Zero pollution of Persistent, Mobile substances

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TOP-Assay fitness check and Passive Sampling Device Validation

Part 1: TOP-Assay fitness check

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Summary

This report is the first in the series of "TOP-Assay fitness check and Passive Sampling Device Validation", which is a deliverable for the ZeroPM research project. Both reports outline the state-of-the-art for developing novel approaches for per- and polyfluoroalkyl substances (PFAS) monitoring. This first report focuses on the total oxidisable precursor (TOP) assay.

The recent OECD definition of per- and polyfluoroalkyl substances (PFAS) [1] includes over 7 million different chemical compounds that can be found on chemical databases. It is therefore evident that the development of a meaningful sum parameter is of great interest in a regulatory context. The total oxidisable precursor (TOP) assay, a chemical digestive method, has been identified as a potential candidate for such a parameter. This assay converts a very broad range of potentially extremely difficult to analyse PFAS precursors, into analytically accessible perfluorocarboxylic acids (PFCAs) (and, to a lesser extent, to other reaction products, such as perfluoroalkyl sulfonic acids (PFSAs)). The original TOP assay, which was persulfate-based, was designed for the analysis of aqueous samples. Currently, various persulfate-based TOP assay modifications are available for the analysis of solids. These include the eTOP (where e stands for extract), in which extracts of, e.g., soils, suspended solids or biota are oxidised, and the dTOP (where d stands for direct), in which an aliquot of the solid is used directly and without prior extraction.

The present report describes a so-called fitness-check for the persulfate-based TOP assay, which is considered a potential proxy for the parameter "PFAS Total", in the Directive (EU) 2020/2184 of the European Parliament and of the Council of December 16, 2020, on the quality of water intended for human consumption (The Drinking Water Directive). This fitness-check aimed to investigate if a generalised TOP assay protocol would exist or could be developed, and if it could also be applied to other matrices than drinking water, e.g. soil and sewage sludge. For this purpose, both a systematic and comprehensive literature review and laboratory experiments were carried out. The goal of the present study was to check if the criteria *completeness, sensitivity, and uncertainty* can be fulfilled by a certain TOP assay protocol in order to serve as an acceptable proxy for "PFAS Total". The primary outcome of the investigation is that a persulfate-based TOP assay does not align with the defined criteria. A dTOP approach is needed in order to achieve the most comprehensive digestion of samples. However, this persulfate-based approach hampers the analysis of ultrashort-chain oxidation products, such as TFA and PFPrA, due to high salt contents in the digested samples.

Therefore, an eTOP assay approach, (developed in house at DVGW-TZW) for soil sample extracts, was tested for expansion to a more generalised dTOP approach. However, a cleanup-step, which worked for the eTOP, failed when using the harsher reaction conditions of the dTOP. The reason was the partial oxidation of the solvent acetonitrile under these conditions. Several modifications (variation of pH, addition of a reducing agent) were not successful. As a consequence, the combination of dTOP conditions and subsequent analysis including the ultrashort-chain PFCAs TFA and PFPrA was not successful. Therefore, future research should focus on the promising chemical-free technique called PhotoTOP. This photochemistry approach was reported recently in a proof-of concept paper. Due to the salt-free reaction matrix and only little chain shortening (likely due to the lower reaction temperature compared to the heat-activated persulfate-based TOP assay) this new approach might allow to assess the ultrashort-chain PFCAs or makes their detection superfluous. However, the further development, harmonisation and standardisation of this new approach was out of the scope of the ZeroPM research in WP7.

Abbreviations

PFAS	**Per- and polyfluoroalkyl substances**[1]
ΔPFAS	The difference between pre-oxidation and post-oxidation concentrations of PFAS
PFAAs	**Perfluoroalkyl acids**
PFCAs	**Perfluoroalkyl carboxylic acids**
TFA	Trifluoroacetate (also used for trifluoroacetic acid, TFAA)
PFPrA	Perfluoropropanoic acid
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFTeDA	Perfluorotetradecanoic acid
ΔPFCAs	The difference between pre-oxidation and post-oxidation concentrations of C_4-C_{10} PFCAs
$\Delta PFCA_i$	The difference between pre-oxidation and post-oxidation concentrations of a specific PFCA

Perfluoroalkane sulfonyl fluoride-based PFAS

PFSAs	Perfluoroalkyl sulfonic acids
PFEtS	Perfluoroethane sulfonic acid
PFPrS	Perfluoropropane sulfonic acid
PFBS	Perfluorobutane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFOS	Perfluorooctane sulfonic acid
FOSA	Perfluorooctane sulfonamide
MeFOSA	*N*-methyl perfluorooctane sulfonamide
EtFOSA	*N*-ethyl perfluorooctane sulfonamide
FOSAA	Perfluorooctane sulfonamidoacetic acid
MeFOSAA	*N*-methyl perfluorooctane sulfonamidoacetic acid
EtFOSAA	*N*-ethyl perfluorooctane sulfonamidoacetic acid
FOSE	Perfluorooctane sulfonamido ethanol

Fluorotelomer-based PFAS

n:2 FTCA	n:2 fluorotelomer carboxylic acid
n:2 FTUCA	n:2 fluorotelomer unsaturated carboxylic acid
n:3 Acid	n:3 fluorotelomer carboxylate
n:2 FTSA	n:2 fluorotelomer sulfonic acid
n:2 FTOH	n:2 fluorotelomer alcohol

[1] PFAS nomenclature according to [2]

n:2 diPAP	n:2 fluorotelomer phosphate diester
n:2 FTAC	n:2 flourotelomer acrylate
n:2 FTMAC	n:2 fluorotelomer methacrylate

Per- and polyfluoroalkyl ethers

PFECAs	Perfluoroalkyl ether carboxylic acids
DONA	Dodecafluoro-3*H*-4,8-dioxanonanoic acid
PFMOPrA	Perfluoro-3-methoxypropanoic acid
GenX	The ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA)

Other PFAS

PFCSAs	Perfluoroalkyl diacids with a carboxylic and a sulfonic acid group
H-PFCAs	Hydro perfluoroalkyl carboxylic acids
UPFECAs	Unsaturated perfluoroalkyl ether carboxylic acids

Other abbreviations

ACN	Acetonitrile
AFFF	Aqueous film forming foams
$C_{V,R}$	Coefficient of variation under reproducibility conditions
DIN	Deutsches Institut für Normung (German Institute for Standardization)
DOC	Dissolved organic carbon
DOI	Digital object identifier
dTOP assay	Direct total oxidisable precursor assay
DWD	Drinking Water Directive
eTOP assay	Total oxidisable precursor assay after sample extraction
H_2O_2	Hydrogen peroxide
HPLC	High performance liquid chromatography
IC-MS/MS	Ion exchange chromatography-tandem mass spectrometry
ILT	Interlaboratory trial
$K_2S_2O_8$	Potassium persulfate (potassium peroxydisulfate)
LC	Liquid chromatography
LOQ	Limit of quantification
MeOH	Methanol
MS/MS	Tandem mass spectrometry
NaOH	Sodium hydroxide
OC	Organic carbon
OECD	Organisation for Economic Co-operation and Development
$^{\cdot}OH$	Hydroxyl radical
PhotoTOP	Photocatalytical total oxidisable precursor assay
PM substances	Persistent and mobile substances
PP	Polypropylene
RP	Reversed phase
SPE	Solid phase extraction
TiO_2	Titanium dioxide
TOP assay	Total oxidisable precursor assay
TZW	TZW: DVGW-Technologiezentrum Wasser (German Water Centre)

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1 Introduction

ZeroPM, which stands for Zero pollution of Persistent, Mobile substances, is a 5 year long European research project funded under the Horizon 2020 research and innovation program. ZeroPM will interlink and synergise three strategies to protect the environment and human health from persistent and mobile (PM) substances: Prevent, Prioritize and Remove. To do this, ZeroPM will develop an evidence-based multilevel framework. The framework will guide policy, technological and market incentives to minimise use, emissions and pollution of entire groups of PM substances.

ZeroPM will go beyond the state-of-the-art to support policy developments in cases where state-of-the-art analytical methods are not in place. One of the objectives of Work Package 7 – "Technical Solutions, Method Development and Analysis" (WP7) is to develop and optimise methods of analysis for PM substances to provide tools for their monitoring.

This report is related to deliverable 7.4: TOP-Assay fitness-check and passive sampling device validation. This deliverable is a result of task 7.1 where monitoring methods and strategies are developed and applied to facilitate the evaluation of the different water treatment methods. The PFAS sum parameter "Total Oxidisable Precursor" (TOP) assay was evaluated for its suitability to be used as the parametric value 'PFAS Total' in the revised EU drinking water directive (DWD). Results are used in task 3.2 and 3.3 to inform policy needs. Samples to test were obtained from task 7.2, 7.3 and 7.4. This first report focuses on the TOP assay, the second report in this series (Deliverable 7.4b) will focus on the passive sampling validation.

ZeroPM has investigated potential barriers to the measurement of the parameter "PFAS Total" in the EU Drinking Water Directive to be determined by the TOP assay, a digestive method, in which potentially extremely difficult to analyse precursors to perfluoroalkyl acids (PFAAs) are converted into analytically accessible perfluoroalkyl carboxylic acids (PFCAs) and, to a lesser extent, perfluoroalkyl sulfonic acids (PFSAs) and other products. ZeroPM will advance the state-of-the-art by providing a TOP assay fitness-check. To do this ZeroPM will investigate if there is an existing TOP assay protocol fit for purpose to serve as a method for compliance testing of drinking water and resources, and, because of its specific relevance to the project due to the known soil-groundwater contamination pathway, will also evaluate the soil matrix.

Within the fitness-check, it was important to consider not only the current legislation, but also to ensure that the protocol would meet the now very broad PFAS definition, so that the methodology would provide both a comprehensive, meaningful tool for determining the current exposure situation and an efficient tool for future monitoring, e.g. after a possible restriction of PFAS. For this purpose, a literature review and laboratory experiments were carried out. The results are described in the present report.

2 Task definition

The Directive (EU) 2020/2184 of the European Parliament and of the Council of December 16, 2020, on the quality of water intended for human consumption (The Drinking Water Directive) was published on December 23, 2020, and had to be transposed into national laws of the member states [3]. The revised Directive 2020/2184 also includes two new parametric values for PFAS: “Sum of PFAS” and “PFAS Total”. These new parameters should only be applied once technical rules for monitoring this parameter have been developed. At the time of the ZeroPM proposal submission, no such technical guidelines existed. These technical guidelines were originally supposed to be available by January 12, 2024, however, were actually published on August 7, 2024, with the Commission Notice C/2024/4910 “Technical guidance on analytical methods for the monitoring of per- and polyfluorinated alkyl substances (PFAS) in water intended for human consumption” [4]. DVGW-TZW researchers from WP7 were involved in supporting DG Environment in the preparation of this Commission Notice [5].

Annex I of the revised Drinking Water Directive provides a parametric value of 0.1 µg/L for “Sum of PFAS”, i.e. for the sum of the concentrations of a selection of 20 perfluoroalkyl acids (PFAAs) containing a perfluoroalkyl unit with three or more (maximum 13) carbon atoms as listed in Annex III. The parameter “Sum of PFAS” can be determined by liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis using a recently released European standard method (EN 17892) [6]. This method is recommended in the above-mentioned Commission Notice C/2024/4910 [4].

In addition, the sum parameter “PFAS Total” was introduced with a parametric value of 0.5 µg/L for the sum of all PFAS. However, no definition of the term PFAS can be found in the EU Directive. In consultation with DG Environment it was decided that the OECD definition of PFAS from 2021 [1] should be applied. According to this definition, any substance that contains at least one $-CF_2$ or $-CF_3$ group is considered as a PFAS, with a few exceptions. In total, over 7 million compounds belong to this group of substances [7]. These include, for example, many active ingredients of pesticides and pharmaceuticals and their metabolites as well as the ultra-short-chain PFAAs trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPrA). Against this background, the TOP assay was discussed as one possible approach for the determination of “PFAS Total”.

Different requirements to the TOP assay result from the boundaries given in Directive (EU) 2020/2184 for the parameter “PFAS Total” and the agreement that it shall comprise all PFAS according to the OECD (2021) definition:

- Completeness: All PFAS according to the OECD (2021) definition must be assessed. In particular, both ultrashort-chain PFAAs, such as TFA and others, as well as long-chain PFAS must be included.
- Sensitivity: The limit of quantification (LOQ) must be 30% of the parametric value of 0.5 µg/L, i.e. LOQ ≤0.15 µg/L.

- Uncertainty of measurement: The uncertainty of measurement must be ≤50 % at the environmental relevant level, i.e. at the level of the parametric value of 0.5 µg/L.

All three criteria must be fulfilled for the TOP assay to be a valid approach to measure "PFAS Total". The greater the deviations from this ideal picture, the more the TOP assay can then only be considered as a proxy for "PFAS Total".

Furthermore, a comprehensive, comparable and meaningful analysis of the environment is best ensured if the analytical method is largely independent of the matrix (water, soil, sludge, biota, etc.) and therefore applicable to samples from different environmental compartments. Otherwise, the discrimination of different substances or substance groups in the analysis of individual matrices may lead to a significant misinterpretation of the degradation, transformation, and transport/migration behaviour and thus of their risk potential.

In the fitness-check of the TOP assay presented here, it was investigated, if or to what extent the above-mentioned requirements could be fulfilled by existing TOP assay protocols or if the TOP assay can be further developed and validated to meet this goal. For this purpose, both, a comprehensive review of the existing literature and orientating laboratory experiments were conducted.

3 Systematic and comprehensive literature review

As part of this deliverable, an open access peer reviewed publication was published [8]. This article presents a literature review and considers publications on existing persulfate-based TOP assay protocols until mid-2024 and comprises a diversity of PFAS contaminated liquid and solid matrices, including precipitation, street runoff, surface water, drinking water, wastewater, groundwater, aqueous film-forming foams (AFFFs), AFFF surfactants, soils, sediments, surface water suspended particulate matter, sewage sludge, indoor and outdoor dust, biota, human blood serum, and consumer products, such as papers, textiles, and textile finishing agents. The analytical conditions (including reaction endpoints and quality control) of the persulfate-based TOP assay were compiled in an excel spreadsheet included in the article as supplementary information that can be found here:
https://www.sciencedirect.com/science/article/pii/S2214158824000187?via%3Dihub.

This literature review was the basis for evaluating the existing protocols to meet the three requirements of completeness, sensitivity, and uncertainty of measurement as specified in chapter 2. Given the focus of ZeroPM on *drinking water* and given the need to specify a protocol for the determination of the sum parameter "PFAS Total" in the Directive (EU) 2020/2184, this matrix was investigated. Furthermore, other water matrices, soil, and other environmental solids (sediments, suspended solids, biosolids, biota) were also considered in the work.

3.1 Completeness

The criterion of completeness has three components: (i) complete assessment of all existing groups of PFAS, (ii) complete transformation of PFAA precursors, and (iii) complete determination of all transformation products. As demonstrated in the following paragraphs, full completeness does not exist in any of these three components.

In the TOP assay, $^{\cdot}OH$ radicals are formed from persulfate and OH^- following equations 1 and 2.

$$S_2O_8^{2-} \xrightarrow{\Delta} 2\ SO_4^{\cdot -} \qquad \text{Equation 1}$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \qquad \text{Equation 2}$$

These $^{\cdot}OH$ radicals transform precursors to measurable products (Figure 3-1).

3.1.1 The TOP assay cannot give a complete assessment of all existing groups of PFAS

Only perfluoroalkane sulfonamide-based, fluorotelomer-based, and polyfluoroalkyl ether-based precursors are known to transform to the perfluoroalkyl acids shown in Figure 3-1. Other compound classes, e.g. perfluoroalkyl ethers, such as GenX cannot be oxidised. In addition, side-chain fluorinated polymers (SCFPs), such as polyfluoroacrylates, -methacrylates and others are not, or are only incompletely digested by the TOP assay under comparatively mild conditions. Harsher conditions as in the so-called direct TOP (dTOP) assay, which applies higher persulfate and OH^- concentrations directly to a sample, are needed to release measurable products. Due to the high alkalinity and high oxidant concentration under dTOP conditions, other additional products can be formed, e.g. PFSAs from perfluoroalkane sulfonamide-based precursors. The latter is not necessarily a disadvantage, as PFSAs can easily be integrated into the PFCA detection method. However, this needs to be taken into account.

