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Methodological recommendations for the monitoring and assessment of PFAS in the aquatic environment

EMPEREST – ELIMINATING MICRO-POLLUTANTS FROM EFFLUENTS FOR REUSE STRATEGIES

Markus Raudkivi et al, 2025

Imprint

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Project note

The EMPEREST project supports local authorities, service providers and policy-making community in finding ways to reduce PFAS (Per- and polyfluoroalkyl substances) and other organic micropollutants from the water cycle. The project has four activity strands to fulfil its aims. First, in close cooperation with HELCOM EMPEREST prepares methodological recommendations to monitor PFAS group in the aquatic environment. Second, local authorities address the subject on the city level by developing a PFAS risk assessment framework to identify and assess PFAS-related risks and propose relevant risk mitigation strategies. Third, EMPEREST supports water utilities in making informed decisions about cost-effective treatment strategies and investments for removing micropollutants from wastewater. Finally, capacity building takes place for both local authorities and public service providers to inform them about the recent developments in the field and train them with tailored materials and tools.

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Methodological recommendations for the monitoring and assessment of PFAS in the aquatic environment

List of Abbreviations

Abbreviation	Definition
AA-EQS	annual average environmental quality standard
ABS C	absolute concentration
AFFFs	aqueous film forming foams
BSR	Baltic Sea region
CAS-number	Chemical Abstracts Service number
C-F	carbon-fluorine (bond)
DE	Germany
DK	Denmark
ECHA	The European Chemicals Agency
EE	Estonia
EFSA	The European Food Safety Authority
EQS(D)	Environmental Quality Standard(s Directive)
EU	European Union
FI	Finland
HELCOM	The Baltic Marine Environment Protection Commission
HOLAS 3	The third holistic assessment of the Baltic Sea
JRC	Joint Research Centre
L>M	comparison between liver and muscle tissue
LOD	limit of detection
LOQ	limit of quantification
LT	Lithuania
LV	Latvia
MSFD D8/D9	Descriptor 8/9 of the Marine Strategy Framework Directive
OC	organic carbon
OECD	Organisation for Economic Co-operation and Development
OF	organic fluorine
PFAS*	per- and polyfluoroalkyl substances
PFAS 24	list of 24 PFAS proposed by the new EQSD update
PL	Poland
RPF	relative potency factor
SCHEER	Scientific Committee on Health, Environmental and Emerging Risks
SE	Sweden
TH	threshold
TOF/EOF	total organic fluorine/extractable organic fluorine
TOP(A)	total oxidizable precursor (array)
TWI	tolerable weekly intake
WFD	Water Framework Directive
WG Chemicals	Chemicals Working Group
WGS 84	World Geodetic System v84, a standard coordinate system
WWTP	wastewater treatment plant
µg/kg dw	micrograms per kilogram of dry weight (default unit for sediments)
µg/kg ww	micrograms per kilogram of wet weight (default unit for biota

* Individual names and acronyms of the PFAS compounds can be found in Table 1

Foreword

The Baltic Sea is a delicate aquatic ecosystem, which faces unique challenges due to its low water exchange rate with the Atlantic, shallow depths, and distinctive low-salinity environment. Shared by multiple countries with diverse backgrounds and policies, we collectively strive to maintain the sea in a condition that benefits us all.

One critical threat to local ecosystems is the presence of hazardous substances. Despite our awareness of this issue for nearly a century, and active efforts to protect the sea over the past 50 years, we still grapple with insufficient solutions. Our society constantly introduces new chemical agents and reagents, serving various purposes—from detergents, self-care products, and cosmetics to pesticides and herbicides. Unfortunately, the current environmental safety system for new chemicals operates in a counterproductive manner, lacking the necessary assurance of environmental safety before mass production of a new substance begins. Consequently, we find ourselves reacting to increased concentrations of hazardous substances in our basins rather than proactively preventing their impact.

Per- and polyfluoroalkyl substances, commonly known as PFAS, have come to the forefront of environmental concern in the last few decades. Despite their widespread use in industry and the considerable variations among different substances, the environmental assessment of this group is still lagging behind. Frequently, monitoring efforts focus solely on PFOS, while the industry has been moving away from using the substance since its inclusion in the Stockholm convention in 2009 [1]. As new information about the ecotoxicity of other PFAS has been published, it has become increasingly apparent that more PFAS, rather than only PFOS should be assessed to get a better picture of the PFAS environmental pollution.

Currently the assessment of PFAS pollution in the Baltic Sea is based on PFOS concentrations in biota and water. However, many HELCOM contracting parties do already monitor a number of other PFAS in the environment, including from the sediment matrix. So far, concentrations of several PFAS compounds have often been summed up into different groupings, which often causes the loss of valuable information on specific substances including about their different levels of toxicity. Therefore, a good summing or categorisation approach for the different PFAS is needed in order to carry out better assessments of their impact on the Baltic Sea ecosystem.

As a part of the new EU Zero Pollution Action Plan [2], a proposal to update the current surface waters pollutants list and limit values was published in October 2022, including a new approach to summarise the concentrations of 24 different PFAS based on their liver toxicity. Although this group of 24 PFAS does not necessarily include all substances potentially found in the environment in alarming concentrations, it does provide a novel approach for a group assessment that could be in the future amended with additional PFAS substances besides the initial 24 and information about their respective toxicity compared to PFOA.

This output 2.1 by the Interreg BSR funded EMPEREST project, is proposing methodological recommendations for the monitoring and assessment of PFAS in the aquatic environment, with the main focus on the marine environment of the Baltic Sea. The approach is based on the latest developments in the assessment of PFAS, especially the PFAS sum of 24 EQS value proposed as part of the EU Zero Pollution Action Plan, combined with additional RPF values for other substances based on a precautionary approach. The output also includes an example of the assessment based on a collection of PFAS monitoring data from the Baltic Sea region from 2000-2022, collected through a data call carried out by the EMPEREST project in 2023. The general statistics and some extra data not fitting into the assessment are also added as annexes to the main document to provide extra information should it be needed.

PART A - Methodological recommendations

1. Introduction

Per- and Polyfluoroalkyl Substances (PFAS), a class of artificially manufactured organic chemicals, contain at least one fully fluorinated carbon atom (OECD 2021 definition). Although the total number of different PFAS has been under debate for a while, the latest estimates show that the total number of chemical compounds fulfilling the criterion might be more than 7 million [3]. Other estimations show that 5000-15 000 of these substances are commercially relevant and currently on the market. Their structures range from ultrashort-chain variants (with carbon chain lengths of 2–3 atoms) to linear or branched long-chain PFAS and polymers.

Generally, most of these compounds exhibit a unique blend of physical and chemical properties, including hydrophobic and lipophobic characteristics, resulting in robust water and oil repellence as well as friction resistance [4]. Consequently, PFAS find widespread use due to their useful qualities, including wide use in both industrial and commercial applications from machine lubricants to sandwich papers, providing ample opportunities for emissions into the environment from a multitude of different processes.

One of the main issues with PFAS in the environment comes from their very high stability – resulting in the group of substances often being called the “forever chemicals”. This remarkable stability is due to the presence of carbon-fluorine (C-F) bonds, which are under typical environmental conditions resistant to degradation, whether it be chemical, physical, or biological. While perfluorinated compounds are fully fluorinated and especially difficult to degrade, polyfluorinated compounds contain carbon atoms that are not fully fluorinated, resulting in less stable bonds with other atoms. These weaker bonds can be broken down, leaving behind the robust perfluorinated segments as stable end products. Consequently, polyfluorinated compounds are often labelled as ‘precursors’ and the resulting perfluorinated compounds labelled as “arrowheads”. This degradation is also the basis for newer analytical methods in development, e.g. the Total Oxidizable Precursor Assay, often referred to as TOP Assay or TOPA.

Nowadays, the PFAS monitoring mainly relies on analysing single PFAS substances from a sample. Although the total number of PFAS in use is thousands if not tens of thousands of different substances, the current laboratory practises allow quantifying only a fraction of them. The state-of-the-art academic laboratories, such as Harvard in the United States and Swedish University of Agricultural Sciences in Sweden, can nowadays measure a bit more than a hundred different PFAS compounds, while commercial laboratories are currently commonly capable of analysing anywhere between 20 to 50 compounds. The key issues laboratories are facing are related to the availability of reference materials for different PFAS and reaching the very low limits of detection and quantification the newer standards are expecting.

This all plays a vital role in the monitoring and assessment of PFAS pollution in the Baltic Sea area, as the possible methods and parameters that can be used here need to be common and robust enough to be used by all the countries around the sea, while still analytically good enough to provide clear information. In the next sections the document proposes some important parameters for the monitoring and assessment, which have been selected based on the assessment of monitoring data in the Baltic Sea region collected within the EMPEREST PFAS data call or based on communications with experts. A “sample” assessment of the collected PFAS monitoring data itself can be found in part B of the document, to provide some supporting evidence. EMPEREST partners also worked on testing the approach and explored some of the current monitoring gaps, the results of which are presented in part C of the document.

2. Key parameters

2.1. Indicative PFAS for monitoring

As the PFAS group of substances is very large and impossible to monitor in its entirety, it is vital to select some of the substances as indicators. These substances would need to be representative of the whole group, to enable extrapolating the bigger picture of PFAS pollution from the concentrations of a limited number of substances. So far, most of the PFAS assessment in the aquatic environment has been based solely on monitoring PFOS, which might not be indicative enough for the future considering the international bans together with widescale regretful substitutions of the compound with other PFAS compounds.

Selecting the specific PFAS substances that should be monitored is not as straightforward as it might seem, as there is a big discrepancy between the amount of information available for PFOS and PFOA, compared to most of the other substances. As two of the most common PFAS in aqueous film forming foams (AFFFs), their environmental and toxicological effects have been studied the most, which in turn causes these two substances to be the most common ones analysed in the environment. At the same time, both of these substances have been targeted by various international agreements, such as the Stockholm convention (PFOS added in 2009 and PFOA in 2019), which means they have been substituted with other PFAS in most industrial uses. This however means that the current environmental monitoring and assessment should not only be based on these substances, as many others PFAS compounds are potentially now on the rise in the environment and could be easily missed with too narrow of a focus.

Within the collected PFAS monitoring data available in the region, a total of 55 different PFAS compounds have been reported between 2000 and 2022, which can be seen in Table 1. As some of the compounds only had a few measurements reported (often coming from scientific studies), a total of 40 PFAS compounds can be said to be common in the Baltic Sea environmental monitoring. It is complicated though to assess each of these values separately, as there are very few threshold or limit values available for assessment use. Most evaluations for PFAS done by HELCOM have so far only focused on PFOS, using the surface water Environmental Quality Standard (EQS) value proposed by the EU in relation to the Water Framework Directive (WFD).

In October 2022 however, as a component of the Zero Pollution action plan, the European Commission proposed significant modifications to the current Water Framework Directive's priority substances list (Annex X) and respective EQS values. The PFOS specific entry was suggested to be replaced with a collective entry for 24 PFAS with a new EQS based on liver toxicity results of different PFAS. Each of these 24 PFAS was assigned a Relative Potency Factor (RPF) in relation to PFOA, facilitating the aggregation of different substance concentrations. The newly proposed EQS value for the combined 24 PFAS stands at 0.0044 µg/l for water and 0.077 µg/kg wet weight for biota.

Considering the new EU list of 24 PFAS, 19 substances have been commonly reported in the Baltic Sea region (BSR), with the other 5 substances included in the sum value having no (or almost no) reported measurements from the Baltic Sea environment. The main categories of the 24 PFAS could be summarised as following:

- C4-C14, C16 and C18 perfluoroalkyl carboxylic acids (PFCAs) – all commonly monitored in BSR.
- C4-C8, C10 perfluoroalkyl sulfonic acids (PFSAs) – all commonly monitored in BSR.
- Fluorotelomer alcohols (6:2 FTOH and 8:2 FTOH) – no monitoring reported.
- New PFAS alternatives (HFPO-DA/Gen X, ADONA, C6O4) – no marine monitoring reported (ADONA reported from a few wastewater treatment plant (WWTP) effluents)

As these 24 PFAS are probably going to be prioritized by the EU in surface waters, it is clear these compounds should also be part of the Baltic Sea monitoring system. At the same time, based on the current monitoring results it is clear that there are other PFAS commonly detected in the environment (Table 21, Table 25), which are not part of the sum of 24. These could be categorized as followed (bold names indicate more than 50% average detection frequency in biota):

- Other PFCAs (C7* - **HPFHpA**, C15 - **PFPeDA**) and PFSAs (C9 - PFNS, C11 - PFUnDS, C12 - PFDoDS, C13 - PFTrDS) left out of the sum of 24.
- Perfluoro sulfonamides and derivates such as FHxSA, **FBSA** and the C8 versions (**FOSA, FOSAA, N-MeFOSA, N-MeFOSAA, N-MeFOSE, N-EtFOSA, N-EtFOSAA, N-EtFOSE).**
- Other fluorotelomers, such as **4:2, 6:2**, 8:2 and **10:2 FTS; H2PFDA** and **H4PFUnDA.**
- Other PFAS, such as **PF-3,7-DMOA** and **PFECHS.**

These extra substances deserve additional focus in monitoring, especially in biota from the Baltic Sea environment, although unfortunately there is not enough information about the toxicity of these substances (or official RPF factors) to add them to the same assessment system as the new PFAS sum of 24. Still, from discussions with EU Joint Research Centre (JRC), it seems there is work ongoing to find respective RPF values to other PFAS as well. Therefore, it would be good to monitor the potential additional PFAS in the marine environment, if possible, as it might be possible to add the other PFAS to the assessment retrospectively as new RPF values are produced. For the sample assessment produced in this document, precautionary approach was used to assign all PFAS a RPF factor (more details in Chapter 0) to allow every measured PFAS compound to be assessed in the same system.

Based on the sample assessment, around 90-95% of the total PFAS pollution currently monitored could be attributed to only a few PFAS compounds, while they differ somewhat between the sample matrices. The tables provided in Part B of this document, namely Table 4 for water matrix, Table 8 for biota matrix and Table 13 for the sediment matrix could be considered as basis to select the most important PFAS for each matrix. Another set of tables is also provided in each of these sections (Table 5, Table 9 and Table 14), showing lists of PFAS with the highest detection frequency in each of the matrices, regardless of how many times the compounds have been measured from samples. These PFAS on those tables should also be under higher monitoring importance, because their influence currently in the environment might be severely undervalued due to lower monitoring frequency.

As the individual PFAS compounds can make the monitoring and assessment of PFAS quite complicated, the TOP Assay analysis method could be a viable alternative in the future. This method uses strong oxidation to degrade all more complicated PFAS substances into a limited number of “dead end perfluoroalkyl acids”, commonly called “arrowheads”. Analysing these arrowhead substances before and after oxidation allows to estimate the total amount of PFAS in the sample, catching even the compounds that would not be analysable otherwise.

This method might be a good alternative, as on a larger scale the long-term toxicity of perfluorinated arrowhead substances appears to be more significant and impactful than their polyfluorinated precursors. However, the current level of information available may not be sufficient to fully support a shift away from substance-specific analysis, as through the oxidation there is a risk of losing crucial information associated with the specific structures of the precursor molecules. As the TOP Assay as a method and the assessment of the complicated results acquired is currently under fast development, it is recommended to keep an eye out for the advancements of the method for the near future.

2.2. Spatial and temporal parameters

Although the PFAS pollution is often connected to pollution hotspots, especially due to large scale uses of AFFFs, the current evaluation of the Baltic Sea shows the PFAS pollution to be fully distributed among the whole area (Figure 7 and Figure 15). At the same time, as PFAS industry has been going through multiple stages of substitution, the specific compounds might have more spatial differences, with newer PFAS from households entering the environment mainly via WWTPs, which often end up in the Baltic Sea via riverine inputs. Therefore, although the spatial distribution of the more common PFAS might not provide a lot of new information, looking at the spatial distribution of newer PFAS alternatives or substitutions (HFPO-DA, ADONA, C6O4) might reveal new hidden pollution sources and emitters. This means, that when choosing locations for PFAS monitoring, the coastal areas, especially next to major rivermouths should be especially targeted for analysis of newer PFAS compounds.

The assessment of the PFAS data call results also hint at differences between PFAS sedimenting in freshwater versus marine environments, with analysis from lakes and rivers showing a higher ranking for different FOSE/FOSA/FOSAA compounds (N-Et-X and N-Me-X variations) on average than in marine samples. Although the current amount of data is not enough to clearly show this difference, similar tendencies between different sampling environments can be expected to be revealed in the long run.

When talking about temporal parameters, the PFAS pollution in general does not follow significant seasonal trends, while use of specific PFAS-containing products (such as ski waxes) might have seasonal tendencies. At the same time, longer temporal parameters are very important with a substance group like PFAS, as multiple substances have been banned or phased out, replaced by new alternatives which have entered the market at different times. With long time trends on a larger number of PFAS substances, it should be possible to see these introductions of new PFAS compounds into the environment and even possible look at their spread. As the pathways of new PFAS entering the environment are often very similar, the best way to detect the changes in the longer time trends is to have a more **thorough monitoring for coastal areas, rivermouths, WWTPs and recipient water bodies**, which might increase the efficiency of future data analysis and advanced assessments.

According to some of the piloting activities concluded in the EMPEREST project, seasonal differences can potentially have a large effect on water sample concentrations, especially in the streams with lower flow rates and coastal waters and bays receiving significant riverine inputs. These seasonal differences are not due to differences in use-patterns of PFAS, but mainly the result of weather patterns – there is evidence to believe that PFAS concentrations might be up to 5 times higher in streams during dry weather and lower by the same amount in nearby coastal waters. Therefore, for the analysis of streams, rivermouths and coastal areas with high riverine input, sample taking time could be important and have a significant effect on the water sample concentrations.

2.3. Prioritisation of matrices

The main three matrices for samples used for marine environment assessment – water, biota and sediment – all provide us with different information about the spread of pollution. Generally speaking, the water results show the ongoing situation, the biota shows the near past, and the sediment results can show the situation at different points of time from present to far past, depending on the depth the sample is taken. Comparing the three can also provide information about long term trends in compound use and enable to predict or model the trends towards future.

At the same time, the primary assessment proposed by the EU with the new sum of 24 PFAS approach is missing an EQS value for sediments, meaning the approach as it was proposed could only be used for assessing water and biota. Even outside this new approach, sediment threshold values for PFAS are very rare, with no applicable options findable in the scientific literature. Although PFAS in sediment should not be of a lower priority in environmental monitoring, it currently has very little support in legislation. In order to provide an assessment for sediment in the current document, a SCHEER endorsed PFOS quality standard for sediments is combined with the PFAS RPF approached used for other matrices. It is vital to point out that this approach should not be considered official and a proper threshold value and assessment criteria development for all PFAS in sediments should be of the highest priority in the future. Until that, this document makes do with the information currently available to provide any kind of assessment for the sediment matrix, while also collecting and collating the available data, as a future threshold could easily also be applied to historical data and provide a more official assessment on a later date.

As both water and biota have EQS standards proposed for PFAS (a previous value for PFOS only and a new proposal for the sum of 24 PFAS), these matrices can be properly assessed. At the same time, as many of the PFAS are highly bioaccumulative, the biota matrix should hold a higher priority for coastal and open sea areas to be able to estimate the total loads coming from the land-based pollution sources. Water matrix should be held to a higher priority in the monitoring of rivers, pollutions hotspots (airports, landfills, fire-fighting training areas) and WWTPs, allowing for a better pollution control and detecting pollution point-sources. The latest EU EQS dossier also has an update that *“The critical EQS is the biota EQS (relating to fish consumption) and must therefore be complied with. The AA-EQS are not equivalently protective.”*, which means **the biota EQS should be considered as the highest priority assessment.**

For biota, the main species monitored for PFAS so far are herring (*Clupea harengus*) and perch (*Perca fluviatilis*), while dab (*Limanda limanda*), cod (*Gadus morhua*), flounder (*Platichthys flesus*), and eelpout (*Zoarces viviparus*) are recommended for the monitoring list for the Baltic Sea. As experts have highlighted problems with the availability of these fish in different areas of the Baltic, bream (*Abramis brama*) and roach (*Rutilus rutilus*) should be also considered for monitoring, especially in the inner coastal areas. In the current situation, when no conversion factors between different species for PFAS have been proposed, all data should be treated equally until scientific clarity on the matter is achieved.

For tissues, liver has been generally considered the most suitable for PFAS analysis, as the substances are highly bioaccumulative and easily analysed from the tissue. Muscle tissue however is now recommended due to harmonisation between the monitoring criteria set in Marine Strategy Framework Directive for descriptors 8 and 9 (MSFD D8 and D9). Analysis for liver tissue can in some cases be converted to muscle, as there is scientific evidence of the conversion factors for some species and substances (17.9 as the conversion for PFOS in herring and perch). Based on data collected and analysed, which can be found in subchapter 5.3.2, and expert opinions, the following summary about tissue selection can be made:

- The new EU EQS proposal is based on fish muscle due to the direct link established with human health, therefore all liver concentrations need to be converted to their muscle equivalent for threshold comparison.
- The new EU EQS proposal increases the number of PFAS that need conversion factors, which is further complicated as all different fish species used for monitoring in the Baltic Sea area need their own set of conversion factors for each compound.
- The chance of detecting PFAS in muscle tissue is still lower than for liver, but the difference between muscle tissue has been decreasing with advancements in analytical sensitivity.
- Though the PFAS detection from muscle tissue might be less frequent, compared to the complications of tissue conversion, the recommendation is to focus on muscle as the primary

tissue moving forward, while work on creating conversion factors should continue to enable the use of older liver data in monitoring time series for trend detection.

While the main biota assessment should use data from abovementioned fish, the assessment in this document also makes use of other biota data collected around the region, using a trophic factor of 10 for bird egg samples and a trophic factor of 100 for mammal samples when comparing the results to the fish EQS numbers. Results of the assessment of fish are provided separately from the assessment of all biota, to provide a comparison between the two approaches.

2.4. Sampling, pre-treatment and analysis

For the sampling, sample pre-treatment and analysis, HELCOM has published two previous documents on PFAS, that should be taken as a basis for both water and biota:

- **Guideline on the determination of Perfluoroalkylated substances (PFAS) is seawater** (2018)
- **HELCOM guidelines on PFAS/PFOS in biota** (2021)

Additionally, the general sampling of biota should be in accordance with the Manual for Marine Monitoring in the COMBINE Programme of HELCOM "**Monitoring guideline on biological material sampling and sample handling for the analysis of persistent organic pollutants (PAHs, PCBs and OCPs) and metallic trace elements**" (2019).

As the list of different PFAS relevant for the environment is constantly increasing, with more structurally complicated new compounds added, some specific pre-treatment and analysis methodologies cannot be reliably collected into a document. In general, communications with local monitoring laboratories for specific details are always encouraged, and in some cases scientific literature might need to be consulted, as the field of PFAS analysis is ever evolving. It is important to note that although historically, liquid chromatography combined with tandem mass spectrometry has been enough for the analysis of all PFAS, some newer compounds also need gas chromatography for the separation of compounds before mass spectrometry. In addition, some of the PFAS (such as the C6O4 included in the EU sum of 24), do not yet have a widespread laboratory methodology for analysis.

In addition, for the analysis guidelines for sediments, the current guidelines listed above recommend referring to the following article: Ahrens, L et al (2010) "Determination of perfluoroalkyl compounds in water, sediment, and biota", published in ICES Techniques in Marine Environmental Sciences issue 48 [5].

2.5. Data reporting and quality assurance

Although the general instructions of data reporting, quality control and quality assurance are indicated in the documents and guidelines referred to in the previous sub-section of this output, there are some specific points of note due to the new EU approach:

1) Each PFAS compound should be added into reporting databases separately. Only reporting sum values (especially national sum values such as sum of 4, 9 or 21 PFAS) loses valuable data and makes it impossible to recalibrate should something change in the assessment.
2) The newly proposed EU biota EQS is very low (0.077 µg/kg ww), especially considering some substances have RPF values of 10, bringing the effective threshold value for PFNA down to 0.0077

µg/kg ww. This means, that many laboratory LODs for specific substances might now be higher than the specific exceedance thresholds, resulting in inconclusive data (Table 20, Table 23).

   a. The main substances of concern for this are PFNA, PFDA, PFUnDA, PFDoDA, PFOS, PFDS (relative potency factors ≥ 2) and PFHpA, PFOA, PFPeS, PFHxS (RPF ≤ 1).
   b. The minimum LODs for each substances derived from the new EU approach can be found in Table 19 for water and Table 22 for biota.

3) Isomeric data for PFAS compounds is becoming more common, while for assessment it does not yet serve a strong purpose, especially as it is not always apparent which isomers have historically been measured for which compounds. Isomeric data should be presented clearly in databases, while supporting information should be collected from laboratories reporting isomers, to make it clear on how to use them for long-term time trends and assessment.
   a. Instead of labelling branched PFOS results as an analyte called br_PFOS, it would be recommended to label the analyte just PFOS in the main column and include the isomer information in a separate column as additional information. This allows for an easier use of the main PFOS data and significantly decreases the number of different substance codes (3-4 codes currently used with each PFAS that has isomers reported), while still allowing for isomeric data to be easily used in assessment if needed.
4) Due to the new PFAS sum-based approach, the data reported to databases should especially carefully be checked to include identification IDs for individual samples to enable summing PFAS up based on these ID numbers.
5) Currently the standardisation when it comes to PFAS names is lacking, as many of the newer PFAS compounds have acronyms that have not been unified (PFODA commonly used instead of PFOcDA, which would be in line with the other 11+ chain length PFAS; PFOSA commonly used instead of FOSA, while all related compounds are named N-EtFOSA not EtPFOSA). The acronyms most commonly used are often related to the most popular commercial labs, while a EU or regional standard naming conventions should be aimed for.

3. Assessment of results

The main basis for the assessment of the PFAS environmental monitoring data is taken from the new EU approach, using relative potency factors based on liver toxicity, to sum a larger number of different PFAS into a PFOA-equivalent value sum. The current EU approach is based on the values of 24 different PFAS, while plans to establish values based on the same criteria have been communicated by the JRC. Until official RPF values are provided for other PFAS, a precautionary approach was used to create some indicative RPF values for each PFAS based on two criteria:

a) For precautionary approach, all other PFAS substances could initially be evaluated to have a minimal toxicity equal to PFOA (RPF 1).
b) For many longer-chain PFAS that biodegrade into specific known arrowheads, their potency could be equal to the highest transformation product RPF value, if that is higher than 1 (otherwise minimal potency would be 1 according to the previous point).

These precautionary RPF values are shown in Table 1 inside brackets, established through scientific literature study into different PFAS substance biodegradation pathways and analytics.

While there are currently no widely accepted EQS values for sediment matrix, there is Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) endorsed threshold for 13.5 µg/kg dw for PFOS for a sediment with 5% organic carbon (OC). This is used as a basis for the sediment assessment, combined with the PFOA equivalent RPF system. Although the toxicity mechanisms are completely different for the sediment matrix compared to water and biota, for the example assessment this combination is at least able to provide comparisons with other matrices.

The example assessment, based on the data collected with the EMPEREST PFAS data call in 2023 is presented in Chapter 5. Please note that the assessment and details are not officially endorsed and are meant to be used as an example foremost. Additional information on the details chosen for the example assessment are presented in Chapter 4.2.

