



Review on Methods for Assessing and Predicting Leaching of PFAS from Solid Matrices

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Abstract

Purpose of Review Per- and poly-fluoroalkyl substances (PFAS) are prevalent environmental contaminants detected in materials such as soils, biosolids, and wastes. Understanding PFAS leaching is crucial for assessing risks associated with leaving impacted material in place, reuse, or disposal. However, there is limited guidance on laboratory methods to measure extent and rate of leaching. This review aims to identify the best methods for assessing PFAS leaching that are reflective of relevant release scenarios.

Recent Findings Various methods have been applied to assess PFAS leaching from contaminated materials. The most common are batch leaching methods that simulate particular conditions (e.g. rainfall, landfill), with the intention of providing conservative estimates (worst-case scenarios) of cumulative PFAS release over time. Columns, static leaching, and rainfall simulators are also used to simulate less aggressive field-like conditions. While less common, pan and suction lysimeters have been used to measure PFAS leaching in situ. Most methods use saturated conditions that do not account for the possible influence of air–water interface accumulation and wetting–drying cycles on leaching. A notable gap is the scarcity of data benchmarking laboratory-leached concentrations with real-world PFAS concentrations. Establishing this relationship is crucial for reliable laboratory protocols.

Summary This article reviews methods for estimating leaching of PFAS from contaminated materials. Given the variety of methods, selecting those that best simulate assessment objectives is essential. Specific scenarios requiring PFAS leaching assessment, such as leaving materials in place, reuse, and disposal, are discussed. The knowledge gaps presented could be used to improve existing leaching methods for better predictions and understanding of PFAS leachability.

Keywords PFAS · Leaching · Contaminated soils · Wastes · Biosolids · Desorption

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Introduction

Per- and poly-fluoroalkyl compounds (PFAS) are a large group of complex and diverse fluorinated organic contaminants that vary in their physical and chemical properties. Many PFAS associated with contaminated land and water are known for their amphiphilic nature, surface-activity, and stability [1, 2]. PFAS have been used over several decades as surfactants incorporated into various processes and products, such as firefighting foams, stain- and water-resistant products, and protective coatings. Their widespread use and persistence have led to increasing levels of contamination in the environment, necessitating management of large volumes of diverse materials contaminated by PFAS. However, limited knowledge on their fate and environmental risks contributes to uncertainties in environmental management for both contaminated sites and pollution prevention. For example, this uncertainty can result in loss of opportunities for material reuse and push to a costly and unsustainable approach, where affected materials are either removed and stockpiled awaiting further action [3] or landfilled leading to the loss of the resource value of the soil or other materials. To determine risks associated with release of PFAS from contaminated materials under environmental scenarios, the potential for leaching needs to be assessed.

Leaching refers to the transfer of sorbed chemicals or contaminants from a solid material into a contacting solution. In the environment, leaching following rainfall can occur from materials on or in the ground, potentially resulting in contamination of adjacent soils and/or surrounding groundwater and surface water. The potential for a chemical to leach, i.e. how fast and how much is leached are controlled by different interactions and mass transfer processes. Several leaching methods have been developed to assess the mobility of inorganic and organic chemicals from diverse solid materials, including contaminated soils, stabilised soils, biosolids, concrete, and other waste materials. These methods aim to simulate the leaching behaviour of contaminants under specific field scenarios.

Scenarios relevant to leaching from solid materials can be broadly grouped into (1) site investigations (in situ mobility assessment) to inform whether material can reasonably remain in situ or needs to be treated or disposed, (2) waste classification to determine what level of controls on landfilling is required, (3) assessing risks if material is reused/repurposed in a different location, and (4) assessment of treatment technologies or remediation outcomes, for example, immobilisation in soil using amendments or in concrete using sealants. For instance, hazardous waste classification is typically guided by legislated regulations and varies for different jurisdictions—Toxicity Characteristic Leaching Procedure (TCLP, USEPA 1311 [4]) is used in the US,

while the Australian Standard Leaching Procedure (ASLP-AS4439.3 [5]) is used in Australia. In the absence of more PFAS-specific tests and guidance, these methods that are originally designed for waste classification, however, tend to get used for other purposes such as site investigations, assessing waste management options, and improving material properties for reuse. However, these methods are not designed to simulate the specific conditions relevant to PFAS mobility. Soil structure and air–water interfacial accumulation significantly influence PFAS mobility [6, 7], yet these factors are not adequately addressed by traditional methods. Many methods available, such as batch and packed column methods, disrupt soil structure and are typically carried out under saturated conditions, rendering them unsuitable for in situ PFAS investigations. For instance, batch shaking and column methods completed under saturated conditions demonstrate high PFAS leachability from soils [8]. However, at AFFF-contaminated sites, PFAS predominately persists in the topsoil despite years of discontinued use [6], highlighting the inadequacy of these methods for scenarios that require in situ investigations. Therefore, alternative methods that can simulate these scenarios are needed. More broadly, understanding the applicability and limitations of the methods currently available is crucial for choosing methods that meet assessment objectives.

This review examines the scientific literature for current methods used to assess leaching of PFAS from contaminated materials with a view to (a) determine the suitability of available methods for assessing leaching under different scenarios and (b) identify key knowledge gaps that are important in understanding leaching of PFAS from solid materials and achieving better assessment/predictions of its release.

Leaching Methods

Table 1 summarises documented leaching methods used in PFAS studies, with examples of their application. These methods differ in their leaching mechanisms, with batch methods aiming to achieve equilibrium (or near equilibrium) conditions at the end of leaching, while column and diffusion-type methods focus on the kinetic aspects of leaching. Most methods are standard approaches originally developed for compliance testing, specifically to determine whether contaminants, particularly inorganic contaminants, leached from waste within regulatory thresholds. Another group of methods can be categorised as characterization tests, intended to enhance our understanding of leaching behaviour and mechanisms. A significantly smaller number of methods focus on in situ leachability for on-site verification. Further details regarding their use in PFAS studies are discussed below.

