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Guidelines for PFAS assessment

Recommendations for the uniform nationwide assessment of soil and water contamination and for the disposal of soil material containing PFAS

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Guidelines for PFAS assessment – Recommendations for the uniform nationwide assessment of soil and water contamination and for the disposal of soil material containing PFAS

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1 Background

In recent years, an increasing number of cases of damage by and contamination with organic fluoride compounds (per- and polyfluoroalkyl substances - PFAS) in soil and water bodies have come to light.

As early as 2006, the (illegal) application of contaminated organic waste mixtures and soil conditioners on farmland in the Hochsauerland area in the German federal state (Land) of North Rhine-Westphalia was identified as a key pathway for exceptionally high levels of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) found in the Ruhr region. The subsequent intensive exploration of the issue revealed that, throughout Germany, the causes of soil and water contamination with PFAS are diverse and the cases numerous. One of the most extensive cases, for example, is in Bavaria, where PFOA has been detected in soil, groundwater and surface water samples taken from an area covering 230 km^2 around an industrial estate hosting fluoropolymer producers and users.

In Baden-Württemberg, PFAS contamination was detected for the first time in 2013, in a well supplying drinking water to the city of Rastatt. Subsequent investigations found that soils and groundwater were contaminated with PFAS in the regions of Rastatt, Baden-Baden and Mannheim. It is assumed that the PFAS contamination was caused by mixtures of paper sludge and compost that were applied to farmed land over a period of several years. In the central and northern Baden region a mosaic of sites totalling several hundred hectares are contaminated with PFAS, in some instances substantially.

However, across Germany many cases of PFAS contamination of soil and groundwater are linked primarily to the use of fire-fighting foams containing fluorine during firefighting operations and training exercises, and to the use of process materials containing PFAS in industrial facilities, e.g. in electroplating and textile finishing.

In view of the significant environmental impacts, the German Conference of Environment Ministers (Umweltministerkonferenz – UMK) issued a request in late 2016 for a report on the scale of environmental impacts attributable to PFAS. The report was published in late September 2017 under the title “Bericht zu perfluorierten Verbindungen; Reduzierung/Vermeidung, Regulierung und Grenzwerte, einheitliche Analyse- und Messverfahren für fluororganische Verbindungen” (report on perfluorinated compounds, reduction/prevention, regulation and limit values, uniform analysis and measurement procedures for fluoroorganic compounds)[1].

In parallel, the Conference of Environment Ministers resolved that the federal and state governments should elaborate uniform standards governing the assessment and remediation of soil and groundwater contamination and the disposal of PFAS-containing material. To this end, and at the request of the German Working Groups on Soil Protection (LABO) and on Water Issues (LAWA) of the Federal States and the Federal Government, an ad hoc working group (PFC working group) was established that involved representatives of the federal and Land governments[2]. The working group developed the present guidelines. It also identified research requirements and set these out in a separate position paper.

The relevant enforcement authorities in the federal states (Länder), e.g. in Bavaria and Baden-Württemberg, have already gained more in-depth experience with PFAS-related issues on the basis of their own assessments and recommendations. Experience to date has shown that robust enforcement is,

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[1] https://www.umweltministerkonferenz.de/umlbeschluesse/umlaufBericht2017_19.pdf (German only)

[2] Representatives of the Bund-/Länderarbeitsgemeinschaft Bodenschutz (LABO), Bund-/Länderarbeitsgemeinschaft Wasser (LAWA), Bund-/Länderarbeitsgemeinschaft Abfall (LAGA – working group on waste) and Bund-/Länder-Arbeitskreis Abwasser (BLAK Abwasser – working group on sewage) contributed.

in principle, viable on the basis of a preliminary assessment toolbox. What has been lacking up to now, however, is the presence of uniform regulations across Germany.

Both large- and small-scale inputs of PFAS into the environment, from the most varied sources, can impact directly on the drinking water supply and agricultural production. Water utilities face substantial costs for water treatment, with the result that water charges must be increased, while farmers can no longer market their products or have to modify their production processes.

Large-scale contamination gives rise to further problems in relation to the designation of zones for construction and the handling of excavated soil that is contaminated. This in turn affects the provision of landfill capacity – an issue that remains unresolved in many locations.

However, the impacts and extent to which the public is affected vary greatly from region to region, depending on input sources, the patterns of PFAS distribution and the scale of the contamination.

With relatively small-scale contamination, remedial action can generally be taken. Where contamination is more widespread, reasons of proportionality often limit remedial action; in such situations, damage management takes priority.[3] Nevertheless, this can involve major costs for the federal states, for instance for urgently required studies and research projects serving precautionary consumer protection or further regional development “despite damage”.

These guidelines provide an evaluation framework as well as relevant background information for assessments. Their primary purpose is to assist enforcement authorities in their evaluation of PFAS inputs into water bodies and soil. The guidelines also provide benchmarks for evaluating study findings and for taking decisions on further action required where soil or water contamination is identified.

Derogations from these recommendations can be expedient when assessing specific cases. It should be noted that, as a general principle, these guidelines cannot be a substitute for assessments prescribed by national or European law.

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[3] German Environment Agency (2020): Remediation management for local and wide-spread PFAS contaminations https://www.umweltbundesamt.de/sites/default/files/medien/5750/publikationen/2020_11_11_texte_205_2020_handbook_pfas.pdf

2 Introduction

Throughout these guidelines the abbreviation PFAS, which is commonly used internationally, is used instead of the abbreviation PFC (poly- and perfluorinated chemicals) more commonly used in Germany.

PFAS do not occur naturally in the environment but are of anthropogenic origin. Currently, several thousand compounds belong to this group of substances[4]. A common feature shared by all PFAS is the presence of fully (per-) or partly (poly-) fluorinated aliphatic carbon chains with a functional group.

Due to the many different applications of these chemicals, the pathways of their input into the environment are highly diverse. Perfluorinated PFAS are extraordinarily stable in the environment, where they practically do not degrade. This is why their presence is no longer limited to contaminated sites; traces of these substances can be detected everywhere in the environment (ubiquitous), including at locations remote from industrial sites. Most PFAS are polyfluorinated substances. These can degrade under environmental conditions to perfluorinated carboxylic and sulfonic acids and are therefore also referred to as precursors.

These guidelines are concerned with PFAS that have more than three fluorinated C-atoms. PFAS are subdivided into long-chain or short-chain compounds as they have different chemical properties. According to an OECD definition[5], long-chain compounds include all perfluoroalkyl carboxylic acids (PFCA) with eight and more perfluorinated carbon atoms (i.e. beginning with perfluorooctanoic acid – PFOA) and all perfluorosulfonic acids with six and more perfluorinated carbon atoms (i.e. beginning with perfluorohexane sulfonic acid – PFHxS). The name of a substance frequently indicates the number of carbon atoms.

Long-chain PFAS are persistent and bioaccumulative. In the human body, long-chain PFAS can bind to proteins in the blood, liver and kidney. Compared to other chemicals, long-chain PFAS are excreted very slowly and can therefore accumulate in the body. The transmission of long-chain PFAS from mother to child during pregnancy and the breastfeeding period is a particularly critical aspect. Elevated PFOA and PFOS concentrations in human blood can suppress the effectiveness of vaccinations, increase susceptibility to infections, cause elevated cholesterol levels and lead to reduced infant birth weight. Long-chain PFAS are detectable in breast milk and in human blood in the general population. According to the European chemicals regulation REACH (see Annex II.1), some of these compounds are classified as substances of very high concern.

Long-chain perfluorinated carboxylic and sulfonic acids were increasingly substituted in the various applications by complex, mostly polyfluorinated compounds which act as precursors. Their degradation products – mostly short-chain perfluorinated compounds – are just as poorly degradable as the long-chain perfluorinated molecules. Because of their low adsorptive propensity, short-chain PFAS are not retained to the same degree in the soil and thus contaminate groundwater and raw water more rapidly. In contrast, long-chain PFAS such as perfluorooctane sulfonic acid (PFOS) or perfluorodecanoic acid (PFDA) are usually washed out of soils very slowly. Groundwater contamination thus often only occurs years or decades after soil exposure, e.g. after spreading PFAS-containing material on land. This applies particularly if these materials contain precursors that take time to break down into persistent PFAS degradation products (see Section 4.1).

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[4] http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

[5] http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutPFAS/Figure1-classification-of-per-and-polyfluoroalkyl-substances%20-PFAS.pdf

Short-chain PFAS, in particular, can be absorbed by plants and thus enter the food chain. No specific transfer factors have yet been identified for the soil-plant pathway. With a few exceptions (such as PFOS and PFOA), little research has been conducted on the ecotoxicological and human toxicological impacts of most PFAS, which makes the precautionary principle an important factor in the assessment.

3 Basis for deriving assessment standards

TDI (Tolerable Daily Intake) values are a key basis for assessing soil and groundwater contamination. TDI indicates the quantity of a substance that can be ingested daily over the course of a lifetime without adverse health effects. TDI values are expressed as the acceptable quantity of a substance per kg body weight (BW) and day (d) (mass/(BW*d)). A weekly or monthly reference period (TWI – Tolerable Weekly Intake, or TMI – Tolerable Monthly Intake) can also provide a basis for assessment.

In 2017, the joint LAWA-LABO working group "Derivation of insignificance threshold values for PFAS" (Kleingruppe "Ableitung von Geringfügigkeitsschwellenwerten für PFAS") published studies to determine TDI-analogous values for seven PFAS compounds – e.g. 28.6 nanograms per kilogram body weight and day (ng/kg BW*d) for PFOA, and the same figure for PFOS. Comparison of human toxicological impacts (whereby drinking water is the protected endpoint) with ecotoxicological impacts (aquatic organisms as subject of protection) reveals that the drinking water is more sensitive to all compounds than the protection endpoint of the trophic level of aquatic organisms. The insignificance threshold values for PFAS are therefore based throughout on human toxicological impacts and on the provisions of the German Drinking Water Ordinance (Trinkwasserverordnung – TrinkwV). In view of the solubility of many PFAS and their associated relevance to the soil-groundwater pathway, the insignificance threshold values are directly connected to the values applied to classify soil material (see Section 6).

The 2021 revision of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz und Altlastenverordnung - BBodSchV) includes the insignificance threshold values as trigger values for the soil-groundwater pathway.

The revised EU Drinking Water Directive (Directive (EU) 2020/2184 of 16 December 2020) – which entered into force at the beginning of 2021 – lists substances belonging to the PFAS group as pollutants for the first time. For the 20 individual compounds listed, a sum value of 0.1 µg/l is applied or, alternatively, 0.5 µg/l for the entire PFAS group. National implementation of this directive will lead to intensified monitoring. In the past, PFAS contamination detected in groundwater or drinking water tended to be more the result of chance findings than of systematic monitoring.

In 2018, the European Food Safety Authority (EFSA) published a re-assessment of the health risks related to the presence of PFOA and PFOS in food, from which it derived substantially lower thresholds than in the past[6]. The Tolerable Weekly Intake values of 6 ng/kg BW for PFOA and 13 ng/kg BW for PFOS published there are also well below the TDI-analogous values established by the LAWA-LABO working group[7]. The EFSA revised its assessment in 2020 once again and now recommends a TWI for the sum of four compounds – PFOA, PFOS, perfluorohexane sulfonic acid (PFHxS) and perfluorononanoic acid (PFNA) – of 4.4 ng/kg BW. It has thus tightened its recommendation once more. For the first time, combined toxicity for groups of contaminants was taken into account (cocktail effects).

Due to the developments listed above, a decision will have to be taken on whether to adjust the previous basis for assessment at national level. This includes revising the insignificance threshold values and, if necessary, adapting the guidelines accordingly. Until further notice, the insignificance threshold values for

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[6] https://www.efsa.europa.eu/en/efsajournal/pub/5194

[7] The intake values derived by EFSA indicate the dose that is not expected to cause adverse health effects in humans when ingested over a lifetime. Until the re-assessment in 2018, the TDI value was 150 ng/kg BW for PFOS and 1500 ng/kg BW for PFOA. The United States Environmental Protection Agency (EPA) had already set a substantially lower combined reference dose for the two compounds in 2016. This is now 13 nanograms (ng) per kilogram (kg) body weight per week for PFOS, and 6 ng/kg body weight per week for PFOA.

seven PFAS compounds from 2017 will be used. These values were derived by a LAWA-LABO working group using TDI-analogous values.

It should be noted at this point that the environmental quality standard introduced for PFOS under the German Surface Waters Ordinance (Oberflächengewässerverordnung – OGewV) (Section 5.1.2) is still based on the outdated EFSA value of 2008.

4 Analysis

4.1 Range of substances

The PFAS chemical group comprises a large number of different individual substances. These guidelines primarily cover the 13 compounds listed in Table 1 for which insignificance threshold values or health advisory levels (HAL) are available and can be analysed in accordance with DIN standards[8]. An assessment framework is thus lacking for several compounds.

If, in justified cases (e.g. contamination with polyfluorinated compounds), more than the PFAS listed in Table 1 are to be investigated, the range of parameters to be analysed should be decided according to the individual circumstances.

Table 1: PFAS analysable according to DIN standards

Substance	Abbreviation	Molecular formula	CAS No	Perfluorinated chain length
Perfluorobutanoic acid	PFBA	$C_4HO_2F_7$	375-22-4	short-chain
Perfluoropentanoic acid	PFPeA	$C_5HO_2F_9$	2706-90-3	
Perfluorohexanoic acid	PFHxA	$C_6HO_2F_{11}$	307-24-4	
Perfluoroheptanoic acid	PFHpA	$C_7HO_2F_{13}$	375-85-9	
Perfluorooctanoic acid	PFOA	$C_8HO_2F_{15}$	335-67-1	long-chain
Perfluorononanoic acid	PFNA	$C_9HO_2F_{17}$	375-95-1	
Perfluorodecanoic acid	PFDA	$C_{10}HO_2F_{19}$	335-76-2	
Perfluorobutane sulfonic acid	PFBS	$C_4HO_3F_9S$	375-73-5	short-chain
Perfluorohexane sulfonic acid	PFHxS	$C_6HO_3F_{13}S$	355-46-4	long-chain
Perfluoroheptane sulfonic acid	PFHpS	$C_7HO_3F_{15}S$	357-92-8	
Perfluorooctane sulfonic acid	PFOS	$C_8HO_3F_{17}S$	1763-23-1	
6:2 Fluorotelomer sulfonic acid	6:2 FTSA (H4PFOS)	$C_8H_5O_3F_{13}S$	27619-97-2	
Perfluorooctanesulfonamide	PFOSA	$C_8H_2F_{17}NO_2S$	754-91-6	

In particular, fluorine-containing fire-fighting foams such as AFFF[9] can cause forms of PFAS contamination that are not included in this list. The range of substances analysed therefore needs to be broadened whenever such fire-fighting foams are used. In particular, polyfluoralkyl betaines need to be considered in such cases; these are contained as PFOS substitutes in Capstone™ products[10], for instance. Not all of these betaines can be detected as individual substances. In certain situations, it may therefore be appropriate to record them as a sum parameter (see Section 4.2).