Table 1 - PFAS compounds reported within the EMPEREST environmental monitoring data call (including a few substances of concern with no reported measurements); The C-F chain length for perfluorinated compounds also includes the functional group carbon. Some values are marked with asterix (*) due to more complicated structural models (indicated values taken from OECD PFAS table). RPF values in brackets are unofficial values generated via a precautionary approach.

#	Substance name	Acronym	Alternative acronyms	CAS-number	C-F chain length	Grouping	Organic F % in mass	RPF	# of reported measurements
1	Perfluorobutanoic acid	PFBA		375-22-4	4	Carboxylic acid	62.13	0.05	4,963
2	Perfluoropentanoic acid	PFPeA		2706-90-3	5	Carboxylic acid	64.76	0.03	4,167
3	Perfluorohexanoic acid	PFHxA		307-24-4	6	Carboxylic acid	66.54	0.01	6,511
4	Perfluoroheptanoic acid	PFHpA		375-85-9	7	Carboxylic acid	67.84	0.505	5,598
5	Perfluorooctanoic acid	PFOA		335-67-1	8	Carboxylic acid	68.82	1	8,874
6	Perfluorononanoic acid	PFNA		375-95-1	9	Carboxylic acid	69.59	10	7,015
7	Perfluorodecanoic acid	PFDA		335-76-2	10	Carboxylic acid	70.22	7	7,021
8	Perfluoroundecanoic acid	PFUnDA	PFUnA	2058-94-8	11	Carboxylic acid	70.73	4	6,198
9	Perfluorododecanoic acid	PFDoDA	PFDoA	335-77-3	12	Carboxylic acid	71.15	3	5,567
10	Perfluorotridecanoic acid	PFTrDA		791563-89-8	13	Carboxylic acid	71.52	1.65	4,036
11	Perfluorotetradecanoic acid	PFTeDA		376-06-7	14	Carboxylic acid	71.83	0.3	3,609
12	Perfluorohexadecanoic acid	PFHxDA		67905-19-5	16	Carboxylic acid	72.34	0.02	2,302
13	Perflorooctadecanoic acid	PFOcDA	PFODA	16517-11-6	18	Carboxylic acid	72.74	0.02	2,281
14	2-(Perfluorohexyl)ethyl alcohol	6:2 FTOH		647-42-7	6	Fluorotelomer alcohols	67.83	0.02	-
15	2-(Perfluorooctyl)ethanol	8:2 FTOH		678-39-7	8	Fluorotelomer alcohols	69.59	0.04	-
16	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	HFPO-DA	Gen X	13252-13-6	6*	Other	63.32	0.06	8
17	2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy)propanoic acid	ADONA	DONA	919005-14-4	7*	Other	60.30	0.03	16
18	2,2-difluoro-2-((2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl)oxy)-acetic acid	C6O4	F-DIOX	1190931-41-9	6*	Other	50.28	0.06	-
19	Perfluorobutane sulfonic acid	PFBS		375-73-5	4	Sulfonic acid	56.98	0.001	5,334
20	Perfluoropentane sulfonic acid	PFPeS		2706-91-4	5	Sulfonic acid	59.69	0.3005	2,104

#	Substance name	Acronym	Alternative acronyms	CAS-number	C-F chain length	Grouping	Organic F % in mass	RPF	# of reported measurements
21	Perfluorohexane sulfonic acid	PFHxS		355-46-4	6	Sulfonic acid	61.73	0.6	5,985
22	Perfluoroheptane sulfonic acid	PFHpS		375-92-8	7	Sulfonic acid	63.31	1.3	3,252
23	Perfluorooctane sulfonic acid	PFOS		1763-23-1	8	Sulfonic acid	64.58	2	11,828
24	Perfluorodecanesulfonic acid	PFDS		335-77-3	10	Sulfonic acid	66.48	2	5,215
25	Trifluoroacetic acid	TFA		76-05-1	2	Carboxylic acid, ultra short-chain	49.99	0.002	104
26	Perfluoropropanoic acid	PFPrA		422-64-0	3	Carboxylic acid, ultra short-chain	57.91	[1]	5
27	7H-perfluoroheptanoic acid	HPFHpA		375-85-9	7	Carboxylic acid	65.88	[1]	1,466
28	Perfluororpentadecanoic acid	PFPeDA		141074-63-7	15	Carboxylic acid	72.10	[1]	901
29	Perfluorononane sulfonic acid	PFNS		68259-12-1	9	Sulfonic acid	65.61	[2]	1,975
30	Perfluoroundecanesulfonic acid	PFUnDS	PFUnS	749786-16-1	11	Sulfonic acid	67.21	[2]	370
31	Perfluorododecane sulfonic acid	PFDoDS		120226-60-0	12	Sulfonic acid	67.84	[2]	1,607
32	Perfluorotridecanesulfonic acid	PFTrDS	PFTrS	791563-89-8	13	Sulfonic acid	68.38	[2]	269
33	2H,2H,3H,3H-Perfluorohexanoic acid	3:3 FTA	3:3 FTCA	356-02-5	3	Fluorotelomer carbonate	54.93	[1]	8
34	2H,2H,3H,3H-Perfluorooctanoic acid	5:3 FTA	5:3 FTCA	914637-49-3	5	Fluorotelomer carbonate	61.09	[1]	8
35	2H,2H,3H,3H-Perfluorodecanoic acid	7:3 FTA	7:3 FTCA	812-70-4	7	Fluorotelomer carbonate	64.46	[1]	8
36	2H,2H-Perfluorodecanoic acid	**H2PFDA**	8:2 FTA, 8:2 FTCA	27854-31-5	8	Fluorotelomer carbonate	67.55	[1]	25
37	2H,2H,3H,3H-perfluoroundecanoic acid	**H4PFUnDA**	8:3 FTA, 8:3 FTCA	34598-33-9	8	Fluorotelomer carbonate	65.63	[2]	108
38	4:2 Fluorotelomer sulfonic acid	4:2 FTS	4:2 FTSA, NFHxSA	757124-72-4	4	Fluorotelomer sulfonates	52.11	[1]	1,681
39	6:2 Fluorotelomer sulfonic acid	6:2 FTS	6:2 FTSA, THPFOS	27619-97-2	6	Fluorotelomer sulfonates	57.68	[1]	3,237
40	8:2 Fluorotelomer sulfonic acid	8:2 FTS	8:2 FTSA	39108-34-4	8	Fluorotelomer sulfonates	61.15	[1]	1,861

#	Substance name	Acronym	Alternative acronyms	CAS-number	C-F chain length	Grouping	Organic F % in mass	RPF	# of reported measurements
41	10:2 Fluorotelomer sulfonic acid	10:2 FTS		120226-60-0	10	Fluorotelomer sulfonates	63.51	[10]	242
42	Perfluorobutylsulfonamide	FBSA	PFBSA	30334-69-1	4	Sulfonamides and derivates	59.56	[1]	21
43	Perfluorohexanesulfonamide	FHxSA	PFHxSA	41997-13-1	6	Sulfonamides and derivates	61.88	[1]	15
44	Perfluorooctane sulfonamide	FOSA	PFOSA, PFOSD	754-91-6	8	Sulfonamides and derivates	64.71	[2]	5,058
45	N-Methyl perfluorooctane sulfonamide	N-MeFOSA	MeFOSA	31506-32-8	8	Sulfonamides and derivates	62.94	[2]	1,455
46	N-Ethyl perfluorooctane sulfonamid	N-EtFOSA	EtFOSA	4151-50-2	8	Sulfonamides and derivates	61.26	[2]	1,418
47	Perfluorooctane sulfonamido-ethanol	FOSE	PFOSE	10116-92-4	8	Sulfonamides and derivates	59.46	[1]	-
48	N-Methyl perfluorooctane sulfon-amidoethanol	N-MeFOSE	MeFOSE	24448-09-7	8	Sulfonamides and derivates	57.96	[2]	1,415
49	N-Ethyl perfluorooctane sulfon-amidoethanol	N-EtFOSE	EtFOSE	1691-99-2	8	Sulfonamides and derivates	56.54	[2]	1,418
50	Perfluorooctane sulfonamidoacetic acid	FOSAA	PFOSAA	2806-24-8	8	Sulfonamides and derivates	57.97	[2]	1,390
51	N-Methyl perfluorooctane sulfon-amidoacetic acid	N-MeFOSAA	MeFOSAA	2355-31-9	8	Sulfonamides and derivates	56.54	[2]	1,424
52	N-Ethyl perfluorooctane sulfon-amidoacetic acid	N-EtFOSAA	EtFOSAA	2991-50-6	8	Sulfonamides and derivates	55.19	[2]	1,569
53	Mono[2-(perfluorohexyl)ethyl] phosphate	6:2 monoPAP		57678-01-0	6	Phosphate monoesters	55.61	[1]	1
54	Mono[2-(perfluorooctyl)ethyl] Phosphate (8:2 PAP)	8:2 monoPAP		57678-03-2	8	Phosphate monoesters	59.36	[1]	1
55	10:2 Fluorotelomer phosphate diester	10:2 diPAP		1895-26-7	2x4	Diester diPAPs	57.95	[1]	8

#	Substance name	Acronym	Alternative acronyms	CAS-number	C-F chain length	Grouping	Organic F % in mass	RPF	# of reported measurements
56	4:2 Fluorotelomer phosphate diester	4:2 diPAP		135098-69-0	2x6	Diester diPAPs	62.51	[1]	16
57	6:2 Fluorotelomer phosphate diester	6:2 diPAP		57677-95-9	2x8	Diester diPAPs	65.23	[1]	47
58	8:2 Fluorotelomer phosphate diester	8:2 diPAP		687-41-1	2x10	Diester diPAPs	67.04	[10]	9
59	6:2/8:2 Fluorotelomer phosphate diester	6:2/8:2 di-PAP		943913-15-3	6+8	Diester diPAPs	64.03	[1]	3
60	8:2/10:2 disubstituted polyfluoroalkyl phosphate	8:2/10:2 diPAP		1158182-60-5	8+10	Diester diPAPs	66.22	[10]	1
61	Perfluoro(2-((6-chloro-hexyl)oxy)ethanesulfonic acid)	6:2 Cl-PFESA	6:2 Cl-PFAES, 9Cl-PF3ONS, 9-Cl-PF	756426-58-1	8	Other	57.08	[2]	28
62	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	8:2 Cl-PFESA	8:2 Cl-PFAES, 11Cl-PF3OUdS, 11-Cl-PF	763051-92-9	10	Other	60.06	[2]	28
63	Perfluoro-3,7-dimethyloctanoic acid	PF-3,7-DMOA	P37DMOA	172155-07-6	9*	Other	70.22	[1]	1,224
64	perfluoro-4-ethylcyclohexane-sulfonate	PFECHS	PFEtCHxS	646-83-3	8 (6-cyclic)	Other	61.67	[1]	23
65	6-Chloroperfluorohexyl phosphonic acid	Cl-PFHxPA		1283087-54-6	6	Other	54.74	[1]	1
66	Perfluoromethoxypropionic acid	PFMOPrA		377-73-1	1+3	Other	57.81	[1]	2

PART B – Assessment of PFAS pollution in the Baltic Sea

4. Methodology of the assessment

4.1. Overview on the data used for the assessment

The PFAS data call for the EMPEREST project was sent out to all contracting parties of HELCOM for summer 2023, with the initial deadline of 30th of September 2023 and final data call closure on the 3rd of November 2023. The first pass of data analysis was completed for the EMPEREST Monitoring Workshop, that took place on the 30th of November 2023. The second pass of data analysis with more in-depth consolidation of the data, removal of duplicate datapoints and thorough check of reported substances was completed by the 31st of January 2024. The data and results were further discussed with national representatives in the first half of 2024, after which the database went through a third and final pass, including a few new sources for Germany that had been mistakenly cut from previous runs. The data work was finalised by September 2024.

The 3rd pass database consists of 137,927 datapoints of individual PFAS results for water, biota, and sediment matrices, including mainly samples taken from marine environments and inland waters, but also some data from groundwater, wastewater treatment plants and other points of interest for PFAS. The division of reported data by country varied greatly, with more than half of all collected data reported by Sweden (Figure 1). The figure only includes reported data added to the final database – additional data and sources were submitted to the data call (scientific articles, reports, etc), which could not be included in the database due the data being sent as non-extractable sources; missing individual data points or supporting parameters; or failing to pass initial quality control criteria.

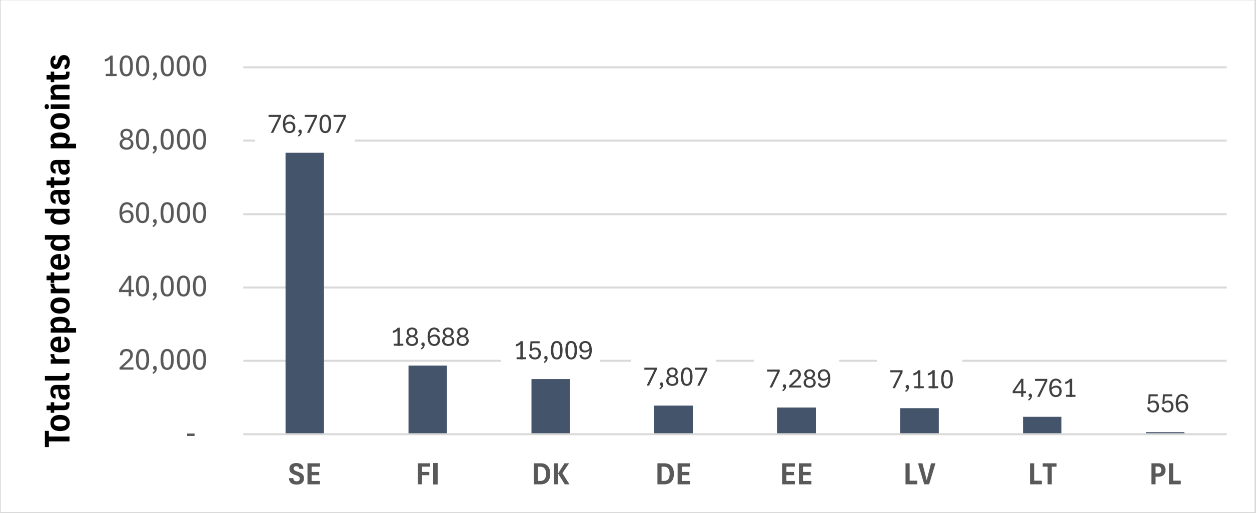


Figure 1 – Total data points reported by country.

When divided up by reported matrices (Figure 2), more than 2/3 of the datapoints represent water samples, with most of the remaining ones representing biota samples. Compared to other matrices, data from sediment samples is significantly underrepresented, which is to be expected, as PFAS are considered a new pollutant group, and PFAS sediment limit values have not been widely proposed as of the end of 2024.

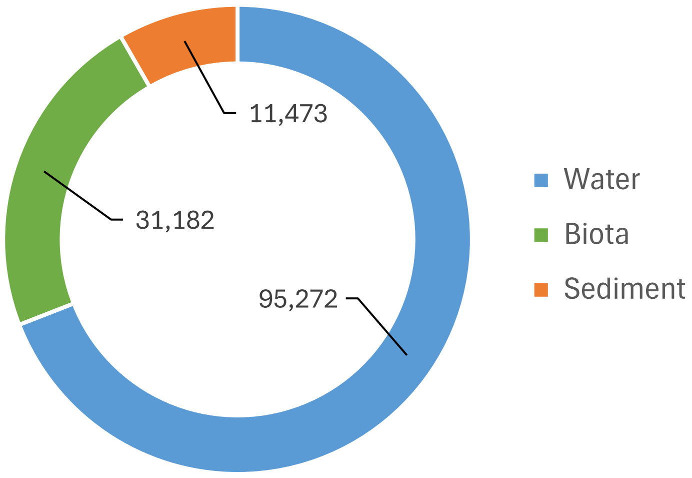


Figure 2 - Division of reported data by matrices.

The current assessment database (Table 1) includes additional data for 66 individual PFAS substances, 62 of which have at least 1 monitoring data point included. The 4 substances without data are 6:2 FTOH, 8:2 FTOH, C6O4 (included as they are part of the new EU PFAS sum of 24) and FOSE (background data included as a core part of the perfluorooctane sulfonamides and a precursor of N-EtFOSE and N-MeFOSE).

Besides the individual datapoints, isomeric data was reported for a total of 27 substances (linear, branched or isomermix). A total of 16 different sum-parameters were reported and are included in the database, while the data is not used in most assessments due to complexities of differentiating individual results from the sum values, especially when results use either RPF or %F. A total of 19 different results from TOP-assay analysis have also been included in the database but are not used in the evaluations and assessment either. The gathered database will be made public and can be used further to explore additional nuances outside of the EMPEREST project scope.

Additional statistics for the data used in the assessment can be found in ANNEX I – PFAS database statistics by matrix at the end of the document

4.2. Additional notes on the methodology of the assessment

As part of the further work with the data collected during the data call, the following major steps were taken within the final database:

- The database was sorted based on sample identities, in many cases sample identities were created based on sample matrix, location and date of sampling. All reported geodata was converted into a uniform WGS 84 format and checked, in some cases (mainly for WWTPs) coordinates were manually found for missing points. Data sources that included large amounts of replicates data for the same samples were reworked and averaged (especially for biota).
- The close to 140,000 separate PFAS compound data points were summed up into 10,175 different environmental samples. Some samples only included data about 1 of the 24 PFAS, while on average 10 different PFAS compounds were analysed from each sample.

- The samples were also grouped to unofficial “monitoring stations”, calculated based on the coordinates provided. All samples within less than a 0.005 sum difference between their WGS84 latitude and longitude points (around 560 meters in total) were grouped to one “station”. This resulted in a total of 3,102 unique sampling locations.
    - This step might not be needed for future assessments based online on harmonised national monitoring data, as the “monitoring stations” data can be officially collected from the reporting agencies. In this database however, due to the compilation of freshwater, marine, WWTP and in smaller amounts groundwater data, the reported station data was too uneven to use without additional calculative approach.
- Measures were taken to avoid isomeric data or multiple analytical parallels overrepresenting some compounds in the sum value Therefore, before summing was done an average for each PFAS and each isomer in each sample was calculated for all 27 substances with isomeric data included in the database. An overall averaging was done for all substances without isomeric data as well, making sure the sum values did not accidentally include multiple measurements of the same compound.
    - The general averaging for each substance was mainly needed as quite often samples had some compounds listed twice (often due to large differences in analytical results). As these were unique results, they were not excluded from the general database but for calculating sums for the samples they needed to be averaged.
- Three different statistical approaches were tested based on different recommendations given for WFD monitoring:
    a) summed and averaged values including only quantified results (under LOD or under LOQ values ignored)
        - This approach was selected to be used in the assessment as the main one.

    b) summed and averaged values including 50% of LOQ value as a monitoring result for all samples over LOD, but under LOQ (under LOD values set as 0 for averaging purposes). This approach is recommended in WFD to be used for calculating annual averages for single substances.
        - As different countries report LOD and LOQ differently, this approach resulted in very similar sums as the first approach, with 0 – 4% difference in threshold exceedances. As the use for sum values is not recommended in the WFD guidance, the approach was not chosen to be used in the assessment.
        - In the future, this approach could be applied with including 50% of LOD values as results, while in a move towards sum values for PFAS it might not be feasible.

    c) summed and averaged values including all under LOQ or LOD values as zero. This approach is recommended in WFD for calculating arithmetic means for groups of substances –
        - This approach was used to calculate some average values for individual PFAS, while for sums the values are identical to the first statistical approach.
- Three different summing approaches were used in parallel with each other, based on different discussions on EU level, potential EQS values set for surface waters in the future, and a need to provide a comparison with previously used sum values:
    a) PFAS sum value using the proposed RPF system – different sums are provided for the EU PFAS 24 with “official” RPF values and all reported PFAS using additional RPF values set based on the precautionary approach explained in Chapter 0 and shown in Table 1.

    b) PFAS sum value based on total organic fluorine – as measurements of total organic fluorine are becoming more common and a surface waters EQS value for this approach has been proposed in WG Chemicals, all PFAS concentrations are converted into organic F concentrations based on the percentage of fluorine from their total mass, as shown in Table 1.

   c) PFAS sum value based on absolute concentrations – as a large number of different sum parameters summing together the absolute concentrations of PFAS without any additional factors have been used in the region, an absolute sum of all individual PFAS compound concentrations is also provided for each sample in the database.

- "Exceedances from threshold" are calculated based on the different types of sum values and different matrices, using new proposed EQS (Table 2) values not officially in effect yet at the time of this report (end of 2024). This means the reported exceedances use future values and might not exceed any currently standing EQS values. This is also true for any tables or figures showing problems with analytical LODs/LOQs being too high for good results – the new standards for these only come to effect with new EQS values being approved, as according to Directive 2009/90/EC, the LOQ should be equal or below a value of 30% of the relevant EQS.

Table 2 - New proposed thresholds for various PFAS analysis used in the assessment

Threshold description	Matrix	Value	Source	Use in assessment
EU proposed update for surface water EQS for PFAS sum of 24	Surface waters (inland and marine)	0.0044 µg/l PFOA equivalents	Zero Pollution Action Plan, further updates on ongoing EQS change process via WG Chemical proceedings	Any PFAS sum values in water except for organic F based sums
	Biota (fish)	0.077 µg/kg ww PFOA equivalents		All PFAS sum values for biota
Additional EQS proposal for PFAS total in surface waters	Surface waters (inland and marine)	0.05 µg/l organic fluorine (F)	WG Chemicals discussions	Organic F based sum values for water
Quality standard for PFOS in sediments	Sediments	13.5 µg/kg dw with 5% organic carbon (C)	SCHEER expert opinion from August 2022	All PFAS sum value assessment for sediments

- A secondary threshold exceedance was calculated for all liver samples, using the conversion factor of 17.9, which was applied in HOLAS 3 for PFOS in perch and herring.
    - As different PFAS compounds would have a different ratio between liver and muscle bioaccumulation, the value of 17.9 might not be suitable for this exercise, therefore both results with and without the conversion factor are shown where possible.

The results of the summed samples and spatial distribution maps are presented in the following subsections. The assessment and details are the result of the EMPEREST project work and not officially endorsed by EU, HELCOM or the Contracting Parties of HELCOM. They should be at most used an example for the proposed new assessment, not as official assessment results.

5. Results of the assessment

5.1. Overall notes from the assessment

Though several different sum parameters and statistical methods were applied to the full database, not all of them will be displayed in the assessment results figures and tables. Different interesting dependencies and notes on the applicability of the applied approaches were found during the sample assessment, while not all of them have enough supporting data to be discussed separately. Two of the more important key discussions are included in this sub-chapter, as they can relate to decisions taken for the rest of the sample assessment provided in this chapter and change how we view the future assessments.

5.1.1. Total organic fluorine (OF) sum values

As explained in the sub-chapter 4.2, four different sum parameters were applied to the database. The sum of PFAS 24 and sum of all PFAS were both decided to be used for the assessment, the first of these to exemplify the new EU EQSD system, the second to show the same approach if more PFAS than the 24 listed in the new EQSD proposal. Though in many cases these two values are almost exactly the same due to limited amount of PFAS compounds analysed from a sample, the small differences already indicate significant changes in use profiles and might have an even larger role to play in the future assessments.

Considering the absolute concentration of PFAS and the calculated total organic fluorine sums, the results are also highly correlated for this assessment. As most PFAS have an organic fluorine content of around 50-73% based on mass (Table 1), the calculated OF sum corresponds directly to the absolute sum of PFAS concentrations, as can be seen on Figure 3. On average, the OF sum corresponds to 65% of the absolute sum of all measured PFAS.

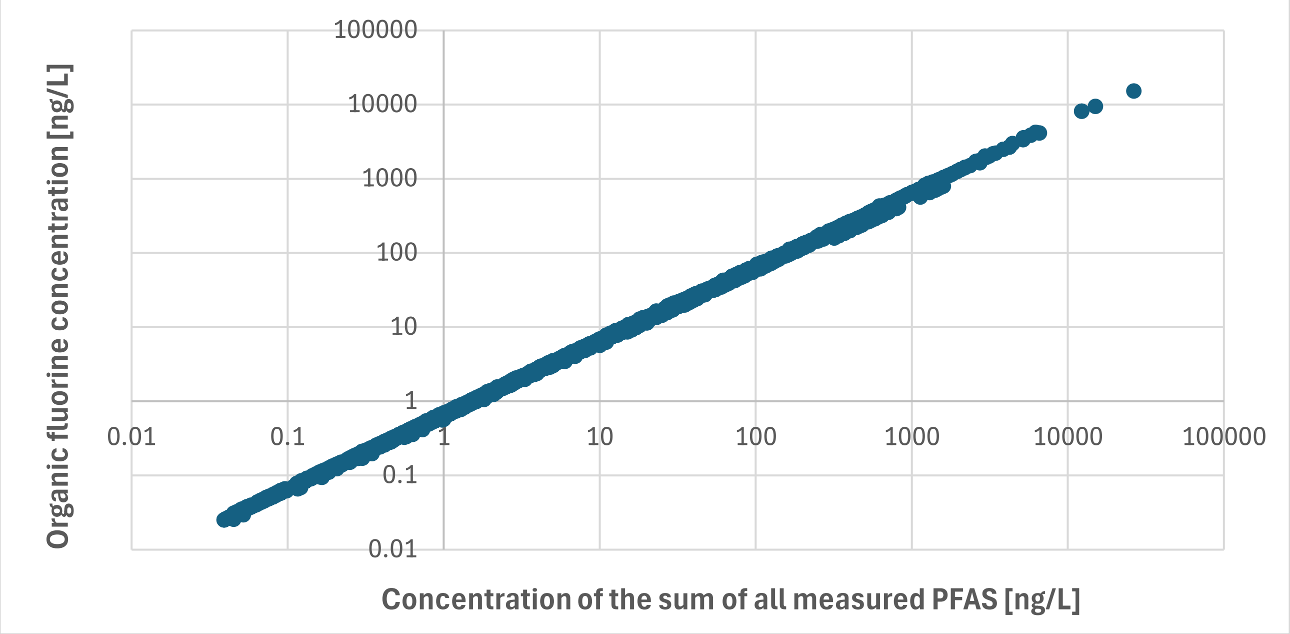


Figure 3 – Correlation between calculated concentrations of total organic fluorine (OF) and absolute concentration of the sum of all measured PFAS (ABS C).

Although there is a separate threshold proposed for OF sum in the water matrix, it is important to note that in most cases, this sum should correspond to a chemical analysis method directly analysing total organic fluorine in the sample. In most cases, the calculated OF sum does not even come close to the proposed threshold, while the main reason behind the difference is in the ultra-short-chained PFAS, such as TFA. As TFA alone can correspond to most of the organic fluorine in a sample – the average OF concentration in a water sample was 32 ng/l organic fluorine, and the average for a TFA measurement was 188 ng/l of organic fluorine, there is almost no point calculating the sum of organic fluorine without TFA included in the sample. Coupled with the fact that TFA only has a total of 100 reported entries in the database, all from German marine water sampling between 2019 and 2021, there is just not enough information to justify showing total organic fluorine sum values in the current assessment. As a sidenote, the current lowest LOD reported for TFA measurement in water matrix was 150 ng/L, which unfortunately corresponds to roughly 75 ng/L organic fluorine, which is 1.5 times higher than the proposed threshold of 0.05 µg/L, showing the TFA analysis still needs some additional sensitivity development to be used with the proposed threshold.