Table 1 Summary of leaching methods applied for assessing PFAS leaching from contaminated materials

Leaching methods		Assessment and related studies		Application*
Standard/ conventional approaches	Batch leaching			
	AS4439.3:2019: Australian Standard Leaching Procedure	ASLP	PFAS leaching behaviour from AFFF-contaminated soils: [8] Performance of sorbents in treated soils: [9, 10]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	British standards EN12457-1–4: Compliance test for leaching of granular waste materials and sludges	EN2457-1–4	Performance of sorbents in treated soils: [11–15]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	DIN 19529: Leaching of solid materials—batch test for the examination of the leaching behaviour of inorganic and organic substances at a liquid to solid ratio of 2 L/kg	DIN 19529	PFAS leaching behaviour from soils without known local PFAS source: [16]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	USEPA 1311: Toxicity characteristic leaching procedure	TCLP	Performance of sorbents in treated soils: [17]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	USEPA 1312: Synthetic precipitation leaching procedure	SPLP	Performance of sorbents in treated soils: [18]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	USEPA 1313: Leaching Environmental Assessment Framework (LEAF), liquid solid partitioning as a function of extract pH using a parallel batch extraction procedure	LEAF 1313	Performance of sorbents in treated soils: [9, 18]	Conservative (leaching over a range of pH, extended time) Saturated conditions Disturbed (crushed material)
	USEPA 1316: LEAF, Liquid–solid partitioning as a function of liquid–solid ratio using a parallel batch extraction procedure	LEAF 1316	PFAS leaching from AFFF-contaminated soils—comparison with expected leaching utilising an equilibrium-based partitioning equation employed by regulatory agencies to establish soil screening levels: [19]	Conservative (leaching over a range of L/S ratios, extended time) Saturated conditions Disturbed (crushed material)
	SW 846 USEPA 1320: Multiple extraction procedure	MEP 1320	Performance of sorbents in treated soils: [10, 18]	More conservative (leaching over extended time) Saturated conditions Simulate changes in pH Disturbed (crushed material)
	Non-standard	Batch shaking, variable conditions	PFAS leaching behaviour from impacted materials in AFFF-contaminated soils [20]; understand factors affecting sorption/desorption using uncontaminated soils [21–23] sediments [24], sludge [25], humic acids [26, 27], sorbents [28, 29]; performance of sorbents in treated soils: [30–32]	Conservative (leaching over extended time) Saturated conditions Disturbed (crushed material)
	Column leaching			

Table 1 (continued)

Leaching methods		Assessment and related studies	Application*
Standard	USEPA 1314; LEAF, Liquid–solid partitioning as a function of liquid–solid ratio for constituents in solid materials using an up-flow percolation column procedure	LEAF 1314 PFAS leaching behaviour from AFFF-contaminated soils—understand release kinetics: [8]	Conservative (leaching over a range of contact rates L/S) Kinetics Saturated conditions Disturbed (packed columns) or intact (cores)
Non-standard	Saturated packed-column leaching	PFAS leaching behaviour from impacted soils—understand release kinetics in AFFF-contaminated soils [33–38] Performance of sorbents in treated soils: [39, 40] Understand effects of remediation practices on PFAS leaching: [37, 41]	Conservative (leaching over a range of contact rates L/S) Kinetics Disturbed (packed columns)
	Saturated intact-core leaching	Simulate PFAS in situ leaching: [42•]	Conservative (leaching over a range of contact rates L/S) Kinetics In situ leaching Saturated conditions Intact (cores)
	Unsaturated/variably saturated column leaching	Simulate PFAS leaching under cold climatic conditions and infiltration: [34] PFAS leaching behaviour from biosolid-amended soils [43]	Conservative (leaching over a range of contact rates L/S) Kinetics Unsaturated/variably saturated conditions Disturbed (packed columns)
	Unsaturated/variably saturated intact-core leaching	PFAS leaching from biosolid-amended soils, with and without biochar treatment: [44]	Less conservative (leaching over a range of contact rates L/S) Kinetics Unsaturated/variably saturated conditions Intact (cores)
	Other leaching methods		
Standard	USEPA 1315; LEAF, Mass transfer rates of constituents in monolithic or compacted granular materials using a semi-dynamic tank leaching procedure	LEAF 1315 Performance of stabilisation/solidification for PFAS: [15]	Conservative (leaching over time) Kinetics Saturated conditions Intact (monoliths) or disturbed (packed columns)

Table 1 (continued)

Leaching methods	Assessment and related studies	Application*
Non-standard	PFAS leaching from AFFF-contaminated soils: [45•] Performance of sorbents in treated soils: [40]	Conservative (leaching over time) Kinetics Saturated conditions Disturbed (crushed/packed material)
Static leaching	PFAS leaching behaviour from impacted soils—simulate in situ leaching: [42•]	Simulates in situ leaching (point-in-time) Saturated conditions Disturbed (Crushed material)
Tray leaching—irrigation/rainfall simulation	Performance of stabilisation/solidification for PFAS: [15, 46] PFAS leaching behaviour from impacted soils and treated soils—simulate 1-in-100 year storm events: [47] PFAS leaching behaviour from AFFF-contaminated concrete: [48–50]	Conservative estimate of leaching and/or runoff Variable saturation; Wetting and drying cycles Intact (monoliths) or disturbed (packed columns)
In situ leaching	Long-term PFAS leaching monitoring (pan lysimeter): [51] Combined plant uptake and leaching (pan lysimeter): [52] Performance of sorbents in treated soils (~ pan lysimeter): [40] Monitoring of PFAS from bio-solid-amended soils (pan lysimeter): [53] Assessing role of air–water interfacial sorption on release of PFAS from AFFF-impacted soils (suction lysimeter): [54, 55] Soil in situ flushing (suction lysimeter): [56]	In situ leaching (point-in-time) Variable saturation; Wetting and drying cycles Intact or disturbed (packed systems)

* Application considers the following: leaching extent/rate estimated, conditions of test (saturated vs unsaturated vs wet/dry), and material form/type

Table 2 Test specification for Australian and European leaching methods (US methods are continued in Table 3)

Standard test	Australian Standard Leaching Procedure, ASLP ^a [5]	German standard ^d [57]	British standards
	AS4439.3	DIN 19529	EN 12457-1 [58] EN 12457-2 [59] EN 12457-3 [60] EN 12457-4 [61]
Description	Standard method developed to determine the contamination potential of groundwater with COPC ^c from liquid and solid wastes, soils, sediments, and sludges in a variety of disposal-to-land scenarios	Standard method used for assessing the leaching behaviour of inorganic and organic substances from solid materials. It is relevant in environmental testing, quality control, and compliance with regulations	Compliance test used to provide information on leaching of granular wastes and sludges under the experimental conditions
Solid material	Wastes, sediments, soils, sludges	Wastes, sediments, soils, sludges	Granular waste materials, sludges with high solid content, and monolithic waste materials with specific dimension
Target constituents	Metals and non-volatile compounds	Inorganic and organic substances	
Test description	Batch leaching with agitation	Batch leaching with agitation	One-stage batch test One-stage batch test Cumulative two-stage batch test
Leaching time	18 ± 2 h	24 h	24 ± 0.5 h 24 ± 0.5 h 6 h (1st stage) 8 h (2nd stage) 24 ± 0.5 h (cumulative)
Particle size	< 2.4 mm	< 2.4 mm	< 4 mm (without or with size reduction) < 4 mm (without or with size reduction) < 10 mm (without or with size reduction)
Eluent volume (L to S ratio)	20:1	2:1	2:1 10:1 2:1 (1st stage) 8:1 (2nd stage) 10:1 (cumulative)
Solid mass	100 g (or less if < 2.4 mm particle size)	100–500 g	175 g 90 g 90 g
Eluent composition	Acetate buffer, sodium tetraborate buffer, or unbuffered aqueous solutions (depending on relevant landfill type) ^b	Reagent water	Distilled water, demineralised water, de-ionised water or water of equivalent purity (5 < pH < 7.5) with a conductivity of 0.5 mS/m, or HNO ₃ 0.1 mol/L
Number of test fractions	1	1	1 1 2 1
Agitation	End-over-end rotation at 30 ± 2 rpm	Overhead agitator	End-over-end tumbler (5–10 rpm) or roller-table inducing rotation of the bottle at about 10 rpm
Assay	pH of fluid used, final pH of leachate, and COPC ^c		pH and COPC ^c
Filtration	Filtration through a 0.6 to 0.8 µm glass fibre filter ^a	Filtration	Filtration at 0.45 µm

