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A Review of Immobilisation-Based Remediation of Per- and Poly-Fluoroalkyl Substances (PFAS) in Soils

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Abstract

Purpose of Review This review provides an overview of the latest developments in immobilisation of per- and poly-fluoroalkyl substances (PFAS) for soil remediation. It examines the efficacy of a range of amendments, including those with binding agents, along with a discussion of immobilisation mechanisms and post-immobilisation assessment needs.

Recent Findings Researchers have recently applied a variety of soil amendments to soil for PFAS immobilisation. Efficacy of these has varied widely, both between amendment and soil types and for individual PFAS molecules present in contaminated soils. Activated carbon based amendments, including composite amendments exhibit the highest efficacies of the examined studies.

Summary Immobilisation of PFAS is complex, with efficacy of immobilisation varying with soil properties including pH, clay and organic matter content, amendment properties, and molecular properties of the individual PFAS. Optimal remediation strategies need to be adjusted accordingly to site specific soil properties and contamination profiles. Additionally, bioavailability testing needs to supplement standard leaching approaches to determine effectiveness of PFAS soil immobilisation strategies.

Keywords PFAS · Soil remediation · Immobilisation · Soil amendments · Leachability

Introduction

Per- and poly-fluoroalkyl substances (PFAS) are a group of man-made chemicals found in fire-fighting foams, water repellent coatings, and consumer products such as carpets, textiles and food packaging [1, 2]. In recent years, PFAS have emerged as contaminants of concern due to their potential for persistence, mobility and bioaccumulation in humans and the environment. PFAS contamination is complex, with PFAS consisting of thousands of different compounds (over 3,000 of these commercially available) [3] although only a limited number are routinely assessed in environmental samples. Of these, perfluorooctan`e sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonyl fluoride (PFOSF) are listed in the Stockholm convention, and perfluorohexane sulfonic acid (PFHxS) is listed as potential compounds to be added [4]. Consisting of a fully or partially fluorinated carbon chain and a functional group, PFAS exhibit surfactant-like properties, are characterised by high octanol-water partitioning coefficients (e.g. log K_{OW}=3.94-6.56 for a range of PFAS [5]) but high aqueous solubility and are proteinophilic rather than lipophilic like other persistent organic pollutants. Exposure to PFAS has been shown to result in a number of adverse health effects [6] including hepatotoxicity [7], immunotoxicity [8], neurotoxicity [9], and developmental toxicity [10] although the molecular mechanisms influencing these effects are only beginning to be elucidated [11]. Environmental concentrations in some organisms have also been measured that exceed experimentally derived lowest observable adverse effect levels (LOAEL) [12, 13].

Over the past 5 years, there has been a substantial increase in research on PFAS[1], including the fate of PFAS in the environment, their bioaccumulation in aquatic and terrestrial food webs and approaches for remediation and risk management. While a large proportion of research has been undertaken on

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[1] Web of Science topic search results for “PFAS” 2016: 141, vs 2020: 561, accessed 15/06/2021.

PFAS impacted water, and associated technologies for its removal, less information is available on strategies for the treatment of contaminated soil. PFAS contamination of soil is prevalent at fluorochemical manufacturing sites [14], fire-fighting training grounds [15], landfill sites [16], airports and air-force bases [17] along with sites where PFAS contaminated biosolids [18], wastewater [19] or recycled water [20] have been utilised. Given the number of possible per and polyfluoroalkyl congeners in commercial products, PFAS contamination from different sources may vary widely in terms of concentration and composition. For example, Brusseau et al. [21] determined that the median background concentration of

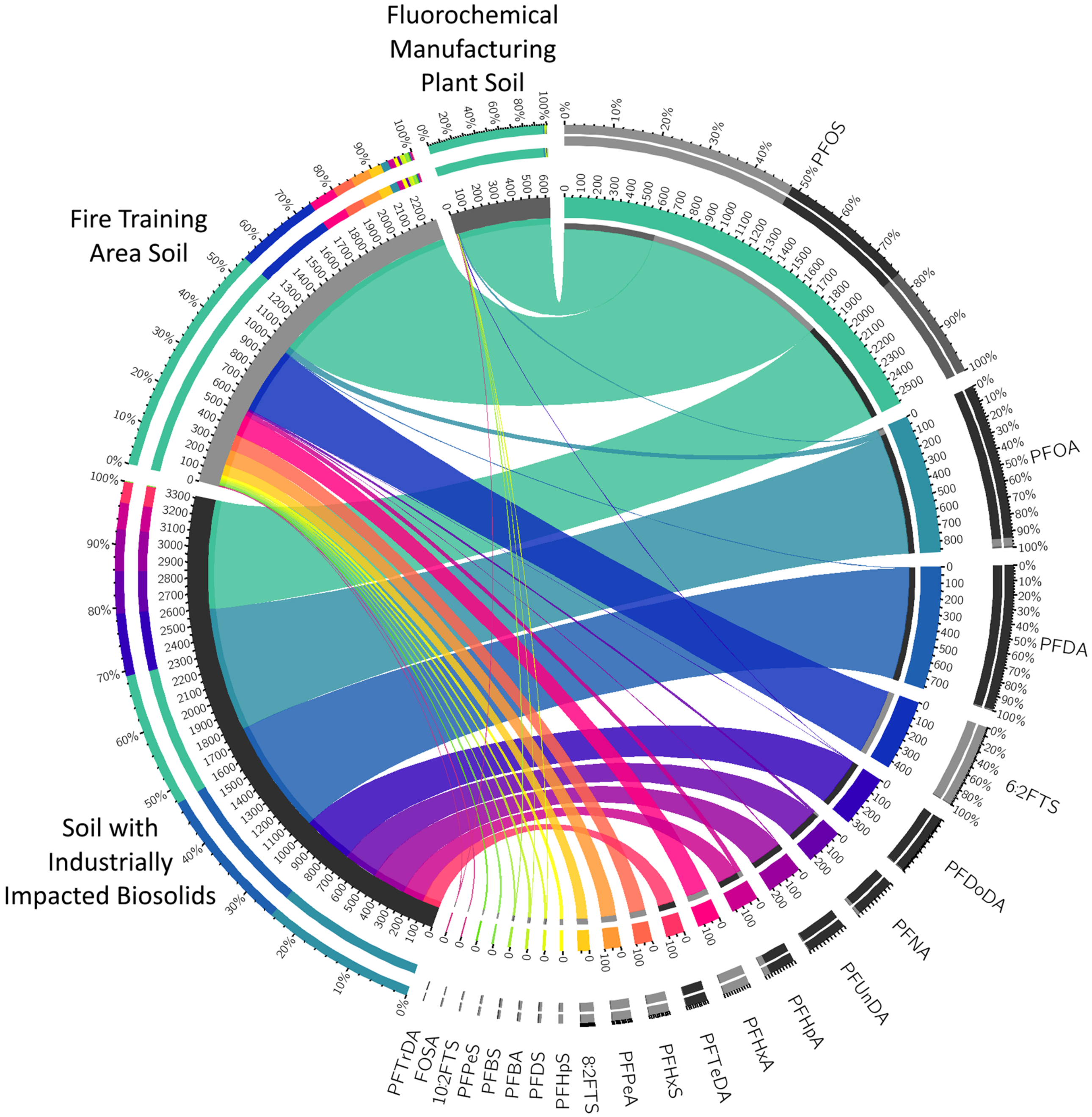

Fig. 1 Composition of PFAS contamination from three locations; soil from an AFFF fire-fighting training ground, a soil with industrially impacted biosolids [22], and a soil from a fluorochemical manufacturing plant [14]. On the right hand side of the circle, moving clockwise, individual PFAS are shown ordered by decreasing concentration (μg kg^{-1}). This is followed by location type, ordered by decreasing total PFAS concentration. The size of the link connecting an individual PFAS with a location type represents the concentration, sized according to the inner numbered scale (μg kg^{-1})