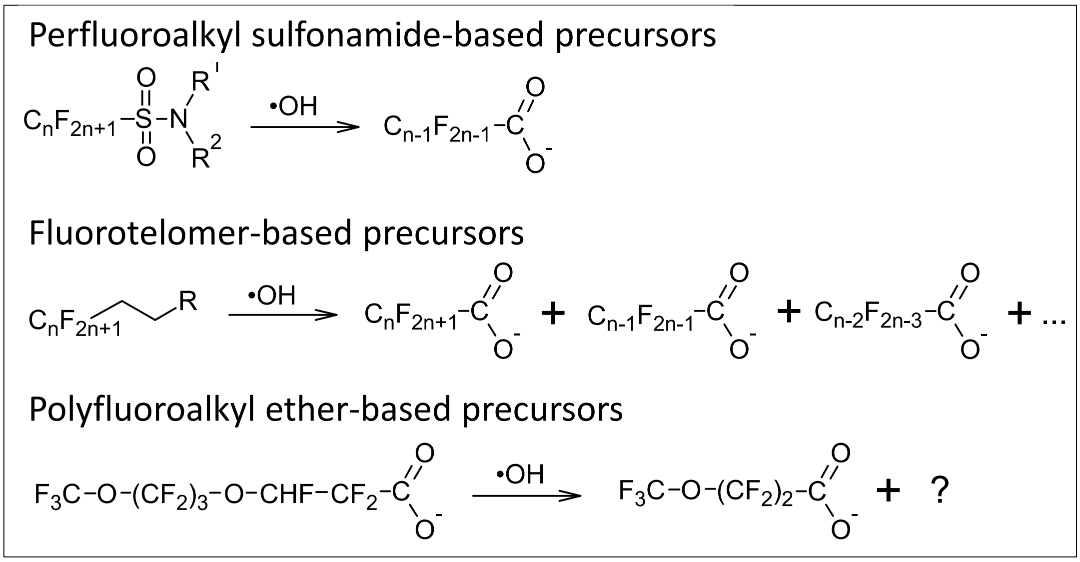

Figure 3-1: Reaction of precursors to PFCAs and PFECAs in the TOP assay [8].

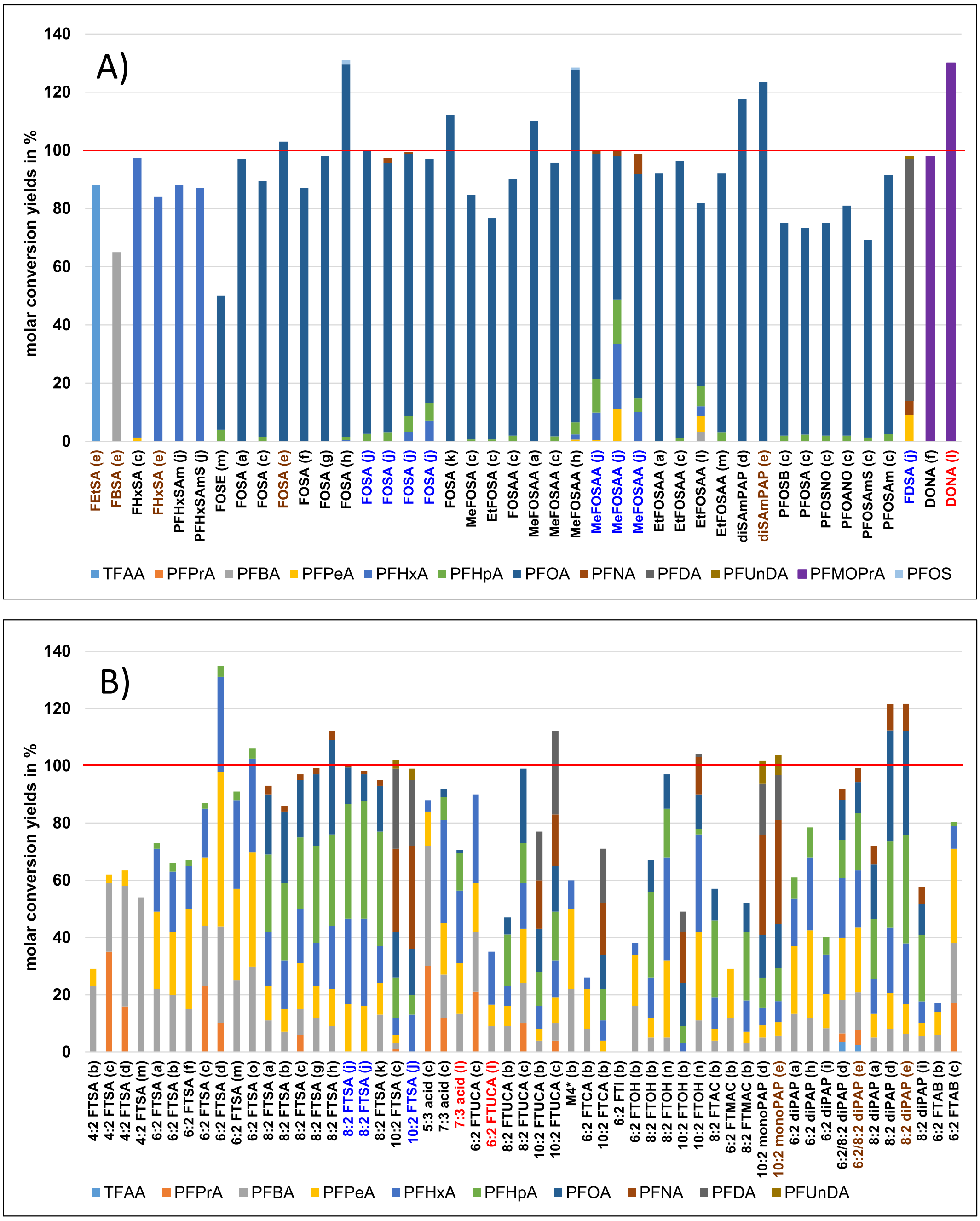

Figure 3-2: Molar conversion yields of A) perfluoroalkane sulfonamide-based precursors and the polyfluoroalkyl ether acid DONA and B) fluorotelomer-based precursors in heat-activated persulfate oxidation experiments with model precursors. References in brackets: (a) Houtz & Sedlak (2012) [9], (b) Boiteux et al. (2016) [10], (c) Martin et al. (2019) [11], (d) Janda (2019) [12], (e) Janda et al. (2019) [13], (f) Zhang et al. (2019) [14], (g) Wang et al. (2022) [15], (h) Simonnet-Laprade et al. (2019) [16], (i) Göckener et al. (2020) [17], (j) Pickard et al. (2022) [18], (k) Wang et al. (2020) [19], (l) Cioni et al. (2022) [20], (m) Joerss et al. (2020) [21], (n) Mumtaz et al. (2019) [22], (o) Fredriksson (2022) [23]. The font color of the analyte names indicates the sample matrix: ultrapure water (black), soil (brown) fish muscle tissue extract (blue), blood serum (red). Figure from [8]. For acronyms refer to the list of abbreviations (nomenclature according to Buck et al. [2], where applicable).

Therefore, none of the existing persulfate-based TOP assay protocols can assess all existing PFAS groups. Thus, all TOP assay protocols are not comprehensive and may underestimate "PFAS Total" to a certain extent depending on the PFAS groups present in a sample. In conclusion, all TOP assay protocols and alternatives, such as the PhotoTOP approach [24], discriminate certain PFAS and can only be considered as proxy methods for "PFAS Total".

3.1.2 Transformation of PFAA precursors is incomplete

Incomplete precursor transformation according to (ii) and incomplete assessment of transformation products according to (iii) (see above) can be recognised by molar conversion yields <100% (Figure 3-2).

For example, short-chain 4:2 and 6:2 fluorotelomer precursors have apparently reduced conversion yields when the ultrashort-chain TFA and PFPrA are missing in the mass balance as they are often not measured as TOP assay end points (Figure 3-2B). Extensive chain-shortening during oxidation of fluorotelomer precursors can be avoided by replacing heat-activation with UV activation [25–27] or, alternatively, by application of the PhotoTOP, a chemical-free approach [24]. This can reduce the necessity to analyse ultrashort-chain TFA and PFPrA as oxidation endpoints in order to achieve a full mass balance.

Non-ionic volatile precursors, such as FOSE, MeFOSA, EtFOSA (Figure 3-2A), FTOHs, FTACs, FTMACs, and FTI (Figure 3-2B), might be lost from the reaction batches, if no appropriate counter measures are taken. Conversion yields close to 100% have been achieved for 8:2 and 10:2 FTOHs with minimised headspace in tightened and sealed 50 mL centrifuge tubes [66].

Incomplete transformation of precursors is a major challenge of the TOP assay, especially in samples with a high organic carbon (OC) content or that contain other oxidisable matrix components. Therefore, for drinking water samples, where neither of these conditions is present, there is little concern about incomplete precursor transformation. However, it is an important factor for sample matrices such as wastewater or OC-rich solids such as suspended solids and sewage sludge.

The reason for incomplete transformation is that the $^{\cdot}$OH radicals might be depleted by reaction with matrix components, so that there is an insufficient amount of reagent left for complete precursor transformation. Measures to check for complete transformation include the disappearance of known precursors after oxidation of a sample or the addition of an isotopically-labelled oxidation standard (i.e. *in-situ* quality control) before digestion and the subsequent quantification of the labelled reaction product (^{13}C-PFCA) [28].

If incomplete transformation is detected, samples can be diluted (resulting in higher LOQs) or sample extracts can undergo a cleanup step, e.g. by carbon cleanup or by primary matrix oxidation using H_2O_2 [29].

3.1.3 Challenges in the quantitative assessment of all transformation products

In the original TOP assay protocol of Houtz and Sedlak [9] only C_5-C_{14} PFCAs were analysed as oxidation products. Ultrashort-chain PFCAs, such as TFA and PFPrA, and longer-chain PFCAs were not included in the analytical method. This, however, is needed for a complete assessment of all PFAS. In addition, other reaction products, such as PFEtS, PFPrS, PFMOPrA, *H*-PFCAs, UPFECAs, and perfluoroalkyl diacids with a carboxylic and a sulfonic acid group (PFCSAs) were (tentatively) identified in reacted samples in the TOP assay. The stability of some of these products, e.g. *H*-PFCAs, seems to depend on the individual reaction conditions (i.e. oxidation strength). All these additional products need to be quantified to achieve completeness of oxidation product assessment. However, for some of the reaction products, reference standards are not available for quantification.

In addition, existing TOP assay protocols are not optimised for volatile precursors. If these are present in a sample, they might be lost through volatilisation, e.g. during the oxidation step or during sample preparation steps (solvent blow down) before LC-MS/MS analysis of reaction products. Examples can be seen in Figure 3-2 for the volatile groups of fluorotelomer iodides (FTIs), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTACs), and fluorotelomer methacrylates (FTMACs).

In conclusion, the gap in the assessment of transformation products also makes the TOP assay incomplete.

3.2 Sensitivity

The criterion of sensitivity in terms of LOQ is most important in the low contaminated matrix of drinking water given the legal background of Directive (EU) 2020/2184 [3]. This directive sets a parametric value of 0.5 µg/L from which derives a required LOQ of ≤0.15 µg/L (30% of the parametric value).

The sensitivity of the TOP assay mainly depends on the sensitivity of the LC-MS/MS method used for detection of the reaction products in the oxidised samples and on the matrix, i.e. salt content in these samples. The standard method EN 17892:2022 [6] for the determination of PFAAs (C_4-C_{13} PFCAs and C_4-C_{13} PFSAs) in drinking water (without oxidation in the TOP assay) has been validated.

A survey of European expert laboratories within the validation interlaboratory trial (ILT) demonstrated that the mean LOQ of all 20 PFAA targets is low enough to allow compliance testing of the “Sum of PFAS” parametric value of 0.1 µg/L (≙ 100 ng/L for 20 analytes, i.e. on average 5 ng/L per PFAA; LOQ must be 30 % hereof, i.e. 1.5 ng/L) for a drinking water matrix [4,5]. This sensitivity would also fit the necessary sensitivity for compliance testing for “PFAS Total” (parametric value of 0.5 µg/L) using the TOP assay. However, the survey did not take into account the matrix of TOP assay reaction solution post oxidation. The LOQ will rise if dilution is necessary prior to LC-MS/MS analysis. Therefore, additional validation would be needed.

It is important to recall that the mass concentrations given as parametric values for PFAS in Directive (EU) 2020/2184 refer to the PFAS concentrations in an original drinking water sample and not to the (lower molecular weight) transformation products after oxidation in the TOP assay. Based on this fact, the TOP assay would not be acceptable as a method for compliance testing of drinking water, unless an additional convention would be given in a technical guideline for practical application. Such a convention was recently defined in the Commission Notice C/2024/4910 "Technical guidelines regarding methods of analysis for monitoring of per- and polyfluoroalkyl substances (PFAS) in water intended for human consumption" [4]:

> *TOP assay methods entail applying oxidation with persulfate in alkaline solution. TOP assay approaches are specifically for PFAS that oxidise to perfluorinated carboxylic acids and pose a very small risk of overestimating the PFAS load at the level of concern. Perfluorinated ether compounds, and possibly other classes, do not oxidise to perfluorinated carboxylic acids. Together with risks for incomplete precursor conversion, there is a high risk of underestimating 'PFAS Total'. All oxidation products need to be quantified and summarised in the proxy analytical result presented as "PFAS Total$_{TOP}$" in ng/l.* [4]

These aspects on the shortcomings associated with the application of the TOP assay for testing of "PFAS Total" were communicated to and were adopted by in the Commission Notice in a parallel consultancy project carried out by a scientific consortium including DVGW-TZW researchers from ZeroPM's WP7.

3.3 Uncertainty of measurement

Most of the scientific articles on TOP assay are either a proof of concept or an exemplary application to a limited number of (in most cases medium to highly PFAS contaminated) samples. Only one standard method for TOP assay exists, DIN 3608:2024-08 [30]. This standard describes a method for measuring the increase of C_4-C_{10} PFCAs, ΔPFCAs, in aqueous batch leachates of soil samples (liquid/solid ratio of 2 L/kg).

In this standard protocol the oxidation conditions are kept within narrow boundaries, e.g. regarding oxidation reagent (1.5 g $K_2S_2O_8$ and 1.5 mL NaOH (30%) per 50 mL soil leachate), reaction temperature (85±3) °C, pH (>11 during the entire reaction), and reaction time (6 h with shaking, overnight or >12 h without permanent shaking). The validation ILT using the standard protocol resulted in coefficients of variation under reproducibility conditions ($C_{V,R}$) for ΔPFCAs (C_4-C_{10} PFCAs) of 10% and 24% (on mass concentration basis) for two soil leachates with a dissolved organic carbon content (DOC) of 3.5 mg/L and 2.3 mg/L, respectively.

However, the $C_{V,R}$ of $\Delta PFCA_i$ for specific PFCA homologues increased systematically with increasing PFCA chain length from 7% (PFBA) to 228% (PFDA) in one leachate and from 23% (PFBA) to 827% (PFNA) in a second leachate, respectively. The large relative differences result from very small changes in concentration between pre and post oxidation samples at low levels of the longer chain PFCAs (C_9 and C_{10}).

For drinking water there is no comparable standard method available yet. The uncertainties of measurement reported in ILTs with other sample matrices than drinking water in part revealed values >50%, which would be unacceptable with regard to the requirement of values ≤50% according to the Directive (EU) 2020/2184.

Despite the circumstance that TOP assay is mentioned as one of three possible sum parameters for a proxy of "PFAS Total" in the Commission Notice C/2024/4910, the application of any TOP assay protocol to drinking water seems to be questionable with regard to the very often observed low precursor concentrations in drinking waters [31]. Thus, (molar) concentrations measured before and after oxidation in the TOP assay are very similar. Calculating ΔPFCAs or ΔPFASs by subtraction of pre oxidation concentrations from post oxidation concentrations frequently leads to inconclusive results (small difference of nearly equal values). This taken together with the uncertainty of measurement, can even result in negative values for ΔPFCAs or ΔPFASs. When applying mass concentration (as done in [31]), due to the mass loss (elimination of the non-fluorinated moiety in a precursor molecule and chain shortening with loss of fluorine) in the transformation of precursors to oxidation products, negative differences will result due to these principle reasons.

ILTs on the TOP assay with aqueous samples in Australia with three [32] and 22 [33] participating laboratories revealed differences between non-harmonised in-house methods. In both studies, it was reported that the participating laboratories used modified versions of the Houtz and Sedlak method [9], e.g. by increasing the amount of oxidation agent, increasing the oxidation time, diluting samples, or conducting additional oxidation cycles. The method modifications indicated that the original Houtz and Sedlak method may yield an incomplete oxidation when high levels of matrix OC or high loads of precursors are present in the samples. While the study with three laboratories reported high coefficients of variability of 27%–67%, the study with 22 participants reported that the majority of values were in a satisfactory range, i.e. 91% with z-scores ≤ 2.0 and 73% with E_n-scores ≤ 1.0, and most laboratories fulfilled the set quality assurance requirements. For definition of z-score and En-score refer to [33]. The latter study explicitly highlighted the underreporting of long-chain PFAAs and their expanded analytical uncertainty.

The results of another ILT with a soil sample and five participating laboratories is given in [34]. Four laboratories applied TOP assay after soil extraction with an organic solvent (eTOP) and one dTOP. While the results for the pre oxidation samples were very similar for all five laboratories, the post TOP results differed greatly due to inconsistent oxidation protocols. The highest ΔPFCAs value appeared under dTOP conditions (up to approximately one order of magnitude increase), and, in addition, PFOS was also produced during dTOP (more than double the value than pre oxidation).