Table 2 (continued)

Standard test	Australian Standard Leaching Procedure, ASLP ^a [5] AS4439.3	German standard ^d [57] DIN19529	British standards EN 12457-1 [58] EN 12457-2 [59] EN 12457-3 [60] EN 12457-4 [61]
Leaching QA/QC	A single leaching test for each sample plus duplicate test portions from selected test samples at a rate not less than one duplicate leach in every 10 test portions or one duplicate leach for each batch of samples		Blank tests shall be carried out. A 0.95 L volume of leaching solution is submitted to the whole procedure

^aASLP, specific instructions for PFAS: if PFAS retention onto filters is > 10%, centrifugation is recommended, smaller sample size allowed, albeit maximum sample size must always be used where possible; using fit-for-purpose containers

^bFor landfill acceptance, PFAS NEMP 2.0 specifies use of both pH 5 and unbuffered reagent water (approximating 'worst-case' for leaching conditions) [3]

^cContaminants of potential concern

^dSpecifications only added where information was accessible from published studies

Batch Methods

Batch methods have been widely used to study leaching from PFAS-contaminated materials, particularly in contaminated soils, and soils treated with sorbents. In these approaches, solid material is subjected to a shaking process with an aqueous leaching solution for a specified period (typically 18–24 h) and liquid to solid ratio (L/S, from 0.5 to 20). During this process, the material is mechanically broken down and dispersed, particularly at higher L/S values. These short, typically single step methods are frequently employed as a conservative measure of leaching over extended time (versus leaching at a particular point in time).

Standard Methods

Most studies that assessed the leachability of PFAS have used conventional batch methods, which are standardised and have been used for regulatory compliance (see Table 1). The conditions simulated in these methods are summarised in Tables 2 and 3. The methods typically simulate a single leaching condition using 'reagent water' as leaching solution and just differed in the L/S used. On their own, the short timeframes and high reproducibility of these single step leaching methods can be very useful for their original purpose, which is for compliance (e.g. acceptance of waste in landfills) and similar scenarios. However, these methods do not provide information on leaching rates or concentrations at specific points in time that are crucial for understanding risk and transport dynamics.

While most standard batch methods simulate a single leaching condition, there are other approaches that consider multiple leaching conditions that provide more context of test results obtained from a single-step method. Some of these methods that have been used to assess PFAS leaching include the multiple extraction procedure (MEP, USEPA 1320 [67]), the Leaching Environmental Assessment Framework (LEAF) method 1313 [63], and method 1316 [66]. MEP involves extractions similar to the synthetic precipitation leaching procedure (SPLP, USEPA 1312 [62]) but completed 10 times. This simulates leaching that a sample may undergo from repetitive precipitation. Suggested to simulate over 1000 years of leaching in acid rain conditions in an improperly designed landfill, this method has been used for long-term performance testing of stabilised soils [3, 9, 18]. LEAF, an integrated suite of USEPA methods [68], also encompasses approaches that simulate various leaching conditions. Among the four methods, LEAF 1316 was used to determine PFAS leachability across varying L/S ratios to determine how well laboratory leaching assessments compared to leachability-based

provisional soil cleanup target levels [19]. LEAF 1313 method, which involves leaching at multiple pH values (2–12), has been used in PFAS studies to provide more insights on PFAS behaviour under varying pH conditions. Findings from various studies indicate that pH can influence the leachability of PFAS, with a more pronounced impact on long-chain PFAS (e.g. ≥ 6 perfluorinated carbons for perfluorosulfonates and ≥ 7 for perfluorocarboxylates) from soils compared to short-chain PFAS [9, 18, 42]. However, in comparison to metals and metalloids, for which these methods were originally developed, the mobility of PFAS is not solely influenced by pH [8, 69].

Most studies on PFAS employed modified standard methods (i.e. based on a comparison of the conditions stipulated in the standard methods with those described in the leaching studies). The most common modification is reduction of the solid mass used for leaching (e.g. leaching 2 g of sample instead of 100 g) while maintaining the L/S ratio. Other modifications include (a) use of dried samples instead of field-fresh samples (as prescribed in DIN 19529 [13]) for storage and preservation [16], (b) reduction in particle size of material to improve homogeneity in samples [13], (c) changes in chemistry of leaching solution to investigate effects of different electrolytes on leaching (e.g. [10]), (d) changes in extraction times to reach equilibrium [13], (e) subsampling over time to evaluate leaching rates [15], and (f) changes to containers used and leachate collection steps [17]. While most are driven by the study objectives (e.g. investigate the effect of electrolytes), the implications of these modifications when it comes to interpretation and decision making are unclear. For example, most standard methods recommend leaching using large amounts of solids (i.e. 20–500 g depending on particle size) to ensure subsampled material is representative of the material to be leached. This precaution is particularly crucial when dealing with bulk solid materials like construction and building materials, as using smaller mass of subsamples may result in a non-representative assessment of the contaminated material.

Non-standard Methods

Non-standard batch shaking methods have been used to investigate leaching from contaminated soils, to investigate sorption (and desorption) of PFAS from soils, sediments, sludge, humic acids, and sorbents and to assess performance of sorbents in treated soils (Table 1). For studies that investigated leaching from contaminated and remediated soils, some used leaching conditions that were similar to standard leaching procedures (i.e. ASLP) [20, 30]. For the studies assessing performance of remediation materials [32], conditions could also be based on standard methods, e.g. in reagent water, albeit for 7 days at 7 L/kg. These non-standard conditions could very well have been

driven by the objective of the assessment. In the study by Söregard et al., longer extraction times were possibly chosen to attain equilibrium conditions in the leaching assessment for PFAS-contaminated soil treated with colloidal activated carbon [32].

To understand mechanisms governing mobility of contaminants, sorption–desorption studies are typically undertaken based on OECD guidelines where a dilute salt solution is used as a background electrolyte for sorption and desorption [70]. Other conditions, i.e. L/S ratio and extraction times, however, are different from standard batch leaching methods (Tables 2 and 3) as these are typically determined following OECD guidelines [21–28, 31]. While not exactly applied to leaching of contaminated waste materials, this approach has been used in the prediction or estimation of contaminant leaching [70].