The large influence of TFA in the OF sum is also a concern when considering the assessment based on the sum value – TFA has not been connected to significant toxicity as of yet, especially compared to many long-chain PFAS. Therefore, for a more meaningful assessment of the "unknown PFAS" influence in the sample (which is one of the main drivers behind the OF sum analysis) the concentration of TFA should be subtracted from the OF sum value. This means TFA as a compound would always need to be analysed additionally with the TOF/EOF analysis, resulting in additional costs and complexity. Coupled with the current high LODs for TFA analysis, the organic-fluorine-based sum value might be considered not developed enough for a wide-scale used in PFAS assessment in the marine environment as of the end of 2024.

5.1.2. Assessing additional PFAS besides EU list of 24

The new PFAS assessment approach proposed by the EQSD update is based on a conversion system, which allows other PFAS to be converted into PFOA equivalents and summed up based on that. Although the approach officially has the conversion values for 24 different PFAS compounds, the system seems to be designed to be more dynamic. The proposed threshold for water, 0.0044 µg/L of PFOA equivalents should show the maximal allowable limit of PFAS in the water based on PFOA toxicity, therefore any number of PFAS could be added to the sum value, if a conversion value (a relative potency factor or RPF) could be found to convert them into the PFOA equivalents.

In the current assessment, this estimation of new RPFs was done based on scientific literature and expert opinions in order to allow assessing all currently measured PFAS in the Baltic Sea area. As it is already known that the 24 PFAS on the list of EU (plus an additional official RPF for TFA as the 25th PFAS) do not necessarily correspond to the 24 most common or important PFAS for the region, it was decided to include a secondary sum value of all measured PFAS in the assessment.

An important consideration for the future assessment in the Baltic Sea region would be to not get too fixed in the current list of 24 PFAS provided by EU monitoring, as at least some indicator compounds of other sub-groups of PFAS compounds should continue to be analysed. Some of the more important sub-groups would be fluorotelomer carbonates and sulfonates (6:2 FTS etc) and sulfonamide derivates ((P)FOSA, N-EtFOSA etc), which already are found in the environment in high concentrations, often significantly more than most of the 24 PFAS included in the EU list. Besides those sub-groups, as industrial substitution of known PFAS is currently going on in rapid pace, it would be good to keep the PFAS assessment flexible, allowing for a dynamic list of PFAS for both monitoring and assessment.

5.2. Water matrix

The database used for the assessment included a total of 6,882 water samples, most of which were taken from freshwater sources (Figure 4), with some samples also from various other water sources, such as groundwater, wastewater and other (including samples from leachates, process water and ditches).

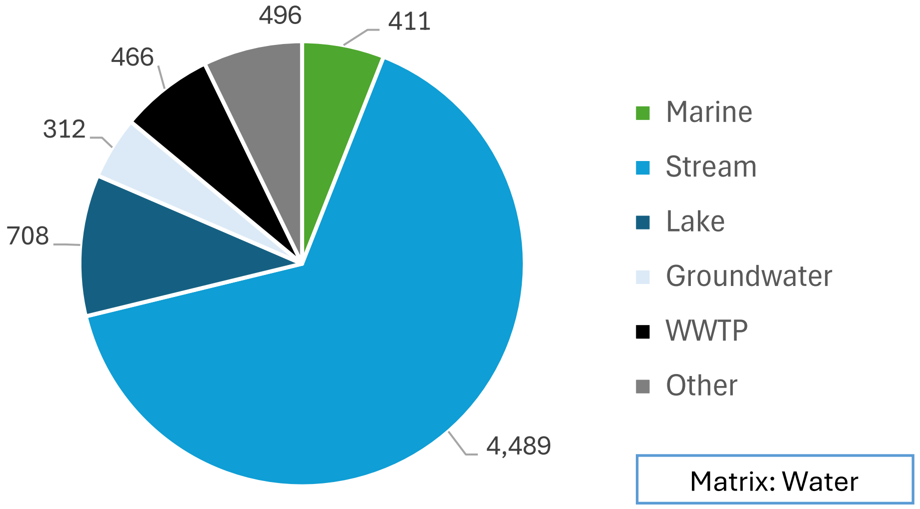


Figure 4 – Distribution of environmental monitoring samples for the water matrix.

Regular data reporting for PFAS in water matrix starts in 2014, with only around 30 samples reported earlier. Therefore, the assessment focuses mostly on the period of 2014-2022, with the earlier samples included in statistics, but not always shown on figures. Only data from marine, stream and lake environments are used in most of the following assessments in this subchapter, with a note on each figure specifying the subsets. Some additional figures and tables for other subsets can be found in ANNEX II – Additional maps, figures and tables of the document.

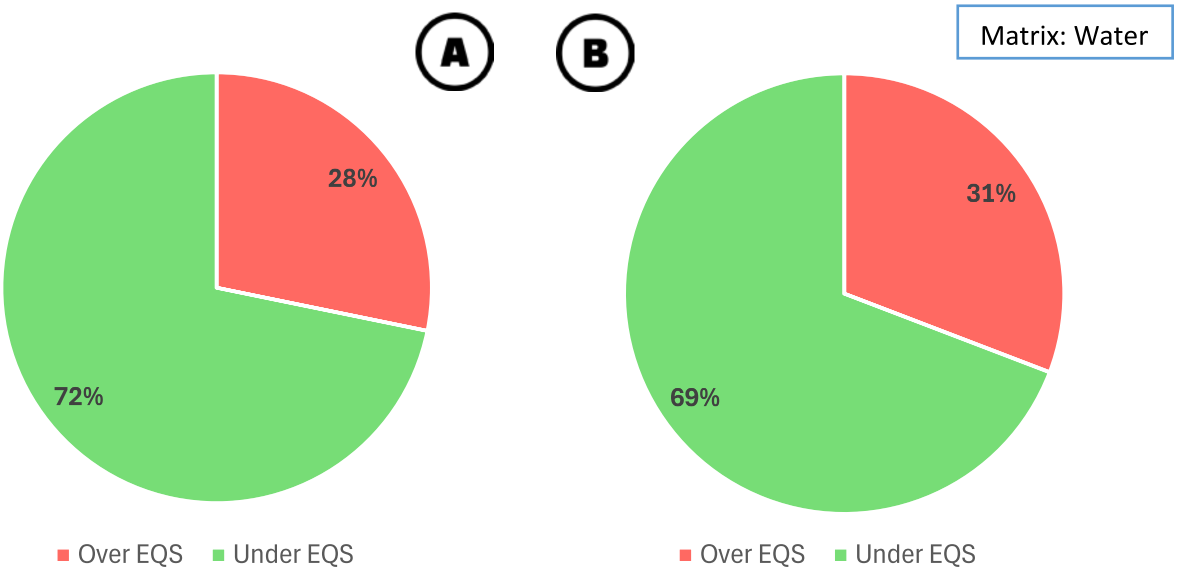


Figure 5 – Overall threshold exceedance of all water samples for the sum of PFAS 24 (A) and sum of all measured PFAS (B). The threshold used (4.4 ng/L) is the from the new EQSD proposal not yet finalised.

When comparing all the samples with the new proposed threshold values in the EU EQSD update (4.4 ng/L), about a quarter of the samples would be over the threshold value considering only the 24 PFAS listed by EU (Figure 5). When considering all PFAS measured from the samples, the number of threshold exceedances increases by a few percentage points, coming to almost a third of all samples. As the new proposed water threshold is in some ways less strict than the current one (0.00013 µg/L or 0.13 ng/L for PFOS only), the status of the marine environment is significantly better than the PFOS water matrix assessment in HOLAS 3 [6]. The average exceedance in the marine environment is only 7.3% with the new threshold (Table 3), while the amount of marine water samples is very low compared to other environments.

Table 3 – Threshold exceedance of water samples based on the sum of all PFAS (in PFOA equivalents), divided by the sampling environment

	Marine	Rivers/streams	Lakes	WWTPs
# of samples	411	4,489	708	338
# over threshold	30	1,420	152	232
% over threshold	7.3%	31.6%	21.5%	68.6%

Figure 6 represents a simplified exploration of time-trends, looking separately at freshwater (A) and marine samples (B). Comparing average annual concentrations of different PFAS sums to new proposed thresholds shows a continuous high exceedance for all years for samples taken from rivers and lakes – on average 6 to 20 times higher the proposed surface water threshold. Still, there is a strong decreasing trend for both sum values using RPFs (correlations over 0.5), even when excluding 2014, which could be considered as an outlier, from the calculations. At the same time, the absolute concentrations (ABS C) of PFAS show a weak increasing trend for freshwater samples, indicating commercial substitutions of known (and high potency) PFAS to newer compounds.

Comparing the "PFAS 24 RPF" and "ALL PFAS RPF" sums, the splitting of the two can also be witnessed from 2019, indicating freshwater PFAS monitoring increasing to encompass substances (such as FOSA, FOSAA and the related compounds) not included in the current EU sum of 24 PFAS. The overall average number of substances (dark blue area and numeric labels) also shows this change between periods of 2014-2018 (average of 9 unique PFAS substances measured from each sample) and 2019-2022 (average of 20 unique PFAS). The total number of surface water samples from lakes and rivers has seen two rapid increases, one from 2015 to 2017 (3x increase in 2 years) and the other from 2019 to 2021 (additional 1.5x increase in 2 years).

Part B of Figure 6 represents the simplified time-trend analysis for marine water samples, while the average number of samples from the medium are ten times lower than for freshwater. There were no reported water samples for 2014, and only around 25 samples for 2015-2018, while the number has increased from 2019 onwards. The amount of unique PFAS measured is also significantly lower, on most years the average sample included measurement of only 2-4 separate PFAS.

The average concentrations for both RPF-based sum values have been under the proposed new threshold since 2016, while sum of PFAS based on actual concentrations had a significant jump in 2019-2021, mostly due to several TFA measurements in German samples, which has very high concentration, but low potency factor. As TFA has not been measured in any other samples (freshwater, biota nor sediment), it can be expected to have very high absolute concentrations in many other samples as well based on scientific literature.

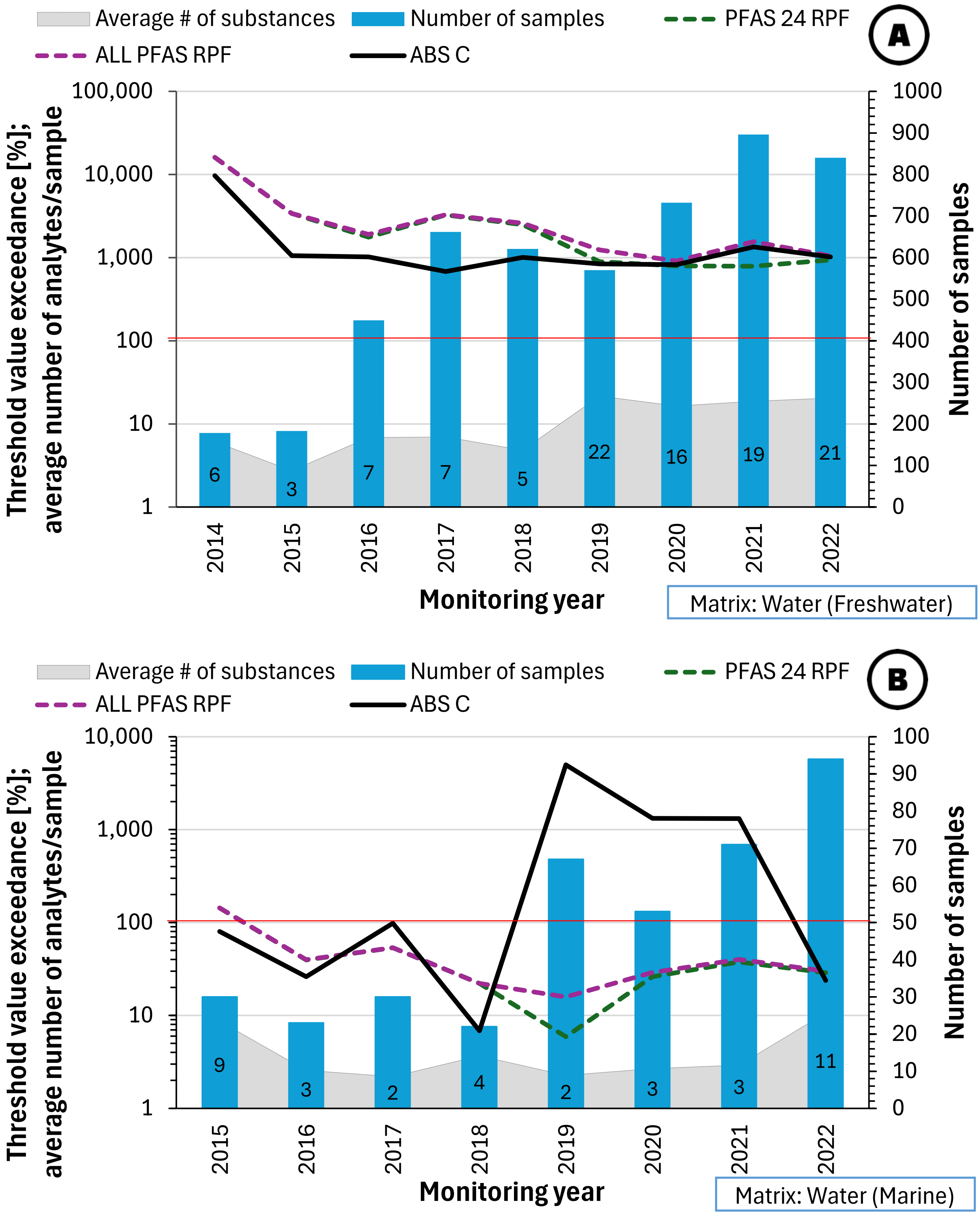


Figure 6 – Time-trends for different PFAS sum parameters in A - freshwater (lakes and rivers) and B – marine samples. Three different sum parameters are represented with different lines, showing the yearly average on how much samples exceeded the new proposed thresholds (0.0044 µg/l PFOA equivalent). Gray area on the background indicates the number of different PFAS compounds on average included in samples each year (also supplied with numeric value labels) and lighter blue columns the total number of samples included that year (corresponds to secondary y-axis).

5.2.1. Key PFAS in the water matrix

To assess which of the PFAS compounds individually has the highest influence on the pollution of surface water samples (including lake, stream and marine samples), the TOP 10 PFAS based on two different statistical approaches are presented in Table 4 and Table 5. Full tables, showing the ranking of all reported PFAS can be found in ANNEX II of the document.

Matrix: Water (Surface water)

Table 4 – TOP 10 PFAS from all water samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentrations (ng/L PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFNA	3381	965	244.32	5358487.15	44.88	44.88
PFOS	5644	2999	50.06	3411748.23	28.58	73.46
6:2 FTS	2252	556	81.71	1032574.22	8.65	82.11
PFOA	4338	2677	11.10	675554.91	5.66	87.77
PFUnDA	2950	191	106.38	461767.36	3.87	91.63
PFHxS	2747	1194	14.10	382492.96	3.20	94.84
PFDA	3398	370	21.09	177389.02	1.49	96.32
PFHpA	2788	1966	3.08	137714.10	1.15	97.48
N-EtFOSA	1054	150	40.00	136363.64	1.14	98.62
PFHpS	2037	221	4.77	23980.02	0.20	98.82

Matrix: Water (Surface water)

Table 5 – Top 10 PFAS measured from water samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into how often a compound has been measured and total impact of a compound for the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (ng/l PFOA eq)	Average TH exceedance amount (%)	Rank
PFNA	3381	497	15	244	5553	1
6:2 FTS	2252	346	15	82	1857	2
PFOS	5644	867	15	50	1138	3
FHxSA	15	15	100	17	379	4
N-EtFOSA	1054	150	14	40	909	5
PFUnDA	2950	122	4	106	2418	6
FBSA	3	3	100	10	227	7
PFDA	3398	167	5	21	479	8
N-MeFOSE	1054	4	0	208	4725	9
PFHxS	2747	216	8	14	320	10

Comparing these two approaches, with one calculated based on how much a single substance has contributed to the total threshold exceedance (based on the new proposed threshold of 0.0044 µg/l PFOA equivalent) and the other method based on how frequently a compound exceeds the thresholds and the average concentrations of >LOQ samples, shows a more nuanced picture of problematic PFAS compounds. Considering the TOP 10 PFAS from both approaches, a total of 7 PFAS (PFNA, PFOS, 6:2 FTS, PFUnDA, PFHxS, PFDA and N-EtFOSA) are the same on both, representing the PFAS that both have a relatively high cumulative impact and high exceedance frequency. It is also important to note, that 2 of these (6:2 FTS and N-EtFOSA are not part of the EU PFAS list of 24, which could potentially be considered an oversight.

The other 6 PFAS, that reach the TOP 10 only with one of the approaches are PFOA (11th on the other approach), PFHpA, PFHpS for cumulative impact and FHxSA, FBSA and N-MeFOSE (11th on the other approach) on exceedance frequency. The latter 3 are also not part of the EU PFAS list of 24.

While the total amount of data for water samples only from the marine environment is rather low with only a handful of different PFAS compounds usually measured, most of the TOP PFAS stay the same, with PFOS, PFOA, PFNA and PFUnDA having high scores with both methods. Surprisingly, TFA, which only has around a hundred measurements from the German marine waters, is also showing up as a TOP 4 issue with both methods in the marine water samples. Other PFAS with a higher importance to marine water samples than for other water samples were PFBA and FOSA. The full tables showing the rankings of marine water samples only can also be found in ANNEX II of the document (Table 29 and Table 31).

5.2.2. Spatial distribution of PFAS from water samples

When looking at the spatial distribution of the samples (Figure 7), it is clearly visible that the overall situation with the water samples is promising – only a limited number of the points are red, representing samples exceeding the new proposed water threshold. It is also clear from the map that most marine samples are taken from coastal waters, with almost no water samples taken from the open sea areas. Quite a few of the coastal samples do exceed the threshold values, and similar status could also be expected from the open sea areas, as according to other matrices the PFAS pollution is spread around the whole region.

Quite many of the total points are represented on the map in white, meaning they showed results under the LOD. In many cases, that does not however mean these samples were under the threshold. As the new proposed threshold is 4.4 ng/L for the PFOA equivalents and some PFAS with the new system are multiplied by a factor of 10, 0.44 ng/L is the lowest LOD required by the new system in practice. Unfortunately, using historical monitoring data dating back to 2010 means a significant amount of data before 2019 use LODs between 1 and 10 ng/L – therefore depending on the specific compound and its RPF, even results shown as <LOD could have been over the new threshold. This is rarely the case with more recent data and the high emphasis on PFAS in the world has resulted in rapid development of PFAS analytical methods and sensitivity.

The data on Figure 7 includes only natural monitoring points, while the collected database also included a lot of data from potential pollution point sources – wastewater treatment plans. The geographic distribution of that data can be found in ANNEX II of the document (Figure 45), as the amount of extra data points made the map presented in this subchapter too difficult to read. Although WWTPs have not been legally tasked with eliminating PFAS from the effluent (PFAS were not included in the 2024 updated Urban Wastewater Treatment Directive as micropollutants that need to be eliminated either), the effluents can be seen as pathways of municipal PFAS pollution finding its way to natural water sources. Most WWTP effluents and recipient water bodies (when no problems with LOD values as described above were present) did end up showing PFAS concentrations above the new proposed EQSD threshold.

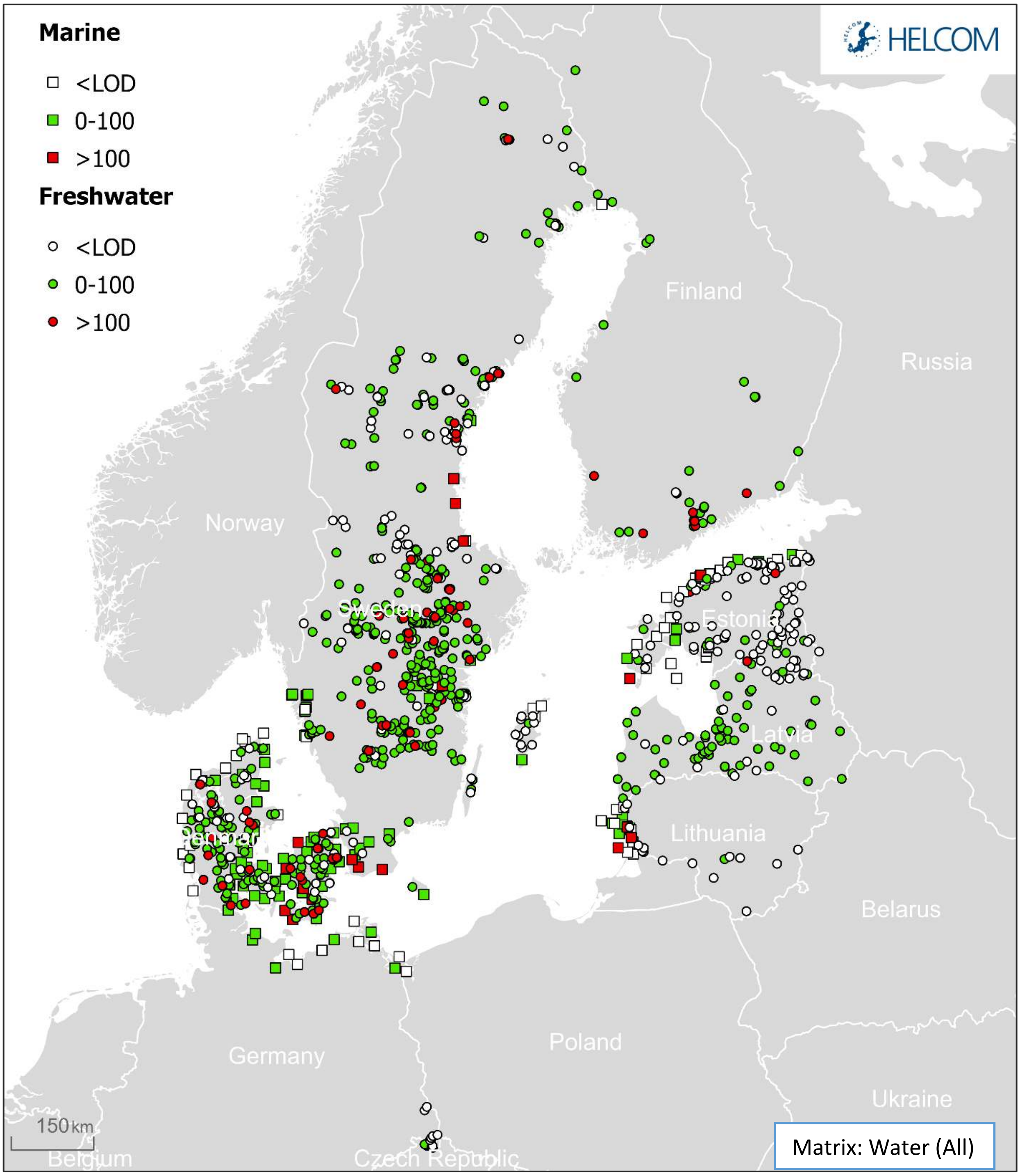


Figure 7 – Geographic distribution of the summed results of all measured PFAS in the water matrix. Only the latest sample from each location is shown. The colours correspond to the new proposed threshold of 4.4 ng/L PFOA equivalents, with red samples over the threshold value. Samples marked <LOD are not necessarily under the threshold value due to LOD sensitivity issues in older data.

It is also important to note that the water matrix problems were already highlighted in HOLAS 3 indicator report, while in some cases the new water EQS proposed by EU (0.0044 µg/l) can be considered more lenient than the previous one (0.00013 µg/l for PFOS). Although the new sum applies to a sum of 24 PFAS and PFOS concentrations are multiplied by 2, in many historic samples only PFOS has been measured. Therefore, as all samples are shown on the figures despite the number of compounds included, the new proposed threshold shows those points now as green, while HOLAS 3 indicated them as red. Still, the water matrix state might be significantly better than estimated previously with the new approach, especially as PFOS used for assessment so far represents one of the most significant drivers of PFAS pollution according to Table 4 and Table 5.

From all the collected marine water samples, only 30 out of a total of 411 exceeded the threshold for the sum of 24 PFAS, further showing the new assessment might show a less severe pollution picture when used for the assessment of the Baltic Sea water matrix. As almost no samples represent the open sea areas however, it is important to increase the number of water samples there to get a better picture of the state of the sea currently.

5.2.3. Water sample trends in monitoring stations

For a better understanding of the PFAS temporal trends in the Baltic Sea region, samples were grouped together into unofficial "monitoring stations" based on the sample locations, as discussed previously in Chapter 4.2. For temporal trend analysis, only locations with at least 2 samples from different years were included and multiple samples from the same year were automatically averaged. The analysis included only samples from streams, lakes and marine environments.

Matrix: Water (Surface water)

Table 6 – Overall status and direction of trends in unofficial water "monitoring stations"

Confidence	Trend	Total	Stream	Lake	Marine
	Stations with no PFAS quantified	18	10	2	6
	Stations with no apparent trends	143	114	19	10
HIGH	Stations with DECREASING PFAS conc.	50	30	7	13
HIGH	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	19	16	0	3
HIGH	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	39	30	3	6
MODERATE	Stations with DECREASING PFAS conc.	24	18	5	1
MODERATE	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	2	0	2	0
MODERATE	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	9	7	2	0
LOW	Stations with DECREASING PFAS conc.	24	21	3	0
LOW	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	5	5	0	0
LOW	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	11	9	1	1
	Total stations	344	260	44	40

The trend analysis was based on two criteria – the linear regression value based on the change of PFOA equivalent sum of all PFAS through years and the confidence value of the regression. Any linear regressions smaller than 5% of threshold value per year were marked as "no trend". Based on the confidence of the linear regressions, results were categorised into "high" (r^2>0.5), "moderate" (r^2>0.3), "low" (r^2>0.15) and "none" (r^2<0.15) confidence groups. For samples showing increasing PFAS concentrations, a secondary analysis was performed to identify if the number of different PFAS compounds measured from the sample has also increased in time. The trend itself does not take into account if any of the samples from the location have exceeded the new proposed threshold values or not, just the direction of concentration change.

The trends in the water matrix are presented in Table 6 with all the relevant confidence assessments and on Figure 8 in a simplified form without the confidence values. About three quarters of the monitoring stations represent streams and rivers, half of which have no visible trends and the other half showing almost an equal amount of long-term decreasing and increasing trends. On average, the increasing concentration trends have higher certainties than the decreasing trends. Although the overall view of water matrix shows some decreasing trends for PFAS, the monitoring station-based view does not support the assessment that PFAS concentrations in water are noticeably decreasing.