In summary, uncertainties of measurement for a most comprehensive TOP assay protocol (including ultrashort-chain and long-chain PFCAs ($>C_{10}$) and other oxidation products) for drinking water are not available, yet.

4 Laboratory experiments

4.1 Preliminary considerations: Challenges of the (d)TOP assay for analysis

It is imperative that a comprehensive and meaningful oxidative method (i.e. any kind of oxidisable precursor assay) includes all PFAA precursors, as well as PFCAs comprising a broad range of chain-length as reaction products (e.g. including the ultrashort-chain PFCA TFA). For this reason, any sample preparation procedures that could lead to substantial discrimination of precursors and reaction products, both before and after the oxidative process, must be avoided. Furthermore, given the risk of sample contamination, all sample preparation should be kept to a minimum. This is particularly true for PFAS due to the ubiquitous nature of this large group of substances and possible contaminations in the laboratory environment (instruments, solvents, expendables, dust, etc.). In the context of a vast and varied group of substances such as PFAS, it is imperative to establish a matrix-independent oxidative approach for investigation. Without such an approach, the complex transformation and translocation processes in natural and technical systems cannot be comprehensively understood. Consequently, it is essential to devise a universally applicable approach ("one-size-fits-all") for the analysis of solid and liquid samples.

Regarding the inclusion of all relevant precursors in the analysis of solid samples (soil, sludge, biota, etc.), their extraction and subsequent oxidation must therefore be viewed critically. Important processes that may lead to discrimination of individual substance groups are the extraction itself, in which poorly extractable substances are hardly included, and the subsequent essential removal of the extraction solvent by evaporation, in which, in turn, volatile precursors are also removed (the removal of the extraction solvent – typically methanol – is necessary because otherwise it would compete with the precursors for the oxidising power in the TOP assay).

To determine the potential extent of such a discrimination within the TOP assay fitness-check in WP 7 samples from the polluted Rastatt site (Test Site 1) were used. This site was contaminated by illegal PFAS soil amendment with compost, which was mixed with paper-fibre biosolids. A soil core was divided into segments of 30 cm thickness (A: 0–30 cm, B: 30–60 cm, C: 60–90 cm) and were analysed individually for selected PFAAs (PFBA–PFDoDA, PFOS). The concentrations were determined in the original sample (i.e. native concentrations) and after oxidation of a methanolic soil extract by the TOP assay (method described in [13]), as well as after direct oxidation of soil by the dTOP without any extraction prior to the oxidation (method described in [35]). The results are presented in Figure 4-1.

In terms of assessing the PFAS contamination of the soil sample, the results in Figure 4-1 clearly demonstrate the benefit of oxidative digestion of the soil extract (or soil sample) compared to a PFAA-only target analysis of the soil sample after extraction without any further oxidation of precursors to PFAA. The comparison of the contamination of the different sampling depths also shows that the PFAA precursors are largely immobile in the soil (i.e. sorptive, poorly water soluble) and that the information gained from carrying out the oxidative processes is the highest in the top-soil. This test site example shows that it is not useful to analyse groundwater and drinking water samples by TOP assay, because possible precursors are retained in the upper soil zone and only appear in the water phase after the transformation (predominantly to PFAAs) has already taken place. Furthermore, the results for such samples with low concentrations of precursors are often inconclusive due to the high uncertainty of measurement caused by similar PFAA concentrations pre and post oxidation (refer to 3.3).

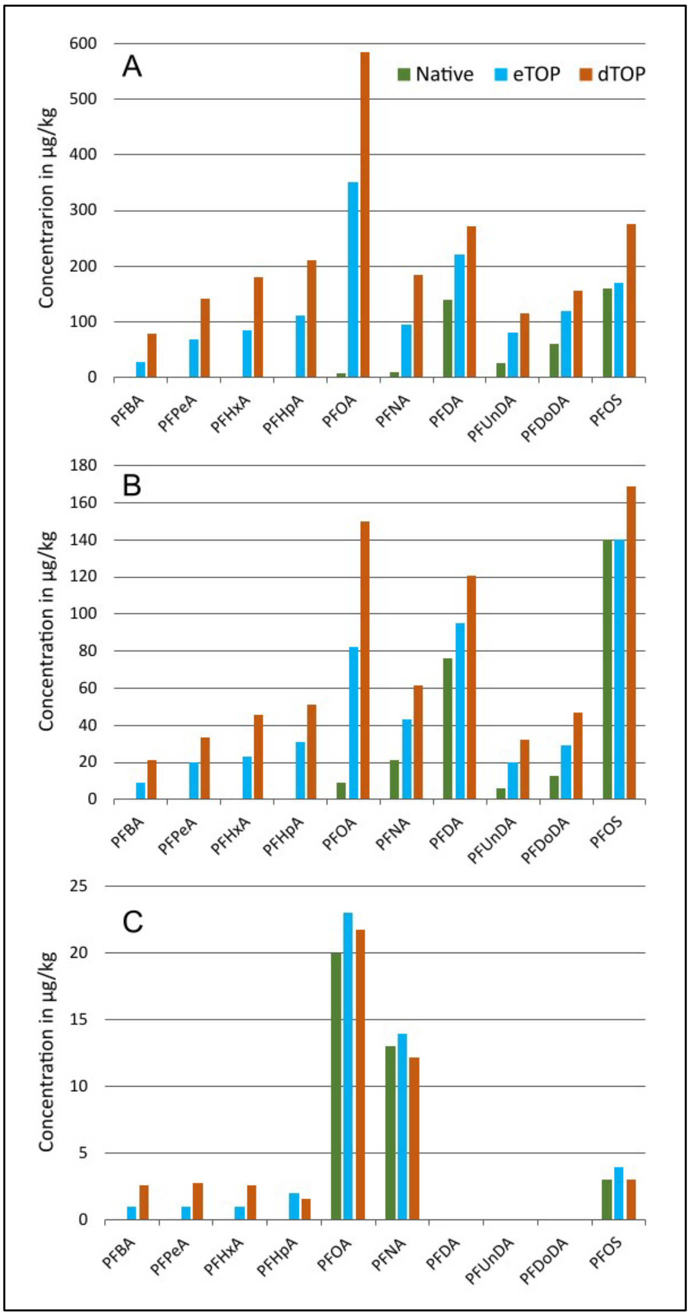

Figure 4-1: Analysis of a soil core from the Rastatt area (Test Site 1), A: 0–30 cm, B: 30–60 cm, C: 60–90 cm. Comparison of native concentrations of selected PFAAs, after eTOP, and dTOP; note the different concentration ranges of PFAAs in the core segments.

Most importantly, the results demonstrate the superiority of the dTOP over a post-extraction TOP assay (eTOP). The results fit well with the fact that Test Site 1 is known to be contaminated with widely used per- and polyfluorinated alkyl phosphate esters (SAmPAP, mono/di/triPAP), which are often difficult to extract from solid matrices. However, the dTOP requires higher oxidising power (i.e. higher concentrations of persulfate and OH^- and a generally higher volume of oxidising solution) compared to the post-extraction TOP assay.

The persulfate-based TOP assay (eTOP and dTOP) produces high concentrations of sulfate (Na and K sulfate) that must be removed before the reaction products can be analysed. Otherwise, the analysis is severely compromised, or, in the case of ion exchange chromatography for the analysis of ultra-short chain PFAAs, rendered impossible. At the same time, however, significant losses of reaction products during salt separation must be avoided, which is not an easy challenge given the wide range of reaction products in terms of chain length.

A highly prevalent method for a broad spectrum of applications of the eTOP/dTOP assay is solid-phase extraction (SPE) using an anion exchange resin [8]. This procedure is successful for the extraction of PFAAs with a chain length greater than or equal to 4 (i.e. PFBA). TFA and PFPrA are poorly retained at the sorbent in the highly saline matrix and/or are washed out of the sorbent during the rinsing step prior to drying and intended elution. However, oxidation of short-chain precursors in the TOP assay may produce significant amounts of PFCAs with chain lengths shorter than C_4, which were not considered in the above procedure. In addition, the wide range of CF_3-substituted pesticides and pharmaceuticals is not considered, which means that the picture of environmental contamination with PFAS including TFA release potential in a catchment is incomplete. This is unacceptable, especially in the light of current discussions about the appearance and regulation of TFA [36]. Therefore, an alternative cleanup for salt removal from oxidised samples was tested in WP 7 within the fitness-check of the TOP assay.

4.2 Testing of alternative cleanup steps for salt removal from oxidised samples

4.2.1 Cleanup by solvent exchange

One method that has been successfully developed and tested by DVGW-TZW is to remove the water using a rotational vacuum concentrator and then extract the reaction products (i.e. PFAAs) from the residue with acetonitrile (ACN). By this solvent exchange, the reaction products (including TFA) are efficiently extracted, while the inorganic salt residue is virtually absent from the extraction solvent [13]. However, this method has so far only been used in a post-extraction TOP assay consisting of <10 mL aqueous solution containing ~14 g/L sulfate. An experimental strategy within the TOP assay fitness-check was to adapt this treatment method to the requirements of a dTOP, i.e. after scaling up regarding size and persulfate concentrations.

Three different dTOP blank matrices were prepared for a series of recovery experiments. For this, 25 mL ultrapure water was mixed with different amounts of $K_2S_2O_8$ and NaOH in PP centrifuge tubes with a nominal volume of 50 mL:

Matrix 1: 1.25 g $K_2S_2O_8$ + 0.5 g NaOH

Matrix 2: 2.5 g $K_2S_2O_8$ + 1.0 g NaOH

Matrix 3: 5.4 g $K_2S_2O_8$ + 2.0 g NaOH

Duplicates were prepared for each matrix. The volume of 25 mL was determined by the maximum volume that could be processed with the available centrifuge rotors. The matrices were incubated in a drying oven at 85 °C for 20 h. After cooling, each matrix was spiked with 5 ng of the analytes (PFCAs: TFA → PFTeDA; PFSAs: PFBS, PFHxS, PFOS as stable compounds in the dTOP; GenX as a representative of a stable perfluoroalkyl ether). Isotope-labelled analogues of the analytes were used to avoid the possible influence of blanks in the determination of recoveries.

It was known from preliminary tests with increased sulfate concentrations that boiling delays and associated cross-contamination and contamination of the centrifuge could occur. These effects become more significant as the concentration of dissolved substances increases. Therefore, it is vital that the water is removed as gently as possible. In collaboration with a manufacturer, a sensor was used to better control the evaporation endpoint. This also allowed for a controlled evaporation process, with the volume being reduced to dryness (A) as well as to a range of 1–2 mL (B). Following treatment, the analytes were extracted from the salt precipitate using ACN, the extract was isolated from the precipitate, the solvent was evaporated, the residue was dissolved in injection solution and analysed using ion exchange chromatography-tandem mass spectrometry (IC-MS/MS) for TFA and PFPrA and reversed-phase liquid chromatography-tandem mass spectrometry (RP-LC-MS/MS) for all other analytes. The results as shown in Figure 4-2.

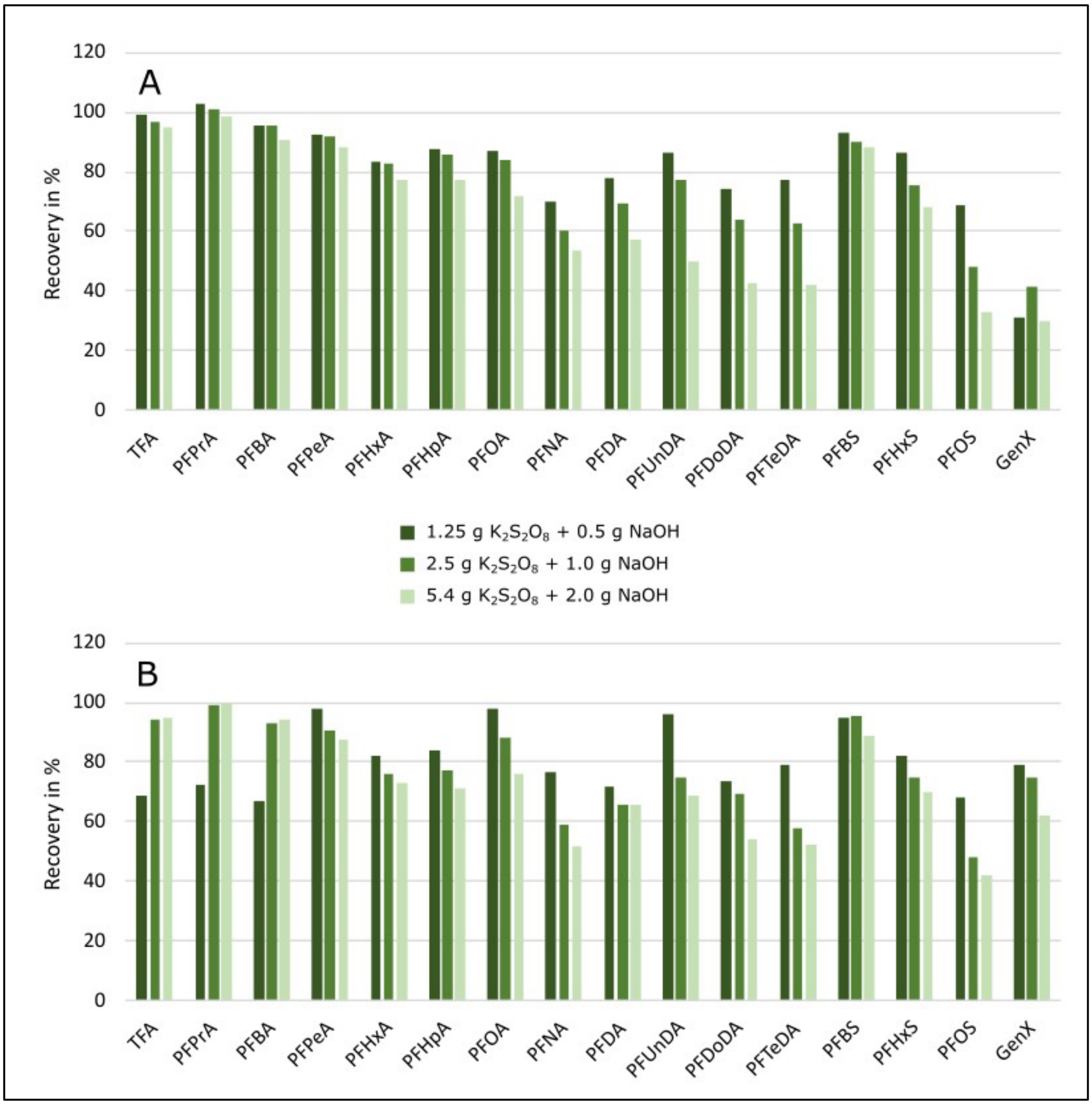

Figure 4-2: Recoveries of selected PFAS (isotopically labelled) from reacted dTOP-solution, extraction with ACN after the evaporation of water by rotational vacuum concentration; A: Evaporation to dryness, B: Evaporation to 1–2 mL supernatant.

These experiments demonstrated that the method could, in principle, also be applied to samples from the dTOP. However, an increased salt load – the sample with the highest salt load corresponds roughly to that of a dTOP – has a negative effect on the recoveries of long-chain PFAAs. Overall, the variant with supernatant water (1–2 mL, variant B) appears to be more favourable for the recovery of the analytes. This may be attributed to reduced volatilisation and enhanced extraction efficiency within the three-phase mixture (salt/water/ACN) in comparison to the two-phase mixture (salt/ACN).

However, there are significant limitations that would render the method unsuitable for implementation as a routine procedure. Due to the high salt concentration of the matrix, the method remains susceptible to boiling delay, which can lead to contamination of the centrifuge interior and other samples. The enhanced controllability afforded by the measuring probe necessitates a significant investment to optimise the process parameters, as minor deviations can result in the complete failure of an entire batch due to potential carry-over events. Moreover, the method is both time-consuming and energy-intensive. It should be noted that, depending on the desired detection sensitivity, higher volumes (100 mL and more) may have to be treated, which further increases the resource requirements. Scaling down the dTOP in terms of total volume is ultimately also limited by sample heterogeneity and weighing accuracy. This is particularly evident in samples with low background pollution. Therefore, in terms of a fitness-check of this method, this procedure is not favourable.

4.2.2 Cleanup by direct liquid-liquid extraction

The observation that variant B (i.e. 1–2 mL of water supernatant) proved advantageous for the recoveries of analytes led to the consideration of direct liquid-liquid extraction without prior water removal. This process takes advantage of the fact that ACN and water saturated with the sulfate salts do not mix. However, significant interference was detected during the subsequent analysis of the PFAAs. During the investigation of the causes, in the ACN phase, high nitrate concentrations (~2 g/L) were detected. The initial suspicion that the contamination was already present in the ACN before the extraction could not be confirmed. The nitrate was therefore formed during the process. In addition, extraction experiments at different pH values (pH 5, 7, 8, 9, 10, 11 and 13) showed that hydrolysis (and subsequent oxidation) of ACN could also be excluded under these conditions. The most likely cause was therefore direct oxidation with residual oxidising power (i.e. $^{\cdot}OH$ radicals or secondary reactive species) still present in the dTOP solution.