PFOS and PFOA in soil from a large range of international sites where neither primary nor secondary PFAS contamination occurred, was 2.7 μg kg^{-1} compared to up to 460 g kg^{-1} (PFOS) and 11 g kg^{-1} (PFOA) at contaminated sites. PFAS congeners in contaminated soil may vary considerably, as depicted in Fig. 1 where three example PFAS contamination profiles representing impacts from fluorochemical manufacturing, the use of aqueous film-forming foam (AFFF) at fire-fighting training grounds and biosolid amended soil are shown. PFAS profiles may range from being dominated by a single compound (e.g., perfluorooctane sulfonic acid, PFOS) in impacted soil from a manufacturing plant [14] to having a wide range of congeners present. A soil from a fire-fighting training area contained significant proportions of both PFOS and 6:2 fluorotelomer sulfonic acid (6:2 FTS), along with smaller amounts of perfluorohexanoic acid (PFHxA) and PFHxS among others. Due to wastewater treatment plants (WWTPs) having PFAS inputs from multiple sources, biosolids and biosolid-amended soil [22] may contain a range of PFAS often dominated by long-chain PFAS ($\geq C_7$) due to their preferential retention (in biosolids) during wastewater processing [23].

Irrespective of the activity leading to soil contamination, potential adverse environmental health effects associated with PFAS exposure has necessitated the development and application of remediation technologies. However, due to the unique physicochemical properties of PFAS, some traditional remediation strategies are ineffective for PFAS remediation. In particular, the strength of the C-F bond limits the application of chemical oxidation and bioremediation strategies and in some cases, oxidation of poly-fluoroalkyl and/or precursor compounds may increase the concentration of recalcitrant perfluorinated carboxylic acids (PFCAs) [24]. Soil washing results in secondary liquid waste that requires additional treatment, while phytoremediation is slow, treatment zones are dependent on plant root depth, and uptake may be limited by mass transfer effects. While thermal treatment technologies, such as incineration with excess oxygen, gasification and pyrolysis have the potential to destroy PFAS by breaking C-F bonds, temperatures in excess of 1000 °C are required to minimise the production of greenhouse gases [25, 26].

Immobilisation techniques, whilst not removing PFAS from the soil matrix, offer a risk management strategy through a reduction in leachability and/or bioavailability. The effectiveness of immobilisation strategies is influenced by a wide variety of parameters, including soil and amendment properties in addition to PFAS profiles in contaminated soil. While recent PFAS remediation reviews have provided a synopsis of the application of established technologies for PFAS contaminated soil and sediment [27–31] or focused on emerging treatment strategies [32], this paper provides a comprehensive overview of soil-based PFAS immobilisation approaches including amendment properties, treatment efficacy, immobilisation mechanisms, existing data gaps and future research priorities.

Immobilisation

Immobilisation is a strategy which reduces the mobility and bioavailability of contaminants through the addition of 'sorptive' soil amendments, thereby reducing exposure for human and ecological receptors. Amendments may be applied either in situ or ex situ and used with or without additional binding agents (e.g. Portland cement). Soil amendments offer the advantage of ease of application, cost-effectiveness and commercial viability, however, selecting suitable amendments that exhibit high sorptive capacity is critical for delivering sustainable immobilisation approaches. While immobilisation strategies are well developed for many legacy contaminants (e.g. metal(loid)s, PAHs), amendments and immobilisation approaches for PFAS have only recently gained research, development and commercial attention. Table 1 provides details of amendments that have been applied for PFAS immobilisation including activated carbon, biochar, clay, polymer and composite sorptive phases. A comparison of physicochemical properties which influence PFAS sorptive capacity and immobilisation efficacy, which in many cases, may be manipulated during amendment development; along with advantages and disadvantages of each amendment type are discussed in detail in the following sections.

Activated Carbon-Based Amendments

Activated carbon is a commonly used sorbent for the removal of contaminants from (waste)water due to its high surface area, high pore volume and surface functional groups. This sorbent has also been applied to contaminated soil for the immobilisation of a variety of organic and inorganic compounds including PFAS [43, 45, 46]. Activated carbon's effectiveness for PFAS sorption is due its high surface area, size and number of pores. However, physicochemical properties and sorptive potential of activated carbon varies depending on the carbon source and temperature used for its production [47]. These parameters influence porosity, surface area and surface functional groups whereby increased production temperature decreases surface functional groups, and in doing so, increases surface charge [47]. Activated carbon has the ability to form both electrostatic and hydrophobic interactions with PFAS, and possibly hemi-micelle and micelle formation in pores [48]. Charge-assisted hydrogen bonding was also suggested from experimental spectroscopy of PFAS interacting with functional groups on the surface of activated carbon [49].

Table 1 Laboratory and field-based immobilisation studies detailing the impact of soil amendment on PFAS leachability