As anticipated, results from batch shaking experiments reveal that PFAS leaching is dependent on perfluorocarbon (CF_2) chain length and functional head group, particularly for PFAS with $\text{CF}_2 \geq 6$, and properties of the material (e.g. soil properties [71]). Differences in leaching for shorter chain PFAS are generally less pronounced, especially under conditions simulated by standard methods. PFAS, particularly anionic PFAAs, could be expected to be leached more from sandy soils than from soils with higher clay or OC contents (e.g. [69, 71]). Leaching is also affected by the surrounding pH, especially for long-chain PFAAs [9]. Leaching of long-chain PFAAs with $\text{CF}_2 \geq 6$ from soil was found to increase with an increase in pH, with the highest number and concentrations of PFAAs observed at pH above 9 (LEAF 1313), albeit this condition is not commonly found in the natural soil environment. On the other hand, leaching of short-chain PFAAs ($\text{CF}_2 < 6$) was higher and was not pH dependent. Zwitterionic and cationic PFAS, which exhibit higher soil sorption, are anticipated to leach less, albeit there are only very few studies that have covered these PFAS. More work on these polyfluorinated PFAS is required given that these have been reported to represent a large proportion of PFAS present at some AFFF-contaminated sites in the US [72]. Because of the rigorous leaching procedure involving end-over-end shaking and high L/S ratios extended over 24 h, these batch methods are frequently employed to replicate worst-case scenarios for leaching, such as waste disposal or extreme rainfall events. As such, the methods have been valuable in assessing the effectiveness of treatment techniques, such as soil stabilisation/immobilisation, as already applied in a few studies with RemBind [9, 10, 30], activated carbon [18, 32], biochars [18, 31, 73], and combined with solidification [15, 46]. Considering the nature of these methods, they should not be expected to replicate field conditions, where the matrix structure plays a significant role.

Table 3 Test specification for US leaching methods. (Continued from Tables 2)

Standard test	Leaching Environmental Assessment Framework, LEAF		Multiple extraction procedure, MEP				
	pH-dependent liquid solid partitioning	Rates of mass transfer Semi dynamic tank leaching		L/S-dependent liquid solid partitioning			
Toxicity characteristic leaching procedure, TCLP [4]	Synthetic precipitation leaching procedure, SPLP [62]	Percolation column	USEPA 1313 [63]	USEPA 1314 [64]	USEPA 1315 [65]	USEPA 1316 [66]	USEPA 1320 [67]
USEPA 1311	USEPA 1312	USEPA 1314 [64]	USEPA 1313 [63]	USEPA 1314 [64]	USEPA 1315 [65]	USEPA 1316 [66]	USEPA 1320 [67]
Description	Standard method designed to assess impact of landfilled waste to underlying groundwater.	Standard method to simulate the conditions of acidic precipitation where rainwater may pass through the waste and carrying soluble materials into the groundwater.	A leaching evaluation system with four leaching methods, data management tools, and scenario assessment approaches. It can be used individually or together to describe release of COPCs ^a . The methods have been designed to consider the effect of key environmental conditions and waste properties on leaching.		Standard method designed to simulate the leaching that a waste will undergo from repetitive precipitation.		
Solid Material	Liquid, solid, and multiphase samples	Liquids, soils, and wastes	Solid waste matrices - wastes, treated waste (solidified/stabilised soils and sediments), secondary materials (blast furnace slags), energy residuals (coal fly ash air pollution control residues), industrial processing residuals (mining and mineral processing wastes, and contaminated soils and sediments)		Liquid, solid, and multiphase samples		
Target Constituents	Organic and inorganic species	Organic and inorganic species	Inorganic, non-volatile, and semi-volatile organic species		Inorganic, non-volatile, and semi-volatile organic species		
Test Description	Batch leaching with agitation	Batch leaching with agitation	Parallel batch extraction as a function of pH	Saturated column test in up-flow mode	Tank test with periodic eluant renewal	Parallel batch extraction as a function of L/S	Repetitive batch extraction with agitation
Leaching Time	18 +/- 2 h	18 +/- 2 h	24, 48, 72 h (dependent on max particle size)	Based on flow rate -total test duration ~10 days	0.08, 1, 2, 7, 14, 28, 42, 49, 63 days (cumulative leaching time)	24, 48, 72 h (dependent on max particle size)	24 h each extraction -10 days in total
Particle Size	<9.5 mm	<9.5 mm	< 0.3, 2.0, or 5mm (85% by mass)	< 2 mm (85% by mass); <5mm (100% by mass)	Monolith: 40 mm cylinder or cube; Compacted granular: cylinder with 40 mm minimum height	< 0.3, 2.0, or 5mm (85% by mass)	< 9.5 mm; Monolith: 3.3x7.1 cm
Eluent Volume (L:S ratio)	20:1	20:1	10:1	L/S varies with percolation time	Liquid-surface area ratio of 10mL/cm ²	L/S of 10, 5, 2, 1 and 0.5 mL/g dry	20:1
Solid Mass	100 g	100 g	20, 40 or 80 g per extract depending on sample particle size; 400 g required pre each test and test replicate	600 g per column	1400 depending on packed density	25 to 500 g per extract depending on L:S ratio; 900 g required for per test and test replicate	100g

Table 3 (continued)

Standard test	Leaching Environmental Assessment Framework, LEAF				Multiple extraction procedure, MEP
	Toxicity characteristic leaching procedure, TCLP [4]	Synthetic precipitation leaching procedure, SPLP [62]	pH-dependent liquid solid partitioning	L/S-dependent liquid solid partitioning	
USEPA 1311	Acetic acid buffer pH 2.9 or 4.9, depending on alkalinity of waste, and reagent water	Unbuffered acid mixture (60/40 weight % of H ₂ SO ₄ /HNO ₃) with pH 4.2 or 5.0, and reagent water	USEPA 1312	USEPA 1313 [63]	USEPA 1320 [67]
USEPA 1314	Acetic acid buffer pH 2.9 or 4.9, depending on alkalinity of waste, and reagent water	Unbuffered acid mixture (60/40 weight % of H ₂ SO ₄ /HNO ₃) with pH 4.2 or 5.0, and reagent water	USEPA 1315 [65]	USEPA 1316 [66]	USEPA 1320 [67]
Number of Test Fractions	1	1	9	5	1
Agitation	End-over-end rotation at 30±2 rpm	End-over-end rotation at 30±2 rpm	None	End-over-end rotation at 30±2 rpm	End-over-end rotation at 30±2 rpm
Assay	pH of fluid used, final pH of leachate and COPC ^a	pH of fluid used, final pH of leachate and COPC ^a	None	End-over-end rotation at 30±2 rpm	pH of fluid used, final pH of leachate and COPC ^a
Filtration	Filtration through a 0.6 to 0.8 µm glass fibre filter	Filtration through a 0.6 to 0.8 µm glass fibre filter	Settling/Centrifugation; filtration at 0.45 µm	Method blanks should be tested on the extremes of acid and base additions as well as reagent water	Centrifugation, separation
Leaching QA/QC	A minimum of one blank (using the same extraction fluid as used for the samples) must be analysed for every 20 extractions that have been conducted in an extraction vessel A matrix spike shall be performed for each waste type A minimum of one matrix spike must be analysed for each analytical batch.	A minimum of one blank (using the same extraction fluid as used for the samples) must be analysed for every 20 extractions that have been conducted in an extraction vessel A matrix spike shall be performed for each waste type A minimum of one matrix spike must be analysed for each analytical batch.	At least one eluant blank should be tested. If multiple batches of the eluant are employed, one eluant blank from each batch should be analysed	Method blanks including eluant and sample contact surface (e.g. bottle without solid material but with eluant, filtration and analytical sample preparation process) should be tested	One blank per sample batch to test the quality of the reagent or container