To suppress this reaction, the addition of various reducing agents was tested. The dose-response relationship between the addition of sodium thiosulfate prior to extraction and nitrate concentration in ACN is shown in Figure 4-3. Although the results support the nitrate formation hypothesis, the addition of thiosulfate is not a viable strategy as it would require unrealistically high doses, which would also carry the potential for PFAS contamination of the extract. The addition of other reducing agents such as methanol, tert-butanol and hydrogen peroxide (H_2O_2) (under alkaline conditions, H_2O_2 is a reductant) did not show a sufficiently large effect either. Alternative extraction agents were not tested due to low chances of success and incalculable side reactions, so the liquid-liquid extraction approach was discarded.

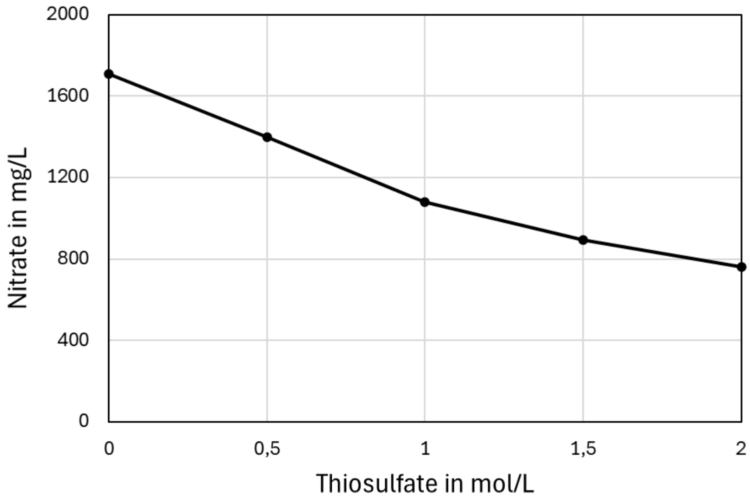

Figure 4-3: Dose-response relationship between the addition of thiosulfate prior to extraction and nitrate concentration in ACN.

Within the scope of the fitness-check task, it can be concluded from the experiments that a comprehensive (e)TOP/dTOP assay based on persulfate-driven oxidation reactions does not appear to be suitable for routine use in environmental monitoring towards regulatory compliance.

5 Future perspectives

The present research aimed to identify a generalised dTOP protocol which would be matrix independent due to a high oxidation reagent excess and which includes also ultrashort-chain oxidation endpoints such as TFA. As was demonstrated by experiments, due to the interferences caused by the high salt concentrations in the post-oxidation samples this challenge cannot be easily solved. Thus persulfate-based TOP assay is not regarded as a versatile and reliable tool for routine use, that should be taken into account for further standardisation activities.

Alternative assays, such as substitution of heat-activation with UV activation [25–27] or by application of the PhotoTOP, a chemical-free approach [24], are regarded as more promising. These new approaches were also taken into account in the TOP assay fitness check within the literature review [8]. Table 5-1 summarises the main characteristics of these TOP assay alternatives.

In contrast to the persulfate-based protocols, extensive chain-shortening during oxidation of fluorotelomer precursors can be avoided by these alternative methods. This can either reduce/annul the necessity to analyse ultrashort-chain TFA and PFPrA as oxidation endpoints in order to achieve a complete mass balance or allows for interference-free LC(or IC)-MS/MS detection without a further cleanup-step provided that specific TFA-precursors such as selected pesticides or pharmaceuticals are present in the sample. Therefore, these alternative oxidative digestion methods should be optimized and harmonised in order to establish a standard method.

Table 5-1: Comparison of important properties of thermal-activated TOP/dTOP, UV-activated TOP and PhotoTOP.

Characteristic	Heat–activated TOP	Heat–activated dTOP	UV-activated TOP	PhotoTOP
References	[8,9]	[8,17,37]	[25–27]	[24]
Reagent	Alkaline persulfate solution ($K_2S_2O_8$/NaOH)	Alkaline persulfate solution ($K_2S_2O_8$/NaOH)	Alkaline persulfate solution ($K_2S_2O_8$/NaOH)	Photons/ TiO_2 (Anatase) catalyst
Energy input	Heat	Heat	UV light	UV light
Chain-shortening for fluorotelomer compounds	Strong	Strong	Strong	Weak
Formation of transformation products other than PFCAs, e.g. PFSAs	Weak	Strong	Weak	Weak
Inclusion of ultrashort-chain PFCAs (TFA, PFPrA) as oxidation endpoints	Possible (after cleanup)	Extremely challenging (due to high salt content)	Possible (after cleanup)	Possible
Yield of precursor transformation	High (if enough oxidant is present)	High (if enough oxidant is present)	High (if enough oxidant is present)	Low to medium, conditions to be optimised

6 Conclusion

This ZeroPM deliverable is one of the outcomes of ZeroPM Task 7.1, where monitoring methods and strategies were developed and applied to facilitate the evaluation of the different water treatment methods.

The PFAS sum parameter "Total Oxidizable Precursor" (TOP) assay was evaluated for its suitability to be used as the parametric value 'PFAS Total' in the revised EU drinking water directive (DWD). The so-called TOP assay fitness-check demonstrated that the TOP assay is not considered a versatile tool for drinking water compliance monitoring for the EU drinking water directive, in terms of a proxy for "PFAS Total" due to often found low precursor concentrations in drinking waters.

The extensive review of methods and the practical tests clearly indicate that a persulfate-based approach to the TOP assay, regarding the necessary completeness defined here, is not a promising strategy for comprehensive, future-oriented and environmentally friendly PFAS analysis. Conversely, strategies such as the PhotoTOP, which have been developed in proof-of-concept work, should be further developed, as these can be expected to have a greater potential for success.

7 Acknowledgements

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8 Appendix

Additional Information

Some of the work conducted in this deliverable were published in the scientific literature:

B. Göckener, F.T. Lange, L. Lesmeister, E. Gökçe, H.U. Dahme, N. Bandow, A. Biegel-Engler, Digging deep—implementation, standardisation and interpretation of a total oxidisable precursor (TOP) assay within the regulatory context of per- and polyfluoroalkyl substances (PFASs) in soil, Environ. Sci. Eur. 34 (1) (2022) 2345.
https://doi.org/10.1186/s12302-022-00631-1.

F.T. Lange, F. Freeling, B. Göckener, Persulfate based total oxidizable precursor (TOP) assay approaches for advanced PFAS assessment in the environment–a review, Trends in Environ. Anal. Chem. 18 (20) (2024) e00242.
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ZeroPM

Zero pollution of Persistent, Mobile substances

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TOP-Assay fitness check and Passive sampling device validation

Part 2: Passive sampling device validation

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Summary

The European research project ZeroPM – "Zero pollution of Persistent, Mobile substances" combines three interlinked strategies to tackle pollution with persistent and mobile (PM) substances: Prevent, Prioritize and Remove. Work Package 7 – "Technical Solutions, Method Development and Analysis" (WP7) is dedicated to the removal of persistent and mobile substances. Among other things, WP7 will develop innovative monitoring and treatment methods for persistent and mobile substances in drinking and waste waters. Part of this work package focuses on developing passive sampling methods for the monitoring of persistent and mobile substances in various aqueous matrices and for the evaluation of drinking and wastewater treatment efficiency. Prior to their application and use under field conditions, the performance of passive samplers for the sampling of persistent and mobile substances of interest needs to be established.

This document is part 2 of Deliverable 7.4 – "TOP-Assay fitness check and Passive sampling device validation". Herewe focus on passive sampling validation, and report on field testing and validation of different types of passive sampling devices for the measurement of persistent and mobile substances. This activity was a joint effort between NIVA and DVGW. The work involved deploying three types of passive samplers at different stages of two drinking water treatment plants in Germany. A procedure to expose samplers to water at different stages of treatment was tested. The work was undertaken at two case study sites on the Upper Rhine (ZeroPM test site 2) and in Rastatt (ZeroPM test site 1). Commercially available samplers as well as samplers prepared in the laboratory at NIVA were exposed to drinking water at different steps of the treatment for a period of three weeks. Samplers were brought back to NIVA and analysed for a set of benzotriazoles and per- and polyfluoroalkyl substances (PFASs). Spot water samples were collected during deployment and retrieval of the samplers at different steps of the treatment processes by DVGW and analysed for the same set of substances. Data obtained with the passive samplers were compared with those from grab sampling and this forms a preliminary passive sampling performance evaluation and validation of the working principle of passive samplers tested here. A key difference between the passive sampler deployment and grab sampling is that the grab sampling corresponds to a single point in time, where as the passive sampling concentrations interact with the water for three weeks. Consistent dissolved water concentrations derived for benzotriazoles from passive samplers were obtained at the Upper Rhine case study. For PFAS in Rastatt, some robust time-average concentrations were obtained for one of the sampler types, while over and underestimates were observed with the two other types of samplers. In general, passive samplers were capable in all cases of identifying the same trends in concentrations as grab sampling with often a possibility to quantify lower concentrations than the grab sampling undertaken here routinely. More work is needed to understand the discrepancies between passive sampler-derived and grab sampling-based water concentrations. This work is underway within ZeroPM.

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Table of abbreviations	
AC	Activated carbon
ATZ	Atrazine
BTZ	Benzotriazole
DGT/o-DGT	Diffusive gradients in thin films
G-TIP	Gradient time integrative passive sampler
HLB	Hydrophillic and lipophilic balance sorbent
K_{sw}	Sorbent-water partition coefficient
K_{pw}	Polymer-water partition coefficient
MCX	Mixed-mode cation exchange
MPT	Microporous polyethylene tube
MW	Molecular weight
OH-BT	2-hydroxybenzothiazole
PAHs	Polycyclic aromatic hydrocarbons
PES	Polyethersulfone
PFAS	Per- and poly-fluoroalkyl substances
PM	Persistent and mobile chemicals
POCIS	Polar organic chemical integrative sampler
PRCs	Performance reference compounds
PS	Passive sampling/samplers
RPD	Relative percentage difference
Rs	Sampling rate
SPE	Solid phase extraction
QAQC	Quality assurance and quality control
WAX	Weak anion exchange
XAD	Amberlite® XAD®-2 styrene-divinylbenzene resin
XTR	5,6-dimethyl benzotriazole
5Me-BTZ	5-methylbenzotriazole
5Cl-BTZ	5-chlorobenzotriazole

1 Introduction

ZeroPM, which stands for Zero pollution of Persistent, Mobile substances, is a 5 year long European research project funded under the Horizon 2020 research and innovation program. ZeroPM will interlink and synergize three strategies to protect the environment and human health from persistent and mobile substances: Prevent, Prioritize and Remove. To do this, ZeroPM will develop an evidence-based multilevel framework. The framework will guide policy, technological and market incentives to minimize use, emissions and pollution of entire groups of persistent and mobile substances.

Work Package 7 – "Technical Solutions, Method Development and Analysis" (WP7) has the overall objective to demonstrate how and if legacy and prioritized persistent and mobile substance pollution can be remediated. WP7 investigates innovative treatment and monitoring methods for water (ground, surface, bank filtrate, waste) and sludge to protect water resources, provide safe drinking water and protect human health and the environment, with a focus on persistent and mobile substances and media from three different test sites.

Passive sampling is an effective technique used to monitor the presence and concentration of contaminants in aquatic environments. Unlike traditional grab sampling methods, passive sampling involves the deployment of devices that accumulate contaminants over a defined period, providing a more accurate representation of time-weighted average concentrations (Vrana et al., 2005). Passive sampling has been used to measure contaminant concentrations in the sea as well as in freshwater environments including groundwater (Alvarez et al., 2005; Martínez Bueno et al., 2016). Applications of passive samplers (PSs) to wastewater environments and drinking water have also taken place (Clokey et al., 2023; Gobelius et al., 2019; Schulze et al., 2021). PSs are generally suited to the measurement of ambient levels of contaminants in water but can also target the low levels of contaminants that can be found in remote locations. Passive sampling devices are ideally suited to the evaluation of remediation efficiency, i.e. by determining concentrations before and after water or sediment treatment processes. Passive sampling has been applied to the evaluation of sediment remediation efficiency such as when using capping (Eek et al., 2010; Oen et al., 2011) or the treatment/removal efficiency in drinking water treatment plants (Gobelius et al., 2019). Passive sampling can be used to assess the impact from effluent release into the environment (e.g. upstream and downstream an wastewater effluent release point in a riverine environment) particularly when concentrations are likely to vary in time or to track pollution sources (Estoppey et al., 2015; Lombard et al., 2023).

While much research has been conducted to develop passive sampling devices for a wide range of chemicals, passive sampling targeting persistent and mobile substances is relatively less advanced. For a passive sampling device to be used reliably, its performance needs to be evaluated to understand the uptake of chemicals into the sampler and assess the impact of environmental factors on this uptake. One important step in the validation of PSs is a comparison with other water sampling methods. Such testing generally involves deploying samplers at one or more locations and measuring contaminant concentrations with one or more relatively more standardised methods such as repeated grab sampling. One crucial aspect of such comparisons is the selection of an adequate grab sampling frequency to obtain a reliable average water concentration for comparison with passive sampling data output.

ZeroPM aims to develop the passive sampling tools necessary for the measurement of ambient levels of persistent and mobile substances in water and to enable the assessment of the efficiency of drinking water and wastewater treatment at the pilot scale. This deliverable focuses therefore on a field validation of different passive sampling devices deployed at two different drinking water treatment plants. The two hypotheses for this work are that (i) a robust understanding of working principles of passive sampling allows the estimation of passive sampler-based time-averaged concentrations in line with water concentrations obtained through grab sampling and (ii) passive samplers are able to track changes in persistent and mobile substance concentrations throughout a drinking water treatment system.

2 Task definition

Task 7.1 aims at obtaining an innovative passive sampling strategy targeting persistent and mobile substances including benzotriazoles, long chain PFAS (≥C6), short chain PFAS (≤C5) and triazines. Passive sampling devices are used to enable time-integrated sampling of persistent and mobile substances in water and to assess pilot and full-scale drinking water and wastewater treatment technologies. A sampler of relatively straightforward construction (with commercially available materials of a stainless steel mesh and solid-phase extraction sorbent discs) was calibrated in the laboratory in the first step. Uptake into the sampler was shown to be more influenced by water turbulences around the sampler than anticipated. Therefore, the standard procedure for sampler deployment was complemented by using a sampler purposely made to estimate *in situ* boundary layer conditions and correct sampling rates. This versatile tool enables the sampling of different aquatic environments and allows the assessment of drinking water treatment processes (Tasks 7.2 and 7.3) and wastewater treatment processes (Task 7.4).

3 Passive sampling for persistent and mobile substances in water

3.1 Theory and principles of passive sampling in water

Passive sampling in water monitoring is an innovative and effective technique used to assess the presence and concentration of various contaminants in aquatic environments. Unlike traditional grab sampling methods, passive sampling involves the deployment of devices that accumulate contaminants over a defined period, providing a more accurate representation of long-term exposure levels (Vrana et al., 2005).

The theoretical basis for passive sampling in water is rooted in the principles of diffusion and equilibrium. When contaminants are present in water, they naturally tend to move from areas of higher concentration to areas of lower concentration, driven by the process of diffusion. Passive sampling devices, made of one or more materials with an affinity for specific contaminants, are designed to exploit this process to accumulate contaminants over time.

The sampling devices contain a sorbent material with a high affinity for the compounds of interest and this retains them from the surrounding water. When exposed to water, contaminants diffuse through one or more layers or membranes into the sorbent, initially free of contaminants, until an equilibrium is reached, where the concentration of contaminants in the sorbent is proportional to the concentration in the water. This equilibrium condition allows for accurate estimation of contaminant concentrations over extended periods.

The rate of diffusion, uptake and the capacity of the sorbent material influence the sampling rate and sensitivity of the device. Factors such as temperature, water flow rate, and the properties of the contaminants also play a role in determining how efficiently passive sampling operates.

Overall, the theoretical basis of passive sampling leverages the fundamental principles of diffusion and equilibrium to capture a representative snapshot of contaminant levels in water over time, offering a more comprehensive understanding of environmental conditions compared to traditional grab sampling methods.