Amendment category	Amendment type(s)	Technique	Application rate (w/w)	Ageing period	Soil properties	Initial soil conc. (μg kg^{-1})	PFAS tested	Leaching method/details	Author, year and reference
Activated carbon	CB + GAC	Stabilisation and solidification	15% CB, 0.2% GAC	12 months	AFFF contaminated (sand 30%, clay 42%, silt 28% pH 8.6, OC 6%)	Not stated	C_{5-8} PFCAs, $C_{4,6,8}$ PFSAs, 6:2 FTS, PFOSA, 3:2 FTOH, HpF-PipB	EN 12457/in situ, 0.1-2.0 mm particles	Sörengård et al. (2021) [33]
Activated carbon	Colloidal activated carbon (PlumeStop®)	Sorbent amendment (injection)	1%	10 months	Spiked 0.6 mg kg^{-1} 10 soils with varying OC, clay	Σ_{18}=10,800	$C_{3-11,13,15,17}$ PFCAs, $C_{4,6,8}$ PFSAs, 6:2,8:2 FTS, PFOSA	1:7 liq:soil, 0.45 μm filter	Sörengård et al. (2019b) [34]
Biochar	Activated and unactivated waste timber biochar	Sorbent amendment (ex situ)	0-5%	Not stated	AFFF contaminated, 1 low, 1 high TOC	Σ_{21}=1200-3800	$C_{4,6,7,8,10}$ PFSAs, $C_{4-10,12-14,16}$ PFCAs, 4:2, 6:2, 8:2 FTS, HPFHpA, DMOA	Modified CEN EN 12457 <1mm, 1.2 μm filter	Sørmo et al. (2021) [35]
Biochar	Biochar (pine, 750 °C)	Sorbent amendment	0-5%	Not stated	Spiked sandy clay, loamy sand	Not stated*	$C_{6,8}$ PFCAs, $C_{6,8}$ PFSAs	0-96 hours, 0.22 μm	Askeland et al. (2020) [36]
Biochar	Activated and unactivated biochar	Sorbent amendment	0-20%	2 weeks	Industrially contaminated	Σ_4=1,125-3,671	$C_{6,8}$ PFCAs, $C_{6,8}$ PFSAs	EN 12457-2	Silvani et al. (2019) [37]
Composite	RemBind®, RemBind Plus®	Sorbent amendment	5-30%	2 months	AFFF contaminated	Σ_{12}=2,400-14,000	$C_{4,6,8}$ PFSAs, C_{4-10} PFCASs	24 h, 0.45 μm filter	Bräunig et al. (2021) [38]
Composite	Modified clay (MatCARE^{TM})	Sorbent amendment	10%	1 week-1 year	AFFF impacted sandy, clay and sandy clay loams	Σ_1=9,262-74,379	PFOS	0.45 μm filter, 24 h	Das et al. (2013) [39]
Multiple	RemBind® PAC (FiltraSorb^{TM} 400)	Sorbent amendment	5%	2 weeks	AFFF contaminated. loamy sand (1), sandy (1)	Σ_{21}=700-37,200	$C_{4-8,10}$ PFSAs, C_{4-13} PFCAs, PFOSA, 4:2, 6:2, 8:2, 10:2 FTS,	ASLP	Kabiri et al. (2021a,b) [40, 41]
Mulitple	CB + bentonite, CaCl, chitosan, hydrotalcite, PAC, pulverized zeolite, RemBind®	Stabilisation and solidification	10% CB 0.2% amend	4 months	Loamy sand (spiked)	Σ_{14}=6240-7310	C_{3-10} PFCAs, $C_{4,6,8}$ PFSA, 6:2, 8:2 FTS, PFOSA	0.1-2.0 mm particles, modified EN-12457-1	Sörengård et al. (2019a) [42]

Table 1 (continued)

Amendment category	Amendment type(s)	Technique	Application rate (w/w)	Ageing period	Soil properties	Initial soil conc. (μg kg^{-1})	PFAS tested	Leaching method/details	Author, year and reference
Mulitple	Activated carbon, compost soil, montmorillonite	Sorbent amendment	3%	Not stated	Sandy AFFF contaminated	Σ_{12}=6.4-2,510	C_{4-10} PFCAs, $C_{4,6,8}$ PFSAs, 6:2, 8:2 FTS	Modified EN 12457-2. 1:1 soil water, 8 days, 0.7 μm filter	Hale et al. (2017) [43]
Multiple	AC (coal-based), Biochar (mixed wood, paper-mill waste)	Sorbent amendment	4%	2 weeks (sorption)	Natively AFFF contaminated	Σ_{15}=780-3,600	PFOS, PFOA, PFHxS	47 μm filter	Kupryianchyk et al. (2016) [44]

AC activated carbon, *ASLP* Australian Standard Leaching Procedure, *CB* concrete binder, *DMOA* perfluoro-3,7-dimethyl octanoic acid, *FTOH* fluorotelomer alcohol, *FTS* fluorotelomer sulfonate, *GAC* granular activated carbon, *HPFHpA* 7H-dodecafluoro heptanoic acid, *HpFPipB* heptafluoropiperidin butane, *OC* organic carbon, *PAC* powdered activated carbon, *PFCAs* perfluoroalkyl carboxylic acids, *PFSAs* perfluoroalkyl sulfonic acids, *PFOSA* perfluorooctanesulfonamide, *TOC* total organic carbon

**Spiked with 5 μg L^{-1} per PFAS

A number of activated carbon products are available for PFAS sorption including powdered activated carbon (PAC), granular activated carbon (GAC) and colloidal/liquid activated carbon, such as PlumeStop®. Smaller particle size activated carbon has the advantage of higher surface area but is problematic to apply due to dust issues, however, colloidal/liquid activated carbon formulations have overcome these issues. Activated carbon amendments have been found to have the highest sorption capacity across a range of PFAS compared to other immobilisation amendments. In a PFAS sorption study using 44 adsorbents in water, Sörengård et al. [50] identified that activated carbon amendments (GAC, PAC, RemBind®) had the highest sorption capacity across most PFAS, with mean log K_d values of 3.5 for PFCAs and 4.2 for PFSAs, PFOSA and fluorotelomer sulfonates (FTSAs). Similarly, GAC was found to be superior at removal of PFAS compared to zeolite and sludge in another comparative study [51].

Biochar-Based Amendments

Biochar is used as an amendment due to its high cation exchange capacity (CEC), surface area and pore volume [52]. It is a carbonaceous material alternative to activated carbon, being produced from sustainably sourced materials [53] for carbon sequestration. As with activated carbon, biochar physico-chemical properties are influenced by carbon source material and pyrolysis temperature. Higher pyrolysis temperatures result in more organised carbon layers, with less functional groups, especially those containing O-H groups (a result of deoxygenation and dehydration) [52]. Higher temperatures also result in higher porosity, specific surface area, pH and ash content with a concomitant decrease in CEC and volatile matter [52]. Animal and solid-waste biochars tend to have lower surface area and volatile matter, but higher CEC than wood and crop-based biochars. The impact of these properties on PFAS sorption are complex, but generally result in biochars being less effective in sorption compared to their more homogenous activated carbon counterparts.

In an attempt to increase sorption capacity, research has been undertaken whereby surface functional groups are modified through biochar treatment. For example, biochar treated with $MgCl_2$ was found to have the highest mean log K_d for PFCAs (0.93) and PFSAs (0.87) of the non-activated carbon sorbents, while the untreated, MnO and $FeCl_3$ treated biochars were less effective at sorbing PFAS [50].

Clay-based Amendments

Of the non-carbon-based amendments, clays, such as zeolite, bentonite, hydrotalcite, montmorillonite and kaolinite have been utilised as a sorbent phase for PFAS immobilisation due to their large surface area and recognised potential to sorb organic contaminants (e.g. PAHs). Clay minerals are hydrophilic, chemically stable and have high cation exchange capacities [54]. The abovementioned clays differ in their constituent molecules, structures and interlayer spacing which drives sorptive capacity. For example, Zhang et al. [55] determined that kaolinite had a higher PFOS sorption capacity (77.6 μg g^{-1}) than montmorillonite (54.5 μg g^{-1}), however, PFOS was observed to sorb in the montmorillonite interlayer. A study of PFAS sorption on kaolinite in water [56] found that adsorption of $\leq C_4$ molecules was not thermodynamically favourable. Clay minerals may also be modified to increase their PFAS sorptive capacity [54]; some of these modified clays are discussed in the following section on composite amendments.

Composite and Other Amendments

To improve the efficacy of soil amendments for PFAS immobilisation, composite products have been developed that comprise a variety of sorptive phases in combination. The philosophy behind composite amendments is to utilise different components exhibiting different physicochemical properties to enable multiple sorptive mechanisms for PFAS retention. Composite amendments used for PFAS immobilisation include RemBind®, RemBind Plus® and MatCARE.