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[8] For the analysis of water samples as per DIN 38407-42 and of sludge, compost and soils as per DIN 38414-14, the applicability of the relevant procedure to further substances is not excluded, but needs to be appraised on a case-by-case basis.

[9] AFFF or A3F is the abbreviation for Aqueous Film Forming Foam.

[10] PFOS-free commercial product (DuPont) used in fire-fighting agents; contains polyfluoralkyl betaines.

With ISO 21675:2019-10[11], a standard is now available that offers a procedure for up to 30 individual substances (see Annex IV for its scope).

4.2 Methods of analysis

In drinking water, groundwater, surface water and treated waste water, the analysis of per- and polyfluorinated carboxylic and sulfonic acids is conducted in accordance with German standard DIN 38407-42 (F42): “Determination of selected polyfluorinated compounds (PFAS) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction” (March 2011). Investigating bodies/laboratories mostly cite a quantitication limit in soil eluates of 5 to 10 ng/l for single compounds; in some cases quantitication limits of 1 ng/l are achievable.

In order to estimate the potential contamination of materials with PFAS, it may be necessary to determine solids content. In aquatic sediments, sewage sludge, compost and soil, these are determined in accordance with German standard DIN 38414-14 (S14): “Determination of selected polyfluorinated compounds (PFAS) in sludge, compost and soil - Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS)” (August 2011). The method’s lower limit of quantitation and detection is given as 10 µg/kg. Quantitication limits for individual substances currently range from 1 to 10 µg/kg, and 0.1 µg/kg in exceptional cases. A lower limit of quantitation and detection of 0.1 µg/kg is required to determine the background contamination of soils (ubiquitous contamination).

In cases of contamination of soils or groundwater, the types of fluoroorganic compounds present and their concentrations are often unknown. In the environment, many polyfluorinated substances are converted into more stable PFAS compounds (e.g. PFOS, PFOA), mostly through oxidative processes. To assess the PFAS contamination, it is therefore crucial to not only determine the concentrations of each of the individual PFAS, but also the maximum concentrations of the stable PFAS that can form from the PFAS mixture present in each case. To date, only a limited number of compounds in this group of pollutants are available as reference substances for analysis and/or can be determined by means of routine methods. For this reason, a number of projects are currently underway to develop sum parameters. As guidance values, these will enable initial estimates to be made of potential contaminations with fluoroorganic compounds. They include the following parameters:

- AOF (adsorbable organic fluorine) for aqueous samples: This is based on the accumulation of fluoroorganic compounds on suitable activated carbon and on the identification of the adsorbed compounds following their combustion as fluorides. The current quantitication limit is ≤ 2 µg/l (draft DIN standard).
- EOF (extractable organic bound fluorine) for solid samples: The analysis is performed analogously to the determination of AOF following extraction from solid samples. The current quantitication limit is approximately 10 µg/kg.
- TOP assay (total oxidisable precursor): In eluates of solids, soil extracts and aqueous samples, defined oxidations are used to transform precursor compounds into persistent PFAS degradation products – primarily perfluorinated carboxylic acids – rendering them analytically detectable. The low quantitication limits of PFAS routine analysis can also be achieved (generally < 5-10 ng/l).

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[11] ISO 21675:2019-10: Water quality – Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water – Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS).

Due to the great number of unknown PFAS compounds, an analysis focussing on single substances can lead to the risk potential being underestimated in certain cases. Irrespective of ongoing standardisation work, sum parameters do provide valuable additional information on the level and spatial distribution of PFAS contamination in soils and water.

For investigations in close proximity to the source of pollution, the recommendation is to complement single compound analysis with analysis of the sum parameters AOF, EOF or TOP assay[12]. When conducting the AOF analysis, however, it needs to be considered that high fluoride concentrations in water samples can impact AOF analysis and thus result in excessive readings and misinterpretations. A comparison of the results for the known individual substances with the results for the sum parameters gives an indication of the proportion of unknown organic fluorine compounds. For investigations far from the source of pollution, e.g. in drinking water, single compound analysis for the known PFAS compounds generally allows for an assessment of the PFAS contamination. This is based on the assumption that polyfluorinated PFAS will have undergone a transformation into analytically detectable compounds along the pathway from the source of pollution. Here, too, the analysis of sum parameters can provide certainty.

4.3 Production of eluates for soil analysis

The testing of soil samples for the purposes of assessing leachate should be undertaken by means of a batch test as per German standard DIN 19529 or by means of the column percolation method as per DIN 19528 at a liquid-to-solid ratio of 2:1.

In accordance with DIN 19529:2015-12, fresh field samples or possibly also dried samples are to be used for testing. It should be noted, however, that both the elution process and the level of desiccation can lead to substantially different results, particularly when testing soils with low levels of contamination, such as those found at long-term soil monitoring sites[13]. This must be factored in when comparing study findings. The inclusion of a drying step therefore improves the comparability of the results.

Based on the DIN standards above, the following additional recommendations for the preparation of samples are therefore made with the aim of improving the comparability of analysis results:

- Drying the sample at a maximum temperature of 40°C until constant weight is reached (exception: humus-rich soils with > 8% SOM content may exhibit high hydrophobicity following the drying process and should therefore only be analysed as fresh field samples); the loss of water content through drying is to be noted in the protocol.
- Conducting the elution using 250 g (DM) in a 1-L PP bottle following separation of the fraction >10 mm; its percentage by weight (WT%) in the total sample is to be noted in the protocol and must be taken into account in the evaluation of the results.
- Foregoing the filtration step after centrifugation as filtration losses have been documented, particularly for precursors. If the samples are too cloudy for a direct measurement, it may be useful to carry out ultracentrifugation (to be noted in protocol).

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[12] AOF or EOF cost approximately 200 euros, while a TOP assay costs approximately 500 euros at private laboratories (prices requested October 2019).

[13] Preliminary results of comparative investigations conducted by the Baden-Württemberg State Institute for the Environment, and the German Water Centre (DVGW) show that for soil samples without specific PFAS contamination column testing generally yields significantly higher eluate values than a batch test (*https://pd.lubw.de/42387*, German only). Moreover, PFAS concentrations in the eluate can be up to 10 times higher than those found in fresh field samples.

- In highly organic soils with > 8% SOM content, a liquid-to-solid ratio of 2:1 cannot produce the quantities of eluate necessary for analysis as the soil binds water too strongly. In such instances, a liquid-to-solid ratio of 10:1 can be used and this deviation is to be noted in the protocol.

Deviating from the process described above, for activities subject to waste law, eluate analyses are generally performed at a liquid-to-solid ratio of 10:1 as per German standard DIN EN12457-4:2003-1 to test to what degree the soil material can be landfilled. If no second analysis with a liquid-to-solid ratio of 2:1 is to be carried out to assess potential waste recovery, the values obtained in the first analysis can alternatively be multiplied by a factor of five. However, these must be significantly above the quantitication limit, i.e. by at least a factor of two, otherwise the inaccuracy is too great.

Scientifically based conversion factors are not available. While the conversion factor may in reality be lower than five due to adsorption effects, especially in the case of long-chain PFAS, this process is sufficient to ensure that the higher dilution of the 10:1 eluate does not result in an underestimation of the load. However, duplicate tests would generally be more robust, satisfying the relevant applicable assessment standards.

The chemical analysis of eluates/percolates is performed analogously in accordance with DIN 38407-42. As a minimum, the analysis parameters for PFAS in the eluate should include the substances listed in Table 1 (Section 4.1). The analytical quantitication limit for PFAS in the eluate should be ≤ 10 ng/l. In practice, the quantitication limits in soil eluates cited by the investigating bodies/laboratories currently range between 5 and 10 ng/l for single compounds in most cases. Optimised process flows can attain quantitication limits of 1 ng/l.

5 Assessment criteria and instructions for use

5.1 Water

5.1.1 Groundwater

Based on information on the occurrence and distribution of PFAS as well as on individual case reports, the LAWA-LABO working group identified a list of priority substances consisting of 13 PFAS with respect to groundwater[14]. For seven of these compounds, they were able to derive insignificance threshold values on the basis of human toxicological data. In accordance with the principles of applying these limits as set out in the LAWA report on insignificance threshold values[15], exceeding the limits constitutes a detrimental change in groundwater quality.

The Drinking Water Commission at the German Environment Agency has deemed the available data to be sufficient to establish seven of the derived insignificance threshold values as guide values under TrinkwV. Due to insufficient data for assessment for a further six PFAS, the LAWA-LABO working group defined health advisory levels (HAL) (see Table 2).

For non-assessable PFAS, the recommendation (as a fallback) is to use a value of 0.1 µg/l per single compound following the ALARA principle (As Low As Reasonably Achievable).

Where multiple PFAS for which insignificance threshold values have been established occur in groundwater at the same time, the quotient sum (QS) can be used for the risk assessment of such mixtures of substances analogous to the cumulative risk assessment of the Technical Rules for Hazardous Substances (TRGS 402). It is up to the federal states to apply them. The application of the QS involves the division of the measured concentration of each individual compound by its insignificance threshold and the summation of these quotients. In this manner, similar effect mechanisms and potential cumulative effects on human health are taken into consideration.

$$Quotient\ sum = \frac{PFC_1}{GFS_1} + \frac{PFC_2}{GFS_2} + \cdots + \frac{PFC_n}{GFS_n}$$

PFAS with insufficient data for assessment and for which therefore only health advisory levels (HAL) are available are not included in the summation. Similarly, analysis results below the quantitication limit are not taken into account.

If, in the assessment of groundwater properties, the quotient sum exceeds a value of 1, then the assumption is that a detrimental change to the groundwater has occurred. Decisions as to whether the exceeded value means that action must be taken (e.g. remediation) depends on the specific circumstances (e.g. groundwater use for drinking water, agricultural irrigation). In contrast to insignificance threshold values, HAL are guidance values, i.e. exceeding these values, which are valid for

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[14] LAWA (2017): Derivation of insignificance threshold values for groundwater - Per and polyfluorinated compounds" (*Ableitung von Geringfügigkeitsschwellenwerten für das Grundwasser – PFAS*). https://www.lawa.de/documents/03_anlage_3_bericht_gfs_fuer_PFAS_endfassung_22_11_2017_2_1552302208.pdf (German only)

PFAS data sheets: https://www.lawa.de/documents/02_anlage_2_bericht__gfs_datenblaetter_2_1552302232.zip (German only)

[15] LAWA (2016): Derivation of insignificance threshold values for groundwater - updated and revised version 2016 (*Ableitung von Geringfügigkeitsschwellenwerten für das Grundwasser – Aktualisierte und überarbeitete Fassung 2016*). https://www.lawa.de/documents/geringfuegigkeits_bericht_seite_001-028_1552302313.pdf (German only)

drinking water assessment, indicates a detrimental change in groundwater quality[16]. The same approach applies to PFAS that are assessed based on the ALARA principle.

Table 2: Insignificance threshold values and health advisory levels (HAL) for PFAS in groundwater

Substance	**Insignificance threshold [µg/l]**	**HAL [µg/l]**
Perfluorobutanoic acid, **PFBA**	10.0	
Perfluoropentanoic acid, **PFPeA**		3.0
Perfluorohexanoic acid, **PFHxA**	6.0	
Perfluoroheptanoic acid, **PFHpA**		0.3
Perfluorooctanoic acid, **PFOA**	0.1	
Perfluorononanoic acid, **PFNA**	0.06	
Perfluorodecanoic acid, **PFDA**		0.1
Perfluorobutane sulfonic acid, **PFBS**	6.0	
Perfluorohexane sulfonic acid, **PFHxS**	0.1	
Perfluoroheptane sulfonic acid, **PFHpS**		0.3
Perfluorooctane sulfonic acid, **PFOS**	0.1	
6:2 Fluorotelomer sulfonic acid, **6:2 FTSA (H4PFOS)**		0.1
Perfluorooctanesulfonamide, **PFOSA**		0.1
Other PFAS with R1-(CF2)n-R2, and n>3		0.1

* Simultaneously serve as guidance values for drinking water pursuant to TrinkwV

5.1.2 Surface waters

In the assessment of surface waters and requirements with regard to discharges, a distinction must be made between two different levels of consideration:

a. The level of the water body within the meaning of § 27 of the Federal Water Act (Wasserhaushaltsgesetz - WHG) (management objectives in the context of discharge permits, with reference to the representative surveillance monitoring point), and

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[16] If the HAL are exceeded, drinking water suppliers are required to ensure compliance with these values in the medium term.

b. the local level, i.e. the surroundings of the point of discharge.

Re a.) Water body level

Pursuant to § 27(1) WHG, bodies of surface water shall be managed in such a way that any deterioration in their ecological and their chemical status is avoided, and a good ecological and a good chemical status are preserved or attained. To this end, environmental quality standards (EQS) have been established for a number of different substances. With EQS Directive 2013/39/EU, PFOS was added to the EU-wide list of priority substances in 2013 as the only representative of its contaminant group to date. As such, the legal requirement to take into account the entire body of water applies only to PFOS. For bodies of water, the focus is on the assessment of the chemical and ecological status pursuant to the specifications set out in OGewV of 20 June 2016. With regard to PFOS, compliance with the EQS with reference to the body of surface water is particularly important. A water body is a significant, uniform section of surface water (§ 3(6) WHG). Management objectives include avoiding any deterioration and achieving the set objectives (§ 27 WHG). The relevant data for assessment in this regard are those obtained at the representative surveillance monitoring point for the surface water bodies concerned.