^aContaminants of potential concern

Column Methods

Compared to batch methods, column methods are considered less aggressive and are often assumed to provide a closer approximation of leaching under field conditions than provided by batch shaking tests. In general, column methods are designed to evaluate release of chemicals under either local equilibrium or advection conditions as a function of time or L/S and include hydrodynamic dispersion of solutes during perfusion [74]. When the flow rate through the column is low, local equilibrium conditions are typically assumed to govern constituent release while at higher flow rates, column testing aims to determine rates of constituent leaching during advective mass transport. For PFAS, column methods have been used to investigate leaching and transport from contaminated soils and from soils amended with biosolids, to assess effectiveness of sorbents in treated soils, and to understand implications of groundwater remediation activities such as biosparging and in situ chemical oxidation on PFAS release (Table 1). Most of these studies were carried out in packed columns under saturated conditions and did not conform to standard methods. LEAF 1314 (Table 2) is the only standard column method we identified to have been applied to studying leaching of PFAS (e.g. [10]). In this method, reagent water or a dilute calcium chloride solution is introduced to moderately packed columns with granular material through continuous upward flow to minimise air entrainment and flow channelling. Flow rate is slow (0.5–1.0 L/S per day) to increase likelihood of equilibrium between the solid and liquid phases. Other studies had very similar conditions and varied in the number of leachate fractions collected (up to 100 pore volumes) or L/S, where longer run times and higher L/S may be needed for assessments of PFAS soil immobilisation [40], and used different leachate solutions (e.g. artificial groundwater at varying pH and ionic strength) to investigate effects of solution chemistry on leaching [38].

The results from the column studies agree with observations in batch experiments, where longer CF_2 chains are more retained than shorter chain PFAS. However, disparities in leaching patterns among PFAS with different chain lengths are more apparent in the column studies than in the batch experiments, especially for shorter chain PFAS. While shorter chain PFAS like PFBA appeared to be readily displaced by longer chain PFAS resulting in fast elution, shorter chain PFAS could still be retained in the soil in the absence of long-chain PFAS [33]. This is quite different from results of batch studies where short-chain PFAS are readily leached. While most studies only report on anionic PFAS, a few soil column studies have reported on leaching of polyfluorinated precursors, particularly

zwitterions. In general, PFAAs were found to be released more rapidly than their polyfluorinated precursor counterparts [36]. Nickerson et al. found that zwitterionic PFAS displayed behaviour akin to long-chain anionic PFAS, showing strong retention to soil [38]. However, the mobilisation of zwitterionic PFAS increased as a function of soil pH. In a different study, Nickerson et al. found that biosparging creates conditions conducive to the transformation of certain polyfluorinated PFAS, leading to the release of more persistent PFAS from saturated soils [37].

Most PFAS column studies have been undertaken under saturated conditions. However, considering the strong interfacial properties of some PFAS, it is crucial to acknowledge the role of the air to water interface in controlling leaching, particularly in column leaching under unsaturated conditions. For example, the air to water interface has been reported to significantly enhance retardation of PFOS and PFOA in unsaturated sand columns [7, 75]. Despite this importance, column leaching under unsaturated or variably saturated conditions has been limited in PFAS studies. Høisæter et al. investigated PFAS leaching under cold climate conditions and infiltration during snow melt using packed soil columns [34]. The authors observed strong attenuation of PFOS in the unsaturated zone, with the attenuation rate increasing over time. Similarly, packed soil columns were utilised to study effects of weathering and aging on release of PFAS from biosolid-amended soils/sand over time with natural precipitation [43]. While these studies are conducted under unsaturated or variably saturated conditions, these unsaturated packed columns may still not be ideal for simulating field conditions due to potential alterations in soil structure. Instead, intact cores under unsaturated conditions, such as those used to study leaching of PFAS from biosolid-amended soils over time, with and without biochar treatment [44], may offer a more suitable approach. In addition to understanding PFAS leaching under unsaturated conditions, these methods could also aid in understanding PFAS evapoconcentration and upward flux, which has been suggested to occur in situ when prolonged periods of evapotranspiration (wicking effect) exceed rainfall [6•].

Alternative unsaturated column methods that could be used to study PFAS leaching include methods developed by Brusseau [7], Lyu et al. [75], and Abraham et al. [76] to investigate sorption/retention of PFAS in unsaturated environments. While not suitable for routine use due to their specialised set-up, required equipment, and/or lack of standardisation, these methods have shown potential to achieve steady-state water flow and uniform distributions of water saturation under unsaturated conditions, unlike the unsaturated columns that have been used for PFAS leaching studies.

Considering the complexity and logistical difficulty associated with column experiments (e.g. soil packing, leachate

collection, and long elution times for clayey soils) and the simplicity and accessibility of batch methods, establishing the relationship between these modes of leaching would be useful. For example, work by Lopez Meza et al. compared leaching of inorganic contaminants under batch and column conditions and established conservative interpretation protocols to allow extrapolation from batch data where column data are not available [74]. Leaching assessments comparing results from batch and column methods have yet to be reported for PFAS-contaminated materials. Similar extrapolations would be useful where information on kinetics is not of interest as column methods are time-intensive and batch extraction methods are still more accessible.

Alternative Leaching Methods

Other methods used to assess PFAS leaching include continuous batch leaching (also called infinite sink or tank leaching), static leaching, rainfall simulations (also called ponding or wash-off experiments), and lysimeters (Table 1). These approaches provide a less conservative estimate of PFAS release (than batch shaking methods) with the aim of simulating conditions close to the field. Among the methods we found, LEAF 1315 is the only standard method.