RemBind® is a composite amendment, consisting of aluminium hydroxide, kaolin, and activated carbon. It is proposed that the aluminium hydroxide component of RemBind® interacts via electrostatic forces with anionic PFAS, binding the functional group. The activated carbon and organic matter components of RemBind® bind to the PFAS 'tail' through hydrophobic and Van der Waals forces. This provides a twopronged reaction mechanism for binding PFAS anions. In addition, the kaolinite and organic matter component of RemBind® provides the ability to bind cationic compounds through electrostatic interactions, regardless of the length of the CF backbone. The activated carbon component also binds PFAS cations through hydrophobic interactions. Most long-chain PFAS ($\geq C_8$) bind to activated carbon, however, smaller compounds ($\leq C_4$) may not bind efficiently as there are limited contact points with the carbon surface and Van der Waals forces are weak. In RemBind®, short-chain compounds are bound through electrostatic interactions as detailed above. RemBind Plus® [38] contains a higher quality and amount of both activated carbon and aluminium oxyhydroxides.

MatCARE^{TM}, is another composite amendment that consists of clay (palygorskite-based, an Mg-Al phyllosillicate), which has been modified with an unsaturated fatty amine (oleylamine), and also contains quartz, kaolinite, dolomite, amorphous materials and traces of NaCl [39]. It was reported to have a PFOS adsorption capacity of 0.09 mmol g^{-1}, which was higher than the activated carbon product, Hydraffin (0.07 mmol g^{-1}) from the same study [39]; however, the sorptive performance for other PFAS and environmental implication related to the use of the oleylamine modification has not been reported.

Other amendments investigated for their PFAS sorptive capacities include polymers, carbon nanotubes and nanoparticles with ligands. In an aquifer solids sorption study, the cationic polymers polydiallyldimethyl ammonium chloride (polyDADMAC) and polyamine [57] were found to increase sorption of PFSAs and PFCAs by a factor ranging from 2.0 to 6.1. For example, K_D values for PFOS increased from 1.44 L kg^{-1} for the untreated soil, to 2.94L kg^{-1} and 8.75 L kg^{-1} for polyDADMAC and polyamine respectively. It was proposed that the increase in PFAS sorption was due to the increase in carbon content, but also due to enhanced exchange interactions between the cationic polymers and anionic PFAS [57]. Similarly, a study of two polyquaternium polymers, poly-(dimethylamine-co-epichlorohydrin) and poly-(diallyldimethylamonium) in water/soil suspensions, found that PFOS was bound, predominantly in soil-polymer-PFOS complexes, with respective affinities of 9.3×10^4 and 7.3×10^4 M^{-1} [58].

PFOS sorption onto Gold nanoparticles with different combinations of dual ligands has been demonstrated by Liu et al. [59], while the adsorption of PFOA onto multi-walled carbon nanotubes (MWCNT) and MWCNT with embedded Fe, Co, Al, Mg, Mn, Fe_2O_3, Cu and Zn has been demonstrated in several studies [60–62]. Carbon nanotubes are useful sorbents due to their large surface areas; however, the cost of MWCNT is generally prohibitive relative to GAC and PAC for large scale applications.

Amendment Additions and Binding Agents

The amount of amendment added to a contaminated soil will influence treatment costs, and may also influence whether the soil is able to be reused post-treatment. Application rates for immobilisation studies included in Table 1 range from 0.1% to 30%. Soil amendments may also be added to contaminated soil in conjunction with binding agents such as cement and lime. Binders are added to reduce the hydraulic conductivity and to increase or maintain unconfined compressive strength so that it is compatible with the intended site end use. The co-addition of amendments and binders provides a two-pronged approach for minimising PFAS leaching through adsorptive and encapsulation processes, as described in "Mechanisms of Immobilisation". Binding agents listed in Table 1 have typically been added at 10% w/w, and cured for a number of months.

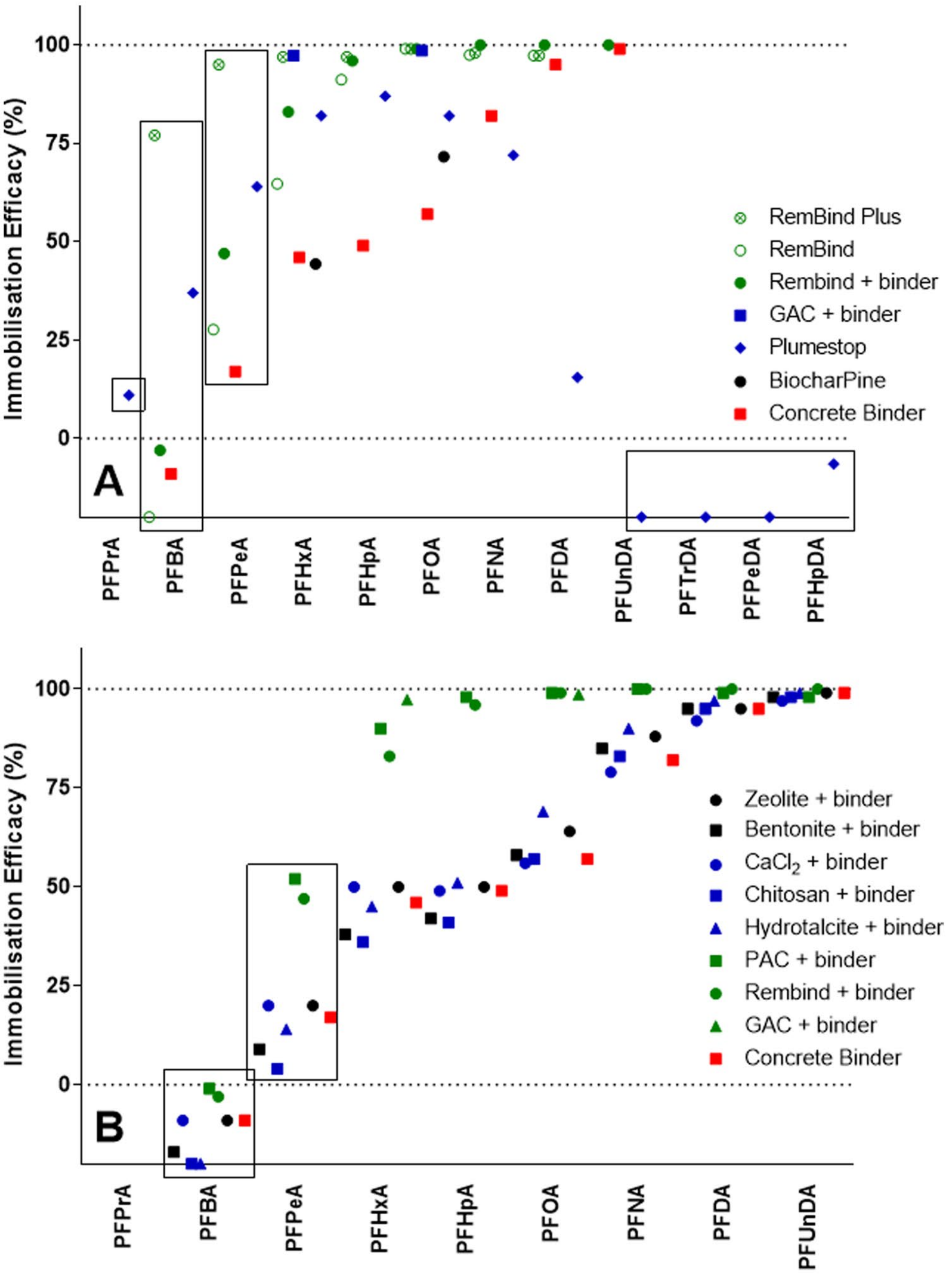

Fig. 2 Comparison of PFCA immobilisation efficacy when different amendment strategies were applied to contaminated soil. Data points may be cross-referenced with information in Table 1 to glean information on application rates, curing times and methods used for the assessment of PFAS leachability. PAC, Rembind® and RemBind Plus® [38], compost, montmorillonite [43], pine biochar [36], MatCARE^{TM} [39], PlumeStop® [34], GAC and CB [33], all other amendments with binder [42]. Points lower than -25 are shown at -25. Some results may be averages over several soil types, conditions and/or replicates, or the most realistic application rate. (**A**) Includes the activated carbon based amendments; (**B**) includes only studies involving a concrete binder

