Immobilization of PFAS in AFFF-Contaminated Soil: Impact on Ecological and Human Exposure

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Introduction

A cost-effective strategy for minimizing PFAS leachability in contaminated soil is through the use of immobilization strategies. Several soil amendments (e.g. activated carbon, biochar and proprietary products) have been shown to decrease PFAS leachability through an enhancement in hydrophobic and electrostatic interactions. Studies utilizing various leaching methodologies (e.g. TCLP, SPLP, ASLP, LEAF) have shown that $\sum_{28}$ PFAS leachability may be reduced by >95% due to electrostatic interactions with inorganic constituents in addition to hydrophobic and Van der Waal interactions with activated carbon and other organic components. While a considerable amount of leaching data is available for PFAS immobilization strategies, limited studies have assessed the impact of soil amendments on biological receptors to assess exposure minimization for ecological and human health. In this study, earthworm and rat bioassays (surrogate human assay) were utilized to determine PFAS immobilization efficacy following treatment of AFFF-contaminated soil using a carbon-based soil amendment

Approach

AFFF-contaminated surface soils were collected from 8 sites across southern and eastern Australia. Soils were characterised using standard wet chemistry methodologies while $\sum_{28}$ PFAS concentrations were determined using LC-MS/MS (Figure 1). Bench scale immobilization studies involved the addition of a composite soil amendment (aluminium hydroxide, activated carbon, kaolin clay) to AFFF-contaminated soil to achieve an application rate of 5% w/w. After thorough mixing and addition of water (to ~30% water holding capacity), soils were cured at room temperature for 5 days before the assessment of PFAS availability in amended and unamended soil.

- PFAS leachability was determined using the Australian Standard Leaching Procedure (Figure 2).
- PFAS bioaccumulation in earthworms (*Eisenia fetida*) was determined using OECD method 222 (Figures 3-5).
- An in vivo rat bioassay (female Sprague-Dawley rats) was utilized to determine the relative bioavailability of target PFAS in soil via oral exposure following the establishment of PFAS toxicokinetics (Figures 6-9).