Continuous Batch/Infinite Sink/Tank Leaching

A departure from traditional batch shaking methods is the continuous batch or infinite sink leaching. Unlike typical batch shaking approaches, this method allows for repeated sampling and continuous desorption, making it valuable for investigating PFAS release over time. This approach has been used to study kinetics of PFAS release from contaminated soils [45•] and those that have undergone immobilisation [15, 40]. Schaefer et al. performed these continuous batch experiments for up to 400 h to determine PFAS desorption kinetics from field-aged soils [45•]. Bierbaum et al. use this method to study the release of PFAS from untreated, sorbent-treated, and solidified soils, over 100–180 days [40]. In these experiments, leaching was facilitated by horizontal shaking at lower L/S (2.5–5), as opposed to end-over-end shaking, and higher L/S (10–20) typically used in batch shaking experiments. Data obtained from this method allowed quantification of desorption rates and cumulative desorbed mass. Slightly different from this is the semi-dynamic tank leaching test (LEAF 1315) that was used by Söregård et al. [15], which is conducted without shaking. The authors used LEAF 1315 to optimise stabilisation/solidification treatment parameters (e.g. additive, binder, binder to soil ratios) and understand leaching of PFAS from the solidified material, which cannot be adequately assessed through batch shaking/leaching experiments. The

authors found good correlation ($p < 0.001$) between results obtained from laboratory (batch leaching EN-12457–1 and LEAF 1315) and pilot scale tests that simulated multiple rain events. While valuable for comparing different treatments, from the perspective of estimating worst-case scenario leaching, this tank leaching approach may not be entirely conservative for concrete. Recent studies have suggested that incorporating wetting and drying cycles can result in significantly greater leaching from concrete cores compared to continuous wet conditions in a tank (see discussion on concrete leaching below—*ponding experiments*). Hence, the application of tank leaching methods may be limited to release assessments consistent with completely saturated conditions.

Static Leaching

A static leaching procedure was developed by Rayner et al. that aimed to better simulate point-in-time leaching and movement of PFAS for intact soils [42•]. Among the methods the authors tested, the saturate-and-spin method (L/S of 3) was found to best represent leaching for in situ soils (leaching from an intact core). This approach could be ideal for assessments that aim to simulate point-in-time field conditions and not worst-case scenarios or cumulative leaching over extended periods.

Rainfall Simulation/Ponding/Wash-off Experiments

Release of PFAS with rainfall/irrigation has been assessed in a few studies on soil [15, 47] and concrete [48–50]. Assessments with contaminated soils have been undertaken using large, packed trays that were then subjected to artificial irrigation or rainfall (tap water). The intensity of the simulated rainfall events varied depending on the study objectives. For instance, Söregård et al. introduced rainfall at rates equivalent to 15 mm/day over 6 months to simulate more than 6 years of natural irrigation [15]. On the other hand, Richardson et al. used more intense events (~1500 mm/day over 6 days) to simulate a 1-in-100-year storm event [47]. Depending on the tray configuration, it is possible to collect surface runoff alongside leachates, allowing investigation of this process as another route for PFAS transport [47]. This is particularly important because replicating surface runoff may not be feasible with many of the currently employed methods. Furthermore, embedded in this method are wetting and drying cycles that occur with each rain event which could be used to investigate PFAS evapoconcentration and upward flux phenomenon [6•]. However, a drawback of this method is its scale, which requires a significant amount of material to conduct such tests.

For concrete, release of PFAS with ponding, rainfall, and wash-off has been investigated on contaminated and sealed

concrete cores [48–50]. This one-dimensional static leaching approach involves repetitive addition of static water to the top surface of the concrete core to assess PFAS release kinetics with multiple ponding events, rain events, or consecutive firefighting training exercises. Data from the successive leaching events with multiple wetting and drying cycles enabled modelling of the leaching kinetics and forecasting of PFAS release from the surface. This study observed PFAS evapoconcentration due to the wicking effect, where each drying period led to new release of PFAS from the concrete core with subsequent rainfall/runoff event. This ongoing replenishment of PFAS at the concrete surface leads to greater leaching compared to assessments conducted under completely saturated conditions (e.g. LEAF 1315), indicating that this method provides a more conservative estimate of leaching from concrete than a tank leaching test.

Lysimeters

Lysimeters are devices/tools that have been used to enable in situ measurements of PFAS leaching. Such measurements have been conducted using pan and suction lysimeters in a few studies involving pilot investigations into long-term leaching of PFAS (5 years), combined simulations of leaching and plant uptake (8 years), PFAS behaviour in agricultural soils (120 days), PFAS in AFFF-contaminated sites and biosolid-amended soils, and investigation of PFAS behaviour during in situ soil flushing (Table 1). The difference between pan and suction lysimeter lies primarily in the manner leachates are collected. Pan lysimeters (also called zero-tension lysimeters) are reservoirs installed in the ground to collect leachates that percolate down via gravity through saturated soils. These were used to investigate natural PFAS leaching as influenced by precipitation, irrigation, and gravitational drainage over an extended period [51, 52]. A similar set-up was also used, albeit smaller scale, to assess leachability of PFAS following immobilisation treatments under variably saturated conditions [40] and leaching of PFAS from biosolid-amended soils with or without biosolids blending with mulch [77]. Conversely, suction lysimeters (also sometimes called sampling, porewater, or rhizon lysimeters) rely on suction or tension to collect pore water. These were used in studies occurring on shorter timescales requiring consistent sampling under controlled pressures to investigate PFAS leaching under field conditions [54] and during in situ soil flushing [56]. Schaefer et al. used this approach to compare PFAS concentrations in porewaters of collected unsaturated soil samples with those in porewaters obtained using field-deployed porous suction cup lysimeters [55]. This comparison aimed to better understand the relationship between these two methods in informing PFAS accumulation at air–water interfaces. Indeed, the ability to measure point-in-time PFAS leaching from undisturbed soil

in the field and subjected to natural and variable moisture changes is a valuable feature of lysimeters for in situ investigations. In the study by Gassman et al., lysimeters enabled modelling of the behaviour of PFAS in soil [52] which suggested the potential formation of desorption-resistant/non-extractable PFAS residues (> 90% of the PFOA and PFOS) over 8 years. In the context of in situ soil flushing, Schaefer et al. reported that such desorption-resistant fractions exist and that this increases with PFAS hydrophobicity [56]. This suggests that PFAS can persist in soil for a long time, despite appearing to leach readily in batch assessments, which further underscores why batch shaking tests should not be used to estimate in situ leaching. Despite the advantage of directly assessing contaminant leaching with lysimeters, factors such as variability (especially for undisturbed soil lysimeters), accuracy (in the case of pan lysimeters), installation challenges, and representativeness (as restricted by depth and size of lysimeter) preclude widespread use for contaminated site assessment [78]. Variations in results from suction lysimeters have also been observed between porewaters extracted from environmental samples and those obtained from lysimeters deployed in the field [55]. However, these may not be an issue in cases where the site is filled with ‘homogeneous’ material (e.g. placement of immobilised soils back to ground). In the absence of field leaching guidance, lysimeters remain useful for comparison with laboratory-based leaching methods which are still scarce in the PFAS literature. The study by Schaefer et al. offers a valuable starting point [54]. The authors noted that while batch desorption results tended to overestimate PFAS porewater concentrations compared to lysimeter data, incorporating air–water interfacial accumulation led to more accurate predicted concentrations, particularly for PFOS.