Remediation Effectiveness

A common strategy for determining immobilisation efficacy is the assessment of contaminant leaching, with a comparison between pre- and post-amendment values. Leaching assays are routinely undertaken to characterise the soil's mobile phase with data then utilised to estimate ground or surface water contamination potential. Leaching assays may also be utilised to classify waste for disposal and/or to demonstrate the effectiveness of soil amendment strategies. This may be achieved through the use of numerous leaching tests, including the Australian Standard Leaching Procedure (ASLP; AS4439-1997), Synthetic Precipitation Leaching Procedure (SPLP; USEPA method 1312), Toxicity Characteristic Leaching Procedure (TCLP; USEPA method 1311), TCLP variations (e.g. ASTM D3987-85), Multiple Extraction Procedure (MEP; USEPA method 1320) and Leaching Environmental Assessment Framework methods (LEAF; USEPA methods 1313-1316). The aforementioned leaching procedures vary in operational parameters including leaching fluid pH, buffering capacity, ionic strength, single versus multiple extractions, solid-to-solution ratio, contact time, agitation, maximum

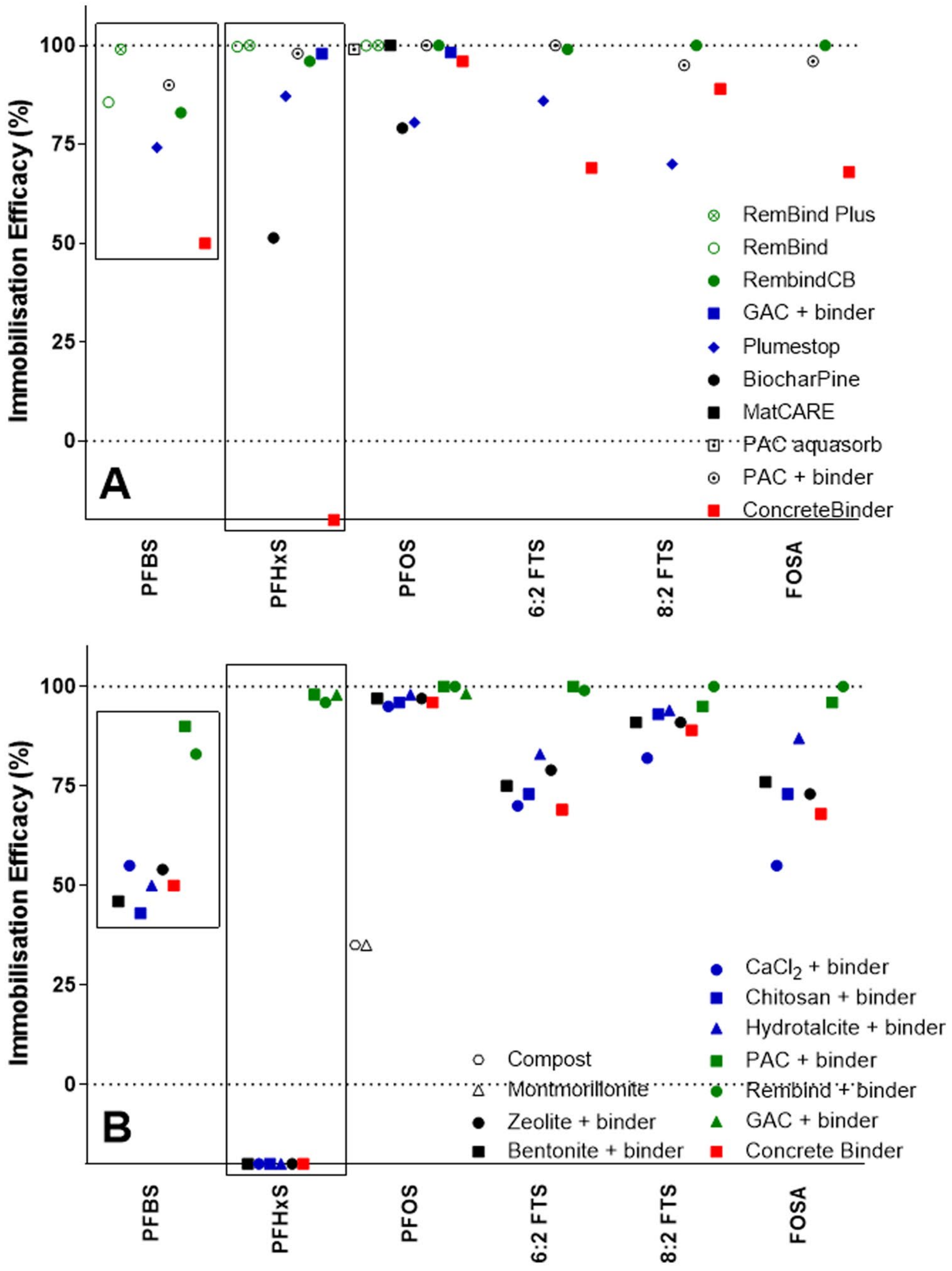

Fig. 3 Comparison of PFSA, FTS and FOSA immobilisation efficacy when different amendment strategies were applied to contaminated soil. (**A**) Includes the activated carbon based and composite amendments; (**B**) includes compost, montmorillonite and studies involving a concrete binder. Data point sources as described in Fig. 2 and Table 1

particle size, batch versus column tests; all of which will influence PFAS leachability outcomes. For example, differences in fluid pH (e.g. buffered TCLP at pH 4.93 versus unbuffered ASLP using deionised water) will influence leachability due to the impact of pH on sorption-desorption (as detailed in "Mechanisms of Immobilisation") while particle size differences (the maximum particle size for AS4439 is 2.4 mm versus 9.5 mm for TCLP) will also influence leaching outcomes due to disparities in reactive surface areas.

Notwithstanding the methodological differences between leaching assays, data from PFAS immobilisation studies (Table 1) are represented in Figs. 2 and 3 to provide an overview of immobilisation efficacy for different amendment strategies applied in both laboratory and field-based studies for PFAS varying in carbon chain length and functional group. Treatment efficacy was calculated, as in Sörengård et al. [34] by:

$$\Delta Re = \left(1 - \frac{c_{aq}^{t}}{c_{aq}^{u}}\right) \times 100 \tag{1}$$

where c_{aq}^{t} is the PFAS concentration in the leachate of the treated soil and c_{aq}^{u} of the untreated soil leachate.