While passive sampling of nonpolar and non-ionised contaminants has progressed much over the last two decades (Booij et al., 2016), passive sampling of polar, mobile and persistent chemicals has been the subject of relatively less development. Different versions of the polar organic chemical integrative sampler (POCIS) have been calibrated in the laboratory or in the field and used in field applications. It is the most used passive sampler for polar chemicals. The device in its most conventional configuration is made of loose OASIS HLB sorbent (commonly used because its relatively high affinity for polar and often mobile substances) sandwiched between two polyether sulfone membrane (PES). However, the understanding of processes that control the uptake remains relatively poorly understood. Despite much effort, the uncertainty linked to the selection and application of a sampling rate or equivalent volume of water extracted per unit of time (R_s, L d^{-1}) to estimate an average concentration in water for the period of exposure remains relatively high. The interaction of certain chemicals with the PES membrane (through sorption) also affects the uptake. In addition, sampling rates are relatively sensitive to water turbulences around the sampler. Higher turbulences result in a smaller diffusive boundary layer at the surface of the water and higher R_s. Conversely, stagnant conditions will increase the thickness of this boundary layer and tend to reduce R_s. For absorption-based PSs, this has been addressed through the use of performance reference compounds (PRCs), which are synthetic chemicals spiked into the samplers and that will dissipate from the samplers during exposure and inform on the water-sampler exchange kinetics. However, such an approach cannot be used with adsorption-based samplers. In order to circumvent this issue and use reliable sampling rates, sampler design for polar and mobile substances has focussed on making the uptake kinetics as independent as possible from the level of turbulences in water. This can be achieved by selecting and modifying membranes to slow the uptake. In other words, kinetics of mass transfer across the membrane needs to be low enough to control the overall uptake kinetics into the sampler. This can be obtained by increasing the thickness of the membrane or selecting a membrane material that is less permeable for the chemicals of interest. This is the working principle of samplers such as the diffusive gradient in thin film (DGT) device making using of relatively thick layers of polyacrylamide or agarose hydrogels or of the microporous polyethylene tube sampler (MPT) sampler with a microporous polyethylene membrane. In the latter, contaminants diffuse from the water into the micropores of the PE membrane.

The resistance to mass transfer into a passive sampling device is the sum of resistances of transfer across the diffusive boundary layer at the surface of the sampler, mass transfer across (and interaction with) the membrane and diffusion and sorption to the sorbent matrix (Figure 3.1-1). SPE sorbent phases can be loose sorbent, as used in the original version of POCIS (Alvarez et al., 2004), but can also be packed into discs (e.g. OASIS/Atlantic™ HLB or Affinisep's HLB disc). However, in these conditions, the disc material or matrix will also have its own resistance to mass transfer.

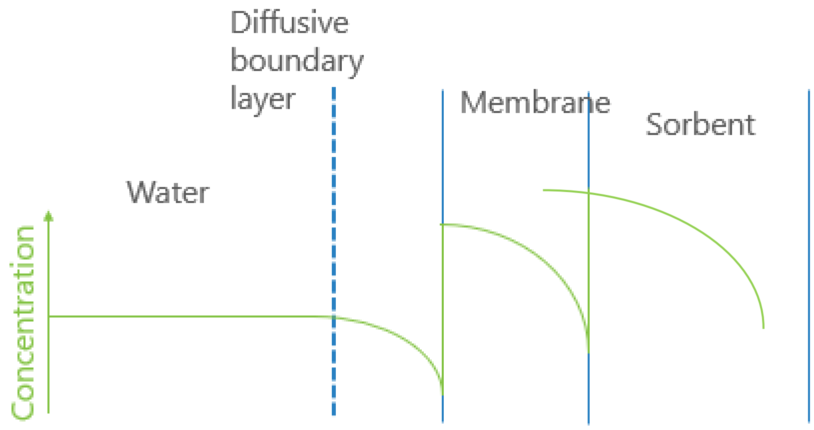


Figure 3.1-1: Principle of the uptake of chemical into an adsorption base passive sampling device

The overall mass transfer resistance to the uptake into a sampler can be decomposed into the sum of mass transfer resistances in each compartment, i.e. the diffusive boundary layer ($1/k_w$), the membrane ($1/(K_{mw}k_m)$) and the sorbent phase ($1/(K_{sw}k_s)$ (Booij et al., 2017):

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{mw}k_m} + \frac{1}{K_{sw}k_s}$$

Eq. 3.1-1

with k_w, k_m and k_s the mass transfer coefficients for the boundary layer, the membrane and the sorbent phase, respectively, and K_{mw} and K_{sw} the membrane-water and sorbent phase-water sorption coefficients, respectively. In the case of a single-phase polymer, the equation reduces to:

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{pw}k_p}$$

Eq. 3.1-2

With K_{pw} the polymer-water partition coefficient (L kg^{-1}) and k_p the mass transfer coefficient for the polymer phase.

For a sampler's R_s to be insensitive to the level of water turbulences (i.e. with $1/k_o$ = constant), the term $1/k_w$ needs to be negligible in comparison with the other terms.

Considering $R_s = Ak_o$, with A the sampling surface area, the equation above can be re-written as:

$$\frac{1}{R_{s(in\ situ)}} = \frac{1}{R_{s,max}} + \frac{1}{Ak_w}$$

Eq. 3.1-3

With $R_{s,max}$ the maximum R_s that can be achieved when mass transfer resistance in the boundary layer is negligible.

Performance criteria when designing a passive sampler are presented in Box 1 and shown in the text below.

Box 1. Performance criteria when designing a passive sampler:
- Appropriate time window for integrative monitoring
- Robust knowledge or derivation of *in situ* sampling rate, R_s.
- High affinity and selectivity for analytes of interest
- Adequate sensitivity, limits of detection/quantification

Appropriate time window for integrative monitoring - The time window for integrative monitoring can be adapted by modifying the surface area to sorption capacity ratio of the sampler.

Robust knowledge or derivation of *in situ* sampling rate, R_s. - Sampling rates independent of water turbulences around the sampler can be achieved by selecting a membrane with relatively low(er) permeability for the analytes of interest or a thick(er) membrane layer.

High affinity and selectivity for analytes of interest - Sampler selectivity can be improved by selecting an appropriate combination of sorption phase and membrane type.

Adequate sensitivity, limits of detection/quantification - The selection of an adequate type of and amount of sorption material contributes to high sorption capacity and lower limits of detection.

Ultimately, a single device configuration will not enable passive sampling of all persistent and mobile substances of interest. Instead, different configurations are required to target different types or classes of persistent and mobile substances.

3.2 Passive samplers used for polar and ionised substances

Different devices have been developed in the last few years to passive sample polar and ionised substances, including persistent and mobile compounds (Figure 3.2-1). DGT and gradient time integrative passive sampler (G-TIP) devices rely on a relatively small sampling window (a few cm^2) compared with POCIS or MPT samplers. Since the overall R_s is proportional to the surface area, these devices will exhibit the lowest R_s. Low sampling rates can in turn affect limits of detection. Depending on the capacity of the receiving phase, the magnitude of the R_s will also dictate how long the uptake of certain chemicals into the sampler can remain in the integrative phase of uptake. For example, a sampler with high R_s and low receiving phase capacity will equilibrate faster than a sampler with low R_s and large capacity for the chemical of interest.

MPT, DGT and G-TIP samplers have been designed to be insensitive to water turbulences during deployment by using relatively thick cylindrical microporous polyethylene membrane for the MPT sampler or an agarose or polyacrylamide hydrogel layer for the DGT device (Fauvelle et al., 2017; Verhagen et al., 2020). The R_s for these devices are generally in the range of 1-10 mL d^{-1}. A different device has also been tested for the sampling of PFAS, also based on diffusion across an agarose layer, but with a larger sampling surface area to try and increase the R_s of DGT (Urík et al., 2020). Values of R_s reported for polar substances with POCIS using a PES membrane are significantly higher and generally in the range of 100-300 mL d^{-1} (Booij and Chen, 2018). These can be even higher when using nylon mesh as the membrane (Belles et al., 2014; Hale et al., 2021). However, the uptake of chemicals into POCIS is most likely partly controlled by transfer across the boundary layer at the surface of the sampler resulting in R_s that will vary with level of turbulences in the water surrounding the sampler. The G-TIP sampler is particularly interesting when working with substances with no affinity to simple, commercially available SPE sorbents. The receiving phase is water that slowly equilibrates with water outside the sampler. The original version of the POCIS made use of loose SPE sorbent which resulted in a very heterogenous distribution of the sorbent sandwiched between two PES membranes.

POCIS 
Sorbent sandwiched between two membranes (~ 40 cm^2)

MPT 
Sorbent enclosed in microporous PE tube (15 cm^2)

DGT 
Hydrogel/PES membrane & sorbent gel layer (3.14 cm^2)

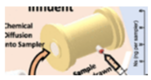
G-TIP 
Sampling cell with small opening for sampling (~ 3 cm^2)

Figure 3.2-1: Different passive sampling devices that have been applied for the sampling of polar and ionised substances in water.

3.3 Passive sampling for ZeroPM persistent and mobile substances

ZeroPM substances principally include PFAS and short-chain PFAS, triazines and benzotriazoles. For PFAS passive sampling, POCIS has been used with Oasis HLB or WAX sorbents (Gobelius et al., 2019; Kaserzon et al., 2014), Strata XAW sorbent (Atoufi and Lampert; Kaserzon et al., 2019) and a combination of both Oasis WAX and Fluoroflash® sorbents (Atoufi and Lampert; Hale et al., 2021) (Table 3.3-1). These sorbents have been used with either a nylon or PES membrane. Higher R_s for short-chain perfluoroalkyl carboxylates with a C3-C6 perfluorocarbon chain lengths and perfluorobutane sulfonate (PFBS) were obtained for POCIS with WAX sorbent than those prepared with HLB sorbent (Gobelius et al., 2019). Interaction of certain chemicals with the PES membrane through sorption renders the understanding of the uptake and prediction of sampling rate more difficult. Such membrane sorption can result in a lag phase in the accumulation of the chemical in the receiving phase. Using 10 µm-nylon mesh allowed the accumulation of a broad range of PFASs with no observable interaction with the membrane (Hale et al., 2021).

For melamine, atrazine and other triazines, a version of the DGT sampler composed of a mixed-mode SPE sorbent MCX cast in a gel and agarose-polyacrylamide diffusive gel covered with a nylon filter (Liu et al., 2021) was tested. Linear accumulation from a 100 µg L^{-1} solution was checked over 6 days. Melamine masses accumulated indicated a R_s just under 10 mL d^{-1}.

An adapted version of POCIS and Chemcatcher was made from an SDB disk behind a protective PES membrane for sampling a range of relatively polar substances (Reymond et al., 2023). These included selected benzotriazoles and atrazine. Maximum sampling rates obtained with this version of the sampler were in the range of 50-100 mL d^{-1}.

Table 3.3-1: Existing passive sampling devices that have been subject to some previous testing in water.

Sampler type	**Membrane**	**Sorbent**	**Sampling (mL d^{-1})**	**Compounds**
DGT	Agarose-polyacrylamide hydrogels	OASIS HLB, MCX, WAX	5-10	PFAS, melamine
POCIS	Polyethersulfone membrane	SDB disk, HLB and WAX powedered sorbent	50-300	Benzotriazoles
MPT	Microporous polyethylene	HLB and WAX Powdered sorbent (or equivalents)	10-20	PFAS ++
G-TIP	Microporous polyethylene	Water	~ few mL	Very polar substances

4 Experimental

After having performed a laboratory calibration of a configuration of POCIS with a stainless steel mesh as membrane, the next step presented here is a performance evaluation of this sampler together with two other types of samplers used for passive sampling of polar substances. The experimental section describes the sampler preparation, sampler deployment and retrieval at two case study sites, grab sampling data, sampler analysis and data interpretation including the calculation of sampling rates for each type of sampler tested.

4.1 Sampler preparation

Diffusion gradient in thin film (DGT) devices were purchased from DGT Research Ltd (UK). The version of DGT used in this work was for the SNW-AP Loaded DGT device specifically made for sampling of perfluorinated compounds in solution. It uses a standard DGT piston/holder and is composed of a 0.8 mm agarose diffusive gel, a polyethersulphone filter membrane and a weak anion exchanger (WAX) binding layer.

MPT samplers were made from microporous polyethylene tubing (4 cm length, 2mm wall thickness, 2.5 µm pore size with 35 % porosity) containing a mix of solid phase extraction sorbents (WAX and HLB). The polyethylene tubing end-plugs were place in a Soxhlet extraction and extracted with methanol to ensure low blank levels. The weak ion exchange resin (WAX) and hydrophilic-lipophilic balance sorbent (HLB) were prepared by soaking in methanol. The methanol was regularly replaced by clean methanol to ensure the samplers were as clean as possible of chemicals of interest. Small aluminium trays were used to weigh the sorbent into the tubes (200 mg of WAX and 200 mg HLB). Once samplers assembled these were placed in a glass jar filled with ultrapure water and kept at room temperature until deployment.

Two versions of POCIS were prepared for this field deployment. The first version tested in the ZeroPM calibration experiment was composed of two stainless steel mesh membranes (5 µm pore size) superimposed on each side of a HLB disc from Affinisep. This version will be used for the sampling of benzotriazoles. A second version making use of a WAX disc also from Affinisep was used for sampling PFAS. Discs were soaked in methanol, with the methanol regularly replaced by clean methanol. The stainless-steel mesh was also soaked in methanol prior to use. Discs were transferred to ultrapure water prior to preparing the samplers. POCIS devices were assembled with wet discs, wrapped in aluminium and stored at 5 °C until use.

A third type of POCIS devices was prepared using silicone rubber. These samplers were loaded with performance reference compounds (PRCs) and the dissipation of these compounds during exposure provides information about silicone-water exchange kinetics and more specifically of boundary layer conditions at the surface the silicone. Since this device's geometry is the same as for the POCIS aimed at sampling benzotriazole and PFAS, boundary layer conditions from POCIS-silicone samplers were extrapolated to those with stainless steel mesh and Affinisep discs. Silicone rubber from Speciality Silicone Product Inc was placed in a Soxhlet extractor and cleaned for 24 hours with ethyl acetate to remove contaminants and oligomers that can interfere with analysis. The Soxhlet extractor was then run with methanol to further clean the silicone. Once cleaned, the silicone was spiked with PRCs using a co-solvent method with methanol and water (Booij et al., 2002). PRCs comprised a suite of deuterated polycyclic aromatic hydrocarbons.

4.2 Sampler deployment at two experimental sites

4.2.1 ZeroPM test site 2 – Upper Rhine

Passive sampler deployment at the Upper Rhine (Bodenheim) was conducted on the 10th June and retrieval was on the 2nd July 2024. A total of five deployment sites were selected and these included a location in the Rhine River, sampling of raw water into the treatment plant (from bank filtration), after ozonation, after sand filtration and after activated carbon (AC) filtration. No samplers were placed after the UV disinfection step. A diagram showing the placement of the sampler is shown below. Sampler deployment in the Rhine was undertaken in the town of Worms (coordinates: 49.631160N; 8.378015E).

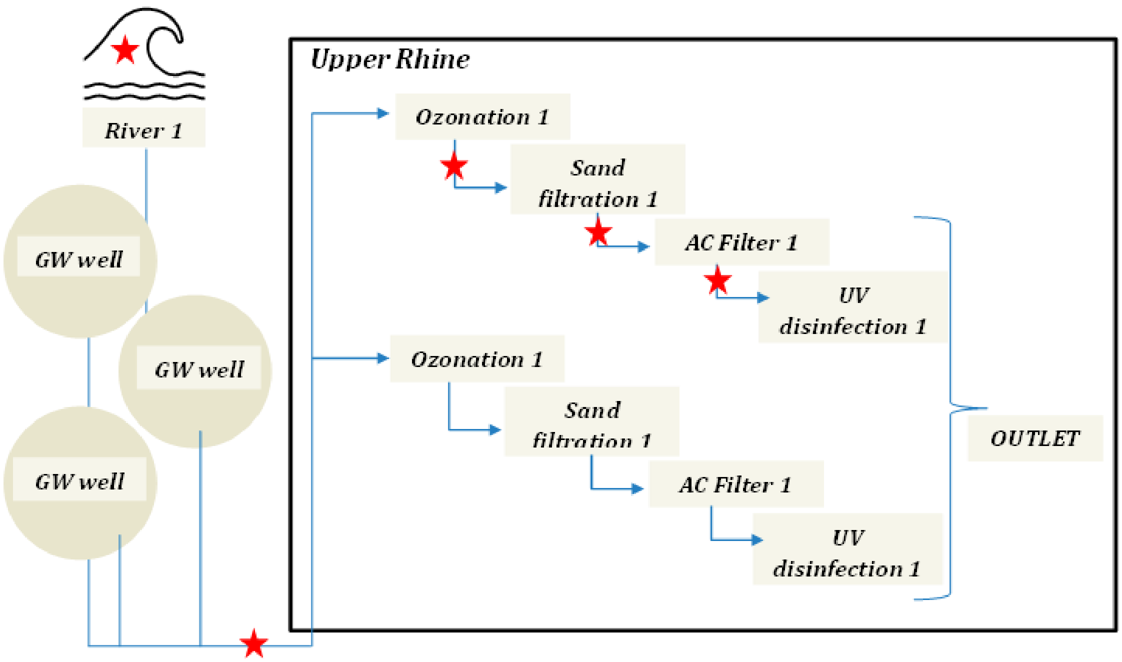


Figure 4.2-1: Flow chart of the test site at the Bodenheim, Upper Rhine River waterworks. The red stars indicate the sampling locations.

