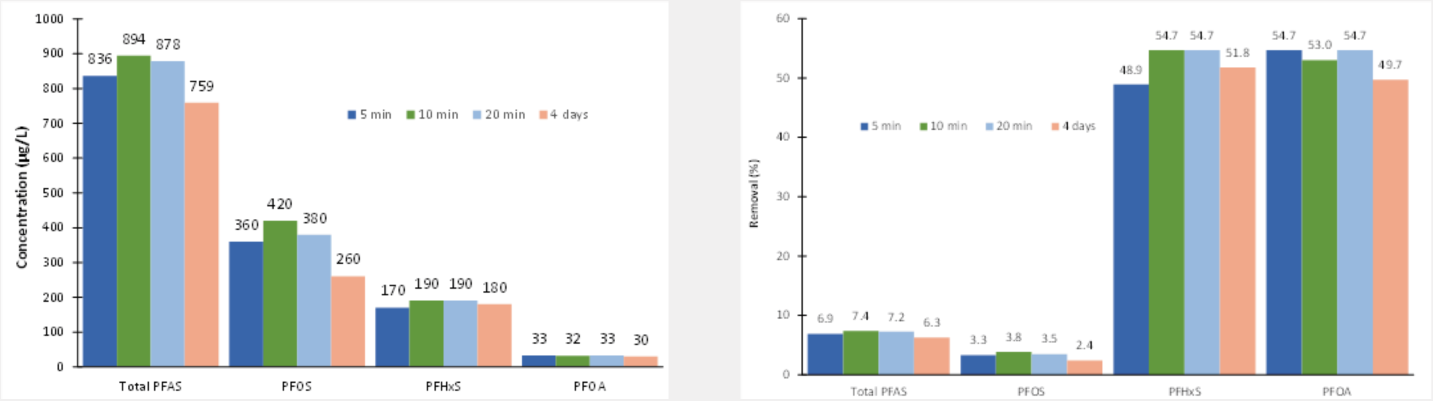
Property	**PFOS (Potassium Salt)**	**PFOA (Free Acid)**	**PFHxS**
Molecular weight (g/mol)	538.23	414.07	400.11
Water solubility (25 ℃) (mg/L)	550-570 (pure water)	9500 (pure water)	1400
Organic carbon-water partition coefficient (Log (KOC))	2.57	2.06	2.4

Note: Log(KOC) is one of the most important parameters describing partitioning of chemicals in soil/water system and measuring their relative potential mobility in soils (Jagiello et al., 2014). PFOS potassium salt is used as an approximate approach based on the soil pH.

INFLUENCE OF EXTRACTION TIME ON PFAS REMOVAL

Figure 3 shows the influence of extraction time on PFAS removal from soil based on the optimum W:S ratio of 2. It can be observed in Figure 3a that except for PFOA, which reaches the maximum concentration in 5 min, all studied PFAS reached their maximum concentrations in the water phase in 10 min. In comparison with the maximum concentration in the water phase, the concentrations of all PFAS declined more than 5% (error =±5%) after an extraction for 4 days, in which the concentration of PFOS in the water phase had the most significant reduction of 38%.

Figure 3. Influence of extraction time on PFAS removal from soil (W:S mass ratio= 2, error = ±5%)



a. Total PFAS and regulated PFAS in water phase

b. Total PFAS and regulated PFAS removal from soil

The fluctuation of PFAS in the water phase with time could be attributed to the property change of clay in the water. It is well known that dry clay will swell in the water and reach a new equilibrium within a certain time, during which its adsorption of anions and cations will vary (Tertre et al., 2021). Diffusion of anions (PFAS) from the bulk solution toward the region of low anion concentration near the soil surface are retarded by the electrostatic repulsion from the negatively charged surfaces (Laird, 2006). However, clay swelling may allow anions to enter the interlayer of clay and increase anion adsorption (Frenkel et al., 1992; Laird, 2006). Hence, as the clay gradually swells, the PFAS in the solution were adsorbed back into the clay, which led to a lower PFAS concentration in the water phase for a longer extraction time.

The influence of extraction time on PFAS removal from soil presented a similar trend to that of the PFAS concentration in the water phase, as shown in Figure 3b. The maximum removals of total PFAS, PFOS, PFHxS and PFOA were respectively 7.4%, 3.8%, 54.7% and 54.7%. Since 90% of the total PFAS are PFOS in the tested soil, 10 min is considered as the optimum extraction time for PFAS removal by soil washing, where both maximum removals of the total PFAS and PFOS were achieved.

INFLUENCE OF SOIL PARTICLE SIZE ON PFAS REMOVAL

PFAS removal from ground soil and the decline of the removal compared to unground soil are shown in Figure 4. The particle size of the ground soil was analysed and reduced as: 10% ≤ 5.8 μm, 50% ≤33.5 μm, 90% ≤75.4 μm (compared to the unground soil particle size shown in Table 3). Previous studies indicated that mortar and pestle grinding reduces the particle size of the soil and increases the number of particles (Hodson et al., 1997; Walsh and Walsh, 2011). It was hypothesised that soil grinding would enhance the extraction of PFAS from soil by making finer soil particles with greater specific surface areas, and reduce extraction length associated with PFAS adsorbed within internal pores. However, it can be seen from Figure 4 that the removal of total PFAS, PFOS, PFHxS and PFOA declined by 17.5%, 35.7%, 10.5% and 18.8%, respectively, with finer soil particles, which had also been observed in a previous study (Sarsby, 2013). The removal declines are closely related to the PFAS removal efficiency whereby the higher the removal efficiency, the lower were the declines in PFAS removal with diminishing particle size. This phenomenon demonstrates that the particle size of the soil and the specific surface area of the soil particles could affect the PFAS removal.

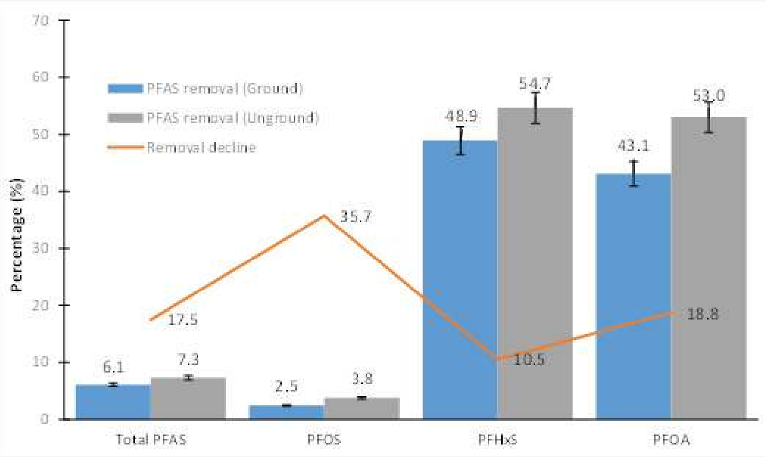


Figure 4. PFAS removal efficiency of ground and unground soil and removal decline compared to unground soil (W:S ratio=2, extraction time = 10 min)

Grinding soil to finer particles would have accelerated the clay swelling rate due to increased surface area (Katti and Katti, 2001), and shortened the optimum extraction time. Hence, the optimum extraction time would vary based on clay particle sizes, which will change the swelling time of the soil.