Multiple Leaching Methods Approach

While most studies use one leaching method, a growing number of studies have used multiple leaching methods, simulating different leaching conditions. For example, in the studies assessing robustness of immobilisation in soils treated with sorbents [9, 10, 18], a combination of approaches (e.g. SPLP, ASLP, LEAF 1313, LEAF 1314, and/or MEP) were used to investigate the effect of varying pH conditions, repeated rain/leaching events, temperature, ionic strength, and/or effect of competing ions. Such comprehensive assessment demonstrated robust immobilisation of treated soils under aggressive leaching conditions (i.e. ASLP, LEAF 1313, and MEP). The use of leaching methods of varying scale, flow, and saturation conditions was also assessed in a few studies on soil immobilisation [15, 40] and to understand role of air to water interfacial sorption on PFAS leaching [54]. In the context of soil immobilisation,

Table 4 Examples of scenarios requiring a leaching assessment and relevant methodologies

Description	Scenario 1		Scenario 2		Scenario 3		Scenario 4	
	Site investigations		Waste classification to determine landfilling controls, i.e. landfilling of impacted material		Risk evaluation for material reuse or repurposing, i.e. reuse of impacted material		Remediation assessments (e.g. soil immobilisation, concrete sealing)	
Specific objective (example)	To predict mobility to assess risk of immediate impacts. For example, to understand impacts to human drinking water or comparison with an aquatic guideline value, from soil or concrete left in situ	To predict mobility for assessment of long-term risks. For example, to understand load that could contribute to bioaccumulation and redistribution of PFAS in the environment over an extended period, from soil or concrete left in situ	To assess downgradient risks to drinking water (e.g. using a dilution attenuation factor)	To assess downgradient risks to drinking water (e.g. using a dilution attenuation factor)	To assess PFAS that can be released over the lifetime of the landfill	To assess downgradient risks to drinking water (e.g. using a dilution attenuation factor)	To determine effectiveness of treatment over a long-period of time	
Material structure	Intact	Intact	Disturbed	Disturbed	Disturbed	Disturbed	Disturbed	
Assessment required	Point-in-time leaching	Conservative—leaching over extended time (long-term load)	Point-in-time leaching	Point-in-time leaching	Conservative—leaching over extended time	Point-in-time leaching	Conservative	
Relevant methods	Lysimeters Static and intact core leaching (e.g. [42•]) For concrete monoliths: ponding/wash-off experiments (e.g. [48–50])	Intact core leaching (e.g. [42•]) Column leaching (e.g. LEAF 1314) Batch leaching (e.g. SPLP, ASLP, MEP, LEAF 1313, LEAF 1316)	Static leaching (e.g. [42•]) For concrete monoliths: LEAF 1315	Static leaching (e.g. [42•]) For concrete monoliths: LEAF 1315	Batch leaching (e.g. ASLP, MEP, LEAF 1313, LEAF 1316) For concrete monoliths: LEAF 1315	Static leaching (e.g. [42•]) For concrete monoliths: LEAF 1315	Batch leaching (e.g. SPLP, ASLP, MEP, LEAF 1313, LEAF 1316) For concrete monoliths: LEAF 1315	

adopting a variety of testing strategies can provide multiple lines of evidence in assessing efficacy of chosen sorbent treatment. In broader terms, this approach enables a more in-depth understanding of the release behaviour of PFAS from contaminated materials and provide site owners and regulators a high level of confidence of effectiveness under different release scenarios. The methods employed allow for an assessment of the extent (magnitude) and rate of leaching, under conservative to more realistic conditions (e.g. batch to lysimeters).

Application of Leaching Methods

Reliability of Leaching Methods for PFAS

It should be noted that while several standard leaching methods are available, the majority of these methods have only been validated for inorganic contaminants [79–81] and equivalent work for PFAS is lacking. While some studies have adapted existing leaching protocols for PFAS, there remains a critical need for systematic validation and standardisation of leaching methods specifically tailored to PFAS compounds to ensure accurate and reliable measurement of leachability. For example, the LEAF set of methods was originally designed to simulate factors that control release of inorganics, such as pH [68]. However, leaching of PFAAs is not solely governed by pH [8, 69]. This underscores the importance of validating existing methods and developing tailored leaching approaches that address the unique properties and behaviour of PFAS (e.g. interfacial accumulation). The validation process should encompass a comprehensive assessment of factors influencing PFAS leaching efficiency, such as sample matrix composition, pH, temperature, and contact time. Furthermore, interlaboratory comparisons are essential along with establishing the relationship between laboratory data and field measurements. It is worth noting that the latter may face additional challenges due to the absence of widely accepted standardised methods for measuring field leaching of PFAS. Therefore, in the absence of fully validated methods, a degree of uncertainty in interpreting results from lab leaching may need to be accepted, while recognising that they still provide a valuable line of evidence.

Method Selection for PFAS Leaching Assessment Across Different Scenarios

Leaching assessments may be performed to simulate certain environmental conditions in line with study objectives, which then dictates the appropriate methods to use. Below, different scenarios are outlined, accompanied by recommendations for suitable leaching methods (Table 4). This list is not meant to be exhaustive, but rather a demonstration of how a leaching method could be selected based on the

objective. While the main emphasis is on soil, separate discussions address unique considerations for materials such as concrete, which may require monolith testing.

Scenario 1: Site Investigations

For site investigations, one could envision undertaking a leaching assessment to (a) predict mobility to assess risk of immediate impacts, for example, to understand impacts to human drinking water or comparison with an aquatic guideline value, from soil or concrete left in situ, and (b) predict mobility for assessment of long-term risks, for example, to understand load that could contribute to bioaccumulation and redistribution of PFAS in the environment over an extended period, from soil or concrete left in situ. In scenario 1a, the material structure will remain intact and point-in-time concentrations being mobilised are relevant. In scenario 1b, the structure will also remain intact but in this case, the long-term load of PFAS released is relevant.

For both scenarios, current batch leaching procedures (e.g. SPLP, ASLP, MEP) will likely be conservative, especially as the soil structure and air to water interface is destroyed and contact between water and soil pores is expected to be much greater than the real-world situation for intact soils. Current column methods also may be conservative due to saturation of the soil column and disruption of the soil structure when homogenising and packing soils in columns. For scenario 1a, this conservatism will be particularly pronounced and may be too conservative for practical application. In this case, the static leach test being developed (e.g. [42•]) may be useful for reducing the degree of conservatism but requires further development. In some cases, field lysimeter testing might be useful but is resource intensive and application and interpreting results have not yet been standardised. For scenario 1b, the conservative approach might have value for some regulatory purposes but be less helpful for estimation of actual risks.

For solid materials in scenarios 1a and 1b, such as concrete, batch monolith procedures may also not be truly representative, but it is harder to predict if leaching measurements will be over- or under-conservative. Recent studies indicating the variability of PFAS concentrations in concrete and potential for preferential transport pathways [81] are unlikely to be well-replicated in small monoliths. For intact concrete, predicting risks might be better informed by simple field wash-off tests and may not be onerous to perform [48–50]. However, it would be useful to have a better understanding of whether field wash-off testing is likely to be conservative or under-conservative compared to real-world precipitation events (or other relevant conditions, e.g. washing vehicles).