For the marine water samples, most of the stations showed high confidence trends, 13 of which had decreasing PFAS concentrations and 9 increasing concentrations. Most of the increases were not due to increased number of PFAS measured in the station, rather showing many coastal marine water stations are showing the trend of increasing PFAS concentration. 25% of marine monitoring stations show no apparent trends and 15% have never detected any PFAS in the stations (latest measurements from 2021/2022 for each these).

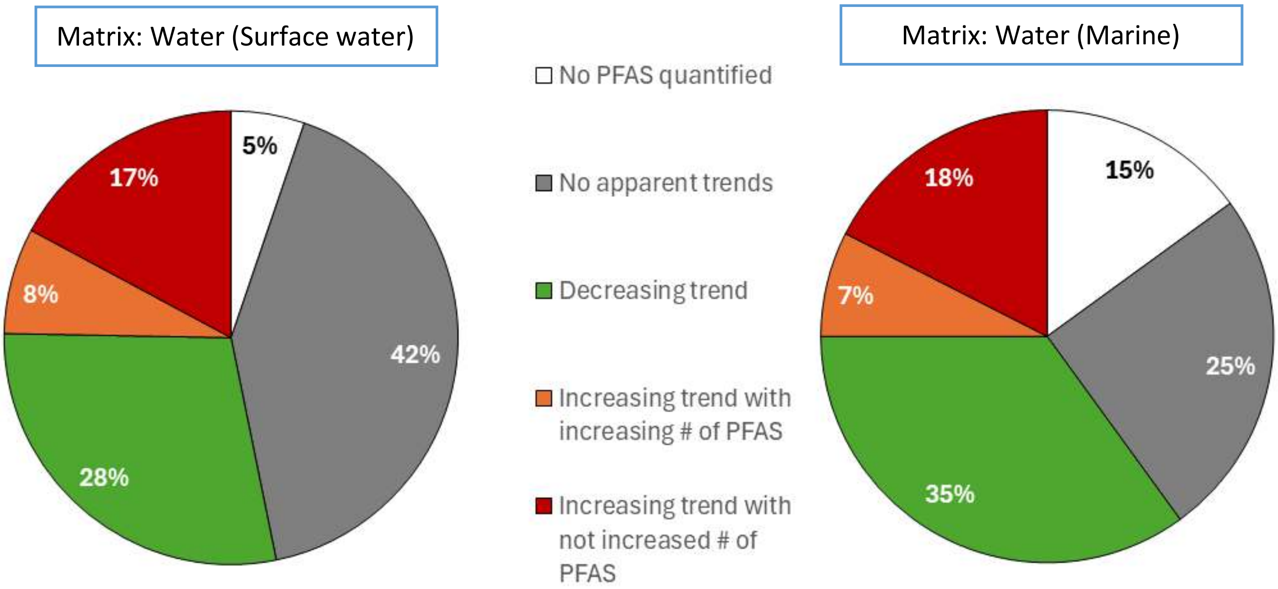


Figure 8 – Overall temporal trends in water samples based on unofficial monitoring stations in lakes, streams and marine environment (left side) and in marine environment only (right side)

The geographic distribution of the station is displayed on the Figure 9. There seems to be a small trend around the coastal waters around Denmark, Germany and southern parts of Sweden with decreasing marine PFAS concentrations, which have also been previously reported by the national experts. At the same time, the rest of the Baltic does not show the same trends, highlighting it might be only a regional trend. As that area is the most influenced by the inflow of salty water from the North Sea, the trend might have a basis in hydrological effects. There is also a potential link to seafoam generation, which could be connected to higher salinity and wave-action of that part of the Baltic Sea and have been shown to be a significant carrier of waterborne PFAS back to land [7].

Matrix: Water (All)

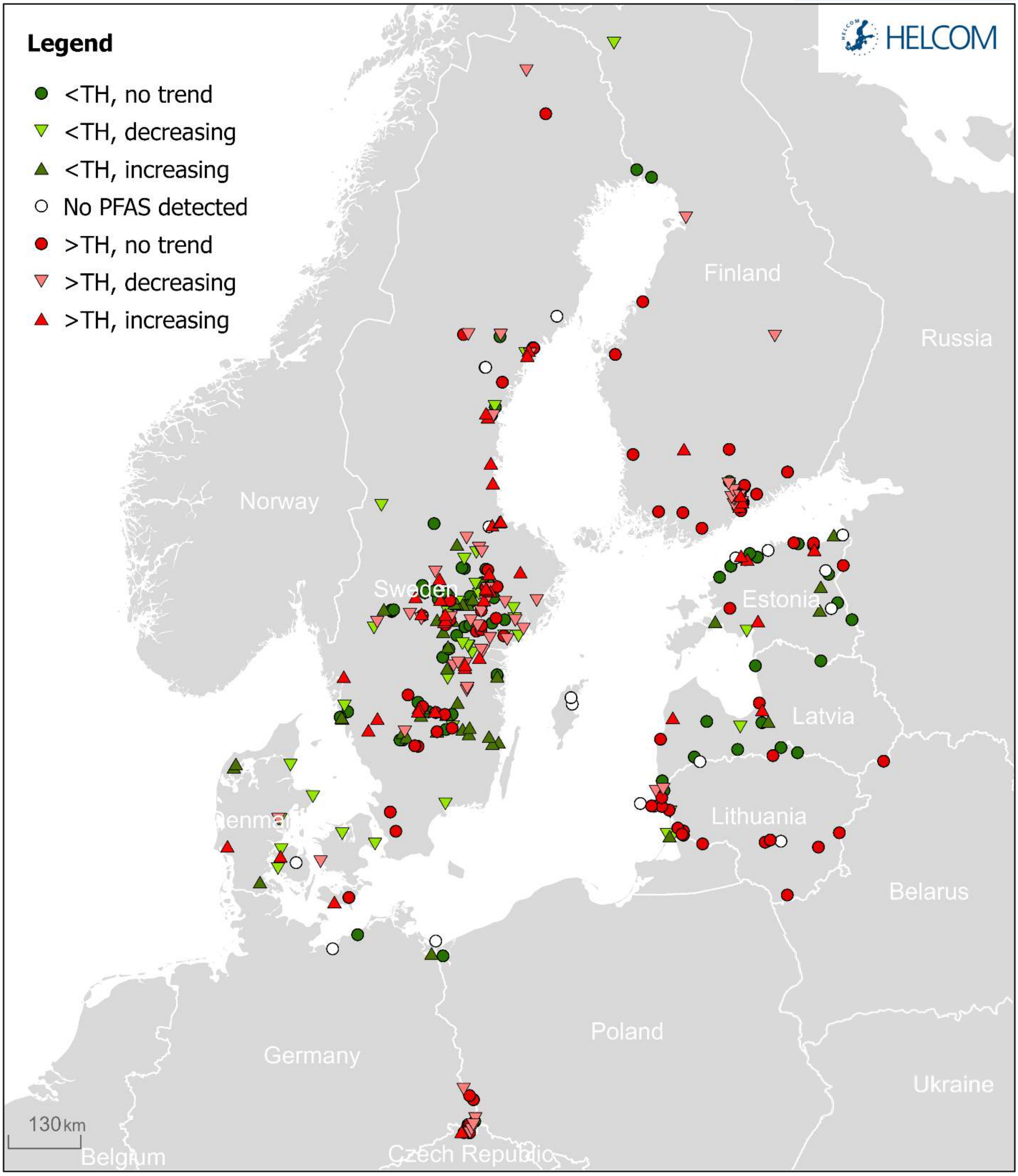


Figure 9 – Direction of trends in the water matrix for monitoring stations with at least 2 different years of data included in the database. The red and green colours indicate if any of the samples in the station have exceeded the new proposed EU EQSD threshold (TH) value of 4.4 ng/L for a sum of PFAS (sum of all measured PFAS included).

5.3. Biota matrix

For biota, the consolidation of the database down to unique samples resulted in a total of 2385 entries (Figure 10), about half of which were taken from the marine environment. The database does also include 41 samples from Sweden, with sample environment marked as “terrestrial”, most of it from otter (*Lutra lutra*) and a few from reindeer (*rangifer tarandus tarandus*). These are included in some of the figures and statistics as “mammals” to avoid confusion, while most of the statistics are displayed as either all biota or fish specifically.

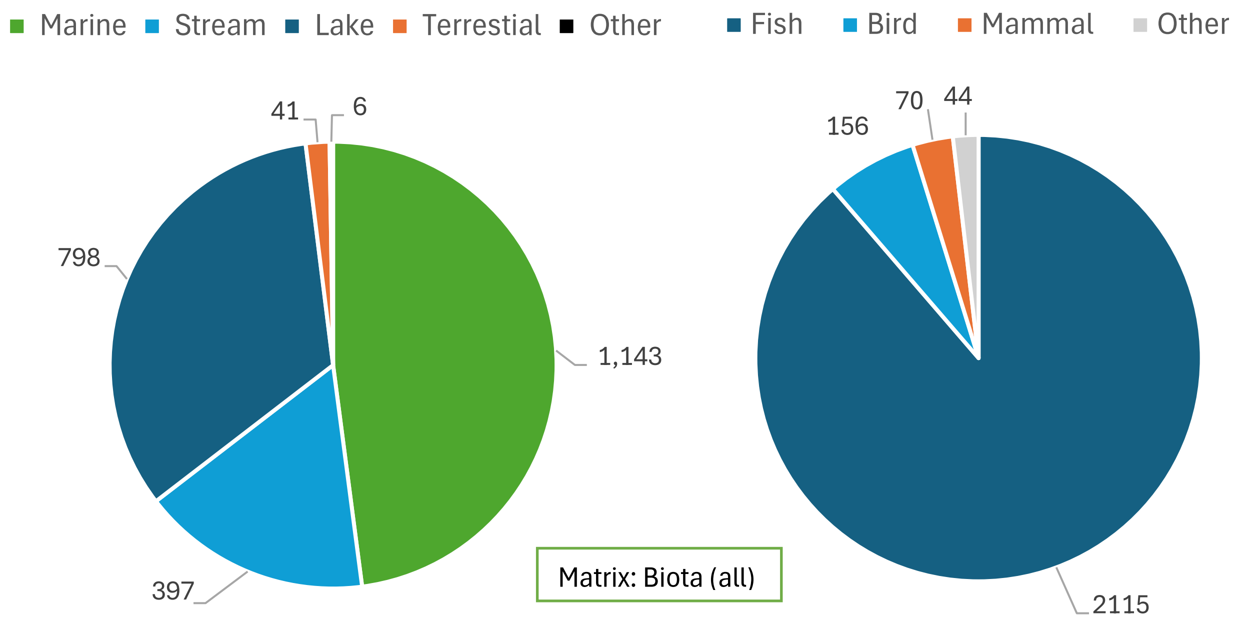


Figure 10 – Distribution of environmental monitoring samples for biota based on sampling environment (left side) and monitored species (right side)

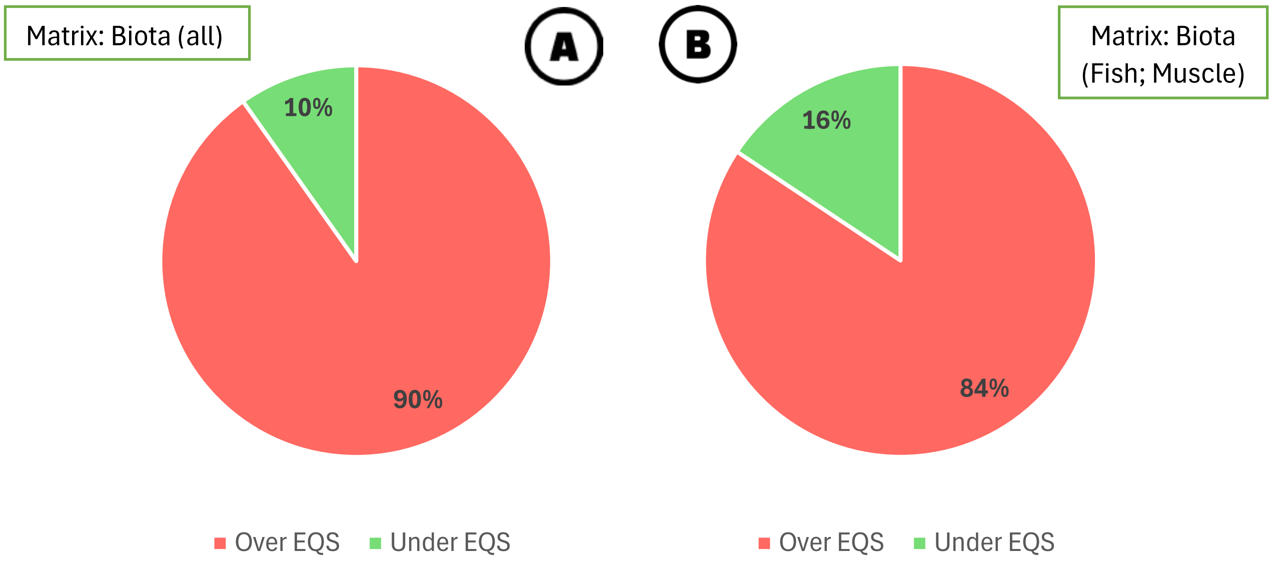


Figure 11 – Threshold exceedance frequency of all reported biota samples (A) and biota sample subset containing only fish muscle/fillet samples (B). All measured PFAS in each sample were summed according to the RPF system.

Compared to water samples, the biota samples show significantly higher threshold exceedance according to the new EU EQSD proposal (Figure 5). A total of 90% of all biota samples would exceed the new proposed threshold of 0.077 µg/kg ww, and this number is the same for both the sum of PFAS 24 and the sum of all PFAS (only an extra 5 samples out of the collection of over 2000 exceeded the threshold with additional PFAS being added to the sum parameter). If the new threshold is used only specifically for fish muscle samples (which it is designed for), with no conversions of other tissues or trophic levels, the threshold exceedance would be 84% for both the sum of PFAS 24 and the sum of all PFAS.

This creates an interesting issue with the assessment, as the new thresholds in the EU EQSD are set with human health in mind, bridging the gap between MSFD descriptor 8 (concentrations of contaminants in the marine environment) and descriptor 9 (concentrations of contaminants in fish and other seafood for human consumption). Based on the new EQSD values, it would mean that 84% of the fish sampled in the Baltic Sea region would not be safe for human health; while the actual food safety standards are set by EFSA for different food categories and are currently set at 2-45 µg/kg ww for a sum of PFOS, PFOA, PFHxS and PFNA for different categories of fish (updated in 2022). The difference between these two sets of legislation (one upcoming and the other in effect) is multiple magnitudes. A recommended tolerable weekly intake (TWI) has also been set by EFSA at 4.4 ng PFAS 4 per kilogram of body weight, which is more in line with the new EQSD levels than the current food safety standards. This inconsistency with the current risk assessment in different EU regulations has also been called out by other experts [8].

Still, it is safe to say that the current levels of PFAS in biota, especially in the marine environment, where the average biota sample exceeds the new proposed threshold 95% of the time, are highly concerning and show the true breath of the PFAS pollution. Therefore, it should be taken as undeniable proof that the PFAS issue needs to be on the forefront of the current fight against chemical pollution in the environment and could justify large-scope actions such as the general PFAS ban proposed by five EU member states and currently in consideration process in ECHA.

On average, the biota living in the marine environment is showing the highest PFAS concentrations, with fish in lakes coming in as a close second, while biota in rivers showing the lowest PFAS concentrations, corresponding to the lowest threshold exceedance frequency (Table 7). This is almost completely opposite to the corresponding results in the water matrix (Table 3), indicating that the correlation between high water matrix results to high biota matrix results might not be direct, and be significantly influenced by other parameters, including flow rates, species and differences in trophic habits.

Table 7 – Threshold exceedance of biota samples based on the sum of 24 PFAS/sum of all PFAS (in PFOA equivalents, different only for marine samples), divided by the sampling environment. Trophic conversion factors of 10 and 100 were used for fish egg/mammal samples respectively and a general liver to muscle conversion factor of 17.9 was used regardless of the specific species or compound for a general estimation.

	Marine	Rivers/streams	Lakes	Mammals
# of samples	1143	397	798	41
# over threshold	1069/1072	307/309	731	34
% over threshold	93.5%/93.8%	77.3%/77.8%	91.6%	83.9%

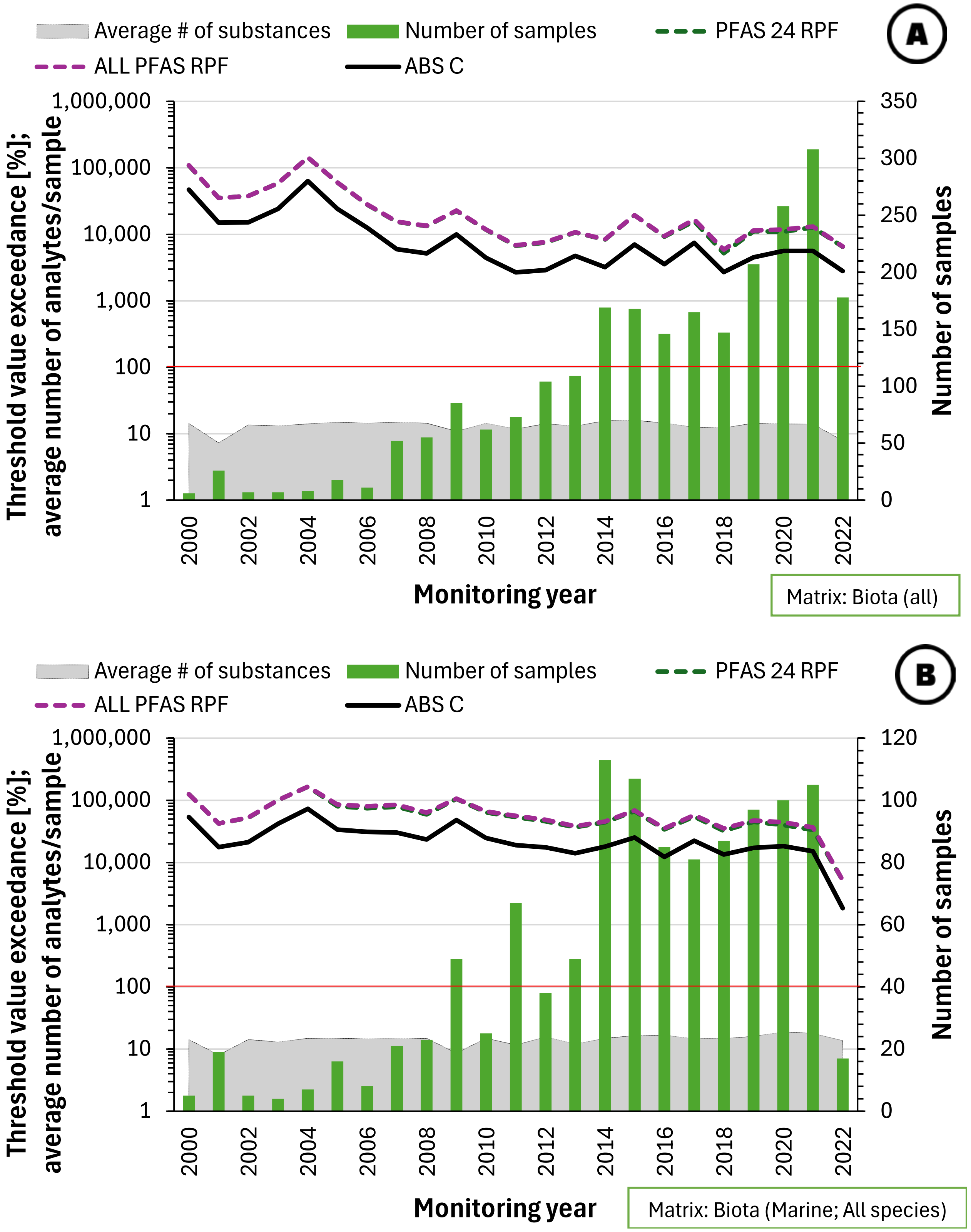


Figure 12 – Time-trends for different PFAS sum parameters in A – all water and B – only samples from marine environment. Data from all reported species are included, with trophic conversion factors applied, while a simplified conversion factor of 17.9 applied was applied for all liver samples. Three different sum parameters are represented with different lines, showing the yearly average on how much samples exceeded the new proposed thresholds (0.077 µg/kg ww PFOA equivalent). Gray area on the background indicates the number of different PFAS compounds on average included in samples each year and lighter green columns the total number of samples included that year (corresponds to secondary y-axis).

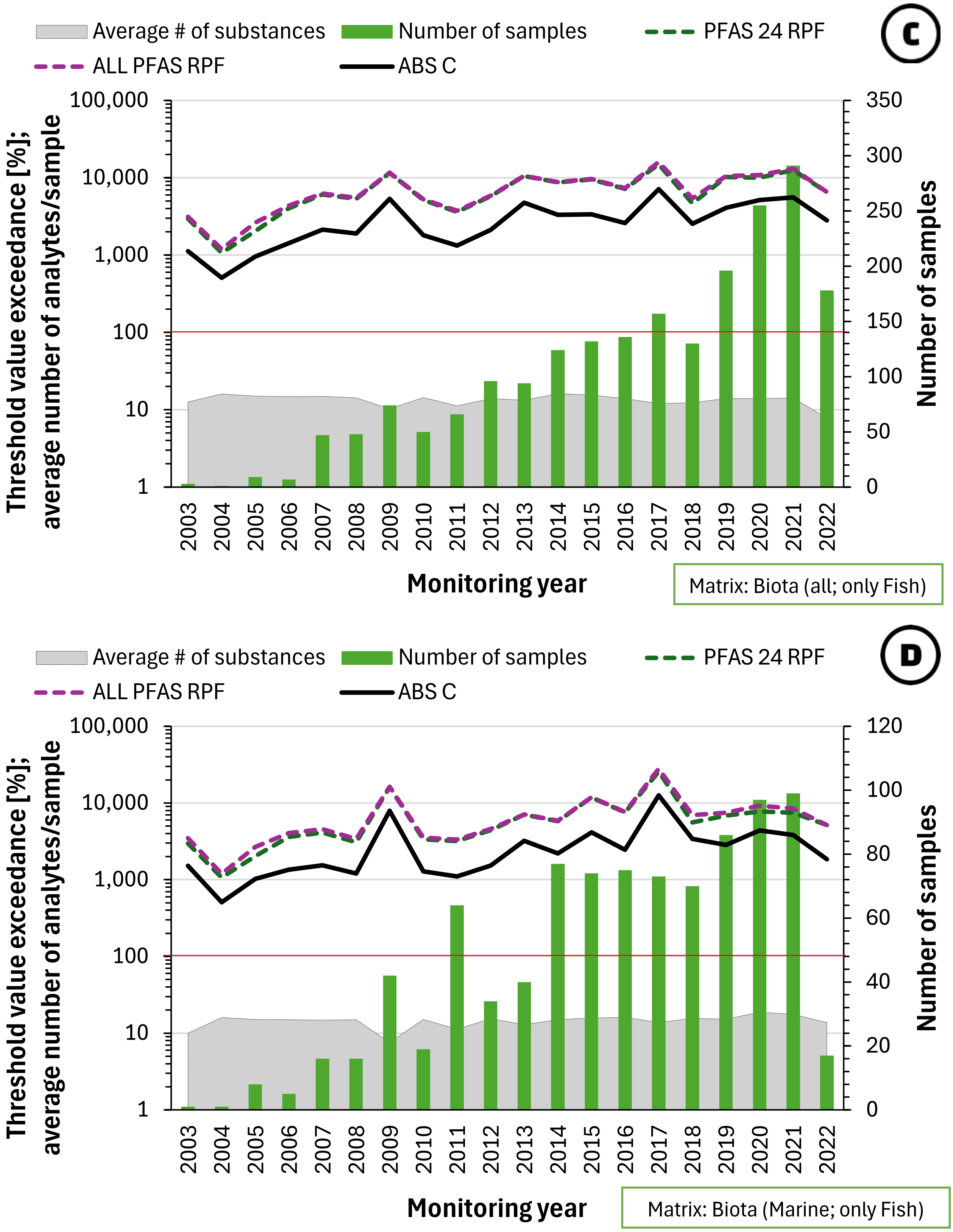


Figure 13 – Time-trends for different PFAS sum parameters in C – all Fish samples and D – Fish samples from the marine environment. All liver data has had a simplified conversion factor of 17.9 applied to better compare it to data from muscle tissue. Three different sum parameters are represented with different lines, showing the yearly average on how much samples exceeded the new proposed thresholds (0.077 µg/kg ww PFOA equivalent). Gray area on the background indicates the number of different PFAS compounds on average included in samples each year and lighter green columns the total number of samples included that year (corresponds to secondary y-axis).

Looking at the general trends in all measured biota samples presented in Figure 12 and all fish samples presented on Figure 13, while there is a general downwards trends when looking at all biota together, excluding all samples besides fish shows a completely different picture. Whether the slightly increasing trend (though mathematically no trend can be detected from 2007 to 2021) in fish samples could be connected to increased monitoring frequency is not clear, but the picture is the same for both freshwater and marine environments. At the same, the amount of different PFAS compounds analysed from biota matrix has not changed much in the last two decades, with the average number of measured compounds in a sample staying between 12 and 16 throughout the years with only a few exceptions when data is divided into sub-matrixes.

The trends for all biota samples on Figure 12 are mathematically more confident, with the r^2 values of all decreasing trends between 2007 and 2021 between 0.31 and 0.47. 2007 has been chosen as the starting year for the trends, as the years before have a high variation in the number of samples. All years between the chosen timeframe have at least 50 total biota samples and at least 20 of them from the marine environment. It is important to note, that as different species could have different conversion factors for each PFAS compound, the statistics might slightly change with more conversion factors being applied than the simplified 17.9 used in this example. At the same time, as shown in sub-chapter 5.3.2, the monitoring has been moving towards muscle tissue monitoring since 2011, meaning the need for hundreds of conversion factors for a more complex assessment might be reduced in the future.

Looking at the numerical values of threshold exceedance enforce the importance of PFAS monitoring in biota even further – using the proposed new EU EQSD human health threshold of 0.077 µg/kg ww, the average samples are magnitudes over the proposed threshold value. Even with trophic conversion factors of 10 and 100 applied for bird eggs and mammals respectively, the average PFAS 24 sum value has still been between 100 and 1000 times over the proposed new threshold. Looking only at fish, the exceedance has been on average between 10 and 250 times the proposed threshold, which is significantly less than for all biota, while still extremely concerning. As the current EQSD threshold (disregarding the update in process) in biota is 9.1 µg/kg ww for PFOS – effectively about 250 times less strict – most of the fish samples would be considered under the threshold, as was also the case in HOLAS 3 assessment [6].

Comparing the absolute concentrations of PFAS (summed without RPF values applied) to RPF-based sum values, can indirectly correlate to which chain-lengths of PFAS are prevalent. This is due to the longer-chain PFAS being generally associated with higher toxicity (except for ultra-long chain PFAS), resulting in higher RPF factors than shorter-chain PFAS (with ultrashort PFAS having RPF values around 0.001 and 0.002). Having the RPF-based sum value higher than absolute concentrations indicates that the higher concentrations come from PFAS with RPF factors over 1, which is the case for all biota results. As discussed previously, this might also be due to ultra-short PFAS not having any reported measurements in biota, as the few measurements from marine water samples including TFA (Figure 6), was immediately apparent the absolute concentration of PFAS being higher than the RPF-factor based.