The biota EQS for PFOS and its derivatives for surface waters is 9.1 µg/kg and may not be exceeded in fish (biota). This value was derived on the basis of human exposure through the consumption of fish to protect human health. The corresponding value for the aqueous phase is 0.65 ng/l as an annual average (AA-EQS). The maximum allowable concentration (MAC) is set at 36 µg/l (MAC-EQS) as derived from an analysis of algae. Compliance with EQS is to be demonstrated by means of biota monitoring. Only where this is not feasible, the AA-EQS in the aqueous phase can be used as an alternative. At the same time, the MAC-EQS must not be exceeded.

Where an ESQ in a body of surface water is not being met, appropriate measures must be determined to ensure compliance by 22 December 2027. Pursuant to OGewV, a monitoring programme for PFOS as well as a preliminary programme of measures was established as at 22 December 2018.

As a priority contaminant with a ubiquitous distribution, permits for waste water discharges or for the reinjection of (treated) groundwater into a surface water body must assess the impacts on the water body taking into consideration the no-deterioration principle and the imperative to achieve set objectives.

No-deterioration principle

A deterioration of the chemical status of a surface water body essentially occurs when a development results in the EQS of a substance included in Annex 8 to OGewV being exceeded. Where the EQS is already exceeded in the surface water body in question prior to the development, any additional discharge (of the substance in question) constitutes deterioration if it results in an increase in the concentration[17] at the representative surveillance monitoring point. If deterioration is found or forecast, a project may nevertheless be approved if the conditions for an exception pursuant to § 31(2) WHG are met[18].

For reasons of proportionality, short-term deteriorations may not be taken into consideration when it can be assumed with certainty that the original status will be restored in the short-term after the discharge

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[17] Increases in concentrations that can be computed but not detected by measurements are not deemed to constitute deterioration.

[18] Unpublished Resolution 153 on recommended action regarding the prohibition on further deterioration issued by the German Working Group on Water Issues (LAWA) in 2017: LAWA-AR Handlungsempfehlung Verschlechterungsverbot (Beschluss 153. LAWA-VV 16./17. 03 2017)

stops. This situation can arise, for example, where brief discharges occur over a limited time as part of a construction project.

Imperative to achieve set objectives

In addition, for PFOS the imperative to achieve set objectives must be taken into account if the EQS is exceeded in the surface water body pursuant to § 27(1) no. 2 WHG. For the individual discharge, this means that it must be verified as part of the permit procedure whether, in the event that the EQS has already been exceeded, it is possible to reduce the load. The question of whether the imperative to achieve set objectives is met must also take into account whether deadline extensions, divergent management objectives or exemptions (WHG §§ 29, 30 and 31) have been specified in the management plan for the surface water body in question. When approving individual projects, it must be ensured that the attainment of set objectives for the body of water overall is not rendered impossible (for further explanations, please refer to Annex II.3.2).

Re b.) Local level

The local level within the meaning of § 57(1) no. 2 WHG concerns the properties of certain sections of water bodies at the point of discharge (after mixing). At this level, the impacts of other PFAS in the water body must also be taken into account. The assessment at local level is described in Section 5.1.3.2. “Additional immission-related requirements”.

5.1.3 Waste water

5.1.3.1 Emission-related requirements

§ 57 (1) no. 1 WHG stipulates that where waste water is discharged, the harmfulness of the contaminants must be minimised using the best available technology (§3 no. 11 WHG). Generally PFAS are not specifically recorded in the waste water discharged directly by operators or by municipal waste water treatment plants.

The sum parameters COD and TOC are not conclusive with respect to PFAS as they only record extractable organic fluoride compounds which only occur at relatively low concentrations. To date, no sector-specific limit value for PFAS has been established as “best available technology”. Substance-specific rules are set out in the general requirements in Part B of the Appendices to the German Waste Water Ordinance (Abwasserverordnung – AbwV) (e.g. avoidance or minimisation of specific input substances).

The PFAS issue was addressed in the sector-specific appendices to AbwV, which was amended in 2016. Appendix 28 *Production of paper and cardboard, Part B General Requirements*, for example, sets out requirements for avoidance and minimisation. This is a first step to finding a solution to this issue in Germany and Europe.

These minimisation requirements also apply to indirect dischargers, but only insofar as the Appendix sets out requirements for waste water at the site of occurrence (Part E) and prior to mixing (Part D). The procedure (DIN 38407-42, March 2011 issue) to identify PFAS in waste water analyses is set out in Appendix 1 to Article 4 AbwV (analysis and measurement procedures) (also see Section 4.2).

5.1.3.2 Additional immission-related requirements

§ 57 (1) no. 2 WHG stipulates that when granting a permit to discharge waste water, the requirements for water body properties must be taken into consideration, i.e. a prognosis and assessment of the impacts on the water body resulting from the discharge. PFAS inputs, where they cannot be entirely avoided, must therefore be limited to such a degree that the predicted PFAS concentrations in the body of water following mixing with the waste water will not result in detrimental changes to the water body at the site of occurrence beyond the requirements already assessed under § 27 WHG.

In this context, not only the discharge itself, but also any potential pre-existing PFAS contamination of the water body must be taken into account. Moreover, limits imposed on discharges into surface waters must take into consideration potential adverse impacts on groundwater (e.g. where there is significant infiltration of surface water into groundwater) and impacts on drinking water use (e.g. where bank-filtered water is used).

For an ecotoxicological assessment (at local level) related to the protection of the aquatic community, the AA-ESQ concentration levels in the aqueous phase (currently only available for PFOS) or PNEC (Predicted No Effect Concentration) can be used for orientation in the context of discharge permits for PFAS. The latter are generally derived exclusively in relation to the protection of the aquatic community based on ecotoxicological data ($\mathrm{PNEC}_{\mathrm{aquatic}}$). Of the parameters to be assessed under the present guideline, $\mathrm{PNEC}_{\mathrm{aquatic}}$ values are currently only available for four short-chain PFAS.

Given the relatively high PNEC values, assessments will generally conclude that the aquatic community is sufficiently protected. In contrast to the EQS for PFOS, however, the PNEC values do not take into account the protection of animals that eat fish (secondary poisoning), human consumption of fish or the potential impacts on groundwater as a drinking water resource. For further information please refer to Annexes II.1 and II.3.

As a precautionary measure due to the high persistence and mobility of PFAS, assessment criteria other than ecotoxicological criteria (e.g. secondary poisoning, human toxicology) can take precedence in waste water discharges and may require more far-reaching minimisation measures.

Moreover,under REACH several PFAS have already been classified as Substances of Very High Concern (SVHC) for which no PNEC values can be established (see Annex II.1)[19]. As a general rule, efforts should be made to establish minimisation measures within the scope of REACH for compounds of this nature.

In individual discharge cases, it must be ensured that the quantity and harmfulness of the waste water are kept as low as possible in compliance with the respective best available technology. Key criteria for additional requirements include not only the level of concentration in waste water, but also the achievable load reduction, the effort required and the local conditions. When prioritising any necessary measures, it is advisable to proceed according to the amount of PFAS detected in the treated waste water. Please refer to the examples in Annexes IV.2 and IV.3 and the guidance values applied there.

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[19] SVHC (Substances of Very High Concern) are, for example, substances that are simultaneously persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB). Given these combinations of characteristics, it is not possible to define “safe” long-term concentrations in the environment.

In addition, the information set out in Section 5.1.2 shall apply to PFOS. It should be noted that the EQS does not need to be met at the point of discharge, but at the surveillance monitoring point representative for the surface water body in question.

In the absence of legally binding immission (input) values, the decision on a discharge permit is to be taken on the basis of due discretion in accordance with § 12 WHG.

In individual cases, exceeding immission (input) values that are not legally binding (e.g. PNEC) may, following appropriate review and justification, even constitute a detrimental change to water bodies. In this case a permit must be denied. This does not fall under the discretion of the competent authority.

5.1.3.3 Estimating water contamination by mathematical means

In order to assess the additional contamination of a water body, it is generally advisable to use the mean low water discharge (MNQ) of the water body in question to estimate the predicted PFAS concentrations in the water body.

The following equation can be used to mathematically determine a pollution load C_{PL} caused by a point discharge:

$$C_{PL} = \frac{MNQ \times C_{BG} + A_{Ww} \times C_{Ww}}{MNQ + A_{Ww}}$$

where:

C_{PL} = pollution load

MNQ = Mean low water discharge upstream of the point of discharge (volume/time)

C_{BG} = Background concentration (mass/volume)

A_{Ww} = Waste water discharge (volume/time)

C_{Ww} = Substance concentration in waste water (mass/volume)

Please refer to the examples in Annexes IV.2 and IV.3.

5.2 Sewage sludge/fertilisers

The Sewage Sludge Ordinance (Klärschlammverordnung - AbfKlärV) of September 2017 (last amended June 2020) indirectly establishes a limit value for PFAS for the soil-related recovery of sewage sludge by cross-referencing the Fertiliser Ordinance (Düngemittelverordnung - DüMV) of December 2012 (last amended October 2019). The latter generally sets a limit value of 100 µg/kg total PFOS plus PFOA for both the source materials of fertilisers as well as the fertilisers themselves; where the concentration exceeds 50 µg/kg this must be indicated on the label.

The limit value introduced in 2008 is set so high that even if complied with, the application of sewage sludge may result in the insignificance threshold value in groundwater (see Table 2) being exceeded. This is exacerbated by the fact that the precursors contained in the sewage sludge are disregarded. As a precautionary measure, it would therefore be appropriate to adjust the limit value downwards as soon as possible as part of an amendment to DüMV. This view is also supported by the significant reduction in the maximum intake levels via food previously recommended by the EFSA. Furthermore, a PFAS total limit value should not be confined to the two substances, but should at least take into account the representatives listed in Table 2 or else the entire group of substances.

5.3 Soil-pathway-specific risk assessment

5.3.1 Soil-groundwater pathway

Assessments of PFAS in the context of hazard prevention and control have shown the soil-groundwater pathway to be the primarily relevant one (without prejudice to individual cases). Irrespective of the as yet existing uncertainties with respect to the substances' environmental behaviour, especially in the soil matrix, their concentration in leachate at the assessment location is estimated on the basis of the soil eluate analysis (leachate forecast, consisting of material analyses and transport prognosis).

The recommendation is to conduct these material analyses using representative samples[20] from the unsaturated soil zone (sampling location) in elution and percolation tests at a liquid-to-solid ratio of 2:1. Assessments of the substances' contaminant potential should – insofar as this is analytically feasible – take into account results of solids analyses.

A number of different cases of contamination have shown that precursors can also be present. Their transformation potential is often difficult to assess. Such PFAS must however be taken into account in the risk assessment. The sum parameters described in Section 4 give indications in this regard.

Until such time as legally binding trigger values for PFAS are in force, the insignificance threshold values for PFAS (Table 2) are applicable as proposed trigger values for leachate at the assessment location[21]. The assessment of the soil-groundwater pathway does not additionally include the sum quotient as it constitutes a precautionary risk assessment of mixtures of substances as part of drinking water quality assessments. For as yet unassessed PFAS, the proposed trigger value to be used is 0.1 µg/l per single compound, based on the ALARA principle. Similar to the health advisory levels (HAL), this value can serve as orientation for assessment purposes. If the proposed trigger value is exceeded, this does not lead to the determination of an imminent risk, but initiates a further assessment. This assessment then takes into account both concentrations and loads as well as potential metabolites and persistent degradation products.

Where one of these proposed trigger values in the eluate is already exceeded at the sampling location, a transport prognosis (by verbal discussion or possibly supported by software such as SIWA-SP or ALTEX-1D) is to assess whether this can also be expected in the leachate PFAS concentration at the

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[20] See Federal Soil Protection and Contaminated Sites Ordinance as amended, Annex 1 Requirements concerning sampling

[21] The revised version of the BBodSchV has established insignificance threshold values for the seven PFAS listed in Table 2 (Section 5.1.1) as trigger values http://dip21.bundestag.de/dip21/btd/18/122/1812213.pdf (in German).

assessment location (transition from the unsaturated to the saturated soil zone). This requires eluate analyses as well as, where necessary, solids analyses.

For the transport prognosis, it should be noted that short-chain PFAS are retained in the unsaturated zone to a lesser degree than long-chain PFAS. Moreover, in each individual case the site conditions must be taken into account e.g. the nature (geology) and the seepage water's further passage into the ground as well as the risk potential posed by precursors.

A transport prognosis must, insofar as possible, take into account the retention effect for long-chain and thus less mobile PFAS (e.g. PFNA, PFDA or PFOS) and for precursors as well as the degradation kinetics of precursors both in the vicinity of the source and along the seepage water path.

Where the projected concentration at the assessment location *falls short* of the proposed trigger value, the possibility that the substances detected pose a hazard can be ruled out.

Where the projected concentration at the assessment location *exceeds* the proposed trigger values, further investigation is required as per Article 9(2) of the Federal Soil Protection Act (Bundes-Bodenschutzgesetz - BBodSchG) on the grounds that there is sufficient suspicion that a harmful soil change or contaminated site exists. Under suitable hydrogeological conditions, an assessment can additionally take into account the mixing of the leachate into a limited volume of groundwater. The assessment of the groundwater after mixing is to be conducted in accordance with Section 5.1.1.

5.3.2 Soil-plant pathway

Plants can take up PFAS from the soil or from irrigation water and transport the substances into different parts of the plant (leaves, seed).[22] Generally, short-chain compounds (e.g. PFBA, PFPeA or PFHxA) are more likely to be absorbed than long-chain compounds (e.g. PFOA, PFOS). There are, however, indications that in the absence of short-chain PFAS, long-chain PFAS, particularly PFOA, are absorbed by plants and in some cases deposited in the seed. Moreover, plant species differ in their absorption capacity and transfer behaviour into plant organs:

- Short-chain PFAS, in particular, are primarily stored in green plant parts and in plants that have a high water demand (e.g. vegetables, soya beans and wheat). In contrast, long-chain PFAS primarily accumulate in the roots[23].
- Transfers into the seed of the harvested product were observed only in individual instances for grain maize, winter rapeseed and spring barley, while a higher level of transfer was observed for soya beans and winter wheat.

The uptake of PFAS in plants is dependent on the concentrations in the soil or irrigation water as well as on the properties of the compounds in question (i.a. chain length, degree of branching, functional groups) and of the plant species. In addition, it is reasonable to assume that absorption is influenced in particular by the soil type, the soil organic matter content and the pH value of the soil.