4.2.2 ZeroPM test site 1 - Rastatt

PSs were deployed at the site in Rastatt on the 11th June and retrieved on the 2nd July 2024. PSs were exposed to inlet and groundwater well water, as well as after the different AC filters and at different stages of the pilot treatment plant installed and tested at the drinking water treatment plant. Sampling locations are indicated in Figure 4.2-2.

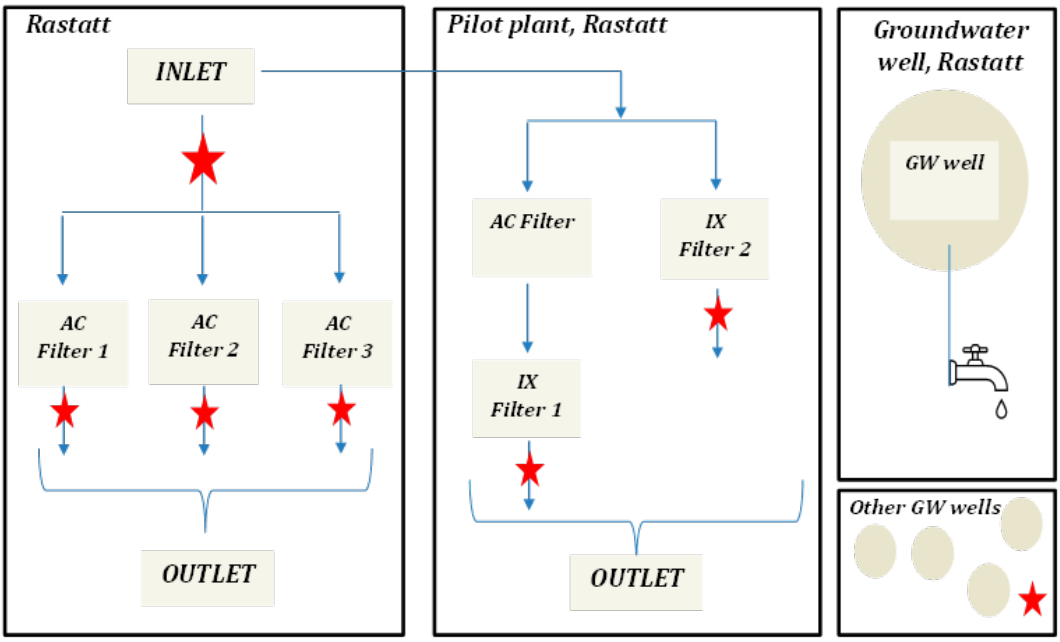


Figure 4.2-2: Flow chart of the test site at the Rauental, Rastatt waterworks. The red stars indicate the sampling locations.

Sampling at the outlet of the AC filters was conducted after three filters out of the four filter units since one unit was offline (AC2). AC units AC1 (Site S2), AC3 (S3) and AC4 (S4) were replaced in December 2023, March 2024 and May 2024, respectively.

4.3 Sampler deployment procedure

4.3.1 Sampler deployments

Duplicate samplers of each kind were deployed at every sampling site, except for the MPT device which was only deployed at the Rastatt site, and the DGT device which was only deployed at the Upper Rhine site with one replicate (Table 4.3-1). Quality assurance measures included the use of field and preparation blanks to check for possible contamination of samplers with persistent and mobile substances of interest during sampler preparation or deployment and retrieval operations. The table below summarises the PS deployments.

Table 4.3-1: Existing passive sampling devices that have been subject to some previous testing in water.

Type of sampler	**Test site: Upper Rhine**	**Test site: Rastatt**	**persistent and mobile substances of interest**
POCIS-WAX		✓	PFAS
POCIS-HLB	✓		Benzotriazole
POCIS-Silicone	✓	✓	No PM substances of interest
DGT WAX		✓	PFAS
DGT HLB	✓		Benzotriazole
MPT	✓	✓	PFAS

4.3.2 Deployments inside the treatment plants

Taps were available for all selected sampling points and this allowed drinking water to be draw for exposure of PSs (Figure 4.3-1 and Figure 4.3-2). For exposure, samplers were placed in stainless steel buckets (10 L) as was previously done in a land-based recirculating aquaculture system (Lusher et al., 2024). POCIS devices were fastened to POCIS holders placed at the bottom of the buckets. A POCIS holder can hold up to three devices. DGT devices were delicately positioned face up at the bottom of the buckets. MPT samplers were fastened to the POCIS holders with fishing line. When possible, buckets were positioned closest to the taps. In other situations, these were placed near drains in the floor and water was brought to the bucket with help of some PEX tubing generally used for drinking water purposes. Water was fed deeper into the bucket and excess water went through an overflow.

The water flow through the buckets was measured at the end of the exposures. Flow through the buckets ranged from 190 to 920 L d^{-1} and on average for all the buckets at the two locations, this was 515 L d^{-1}. It is expected that the flow of water into the buckets was in all cases significantly higher than the removal rate of chemicals by the samplers. In these conditions, it is not expected that the samplers will deplete the water concentration of chemicals of interest.

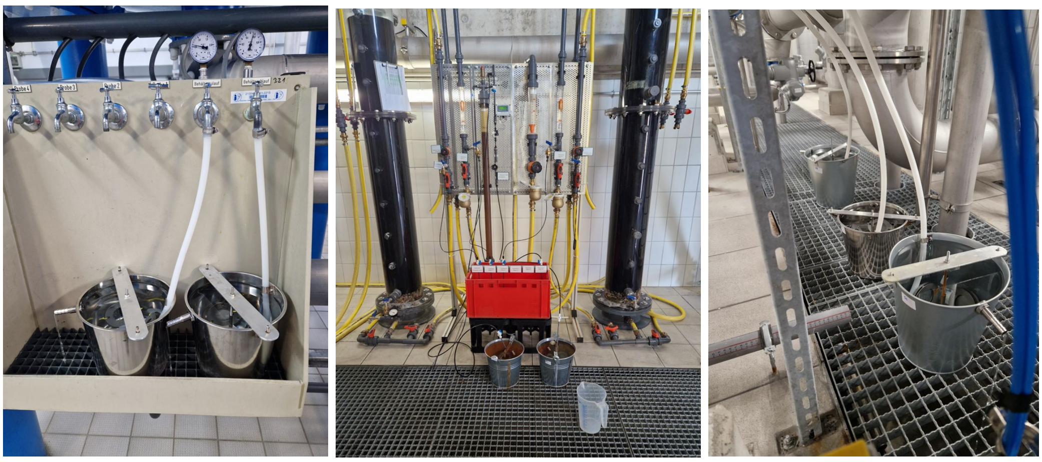


Figure 4.3-1: Examples of exposure systems used at the Upper Rhine and Rastatt test sites.

Figure 4.3-2: Retrieval of passive samplers after 3-week exposure in buckets.

4.3.3 Deployment in the Rhine River

A canister was used to expose PSs in the Rhine River. POCIS devices were placed in the canister using the POCIS holders while DGTs and MPTs were place left loose in the canister. The canister was lowered into the river and held in place with some rope (Figure 4.3-3).

Figure 4.3-3: Retrieval of passive samplers after a 3-week exposure in the Rhine River.

4.4 Sampler extraction and analysis

4.4.1 DGTs and MPTs with WAX sorbent

The MPT samplers were extracted for PFAS by carefully de-capping one end and fortifying the sorbent with internal standards. After at least 30 mins the other end of the tube was de-capped, and the WAX sorbent rinsed into an empty SPE cartridge using ultra-pure water. The empty

SPE cartridge was precondition with 5 mL methanol followed by 5 mL of ultra-pure water. Each sample was rinsed with 10 mL ultra-pure water to remove as much of the loose sorbent from the MPT and caps as possible and was collected in case any analytes were lost in the process, but these have not needed to be analysed. The loose sorbent was then dried under vacuum and then eluted with 5 mL of 0.2% ammonia methanol solution, followed by a further 2 mL. Eluents were evaporated to 1 mL under nitrogen gas (N_2). The 1 mL extracts were cloudy and hence an aliquot of the extract (0.1 mL) was filtered with 5.2 mM ammonium acetate in ultra-pure water (0.2 mL) in a Spin-X nylon centrifuge filter before analysis.

DGT samplers were extracted after carefully dismantling the outer casing and separating the agarose WAX sorbent layer from the sampler. The sorbent layer was placed into a 15 mL tube and artificially fortified with internal standards and left for at least 30 mins before extraction with 5 mL methanol for the analysis of benzotriazoles (Upper Rhine site samples) and 5 mL of 0.2% ammonia methanol solution for analysis of PFAS (Rastatt site samples). The tubes were ultrasonicated for 30 mins and the supernatant collected into a separate tube. The sorbent layer was extracted with a further 3 mL of the same solvents for each type of analysis, sonicated and supernatant collected. The solvent extracts were evaporated using N_2 to 1 mL. The 1 mL extracts for the analysis of samples for Rastatt were cloudy and hence an aliquot of the extract (0.1 mL) was filtered with 5.2 mM ammonium acetate in ultra-pure water (0.2 mL) in a Spin-X nylon centrifuge filter before analysis.

4.4.2 POCIS with HLB and WAX discs

The Affinisep samplers were placed in the fridge until extraction. The POCIS rings were carefully dismantled, and the sorbent membrane was transferred into a 50 mL centrifuge tube. HLB samplers were then artificially fortified with internal standards and were left to rest for 30 mins. Next, the samplers were extracted with 7 mL of 0.1 % formic acid in methanol:acetonitrile (1:1, v/v) and placed to shake at 120 rpm for 60 mins. The solvent was decanted into a 15 mL centrifuge tube and the extraction process was repeated with a further 7 mL 0.1 % formic acid in methanol:acetonitrile (1:1, v/v). The Oasis/Atlantic™ discs were extracted with 10 + 10 mL of 0.1 % formic acid in methanol:acetonitrile as they were completely dry. One millilitre of extract was aliquoted into a LC vial for analysis.

4.4.3 Analysis for benzotriazoles

Analysis of the benzotriazoles was carried out using ultra performance liquid chromatography system coupled to triple quadrupole mass spectrometry system (Acquity UPLC and Xevo TQ-S, Waters™). Detailed information on the analysis can be found in the Appendix.

4.4.4 Analysis for PFAS

The analysis of TFA and other short chain PFAS was conducted separately to longer chain PFAS. The analysis of TFA and other shorter chain PFAS was conducted using the same instrumentation as for the analysis of benzotriazoles. Detailed analytical information can be found in the appendix.

A total of 35 PFAS were quantified using ultra high-performance liquid chromatography (UHPLC, Acquity UHPLC system) coupled with quadrupole time-of-flight mass spectrometry (QToF-HRMS, Xevo G2-S instrument) from Waters™ (Milford, MA, U.S). Mass spectra were acquired in full scan mode across a mass range of m/z 150–1300. Quantitative analysis was carried out by extracting mass chromatograms from the full scan data, utilizing a typical m/z value of 193 with a tolerance of 0.03 ppm to detect the analytes.

4.4.5 Extraction and analysis of silicone samplers for PRCs

Upon returning to the laboratory, blank and exposed silicone rubber samplers were dried and placed in glass jars for soaking in pentane for extraction and to determine the recovery of PRCs. The extraction with 50 mL of pentane was repeated to ensure quantitative recoveries of PRCs. The volume of pentane was reduced to 1 mL under a gentle flow of N_2. Samples were then analysed by gas chromatography and mass spectrometry following methods previously published (Allan et al., 2024; Allan et al., 2021).

4.4.6 R_s determination for DGTs and MPTs

Sampling rates, R_s, are available in the literature for some PFASs but not all (Fang et al., 2021; Yang et al., 2022). In general, these are between 10 and 20 mL d^{-1}. These values enable the estimation of dissolved water concentrations through the following equation:

$$C_w = \frac{m_{acc}}{R_s t} \qquad \textit{Eq. 4.4-1}$$

With C_w the concentration in water (ng L^{-1}), m_{acc} the mass accumulated (ng), R_s the sampling rate from literature (L d^{-1}) and t, the exposure time. In most situations, the relatively thick agarose gel results in sampling rates that are independent of water turbulences. Only in some cases, with very stagnant water conditions, is it needed to consider transport through the boundary layer. As will be shown in this report (through the silicone-water exchange for the PRCs), the water turbulences in the sampling buckets were very low and sufficiently low to require a correction of R_s for DGT to account for resistance to mass transfer in the boundary layer:

$$C_w = \frac{m_{acc}}{\left(\frac{1}{\frac{1}{R_s}+\frac{1}{Ak_w}}\right)t} \qquad \textit{Eq. 4.4-2}$$

With A the sampling surface area of DGT (m^2) and k_w the mass transfer coefficient across the boundary layer (m d^{-1}). It was assumed that DGT samplers remained in the linear uptake phase for most PFAS.

For the MPT sampler, literature-based R_s values were used (Kaserzon et al., 2019) and linear uptake throughout the deployment was assumed. A correction to include the effects of the boundary was applied to these literature-based R_s. However, this had a minor effect on R_s

values. Although, we have chosen these literature values because they included the specific PFAS that were detected and quantified in our study, other references that include R_s for certain PFAS do exist (Clokey et al., 2023; Mackie et al., 2024) with R_s values somewhat higher than those reported in 2019 (Kaserzon et al., 2019).

4.4.7 R_s determination for POCIS with WAX or HLB sorbent disc

$R_{s,max}$ for benzotriazoles was determined in a laboratory calibration experiment conducted with POCIS devices composed of a HLB disc overlayed by two 5-µm stainless steel mesh. Since relatively high $R_{s,max}$ values were obtained, this means that the uptake in this POCIS configuration can be partly boundary layer-controlled. It is therefore necessary in these conditions to quantify boundary layer conditions. Dissolved water concentrations estimated from POCIS exposures are obtained through a similar equation to that presented for DGT:

$$C_w = \frac{m_{acc}}{\left(\frac{1}{\frac{1}{R_{s,max}}+\frac{1}{Ak_w}}\right)t} \qquad \textit{Eq. 4.4-3}$$

Since it is possible that the uptake into POCIS is not linear for the entire exposure duration, an alternative equation is used to take this into account:

$$C_w = \frac{m_{acc}}{K_{sw}m\left(1-exp\left(\frac{-\left(\frac{1}{\frac{1}{R_{s,max}}+\frac{1}{Ak_w}}\right)t}{K_{sw}m}\right)\right)} \qquad \textit{Eq. 4.4-4}$$

With K_{sw} the sorbent-water distribution coefficient (L kg^{-1}). These K_{sw} values were measured in 24h-batch experiments for benzotriazoles and can be obtained from literature for PFASs (Snook et al., 2023).

4.5 Persistent and mobile substance concentrations from grab sampling

Grab sampling was conducted during sampler deployment and retrieval operations to allow comparisons with data generated with the passive sampler exposures (Table 4.5-1 and Table 4.5-2). Sampling at most sampling points was conducted on two occasions. For the Upper Rhine case study site, no grab sampling was conducted in the river. In a few cases, particularly for the Rastatt case study site, some sampling sites were sampled only once.

Table 4.5-1: Mean concentrations of relevant persistent and mobile substances (ng L^{-1}) measured by routine grab sampling undertaken on passive sampler deployment and retrieval dates at the Upper Rhine case study site.

	River	Raw mixed water	Outlet Ozonation	Outlet Sand filtration	Outlet activated carbon	Outlet UV treatment
Benzotriazole	-	120 (17)	81 (12)	79 (9)	-	-
Methylbenzotriazole	-	76 (0)	47 (7)	42 (5)	-	-
Atrazine	-	-	-	-	-	-
TFA	-	1065 (44)	1055 (47)	1065 (44)	1045 (30)	1035 (32)
PFPrA	-	7.6 (29)	7.7 (13)	7.4 (37)	9.0 (45)	8.1 (41)
PFBA	-	5.2 (53)	5.0 (44)	5.0 (48)	3.8 (111)	4.4 (87)
PFPeA	-	3.7 (69)	3.8 (58)	3.7 (48)	1.3	2.2 (100)
PFHxA	-	2.5 (62)	2.5 (62)	2.4 (73)	-	1.4 (58)
PFHpA	-	1.4 (58)	1.4 (52)	1.4 (52)	-	-
PFOA	-	3.0 (0)	2.5 (32)	2.2 (42)	-	-
PFBS	-	2.3 (14)	2.3 (14)	2.2 (19)	-	-
PFPeS	-	-	-	-	-	1.2 (27)
PFHxS	-	1.9 (22)	1.9 (27)	1.8 (34)	-	-
PFOS	-	4.2 (41)	3.9 (65)	3.8 (69)	-	-

Note: Relative percent differences of two measurements (RPD) are given in brackets (%); When one of the two values was below limits of quantification, the limit of detection was used to calculate the mean and the % RPD.

Table 4.5-2: Mean concentrations of relevant persistent and mobile substances (ng L^{-1}) measured by routine grab sampling undertaken on passive sampler deployment and retrieval dates at the Rastatt case study site.