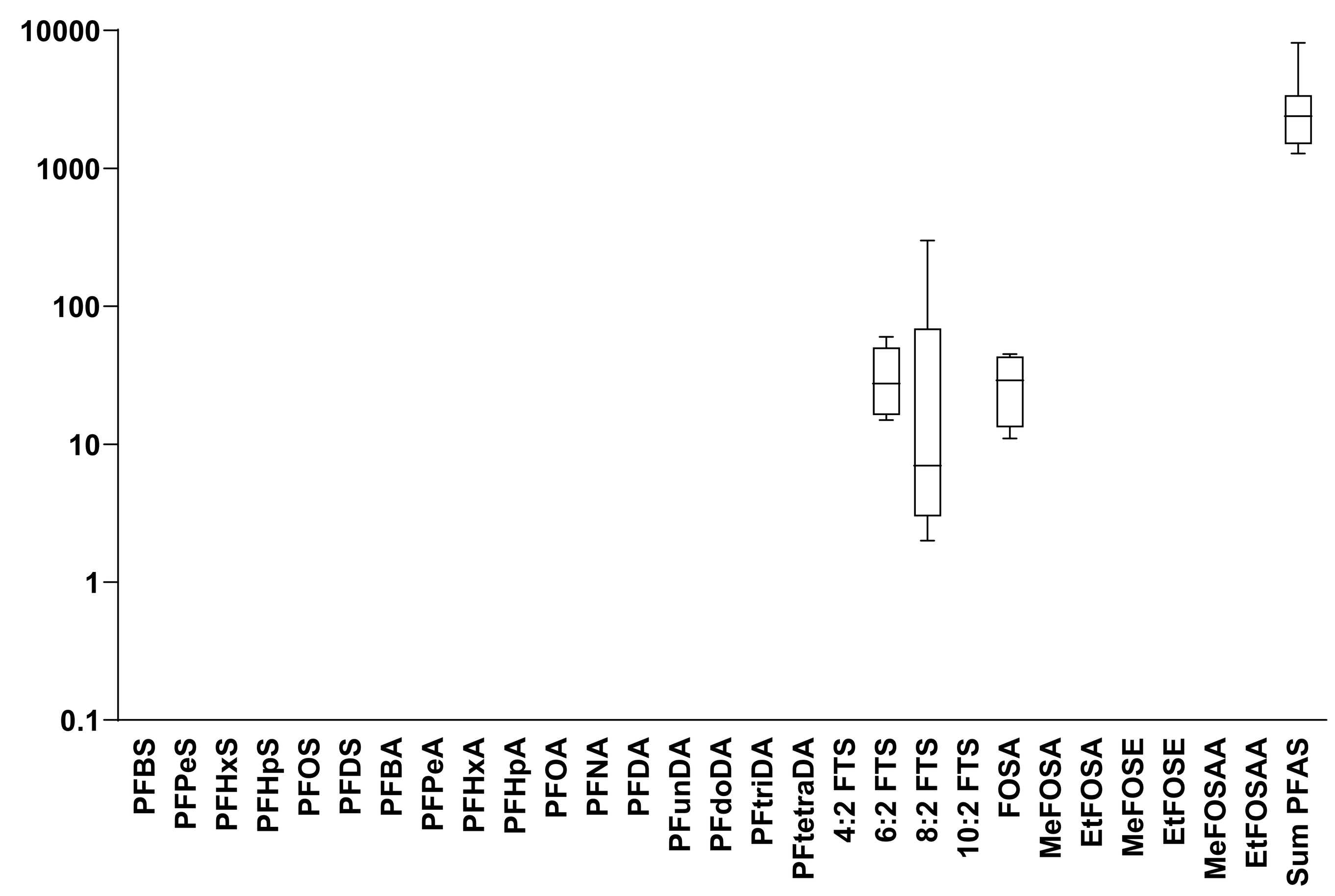

Figure 1. Box plot showing the range in PFAS concentration for perfluoroalkyl sulfonic acids, perfluoroalkyl carboxylic acids, fluorotelomer sulfonates and perfluoroalkyl sulfonamides for soils (n = 8) used in immobilization studies.