GAS FRACTIONATION ENHANCED SOIL WASHING

SOIL WASHING

Comparison of PFAS removal by gas fractionation enhanced soil washing to conventional soil washing

Oxygen fractionation for 10 min was conducted after the water extraction under the optimum conditions (W:S = 2, extraction time = 10 min). Table 6 shows the PFAS concentrations in the soil treated by oxygen enhanced gas fractionation. It can be found that the percentage of PFOS in the total PFAS of the treated soil (91.6%) was similar to that (90.6%) in the total PFAS of the raw soil (Table 4). Hence, compared to solely soil washing, gas fractionation dramatically boosted the PFOS diffusion from the soil phase to the water phase. Since the PFOA concentration was low in the soil sample and under the detection and regulation limits after the treatment, it is not reported in the following gas fractionation enhanced tests.

Table 6. PFAS in soil treated by oxygen fractionation enhanced soil washing (Fractionation time = 10 min)

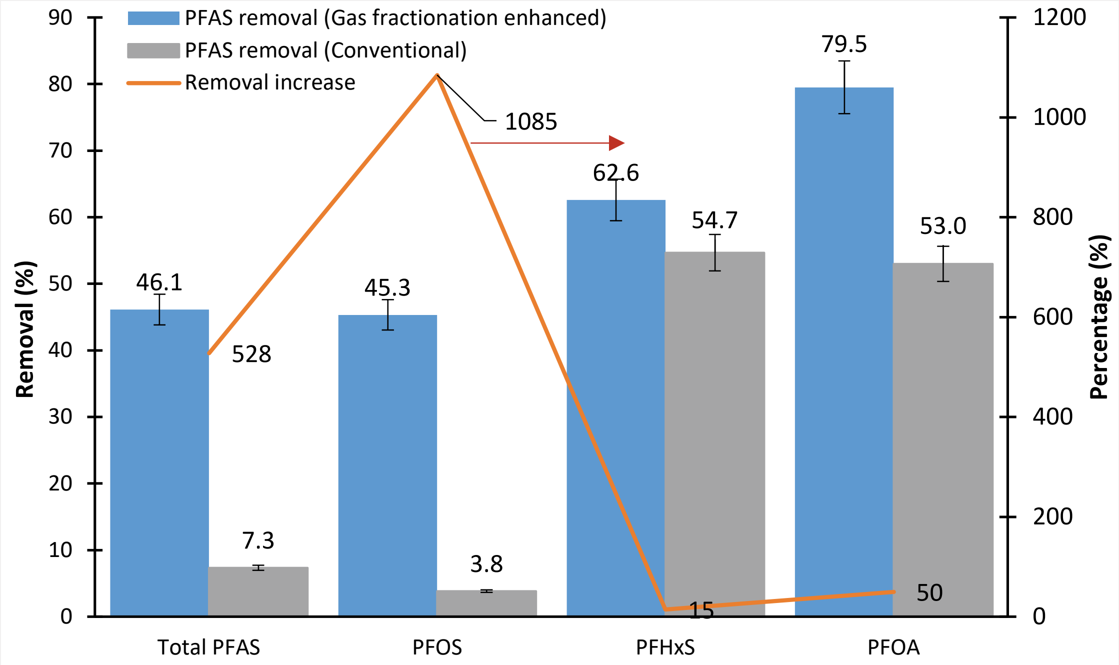
PFAS compound	PFAS in soil (mg/kg)	Percentage (%)
PFOS	12	91.6
PFHxS	0.3	2.2
PFOA	0.002*	0.02
Total PFAS	13.1	100

* estimated by mass balance from the PFOA in the water phase, since the concentration of PFOA was lower the detection limit

It can be observed in Figure 5 that the PFAS removal efficiency by gas fractionation enhanced soil washing was higher compared to conventional soil washing. It can be seen that the removal of total PFAS, PFOS, PFHxS and PFOA were respectively 46.1%, 45.3%, 62.6% and 79.5%, and increased by 528%, 1085%, 15% and 50% in comparison with conventional soil washing.

Since the soil was premixed with water, it was assumed the soil particles were surrounded by water molecules. Hence, firstly the PFAS will transfer from the soil to the water phase. When gas bubbles are introduced into the system, the dissolved PFAS will concentrate at the gas-liquid interface and fractionate into the foam above the water (Dai et al., 2019). Therefore, the PFAS concentration in the liquid phase will be lower than the water washing without gas fractionation enhancement, which encourages more PFAS transferring from the soil to the water phase and fractionating into the foam. The continuing PFAS removal from the water phase into the foam by the gas bubbles will maintain a higher driving force for PFAS transferring from the soil to the water phase than that of solely water washing treatment, thus achieving a higher PFAS removal efficiency than that of solely water washing treatment.

Figure 5. PFAS removal efficiency by gas fractionation enhanced soil washing tests and comparison to conventional soil washing (W:S mass ratio = 2, extraction time = 10 min, oxygen flowrate = 0.2 L/min, fractionation time = 10 min in gas fractionation enhanced test, error = ±5%)



GAS FRACTIONATION ENHANCED SOIL WASHING

SOIL WASHING

Influence of fractionation conditions on PFAS removal from soil

Pre-extraction with water

The influence of pre-extraction (10 min) on removals of total PFAS, PFOS and PFHxS are shown in Figure 6. With premixing the soil with water for 10 min (extraction), the concentration of total PFAS, PFOS and PFHxS in the treated soil reduced from 13.8, 12.0 and 0.23 mg/kg to 12.7, 11.0 and 0.16 mg/kg respectively, and the removal increased from 43.2%, 45.3% and 66.9% to 47.6%, 49.9% and 77.0%, respectively.