5.3.1. Key PFAS in the biota matrix

To assess which of the PFAS compounds individually has the highest influence on the pollution of biota samples, the TOP 10 PFAS based on two different statistical approaches are presented in Table 8 and Table 9. Full tables, showing the ranking of all reported PFAS, can once again be found in ANNEX II of the document.

Matrix: Biota (all)

Table 8 – TOP 10 PFAS from all biota samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. A conversion factor of 17.9 was used for liver samples and trophic factors of 10 and 100 for bird eggs and mammal respectively. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg ww)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	3788	3534	4.82	22102519.76	62.13	62.13
PFNA	1992	1444	2.00	3753102.25	10.55	72.68
PFDA	1994	1613	1.66	3487578.50	9.80	82.48
PFUnDA	1976	1589	1.48	3056724.01	8.59	91.07
PFDoDA	1584	1227	0.68	1079192.83	3.03	94.10
PFTrDA	1336	1166	0.47	710735.83	2.00	96.10
PFDS	2165	563	0.51	375401.34	1.06	97.16
FOSA	2356	1510	0.18	357367.56	1.00	98.16
PFOA	2393	733	0.14	131321.68	0.37	98.53
PFHpS	424	126	0.79	129881.34	0.37	98.90

Matrix: Biota (all)

Table 9 – Top 10 PFAS measured from biota samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. A conversion factor of 17.9 was used for liver samples and trophic factors of 10 and 100 for bird eggs and mammal respectively. This method does not take into how often a compound has been measured and total impact of a compound for the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (µg/kg ww)	Average TH exceedance amount (%)	Rank
PFOS	3788	3302	87.17	4.82	6254.25	1
FBSA	18	18	100.00	2.07	2694.14	2
PFDA	1994	1543	77.38	1.66	2162.17	3
PFNA	1992	1420	71.29	2.00	2599.10	3
PFUnDA	1976	1517	76.77	1.48	1923.68	5
6:2 FTS	231	42	18.18	1.04	1347.75	6
PFDoDA	1584	933	58.90	0.68	879.54	7
10:2 FTS	14	1	7.14	22.60	29350.65	7
PFTrDA	1336	853	63.85	0.47	609.55	9
4:2 FTS	122	16	13.11	0.87	1128.62	9

Once again, the first of the two approaches is based on total threshold exceedance, influenced by the number of times a compounds have been measured over LOQ, while the second approach is based on relative frequency (percentage of measurements over threshold). Comparing these approaches allows to identify which PFAS compounds are currently the main contributors of monitored pollution, and which substances could enter that list should the few measurements included now of them indicate the true breath of their spread. For biota, 6 of the TOP 10 substances are the same for both approaches – PFOS, PFNA, PFDA, PFUnDA, PFDoDA and PFTrDA. The first 4 of these were also in both TOP 10 lists for the water matrix, showing they could currently be considered as the most indicative PFAS for identifying pollution for the whole environment. The biota matrix PFAS besides the shared 4 tend to represent longer-chained compounds, indicating lower mobility in water, while higher bioaccumulation in biota.

Only one PFAS (FOSA) in Table 8 is not part of the EU PFAS 24, while this is often related to the biota matrix having a more traditional list of PFAS usually included in monitoring plans – compared to water monitoring the new PFAS are monitored from biota less often. This is also apparent in Table 9, where 4 of the TOP 10 are not part of the EU PFAS 24, with FBSA rising to 2nd place due to a 100% exceedance rate and quite high measured concentrations. The other 3 new PFAS in the list all belong to a sub-category of fluorotelomer sulfonates (4:2, 6:2 and 10:2 FTS), which should be explored further. 6:2 FTS was also in both TOP 10 lists for the water matrix.

Although the data presented in the TOP 10s is for all sampling environments at once, the results do not significantly differ if looking only at samples from the marine environment, with almost all of the substances staying the same in both tables (besides 10:2 FTS, which does not have a single reported measurement from the marine biota). The full tables showing the rankings of marine water samples only can also be found in ANNEX II of the document (Table 33 and Table 35)

5.3.2. Tissue selection for biota monitoring

The new EU proposed biota environmental quality standard for PFAS is focused on human health; therefore, it should be applied to fish muscle tissue (fillet), which can be directly correlated to fish consumption. Initially, as PFAS measurements were introduced into monitoring programs, the analytical methods had a lower sensitivity than they have today. For some monitoring programs liver was therefore chosen as a target tissue, as PFAS accumulate to a higher degree in fish liver compared to muscle (often in more than a factor 10 higher) (Figure 14). As the sensitivity of the PFAS analytical methods has increased, analysis of muscle tissue has become increasingly more common, making up around half of all the fish samples in the last ten years.

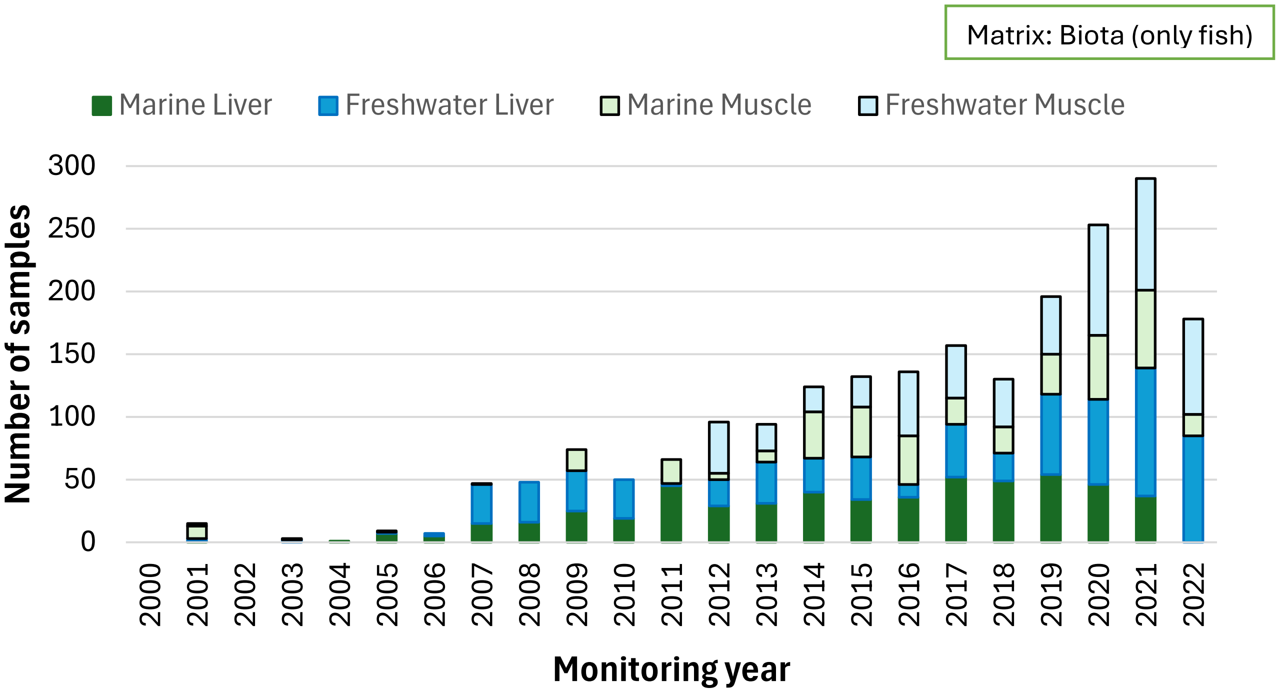


Figure 14 – Annual statistics of the specific fish tissue used for PFAS measurements

In order to use the liver observations for comparison to a threshold set in muscle, liver to muscle conversion factors are needed. Several studies [9] have shown that individual PFAS substances have different liver to muscle conversion factors. Further, there are differences in conversion factors for individual substances between fish species. This makes the conversion between the two tissues complicated, especially as the monitoring shifts focus from PFOS to cover more PFAS substances. A comprehensive list of conversion factors, separate for each PFAS and fish species, would be needed. Using muscle tissue for the PFAS analysis bypass the need for conversion factors and simplify the addition of new PFAS compounds to the assessment when needed. This will be helpful in the Baltic Sea region, where the species used in monitoring programs differ between countries and from the species used in the rest of the world.

Matrix: Biota (Marine; fish)

Table 10 – Difference in PFAS detection, threshold exceedance and LOD issues in marine fish samples according to the analysed tissue. The table shows data for all PFAS together and the TOP 10 PFAS (according to previous subchapter) individually.

	LIVER			MUSCLE			L>M	L>M
Compound	**Samples measured**	**Samples >LOQ %**	**Samples >TH %**	**Samples measured**	**Samples >LOQ %**	**Samples >TH %**	**Change >LOQ %**	**Change >TH %**
ALL PFAS	8,050	63.40	33.93	4,945	45.76	39.51	**17.64**	**-5.59**
PFOS	850	97.65	85.65	1,041	95.00	94.62	**2.64**	**-8.97**
PFNA	538	89.41	86.99	235	74.04	74.04	**15.36**	**12.95**
PFUnDA	537	93.67	86.03	232	65.09	65.09	**28.58**	**20.95**
PFDA	539	93.88	86.27	245	65.71	65.31	**28.16**	**20.96**
PFTrDA	371	85.98	22.37	163	63.80	53.99	**22.18**	**-31.62**
PFDoDA	396	85.35	21.46	243	47.74	47.33	**37.62**	**-25.86**
PFDS	678	20.65	6.64	239	18.83	17.99	**1.82**	**-11.35**
FOSA	854	89.93	34.19	81	46.91	35.80	**43.02**	**-1.61**
PFOA	542	63.28	7.56	439	35.76	18.00	**27.52**	**-10.43**
PFHxS	566	47.70	0.53	214	31.78	9.81	**15.93**	**-9.28**

A comparison between the frequency of detection of different PFAS compounds based on the analysed tissue is presented in Table 10. On average, the absolute percentage of samples quantified is about 18% larger for liver samples (which comes down to around 30% lower chance a PFAS is detected in muscle tissue). This is quite a large difference, showing that on average PFAS are still more often detected from liver tissue. Looking at individual PFAS, the difference of detection for PFOS as the highest impacting PFAS is about the same in both tissues. For other PFAS compounds, the differences vary between 2% and 43%. It would be wise not to make too direct comparisons based on the data however, as the table is not based on simultaneous measurement of both tissues from the same fish.

The table also shows how often PFAS from each tissue have been measured over the proposed new threshold value. This could give some overall indication about the different conversion factors of different PFAS, as currently only a general liver to muscle conversion factor of 17.9 was used for all substances and fish (originally determined for PFOS; [6]). Considering all PFAS, currently muscle samples show concentrations above the new threshold about 6% more often, potentially meaning 17.9 as a general factor might currently slightly underestimate PFAS in liver. The individual differences in specific compounds are much higher, giving further proof different conversion factors would be needed for each different PFAS compound.

Additional information for all reported PFAS compounds can be found in ANNEX II of the document, while for more in-depth consideration the data is presented in two tables, one for all fish samples together (Table 36) and the other for marine fish samples only (Table 37).

In summary:

- The new EU EQS proposal is based on fish muscle due to the direct link established with human health, therefore all liver concentrations need to be converted to their muscle equivalent for threshold comparison.
- The new EU EQS proposal increases the number of PFAS that need conversion factors, which is further complicated as all different fish species used for monitoring in the Baltic Sea area need their own set of conversion factors for each compound.
- The chance of detecting PFAS in muscle tissue is still lower than for liver, but the difference between muscle tissue has been decreasing with advancements in analytical sensitivity.
- Though the PFAS detection from muscle tissue might be less frequent, compared to the complications of tissue conversion, the recommendation is to focus on muscle as the primary tissue moving forward, while work on creating conversion factors should continue to enable the use of older liver data in monitoring time series for trend detection.

5.3.3. Spatial distribution of PFAS from biota samples

The spatial distribution of the biota samples is displayed on Figure 15. Compared to the water samples distribution (Figure 7), biota data does have a fair number of samples also collected from the open sea areas of the Baltic. Also obvious in comparison between the two matrices, is how often biota samples exceed the new proposed EU threshold, which has been discussed in-depth in the previous sub-chapters.

The <LOD samples are much rarer in the biota matrix, while a few earlier measurement campaigns in mainly Estonia and Latvia still suffer from the analytical issue of used LOD values being higher than the new proposed threshold. Therefore, some of the local data mainly about freshwater biota is inconclusive for those areas.

The overall distribution of samples is quite well spread, while based on the map, very high threshold exceedances are more commonly found in Sweden and Finland. Although the specific number of different PFAS compounds included in each sample is not shown on the map, Swedish samples did in general did have higher number of measured PFAS compounds. Including more substances into a sum value is expectedly also increasing the final result, driving the assessment even more over the threshold. On average, each sample included around 10 of the 24 PFAS. Based on the main driver compounds for PFAS pollution in biota, the future monitoring should maybe focus on 6-7 key “legacy” PFAS, plus a few upcoming newer substances identified with screening campaigns to make sure industrial substitutions are not missed when assessing pollution.

Comparing the different species groups, birds (bird eggs) in general had all samples exceed the new proposed threshold, despite a trophic factor of 10 applied to all samples. This might either indicate, that further factors are needed to compare birds in the similar system as fish, or that there is a higher accumulation of PFAS in bird eggs than for other species groups. The mammals group mainly included three different species (T*arandus tarandus, Lutra lutra* and *Phocoena Phocoena*), which compared to the bird samples had a much more varied result. All reindeer samples and one harbour porpoise sample were assessed to be under the threshold (after a multiple conversion factors were applied), while all other samples were on average about 10 times over the threshold.

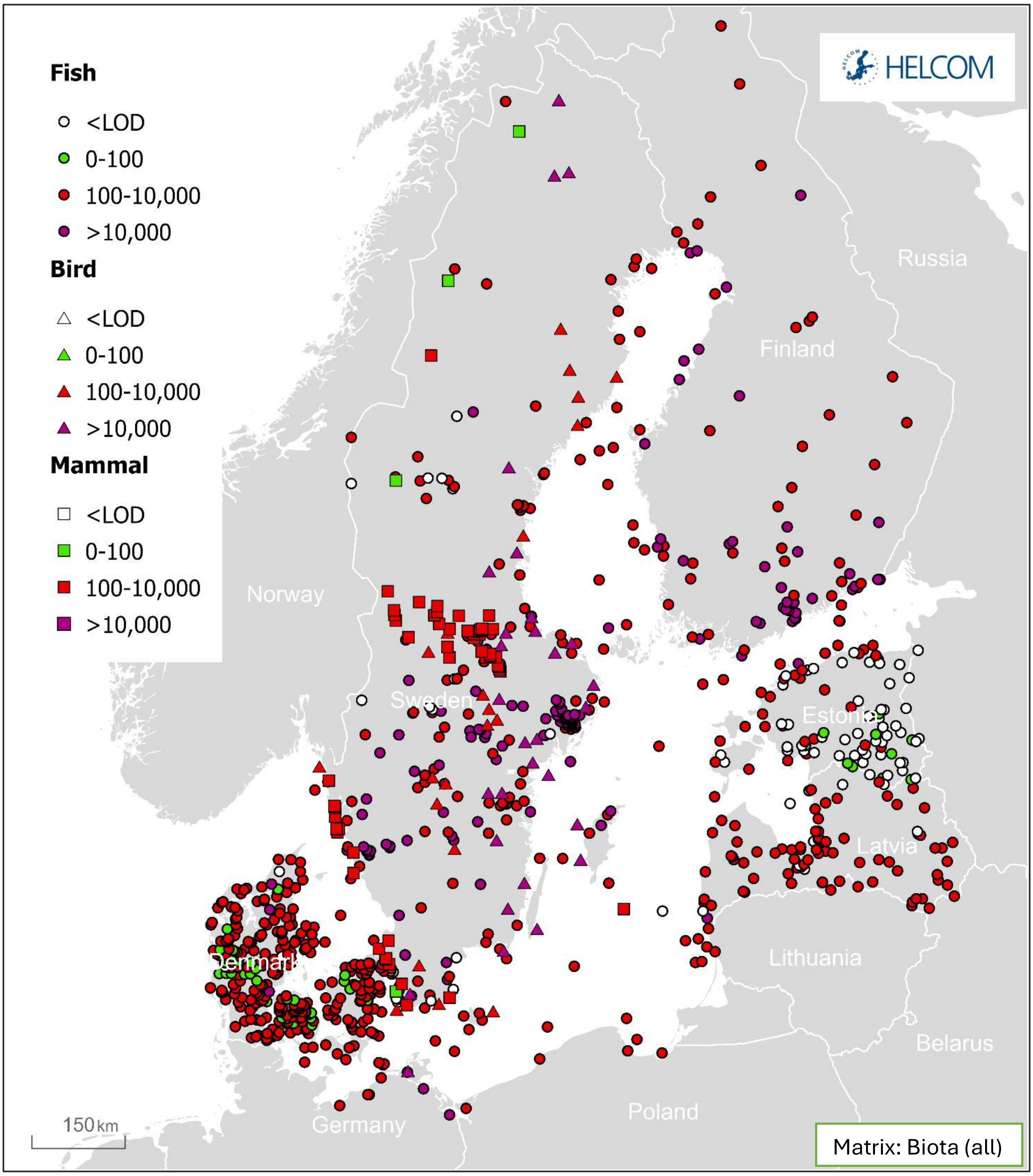


Figure 15 – Geographic distribution of the summed results of all measured PFAS in the biota matrix. Only the latest sample from each location is shown. The colours correspond to the new proposed threshold of 0.077 µg/kg ww PFOA equivalents, with red samples over the threshold value and purple samples over threshold value more than 100 times. Samples marked <LOD are not necessarily under the threshold value due to LOD sensitivity issues in older data.

It is important to note that the new biota EQS proposed by EU (0.077 µg/kg ww) is much stricter than the previous one (9.1 µg/kg ww) used for HOLAS 3, and now applying to a sum of 24 compounds, instead of just

PFOS. This means that all the assessment units in the Baltic Sea would greatly exceed the new threshold and be in a bad environmental status. Overall, this drastically changes the PFAS assessment presented at HELCOM so far and indicates there is a great need for action in order to make sure the general health of the Baltic Sea ecosystem, as well as the 85 million people living in the catchment area would stay properly protected.

5.3.4. Biota sample trends in monitoring stations

As for the water matrix, biota samples were also grouped together into unofficial "monitoring stations" based on the sample locations, with more information about the method discussed in Chapters 4.2 and 5.2.3. All different biota samples were included in this analysis, while each monitoring station has only one type of species included – fish, bird eggs, mammals or others. This was done to make sure trophic conversion factors used for this sample assessment would not influence the general trends.

Matrix: Biota (all)

Table 11 – Overall status and direction of trends in unofficial biota "monitoring stations"

Confidence	Trend	Total	Stream	Lake	Marine
	Stations with no PFAS quantified	6	4	1	1
	Stations with no apparent trends	88	4	38	43
HIGH	Stations with DECREASING PFAS conc.	61	17	11	33
HIGH	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	8	1	4	3
HIGH	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	68	26	28	14
MODERATE	Stations with DECREASING PFAS conc.	10	0	1	9
MODERATE	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	2	0	2	0
MODERATE	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	6	1	2	3
LOW	Stations with DECREASING PFAS conc.	11	0	6	5
LOW	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	3	0	1	2
LOW	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	7	0	4	3
	Total stations	270	53	98	116

The trends in biota are presented in Table 11 with all the relevant confidence assessments and on Figure 16 in a simplified form without the confidence values. While monitoring stations representing streams and rivers were the most common in the water matrix, for biota nearly half of the 270 monitoring stations represented the marine environment (116). About a third of all stations displayed no trend, with another third showing increasing and the last third decreasing concentrations. In marine environment, decreasing trends make up 41% of all stations with only 21% of stations showing increasing concentrations, which could indicate a positive sign. A similar generally decreasing trend was also seen on Figure 12 for all biota samples measured, while this was not apparent when fish samples were assessed separately.

Looking at the specific locations of the stations with decreasing trends however (Figure 17), the decreases seem to be more commonly related to southern parts of the Baltic Sea with northern part showing more increasing trends. Decreasing concentrations are also seen in the coastal stations around Finland and Estonia, with stable or increasing trends in the open sea areas. As blatantly visible form the red colour on the map, almost all biota monitoring stations have had threshold exceedances, with three green points in Sweden representing reindeer monitoring stations. High concentrations of PFAS were detected from those liver samples as well, but multiple different conversion factors were applied (trophic conversion factor of 100 and liver to muscle conversion factor of 17.9, which was designed for PFOS in fish), bringing the results under threshold value. Besides those 3 reindeer stations, 3 harbour porpoise stations were also included, while those stayed red despite the conversion factors applied, two of them displaying additional increasing and one decreasing concentrations.

The overall confidence of the trends was much higher than for water samples. As with water samples, most of the increasing trends were not related to an increase in the number of PFAS compounds measured.

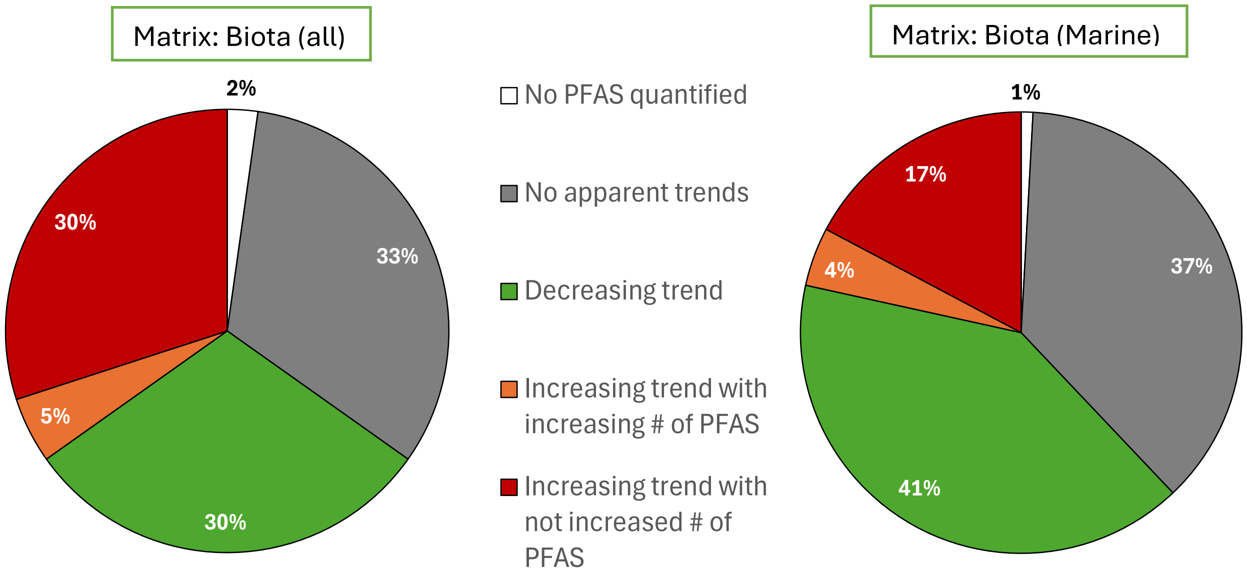


Figure 16 – Overall temporal trends in biota samples based on unofficial monitoring stations in lakes, streams and marine environment (left side) and in marine environment only (right side)

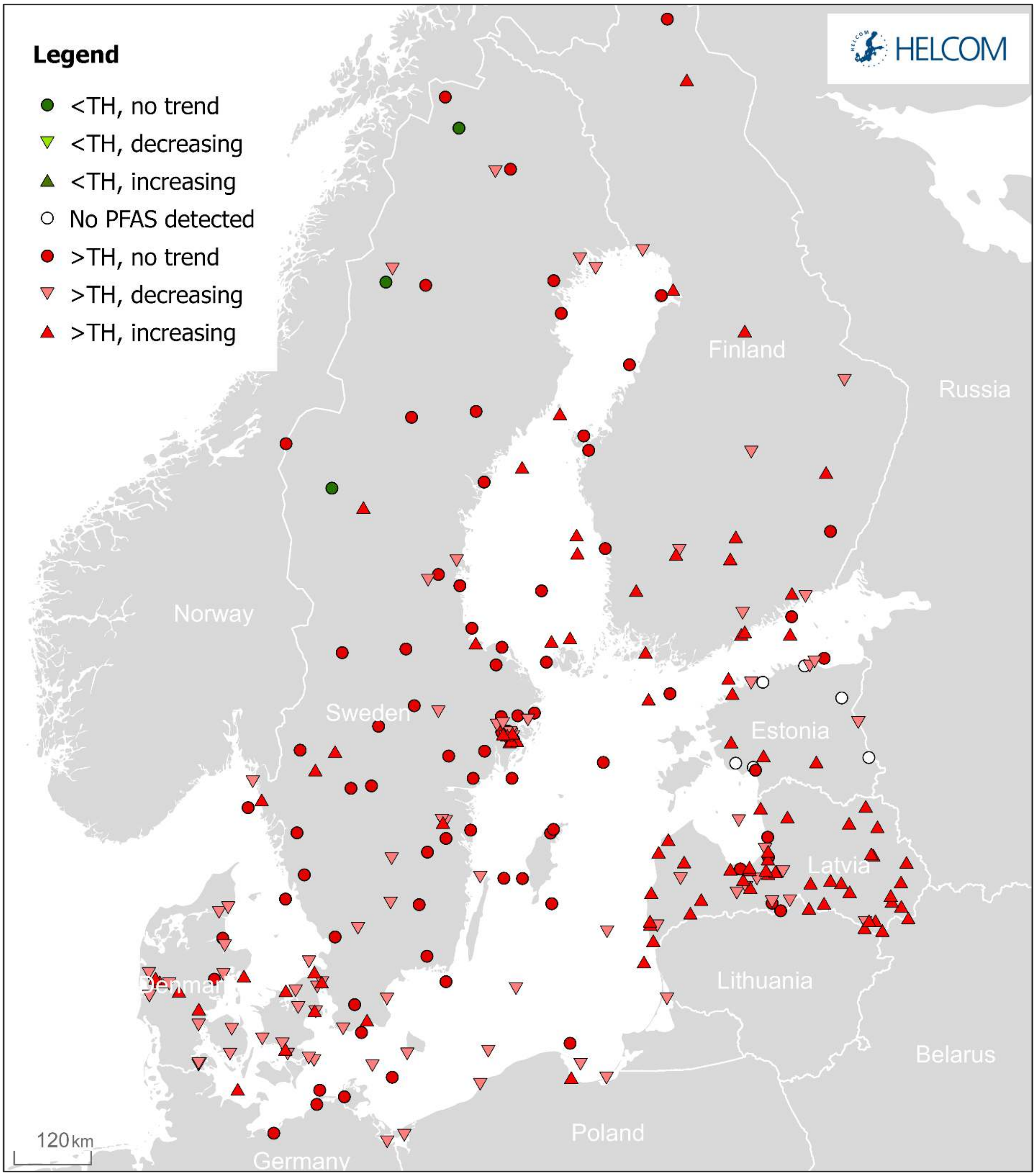


Figure 17 – Direction of trends in the biota matrix for monitoring stations with at least 2 different years of data included in the database. The red and green colours indicate if any of the samples in the station have exceeded the new proposed EU EQSD threshold (TH) value of 0.077 µg/kg ww for a sum of PFAS (sum of all measured PFAS included).