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[22] Stahl, T., Heyn, J., Thiele, H., Hüther, J., Failing, K., Georgii, S., Brunn, H. (2009): Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants. Arch. Environ. Contam. Toxicol. 57, 289-298

[23] Felizeter, S., McLachlan, M.S., De Voogt, P. (2014): Root uptake and translocation of perfluorinated alkyl acids ba three hydroponically grown crops. J. Agric, Food Chem.62, 3334-3342

While there is a need for trigger values for the soil-plant pathway, the data required to calculate the transfer factors are as yet insufficient. It has therefore not yet been possible to define proposed trigger values.

For reasons of precautionary consumer protection, pre-harvest monitoring[24] is therefore recommended on agricultural land contaminated with PFAS, if consumer protection issues have not been unequivocally clarified (see Annex IV.1). Moreover, in suspected cases of contamination, the water that may be used for irrigation should be analysed in order to avoid PFAS inputs.

Wild plants can also absorb PFAS from the soil and deposit the substances in edible plant parts or nectar. Honey for example can be highly contaminated as a result. Especially in cases of widespread contamination of soil material specifically with short-chain PFAS, it is recommended that this aspect is taken into account.

5.3.3 Soil-human pathway (direct contact)

The assessment of soil contamination with regard to the soil-human pathway (direct contact) primarily involves the application of trigger values pursuant to Annex 2 to BBodSchV. However, there are no plans to include relevant values for PFAS in the planned revision of the BBodSchV. Only trigger values for the soil-groundwater pathway are to be included.

The system for establishing trigger values was published in the German Federal Gazette (Bundesanzeiger 51, Nummer 161a) of 28 August 1999[25]. If this system were to be used to establish values for PFAS, these values would be on a scale barely detected in reality to date. In contrast to the soil-groundwater pathway, the soil-human pathway (direct contact) is generally less relevant for remedial actions[26]. With respect to PFAS, the soil-groundwater pathway is generally (without prejudice to individual case assessment) the more sensitive pathway. Only the relevant pathways should be taken into consideration in the concluding risk assessment.

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[24] For information on pre-harvest monitoring see the homepage of the PFAS unit at the Karlsruhe regional council (German only): https://rp.baden-wuerttemberg.de/rpk/Abt5/Ref541/PFC/Seiten/Landwirtschaft.aspx

[25] https://www.lfl.bayern.de/mam/cms07/iab/dateien/ableitung_der_pr__f-_und_ma__nahmenwerte.pdf (German only)

[26] The significance of the soil-groundwater pathway has increased with the new EFSA assessment (see Section 3).

6 Handling soil material containing PFAS

6.1 General notes

PFAS-containing soil material can arise during construction wok or remedial measures, particularly in cases of suspected contaminated sites, detrimental changes to soil or contaminated sites, but also due to diffuse background contamination. If excavated material is surplus to requirements (i.e. there is intent to discard) or if, due to contamination with PFAS (including potential precursors), it may not be reused at the site of occurrence (i.e. there is a duty to present for disposal), it is classed as waste that must be recovered or disposed of properly and without causing damage. Recovery must not lead to any accumulation of contaminants in material cycles.

Preventing occurrences of soil material that must be handled as waste takes priority over recovery and disposal of such material. Binding stipulations, for instance in local development planning (preparatory land-use plans and final zoning plans), can often prevent or at least minimise occurrences of surplus soil material. The requisite reuse and disposal steps can thus be regulated uniformly ex-ante.

In cases in which different grain-size fractions of the soil material are contaminated differently, it is recommended to separate highly contaminated PFAS-containing fractions from fractions with no or low-level contamination. This reduces the soil volume that must be consigned to final disposal. A prerequisite for this is the development of practical technical processes for pre-treating PFAS-contaminated soil material.

When recovering soil material, it is necessary to stay below the threshold limit value. The threshold limit value for the soil-groundwater pathway corresponds to the insignificance threshold values in the leachate as it enters the groundwater (assessment location). The health advisory levels (HAL) are used for orientation due to the lack of human toxicological knowledge. Reliably staying below the threshold limit value (insignificance threshold at the assessment location) is ensured if the eluate in the soil material complies with the insignificance threshold and health advisory levels (Table 3a/b).

General requirements regarding the harmlessness of soil material recovery are set out for various recovery classes, e.g. in the General Part (Part I) of LAGA Note 20 (LAGA-Mitteilung 20 “Anforderungen an die stoffliche Verwertung von mineralischen Abfällen - Technische Regeln - Allgemeiner Teil”). The recovery classes include the allocation values both in the solids content and in the eluate.

Soil material from areas where there are no indications or evidence of PFAS contamination can generally be recovered with no restrictions with respect to PFAS contamination, as long as no other types of contamination prohibit such use. Soil material from areas where there are indications or evidence of PFAS contamination must generally undergo chemical analysis. PFAS pathways giving an indication of PFAS contamination are listed in Annex I.

To date, no corresponding allocation values are available for PFAS, meaning that the recovery of soil material containing PFAS is broken down into three recovery classes (Verwertungskatergorien - VK) on the basis of the eluate values.

- Recovery class 1 (VK 1) = unrestricted open emplacement
- Recovery class 2 (VK 2) = restricted open emplacement in areas with elevated PFAS concentrations
- Recovery class 3 (VK 3) = restricted emplacement in technical structures with defined safety measures

Recovery class 1 (VK 1), soil material can be recovered without restrictions in open emplacement outside and within technical structures.

Recovery class 2 (VK 2) soil material can only be recovered within areas with elevated PFAS concentrations under certain conditions in the root-penetrable soil layer, in soil-like applications and in such areas as well as in technical structures.

Recovery class 3 (VK 3) soil material can only be recovered in technical structures with safety measures.

For the emplacement of VK2 or VK3 soil material, the distance to the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

PFAS-contaminated soil material in VK1 and VK2 may generally only be shifted, in accordance with its classification, to sites with the same or a higher classification (see Tables 3a/b). A risk to groundwater or other hazards must not arise. If treatment of PFAS-contaminated soil material is required, it should be carried out in facilities designed for this purpose. The objective is to prevent the spread of PFAS contamination. Regardless of this, there is also the option to recover PFAS-containing soil material in technical structures (see Section 6.3).

In VK1, no soil material exceeding the allocation values shall be recovered in the following areas:

- Water protection areas that are established, temporarily secured or planned by expert competent authorities (zones I to III B);
- Protected areas surrounding recognised medicinal springs;
- Priority water areas, geographic locations which have been designated in order to secure future water supply;
- Areas which flood frequently e.g. flood-retention basins, river floodplains and outer dike areas.

Other water resource management criteria (e.g. location in relation to drinking water protected areas and surface waters) and the hydrogeological conditions on site are to be the taken into account, particularly with regard to the protective function of soil layers above groundwater surfaces.

Table 3a: Preliminary maximum permissible concentrations in the liquid-to-solid 2:1 eluate in µg/l for the specific recovery classes (insignificance threshold based values)

	VK 1 Unrestricted open emplacement	**VK 2** Restricted open emplacement in areas with elevated PFAS concentrations (*see notes)	**VK 3** Restricted emplacement in technical structures with defined safety measures
Perfluorobutanoic acid, **PFBA**	≤ 10.0	≤ 20.0	≤ 50
Perfluorohexanoic acid, **PFHxA**	≤ 6.0	≤ 12.0	≤ 30
Perfluorooctanoic acid, **PFOA**	≤ 0.1	≤ 0.2	≤ 1
Perfluorononanoic acid, **PFNA**	≤ 0.06	≤ 0.12	≤ 0.6
Perfluorobutane sulfonic acid, **PFBS**	≤ 6.0	≤ 12.0	≤ 30
Perfluorohexane sulfonic acid, **PFHxS**	≤ 0.1	≤ 0.2	≤ 1
Perfluorooctane sulfonic acid, **PFOS**	≤ 0.1	≤ 0.2	≤ 1

Notes on Table 3a:

In view of the lack of sufficient data from which to derive solids content values, it is recommended to use the values listed in Table 3a in the interim when assessing recoverability of soil material. Deviations are possible in the form of regulations specific to individual federal states. This also applies to the application of the sum quotient (see Section 5.1.1). As soon as background levels based on solids content are available and analysis allows, the provisional requirements defined as eluate values are to be replaced by solids content values combined with eluate values.

- **VK 1:** The unrestricted open recovery of soil material must not give cause for concern that detrimental changes to the soil may arise. Soil material may be applied onto or introduced into the root-penetrable soil layer, or may be incorporated into soil-like applications or technical structures if the eluate content used does not exceed the insignificance threshold values specified in Table 3a. These values are based on values that protect groundwater sufficiently.
- **VK 2:** Limited open recovery is possible under certain conditions (*):
  In areas with elevated PFAS concentrations (according to Article 12 (10) BBodSchV or Article 6 (4) of the revised BBodSchV), VK2 soil material with a contaminant concentration up to double the insignificance threshold values in the eluate may be recovered within these zones in restricted open emplacement, if proper and safe recovery is demonstrated in each individual case. Site conditions, in particular the geological and hydrogeological conditions, the natural soil functions of the subsoil and surrounding area, and existing PFAS levels, are to be taken into account. There must be no deterioration of the situation at the site of recovery. The distance to the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

  Under these conditions, the authority responsible for authorising the application and introduction of soil material may, in agreement with the authority responsible for soil protection, allow the PFAS-containing soil material to be applied or introduced. It is recommended to involve the competent water authority.

  These rules do not apply in water protected areas (zone I to III B), protected areas surrounding recognised medicinal springs, priority water areas and areas which flood frequently.

- **VK 3:** For the derivation of the values for recovery in technical structures with defined safety measures in VK3, account was taken of the mobility of short-chain compounds (application of a factor of five) and the elevated retardation of long-chain compounds in the soil (application of a factor of ten). The distance to the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

Table 3b: Preliminary maximum permissible concentrations in the liquid-to-solid 2:1 eluate in µg/l for the specific recovery classes (HAL based values)

	VK 1 Unrestricted open emplacement	**VK 2** Restricted open emplacement in areas with elevated PFAS concentrations (*see notes)	**VK 3** Restricted emplacement in technical structures with defined safety measures
Perfluoropentanoic acid, **PFPeA**	≤ 3.0	≤ 6.0	≤ 15
Perfluoroheptanoic acid, **PFHpA**	≤ 0.3	≤ 0.6	≤ 3
Perfluorodecanoic acid, **PFDA**	≤ 0.1	≤ 0.2	≤ 1
Perfluoroheptane sulfonic acid, **PFHpS**	≤ 0.3	≤ 0.6	≤ 3
6:2 Fluorotelomer sulfonic acid, **6:2 FTSA (H4PFOS)**	≤ 0.1	≤ 0.2	≤ 1
Perfluorooctanesulfonamide, **PFOSA**	≤ 0.1	≤ 0.2	≤ 1
Other PFAS	≤ 0.1	≤ 0.2	≤ 1

Notes on Table 3b:

In view of the lack of sufficient data from which to derive solids content values, it is recommended to use the values listed in Table 3 in the interim when assessing recoverability of soil material. Deviations are possible in the form of regulations specific to individual federal states. As soon as background levels based on solids content are available and analysis allows, the provisional requirements defined as eluate values are to be replaced by solids content values combined with eluate values.

- **VK 1**: The unrestricted open recovery of soil material must not give cause for concern that detrimental changes to the soil may arise. Soil material may be applied onto or introduced into the root-penetrable soil layer, or may be incorporated into soil-like applications or technical structures if the eluate content used does not exceed the health advisory levels values specified in Table 3b. These values provide guidance for these individual substances as long as no insignificance threshold values are available for them.
- **VK 2:** Limited open recovery is possible under certain conditions (*):

  In areas with elevated PFAS concentrations (according to Article 12(10) BBodSchV or Article 6(4) of the revised BBodSchV), VK2 soil material with a contaminant concentration up to double the health advisory levels in the eluate may be recovered within these zones in restricted open emplacement, if proper and safe recovery is demonstrated in each individual case. Site conditions, in particular the geological and hydrogeological conditions, the natural soil functions of the subsoil and surrounding area, and existing PFAS levels, are to be taken into account. There must be no deterioration of the situation at the site of recovery. The distance to the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

  Under these conditions, the authority responsible for authorising the application and introduction of soil material may, in agreement with the authority responsible for soil protection, allow the PFAS-containing soil material to be applied or introduced. It is recommended to involve the competent water authority.

  These rules do not apply in water protected areas (zone I to III B), protected areas surrounding recognised medicinal springs, priority water areas and areas which flood frequently.

- **VK 3:** For the derivation of the values for recovery in technical structures with defined technical safety measures in VK3, account was taken of the mobility of short-chain compounds (application of a factor of five) and the elevated retardation of long-chain compounds in the soil (application of a factor of ten). The distance to the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

6.2 Recovery of soil material on/in or below/beyond a root-penetrable soil layer

The requirements for recovery set out in this section are based on the following principles:

- The measure must serve a useful purpose (Section 3 subsection (23) of the German Circular Economy Act (KrWG)). In accordance with Article 12 (2) BBodSchV, it must not give rise to concerns about the occurrence of detrimental changes to the soil and at least one of the soil functions specified in Article 2(2) nos. 1 and 3 (b) and (c) BBodSchG must be safeguarded or restored in the long term.
- Recovery of wastes must be carried out properly and without causing harm; the latter criterion demands, in particular, that no accumulation of contaminants arises in cycles of recyclable materials.
- There must be no deterioration of the situation at the site of recovery.
- The recovery cannot give cause for concern that detrimental changes to the groundwater may arise.

The contaminant-related requirements for the recovery of soil material under soil protection law are generally based on the precautionary principle set out in Article 9 BBodSchV and the precaution requirements of Article 10 BBodSchV (in the revised BBodSchV the stipulations under Article 3 will apply). BBodSchV generally defines precautionary values in terms of solids content values. To date, it has not been possible to derive precautionary solids content values for PFAS. Consequently, precautionary stipulations are formulated for PFAS as provisional requirements in the form of eluate levels. If the insignificance threshold values are complied with in the eluate of soil material at the site of application, then groundwater protection is sufficient, especially taking into consideration the dilution that occurs when mixed with groundwater.

Soil material that meets the requirements of column VK1 of Tables 3a and b can be recovered without restriction insofar as there are no other grounds for imposing restrictions (e.g. the principle that the situation on site must not deteriorate). The notes on Tables 3a and b, in particular, are to be taken into account.