Values greater than zero indicate that the amendment strategy decreased PFAS leachability compared to unamended soil with increasing values up to a maximum of 100 indicating increasing treatment efficacy up to complete immobilisation. Negative values may also be calculated whereby the addition of the soil amendment results in enhanced PFAS leachability compared to unamended soil. Negative values may also result from analytical variability particularly when PFAS concentrations are being reported near the level of quantification. Conceivably precursor transformation may influence PFAS immobilisation efficacy; however, data illustrating this is lacking due to analytical

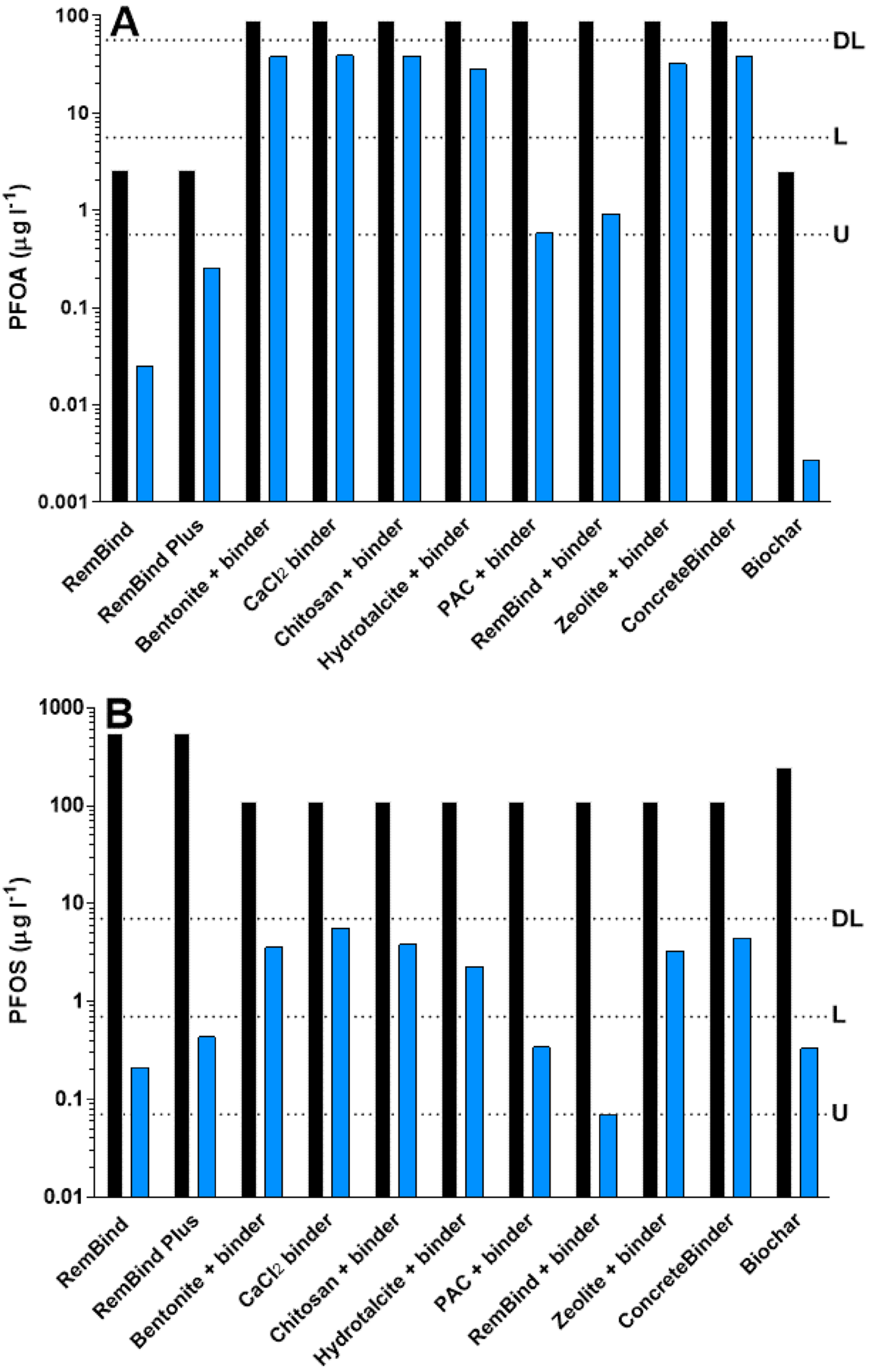

Fig. 4 Change in PFOA (**A**) and PFOS (**B**) leachability following treatment of soil with amendments (as detailed in Table 1). PFOA and PFOS leachability pre- (■) and post-amendment (🟦) is presented in the context of regulatory standards for unlined (**U**), lined (**L**) and double-lined (**DL**) landfills [63]. Amendments shown: RemBind [38], biochar [35], amendments with binder [42]

challenges associated with precursor identification and quantification. The plot of treatment efficacy, depicted in Figs. 2 and 3, provides a high-level approach for comparing data across amendment strategies. However, efficacy calculations do not reflect whether the extent of immobilisation was suitable against regulatory standards (i.e. landfill leaching criteria, water quality standards). As a result, Fig. 4a, b highlight PFOA and PFOS pre- and post-amendment leaching results in the context of regulatory standards.

As shown in Fig. 2, treatment efficacy trends were observed for PFCAs when different amendment strategies were utilised; PFAS immobilisation efficacy increased with increasing carbon chain length although some variability was observed for C_{10}-C_{14} compounds in the study of Sörengård et al. [34]. For $\leq C_6$ PFCAs, immobilisation efficacy for most treatments was <50% with the exception of three amendments incorporating activated carbon. Activated carbon amendments were highly effective at reducing leachability of $\geq C_8$ PFCAs in amended soil as exemplified by RemBind® and RemBind Plus® amendments [38]. At loadings of 25% and 15% w/w respectively, >97% reduction in leachability was observed for C_8-C_{10} PFCAs. For PlumeStop®, a decrease in immobilisation efficacy was observed for $>C_7$ PFCA possibly due to reduced hydrophobic interactions [34]. While only a limited number of studies have assessed the impact of biochar addition on PFCA leachability, Askeland et al. [36] observed increasing immobilisation efficacy with increasing carbon chain length. However, compared to activated carbon amendments, biochar appears to be less effective at reducing PFCA leachability, though further comparative studies with equivalent amendment loadings and leaching assessment methodologies would be beneficial. While the addition of bentonite, $CaCl_2$, chitosan, hydrotalcite and zeolite in conjunction with a concrete binder had little effect on treatment efficacy compared to the binder alone, the addition of activated carbon-based amendments with concrete binders enhanced immobilisation efficacy compared to binder alone, particularly for C_5-C_9 PFCAs. When immobilisation efficacy was compared between RemBind® amendments with and without the addition of concrete binders, C_5-C_7 PFCA treatment efficacy was enhanced by inclusion of the binding agent, however, this effect was not observed for longer chain PFCAs.