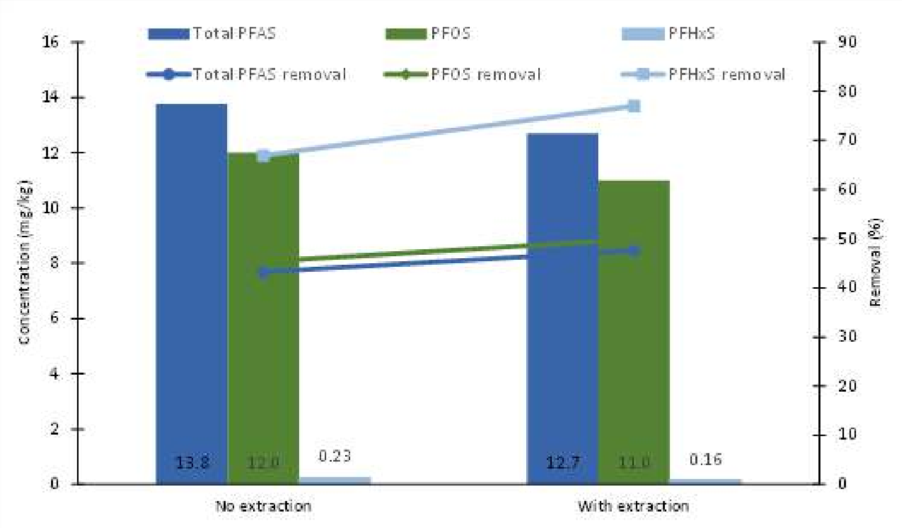


Figure 6. PFAS concentration in the treated soil and removal efficiency from soil varies pre-extraction (W:S = 4, ozonated oxygen flowrate = 0.4 L/min, fractionation time = 10 min, [PFOA] in treated soil < 0.02 mg/kg, error = ±5%)

The improved removal efficiencies can be attributed to the better mixing between water and soil via pre-extraction, which reduced the initial PFAS concentration in the soil and increased the PFAS in the water phase prior to gas fractionation. Compared with direct fractionation without pre-extraction, the pre-extraction facilitated the contact of gas bubbles with soil particles and fractionated more PFAS in water phase to the foam. As a result, PFAS removal improved with soil extraction.

Gas type

It has been demonstrated in previous work (Dai et al., 2019) that PFAS removal efficiency of gas fractionation varied with different types of gases employed in the treatment of PFAS contaminated water. It was suggested that the PFAS removal efficiency from soil could also vary when different types of gases are used for the gas fractionation enhancement. From Figure 7 it can be observed that using ozonated oxygen achieved the highest removals of PFHxS (72.9%), PFOS (58.1%) and total PFAS (55.9%) when compared with other gases (air, oxygen and ozonated air) for fractionation. It can be also seen that the removal of all PFAS increased as oxidation potential and solubility of the gas increased.

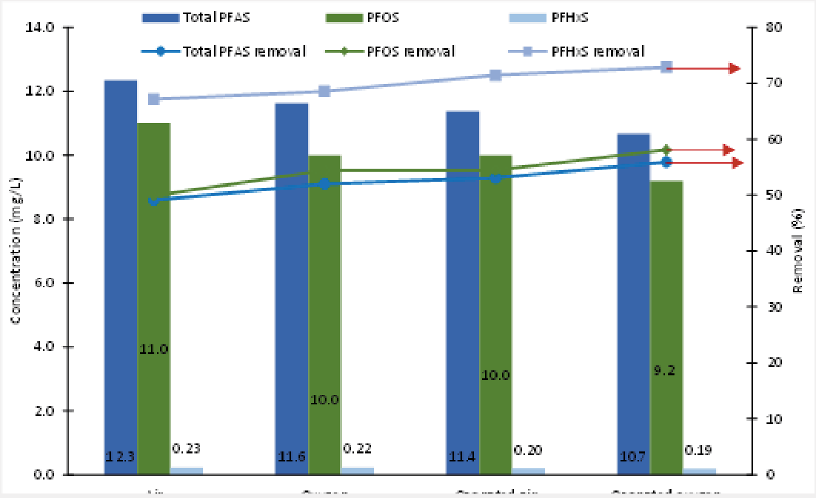


Figure 7. PFAS concentration in the treated soil and removal efficiency from soil varies with gas used in the fractionation (W:S = 4, extraction time = 10 min, gas flowrate = 1.0 L/min, fractionation time = 30 min, [PFOA] in treated soil < 0.02 mg/kg, error = ±5%)

The dissolved gas being hydrophobic acts as a molecular impurity in the water, and it will accumulate to the hydrophobic surfaces (interface between the gas bubbles and water) (Wennerström, 2003) and make the surface more affinity to hydrophobic components. Furthermore, it is reported that the presence of dissolved gas in water can significantly prolong the lifetime of gas bubbles (Wennerström, 2003). Hence, the bubbles formed by gas that has higher solubility would possess interfaces with more affinity to hydrophobic components, and a prolonged lifetime.

The order of the solubilities of the tested gases under testing conditions (25°C, 1 atm) are ozonated oxygen > ozonated air ≈ oxygen > air (Clever and Battino, 2003; Rischbieter et al., 2000). Therefore, the sequence of gas bubble interfaces affinity to hydrophobic components should be ozonated oxygen > ozonated air ≈ oxygen > air. From Figure 7, it can be found that the removal of PFOS and PFHxS also increased greater than that of the total PFAS as the solubility of the gas becomes greater, due to their greater more hydrophobicity (Park et al., 2020) and tendency to attach on more hydrophobic interfaces of the gas bubbles. Furthermore, high oxidation potential could also remove PFAS (mainly short-chain PFAS) by destruction (Dai et al., 2019). Both the oxidation potential and solubility of ozonated oxygen (at 25 °C) were the highest among all gases used, so it resulted in the highest capability of reducing PFAS concentration in the water and enhancing PFAS diffusion from soil to the water phase.