Pursuant to Article 12(2) sentence 2 BBodSchV, the shifting of soil material on sites in connection with the erection or modification of built structures is not subject to the requirements concerning the application and introduction of material onto or into soil pursuant to Article 12 BBodSchV if the soil material is reused at its site of origin. A precondition is that there is no risk or suspected hazard. It follows that soil material can be shifted at the site of origin in connection with the erection and modification of structures and operational facilities if it is certain that there are no contaminated sites or any other detrimental change to the soil due to PFAS (or other contaminant) contents. (This will be regulated under Article 6(3) in the new version of the BBodSchV).

If there are indications or evidence of risks or hazards, investigations and a risk assessment (Section 5.3) are required.

6.2.1 Recovery of soil material on/in a root-penetrable soil layer

The stipulations of BBodSchV apply to the application and introduction of soil material. Particular note is to be taken of the requirements under Article 12 BBodSchV (including the enforcement guidance[27]), e.g. the prohibition of introduction in areas meriting special protection pursuant to Article 12(8) BBodSchV. (In the revised BBodSchV, future provisions under Articles 6 and 7 are to be taken into account in this context). Unrestricted open emplacement is described in VK1 (Tables 3a and b).

Soil material that does not exceed insignificance threshold values for PFAS used instead of precautionary values in eluate may be applied onto or introduced into the root-penetrable soil layer. If the insignificance threshold values (liquid-to-solid ratio of 2:1) are complied with, there is no reason to be concerned about a detrimental change to the groundwater or a detrimental change to the soil. For individual substances for which no insignificance threshold values are known, the provisional values under VK1 specified in Table 3b can provide guidance.

In areas with PFAS concentrations (according to Article 12(10) BBodSchV and Article 6(4) of the new BBodSchV or generally established), in individual cases emplacement values up to double the insignificance threshold values/HAL in the eluate are possible under certain conditions (VK2 with notes according to Tables 3a and b).

Where material is applied onto or introduced into a root-penetrable soil layer, it may be necessary to also consider the soil-plant pathway, especially with regard to short-chain PFAS (see Section 5.3.2).

6.2.2 Application and introduction of soil material below/beyond a root-penetrable soil layer

The recovery of soil material in soil-like applications (backfilling pits, quarries and trenches, landscaping measures, landscape management, site recultivation, or preparatory works to make site reusable) is feasible, in a manner similar to recovery on or in a root-penetrable soil layer, as long as this does not give rise to any concerns regarding detrimental changes to the soil or to groundwater. This is the case if the soil material to be recovered in the eluate (liquid-to-solid ratio of 2:1) does not exceed the provisional values of VK1 in Table 3a. Furthermore, the interim values of VK1 specified in Table 3b can provide guidance.

In areas with elevated PFAS concentrations (according to Article 12(10) BBodSchV and Article 6(4) of the new BBodSchV or generally established), in individual cases emplacement values up to double the insignificance threshold values/HAL in the eluate are possible under certain conditions (VK2 with notes according to Tables 3a and b).

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[27] https://www.labo-deutschland.de/documents/12-Vollzugshilfe_110902_9be.pdf (German only)

6.3 Recovery of soil material in built structures

Soil material in VK1 can be recovered in open emplacement in technical structures. Soil material in VK2 can only be recovered in areas with elevated PFAS concentrations if certain conditions in technical structures are met.

By contrast, soil material in VK3 can only be recovered in technical structures with defined technical safety measures (see notes on Tables 3a and b).

For the emplacement of soil material in technical structures in VK2 and VK3, the distance from the maximum expected groundwater level must be at least 1.0 m plus a safety distance of 0.5 m.

The requirements and stipulations of LAGA M 20 (LAGA Note 20) regarding defined technical safety measures should be applied to the emplacement of PFAS-contaminated soil material. However, other approaches can be adopted by the individual federal states as long as the technical requirements are fully adhered to and thus no concern arises that a detrimental change to groundwater or the soil can occur[28].

In cases where approval or notification is necessary, it is recommended to ensure that the competent authority is informed about the emplacement in question.

6.4 Shifting of soil in the context of remediation

The remediation of contaminated sites and detrimental changes to the soil is regulated by the risk prevention stipulations set out in BBodSchV. Under Article 5(6) BBodSchV, during remediation operations soil material can be applied, introduced or shifted in the area which includes the adverse soil alteration or contaminated site or within the area covered by a remediation plan declared as binding, if no risks, considerable disadvantages or nuisances arise as a result for individuals or the wider public in the long term.

The requirements for investigations and planning for remediation as established by Article 13 BBodSchG in conjunction with Annex 3 to BBodSchV are to be taken into account.

Generally, backfilling or shifting PFAS-containing soil material is possible in agreement with the competent authority if no risks, considerable disadvantages or nuisances are to be expected for individuals or the wider public in the long term. Following case-by-case appraisal and evaluation, this can be achieved by means of appropriate remedial, protective and restrictive measures.

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[28] For VK3, an alternative to emplacement with a covering is emplacement with water-impermeable base liner (analogous to the requirements stipulated by the German Landfill Ordinance (Deponieverordnung – DepV) for a DK (landfill class) I landfill) and a leachate treatment system designed specifically for PFAS (see Section 6.5).

6.5 Recovery and disposal on landfills

In general, the quantity (mass, volume) of PFAS-contaminated soil material that needs to be disposed of is to be reduced as far as possible by means of suitable pre-treatment measures (e.g. classification), and recyclable material is to be consigned to recovery (see note in Section 6.1).

Under KrWG and DepV, deposition of PFAS-contaminated soil material on landfills of landfill class (Deponieklasse – DK) 0 is only permissible for inert waste. Above-ground landfilling of PFAS-containing soil material that is not inert waste is only permissible on DK I, II and III landfills if the preconditions set out below are met. A case-specific assessment may be planned for a further review.

The values set out under VK1 in Tables 3a and b (unrestricted open recovery) can be drawn on to determine what constitutes inert waste. If these values are complied with in the eluate, there is no reason for concern about groundwater damage from deposition on a DK 0 landfill.

Soil material with a guidance value of $PFAS_{total}$ < 100 µg/l in the eluate at a liquid-to-solid ratio of 10:1 ($PFAS_{total}$ < 500 µg/l at a liquid-to-solid ratio of 2:1, see Section 4.3) can be deposited in DK I landfills if the allocation values of DepV are complied with. The $PFAS_{total}$ to be determined here is the sum of the PFAS compounds listed in Table 1.

The following requirements must be met for deposition in DK I to III landfills so that these landfills can fulfil their function as a pollutant sink for PFAS

- It must be ensured that suitable leachate treatment is carried out to meet the specified discharge conditions and that the PFAS can be sustainably removed from the material cycle. This can be done directly by an on-site leachate treatment facility, by treatment in a suitable off-site waste water treatment facility, or by a combination of both options. After this, the PFAS are to be destroyed.
- Until PFAS are included in LAGA M 28 (Technische Regeln für die Überwachung von Grund-, Sicker- und Oberflächenwasser sowie oberirdischer Gewässer bei Deponien – Technical rules for the monitoring of groundwater, leachate and surface water, and above-ground water bodies at landfills), the investigation programme for leachate and groundwater is to be extended to include the relevant PFAS and to include a PFAS sum parameter. If necessary (e.g. when PFAS-contaminated soils are deposited in a mono area), the competent authority can set appropriate trigger levels for groundwater in accordance with DepV. In cases where PFAS-contaminated soil is landfilled, it is therefore recommended that the competent waste authority is informed of the emplacement in question.

To minimise the formation and effectively treat PFAS-containing leachate from the disposal of PFAS-contaminated waste, it may be worth considering placing the soil material in a mono area with separate leachate collection and discharge. The emplacement area should be kept small and covered with waterproof material immediately after emplacement in order to direct the uncontaminated water to the peripheral ditches. The mono-deposition of PFAS-contaminated soils enables the leachate, which is usually only contaminated with PFAS, to be treated much more effectively. Deposition on mono areas also allows for later retrieval of the soils for recovery if suitable treatment processes are then available.

The aforementioned rules also apply accordingly to the recovery as landfill replacement construction materials.

Underground deposition

Under EU Regulation 2019/1021 (EU POPs Regulation), wastes contaminated with persistent organic pollutants (POPs) shall be disposed of or recovered in such a way as to ensure that the POP content is destroyed or irreversibly transformed. As of yet, the Regulation only contains limit values for PFOS specified in Annex IV. Under Article 7(4) of the EU POPs Regulation and Section 7(1) no. 7 DepV, above-ground landfilling of contaminated soil material is permissible up to a PFOS concentration of 50 mg/kg. It is possible that if the regulation is revised this value will be adjusted downward.

If the PFOS concentration exceeds 50 mg/kg, the contaminated material can be disposed of in permanent underground storage facilities for hazardous waste, including salt mines, pursuant to Annex V Part 2 footnote 1 of the EU POPs Regulation. However, such high levels of PFOS contamination have not been detected in Germany. The PFOS limit value is therefore not a determining factor in practice.

Glossary

6:2-FTS	6:2 fluorotelomer sulfonic acid (H4PFOS)
AbfKlärV	Sewage Sludge Ordinance (Klärschlammverordnung)
AbwV	Waste Water Ordinance (Abwasserverordnung)
AFFF	aqueous film forming foam
ALARA	As Low As Reasonably Achievable
BBodSchG	Federal Soil Protection Act (Bundesbodenschutzgesetz)
BBodSchV	Federal Soil Protection and Contaminated Sites Ordinance (Bundesbodenschutzverordnung)
CAS	Chemical Abstracts Service
DepV	Ordinance on Landfill Sites and Long-Term Storage Facilities (Landfill Ordinance – DepV)
DüMV	Fertiliser Ordinance (Düngemittelverordnung)
DK	landfill class (Deponieklasse)
ECHA	European Chemicals Agency
FTOH	fluorotelomer alcohol
GenX	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoic acid
GFS	Insignificance threshold (Geringfügigkeitsschwelle) - assessment basis applied by LAWA for substances in groundwater
HAL	health advisory levels (for drinking water)
KrWG	Circular Economy Act (Kreislaufwirtschaftsgesetz)
LABO	German Working Group on Soil Protection of the Federal States and the Federal Government (Bund-/Länder-Arbeitsgemeinschaft Bodenschutz)
LAGA	German Working Group on Waste of the Federal States and the Federal Government (Bund-/Länder-Arbeitsgemeinschaft Abfall)
LAWA	German Working Group on Water Issues of the Federal States and the Federal Government (Bund-/Länder-Arbeitsgemeinschaft Wasser)
MNQ	mean low water discharge
OGewV	Surface Waters Ordinance (Oberflächengewässerverordnung)
PBT	persistent, bioaccumulative, toxic
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid

PFBS	perfluorobutane sulfonic acid
PFC	per- and polyflourinated chemicals
PFCA	perfluorocarboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFDS	perfluorodecane sulfonic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFOSA	perfluorooctanesulfonamide
PFPeA	perfluoropentanoic acid
PFSA	perfluorosulfonic acid
PFUnDA	perfluoroundecanoic acid
PNECaqua	predicted no effect concentration (for aquatic organisms)
POP	persistent organic pollutant
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (EU chemicals regulation)
SVHC	Substances of very high concern (substance category under REACH regulation)
TWK	Drinking Water Commission of the German Environment Agency (Trinkwasserkommission)
TrinkwV	Drinking Water Ordinance (Trinkwasserverordnung)
EQS	Environmental quality standard (stipulated in OGewV, stated as annual average (AA-EQS) or maximum allowable concentration (MAC-EQS))
vPvB	Very persistent and very bioaccumulative (substance category under REACH regulation)
WHG	Federal Water Act (Wasserhaushaltsgesetz)
WFD	European Water Framework Directive

Annex

I. Pathways into the environment

PFAS emissions can generally arise at any stage of the life cycle – that is, at any point during manufacture, use or disposal. The possible scenarios for input into the environment are therefore many and varied. Known routes include discharge of waste water containing PFAS into treatment plants and water bodies, contamination of water and soil by PFAS-containing AFFFs (aqueous film-forming foams), and the application of organic residual waste material containing PFAS on farmland. By contrast, in cases of ubiquitous distribution, it is likely that the PFAS entered the environment through the air. This atmospheric transport can extend over vast distances, as demonstrated by the discovery of PFAS in very remote regions devoid of industrial activity.

I.1 Fire-fighting foams used by fire brigades

The widespread use of AFFF fire-fighting foams containing PFAS commenced in the early 1970s. These foams were and are used mainly by on-site fire brigades (e.g. at civil and military airports, at refineries and in the chemicals industry), although municipal fire brigades also use them. Until 2000, these fire-fighting foams generally contained PFOS manufactured through electrochemical fluorination (ECF). This process produces a mixture of different PFAS (different chain lengths, branched/unbranched). As a result, a characteristic pattern of PFAS of varying chain length is found in many instances of contamination with fire-fighting foams. Most PFAS manufactured at a later date have been produced using telomerisation (advantages: only even-numbered homologues (C2, C4, C6…), fewer by-products). Fire-fighting foams with a PFOS content of more than 0.001% have been banned throughout the EU since 2011.

More modern AFFF fire-fighting foams now frequently contain telomere-based PFAS (e.g. 6:2 fluorotelomer sulfonic acid (6:2 FTS), also known as H4PFOS, or other C6-based precursor compounds) rather than PFOS. Some cases of PFAS contamination caused by fire-fighting foams, particularly those linked to stationary sprinkler systems, mainly involve PFAS such as perfluoroalkylbetaines that cannot always be detected by routine analysis.

However, recent developments means that fluorine-free fire-fighting foams are now available for the vast majority of fires; AFFF agents are no longer necessary except in very rare instances.[29]

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[29] Fire-fighting foams and the environment: https://www.lfu.bayern.de/analytik_stoffe/pfc/feuerloeschschaeume_und_umwelt/index.htm (German only), or

Fire Safety Research of the German Federal States – Reports:

Investigation of fluorinated tenside-free fire-fighting agents and suitable methods for extinguishing fires involving frequently used polar liquids (i.e. foam-destroying liquids)

https://idf.sachsen-anhalt.de/fileadmin/Bibliothek/Politik_und_Verwaltung/MI/IDF/IBK/Dokumente/Forschung/Fo_Publikationen/imk_ber/bericht_187.pdf (German only)

I.2 PFAS input via organic residual waste material

The cases of extensive PFAS contamination in North Rhine-Westphalia (Arnsberg, 2006) and Baden-Württemberg (Rastatt, 2013) have resulted from the illegal and improper application of organic residual waste material contaminated by PFAS on farmland.
In the Rastatt case, it is thought that compost mixed with paper sludge was applied to agricultural land. This mixture contained polyfluorinated chemicals used to coat paper.