Immobilisation trends were less apparent for PFSAs compared to PFCAs (Fig. 3). For activated carbon-based amendments, higher immobilisation efficacy was observed for short-chain compounds (perfluorobutane sulfonic acid (PFBS) and PFHxS) compared to the equivalent carbon chain length carboxylic acids. Although some variability in PFSA immobilisation efficacy was observed for PlumeStop® [34], the remainder of the activated carbon-based amendments reduced PFSA leachability, irrespective of carbon chain length and degree of fluorination, by >80%. Limited data points are available for biochar amendments, however, similar trends were observed for PFSAs and PFCAs. Similarly, the addition of bentonite, $CaCl_2$, chitosan, hydrotalcite and zeolite in conjunction with a concrete binder had little effect on PFSA treatment efficacy compared to the binder alone [42].

Figure 4 shows PFOA and PFOS leachability pre- and post-amendment addition from selected studies, with reference to landfill regulatory guidelines [63]. In soil containing high PFOA leachability pre-treatment (~90 $\mu g\ L^{-1}$), irrespective of amendment type, leachability post-treatment was reduced to an acceptable level for soil disposal into a double-lined landfill, although for most treatments there was no advantage of adding an amendment (0.2% w/w) over the binder alone (10% w/w, Figure 4a). However, carbon-based amendments (PAC + binder, RemBind® + binder [42]) performed significantly better, reducing PFOA leachability to achieve the single-lined landfill criterion. For soil with low PFOA leachability pre-treatment (<3 $\mu g\ L^{-1}$), addition of RemBind® (25% w/w), RemBind Plus® (15% w/w) [38] and biochar (5% w/w) [35] reduced PFOA leachability to below the unlined landfill criterion. Although landfill acceptance criteria are lower for PFOS compared to PFOA, all treatments were able to reduce PFOS leachability to at least the double-lined landfill criterion (Fig. 4b). However, carbon-based amendments (RemBind® RemBind Plus® Biochar, PAC + binder, RemBind® + binder) achieved the single-lined landfill criterion at application rates ranging from 5-25% w/w.

Mechanisms of Immobilisation

A reduction in PFAS leachability occurs as a result of a number of sorption mechanisms. Sorption mechanisms are dependent on physico-chemical properties of PFAS and amendments and are influenced by the surrounding soil and environmental conditions. The following conditions will impact PFAS sorption:

1. C chain length and function group influence hydrophobic and electrostatic interactions respectively
2. Amendments may influence sorption through changes in soil pH (electrostatic interactions), by providing surfaces for hydrophobic interactions, and cation bridging.
3. PFAS adsorption studies performed on soils with varying characteristics (e.g. OC, clay, pH, anion exchange capacity (AEC) and protein) [64–70] have found that soil pH, organic carbon and clay content all play important roles in sorption through a combination of electrostatic and hydrophobic interactions [71].
4. Most PFAS have pKa<2 and thus are anions under most environmental circumstances. However, some PFAS (e.g. PFOSA, pKa 6.2-6.5), do not form anions under many circumstances [42, 72], which will impact sorption strategies based on direct electrostatic interactions.

PFAS have widely varying physico-chemical properties, and in particular, both the functional group and fluorinated C chain length affect sorption behaviour. PFAS may exist as uncharged, anionic, cationic, or zwitterionic molecules, although the most commonly observed compounds (PFOS and PFOA), both form anions. Charge differences affect sorption and desorption processes, and impacts the efficacy of soil amendments. The sulfonate functional group of PFSAs is considered to be a hard base, having higher sorption onto oxide surfaces than the soft base of the carboxylate group in PFCAs [73]. However, different amendments vary in their PFAS immobilisation efficacy due to the complex interplay of properties. Surface charge is a significant parameter, for example with anionic PFAS, sorption increases with increasingly positive surface charge [74].

Activated carbon and biochar have a number of different functional groups on the amendment surface, depending on the temperature of production, which will influence electrostatic interactions. More functional groups are present on the surface when production occurs at a lower temperature, therefore electrostatic interactions are likely to be higher; however, hydrophobic interactions may be the predominant PFAS sorption mechanism, as carbonaceous material produced at higher temperature have higher PFAS sorption capacities. pH influences will impact electrostatic interactions as an increase in pH will result in competition for sorption sites, between OH- groups and anionic PFAS [73].

PFAS octanol-water partitioning coefficients are influenced by C-chain length (e.g. PFHxA K_{OW}=3.12 versus PFOA K_{OW}=4.59 [75]), while log K_{OC} has been shown to increase by 0.6 and 0.83 with each additional fluorinated carbon for PFCAs and PFSAs respectively [67]. As such sorption efficacy of varying carbon chain length compounds to soil and soil amendments is influenced by K_{OW} through hydrophobic interactions [42, 66]. It has been reported that PFAS hemi-micelles and bilayers may form through self-aggregation on amendment surfaces [76] which is influenced by sorbent pore size, organic matter fraction, surface area and degree of carbonisation [36, 42].

In addition to electrostatic and hydrophobic interactions, PFAS may also form divalent cation bridges, with ions such as Ca^{2+} [77] and Mg^{2+}. Smaller PFAS are more likely to participate in divalent cation bridging, as observed by Campos Pereira et al. [67], potentially due to their shorter C-F tail, which makes them less hydrophobic, and subsequently less likely to sorb via hydrophobic interactions. Carbon nanotubes (CNT) with a variety of metal cations (Co, Mn, Mg and Al) on their outer and inner surface were found to enhance PFOA sorption by a factor of 6 compared to CNT containing inner surface Fe as a consequence of enhanced electrostatic interactions [60]. In addition, ligand exchange may occur between the carboxyl group of PFCAs and hydroxyl groups on metal oxides [76], forming inner sphere complexes via covalent metal-ligand bonds.

Compared to anionic PFAS, fewer sorption studies have been undertaken on cation, zwitterionic and neutral PFAS [42]. A study on cationic and zwitterionic PFAS sorption in soils [78], found that sorption of these compounds was non-linear, in contrast to anionic PFAS, however, electrostatic and hydrophobic interactions were the predominant mechanisms controlling PFAS sorption. Cationic PFAS sorption was correlated with soil organic matter content and was reversible. In contrast, sorption of zwitterionic