	Inlet	Small wells	Outlet AC filter (no 1)	Outlet AC filter (no 3)	Outlet AC filter (no 4)	Outlet IX filter 1	Outlet IX filter 2	Outlet AC filter (coconut shell)	Outlet AC filter (hard coal)	Outlet
Site nb	*S1*	*S9*	*S2*	*S3*	*S4*	*S6*	*S7*	*S5.2*	*S5*	
TFA	790 (3)	1368	808 (9)	801 (1)	842 (8)	798 (5)	804 (5)	855	815	843
PFPrA	18 (18)	24	20 (22)	23 (44)	18 (64)	16 (110)	22 (15)	22	16	22
PFBA	24 (3)	33	34 (12)	15 (105)	<1	14 (187)	26 (5)	25	25	17
PFPeA	67 (5)	81	13 (142)	<1	<1	31 (194)	81 (1)	80	75	9.3
PFHxA	59 (1)	70	<1	<1	<1	5.5 (164)	29 (12)	66	57	<1
PFHpA	30 (9)	37	<1	<1	<1	<1	<1	28	22	<1
PFOA	149 (23)	180	<1	<1	<1	1.3	<1	90	65	<1
PFBS	1.9 (0)	1.2	<1	<1	<1	<1	<1	2.0	1.9	<1
PFHxS	1.3 (8)	1.1	<1	<1	<1	<1	<1	<1	1.3	<1

Note: Relative percent differences of two measurements (RPD) are given in brackets (%); When one of the two values was below limits of quantification, the limit of detection was used to calculate the mean and the % RPD. Only one measurement was conducted at the small wells site (S9), outlet and after the pilot plant coconut shell and hard coal activated carbons.

5 Results and Discussion

5.1 *In situ* calibration of boundary layer conditions

5.1.1 PRC dissipation

In the present context, POCIS-silicone samplers were used to (i) obtain additional information on water turbulences that the samplers were exposed to and (ii) quantify the possible contribution of the boundary layer at the surface of the samplers to the overall sampling rates of persistent and mobile substances by these samplers. POCIS-silicone were deployed on the POCIS holders in the same way as the POCIS for sampling persistent and mobile substances and we assume that we can extrapolate the boundary layer conditions to the other POCIS devices and to the other samplers if needs be. A typical PRC dissipation curve is presented below for the POCIS-silicone sampler deployed at the outlet of the AC filter at the Upper Rhine case study site (Figure 5.1-1). The PRC fraction remaining in the sampler after exposure increases with increasing hydrophobicity. The non-linear least square method (Booij and Smedes, 2010) was applied to each exposure to obtain an equivalent sampling rate and mass transfer coefficient across the boundary layer. PRC dissipation is mainly the result of transport across the boundary layer, and this means that PRC dissipation informs us on transport across this layer.

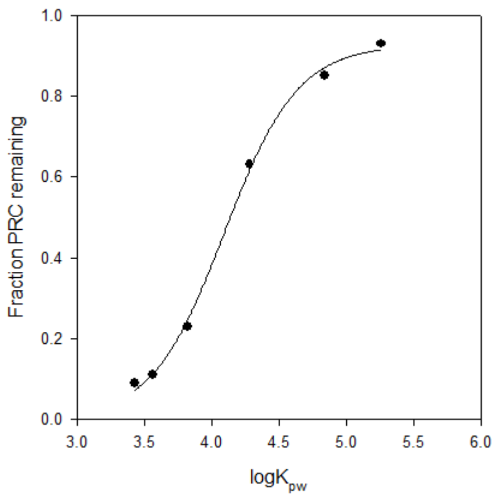


Figure 5.1-1: Example of PRC dissipation from POCIS-silicone sampler during the three week exposure in water from the outlet of the activated carbon filter at the Upper Rhine case study site. The proportion of PRC left in the sampler is obtained from the mass remaining in the sampler over the mean value for non-exposed blank silicones.

The exposure-specific parameter logβ, an equivalent R_s and mass transfer coefficient for the boundary layer (for a molecule with log K_{pw} = 5 and MW = 252 g mol^{-1}) are given in the table below (Table 5.1-1). Values of k_w were in the range 2.4-8.7 cm d^{-1} in the bucket exposures and substantially higher for the cage exposure in the Rhine River.

Table 5.1-1: Characterisation of the boundary layer conditions at the surface of the POCIS devices during exposures at two case study sites using POCIS- silicone and PRC dissipation kinetics.

	S1	S2	S3	S4	S6	S7	S9	S10	S11	S12	S13	S14
Logβ*	-0.41	-0.39	-0.56	0.00	-0.34	-0.10	-0.26	1.01	-0.20	-0.10	-0.27	-0.25
Log β SE	0.03	0.03	0.04	0.03	0.03	0.04	0.06	0.06	0.04	0.02	0.07	0.05
R_s**	155	162	110	398	182	316	219	4074	251	316	214	224
k_w***	3.4	3.5	2.4	8.7	4.0	6.9	4.8	89	5.5	6.9	4.7	4.9

*Exposure-specific parameter and its standard error (SE)
**R_s (mL d^{-1}) given for a chemical with $logK_{pw}$ = 5 and MW = 252 g mol^{-1} (average of the two closest PRCs)
***Mass transfer coefficient (cm d^{-1}) for the boundary layer for a chemical with $logK_{pw}$ = 5 and a sampler surface area of 45 cm^2.

5.1.2 Accounting for boundary layer conditions when estimating R_s

Depending on the level of resistance to mass transfer in the boundary (level of turbulences), this resistance may not be negligible and thus, may need to be considered when estimating *in situ* sampling rates for PSs for persistent and mobile substances. Transport through the boundary layer is mainly through diffusion in water. Hence the mass transfer coefficient is related to the conceptual boundary layer thickness and diffusion coefficient in water. Mass transfer coefficients, $k_{w,PRC}$ were derived for a hypothetical PRC (deuterated polycyclic aromatic hydrocarbons (PAHs)) with a $logK_{pw}$ of 5 and MW of 252 g mol^{-1}. This was used in the following equation to estimate $k_{w,PM}$ for our persistent and mobile substances of interest (Glanzmann et al., 2022; Glanzmann et al., 2023; Reymond et al., 2024):

$$k_{w,PM} = k_{w,PRC} \left(\frac{D_{w,PM}}{D_{w,PRC}}\right)^{2/3} \quad \textit{Eq. 5.1-1}$$

Where D_w are the diffusion coefficients of persistent and mobile substances and PRCs in water. Diffusion coefficients in water were themselves obtained through the following equation:

$$D_w = \frac{2.7\ 10^{-8}}{MW^{0.71}} \quad \textit{Eq. 5.1-2}$$

With MW in g mol^{-1} and D_w in m^2 s^{-1} (Schwarzenbach et al., 2016).

In this way it is possible to estimate the mass transfer coefficient through the boundary layer at the surface of the samplers for each persistent and mobile substance of interest at each sampling location. This method to calibrate the uptake *in situ* has been proposed previously (Glanzmann et al., 2022; Reymond et al., 2023).

5.2 Mass accumulated in samplers over three weeks

5.2.1 Benzotriazoles and atrazine at the Upper Rhine case study site

All benzotriazoles and atrazine accumulated in samplers deployed in the Rhine River (Table 5.2-1). Most of these substances were also found in the inlet water at the drinking water treatment plant with generally decreasing masses accumulated with increasing treatment. Only benzotriazole and 4 and 5-methyl benzotriazole were found above limits of quantification

(LOQ) after AC treatment. The relative percent difference between duplicate measurements ranged from 1 to 84 % depending on the exposure site and compound.

Table 5.2-1: Masses of benzotriazoles (and atrazine) in POCIS-HLB samplers exposed at the Upper Rhine case study site (ng sampler⁻¹).

	Laboratory blanks	Field blanks	River	Inlet	After ozonation	After sand filtration	After AC
ATZ			8.2 (37)	1.0 (50)	1.1 (24)	0.53 (22)	
BTZ	0.1 (1)	4.0 (58)	148 (14)	83 (37)	89 (27)	41 (37)	3.6 (58)
4/5Me-BTZ		17 (84)	274 (24)	86 (34)	77 (14)	39 (83)	17 (68)
5Cl-BTZ		0.3 (51)	6.0 (17)	2.1 (56)	2.5 (63)	1.2 (5)	
XTR			2.2 (36)				
OH-BT	6.7 (9)	6.7 (23)	55 (35)				

Note: Duplicate samplers were used except for the field blanks for which triplicates were available. Relative percent differences of two measurements (RPD) are given in brackets (%)
For visual considerations, cells are left empty for data below limits of quantification

5.2.2 PFAS at the Rastatt case study site

POCIS deployed at the Rastatt case study site accumulated a range of PFAS (Table 5.2-2). These ranged from PFBA that was found throughout the treatment plant to PFOA and PFOS, which were found primarily in the inlet water. Relative percent differences (RPDs) between duplicate measurements ranged from a few percent up to 80 %. Some higher % RPDs were calculated for exposure sites and chemicals for which only one measurement was > LOQ.

Table 5.2-2: Masses of PFAS in POCIS devices exposed at the Rastatt case study site (ng sampler⁻¹)

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
Site	S1	S9	S2	S3	S4	S6	S7
PFBA	14 (53)	20 (29)	16 (52)	12 (68)	1.1 (34)	25 (65)	26 (23)
PFPeA	45 (53)	62 (35)	7.1 (61)			83 (65)	98 (16)
PFHxA	42 (56)	56 (29)				13 (79)	40 (16)
PFHpA	20 (58)	30 (27)				1.5 (64)	1.4 (51)
PFOA	80 (53)	132 (27)				1.8 (59)	
PFNA	0.34 (200)	1.3 (51)					
PFBS	4.3 (18)	3.0 (36)					
PFHxS	2.3 (23)	1.7 (29)					
PFHpS	0.21 (0)	0.14 (25)	0.30 (11)	0.11 (120)	0.17 (150)	0.04 (200)	0.06 (4)
PFOS	6.8 (18)	2.5 (33)					
br-PFOS	3.4 (18)	2.5 (31)					

Relative percent differences of two measurements (RPD) are given in brackets (%)
For visual considerations, cells are left empty for data below limits of quantification

In general, the PFAS accumulated in DGT and MPT devices deployed at the Rastatt case study site mirrored well those accumulated in POCIS, albeit with lower masses accumulated (Table 5.2-3 and Table 5.2-4). This is not surprising considering the lower surface area and sampling rates of the DGT device. Therefore, POCIS has a better potential to reach lower limits of detection (LOD) than the DGT.

Table 5.2-3: Masses of PFAS in DGT samplers exposed at the Rastatt case study site (ng sampler^{-1})

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
	S1	S9	S2	S3	S4	S6	S7
TFA	0.71 (59)	0.80 (44)	0.64 (1)	0.75 (11)	0.73 (65)	0.58 (22)	0.55 (3)
PFBA	2.5 (42)	2.6 (53)	3.1 (2)	1.5 (27)		2.0 (4)	3.6 (50)
PFPeA	11 (20)	12 (58)	1.9 (9)			8.5 (15)	15 (2)
PFHxA	10 (26)	12 (52)				1.5 (18)	6.4 (1)
PFHpA	4.8 (20)	5.9 (52)				0.19 (4)	0.24 (24)
PFOA	20 (22)	24 (59)	0.07 (200)	0.15 (46)		0.20 (7)	
PFNA	0.5 (110)	0.30 (60)					
PFBS	0.26 (13)	0.16 (41)					
PFHxS	0.14 (5)	0.12 (55)					
PFHpS							
PFOS	0.36 (2)	0.10 (74)					
Relative percent differences of two measurements (RPD) are given in brackets (%)							

Table 5.2-4: Masses of PFAS in MPT samplers exposed at the Rastatt case study site (ng sampler^{-1})

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
	S1	S9	S2	S3	S4	S6	S7
TFA	4.4 (9)	4.8 (6)	4.1 (9)	4.1 (15)	4.5 (15)	2.9 (1)	3.5 (45)
PFPrA	1.8 (1)	1.1 (200)	0.6 (200)	1.0 (23)	1.4 (23)	0.5 (200)	
PFBA	1.9 (10)	1.1 (22)	2.6 (54)	0.92 (15)	0.087 (21)	1.6 (17)	2.1 (67)
PFPeA	7.3 (14)	3.5 (12)	1.1 (45)	0.54 (71)		4.8 (4)	7.8 (77)
PFHxA	5.8 (37)	3.7 (40)		0.22 (54)		0.37 (3)	2.2 (42)
PFHpA	1.7 (77)	1.6 (63)					
PFOA	5.5 (64)	6.2 (48)	0.02 (200)				
PFNA		0.1 (42)					
PFBS	0.17 (25)	0.088 (15)	0.026 (70)	0.034 (0)	0.030 (11)	0.029 (32)	0.036 (45)
PFHxS	0.027 (45)	0.014 (200)					
PFOS	0.077 (33)						
Relative percent differences of two measurements (RPD) are given in brackets (%) For visual considerations, cells are left empty for data below limits of quantification							

5.3 Dissolved water concentrations derived from passive sampling measurements

5.3.1 Benzotriazoles and atrazine at the Upper Rhine case study site

Dissolved concentrations in water were calculated from masses of chemicals accumulated in the samplers. In the case of the POCIS devices deployed at the Upper Rhine case study site, benzotriazole and 4/5-methyl benzotriazole are present in river water at the highest concentrations (Figure 5.3-1). These are in the range of 100-250 ng L^{-1} in the river and lower at the treatment plant. There is a relatively good agreement of PS-derived concentrations with those obtained through grab sampling for benzotriazole and 4/5-methyl benzotriazole. Ozonation and sand filtration, as expected, have very little effect on water concentrations for these two chemicals while the most pronounced effect resulted from the AC filtration. Atrazine concentration in the river was estimated at approximately 3 ng L^{-1} reducing to 0.2 ng L^{-1} at the drinking water treatment plant inlet. Ozonation and sand filtration had little effect on the atrazine concentration in water. However, it was < LOD in the water at the outlet of the AC filter. A similar pattern was obtained for 5-chlorobenzotriazole as for atrazine. Finally, 5,6-dimethyl benzotriazole and 2-hydroxybenzothaizole were found > LOQ in the river but were not found in samplers from the drinking water treatment plant.

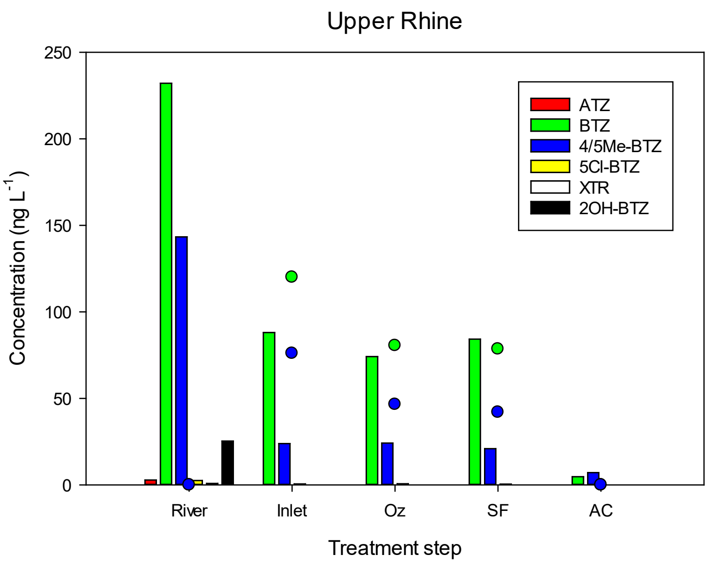


Figure 5.3-1: Comparison of POCIS passive sampler-derived benzotriazole (and atrazine) concentrations in water at the different steps of the drinking water treatment process (bars) with those measured by grab sampling (circles). Grab sampling was not conducted at the River site. Note that Oz, SF and AC indicates sampling after ozonation, sand filtration and activated carbon filtration, respectively.

5.3.2 PFAS at the Rastatt case study site

For the DGT device deployed at the Rastatt case study site, dissolved water concentrations were estimated from PFAS masses accumulated and literature values of R_s corrected for boundary layer conditions. Estimated dissolved water concentrations from passive samplers are given in the table below and compared with mean concentrations from grab sampling. In most cases, concentrations generated by the passive sampler deployments deviate from grab sampling by well under a factor of two (Table 5.3-1). The fingerprint of PFAS found with grab sampling and PS are extremely similar. The concentrations of PFAS at the inlet of the treatment plant were relatively similar to those from the small wells (S9). PSs also confirm the limited treatment efficiency of the two pilot treatment lines at the time of sampling for PFBA and up to PFNA. DGTs were also able to measure water concentrations close to or <LOQs of grab sampling. PFNA, PFUnDA, PFPeS, PFHxS and PFOS were measured at concentrations close to or <1 ng L^{-1} in the inlet water but were not found through grab sampling. Another interesting aspect of these results is the presence of certain compounds in outlet water from the AC filters. PFBA was measured in the effluent of S2 and S3 and PFPeA in the outlet water of S2. Results from passive samplers and grab sampling were in agreement. PFOA was also found using passive samplers in the outlet water of S2, S3 and S4 at concentrations close to or <1 ng L^{-1}. The AC filter at S4 clearly shows the best removal efficiency for PFAS out of the three AC filters. The AC filter at S2 had been online the longest and appears to show highest breakthrough of PFBA and PFPeA. The AC at S4 was placed online the latest and it remained capable of retaining PFBA efficiently since no breakthrough is observed.