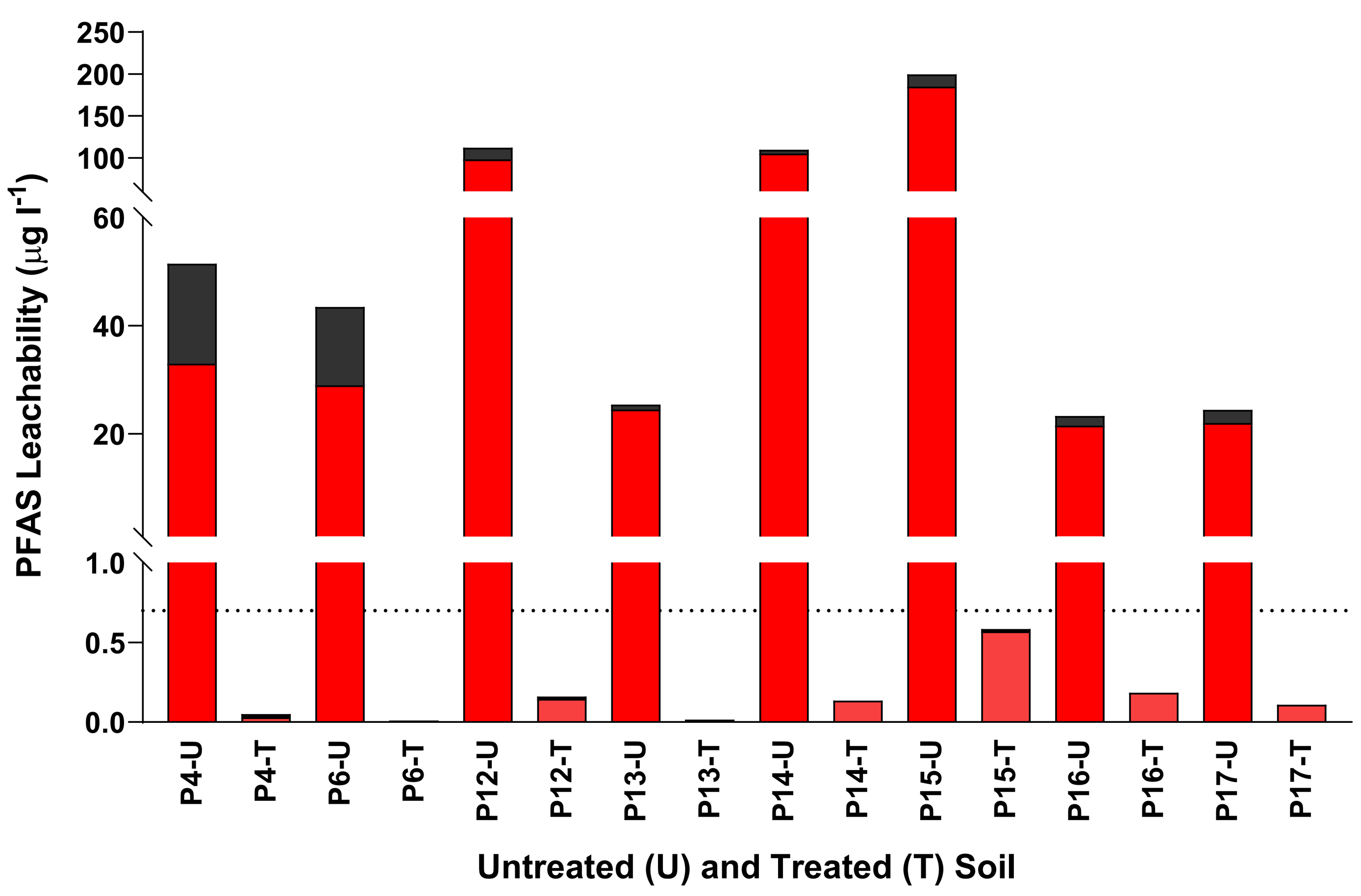

Figure 2. PFOS (■) and PFHxS (■) leachability in unamended soil (U) and following treatment (T) with 5% w/w composite soil amendment. The dashed line indicates the interim landfill acceptance criterion for single composite lined landfills (0.7 µg l[-1] for the sum of PFHxS and PFOS).

Earthworm Bioassay Results

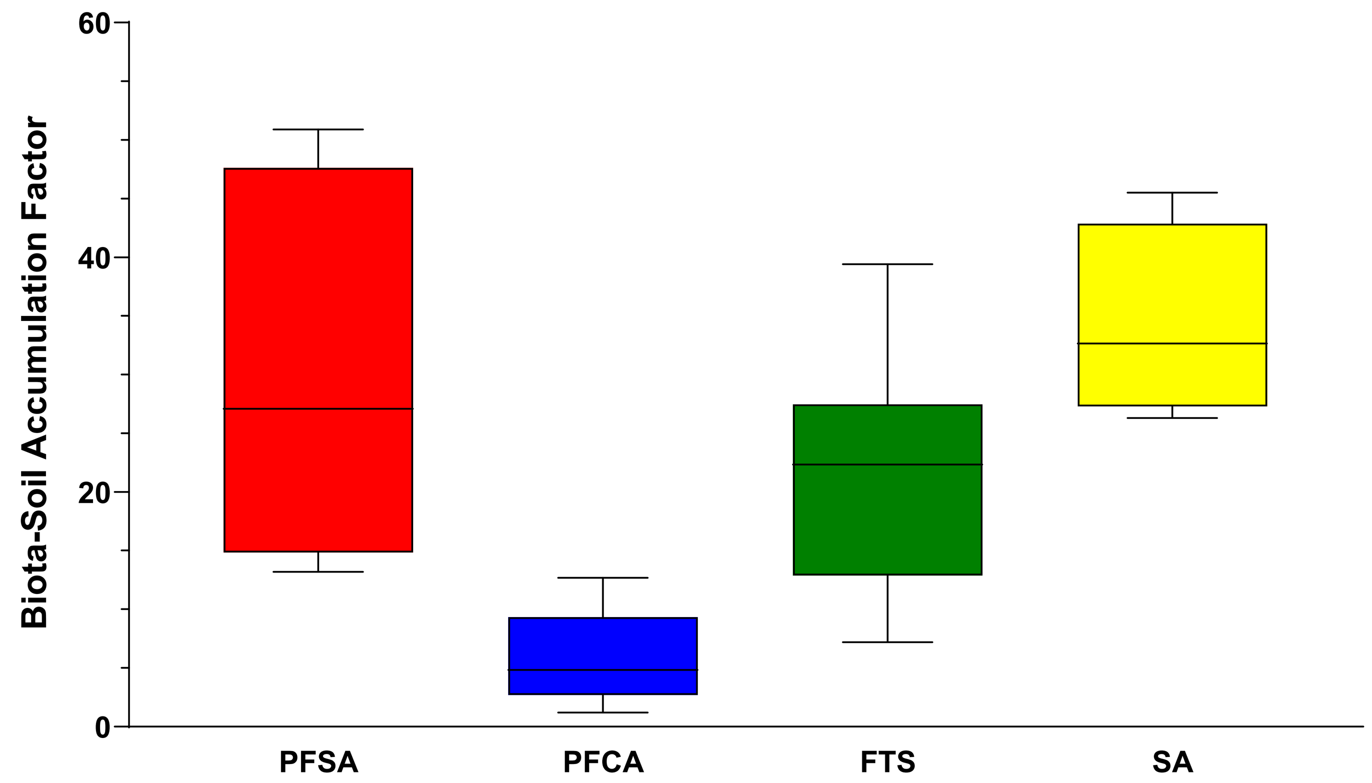

Figure 3. PFAS biota-soil accumulation factors (BSAF) for *E. fetida* and perfluoroalkyl sulfonic acids (PFSA), perfluoroalkyl carboxylic acids (PFCA), fluorotelomer sulfonic acids (FTS) and perfluoroalkyl sulfonamide (SA) following exposure to unamended PFAS contaminated soil.