I.3 Waste water

PFAS are used by manufacturers in various branches of industry (see Annex III). They are often used to treat and finish surfaces e.g. as a mist suppressant and to reduce surface tension on textiles in order to improve water-, oil- and grease-repelling properties (e.g. in outdoor clothing, work clothing, upholstery, carpets), or to coat paper for food packaging or in the field of specialty chemicals, such as for the manufacture of fluorine-containing plastics. Depending on the application, this may mean that PFAS enter the industrial sewage system during the manufacturing process. Given that only a small to moderate share of many PFAS can be removed from the waste water in treatment plants and the AbwV does not at present define the best available technology for any specific pre-treatment to reduce PFAS, the substances are also discharged into the water bodies.

The use of PFOS has with a few exceptions been banned since 2006, and the use of PFOA has been completely banned since 2020. However, the following sources of PFAS emissions are still permitted (a detailed list of the sectors in which PFAS are or have been used is provided in Annex III):

- Diffuse inputs into municipal sewage networks via rainwater (atmospheric transport), groundwater ingress, etc.
- Waste water from industrial operations (e.g. electroplating) that use PFAS other than PFOS or PFOA (conversion of precursor substances into persistent degradation products), or from the manufacture of PFAS compounds.
- In the case of businesses that no longer use PFOS or PFOA but have used them in the past, and/or that have switched to polyfluorinated substitutes; it has been found that PFOS and PFOA discharges from such plants may continue for a number of years after their use is discontinued (“bleeding” of contaminated pipes and parts of the plant).
- Inputs from the remediation of soil or groundwater and from the lowering of groundwater levels (e.g. extraction for construction measures), waste water from water treatment plants, if PFAS were already present in the raw water used.
- Combined sewage overflows and in some cases faulty connections in separate sewage systems
- Fire-fighting foams that contain PFOS in quantities < 0.001% or other PFAS
- PFAS can also enter the environment via numerous consumer products, for example through the washing of textiles such as outdoor and work clothing that has been treated with the chemicals, or via the use of impregnation agents containing PFAS.

I.4 Contaminated sites and detrimental soil changes

I.4.1 Former industrial sites

Pathways via which PFAS enter the environment can result from industrial applications that lead to contamination of soil and groundwater. On former industrial sites, former plants with chrome-electroplating baths are particularly significant; in the old Länder (former West German federal states), PFAS are likely to have been used in these baths since the 1960s (in the new Länder (federal states) of former East Germany, they will probably have been used since the 1990s). They are significant in terms of contaminated sites due to the relatively large quantities of PFAS that were used (usually PFOS, but also PFBS and PFHxS).

Other sites for which it may be necessary to include PFAS in the investigations include, in particular, former industrial sites linked to textile processing, paper manufacturing and the photography and film industry. Detailed information on the relevance of PFAS in individual sectors can be found in the "LABO-Arbeitshilfe zur flächendeckenden Erfassung, standortbezogenen historischen Erkundung und zur orientierenden Untersuchung von Boden- und Grundwasserkontaminationen mit PFC" (LABO working guide to the comprehensive recording, site-related historical investigation and initial investigation of PFC-contamination of soil and groundwater; see also Annex III).

I.4.2 Former waste disposal sites and closed landfill sites

In the case of former waste disposal sites or closed landfill sites, the time at which an industrial site or landfill was closed is important for the relevance of PFAS. If the sites were closed in the 1970s, PFAS are unlikely to be present as intensive use of PFAS did not commence until after that time. Small municipal former waste disposal sites are also unlikely to contain significant levels of PFAS. Exceptions to this may in some circumstances include either company-owned former waste disposal sites, on which the business used PFAS in relevant quantities and closure occurred later than the 1970s, or deposits of rubble from fires (PFAS in fire-fighting agents). Investigations at a number of landfills in some federal states found that PFAS are regularly present in leachate.

I.4.3 Further information

With regard to the use of fire-fighting foams (see I.1), former and operational civil and military airfields, fire brigade training grounds and large fires are typical sites with potential PFAS pollution. Contaminated sites are also found on other sites formerly used for military purposes. Among the principal harmful compounds detected are aromatic and aliphatic hydrocarbons, which are found in the vicinity of tank systems and also near fire brigade training grounds. In many cases, these areas and the sites of major fires are also significant in terms of PFAS.

Mixing of PFAS-containing and PFAS-free soil material may occur at sites used for biological ex-situ remediation processes and in off-site decontamination plants. Carry-over of PFAS when the soil material is reintroduced cannot be ruled out.

For sectors relevant for PFAS contamination, remediated contaminated sites may on occasion require follow-up data recording with subsequent exploration and investigation of PFAS.

I.5 Atmospheric pathways

Systematic investigations at long-term soil monitoring sites in Baden-Württemberg and Bavaria indicate that low concentrations of PFAS, especially PFOA, PFOS and short-chain carboxylic acids are widely detected in eluates from topsoils at sites where contamination is completely unsuspected. The most probable reason for the detection of these substances, even in largely unaltered soils, is ubiquitous atmospheric transport, which contributes to global distribution of the substances.[30/31]

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[30] https://www.lubw.baden-wuerttemberg.de/boden/schadstoffe-im-fokus (German only)

[31] See also https://www.lfu.bayern.de/analytik_stoffe/pfc/pfc_belastung_boeden/index.htm (German only)

II. Legal basis

II.1 International and European regulations

The international Stockholm Convention on Persistent Organic Pollutants (POP Convention)

At international level, persistent organic pollutants (POPs) are regulated in the Stockholm Convention. Since the inclusion of PFOS in 2009 in Annex B of the Convention, parties are required to restrict the production and use of PFOS in their territory. With the inclusion of PFOA in Annex A in 2019, the production, use, import and export of PFOA has been prohibited since July 2020. PFHxS is currently in the process of being included in Annexes A, B and/or C of the Stockholm Convention and is expected to be regulated internationally as a persistent organic pollutant.

EU POPs Regulation

Regulation 850/2004/EC (EU POPs Regulation) transposed the provisions of the Stockholm Convention into European law. In July 2019, this was then replaced by the amended EU POPs Regulation (EU) 2019/2021.

The manufacturing, placing on the market and use of these substances, whether on their own, in mixtures or parts of articles, are prohibited, although some exemptions and certain limit values apply. The use of fire-fighting foams containing >0.001 weight-% PFOS was permitted only until 27 June 2011.

Delegated Regulation (EU) 2020/784 supplemented the POPs Regulation (2019/2021) with the addition of PFOA to Annex I in November 2020. However, the use of articles already in use the Union before 4 July 2020 containing PFOA, their salts and/or PFOA-related compounds shall be allowed.

European chemicals legislation (REACH Regulation)

Directive 2006/122/EC, published on 27 December 2006, introduced significant restrictions on the use of PFOS and their derivatives. This restriction was incorporated into the REACH Regulation (EC) No. 1907/2006 (Registration, Evaluation, Authorisation and Restriction of Chemicals). A restriction under REACH means that a substance is no longer authorised for use, in articles or mixtures. These restrictions are listed in Annex XVII to the REACH Regulation.

With the inclusion of PFOS in the POPs Regulation in 2011 (see above), the corresponding entries concerning PFOS in the REACH Regulation were deleted to avoid duplication of legislation.

With the inclusion in Annex XVII to the REACH Regulation (EU) 2017/1000, EU-wide restrictions also entered into force for PFOA, its salts and precursors. Since 4 July 2020, this Regulation prohibits the manufacture and placing on the market of these substances on their own, in mixtures or in articles; a limited number of exemptions apply. If PFOA, its salts and precursors are used as constituents of other substances, in a mixture or an article – for example, in waterproofing sprays, textiles or plastic food packaging – the applicable limit values are 25 ppb (= 25 µg/l) for PFOA and its salts and 1000 ppb (1000 µg/l) for precursors. Fire-fighting foam mixtures that were placed on the market before 4 July 2020 may be used up with no time limit.

Following the inclusion of PFOA in the POPs Regulation, this entry was also deleted (as was done in the case of PFOS on 15 December 2020) to avoid duplication of legislation at EU level.

Similarly, an EU-wide restriction on the manufacture and use of the long-chain PFAS **C9 - C14** will enters into force on 25 February 2023. If these substances, their salts or PFOA precursors are used as constituents of other substances, in a mixture or an article – for example, in waterproofing sprays, textiles or plastic food packaging – the applicable limit values are 25 ppb (= 25 µg/l) for the substance and its salts and 260 ppb (260 µg/l) for precursors. These regulations include longer exemption periods and concentration limits for individual uses.

EU-wide restrictions on the manufacture and use of **PFHxA** and **PFAS-containing fire-fighting foams**, as well as a comprehensive restriction of the PFAS substance group are currently in preparation.

Restrictions procedure for entire group of substances

In the case of PFAS, furthermore, a restriction on the use of the entire substance group and consistent focus on substitutes with less critical environmental properties appear necessary. German chemicals authorities (BfR, UBA, BAuA) are thus working together with the authorities of four other countries (the Netherlands, Sweden, Denmark and Norway) on a European regulatory proposal under REACH to regulate all other uses of PFAS that are not necessary for society. A proposal is to be submitted to the European Chemicals Agency ECHA in 2022, thus formally initiating the EU restriction procedure. As this is a very complex process, a decision is not expected before 2024.

Candidate list for Annex XIII

Substances of very high concern (SVHCs) may be included in the candidate list under Article 57 of the REACH Regulation. For example, according to Annex XIII to the REACH Regulation, substances which are carcinogenic, mutagenic or toxic to reproduction (CMR), persistent, bioaccumulative and/or toxic to the environment (PBT/vPvB) or pose some other risk are classified as substances of very high concern. When a substance is included on the candidate list, suppliers of an article containing that substance in a concentration above 0.1 % mass percentage are subject to an information obligation to enable safe use of the article and consumer have a right to this information.

Substances which are added to the candidate list may subsequently be included on the authorisation list (Annex XIV to the REACH Regulation). Once a substance has been added to Annex XIV, its use in the EU is prohibited. Businesses may, however, apply for authorisation for certain uses if, for example, no suitable alternatives are available or if there are socio-economic factors justifying the continued use of the substance. In such cases, minimisation measures should be aimed for as a matter of principle.

The long-chain PFAS listed in Table A-1 are already included in the candidate list due to their persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) properties. Toxicity is based on classification of the substance in accordance with the EU CLP Regulation32.

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[32] CLP Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

Table A-1: Overview of PFAS which, due to their SVHC properties, are candidates for inclusion in Annex XIV to the REACH Regulation

Substance	**SVHC property***	**Classification under CLP Regulation (Annex VI CLP)**
Perfluorooctanoic acid (PFOA; C8-PFASA) and the ammonium salt APFO	PBT, CMR	Carc. 2 Repr. 1B Lact STOT RE 1 Acute Tox. 4 Eye dam. 1
Perfluorononanoic acid (PFNA; C9-PFASA) and its sodium and ammonium salts	PBT, CMR	Carc. 2 Repr. 1B Lact. Acute Tox. 4 STOT RE 1 Eye Dam. 1
Nonadecafluorodecanoic acid (syn. perfluorodecanoic acid (PFDA); C10-PFASA) and its sodium and ammonium salts	PBT, CMR	Carc. 2 Repr. 1B Lact.
Henicosafluoroundecanoic acid (syn. perfluoroundecanoic acid (PFUnDA); C11-PFASA)	vPvB	-
Tricosafluorododecanoic acid (syn. perfluorododecanoic acid (PFDoDA); C12-PFASA)	vPvB	-
Pentacosafluorotridecanoic acid (syn. perfluorotridecanoic acid (PFTrDA); C13-PFASA)	vPvB	-
Heptacosafluorotetradecanoic acid (syn. perfluorotetradecanoic acid (PFTeDA); C14-PFASA)	vPvB	-
Perfluorobutane sulfonic acid (PFBS)	vP, very mobile	-
Perfluorohexane sulfonic acid (PFHxS) and its salts	vPvB	-
2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX, HFPO-DA)	-	-

* PBT: persistent, bioaccumulative and toxic; vPvB: very persistent and very bioaccumulative; CMR: carcinogenic, mutagenic or toxic to reproduction

PBT and vPvB substances remain in the environment for long periods of time. The long-term effects of accumulation in organisms are impossible to predict; however, such accumulation is generally irreversible. Due to their persistence, the levels of these substances found in environmental media cannot be lowered to any significant extent by reducing emissions. Furthermore, PBT and vPvB substances can be transported into and hence contaminate locations quite remote from their original sources.

Although for PBT and, in particular, vPvB substances, standard laboratory tests have produced little or no evidence of acute toxicity, prolonged low-dose exposure may have long-term impacts which are almost impossible to predict due to the long life cycles of organisms at the end of the food chain. Long-term effects therefore cannot be ruled out as the levels of PBT and vPvB substances accumulating in humans and the environment over extended time periods are also impossible to forecast.

This currently applies to all perfluorinated carboxylic acids with a chain length ranging from 8 to 14 C atoms, and to PFOS and PFHxS. Accordingly, a PNEC (= Predicted No-Effect Concentration) cannot be determined under REACH for these substances (see also Annex II.3). Emissions of these substances should therefore be minimised as far technically and economically feasible.

EU Chemicals Strategy for Sustainability

The Chemicals Strategy for Sustainability presented by the European Commission in October 2020 contains, among other things, a PFAS action plan. Concrete activities envisaged are the restriction of fire-fighting foams (in preparation at the European Chemicals Agency) and other uses that are not essential for society. In future, PFAS are to be addressed with a group approach under the relevant legislation on water, sustainable products, food, industrial emissions and waste. The Commission also wants to develop an EU-wide approach to the remediation of PFAS contamination and provide financial support for research projects with a view to the substitution of these substances with more environmentally sound chemicals.

Revision of EU Drinking Water Directive

The new EU Drinking Water Directive 2020/2814 of 16 December included PFAS as follows: By the start of 2024, the Commission shall establish technical guidelines regarding methods of analysis for monitoring the new PFAS parameters. Detection limits, parametric values and frequency of sampling. By 2026, member states shall ensure compliance with the values set out.