GAS FRACTIONATION ENHANCED SOIL WASHING

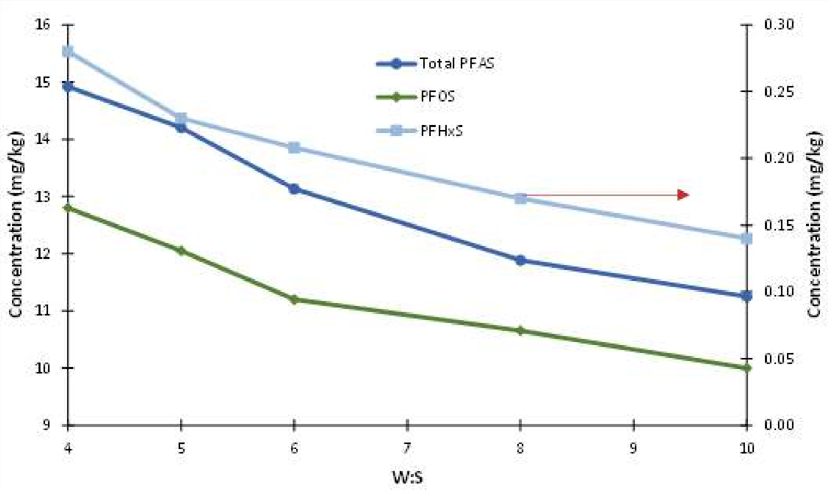
SOIL WASHING

Influence of fractionation conditions on PFAS removal from soil

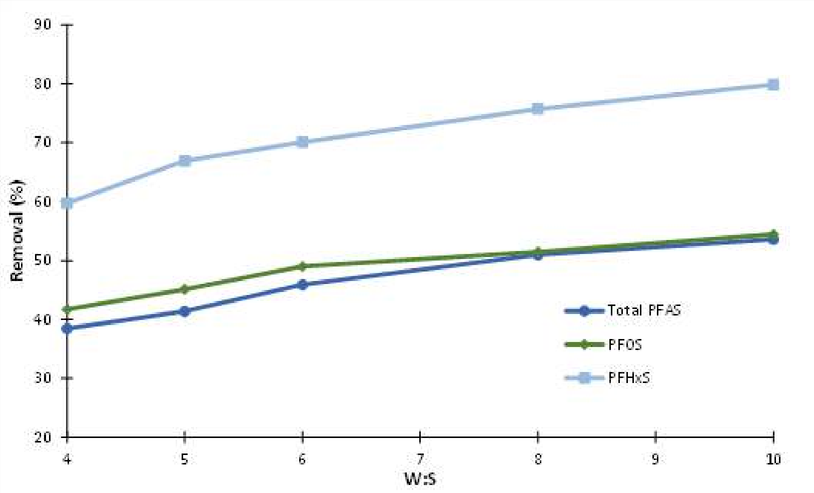
WATER TO SOIL MASS RATIO (W:S RATIO)

The influence of W:S mass ratio on PFAS removal is shown in Figure 8. It can be found that a greater PFAS removal was achieved with an increase of W:S ratio. However, the rate of increase of the PFAS removal slightly plateaued when the W:S ratio continued to increase. Specifically, the PFAS removal increased around 10% when W:S ratio increased from 4 to 6, but the PFAS removal increased ≤10% when W:S ratio increased from 6 to 10. The lowest concentrations of total PFAS, PFOS and PFHxS in the treated soil were 11.3, 10 and 0.14 mg/kg, respectively (Figure 8a), and the maximum removal of total PFAS, PFOS and PFHxS as shown in Figure 8b were respectively 53.6%, 54.4% and 79.9% when the W:S ratio was 10.

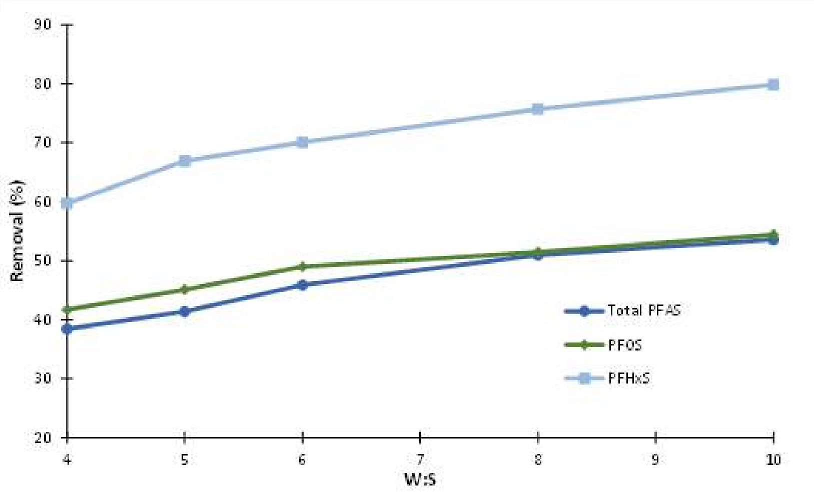
Figure 8. Influence of water to soil mass ratio (W:S ratio) on PFAS removal (extraction time=10 min, ozonated oxygen flowrate = 1.0 L/min, gas fractionation = 30 min, [PFOA] in treated soil < 0.02 mg/L, error = ±5%)



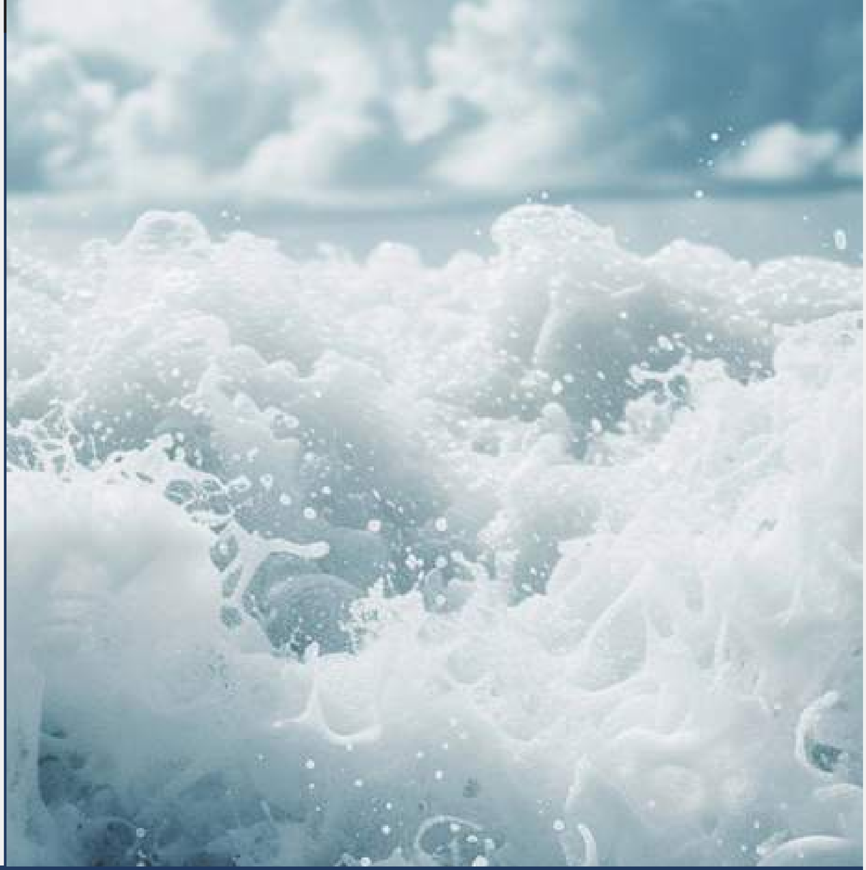
a. Concentration of total PFAS and regulated PFAS in the treated soil