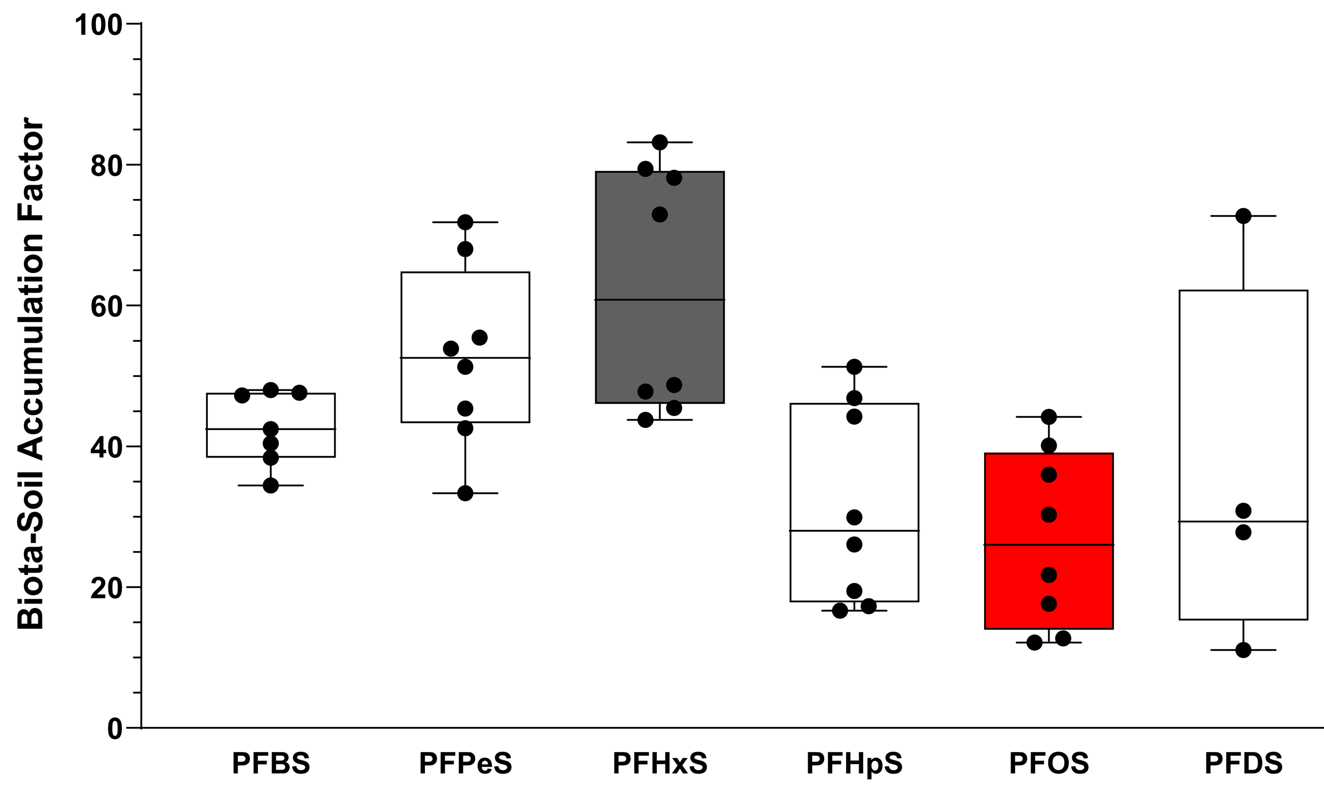

Figure 4. PFAS biota-soil accumulation factors (BSAF) for *E. fetida* and individual PFSA following exposure to unamended PFAS contaminated soil.