Table 5.3-1: Dissolved water concentrations of PFAS derived from DGT sampler exposures at the Rastatt case study site (ng L^{-1}).

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
Site	S1	S9	S2	S3	S4	S6	S7
PFBA	16 (24)	14 (33)	20 (34)	13 (15)		12 (15)	16 (26)
PFPeA	75 (67)	68 (81)	13 (13)			55 (31)	70 (81)
PFHxA	78 (59)	72 (70)				10 (5.5)	33 (29)
PFHpA	40 (30)	39 (37)				1.4 (<1)	1.3 (<1)
PFOA	171 (149)	171 (180)	0.59 (<1)	1.7 (<1)	0.55 (<1)	1.5 (1.2)	0.23
PFNA	4.6 (<1)	2.3 (<1)				2.0 (<1)	0.80 (<1)
PFUnDA	0.32 (<1)						
PFBS	2.0 (1.9)	0.95 (1.2)		0.27 (<1)			
PFPeS	0.22 (<1)	0.091 (<1)					
PFHxS	1.2 (1.3)	0.85 (1.1)					
PFOS	3.5 (<1)	0.80 (<1)					
Mean concentrations from grab sampling are shown in brackets Relative percent difference for dissolved concentrations are the same as for masses accumulated. For visual considerations, cells are left empty for data below limits of quantification							

Data generated from the POCIS exposures at the Rastatt case study site are in line with those from the DGT sampler and from grab sampling (Table 5.3-2). The fingerprint of PFAS detected and quantified with POCIS matches the pattern observed with DGT very well. While some of the dissolved water concentration estimates are fully in line with grab sampling and DGT-derived concentrations, others such as PFPeA, PFHxA, PFHpA and PFOA are clearly underestimated by the POCIS device. Concentrations are underestimated by a factor of three to four for these PFAS. The pattern of PFAS quantified in extracts of the MPT sampler (Table 5.3-3) is also in line with PFAS quantified in extracts from the other samplers and through grab sampling.

Table 5.3-2: Dissolved water concentrations of PFAS derived from POCIS-WAX device exposures at the Rastatt case study site (ng L^{-1}).

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
Site	S1	S9	S2	S3	S4	S6	S7
PFBA	13	17	15	12	0.87	22	21
PFPeA	21	21	3.1			33	24
PFHxA	19	18				5.0	9.0
PFHpA	9.6	10				0.61	0.32
PFOA	41	48				0.80	
PFNA	0.19	0.52					
PFBS	1.9	0.94				0.15	
PFHxS	1.2	0.60					
PFHpS	0.11	0.053	0.15	0.082	0.035	0.017	0.015
PFOS	3.9	1.0					
br-PFOS	1.9	1.0					
Relative percent difference for dissolved concentrations are the same as for masses accumulated. For visual considerations, cells are left empty for data below limits of quantification							

Table 5.3-3: Dissolved water concentrations of PFAS derived from MPT sampler exposures at the Rastatt case study site (ng L^{-1}).

	Inlet	Small wells	Outlet AC	Outlet AC	Outlet AC	Outlet IX filter	Outlet IX filter
Site	S1	S9	S2	S3	S4	S6	S7
PFBA	47	28	66	24	2.2	40	53
PFPeA	138	64	20	10		90	143
PFHxA	100	63		3.8		6.4	36
PFHpA	30	27					
PFOA	97	108	0.30				
PFNA		1.45					
PFBS	2.8	1.4	0.42	0.57	0.46	0.45	0.57
PFHxS	0.42	0.21					
PFHpS							
PFOS	0.89						
Relative percent difference for dissolved concentrations are the same as for masses accumulated. For visual considerations, cells are left empty for data below limits of quantification							

In Figure 5.3-2, we plotted the ratio of concentration estimated by the three different kinds of samplers over the mean values obtained through grab sampling. As mentioned, above, this visually confirms that DGTs provide data most in line with the spot grab sampling. MPTs tend to overestimate water concentrations for PFBA and PFPeA by a factor of two, while data for the other PFAS are closer to a ratio of one. POCIS clearly and consistently underestimates water concentrations for perfluorocarboxylic acids (PFCAs) above. Data are closer to a ratio of one for PFBS and PFHxS. It is not clear at present the reasons for deviations observed with the MPT and POCIS devices. For the sampling of PFCAs by POCIS, the procedure to estimate *in situ* sampling rates from silicone-based PRC dissipation kinetics may need to be improved. It is also possible that the uptake of PFAS into the POCIS devices was not linear over the three weeks of exposure, although this is unlikely due the very high WAX sorbent-water distribution coefficients (Snook et al., 2023).

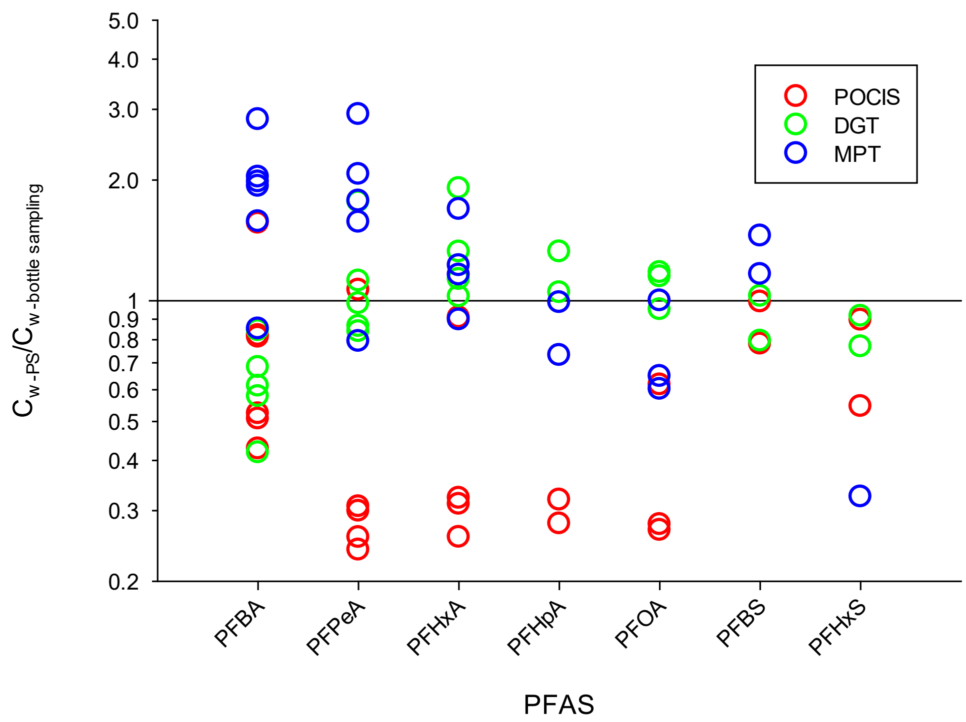


Figure 5.3-2: Ratio PFAS concentrations estimated by three types of passive samplers over that obtained through grab sampling. Data were plotted only when both passive sampling and spot sampling data were above limits of quantification.

6 Conclusions

Three types of PSs were successfully deployed at different stages of two drinking water treatments plants in Germany. It was possible to compare the dissolved water concentrations of a range of persistent and mobile substances obtained through spot, grab sampling with those estimated using the three types of PSs. Key conclusions of this performance evaluation for the three types of PSs are given below:

- The deployment of passive samplers in a drinking water treatment plant using buckets for exposure was successful.
- As shown by the silicone-based PRC dissipation kinetics, the level of water turbulences in the exposure buckets was very low. Therefore, this test represents a relatively extreme set of conditions under which samplers have been tested.
- At the Upper Rhine site, POCIS devices provided data in line with grab sampling for benzotriazoles, they could detect lower levels of contamination than grab sampling, and they demonstrated the removal of persistent and mobile substances throughout the water treatment plant steps.
- After 21 days of exposure, the POCIS devices were no longer in the linear uptake phase.
- The three types of passive samplers deployed in Rastatt provided a similar profile of PFAS contamination throughout the treatment plant. These data were in line with the grab sampling data conducted at the start and end of the passive sampler exposures allowed the quantification of more PFAS than through grab sampling.
- All three types of passive samplers were able to provide information on the removal efficiency of PFAS by the different AC filters and through the pilot treatment plant installed at the Rastatt case study site.
- DGT devices provided the best agreement with the concentrations of PFAS in water measured with grab sampling. In case of POCIS and MPT samplers, some wider deviation than expected were observed. However, these deviations appeared relatively systematic and likely the result of a specific factor, e.g. such as non-linear uptake over the three-week period, or bias in R_s estimation.
- Masses of chemicals accumulated in POCIS were substantially higher than in the other two types of samplers. This can offer improved limits of quantification.
- Further work is needed to understand the reasons for the deviations observed for POCIS and MPT samplers and to investigate the accumulation process for the ultra-short chain PFAS.

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9 Appendix

UPLC-MS/MS parameters for benzotriazoles analysis

LC parameters:

Instrument:	Acquity UPLC, Waters™
Run time:	6 min
Mobile phase A:	0.05% formic acid in 5 mM ammonium formate
Mobile phase B:	Acetonitrile:methanol, 3:1
Flow rate:	0.5 mL min^{-1}
Column:	ACQUITY UPLC BEH C8 1.7µm
Column temp:	50 °C
Injection volume:	2 µL

MS parameters:

Instrument:	Xevo TQ-S, Waters™
Electro-spray ionisation:	positive mode

Table 0-1: Mobile phase gradient

Time (min)	A%	B%
0	97	3
0.5	95	5
3.5	70	30
4.5	30	70
4.6	0	100
5.8	0	100
5.9	95	5
6	95	5

Table 0-2: Target analytes analysed and their corresponding internal/surrogate standards, retention time, parent and daughter ions and limits of detection (LOD).

Analyte	Internal standard/ surrogate	Retention time (min)	Parent (m/z)	Daughter (m/z)	LOD (ng mL^{-1})
ATZ	d5-atrazine	4.95	216.0 216.0	104.0 174.0	0.01
BTZ	d6-5-methylbenzotriazole	2.73	120.1 120.1	65.0 92.0	0.03
5Me-BTZ	d6-5-methylbenzotriazole	3.61	134.1 134.1	77.0 79.0	0.03
5Cl-BTZ	d6-5-methylbenzotriazole	4.00	154.0 154.0	90.0 99.0	0.08
XTR	d6-5-methylbenzotriazole	4.26	148.0 148.0	77.0 93.0	0.04
OH-BT	d6-5-methylbenzotriazole	4.08	152.0 152.0	92.0 124.0	2.64

UPLC-MS/MS parameters for TFA analysis

LC parameters:

Instrument:	Acquity UPLC, Waters™
Run time:	8.5 min
Mobile phase A:	
Mobile phase B:	Acetonitrile:methanol, 3:1
Flow rate:	0.4 mL min^{-1}
Column:	ACQUITY UPLC
Column temp:	50 °C
Injection volume:	50 µL

MS parameters:

Instrument:	Xevo TQ-S, Waters™
Electro-spray ionisation:	negative mode

Table 0-3: Mobile phase gradient

Time (min)	A%	B%
0	80	20
1.2	80	20
4.5	35	65
6.5	0	100
7.5	0	100
7.6	80	20
8.5	80	20

Table 0-4: Target analytes analysed and their corresponding internal/surrogate standards, retention time, parent and daughter ions and limits of detection (LOD).

Analyte	Internal standard/ surrogate	Retention time (min)	Parent (m/z)	Daughter (m/z)	LOD (ng mL^{-1})
ATZ	d5-atrazine	4.95	216.0 216.0	104.0 174.0	0.01
BTZ	d6-5-methylbenzotriazole	2.73	120.1 120.1	65.0 92.0	0.03
5Me-BTZ	d6-5-methylbenzotriazole	3.61	134.1 134.1	77.0 79.0	0.03
5Cl-BTZ	d6-5-methylbenzotriazole	4.00	154.0 154.0	90.0 99.0	0.08
XTR	d6-5-methylbenzotriazole	4.26	148.0 148.0	77.0 93.0	0.04
OH-BT	d6-5-methylbenzotriazole	4.08	152.0 152.0	92.0 124.0	2.64

QToF-HRMS parameters for PFAS analysis

LC parameters:
Instrument: Acquity Ultra UPLC, Waters™
Run time: min
Mobile phase A: 5.2 mM ammonium acetate in ultra-pure water
Mobile phase B: Acetonitrile
Flow rate: 0.5 mL min^{-1}
Column: ACQUITY UPLC BEH C8 (100 x 2.1 mm, 1.8 µm particles)
Column temp: 50 °C
Injection volume: 7 µL

MS parameters:
Instrument: Xevo G2-S QToF-HRMS, Waters™
Electro-spray ionisation: negative mode
Full scan mode mass range: 150-1300 m/z
Capillary voltage: 0.7 kV
Desolvation temperature: 500 °C
Source temperature: 120 °C
Nitrogen desolvation gas flow: 800 L h^{-1}

Table 0-5: Mobile phase gradient

Time (min)	A%	B%
0	88	12
1.5	88	12
11	1	99
13	1	99

Table 0-6: Target analytes analysed and their corresponding internal/surrogate standards, mass and limits of detection (LOD) and limit of quantification (LOQ). The LOD and LOQ were calculated as 3x and 10x the standard deviation of the lowest standard, from repeated measurements from different analysis.

Analyte	**Internal standard/ surrogate**		**Mass**	**LOD**	**LOQ**
	DGT/MPT	**POCIS**	**(m/z)**	**(ng mL^{-1})**	**(ng mL^{-1})**
PFBA	M4PFBA	M5PFPeA	168.99		
PFPeA	M5PFPeA	M2PFOA	196.986 218.986	0.01	0.05
PFHxA	M5PFHxA	M2PFOA	268.98 312.97	0.02	0.06
PFHpA	M4PFHpA	M2PFOA	318.97 362.97	0.01	0.04

Analyte	Internal standard/ surrogate		Mass	LOD	LOQ
	DGT/MPT	POCIS	(m/z)	(ng mL^{-1})	(ng mL^{-1})
PFOA	M8PFOA	M2PFOA	412.96 368.97	0.01	0.04
PFNA	M9PFNA	M2PFOA	418.975 462.965	0.02	0.07
PFDA	M6PFDA	M2PFOA	512.965 468.97	0.03	0.12
PFUnDA	M7PFUnDA	M2PFOA	562.97 518.97	0.02	0.08
PFDoDA	M2PFDoDA	M2PFOA	612.95 568.965	0.02	0.07
PFTrDA	M2PFDoDA	M2PFOA	662.95 618.95	0.03	0.09
PFTeDA	M2PFTeDA	M2PFOA	712.955 668.955	0.08	0.28
PFHxDA	M2PFTeDA	M2PFOA	812.945 768.945	0.01	0.02
PFPrS	M3PFBS	M4PFOS	248.946	0.02	0.06
PFBS	M3PFBS	M4PFOS	298.945	0	0.02
PFPeS	M3PFHxS	M4PFOS	348.94	0.01	0.3
PFHxS	M3PFHxS	M4PFOS	398.94	0.01	0.04
PFHpS	M8PFOS	M4PFOS	448.94	0.01	0.02
PFOS	M8PFOS	M4PFOS	498.93	0.02	0.05
PFNS	M8PFOS	M4PFOS	548.93	0.01	0.04
PFDS	M8PFOS	M4PFOS	598.93	0.02	0.06
PFUnDS	M8PFOS	M4PFOS	648.925	0.02	0.07
PFDoDS	M8PFOS	M4PFOS	698.925	0.03	0.1
PFTrDS	M8PFOS	M4PFOS	748.91	0.01	0.05
PFOSA	M8PFOSA	M4PFOS	497.95	0.01	0.03
meFOSA	d5-etFOSA	M4PFOS	511.965	0.01	0.03
etFOSA	d5-etFOSA	M4PFOS	525.975	0.02	0.07
meFOSE	d9-etFOSE	M4PFOS	602.004 616.01	0.15	0.49
etFOSE	d9-etFOSE	M4PFOS	616.01 630.02	0.05	0.17
PFOSAA	d5-etFOSAA	M4PFOS	555.951	0.07	0.24
me-FOSAA	d5-etFOSAA	M4PFOS	569.978	0.06	0.2
et-FOSAA	d5-etFOSAA	M4PFOS	583.978	0.03	0.09
4:2 FTS	M4:2 FTS	M4PFOS	326.975	0.06	0.21
6:2 FTS	M6:2 FTS	M4PFOS	426.968	0.06	0.19
8:2 FTS	M8:2 FTS	M4PFOS	526.96	0.02	0.08
10:2 FTS	M8:2 FTS	M4PFOS	626.945	0.09	0.13

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