5.4. Sediment matrix

Compared to the water and biota matrices, the sediment matrix is not often considered when talking about PFAS – there are not even any widely accepted threshold values for sediments. Even the new EU EQS update does not propose anything for sediments, which makes the assessment of the sediment matrix very complicated.

PFAS sediment values have though been in discussion and one of the latest has been the 18 August 2022 scientific opinion paper from the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER), which endorses a proposed threshold for 13.5 µg/kg dw for PFOS for a sediment with 5% organic carbon (OC). The opinion also states that further thresholds are needed for other PFAS, and scientific sediment studies need to be further evaluated to verify these conclusions.

Until a more scientifically and politically backed threshold for sediments is proposed or legislated, the 13.5 µg/kg dw with 5% OC for PFOS will be proposed to be used as a basis for the sediment matrix assessment. Although the toxicity mechanisms are completely different for this matrix compared to water and biota, for the example assessment presented here the RPF system will be used for the sediment matrix as well, mainly to be able to make the assessment comparable to the other matrices. As the RPF system is based on PFOA equivalents and PFOS has a RPF value of 2, the sediment assessment will use a placeholder threshold value of 27 µg/kg dw for the sum of PFAS in PFOA equivalents. Unfortunately, most of the monitoring data collected for the sediment matrix did not include any supporting parameters on the organic carbon content, which further decreases the validity of this assessment.

The database used for the assessment included a total of 11,473 data points, divided into 908 unique sediment samples. Similar to other matrices, most of the samples were from freshwater sources (Figure 18), and about 30% of the samples were taken from the marine environment. The 18 samples from WWTPs were from a 2012 Estonian study on treated wastewater sludge, which are excluded from the further assessment in this sub-section.

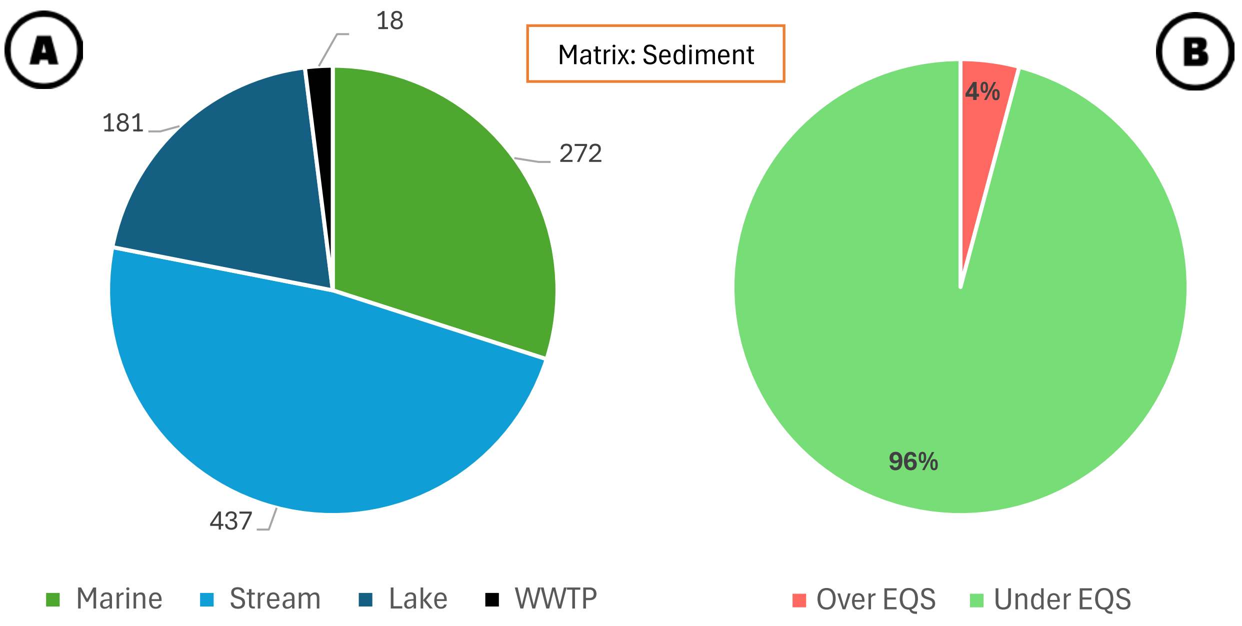


Figure 18 – Distribution of environmental monitoring samples for the sediment matrix (A) and threshold exceedance frequency of all reported sediment samples (B). All measured PFAS in each sample were summed according to the RPF system.

Applying the SCHEER endorsed threshold similarly as the RPF-based system for a sum of PFAS, only about 4% of all sediment samples were exceeding the threshold value. Interestingly, most of the sediment exceedances were measured from marine sediments (Table 12), with about 10% of the samples over the potential threshold. Sediments from streams and lakes exceeded the threshold very rarely, for about 1% of the samples.

Table 12 – Threshold exceedance of biota samples based on the sum of 24 PFAS/sum of all PFAS (in PFOA equivalents, different only for lake samples), divided by the sampling environment. The SCHEER endorsed PFOS threshold was used together with the RPF-based system of other matrices.

	Marine	Rivers/streams	Lakes	Total
# of samples	272	437	181	890
# over threshold	29	5	2/3	36/37
% over threshold	10.7%	1.1%	1.1/1.7%	4.0/4.2%

The regular sediment monitoring for PFAS started mostly in 2014, with a few random samples from 2007 and 2008 with all reported concentrations under LOD. There are two additional earlier samples, one from 2009 and the other from 2011, while the assessment will focus on the period of 2014-2022.

Figure 19 represents the yearly average concentrations and sample amounts for freshwater (A) and marine samples (B). Contrary to similar figures in water and biota sections of the document, the average concentrations displayed in the figures do not exceed the proposed threshold. This could partly be due to the PFAS pollution not having a strong presence in sediments yet, or due to the applied threshold not having complete scientific packing yet. The chosen threshold for the sediment assessment is displayed on the figures as a red line, while only freshwater samples from 2015 are exceeding that by a small amount when RPF factors are used. For absolute concentrations, the average yearly concentrations did not exceed the thresholds on any of the years. As presented in Table 12, there were only a total of 37 sediment samples exceeding the proposed threshold out of the whole dataset.

It is also clear from the figures that there are large variations in the reported data for different years, including very high variations on how many different substances have been measured. Therefore, no time-trends can be found in sediment PFAS results. The only major visual trend can be seen in comparison between freshwater and marine samples – though freshwater samples have more measurements, the measured concentrations have been consistently low (besides a peak in 2015, mostly caused by a single Swedish lake sediment sample). For marine samples, the detected sediment concentrations are much more varying and might be expected to increase in the future due to PFAS in biota sedimenting in the Baltic Sea. Similar spikes in concentrations are visible for multiple years, while these are all open sea samples often from non-urban environments. Most of these high concentration samples have been measured from Bothnian Bay area, which is further explored in sub-chapter 5.4.2.

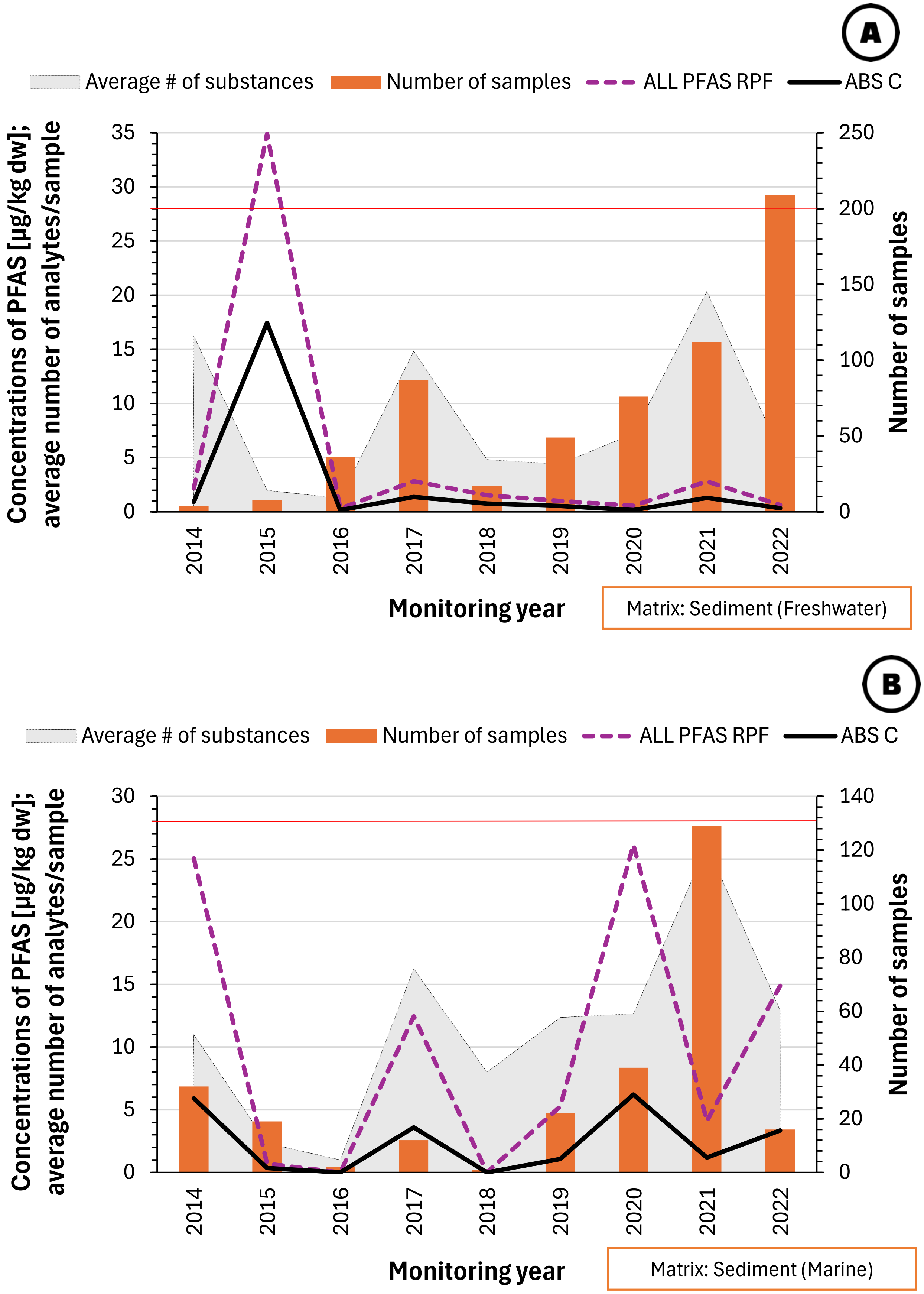


Figure 19 – Time-trends for different PFAS sum parameters in A - freshwater (lakes and rivers) and B – marine samples. Two different sum parameter concentrations are represented with different lines. Gray area on the background indicates the number of different PFAS compounds on average included in samples each year and orange columns the total number of samples included that year (corresponds to secondary y-axis). Potential threshold of 27 µg/kg dw is indicated on both figures as a red line.

5.4.1. Key PFAS in the sediment matrix

To assess which of the PFAS compounds individually has the highest influence in the sediment matrix, the TOP 10 PFAS based on two different statistical approaches are presented in Table 13 and Table 14. Full tables, showing the ranking of all reported PFAS can be found in ANNEX II of the document.

Matrix: Sediment

Table 13 – TOP 10 PFAS from all sediment samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFNA	621	133	12.74	6273.33	38.81	38.81
PFOS	861	424	3.80	5972.67	36.95	75.76
PFDA	620	160	2.61	1549.62	9.59	85.34
PFUnDA	511	214	1.61	1278.81	7.91	93.25
PFOA	738	154	0.76	431.01	2.67	95.92
N-EtFOSAA	137	10	4.30	159.31	0.99	96.91
PFDoDA	440	88	0.30	96.73	0.60	97.50
PFTrDA	256	125	0.20	90.57	0.56	98.06
N-EtFOSE	194	15	1.53	85.25	0.53	98.59
PFHpA	447	53	0.25	48.49	0.30	98.89

Matrix: Sediment

Table 14 – Top 10 PFAS measured from sediment samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into how often a compound has been measured and total impact of a compound for the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (µg/kg PFOA)	Average TH exceedance amount (%)	Rank
PFNA	621	25	4.03	12.74	47.17	1
N-EtFOSA	191	0	0	5.50	20.37	2
PFOS	861	6	0.70	3.80	14.09	3
N-EtFOSAA	137	0	0	4.30	15.93	3
N-MeFOSAA	137	0	0	3.17	11.76	5
PFDA	620	0	0	2.61	9.69	6
N-MeFOSE	191	0	0	2.22	8.22	7
10:2 FTS	137	0	0	2.10	7.78	8
PFUnDA	511	0	0	1.61	5.98	9
N-EtFOSE	194	0	0	1.53	5.68	10

As in previous subchapters, these two approaches use a threshold value as a basis (here the threshold of 27 µg/kg dw PFOA equivalent is used), while it is important to note that the order of substances in the first approach is not dependant on the threshold used, while the ranking in the second approach would change partially (due to different exceedance frequency) with another threshold value applied. Both approaches rely on the RPF system though, which might not find use in the future for the sediment matrix.

Considering both TOP 10 PFAS, PFNA is clearly the biggest current driver of PFAS pollution in the sediment matrix, while it does have and RPF factor of 10, greatly boosting the results. A total of 6 substances are on both lists (PFNA, PFOS, PFDA, PFUnDA, N-EtFOSAA, N-EtFOSE), showing clearly that the sediment PFAS are currently dominated by long-chain PFAS. Looking at the differences between the two approaches, it could be proposed that PFOA, PFDoDA, PFTrDA and PFHpA currently have a measurement frequency bias, which increases their cumulative impact, while N-EtFOSA, N-MeFOSAA, N-MeFOSE and 10:2 FTS have on average higher concentrations in the sediment samples but are on average measured 3 times less frequently. In general, it is concerning that many potentially relevant PFAS compounds for sediments are not the ones included in the EU PFAS sum of 24, which although proposed for water and biota matrices, will most probably become the common “standard” for most PFAS analysis in the coming years.

Looking at the marine sediment samples separately, most of the top substances stay the same and in similar rankings, while the different FOSE/FOSA/FOSAA substances are on average placed lower than for all sediment samples together. Unfortunately, the amount of data is not sufficient to propose a significant difference between the different PFAS sedimenting in lakes/rivers and marine environment, while this subgroup differs the most between the two datasets. The full tables showing the rankings of marine sediment samples only can be found in ANNEX II of the document (Table 39 and Table 41).

5.4.2. Spatial distribution of PFAS from sediment samples

The spatial distribution of the sediment samples is displayed on Figure 20. Compared to the water and biota, the sediment samples do not currently show a high spread of PFAS pollution, with most of the freshwater samples having no PFAS detected from them. While the <LOD points for biota and water are often connected with uncertainty due to historical measurements not having enough sensitivity compared to the new thresholds, this does not seem to be a problem currently for the sediment samples. Of course, this is partly due to the fact sediment currently does not have a strict threshold value. Still, compared to the PFOS threshold of 13.5 µg/kg dw (and the PFOA threshold of 27 µg/kg dw created based on that), only a handful of samples had LODs higher than that. Therefore, most of the <LOD points on the sediment map truly indicate the related sediments should have very low environmental concentrations and are surely under the endorsed threshold.

The marine samples for sediments include both coastal and open sea areas, which is better than the distribution of samples in the water matrix. The open sea samples are the most interesting for sediment, as almost all of the open sea samples taken from Bothnian Bay are over the threshold value. This is especially important trend. as the samples have been taken on multiple different years and by both Finland and Sweden, meaning the chances for sampling or analytical errors are very low. Multiple of these samples have also been marked as non-urban environment background samples, indicating a possible sub-basin-based pollution problem in the whole Bothnian Bay. As almost all biota samples show high concentrations and water samples have not been taken from the open-sea areas, it is difficult to say if this means Bothnian Bay in general has a higher PFAS problem than most other Baltic Sea sub-basins, or if the higher sediment concentrations indicate historic pollution points sources, that are not present today.

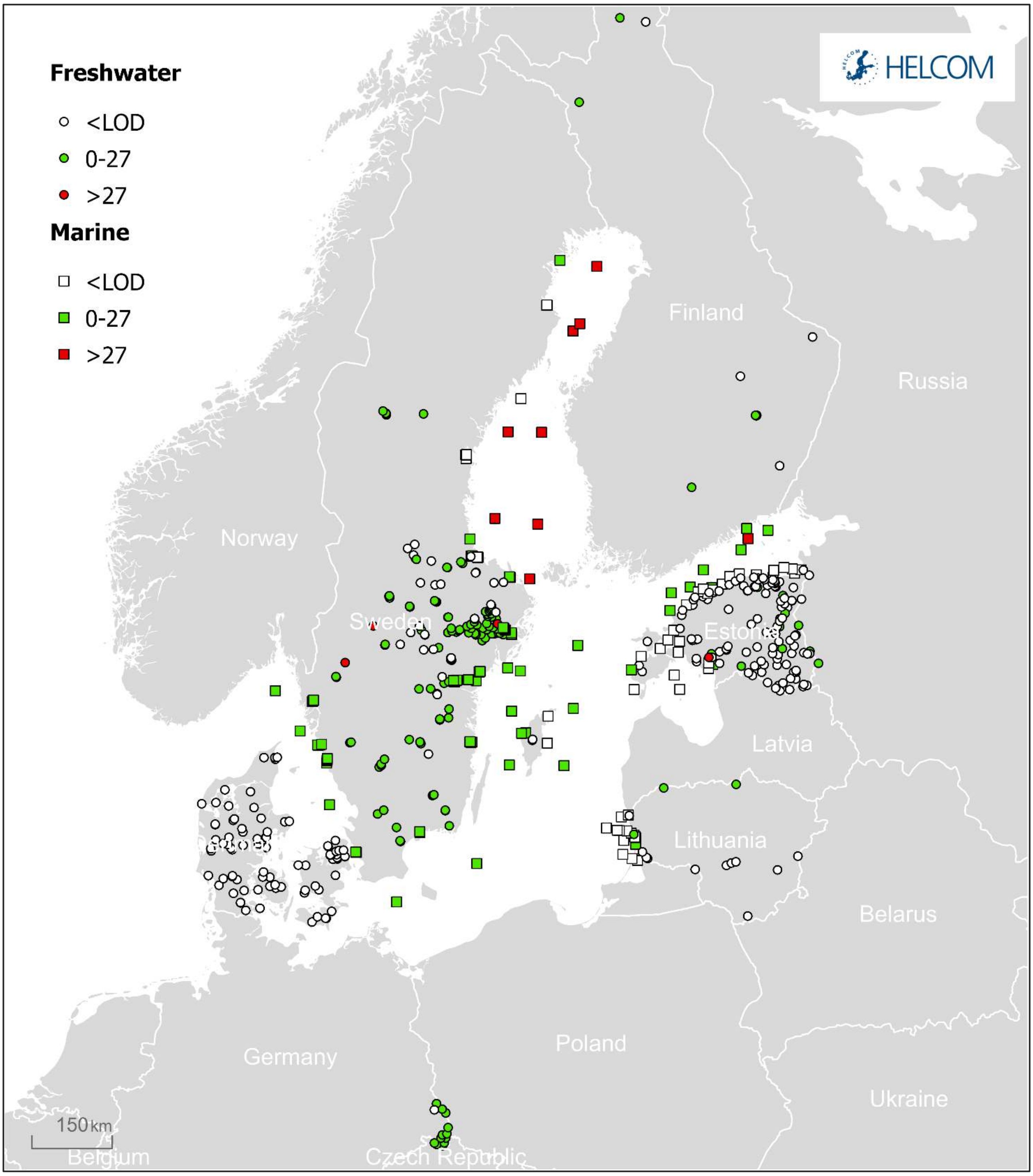


Figure 20 – Geographic distribution of the summed results of all measured PFAS in the sediment matrix. Only the latest sample from each location is shown. The colours correspond to a potential threshold (27 µg/kg) endorsed for PFOS but used together with the RPF-based system of the other matrixes to apply for the sum of all PFAS. Samples marked <LOD have not had a single PFAS compound measured over their respective limit of detection (LOD) values.

5.4.3. Sediment sample trends in monitoring stations

Similar to the previous subchapter for water and biota samples, the grouping into unofficial "monitoring stations" were done for sediment samples as well. A total of 72 "stations" could be detected for sediment samples, which each had at least 2 samples from different years reported to the database. The trends for sediments were calculated based on PFOA equivalent concentrations, without using a threshold value, which should allow assessing the potential trends even without a definite quality standard. Therefore, the trends only show if the concentrations seem to be increasing in the station or not.

Matrix: Sediment

Table 15 – Overall status and direction of trends in unofficial sediment "monitoring stations"

Confidence	Trend	Total	Stream	Lake	Marine
	Stations with no PFAS quantified	25	15	1	9
	Stations with no apparent trends	25	10	3	12
HIGH	Stations with DECREASING PFAS conc.	9	0	4	5
HIGH	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	4	2	2	0
HIGH	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	7	1	0	6
MODERATE	Stations with DECREASING PFAS conc.	1	0	0	1
MODERATE	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	0	0	0	0
MODERATE	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	0	0	0	0
LOW	Stations with DECREASING PFAS conc.	1	1	0	0
LOW	Stations with INCREASING PFAS conc. & INCREASING of number of PFAS measured	0	0	0	0
LOW	Stations with INCREASING PFAS conc. & not increased number of PFAS measured	1	1	0	0
	Total stations	72	29	10	33

The trends for the sediment samples of different sampling environments are displayed in Table 15 and the summary on Figure 21. A very large section (34% of all samples) of the sediment samples have no measured PFAS from them, while another third has no apparent trends appliable. The last third has about equal distribution of increasing and decreasing trends, most of which are marine sediment samples.

In general, the confidence of the trends in sediment are high, while it is often because only 2 different samples are included for the stations (and linear regression between two values is always with a high statistical confidence). This was not a recurring problem for water and biota samples, where most monitoring stations had multiple different samples from different years.

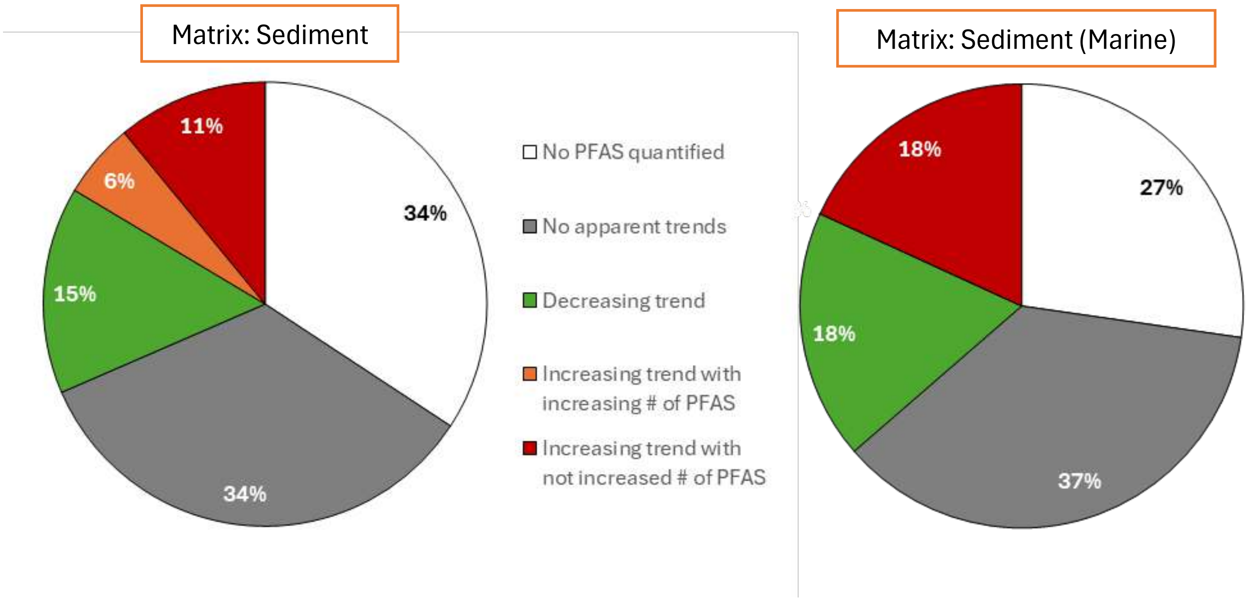


Figure 21 – Overall temporal trends of sediment samples based on unofficial monitoring stations in lakes, streams and marine environment (left side) and in marine environment only (right side)

The geographic distribution of the stations is displayed on Figure 22. Similar to the overall sample distribution map in the previous sub-section, most of the stations showing exceedance have been gathered in the Bothnian Bay. From the few stations in the sub-basin, it seems the concentrations of PFAS in the sediments are still increasing in the northern part of the Bothnian Bay, while southern parts near the Archipelago Sea are showing decreasing trends. This might indicate a PFAS pollution source or pathway into the northern part of the sub-basin, while there is not enough information to support a stronger statement.

Outside of the Bothnian Bay, increasing concentrations in sediment samples can also be seen for some coastal monitoring stations and a few freshwater sediment samples, while none of them are over the proposed threshold used in this assessment. The only other stations over the proposed threshold are a few freshwater stations around the German-Polish border, in the area of Saxony, while one of the two stations is showing stable and the other one decreasing concentrations.

Interestingly, Estonia has the highest number of sediment stations from freshwater sources, indicating the same locations have been used for samples on multiple different years. Compared to Figure 20, both Sweden and Denmark also have a lot of sediment samples reported in the database, but almost none of those relate to monitoring from multiple different years. Therefore, the station map has no points for Danish freshwater sediment monitoring and only a few rare points for Sweden.