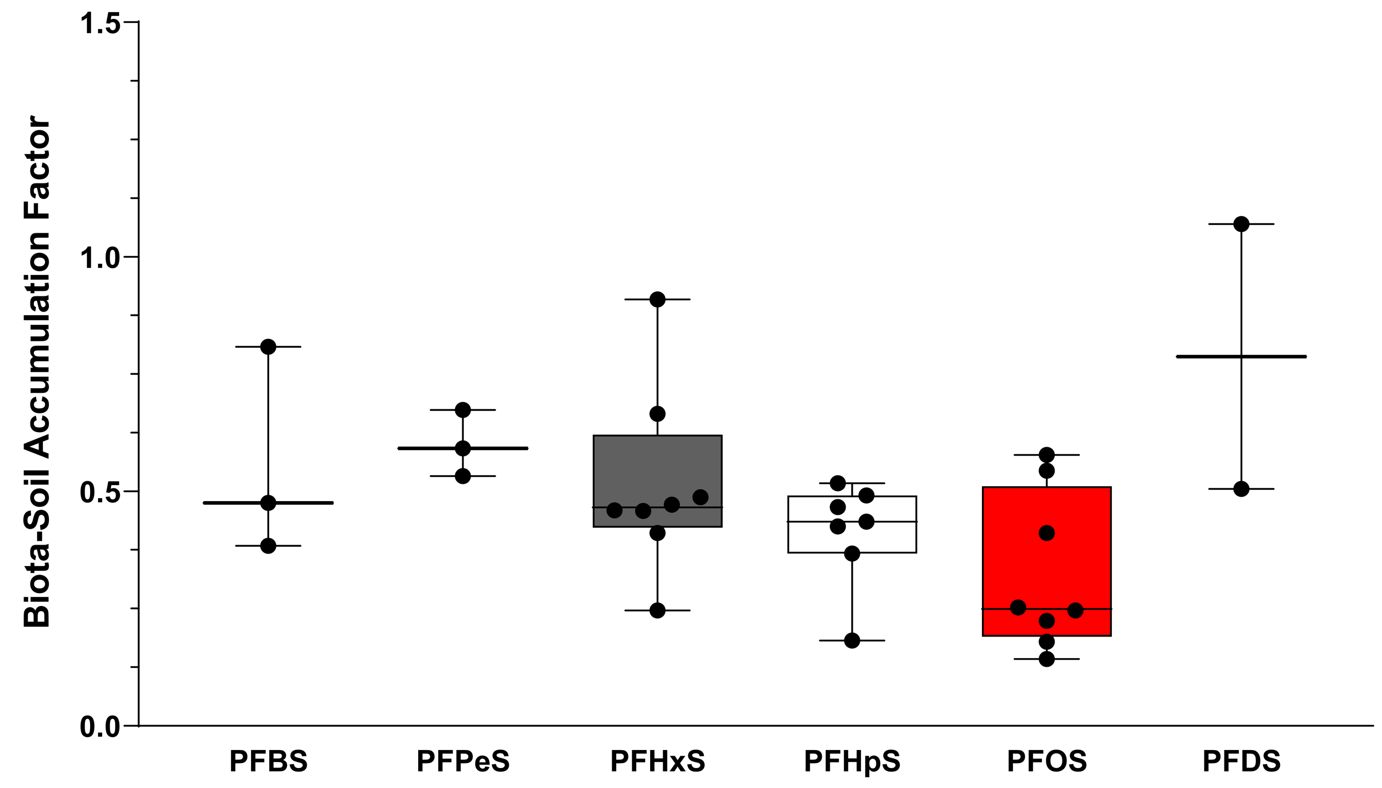

Figure 5. PFAS biota-soil accumulation factors (BSAF) for *E. fetida* and individual PFSA following exposure to PFAS contaminated soil amended with 5% w/w composite soil amendment.