b. Removal efficiency of total PFAS and regulated PFAS

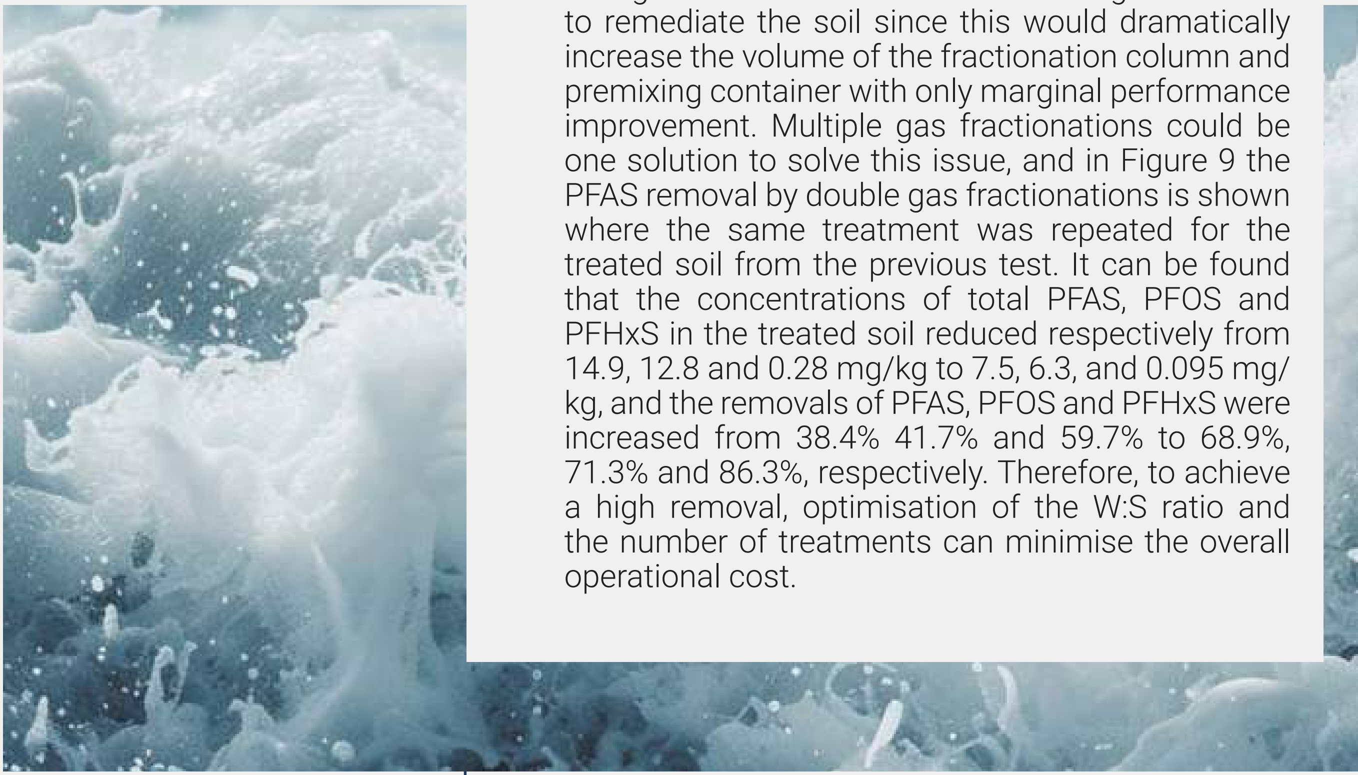


c. Total PFAS concentration in the water phase



SOIL WASHING

The increase of PFAS removal is due to the dilution effect of PFAS in the water phase where the total PFAS removal is the sum of PFAS in the water phase and in the foam. Increasing the W:S ratio as shown in Figure 8c, increases the mass transfer driving force from soil to water based on Equation (1). However, it can be found that the total PFAS removal only increased from 38.8% to 53.6%, when the water volume increased from 4 to 10. Hence, it might not be beneficial to use a high W:S ratio to remediate the soil since this would dramatically increase the volume of the fractionation column and premixing container with only marginal performance improvement. Multiple gas fractionations could be one solution to solve this issue, and in Figure 9 the PFAS removal by double gas fractionations is shown where the same treatment was repeated for the treated soil from the previous test. It can be found that the concentrations of total PFAS, PFOS and PFHxS in the treated soil reduced respectively from 14.9, 12.8 and 0.28 mg/kg to 7.5, 6.3, and 0.095 mg/kg, and the removals of PFAS, PFOS and PFHxS were increased from 38.4% 41.7% and 59.7% to 68.9%, 71.3% and 86.3%, respectively. Therefore, to achieve a high removal, optimisation of the W:S ratio and the number of treatments can minimise the overall operational cost.



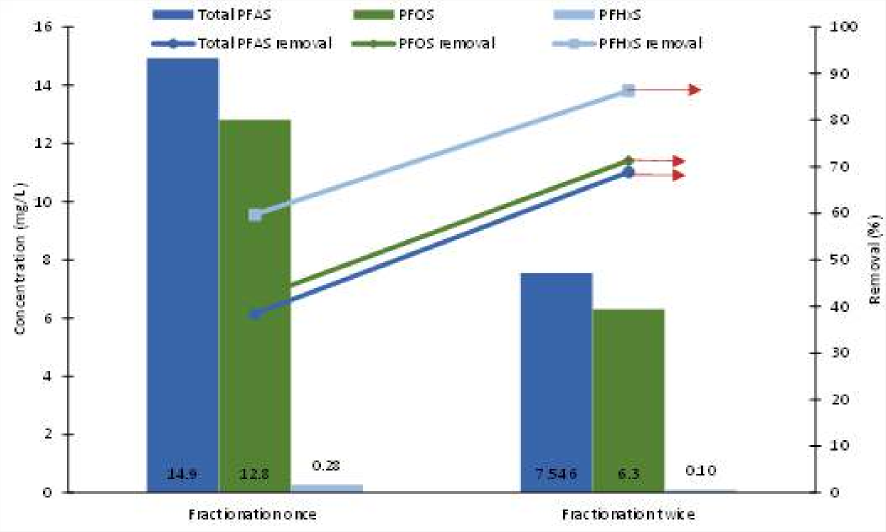


Figure 9. Comparison of PFAS removal from soil by single gas fractionation to double gas fractionation (W:S = 4, extraction time = 10 min, ozonated oxygen flowrate = 1.0 L/min, fractionation time = 30 min, [PFOA] in treated soil < 0.02 mg/kg, error = ±5%)

GAS FLOWRATE AND GAS FRACTIONATION TIME

The influence of gas fractionation time on PFAS removal from soil is shown in Figure 10. The concentration of total PFAS and PFOS in treated soil increased from 13.9 and 9.7 mg/kg to 15.1 and 13.2 mg/kg, respectively, and the removal of the total PFAS and PFOS declined from 42.7% and 55.7% to 37.5% and 39.8%, respectively, when the gas fractionation time increased from 10 min to 20 min. However, PFHxS concentration in the treated soil decreased from 0.33 to 0.28 mg/kg in the same period (Figure 10a). When the fractionation time was greater than 20 min, the total PFAS, PFOS and PFHxS in the treated soil appeared constant with variations in concentration within the error range.