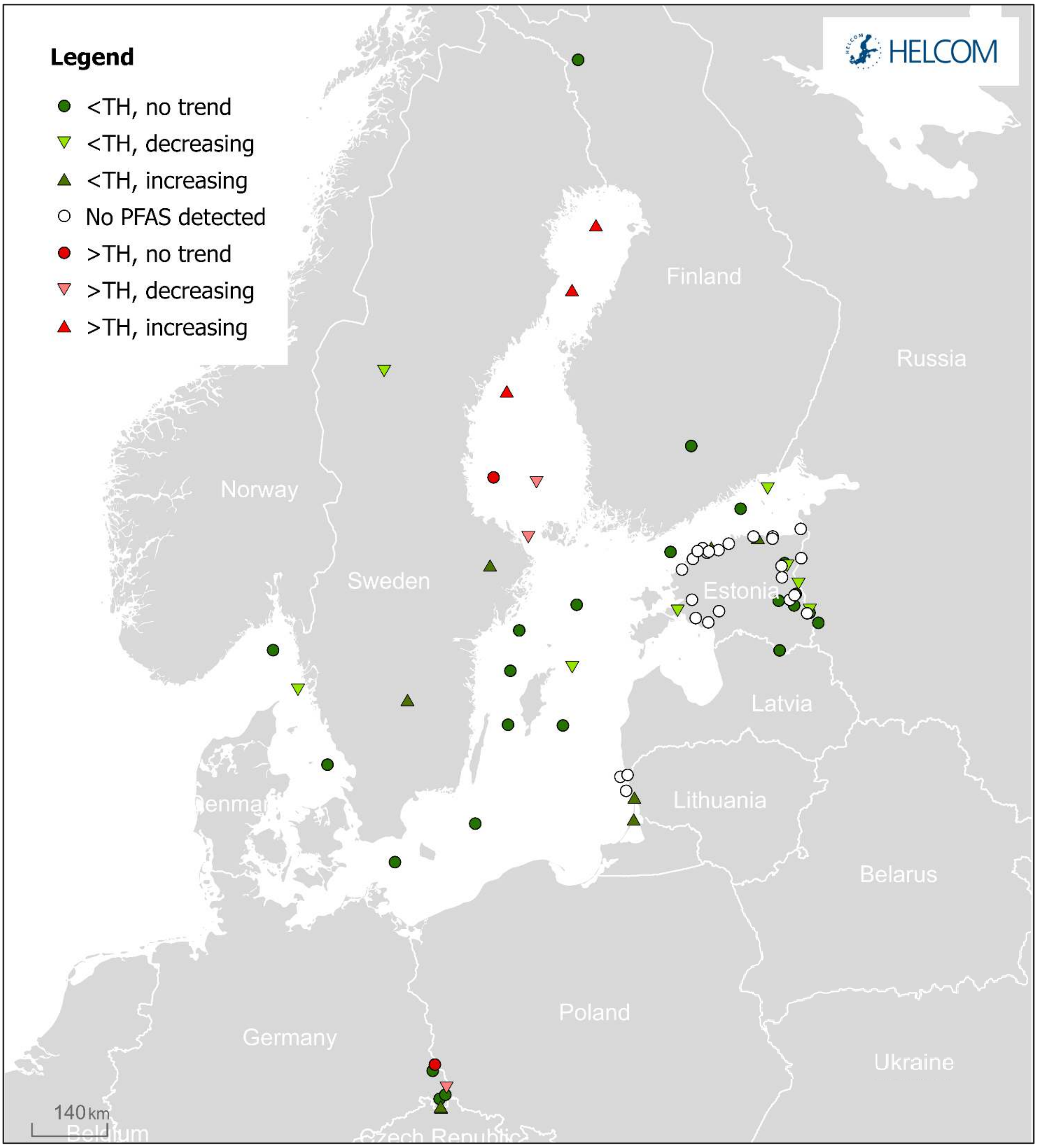


Figure 22 – Direction of trends in the sediment matrix for monitoring stations with at least 2 different years of data included in the database. The red and green colours indicate if any of the samples in the station have exceeded the applied preliminary threshold value of 27 µg/kg dw for a sum of PFAS (sum of all measured PFAS included).

Part C – Additional results from EMPEREST piloting

6. Piloting overview

6.1. Description of activities

Based on some of the preliminary gaps in data identified based on the initial rounds of EMPEREST PFAS data call analysis, three EMPEREST project partners carried out additional sample taking and analysis based on the monitoring guidelines included in the deliverable 1.1. The collection of marine samples was often done in collaboration with respective national authorities, while collected samples were sent to commercial laboratories, for their largest available selection of PFAS to be analysed. Following key gaps were targeted:

a) Berlin University of Technology (TUB) collaborated with the national sampling authority in Germany, to collect and analyse additional marine water samples, focusing on a large selection of PFAS compounds previously not analysed or not frequently analysed from marine samples (Figure 23).
  - 18 water samples (4 estuaries, 14 marine) were collected and analysed
  - 1 reference sample from River Havel in Berlin (outside Baltic Sea catchment)
  - All samples were taken in the same timeframe
  - 57 PFAS compounds were analysed from each sample

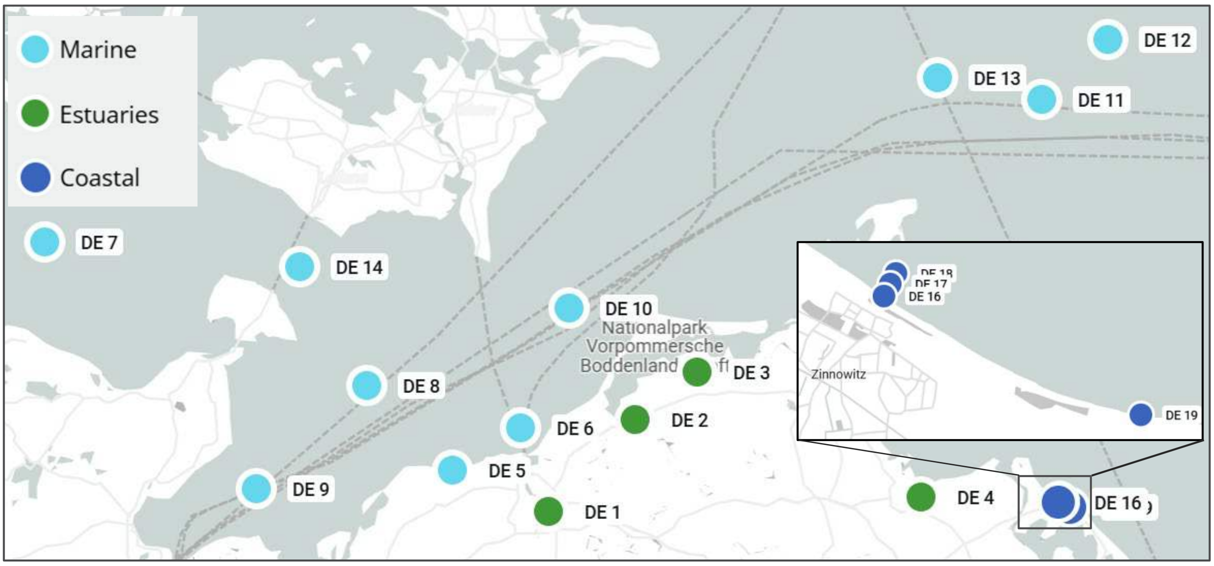


Figure 23– Locations of water samples collected by the Berlin University of Technology, with one section of the map having partial zoom-ins to better display some sample locations. Sample 15 is not displayed on the map as it was taken from a river in Berlin

b) University of Tartu (UT) collaborated with the national sampling authority in Estonia, to collect and analyse additional biota samples from the Baltic Sea, focusing also on a large selection of PFAS compounds, that have only lately become available or have not been analysed as often before (Figure 24).
  - 16 biota samples were collected and analysed (8 perch, 4 herring, 4 flounders)
  - All samples were collected at the same season
  - 50 PFAS compounds were analysed from each sample

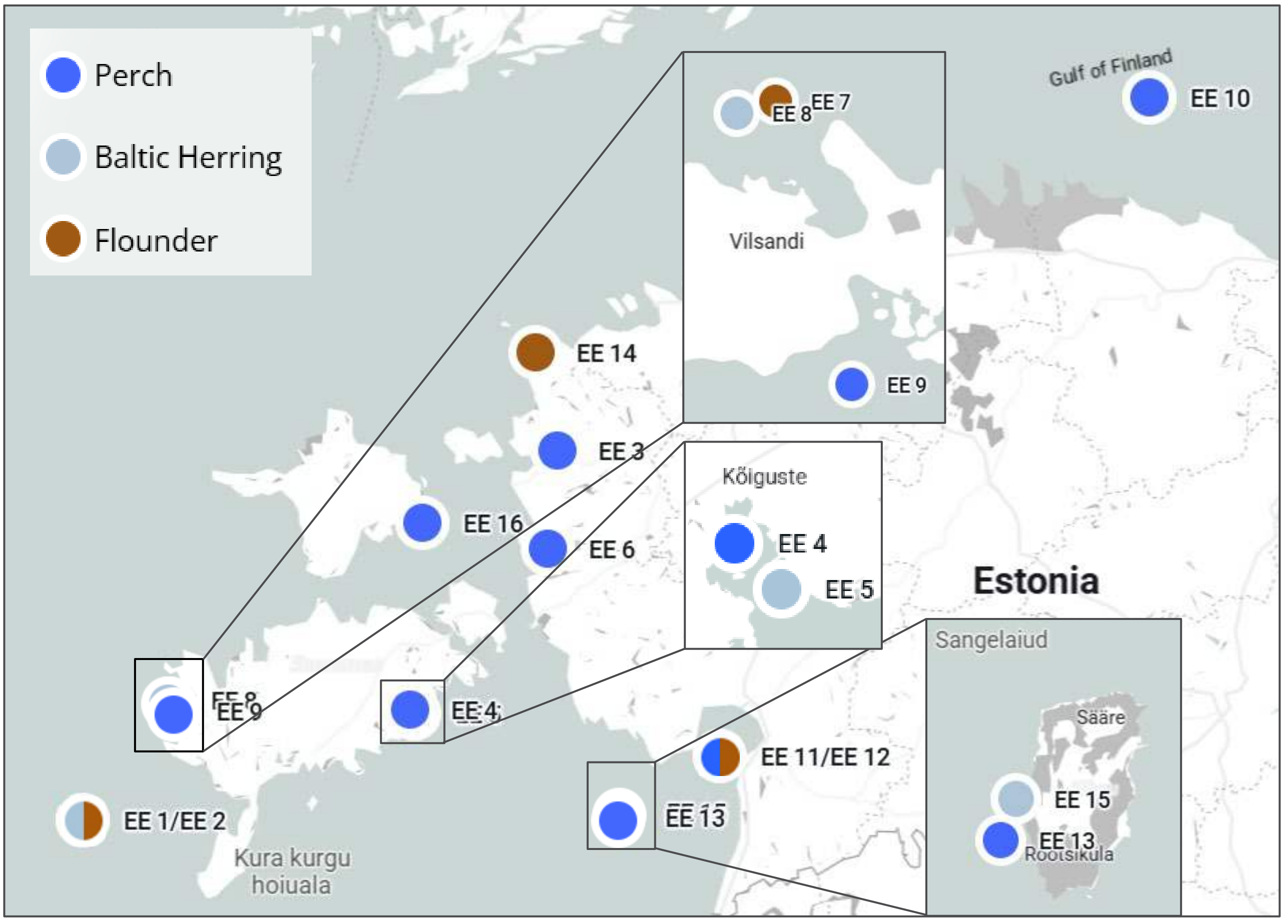


Figure 24 – Locations of biota samples collected by the University of Tartu. Colours of the sample points indicate the sampled species, with three sections of the map having partial zoom-ins to better display some sample locations. In some cases, different fish were caught at the exact same location, which is then indicated in two sample numbers and two colours.

c) Turku University of Applied Science (TUAS) carried out water sampling in different streams entering Turku Archipelago Sea and biota sampling in the Archipelago Sea, focusing on the interaction between different water environments and seasonality (Figure 25).

- 18 water samples were collected from the streams, from 6 different locations
- 10 marine water samples were collected from 5 different locations
- 5 additional water samples were collected from ditches and stormwater channels
- 5 composite perch samples were collected from the Turku Bay
- 51 PFAS compounds were analysed from each biota and water sample

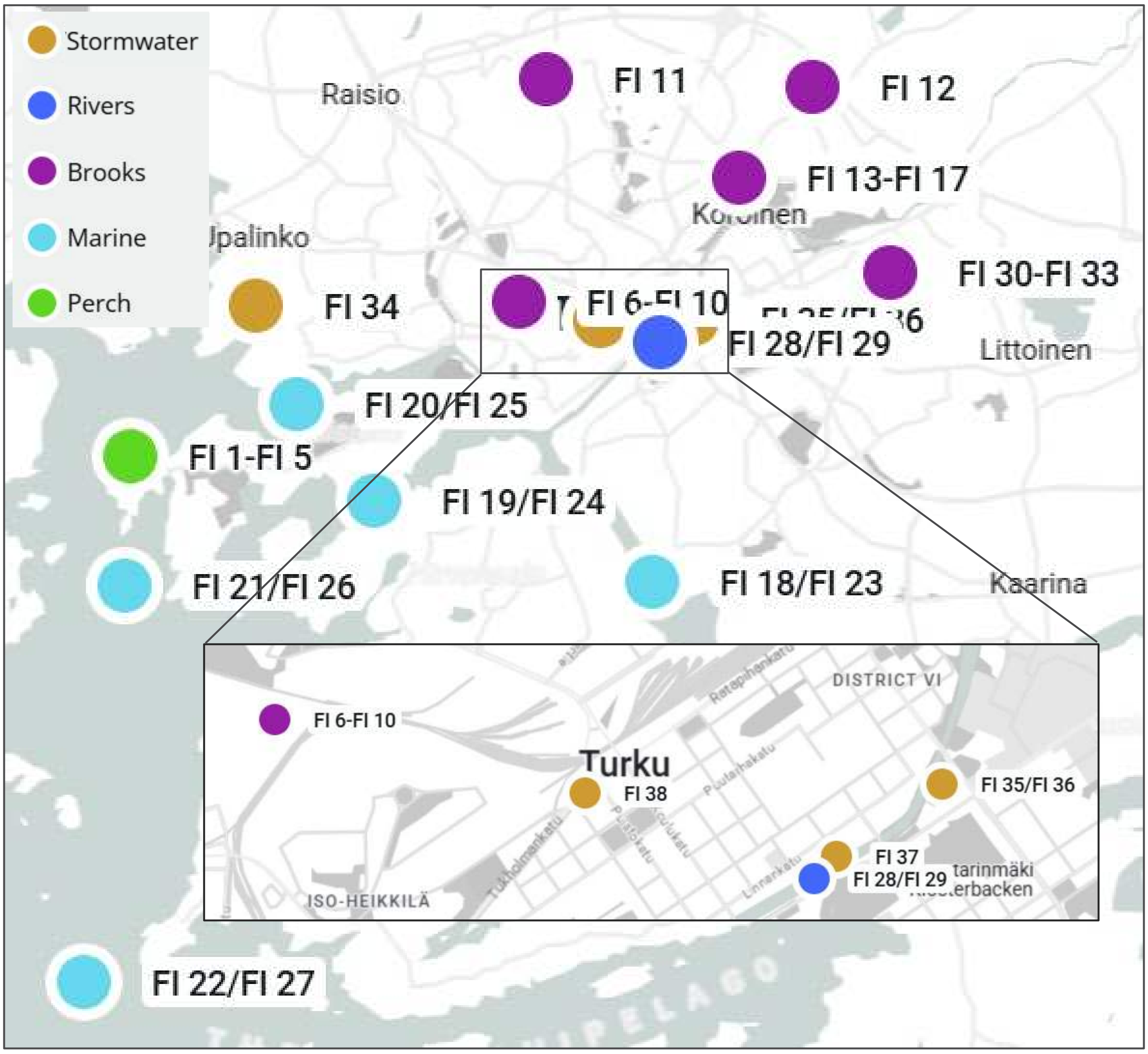


Figure 25 – Locations of water and biota samples collected by the Turku University of Applied Sciences. Colours of the sample points indicate the sample matrix and environment, with one section of the map having partial zoom-ins to better display some sample locations.

The analysis also included 6 new PFAS compounds (Table 16), that had not been reported in the monitoring database previously. This also means these new compounds were not part of the literature review for precautionary RPF allocation. Therefore, as information about their transformation products is not known, for the analysis of piloting results, they have been given an RPF value of 1 as a precaution.

The inclusion of these new compounds indicates a trend in PFAS analysis focusing more and more on short-chained PFAS – all the new PFAS besides HFPO-TA have only 2-4 fluorinated carbon atoms. At the same time, all the new PFAS besides PFPrS belong to a sub-group of perfluoroether (acids), which means the carbon chains have been interrupted with oxygen atoms, making the new PFAS structures quite complicated. Gen X or HPFO-DA is also part of the same subgroup. This is once again emphasising the importance of a broader PFAS approach, as these substances again represent market substitutions to known and restricted PFAS. Thankfully, only PFMPA of these 6 new compounds was actually detected in environmental samples and low concentrations (average of 0.3 ng/L), indicating these substances should not be prevalent in the environment yet.

Table 16 – Information about the new PFAS compounds included in the piloted sample analysis

#	Substance name	Acronym	Alternative acronyms	CAS-number	Grouping	OF % in mass	RPF
67	Perfluoropropanesulfonic acid	PFPrS		423-41-6	Sulfonic acid	53.18	1
68	Perfluoro-3,6-dioxaheptanoic acid	NFDHA	PFDHA	151772-58-6	Ethercarboxylic acid	57.76	1
69	Perfluoro-4-methoxybutanoic acid	PFMBA	PFMOBA	863090-89-5	Ethercarboxylic acid	61.06	1
70	Perfluoro-3-methoxypropanoic acid	PFMPA	PFMOPrA	377-73-1	Ethercarboxylic acid	57.81	1
71	Perfluoro-2,5-dimethyl-3,6-dioxanonanoic acid	HFPO-TA	PFO2NA	13252-14-7	Ethercarboxylic acid	65.11	1
72	Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA		113507-82-7	Ethersulfonic acid	54.09	1

6.2. Summary of piloting results

6.2.1. Overall results

For the water matrix piloting, samples were collected from different mediums, including samples from rivers, brooks, estuaries, coastal areas and open sea areas. The German samples are presented on Figure 26. Interestingly, as a larger group of PFAS than the EU 24 were measured, all water samples (besides river Havel) were under the threshold for the 24 PFAS, while multiple would be over the threshold considering more different compounds. There is also a clear trend showing higher average concentrations in river estuaries, slightly lower concentrations in the immediate coastal areas and even lower in the marine samples, which is in line with the estimate that rivers are the main sources of PFAS entering the marine environment.

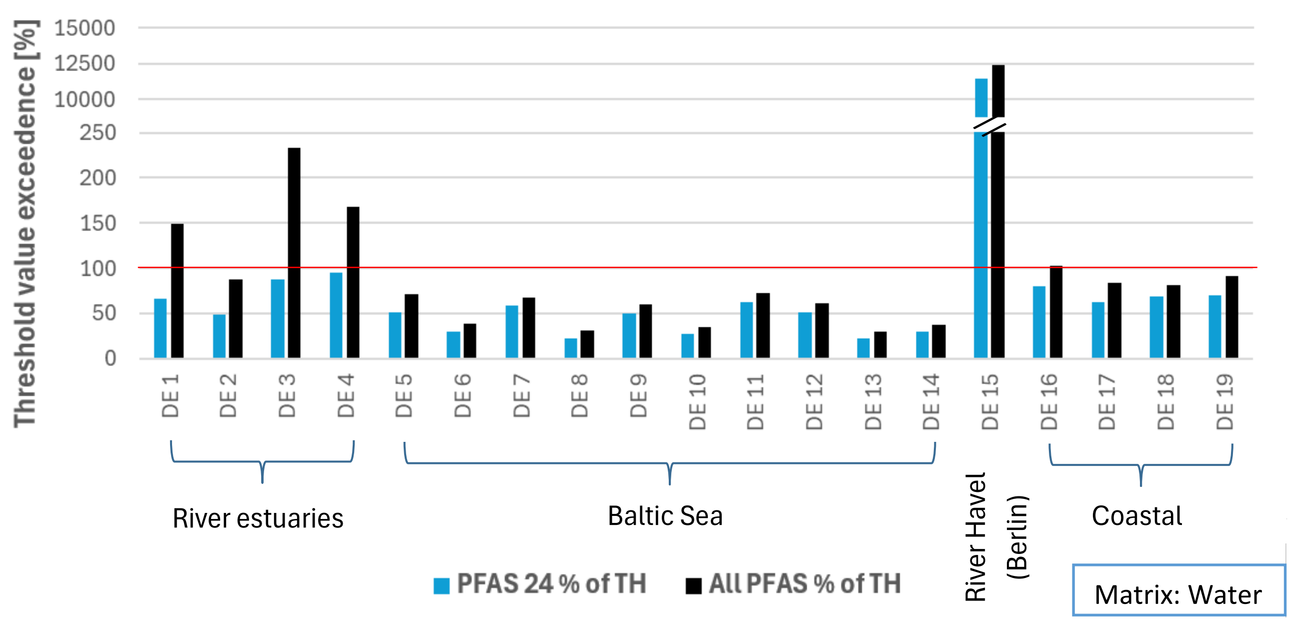


Figure 26 – Overall results of the water samples taken by the Technical University of Berlin as part of the EMPEREST project piloting. The y-axis has a break to show the higher concentrations in the river Havel. Most samples were taken in July-August, while the coastal samples were taken at the end of September.

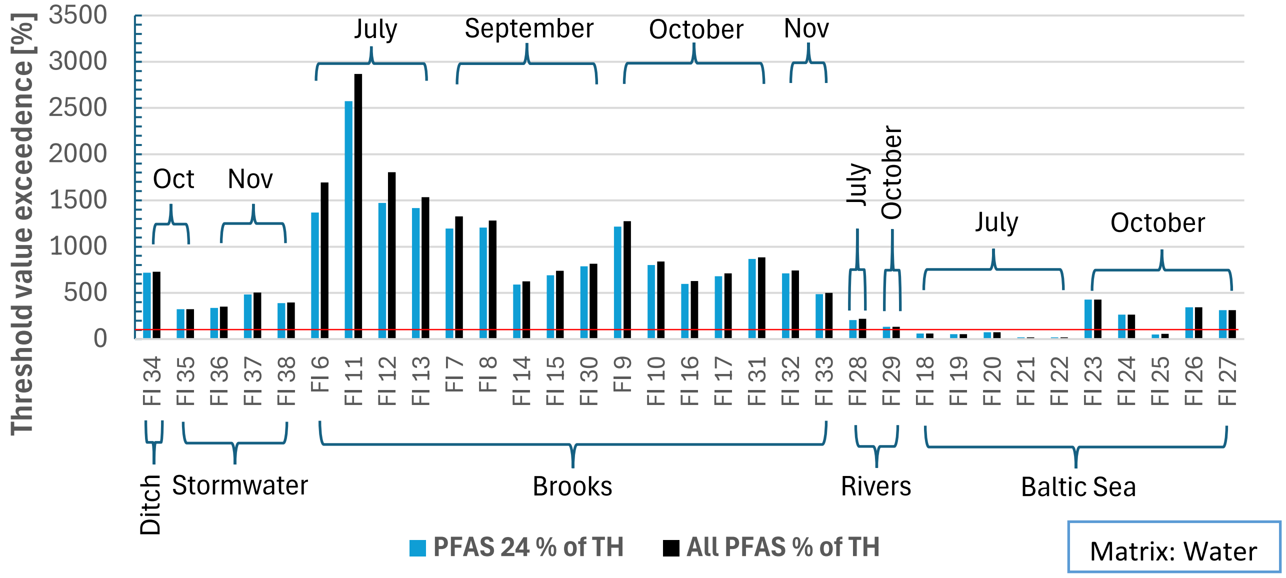


Figure 27 – Overall results of the water samples taken by the Turku University of Applied Sciences as part of the EMPEREST project piloting/screening. Extra information in brackets provide details on the time and location of the collected samples.

The Finnish water samples taken around the Bay of Turku are presented on Figure 27. As more of the samples there were taken from different kind of input sources into the bay, the results vary a great deal based on where the sample was taken from. Some individual variations between samples of the same group also come due to differences in sampling weather, type of sample (grab, 1h composite, 12h composite) and season.

Based on the samples collected, season differences are quite strongly apparent from the data – higher rainfall months show higher concentrations of PFAS in brooks and rivers; while PFAS concentrations in the Bay of Turku are significantly lower in July than in October, potentially indicating a large extra load of PFAS entering with the rainy season. These results also indicate that the sampling time and season might have a strong influence on the coastal water samples. Although open sea area samples are not presented in this piloting study, the influence of weather patterns and seasons should be almost negligible the further from the coastline a water sample is taken. The seasonal influence of the Bay of Turku samples is especially vital for assessment purposes, as all 5 samples would be under the new EU threshold when sampled in July, while four of the five samples would be significantly over the threshold when sampled in October.

Last, but certainly not least, the results of the biota samples collected from the Bay of Turku and the coastal waters around Estonia are presented on Figure 28. As was the case with the samples in the collected monitoring database, the new proposed threshold of 0.077 µg/kg ww is very strict meaning all collected samples would be 20-230 times over the threshold. As samples were collected from 4 different species, the highest average PFAS concentrations were detected from flounders, the second highest from perch and the lowest from Baltic herring. The average concentrations in flounder were 170% and in herring 30% of perch concentrations (for both PFAS24 and all PFAS).

While the samples in Estonia were collected from various places along the coastline, the Finnish samples were all taken from the same place in the Bay of Turku – a total of 28 individual perch caught on the same day were ordered by size and divided into 5 composite samples based on the sizes (36g, 48g, 64g, 153g, 250g of average weigh respectively from FI 1 to FI 5). The concentrations of PFAS were quite different between the samples as well, from FI 2 to FI 5, the PFAS concentrations increased from roughly 4 µg/kg ww to 12 µg/kg ww. The first sample did not follow the same pattern however, having around 6.6 µg/kg ww with the smallest size-category of fish. At the same time, most of the collected perch in samples FI 2 to FI 5 were female (60%, 75%, 100%, 100% respectively), while the FI 1 sample had more individual perch included and only 27% female perch in total. Although the results of one sample are not enough to show if sex of the fish sample has a significant effect on the PFAS concentrations or not, but it is enough evidence to suggest an important connection.

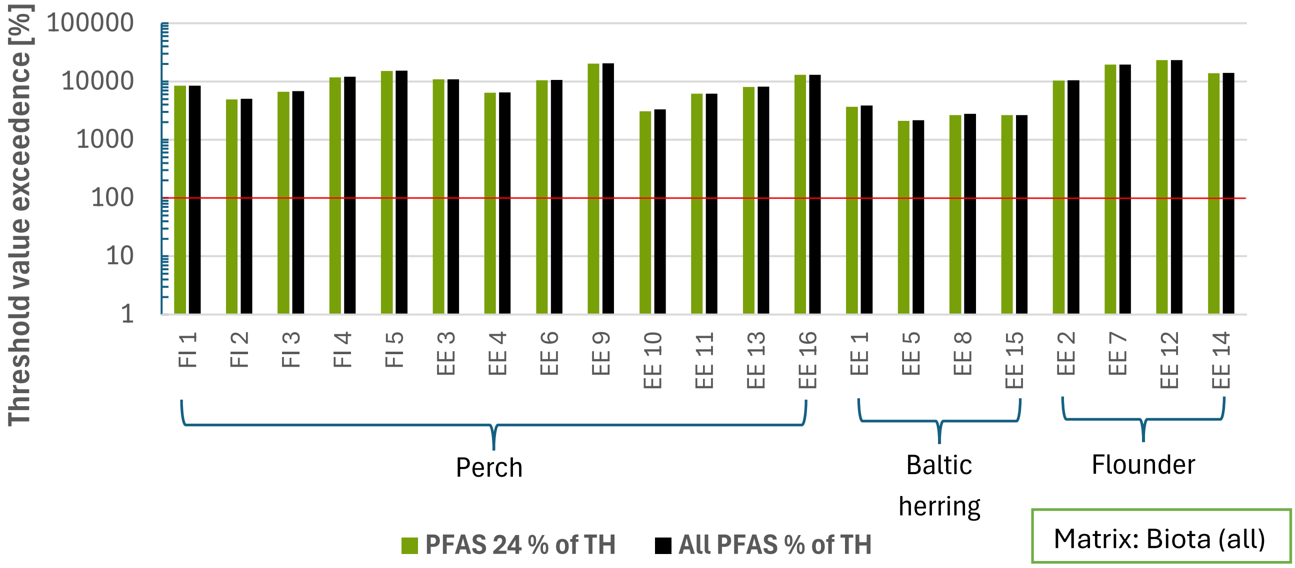


Figure 28 – Overall results of the biota samples taken by the Turku University of Applied Sciences and University of Tartu as part of the EMPEREST project piloting/screening.