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Rat Bioassay Results

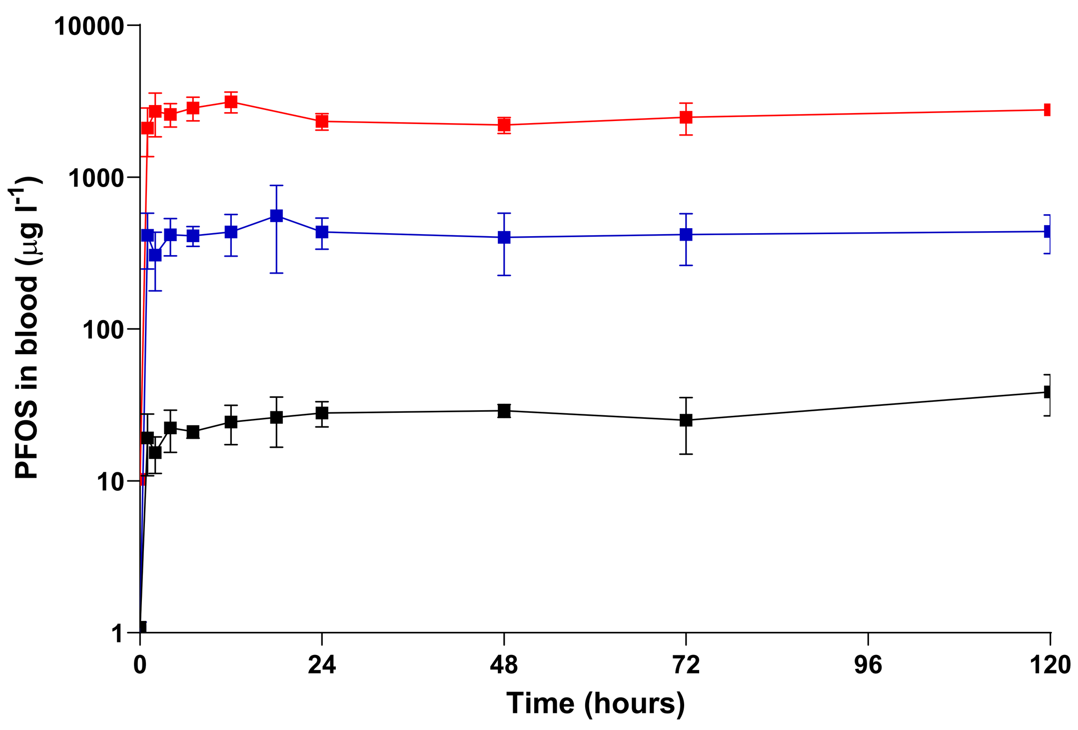


Figure 6. PFOS blood profiles following single dose administration (gavage) of 5-500 µg of PFOS (~20-2,000 µg kg^{-1} body weight) to female Sprague Dawley rats (n = 6).

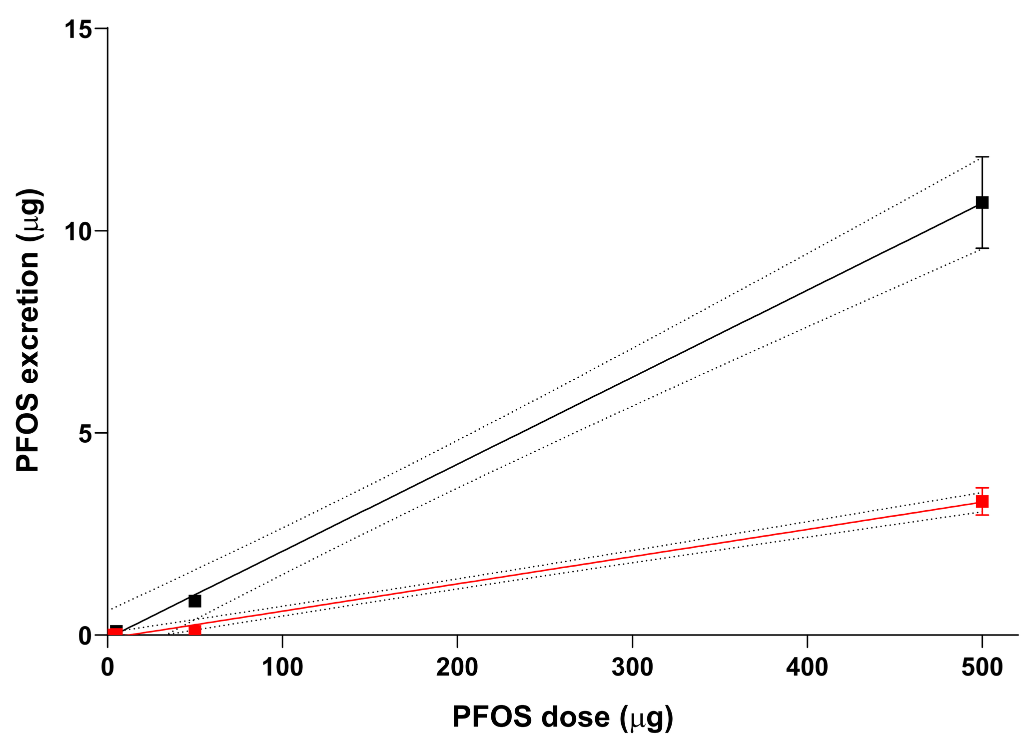


Figure 7. Cumulative PFOS urinary (■) and faecal (■) excretion after 5 days following single dose administration (gavage) of 5-500 µg of PFOS (~20-2,000 µg kg^{-1} body weight) to female Sprague Dawley rats (n = 6).