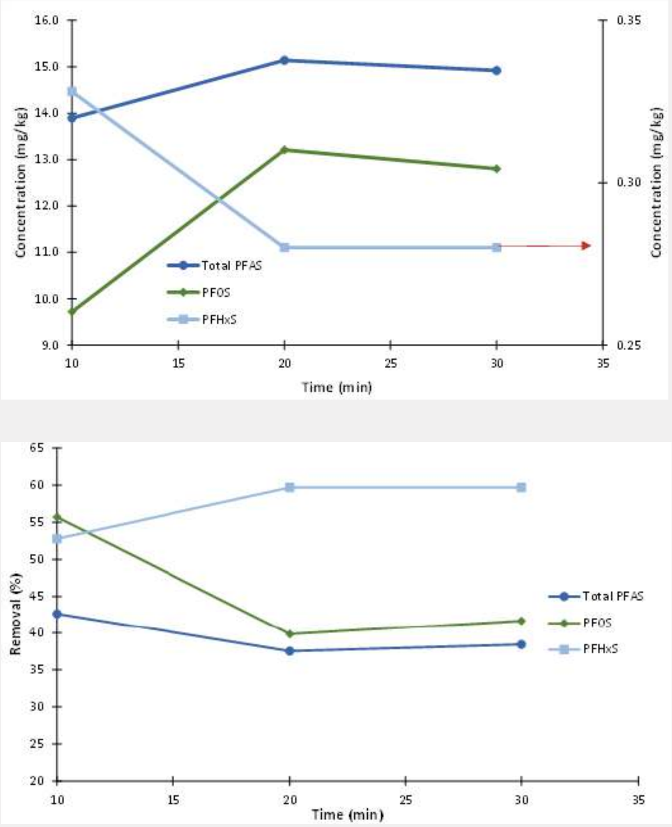
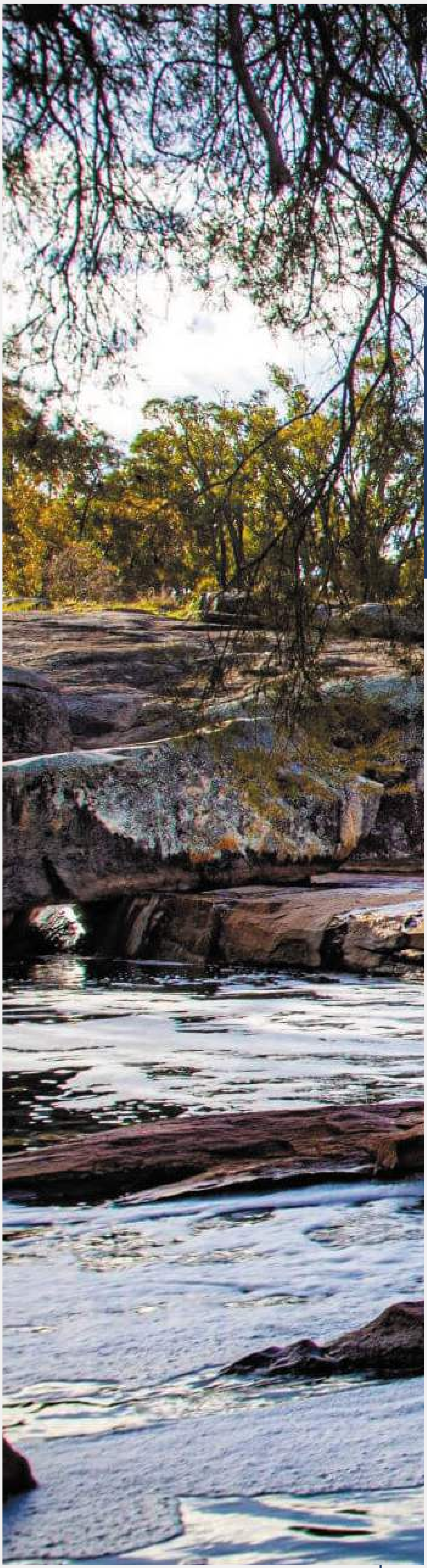


Figure 10. Influence of gas fractionation times on PFAS removal from soil (W:S = 4, ozonated oxygen flowrate = 1.0 L/min, [PFOA] in treated soil< 0.02 mg/kg, error = ±5%)

a. PFAS concentration in the treated soil

b. PFAS removal efficiency



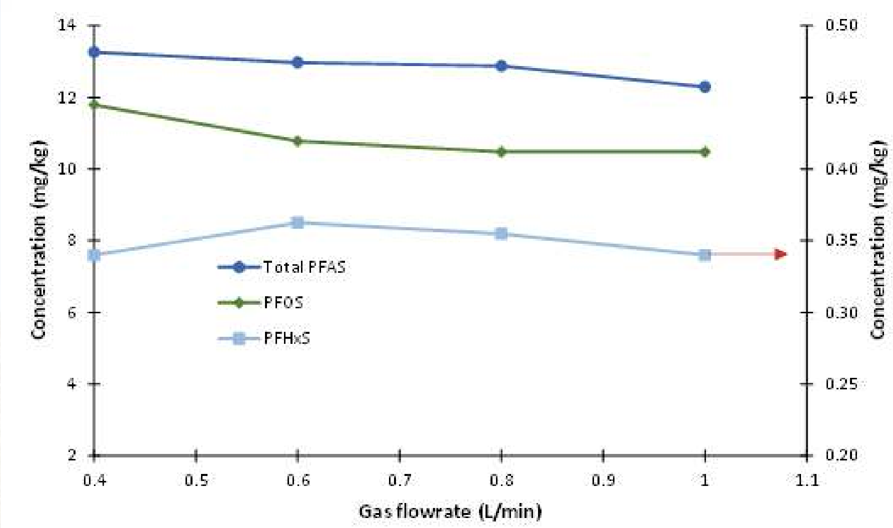
SOIL WASHING

The decline of the removal efficiency of total PFAS (PFOS is dominant) and PFOS (Figure 10b) should be also related to the increased adsorption of clay to PFAS due to swelling in the water (Frenkel et al., 1992; Laird, 2006) as discussed previously. However, clay swelling has less of an effect on adsorption to PFHxS, which was also observed in Figure 3b. Hence, the optimised fractionation time would be cautiously considered based on the properties of the contaminated soil and dominant types of PFAS in the contaminated soil.