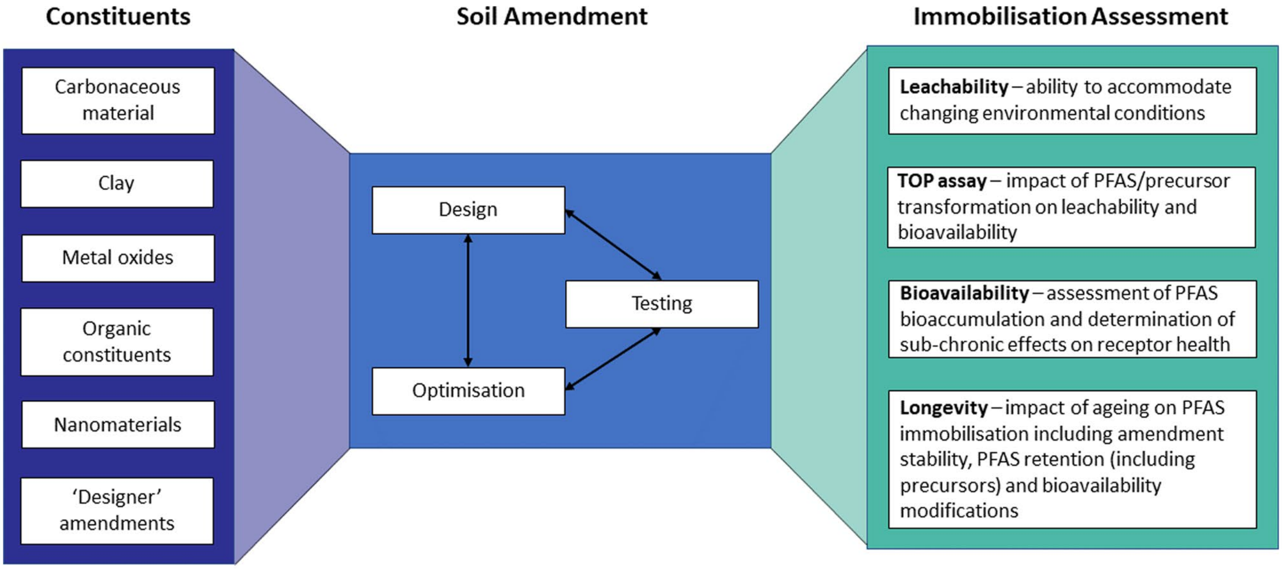

Fig. 5 Assessment framework for the design, optimisation and validation of PFAS immobilisation efficacy and longevity

PFAS was hysteretic rather than reversible and was hypothesised to be due to entrapment in porous structures present in inorganic soil components [78]. Differences in behaviour between cationic and zwitterionic PFAS highlight the necessity of further studies to assess the influence of soil amendments on PFAS fate and transport and immobilisation efficacy.

When binding agents are utilised, encapsulation also contributes to the decrease in PFAS leachability. Although the addition of cement binders may raise the pH to around 10 [42], thereby decreasing the impact of electrostatic interactions, the decrease in surface area and reduction in hydraulic conductivity of stabilised/solidified material results in reduced PFAS leachability.

Conclusions and Future Research Needs

As detailed in "Remediation Effectiveness", a common approach for assessing the efficacy of PFAS immobilisation is the use of leaching methodologies (e.g. SPLP, TCLP, ASLP). These approaches are simplistic, however, differences in operational parameters may restrict true comparison of immobilisation efficacy between treatments and studies. In addition, these approaches for the assessment of PFAS immobilisation utilise operationally defined procedures which may generate methodological artefacts, such as perceived enhanced contaminant mobility via colloidal generation [79–81]. Water-dispersible naturally occurring colloids are generated as a result of vigorous shaking during the batch extraction process or by leaching under elevated pH. Colloids exhibit high specific surface area and charge, which are effective sorbents for PFAS. Although an understanding of colloidal facilitated mobility of PFAS is limited, this transport mechanism has been shown to be significant for other contaminants of concern including metal(loid)s, mono-aromatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides [82–87]. The use of the Leaching Environmental Assessment Framework (LEAF) [88] may overcome some the aforementioned limitations as the framework incorporates a number of standardized testing methods (including assays to assess pH dependency, liquid:solid dependency, percolation and mass transfer) and generic or application-specific release models. In addition, the LEAF overcomes single-point leaching tests that assess a specific environmental scenario and can accommodate defined particle sizes and monoliths (i.e. minimized colloidal generation) which are relevant for solidified materials.

Post immobilisation assessment should provide further consideration to the influence of aging and environmental factors on long-term immobilisation efficacy. Limited studies have assessed immobilisation stability over extended timeframes, however, PFAS immobilisation longevity was demonstrated in RemBind® amended soil following a 3-year aging period [38]. Although small increases in PFAS leachability (ASLP) were observed in aged samples when 2 month and 3-year leachability data was compared, PFAS leachability after 3-years was reduced by >99% compared to unamended soil. Additional studies like this are needed to elucidate the long-term effect of soil amendments on PFAS immobilisation. However, a limiting factor for ageing studies is the timeframe required to assess longevity. Conceivably, wetting and drying (at elevated temperature) cycles could be introduced into protocols as a means to accelerate ageing processes. This may provide indicative information regarding the impact of ageing on immobilisation stability although interpretation of data may be confounded by the difficulty in replicating natural ageing processes in the laboratory [89].

Transformation of PFAS and/or precursor compounds may potentially occur post-treatment via biotic and abiotic oxidation processes. Although little research has been undertaken to investigate the rate and extent of post-immobilisation transformation, the total oxidisable potential (TOP) assay [90] may provide an approach for quantifying transformation. However, as the name suggests, the assay quantifies the impact of oxidation on PFCA formation, although it fails to elucidate timeframes for such processes. Nevertheless, this information may provide a worst-case scenario for PFAS immobilisation stability. In the aforementioned 3-year RemBind ageing study [38], it was proposed that the minor increase in PFAS leachability in aged immobilised soil may have resulted from the generation of labile PFCAs through precursor compound transformation, however, it is conceivable that minor increases in PFAS leachability may have also resulted from immobilising agent breakdown. For some soil amendments with organic modifications (e.g. amine-modified clays), constituents may be utilised by the indigenous microflora as a carbon and energy source, thereby potentially impacting amendment integrity and PFAS sorption. The stability of these and other soil amendments has not been assessed in the context of PFAS sorption and retention; further assessment of this is required to ensure long-term stability of PFAS immobilised soil.

While leaching tests are utilised to understand the leaching profile of immobilised soil and/or determine the regulatory acceptability of stabilised material for disposal, data generated from these methods do not provide information regarding the influence of soil amendments on PFAS biological exposure and impact. If PFAS leachability can be reduced to below the criterion for unlined landfills, conceivably immobilised soil could remain on site; in such a case, other assessment methodologies (i.e. bioavailability assessment) would be required to ensure stabilised material was environmentally benign. Conceivably, leaching approaches may provide a conservative estimate of labile/exchangeable PFAS available to plants, however, other release mechanisms may be pertinent for ecological receptors facilitated by oxidative processes (of precursor compounds or immobilising agent) and/or pH changes (e.g. in gut environments). However, limited studies have been undertaken whereby changes in PFAS bioavailability (e.g. decrease in PFAS bioaccumulation) as a result of amendment application have been quantified. Bräunig et al. [38] reported that PFAS bioaccumulation in *E. fetida* decreased by 74-98% following immobilisation of a soil with 25% w/w RemBind®, although earthworm weight loss was reported, presumably due to decreased nutrient availability. These potential ecological impacts require further investigation in addition to the assessment of potential sub-chronic health effects including oxidative stress, DNA damage and reproductive issues.

Due to the variability in physicochemical properties of legacy and replacement PFAS (e.g. ADONA, GenX), a single agent may not be adequate/suitable to immobilise all compounds of concern in impacted soil. As such, soil amendments may need to be tailored to site-specific conditions. To drive future PFAS soil amendment research and development, a robust assessment framework is essential to elucidate not only immobilisation efficacy but longevity of immobilisation processes. The schematic framework detailed in Fig. 5 provides key assessment components required to test and validate the efficacy, longevity and biological impact of amendments for PFAS immobilisation in soil. This information is critical to provide a lines-of-evidence approach for the application of sustainable, cost-effective, immobilisation strategies to minimise the impact of PFAS on environmental health.

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Declarations

Conflict of Interest The authors declare that they have no conflict of interest.

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