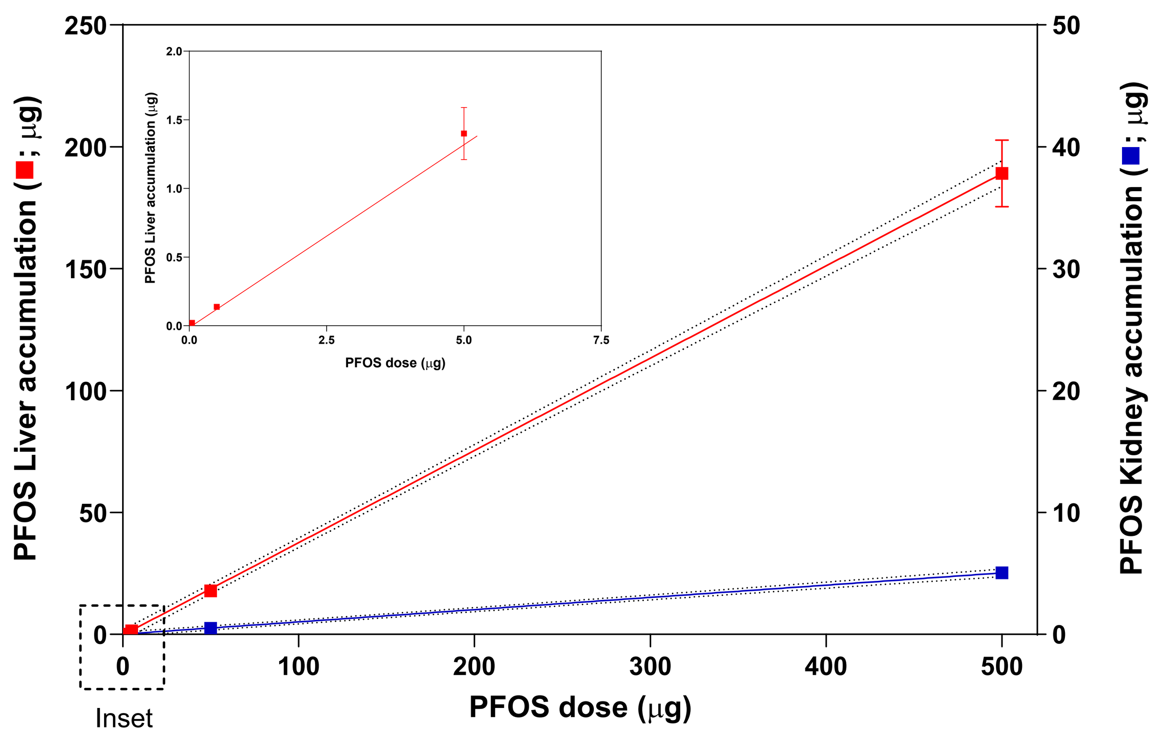


Figure 8. PFOS accumulation in the liver (■) and kidney (■) after 5 days following single dose administration (gavage) of 0.05-500 µg of PFOS (~0.2-2,000 µg kg^{-1} body weight) to female Sprague Dawley rats (n = 6).

PFOS toxicokinetics and relative bioavailability determination

PFOS blood plasma concentrations rapidly increased after administration, however, concentrations remained high during the 5-day monitoring period (Figure 6).

Only a small fraction of administered PFOS was excreted in urine (0.67 ± 0.02%). PFOS faecal excretion was greater than urinary excretion although only 2.15 ± 0.12% of the administered dose was recovered in faeces after 5 days (Figure 7).

Linear dose-responses were observed for PFOS accumulation in liver and kidneys; 37.9 ± 0.55% of the administered dose accumulated in the liver which was ~38-fold higher compared to kidney accumulation (1.01 ± 0.03%; Figure 8).

PFOS absolute bioavailability (ABA) was calculated (102.9 ± 15.6%) by comparing liver accumulation following oral and intravenous doses; values were comparable to PFOS ABA reported by ATSDR (2018) and USEPA (2016).

PFOS relative bioavailability in soil was determined by comparing PFOS liver accumulation for orally administered soil and reference compound doses (following dose normalization).