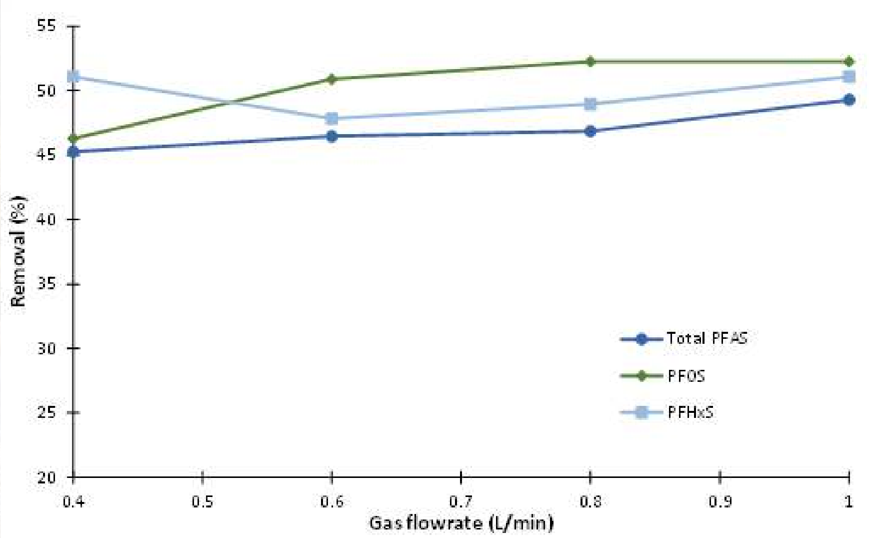
The influence of gas (ozonated oxygen) flowrate during the gas fractionation on the PFAS removal is shown in Figure 11. The concentrations of total PFAS and PFOS in the treated soil reduced from 13.3 and 11.8 mg/kg to 12.3 and 10.5 mg/kg, respectively, and their removals increased from 45.3% and 46.3% to 49.3% and 52.3%, respectively, when the gas flowrate was increased from 0.4 to 1.0 L/min. However, PFHxS removal was observed to fluctuate with increasing gas flowrate. The concentration of PFHxS in the treated soil varied in range of 0.35±0.01 mg/kg (in error range) at the tested gas flowrates.

Although the increased gas flowrate has greater influence on PFOS removal based on the Figure 11, its removal plateaued when the gas flowrate is greater than 0.8 L/min under the experimental conditions. This could be due to the increased collision and emergence of the generated gas bubbles in a confined space at higher gas flowrate, which compromises the interface area increase of the gas bubbles and the PFAS removal efficiency.

Figure 11. Influence of gas flowrate on PFAS removal from soil (W:S = 2, extraction time = 10 min, ozonated oxygen, fractionation time = 10 min, [PFOA] in treated soil< 0.02 mg/kg, error = ±5%)