Minimum requirements:

- PFAS Total: 0.50 µg/l (totality of per- and polyfluoroalkyl substances)
- Sum of PFAS: 0.10 µg/l (sum of the 20 per- and polyfluoroalkyl substances listed in Part B of Annex III):
    - Perfluorobutanoic acid, PFBA
    - Perfluoropentanoic acid, PFPeA
    - Perfluorohexanoic acid, PFHxA
    - Perfluoroheptanoic acid, PFHpA
    - Perfluorooctanoic acid, PFOA
    - Perfluorononanoic acid, PFNA
    - Perfluorodecanoic acid, PFDA
    - Perfluoroundecanoic acid, PFUnDA
    - Perfluorododecanoic acid, PFDoDA
    - Perfluorotridecanoic acid, PFTrDA
    - Perfluorobutane sulfonic acid, PFBS
    - Perfluoropentane sulfonic acid (PFPeS)
    - Perfluorohexane sulfonic acid, PFHxS
    - Perfluoroheptane sulfonic acid, PFHpS
    - Perfluorooctane sulfonic acid, PFOS
    - Perfluorononane sulfonic acid, PFNS
    - Perfluorodecane sulfonic acid, PFDS

- Perfluoroundecane sulfonic acid
- Perfluorododecane sulfonic acid
- Perfluorotridecane sulfonic acid

In addition, the inclusion of PFAS in the Annexes to the EU Groundwater Directive is envisaged.

PFAS in food

In September 2020, EFSA presented its finalised opinion on PFAS in food: EFSA focussed, in particular, on the evaluation of peer-reviewed literature published between January 2007 and September 2018. As a result, a sum TWI for the four long chain PFAS with multiannual half-lifes in humans, PFOA, PFOS, PFHxS, PFNA ,of 4.4 ng/kg BW per week was established in a pragmatic approach. This represents a lowering once again of the current TWI. The most sensitive toxicological endpoint for all four substances was immunotoxicity based on animal testing and epidemiological studies. The exposure estimates of EFSA for PFAS in food indicate a health concern due to the exceedances of TWI.

Discussions began at EU level in November 2020 on establishing, for the first time, a maximum concentration for the four substances for which the sum TWI was set. The initial focus is on the food groups, which, according to the EFSA opinion, are a significant factor in terms of PFAS exposure and for which sufficient data is available. In preparation for the establishment of maximum concentrations, more sensitive methods of analysis for animal- and plant-based food need to be developed due to the new much lower TWI.

First proposals to set maximum PFAS levels in food and to adapt EU Recommendation 2010/161/EU on the monitoring of perfluoroalkylated substances in food were presented by the European Commission in June 2021 to the member states with the opportunity to comment.

II.2 Germany: national regulations to limit PFAS inputs into the environment

Uniform regulations applicable throughout Germany for this class of substances are currently set out in OGewV of 20 June 2016 (last amended 9 December 2020) which defines environmental quality standards (EQS) for PFOS. If these standards are exceeded in a surface water body, appropriate measures must be taken in order to achieve compliance from 2027 at the latest. An additional monitoring programme and a programme of temporary measures to minimise PFOS contamination have been in place since 22 December 2018.

Further provisions are laid down in DüMV, which sets a maximum limit of 100 µg/kg dry matter for the sum of PFOA and PFOS.

For seven individual PFAS on the basis of human toxicological data, insignificance threshold values were established for groundwater and guide values for drinking water. On this basis, trigger values were formulated for the soil-groundwater pathway for these seven PFAS in the revised BBodSchV.

No other national legislation currently defines specific limit values for this class of substances.

II.3 Surface waters - How PNEC and EQS are derived

PFHxS, PFOA, PFNA and PFDA, as well as all perfluorinated carboxylic acids with 11 to 14 carbon atoms in the chain, are currently classified as substances of very high concern (SVHC) under REACH due to their persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) properties (see II.3). PFOS, PFOA, PFDA and PFNA are additionally classed as CMR substances.

The very high concern raised by PBT substances relates to the fact that once they enter the environment, they remain there for a very long time. They can also accumulate in environmental media or in organisms over long periods of time and then cause harm. It is impossible, however, to predict precisely when and where such effects will occur. The damage caused to human health and the environment by PBT or vPvB substances is often irreparable, which is why the precautionary principle is built into the REACH Regulation.

Due to their persistence in the environment and high potential to accumulate in organisms, it is not possible to determine a concentration level in the environment for PBT and vPvB substances under REACH that ensures with certainty that no adverse effects will occur in future. PNECs can be calculated for certain environmental assets (e.g. $\text{PNEC}_{\text{aquatic}}$ for aquatic biocoenoses) based on current data, but do not offer the required certainty for risk minimisation in relation to all the assets under consideration. A PNEC – as an indicator of a “safe” concentration in the environment – is therefore accompanied by a high degree of uncertainty and cannot be derived for the biocoenosis as a whole. One factor to bear in mind, however, is that accumulation of water-soluble PFAS in aquatic organisms is relatively low. In fish, effects are only observed at comparatively high concentrations, and this in turn produces relatively high $\text{PNEC}_{\text{aquatic}}$ values. By contrast, terrestrial apex predators have been shown to be heavily contaminated with PFOA and other long-chain PFAS. There is evidence of this in otters, for example. Interestingly, to date humans have been found to be the organism most sensitive to the effects of PFAS contamination. Humans mainly ingest PFAS in food (e.g. fish), drinking water, air and dust. From a human health perspective, therefore, minimising PFAS inputs into water bodies is extremely important in order to curb any further spread of these substances and reduce human exposure.

The relevant environmental quality standards (EQS) for assessing priority substances such as PFOS in accordance with the Water Framework Directive include criteria for deriving PNEC (protection of the aquatic environment based on species across three trophic levels, i.e. algae, daphnia and fish), protecting fish-eating animals from secondary poisoning and protecting human health during fish consumption.

III. PFAS uses

Apart from their use in fire-fighting foams (see Annex I.1), the other main areas where PFAS are used are the surface treatment of textiles, paper coating and specialty chemicals.

Detailed information about the relevance of PFAS in the individual sectors can be found in LABO's guidance on assessing soil and groundwater contamination with PFAS[33].

An overview of selected sectors of PFAS relevance is provided below:

Chemicals industry

The chemicals industry covers a very broad and diverse range of applications, with widespread distribution all along the product chain. Very little data is available on the sectors listed below. No information whatsoever is available on the quantities used and usage periods, or on whether the area of application is in fact relevant to Germany.

Usage period: from around 1970 to present.

PFAS substances/groups of substances: possible use of chemicals from the entire PFAS product range.

Sectors:

- Production of PFAS and their polymers,
- Production of formulations,
- Use of PFAS (as process chemicals and additives in syntheses) in the manufacture of products which do not ultimately contain PFAS,
- Use of PFAS to manufacture products which contain PFAS.

Electroplating

PFAS are used in surface treatment in hard chromium plating, decorative chromium plating and electroplating of plastics using chromium. Appendix 40 to AbwV applies (no PFAS limit values). Since 2015, the EU POPs Regulation only permits the use of PFAS as mist suppressants for non-decorative hard chromium (VI) plating in closed loop systems.

Usage period: from around 1960 to present (exemption for PFOS)

PFAS substances/groups of substances: PFOS, 6:2 FTSA, PFBS, PFHxS

Sectors: surface finishing/surface technology using the following processes:

1st priority: hard chromium plating, decorative chromium plating, electroplating of plastics using chromium

2nd priority: zinc plating, copper plating, nickel plating, gilding, electroplating, precious metals, anodising

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[33] State finance programme water, soil and waste, section on soil (2016): Soil and groundwater contamination with PFAS on sites with suspected contamination and after use of fire-fighting foams - criteria for recording and historical investigation of soil and groundwater PFAS contamination — Cross-state ALA guide (project level 1). (*Länderfinanzierungsprogramm Wasser, Boden und Abfall, Teil Boden (2016): Boden- und Grundwasserkontaminationen mit PFAS bei altlastverdächtigen Flächen und nach Löschmitteleinsätzen - Kriterien für die Erfassung und historische Erkundung von Boden- und Grundwasserkontaminationen mit PFAS – Länderübergreifende ALA-Arbeitshilfe (Projektstufe 1)*) LFP Project B 4.14 (http://www.laenderfinanzierungsprogramm.de/projektberichte/labo/, Project B 4.14 - German only)

Textiles industry

Textile factories which use wet finishing processes to apply waterproofing and stain protection or produce membranes are relevant in terms of contaminated sites and waste water. Appendix 38 to AbwV applies (no PFAS limit values).

Usage period: from around 1960 to present (with the exception of PFOS: ended 2006)

PFAS substances/groups of substances: fluorocarbon resins, fluoropolymers, PFOS, PFOA, 6:2 FTOH, fluorotelomer acrylates, side-chain fluorinated polymers based on C6

Sectors: manufacturing of textiles, technical textiles, carpets, membranes (e.g. Gore-Tex)

Paper industry

The potential environmental risk is limited to paper and cardboard manufacturing. Appendix 28 to AbwV applies.

Usage period: from around 1960 to present

PFAS substances/groups of substances: side-chain fluorinated polymers (all chain lengths), phosphate esters of N-EtFOSE, fluorocarbon resins, perfluoropolyether (PEPE), PAP, polyfluorinated phosphonic acids (PFOS, PFOA and precursors as relevant secondary contaminants), diPAP, SAmPAP

Sectors: paper and cardboard manufacturing

Paint and varnish manufacturing

It is difficult to make firm statements about the relevance of contaminated sites here. Contaminated sites are most likely when PFAS additives were used in the manufacture of paint/varnish.

Usage period: from around 1960 to present (with the exception of PFOS: ended 2006)

PFAS substances/groups of substances: PFOS and PFOS-related substances, PFBS, fluorinated polyethers, fluoropolymers – PVDF (polyvinylidene fluoride – polymer of C2H2F2).

Sectors: paint and varnish manufacturing – paints/varnishes with water-, stain- and oil-repellent properties; manufacturing of printing inks (paint shops and industrial establishment with painting facilities)

Fire-fighting foams (see also Annex I.1)

Usage period; from 1970 to present

PFAS substance group: Fire-fighting foams containing fluorine: Aqueous Film Forming Foam (AFFF) contained PFOS and PFHxS until around 2010. Newer foams are mainly based on C6 chemistry, i.e. contain precursor substances, which can be degraded to PFHxA or PFHxS. Fluorotelomer betaine and perfluorinated betaine are typical components of the current generation of fire-fighting foams.

Sectors: Fire services (factory, professional, airport and voluntary)

Semiconductor industry

Due to the process used, no specific environmental risk to soil or groundwater is expected. Appendix 54 to AbwV applies (no PFAS limit values).

Usage period: from around 1995 to present (with the exception of PFOS: ended 2006)

PFAS substances/groups of substances: PFOS, precursors based on C8, C6 and C4 chemistry

Sectors: semi-conductor manufacturing

Photography industry

As with the semi-conductor industry, no relevant environmental risk is expected.

Usage period: from around 1995 to present, mainly until 2000

PFAS substances/groups of substances: PFOS, precursors based on C8, C6 and C4 chemistry

Sectors: print media production, developing laboratories, businesses involved in processing developer solutions

Hydraulic fluids

No environmental risk to soil and groundwater is expected from the use of hydraulic fluids in the aviation industry. The quantities of PFOS used are minimal.

Usage period: start date unclear; in use at present

PFAS substances/groups of substances: PFOS, potassium perfluoroethyl cyclohexyl sulfonate (FC-98)

Sectors: aircraft construction, aircraft maintenance (airports)

IV. Overview of compounds analysable under ISO 21675:2019-10

Table A-2 lists the compounds analysable using the ISO 21675:2019 method. This method covers not only the 13 PFAS analysed under DIN 38407-42 (F42), but also other PFAS compounds such as PFOA substitutes GenX and DONA and the main component of F-53B 9Cl-PF3ONS.

Table A-2: Overview of compounds listed in ISO 21675:2019

Substance	**Abbreviation**	**Formula**	**CAS**
Perfluorobutanoic acid	PFBS	$C_4HF_9O_3S$	375-73-5
Perfluorohexane sulfonic acid	PFHxS	$C_6HF_{13}O_3S$	355-46-4
Perfluoroheptane sulfonic acid	PFHpS	$C_7HF_{15}O_3S$	375-92-8
Perfluorooctane sulfonic acid	PFOS	$C_8HF_{17}O_3S$	1763-23-1
Perfluoroundecane sulfonic acid	PFDS	$C_{10}HF_{21}O_3S$	335-77-3
Perfluorooctanesulfonamide	PFOSA	$C_8H_2F_{17}NO_2S$	754-91-6
N-methyl perfluorooctane sulfonamide	N-MeFOSA	$C_9H_4F_{17}NO_2S$	31506-32-8
N-ethyl perfluorooctane sulfonamide	N-EtFOSA	$C_{10}H_6F_{17}NO_2S$	4151-50-2
N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	$C_{11}H_6F_{17}NO_4S$	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	$C_{12}H_8F_{17}NO_4S$	2991-50-6
6:2 Fluorotelomer sulfonic acid	6:2 FTSA (H4PFOS)	$C_8H_5F_{13}O_3S$	27619-97-2
8:2 Fluorotelomer sulfonic acid	8:2 FTSA	$C_{10}H_5F_{17}O_3S$	39108-34-4
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	$C_8HClF_{16}O_4S$	756426-58-1
Perfluorobutanoic acid	PFBA	$C_4HF_7O_2$	375-22-4
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	2706-90-3
Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	307-24-4
Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	375-85-9
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	335-67-1
Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	375-95-1
Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	335-76-2
Perfluoroundecanoic acid	PFUnDA	$C_{11}HF_{21}O_2$	2058-94-8
Perfluorododecanoic acid	PFDoDA	$C_{12}HF_{23}O_2$	307-55-1
Perfluorotridecanoic acid	PFTrDA	$C_{13}HF_{25}O_2$	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	$C_{14}HF_{27}O_2$	376-06-7

Perfluorohexadecanoic acid	PFHxDA	$C_{16}HF_{31}O_2$	67905-19-5
Perfluorooctadecanoic acid	PFOcDA	$C_{18}HF_{35}O_2$	16517-11-6
8:2 Fluorotelomer unsaturated carboxylic acid	8:2 FTUCA	$C_{10}H_2F_{16}O_2$	70887-84-2
8:2 Polyfluoroalkyl phosphate diester	8:2 diPAP	$C_{20}H_9F_{34}O_4P$	678-41-1
Hexafluoropropylene oxide dimer acid	HFPO-DA / FRD-903 / GenX	$C_6HF_{11}O_3$	13252-13-6
4,8-dioxa-3H-perfluorononanoate	DONA	$C_7H_2F_{12}O_4$	919005-14-4

V. Case studies from the federal states

V.1 Baden-Württemberg

Food assessment procedure

Plants can in principle absorb PFAS from the soil or from irrigation water. Studies have shown that it is mainly short-chain PFAS (PFBA, PFPeA, PFHxA) that are absorbed. In addition, different plant species have been found to have different uptake capacities: soya beans, vegetables and wheat absorb PFAS easily, while no transfer to the grain has been detected in maize or rapeseed.