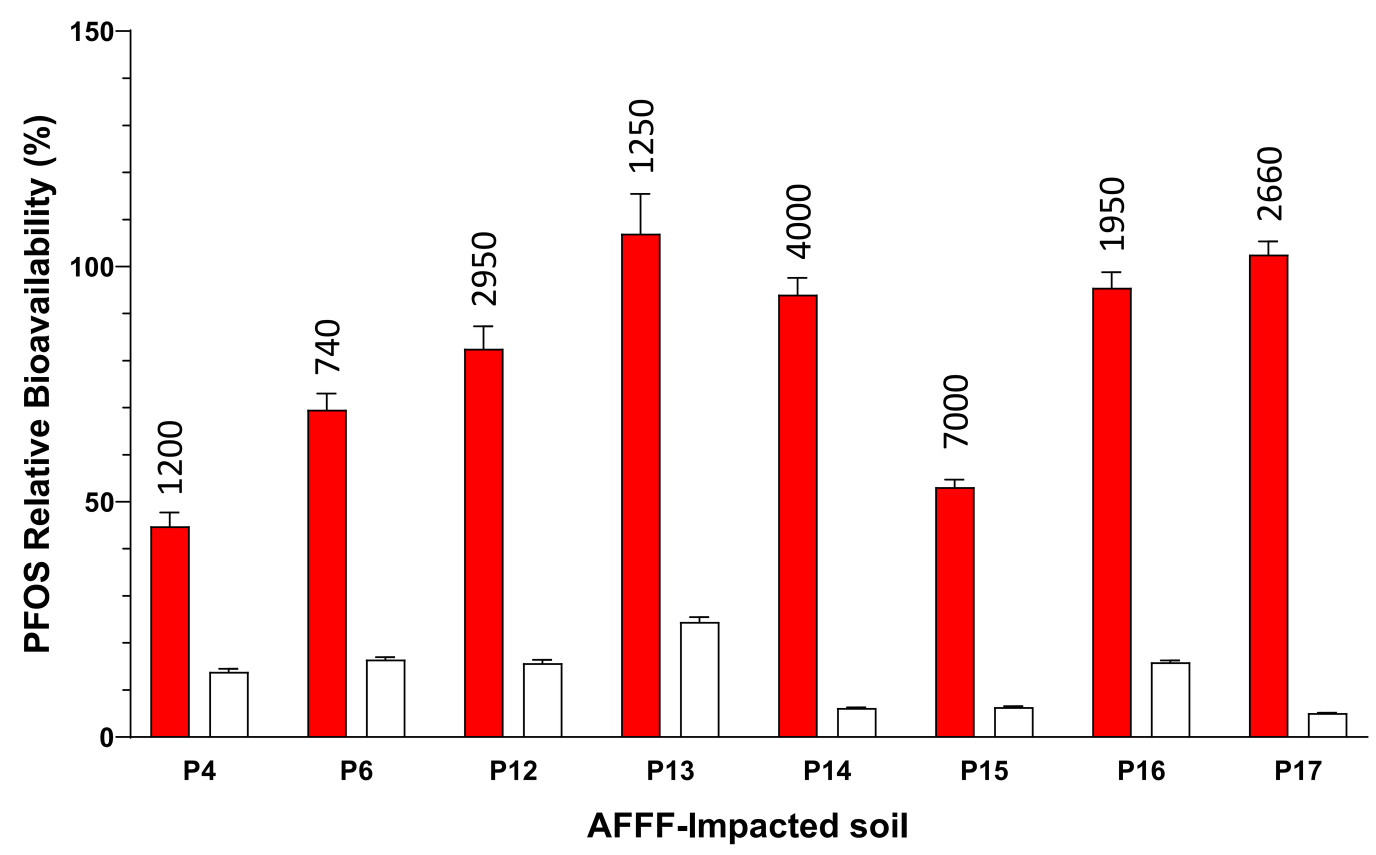
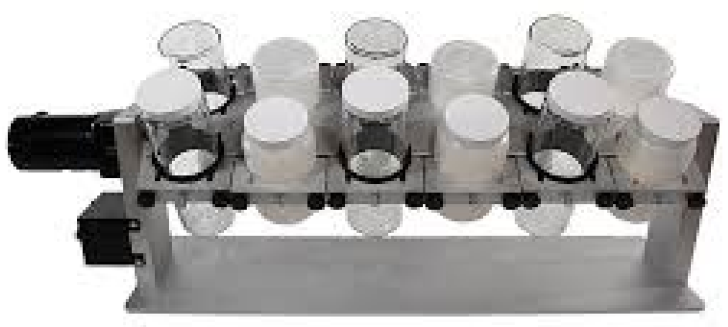


Figure 9. PFOS relative bioavailability in unamended soil (■) and following treatment (□) with 5% w/w composite soil amendment. Values above bars indicate soil PFOS concentration (ng g^{-1})



Lessons Learned

The addition of a composite soil amendment to AFFF-contaminated soil had a significant impact on PFAS availability, however, treatment efficacy varied depending on the endpoint measured.

In unamended soil, Σ_{28} PFAS in ASLP leachates ranged from 26.0-235 µg l^{-1} with PFOS (21.5-185 µg l^{-1}) and PFHxS (0.93-18.5 µg l^{-1}) being the major constituents, driven by their soil concentration. However, in amended soil, Σ_{28} PFAS in ASLP leachates was reduced to ≤ 0.62 µg l^{-1} while PFOS and PFHxS leachability was reduced to 0.01-0.57 µg l^{-1} and ≤ 0.02 µg l^{-1} respectively (≥ 99.1% reduction in leachability).

Earthworm bioassays identified that PFAS in unamended AFFF-contaminated soil were highly bioavailable with biota-soil accumulation factors ranging from 12-44 (PFOS) and 45-83 (PFHxS). However, following exposure of earthworms to amended soil, biota-soil accumulation factors were reduced significantly to 0.2-0.6 (PFOS) and 0.2-0.9 (PFHxS).

The incidental soil ingestion pathway was assessed using a rat bioassay with PFOS accumulation in the liver used as the bioavailability endpoint. PFOS relative bioavailability in unamended soil ranged from 45-107% while significantly lower values (5.1-24%) were observed in amended soil..

Acknowledgements

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