Scenario 2: Waste Classification

For classifying waste for disposal, leaching assessments are typically completed to (a) assess downgradient risks to drinking water (e.g. using a dilution attenuation factor) and (b) assess PFAS that can be released over the lifetime of the landfill. In scenario 2a, the material structure will be disturbed, and point-in-time concentrations being mobilised are relevant. In scenario 2b, the structure will be disturbed and the long-term load of PFAS released is relevant, i.e. where regulation is based on total load on PFAS that can be released over the lifetime of the landfill.

For scenarios 2a and 2b, disturbing soil structure for testing may be reflective of processes occurring for the situation being simulated (removal, transport, and re-emplacement of soil). A static leach test may provide a less conservative estimate of point-in-time leaching for scenario 2a. Current batch procedures (ASLP, MEP) are also well-aligned to these situations, especially for scenario 2b, where conservatism is justified due to the extreme persistence of some PFAS. LEAF 1313 testing over a range of pH values remains well-suited to where there is potential for changing conditions over time, such as in landfill.

For solid materials in scenarios 2a and 2b, such as concrete, monolith testing is valuable (LEAF 1315). For 2a, where point-in-time concentrations is desired, time series data from monolith testing will be informative. For 2b, total loads extracted over time could be useful.

Scenario 3: Risk Evaluation for Material Reuse or Repurposing

For reuse and repurposing, site specific objectives may govern which protocols are more useful. For example, assessment of downgradient risks to drinking water, similar to 2a, could be undertaken. For this scenario, static leach testing could provide a less conservative estimate of point-in-time leaching, while current batch tests also suit, albeit more conservative.

Scenario 4: Treatment Technology and Remediation Assessments (e.g. Soil Immobilisation, Concrete Sealing)

For assessing the efficacy of amendments for immobilising PFAS in soil, conservative batch procedures are useful. These are particularly appropriate noting that long-term immobilisation performance under field conditions has yet to be demonstrated, so using conservative leaching approaches provides additional confidence when using these techniques. Studies to date have shown that a variety of amendments perform well, even under the exaggerated leaching conditions of these tests [9, 10, 18, 32]. Similar arguments may apply for sealants to minimise PFAS egress from PFAS-impacted

concrete. Therefore, LEAF 1315 monolith testing is useful though it is worth noting that systematic data evaluating such products is not yet available.

In summary, there are certain situations where currently available methods are well-suited, but other situations where current methods may be over-conservative or the relevance to real-world conditions is not well-understood. Understanding study objectives, especially for contaminated land regulation or waste management, is important to choosing the most relevant methods.

Summary, Recommendations, and Key Knowledge Gaps

Leaching of PFAS in the scientific literature has mostly been assessed following standard batch methods. In these studies, leaching assessments were conducted to investigate leachability of PFAS from contaminated materials (e.g. soils, sediments, biosolids, concrete) and to understand the general leaching behaviour of PFAS. Other studies have conducted leaching assessments to gauge treatment effectiveness aiming to determine the viability of remediation methods (e.g. sorbents, sealants). Leaching studies are mostly under saturated conditions and closer to field conditions are less common. This is likely due to the complexities, higher costs, longer time requirements, and lack of standardisation associated with methods such as columns, intact cores, and tray leaching. While these are not directly representative of field leachates collected from lysimeters, data collected from these methods are useful in estimating leaching when managed in the field, given the use of lysimeters themselves which have their own challenges with respect to installation, site selection, homogeneity, etc. None of the methods currently used have been validated for PFAS, which then raises a question regarding their reliability for estimating leaching of PFAS under a given condition. In the absence of validated methods, interpreting lab leaching results may entail uncertainty, yet they still offer valuable evidence.

It is also evident that leaching scenarios simulated in the literature are often limited. Most PFAS leaching studies tend to focus on worst-case scenarios or rely solely on single batch leaching methods. Compliance methods like ASLP, which are primarily designed for waste classification, have been applied to scenarios that require conservative leaching estimates and where the long-term release of PFAS is relevant. While this is appropriate in most cases, uncertainties may also arise from variations in environmental/exposure conditions (e.g. pH, redox potential, salinity, organic matter amount and composition, temperature, water content), material heterogeneity, or the generation of large volumes of contaminated material over time. In this context, when conditions differ from those

simulated in the compliance method and a more tailored (i.e. site specific) assessment is required for full scientific understanding, a tiered leaching approach akin to LEAF is recommended [68, 82]

While leaching methods are available, there is a need to further develop methods that account for the unique properties of PFAS, improving predictions and understanding of PFAS leaching from contaminated materials. Some of the key gaps that need to be addressed with respect to leaching methods are described below.

- Methods used to assess PFAS leaching are not validated. Considerable empirical evidence is emerging indicating a disconnect between behaviour observed using batch extraction methods (i.e. high leachability of PFAAs), and results from published studies showing PFAS residue can remain concentrated in the vadose zone for a long time [6•]. Standardisation of field measurements is also needed to better understand how laboratory data corresponds to real-world field data. From the point of view of method robustness, this could involve interlaboratory comparisons, mass balance analysis, investigating effects of sample preparation on leaching, etc. Furthermore, the validations should also consider the implications of different method modifications typically adopted by researchers (e.g. mass used, drying of samples) on leaching results. The approach used by USEPA to validate the LEAF test may be an example worth emulating [79, 80, 83].
- Methods that account for the possible influence of the PFAS accumulation at the air to water interface (under unsaturated conditions) and surfactant-like properties on leaching of PFAS need to be developed. Accumulation of PFAS at the air to water interface has been reported to be a significant contributor to the retention of PFAS in sandy soils. Furthermore, recent studies have alluded to occurrence of PFAS wicking during wetting and drying cycles. Leaching methods that already incorporate these effects (e.g. unsaturated columns, rainfall simulations) provide a good starting point to develop methods suitable for routine assessments.
- Most studies on PFAS leaching focus on soils, with a limited number investigating other solid matrices like concrete, asphalt, biosolids, and other organic materials. Similar to soils, the composition of these samples can significantly influence PFAS leachability. However, there is a notable gap in understanding the influence of sample chemistry for other solid matrices. Future research efforts should be directed toward understanding PFAS behaviour in bulk contaminated wastes such as concrete, asphalt, and biosolids, which are present in large volumes and can exist in forms that may differ from soil. Leaching methods and guidance that account for differences in material attributes will also be important.

- Current ‘worst-case’ scenario assessments rely on protocols simulating single leaching conditions (e.g. SPLP, MEP) that generally do not account for factors that could change in a material over time (i.e. aging and weathering). In some instances (e.g. concrete), a saturated system may not even necessarily provide a worst case. While this approach is widely used at present, it is crucial to improve the guidance to consider prospective environmental changes that could unfold over centuries or millennia and broad range of solid matrices of interest. In today’s dynamic environmental context, climatic conditions and variables like pH and soil salinity can swiftly shift. To ensure robust and forward-looking assessments, researchers should develop tools and models that can adapt to evolving environmental conditions and diverse nature of impacted materials.

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Declarations

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