The need for trigger values for the soil-plant pathway is recognised, but a basis for evaluation is lacking (pre-harvest monitoring is currently carried out in some places e.g. in the Rastatt/Baden-Baden area). There is not yet sufficient data on soil-plant transfer of PFAS for transfer factors to be calculated. It should be noted that transfer depends on a number of different factors, such as PFAS chain length. Systematic studies of soil-plant transfer under field conditions are considered necessary.

With regard to the assessment of PFAS residues in animal- and plant-based foods, the only binding basis for decision making at present is the Tolerable Weekly Intake (TWI) of 4.4 ng/kg, established by the European Food Safety Authority (EFSA) in 2020, for the sum of the four long-chain PFAS compounds PFOS, PFOA, PFHxS and PFNA (see Annex II.1). There are as yet no other TWIs or legally binding limits for short-chain PFAS compounds.

Following a major case of PFAS contamination on various areas of agriculturally used land and in groundwater, surface water and drinking water in three administrative districts in Baden-Württemberg, and in light of the above-mentioned lack of legally binding limit values, the Baden-Württemberg Ministry of Rural Affairs, Food and Consumer Protection calculated and defined its own assessment values for short-chain PFAS in plant- and animal-based foods. These tolerable values for food provide a tool for official food monitoring; they are designed to be used in combination with prior pre-harvest monitoring to ensure that foods contaminated with PFAS are not placed on the market. These assessment values in Baden-Württemberg were derived from the guidance levels and health advisory levels for PFAS in drinking water published and later updated by the German Environment Agency (UBA), taking into account the precautionary and minimisation principles. They also take account of factors such as the average amounts ingested daily from food, as detailed in the national nutrition survey (Nationale Verzehrstudie).

The factors that influence the PFAS absorption of different crops are highly diverse; in most cases they have not been sufficiently researched and cannot be influenced. It is therefore not currently possible to accurately predict PFAS absorption by plants for known values in the soil. Nevertheless, cultivation recommendations for the most important crops have been drawn up based on the data from pre-harvest monitoring and experiment results.

Further information (in German) is available on the website of the Karlsruhe regional council: https://rp.baden-wuerttemberg.de/rpk/Abt5/Ref541/PFC/Seiten/default.aspx

V.2 Bavaria

Discharge into surface waters

Water contaminated with PFAS may need to undergo treatment in line with the best available technology before being discharged into a surface water body. With regard to the groundwater discharge that is extracted for remediation, the requirements are considered met in the example below if at least 90% of PFAS are removed. In addition, the level for the total of all 13 PFAS that can be tested under the DIN standard should not exceed 200 ng/l, and the level of PFOS as a single substance in the treated water should not exceed 20 ng/l. The same procedure applies to the discharge of water used in fire-fighting operations that is contaminated with PFAS.

A practical example:

- The PFOS concentration in an affected water body is on the scale of around 6 ng/l, which at an MNQ of 131 m^3/s corresponds to a load of 786 µg/s
- The volume of groundwater extracted and to be cleaned in the event of contamination with PFAS: 50 m^3/h = 14 litres/s
- Cleaning e.g. via activated carbon, cleaning target values: 200 ng/l total PFAS, 20 ng/l PFOS
- An additional load of 14 l/s x 20 ng/l = 280 ng/s = 0.28 µg/s for PFOS increases the total load in the water body from 786 µg/s to 786.28 µg/s and leads in mathematical terms to an increase of around 0.002 ng/l in the concentration. This is within the fluctuation margin of the measurement technology and cannot be analytically proven.

Extraction for construction measures

The discharge of extracted groundwater into a surface water body is governed by the load-related requirements set out in Section 5.1.3 of this guide. Rules on the assessment of a deterioration in water quality are set out in OGewV using the environmental quality standard for PFOS of 0.65 ng/l. Short-term deterioration of a water body can be ignored if it can be assumed on the basis of a case-specific assessment that the previous status of the water body will soon be restored and the assumption that deterioration has occurred would be disproportionate. Under the Ordinance, all extraction for construction measures must include examination of the duration and extent (volume of water, PFAS concentration/load) of groundwater extraction. Small-scale extraction for construction measures, e.g. for individual residential buildings, may therefore be assessed differently from water inputs from long-running groundwater remediation programmes or long-term extraction for construction measures.

If measures to remediate the groundwater have already been taken or will be taken in the foreseeable future (e.g. as part of the enforcement of soil protection regulations) and this is expected to lead to a significantly more efficient reduction in the contaminant load compared with the mitigation achieved through water removal and cleaning in the context of short-term extraction for construction measures, cleaning before infiltration (reintroduction into the polluted groundwater) is not required in these individual projects.

V.3 North Rhine-Westphalia

Discharge of treated groundwater into a surface water body

After initial evidence from the Duisburg waterworks of elevated PFAS concentrations in an upstream monitoring station of a water extraction plant, the city of Düsseldorf has since 2007 systematically carried out risk-oriented groundwater testing for PFAS in the north of Düsseldorf. The scope of testing is being continuously expanded. Four input points on the grounds of Düsseldorf Airport have been identified. Contaminant plumes flow from these points towards the Rhine.

Sampling revealed concentrations significantly above the general precautionary value of 100 ng/l PFAS at several monitoring stations; in isolated cases values of up to 57,000 ng/l PFAS were found. A similar picture was observed in connection with the artificial lakes in the north of Düsseldorf that have emerged as a result of excavations. Existing groundwater contamination thus directly influences the water quality in the lakes. PFAS concentrations of up to 5,000 ng/l were measured in one lake.

PFAS groundwater remediation at Düsseldorf Airport involves cleaning groundwater contaminated with PFAS using ion exchangers and active carbon filters. Equipment for hydraulic screening of the input sources was put into operation between November 2015 and June 2016. The necessary withdrawal quantities for hydraulic capture of the contaminants in the vicinity of the input points were calculated based on the city of Düsseldorf's groundwater model:

- Former fire-fighting practice basin: withdrawal of 14 m³/h from three wells
- Northern fire station: withdrawal of 18 m³/h from five wells
- Atlas Air accident site: withdrawal of 22 m³/h from two wells

The stationary system is constructed as follows:

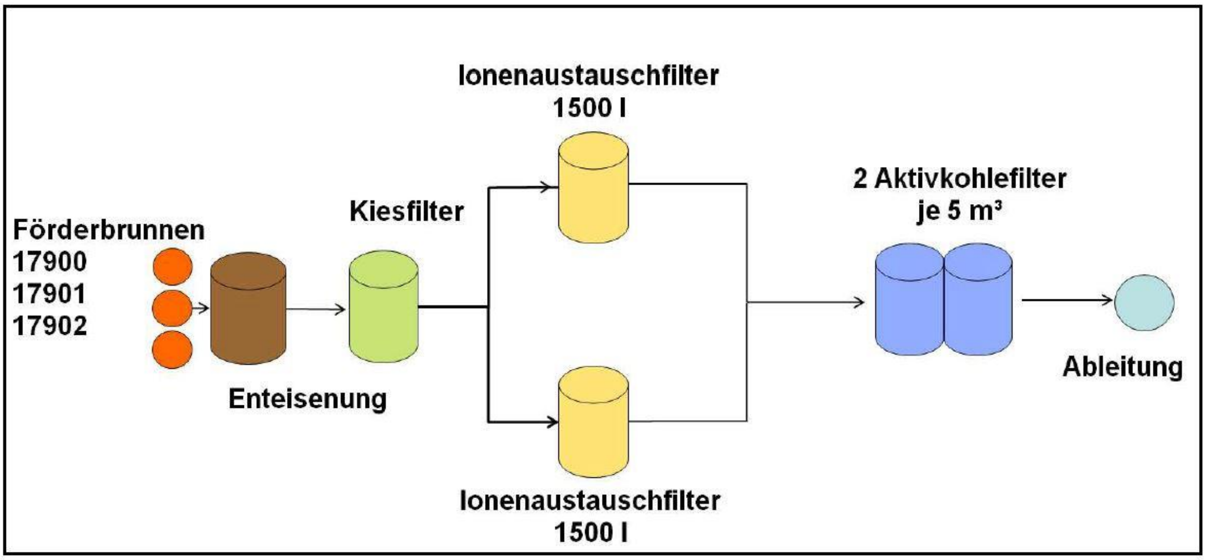

Figure A-3: The principle of the cleaning system at the former fire-fighting basin when complete

The cleaned water from the three remediation systems is discharged into a surface water body. The following water-law requirements were formulated for the water-law permits: for the purpose of remediation, the contaminated groundwater is to be extracted, treated, and discharged either directly or indirectly into a water body. In the present case, the groundwater is discharged after treatment into an above-ground water body. The discharge of treated groundwater into a public or private sewage system is not recommended, as no targeted PFAS reduction is performed in sewage treatment plants that do not have contaminant-specific technology; instead, the additional quantity of water merely increases the hydraulic load on the treatment plant and all related consequential problems.

Reinfiltration of the treated groundwater is also not an option in the present case. Under § 48 (1) WHG, a permit for the introduction or discharge of substances into the groundwater can only be granted if there are no grounds to fear any detrimental changes in the water properties. Given that permeability can vary widely even in a quaternary aquifer, it is very difficult to predict the expected spread of reinfiltrating groundwater underground in either the unsaturated or the saturated soil zone. It is also not possible to control the spread of the reinfiltrating groundwater underground. There is therefore considered to be a risk that reinfiltration causes further spread of the contamination or new long-term damage.

Contaminated groundwater is not classed as waste water in the strict sense for the purposes of the water regulations contained in § 54 WHG and Section 51 of the State Water Act of North Rhine-Westphalia (LWF NRW). The emission requirements defined for waste water discharges could be used as a source of information. However, as the AbwV does not contain any concrete rules on PFAS, the reference points used are the requirements for direct and indirect dischargers established by decree in North Rhine-Westphalia, and the general requirements.[34] According to the decree, the guidance values for waste water are 300 ng/l for PFOS and PFOA combined and 1,000 ng/l for the total of all PFAS. The load-related requirements of OGewV must be met and the no-deterioration principle must be observed.

According to the official monitoring of water quality in the Kittelbach river above the planned input point, the majority of the PFAS concentrations (from 2014 incl. 6:2 FTS) are below the quantitication limit. Concentrations above the quantitication limit were detected at some testing times.

The highest level of PFAS recorded to date was around 200 ng/l.

Based on the data from a water gauge, the mean low water discharge (MNQ) is 0.36 m³/s (1296 m³/h) and the mean flow (MQ) is 0.74 m³/s.

Calculation of the permissible input concentration: $A_{Ww} \cdot C_{Ww} = MNQ \cdot C_{BG}$

MNQ = mean low water discharge (volume/time)

C_{BG} = background concentration (mass/volume)

A_{Ww} = waste water flow (volume/time) or volume flow at groundwater treatment plants

C_{Ww} = substance concentration in waste water (mass/volume) or concentration in discharge from groundwater treatment

Calculation of the maximum permissible sum concentration all measured PFAS in the discharge from groundwater treatment (= input) on the condition that no appreciable elevation of the content in the water body is caused (benchmark: quantitication limit of the analysis process of 10 ng/l):

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[34] Decree of the Ministry for Climate Protection, Environment, Agriculture, Conservation and Consumer Protection of the State of North Rhine-Westphalia of 6 June 2014, ref.: IV-7 096 004 0052

C_{Ww}= MNQ / A_{Ww} ▪ C_{BG} = 1296 m^3/h / 54 m^3/h ▪ 10 ng/l

C_{Ww}. = 240 ng/l (sum of all measured PFAS)

selected: C_{Ww}. = 200 ng/l

Calculation of the maximum permissible concentration of PFOS in the discharge from groundwater treatment (= input) on condition that no notable elevation of the content in the water body is caused (benchmark: EQS = 0.65 ng/l):

C_{Ww} = MNQ / A_{Ww} ▪ CHG = 1296 m^3/h / 54 m^3/h ▪ 0.65 ng/l

C_{Ww} = 15.6 ng/l (PFOS)

selected: twice the detection limit of the analysis process: C_{Ww} = 20 ng/l

Assuming that the remediation measures at the airport initially require 54 m^3/h of treated groundwater to be introduced into the water body, compliance with the maximum concentration of 200 ng/l for total PFAS would result in a load of approx. 10,000 µg/h being discharged into the water body. At MNQ this would result in a mean concentration increase of 10 ng/l, which would accordingly lie within the range of measurement accuracy. The discharge would therefore not cause any notable elevation of PFAS concentrations in the water body. The no-deterioration principle would thus be observed if the above-mentioned values are adhered to.

<u>PFAS values in cleaned groundwater to be observed for discharge into an above-ground water body in a concrete case:</u>

In the concrete case, treatment of the groundwater extracted for remediation is to be carried out, giving due regard to load-related considerations, before discharge into an above-ground water body. In the present case, this requirement is considered to be met if

- the degree of cleaning for PFAS is >90%.

To ensure that the discharge from groundwater remediation observes the no-deterioration principle, even if PFAS concentrations in the extracted groundwater are very high,

- the level of total PFAS < 200 ng/l

in the groundwater to be discharged after treatment must be observed. The environmental quality standard for PFOS must also be adhered to. Taking account of the current analytical options, it was established that these requirements are considered to be met if

- PFOS < 20 ng/l[35]

is adhered to in the groundwater to be discharged. Monitoring of the system should be designed so that breaches are identified promptly, taking into account the time frame of the analysis. Compliance with the no-deterioration principle should be checked through appropriate monitoring. Operational monitoring for recording of the contaminant plume should also be put in place.

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[35] Corresponds to twice the detection limit of 10 ng/l that can normally be achieved