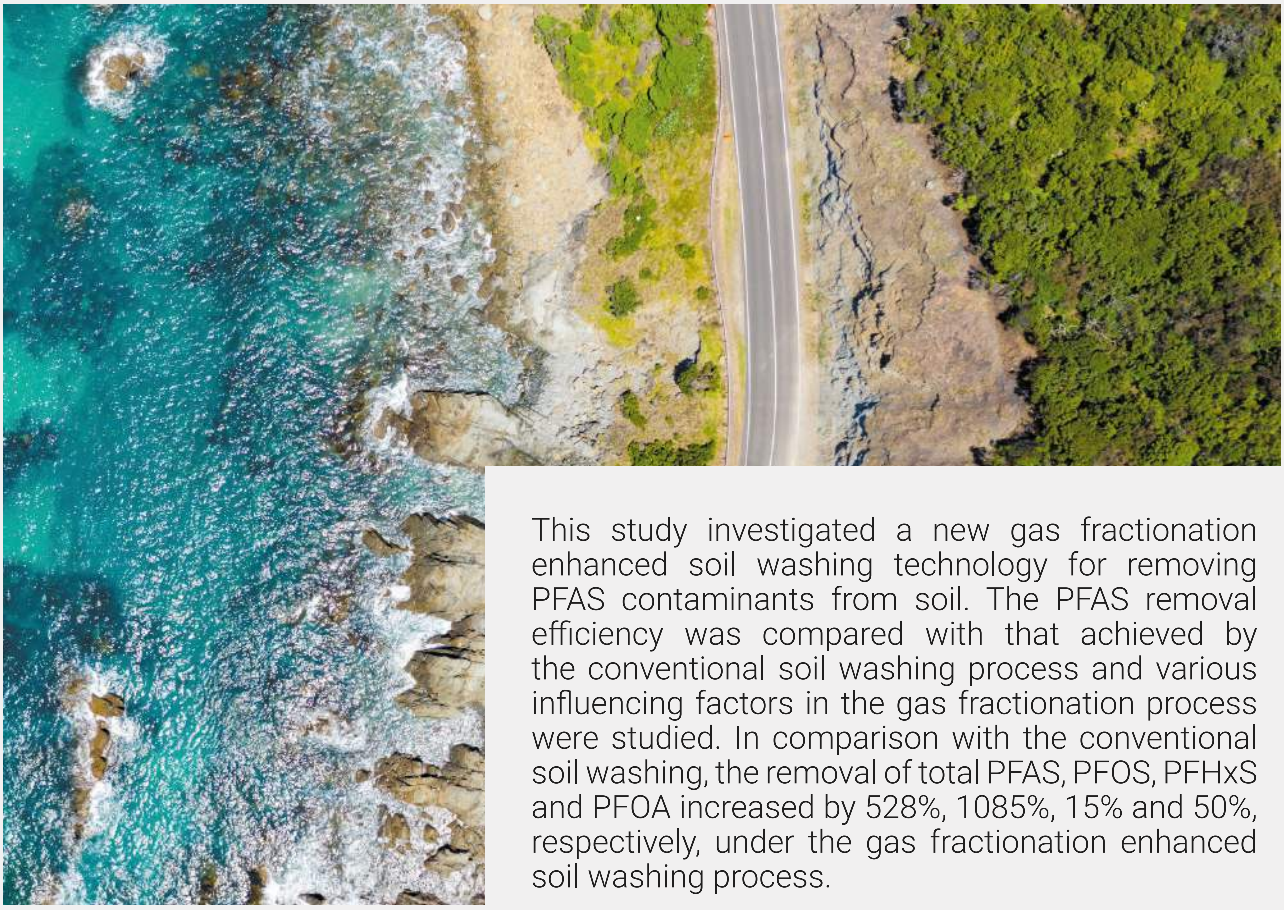


a. PFAS concentration in the treated soil



b. PFAS removal efficiency

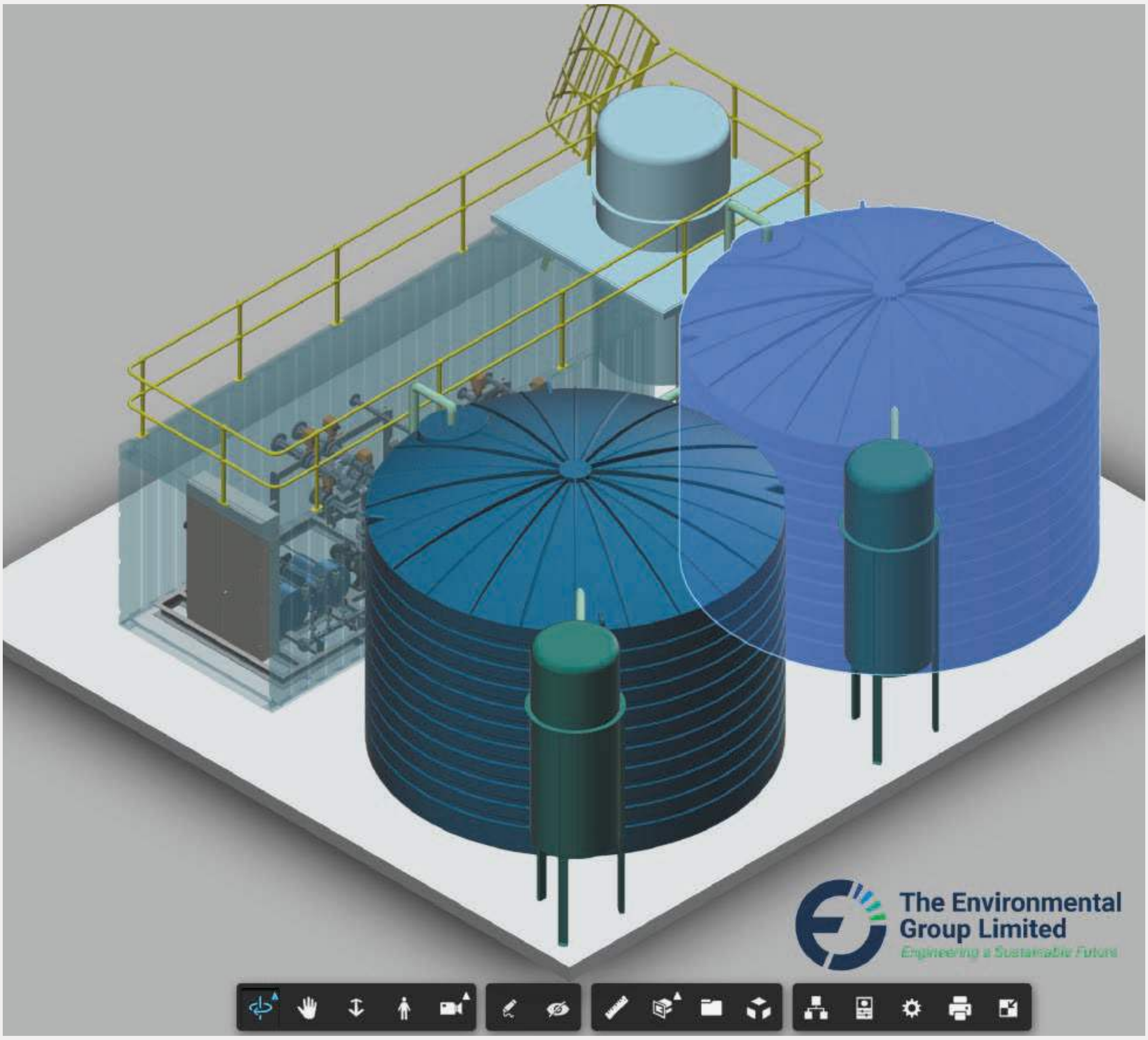
CONCLUSIONS AND FUTURE WORK



This study investigated a new gas fractionation enhanced soil washing technology for removing PFAS contaminants from soil. The PFAS removal efficiency was compared with that achieved by the conventional soil washing process and various influencing factors in the gas fractionation process were studied. In comparison with the conventional soil washing, the removal of total PFAS, PFOS, PFHxS and PFOA increased by 528%, 1085%, 15% and 50%, respectively, under the gas fractionation enhanced soil washing process.

The pre-extraction of the soil for 10 min increased the PFAS removal from the soil. Of the four tested gases (air, oxygen, ozonated air and ozonated oxygen), ozonated oxygen fractionation achieved the highest PFAS removal under the same operational conditions. The influence of water to soil ratios, fractionation time, and gas flowrate were also studied and a high water to soil ratio facilitates PFAS removal, but fractionating the soil twice with a lower water to soil ratio further enhanced PFAS removal. Additionally, there is trade-off between PFAS removal and PFAS absorption that is associated with the fractionation time. During a long fractionation period, PFAS (especially PFOS) will be absorbed back into the soil due to clay swelling, and the equilibrium of PFAS in water and soil phases would change which supress the benefit of continuously removing PFAS from the water phase in the tested period. However, there is no clear evidence that PFHxS removal would be affected by the extended fractionation time and a high gas flowrate influences PFOS removal more than PFHxS removal. However, PFOS removal efficiency was observed to plateau at high gas flowrate.

This study serves as a proof-of-concept work to demonstrate the new developed gas fractionation enhanced technology for effective remediation of PFAS contaminated soil. In the future, comprehensive analyses of X-Ray Diffraction (XRD) and Fourier Transformed Infrared (FTIR) will be undertaken on soil samples pre- and post-treatment to characterise the changes of particular chemical structure of the soil. Different types of PFAS contaminated soil (sandy, clay, silt etc.) with various physiochemical properties will be used for treatment using the developed fractionation method in order to extend the method for wider applications. A pilot trial of the developed fractionation process is necessary to understand the feasibility of the operational conditions and the PFAS removal performance, as well as a dual/multiple-fractionations with solid-liquid separation between stages using counter current flow for minimisation of water use.



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