6.2.2. Key PFAS in the water and biota matrices

One of the benefits of the extra piloting done in the EMPEREST project, is that it allows to compare the TOP 10 PFAS results from both water and biota to a secondary database, where almost all included compounds have been measured the same number of times. This should decrease the undervaluation of some newer PFAS compounds and indicate if the list of PFAS contributing most to environmental pollution seem to be changing.

Matrix: Water (All)

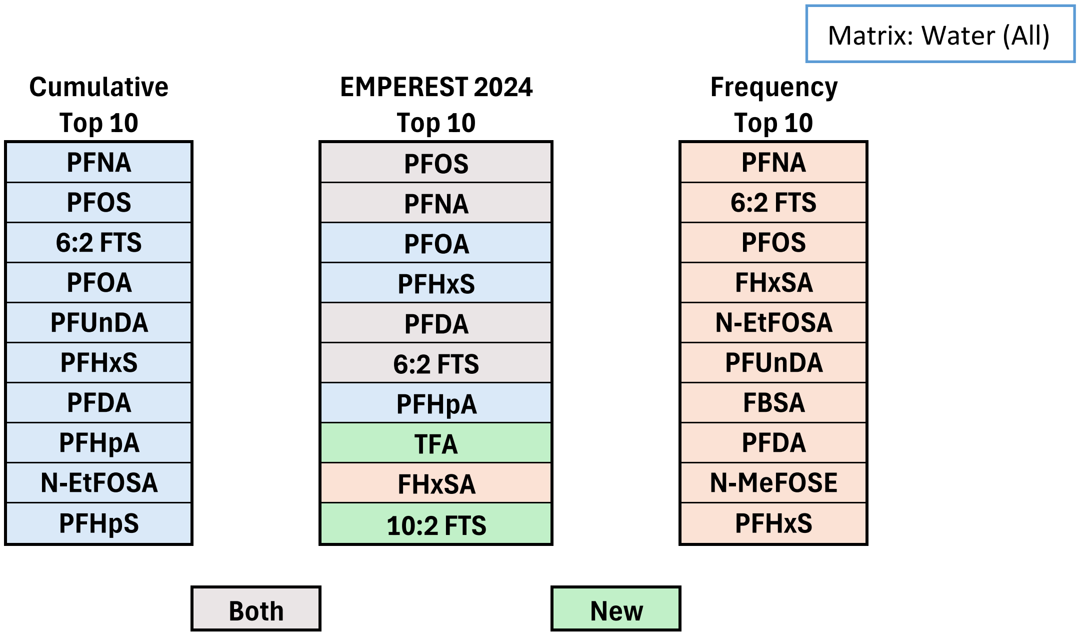
Table 17 – TOP 10 PFAS from all new water samples taken by the EMPEREST project, based on the total amount of "threshold exceedance", calculated based on the number of measurements over LOD/LOQ and average concentrations of those measurements, using the RPF approach to sum the different compounds.

Compound	Samples measured	Samples >LOQ	Average con-centrations (ng/L PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	52	49	15.98	783.08	48.82	48.82
PFNA	52	34	7.91	269.10	16.78	65.60
PFOA	52	52	3.36	174.81	10.90	76.49
PFHxS	52	47	1.73	81.50	5.08	81.58
PFDA	52	10	6.75	67.48	4.21	85.78
6:2 FTS	52	18	3.06	55.09	3.43	89.22
PFHpA	52	52	1.02	53.14	3.31	92.53
TFA	19	19	1.20	22.80	1.42	93.95
FHxSA	52	12	1.35	16.15	1.01	94.96
10:2 FTS	52	1	12.00	12.00	0.75	95.71

The TOP 10 PFAS based on the water matrix are presented in Table 17. While all other PFAS with quantified measurements had the same number of samples (52) included, TFA was unfortunately an exception. It was only measured from the water samples taken on the German coast. There were other minor differences as well between the list of PFAS measured by the Eurofins lab in Germany compared to the other Eurofins labs, while TFA is the most important of these and the only one influenced in the water matrix.

As TFA was measured from only a third of all samples, the cumulative exceedance could actually be a few times larger, up to around 5%, raising TFA a few places in the TOP 10 list. At the same time, even based on the reported measurements it is safe to say TFA is in any way one of the top 10 most important PFAS compounds in the water matrix and should be included in monitoring as often as possible. This is an important result, as TFA based on our current understanding needs a separate analytical method to be measured, resulting in significant extra costs.

The comparison of the new EMPEREST monitoring data TOP 10 PFAS in the water matrix to the two different approaches used in part B of the document is provided on Figure 29. Interestingly, the first 7 substances according to the EMPEREST piloting are exactly the same as identified by the cumulative approach, with minor differences in the order of substances. One substance (FHxSA) from the exceedance frequency approach only and two substances (TFA and 10:2 FTS) not on either of the lists reach the TOP 10 in EMPEREST piloting. Both of these new additions are expected, as they did feature on the respective lists for biota, while not a single measurement in the water matrix had been reported before.



Matrix: Water (All)

Cumulative Top 10	EMPEREST 2024 Top 10	Frequency Top 10
PFNA	PFOS	PFNA
PFOS	PFNA	6:2 FTS
6:2 FTS	PFOA	PFOS
PFOA	PFHxS	FHxSA
PFUnDA	PFDA	N-EtFOSA
PFHxS	6:2 FTS	PFUnDA
PFDA	PFHpA	FBSA
PFHpA	TFA	PFDA
N-EtFOSA	FHxSA	N-MeFOSE
PFHpS	10:2 FTS	PFHxS

Both

New

Figure 29 – Comparison of the TOP 10 PFAS results in water matrix between collected monitoring data and new piloting carried out in the EMPEREST project in 2024. The colours indicate which of the lists the compound initially belonged to, with grey and green used to indicate substances from both or neither list, respectively.

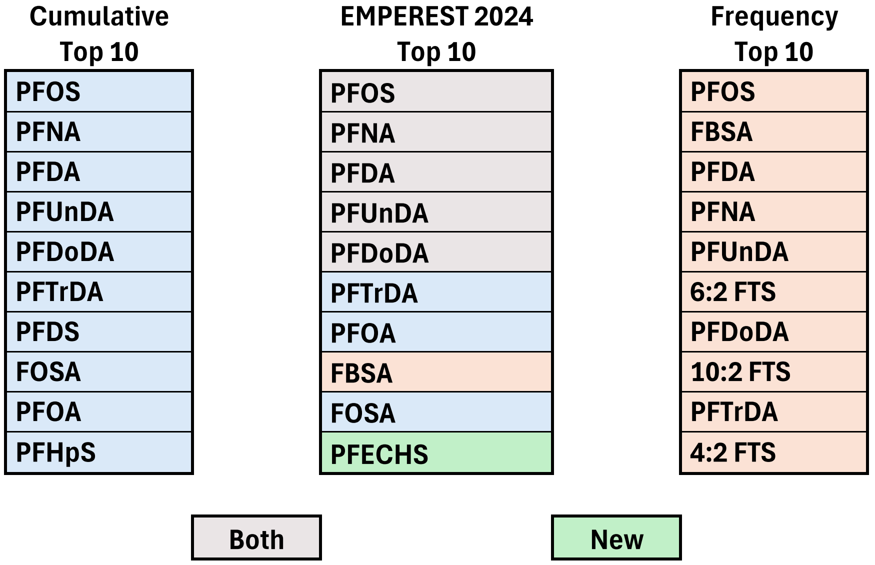
The same statistics for the TOP 10 PFAS in the matrix of biota are provided in Table 18. Unfortunately, no TFA was measured from these samples due it not being available in the laboratories used for these analyses. Interestingly, the share of PFOS and PFNA from the total exceedance are very close, while in total only 4 PFAS are responsible for close to 96% of the pollution and 7 PFAS make up 99% of the pollution. Only 16 of the 51 PFAS compounds were detected from the samples though and only 9 of them in concentrations high enough to exceed the threshold meant for the sum as a single substance. While these biota samples were focused on the Bay of Turku and coastal waters around Estonia only, they lead to believe that at the current state, focusing the main monitoring in biota on the TOP 7 substances would be the most cost-efficient. New substances should continue to be screened though, as the latter 3 substances in the TOP 10 table all represent PFAS not even on the EU list of 24.

Matrix: Biota (all)

Table 18 – TOP 10 PFAS from all new biota samples taken by the EMPEREST project, based on the total amount of "threshold exceedance", calculated based on the number of measurements over LOD/LOQ and average concentrations of those measurements, using the RPF approach to sum the different compounds.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg ww)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	21	21	3.01	63.16	39.88	39.88
PFNA	21	21	2.56	53.74	33.93	73.80
PFDA	21	21	0.89	18.73	11.83	85.63
PFUnDA	21	21	0.76	16.05	10.13	95.77
PFDoDA	21	17	0.13	2.25	1.42	97.19
PFTrDA	21	19	0.10	1.87	1.18	98.37
PFOA	21	9	0.09	0.82	0.52	98.88
FBSA	21	18	0.04	0.77	0.49	99.37
FOSA	21	5	0.06	0.29	0.18	99.55
PFECHS	21	10	0.02	0.23	0.15	99.70

Matrix: Biota (all)



Cumulative Top 10	EMPEREST 2024 Top 10	Frequency Top 10
PFOS	PFOS	PFOS
PFNA	PFNA	FBSA
PFDA	PFDA	PFDA
PFUnDA	PFUnDA	PFNA
PFDoDA	PFDoDA	PFUnDA
PFTrDA	PFTrDA	6:2 FTS
PFDS	PFOA	PFDoDA
FOSA	FBSA	10:2 FTS
PFOA	FOSA	PFTrDA
PFHpS	PFECHS	4:2 FTS

Figure 30 – Comparison of the TOP 10 PFAS results in biota matrix between collected monitoring data and new piloting carried out in the EMPEREST project in 2024. The colours indicate which of the lists the compound initially belonged to, with grey and green used to indicate substances from both or neither list, respectively.

Comparing the TOP 10 substances from the EMPEREST screening to the biota monitoring results (Figure 30), the TOP 6 compounds are the same and in the same order in both lists. Only one substance (FBSA) in the EMPEREST piloting results list is only present in the frequency list and one substance not included in either of the original lists (PFECHS). PFECHS has been measured from biota samples before, while in previous lists it has not been as high up (25th for cumulative and 16th of frequency). As the samples were rather localised, the higher impact of PFECHS might mean a higher localised pollution of the specific compound in the Bay of Turku and the coastal water around Estonia. Full tables of all PFAS measured from both water and biota samples can be found in ANNEX II – Additional maps, figures and tables (Table 42 and Table 43).

Summary and key messages

The monitoring and assessment of PFAS is currently undergoing large changes in Europe, as it has become clear monitoring just PFOS and PFOA is not enough to properly assess the spread of PFAS pollution. With the ongoing update of the Environmental Quality Standards Directive and the new approach with a RPF-based system proposed for the PFAS, large changes are expected for the monitoring of PFAS for the whole Europe.

For the Baltic Sea region, the current monitoring of PFAS varies highly between different countries. Harmonising the monitoring for a better future assessment is highly relevant, while a lot of work on the field is currently at a standstill as the EU EQSD update has been an ongoing process for over two years with no finalisation yet. At the same time, the proposed new approach for PFAS and the threshold values for water and biota have not changed within the process. As part of the methodological recommendations for the monitoring and assessment of PFAS in the aquatic environment, EMPEREST project established a database of collected monitoring results from the Baltic Sea region to test and review this new EU approach and see how it changes the assessment of PFAS in the region. The project also explores what happens if the assessment would be taken a step further and include all monitored and reported PFAS (more than 60) instead of the 24 PFAS included in the current EU-proposed system.

What is clear however from the monitoring side, is that PFAS monitoring will continue from water and biota matrices, involving more PFAS than just PFOS. Though official thresholds for sediments have not been set, sediment monitoring is also recommended based on expert opinion, though it is currently much less common around the region. Another bigger topic concerns the biota analysis – the recommendation is to focus on muscle as the primary tissue moving forward as this can help with the complications of tissue conversion, while the PFAS detection compared to liver might be less frequent. Conversion factors might still be needed for the biota monitoring and assessment, as the PFAS concentrations differ between different fish and depending on the weight (age) of the individuals within a species.

Despite biota being proposed as the highest priority assessment in the latest EU EQSD updates, the EMPEREST project carried out a sample assessment in all three matrices – water, biota and sediment. The overall results show a varied state in the environment. Looking at sediment samples, which have the least amount of information and thresholds available, the PFAS pollution is rare, but concentrated in the Bothnian Bay. For water samples, the situation is more varied, with about third of the samples potentially over the new threshold. It is also concerning, that many of the PFAS compounds driving the pollution in water are not part of the EU list of 24 PFAS, representing newer PFAS and industrial substitutions.

For biota, the new threshold value is very strict compared to the previous one, meaning close to 90% of the biota samples would be over the new limit value. The main driving PFAS for biota are more traditional as 95% of the current pollution is coming from 5 PFAS (PFOS, PFNA, PFDA, PFUnFA and PFDoDA) and 99% of the pollution can be covered by the top 10 PFAS. In most of the fish samples, the concentrations are 10 to 250 times over the threshold, indicating how much work would need to be done on the field of PFAS to reach a good environmental status.

As another part of this output, three of the EMPEREST partners concluded some piloting of the proposed guidelines, while trying to get answers to some outstanding questions on the field of monitoring. Technical University of Berlin and University of Tartu worked closely with their national authorities taking marine samples and sent additional water (DE) and biota (EE) samples to be analysed for a large range of PFAS. As the monitoring results had a disproportionate amount of more common PFAS analysed, it was difficult to determine the potential cumulative impact of newer PFAS in those two matrices. The results of this extra screening indicate that newer PFAS have a large presence in water samples, while TFA especially should be included in the water monitoring. The biota matrix indicated almost the opposite – the number of different PFAS even detected in fish was much lower, while the main compounds with high concentrations were the same identified with the preceding assessment.

The third study was concluded by the Turku University of Applied Sciences, who amongst other things checked the seasonality of PFAS concentrations in brooks and rivers and the bay they feed into. Surprisingly, the effect of dry or rainy season was very high – marine water concentrations in the coastal areas could differ manyfold depending on the season. The concentrations in the bay were up to 5 times higher in the rainy season, while the concentrations in brooks were significantly lower then. Additionally, different sizes of perch were divided into samples, showing a steady increase in PFAS concentrations in them, from 4 µg/kg ww to 12 µg/kg (for fish around 50 g and 250 g average weight respectively). This is in line with previous knowledge on the field but highlights even more that potential correction factors would be needed as differences do not only come from fish species, but also the weight of the analysed specimen.

With all of the above in mind, the output 2.1 from the EMPEREST project proposes a few key messages as a synthesis of all the collected data, the sample assessment and extra piloting carried out by the partners:

1) Although some regional decreases in PFAS concentrations can be seen in the water matrix, especially for marine water in the western parts of the Baltic, the larger Baltic Sea region does not see significant decreasing trends on average in any analysis matrix. This means the current efforts in PFAS legislation have potentially stopped the rapid increase of PFAS in these matrices but are not sufficient for the state to start getting better.
2) The proposed list of 24 PFAS by the new EU EQSD should not be rigidly used in monitoring but adapted to local situation when and if possible. Currently, this is complicated due to a lack of official relative potency factors for other compounds, but there is potential workarounds for now and promises for more official factors to come in the future. For water matrix, the list of 24 does not include a large number of newer PFAS subgroups, which have significant presence in the Baltic Sea aquatic environments already and can degrade into PFOS, PFOA and other more known PFAS. The opposite is true for the biota – most biota pollution comes from only a small number of PFAS, making half of the proposed list unnecessary for the matrix. At the same time, even in biota a few new compounds not on that list are showing up in high concentrations, which should be prioritised in measurements when possible.
3) Based on the overall state of PFAS in the aquatic environments around the Baltic Sea region and the main trends, the EMPEREST project wholly supports the wider PFAS ban in the European Union proposed by five Member States in January 2023. As industrial substitutions for PFAS keeps happening when previously used compounds face legislative restrictions, a broader restriction for the whole group is needed to keep more and more new PFAS being introduced into our environment and finding their way into the food chain, greatly influencing human health in the process.

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ANNEX I – PFAS database statistics by matrix

The annex I presents a large amount of statistic about the monitoring data, collected by the EMPEREST project in cooperation with HELCOM contracting parties from June to October 2023. This annex was initially prepared in April 2024 as the EMPEREST deliverable 1.1. As the database has gone through several edits, the statistics in this annex are presented based on the second version of the database.

The assessment presented in the main document is based on the third version of the database, which has some additional data from Germany and some additional data quality control applied, while these edits represent about 10% of the final data and should not drastically change the statistics outlined in the Annex. This annex should be seen as supplementary material to provide some background statistics and not should not be taken as basis for decision-making.

Part 1 - Water matrix

As the most represented matrix in the PFAS data call, water samples were reported by all countries (Figure 31), while for Germany and Poland the represented water matrix data is from ICES (International Council for the Exploration of the Sea). Some additional water matrix data from inland waters was reported by Germany (separate report was also received from the state of Saxony), which due to some problems with the data were not included in the initial database. A response was also received from Poland that no regular state monitoring from coastal waters, inland waters or groundwater concerning PFAS is currently conducted outside of the Baltic Sea Monitoring Programme.

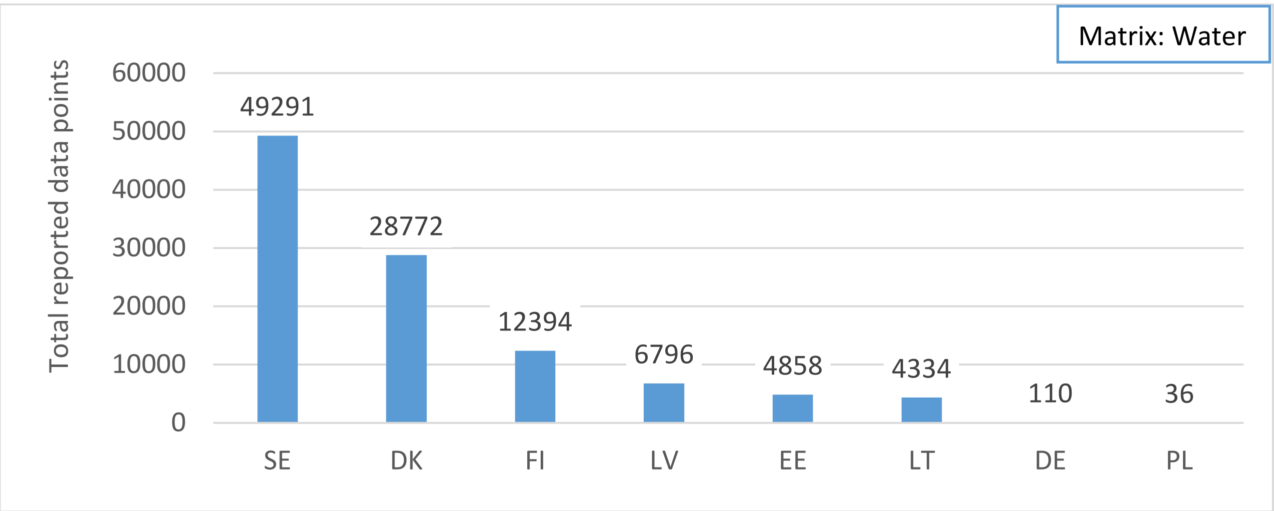

Figure 31 – Water matrix data points reported by country.

Figure 32 illustrates the different water sources the samples have been taken from. The largest proportion (almost 80%) of the water matrix results represent samples taken from inland waters, namely lakes and streams (including rivers), with only about 5% of the water samples representing the marine environment. A large proportion of samples were also collected from wastewater treatment plants (WWTP), which will be looked at separately at a later occasion.

The category “Other” on Figure 32, representing about 7% of the total water samples, includes all other results, including datapoints without indicated source, but also data from leachate water, process waters, permeates and stormwater samples.

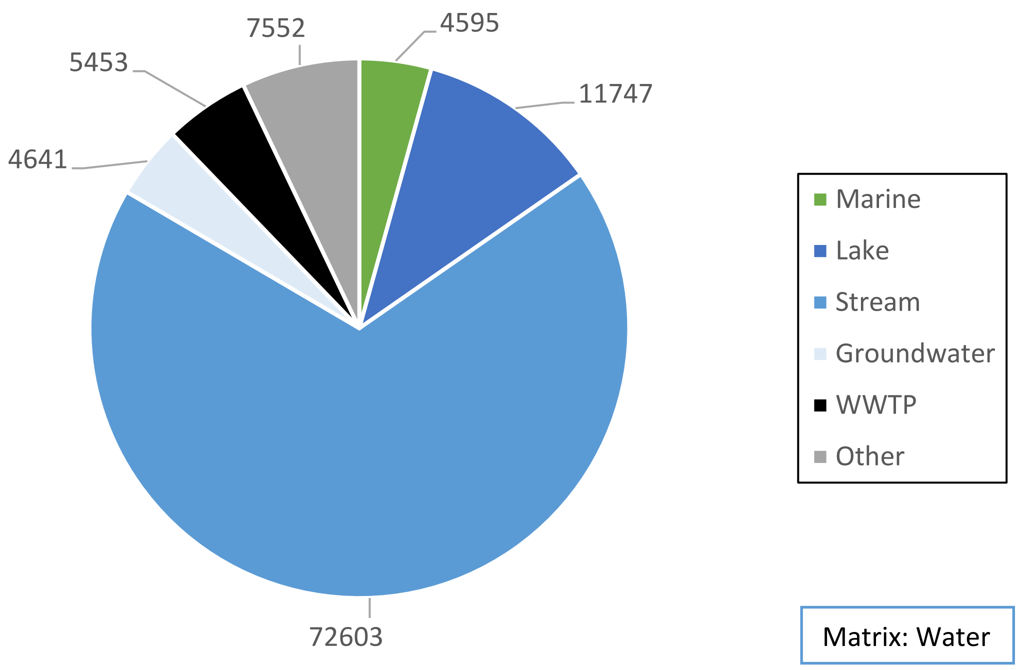

Figure 32 – Water datapoints divided by water source.

Although the data call document sent out in June 2023, highlighted that we are looking mostly for data after 2016/2017 as some monitoring data for micropollutants had been collected in a previous data call, most reporting countries provided us links to their national databases, allowing for a clean download of all relevant data. Highlighted on Figure 33 is the distribution of water matrix data by sample year, which shows a significant increase for PFAS monitoring in the water phase, especially since 2014. The earlier PFAS results generally carry less relevant data, as the limits of detection (LOD) for most substances were 2-3 magnitudes higher than the standard today (30 ng/l of LOD in 2010 vs 0.1 ng/l in 2023).

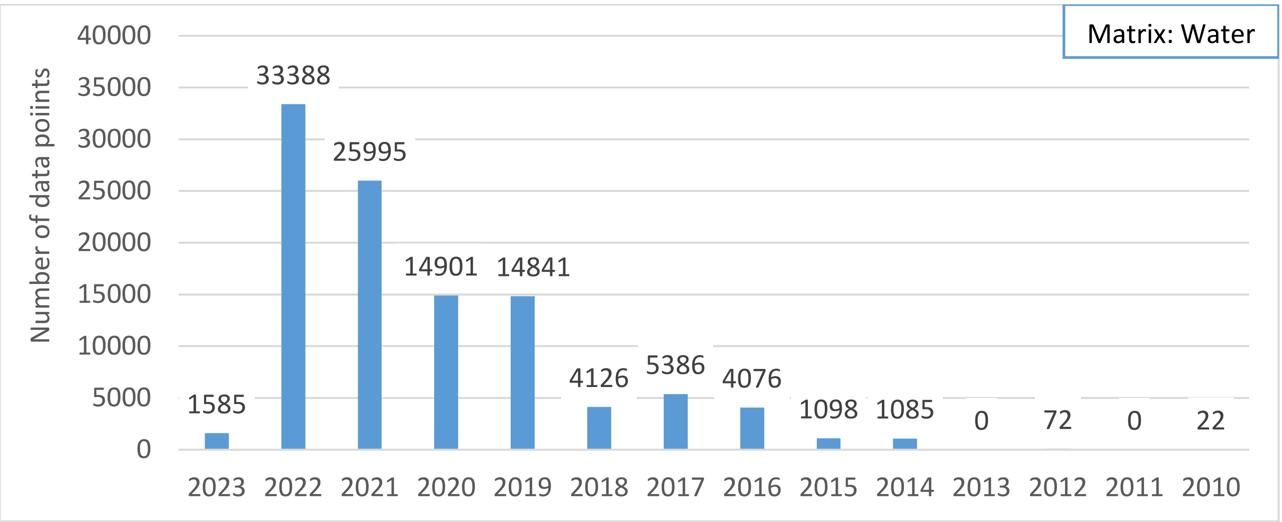

Figure 33 – Yearly distribution of water matrix data.

Although the datapoints in water have a variety of LODs, which get more precise with newer results, only a couple of the reported datapoints fail to fill the current EU limit of reporting (LOR) for PFAS, which based on a specific substance varies from 10 to 50 ng/l. The LOR is used in many environmental standards to show the minimal necessary sensitivity an analytical method should fulfil in order for the results to be considered valid. It is usually defined as a lowest calibration level which can be achieved in 90% of the analytical series performed and must be at or above the limit of quantification (LOQ) of the method, while specifics of how it is determined may differ based on a substance group it is used for.

At the same time, it is important to mention that the current LORs for PFAS have not yet been adjusted based on the new Zero Pollution Action Plan PFAS EQS. As the new threshold value for the PFOA equivalent of a sum of 24 PFAS was proposed as 4.4 ng/l, all current LORs are higher than the new EQS and therefore the LORs should expect to be changed accordingly in the future if the new PFAS EQS approach is adopted into legislation.

Looking at all the water matrix datapoints (Figure 34), PFAS were generally detected over respective LODs on 43% of detections, with 39% of all PFAS analyses in the water matrix being over the limits of quantifications (LOQ).

In order to further analyse the data, some threshold or limit values are needed. Currently, in the HELCOM framework, there is a PFOS indicator with threshold values for biota (9.1 µg/kg muscle ww) and marine waters (0.00013 µg/l or 0.13 ng/l). The current EU Environmental Quality Standards (EQS) for surface waters has an annual average limit value for PFOS in inland waters as 0.65 ng/l. As the water matrix dataset includes datapoints for 51 different PFAS substances and mainly data from inland waters, these thresholds are not sufficient to analyse the bulk of the data.

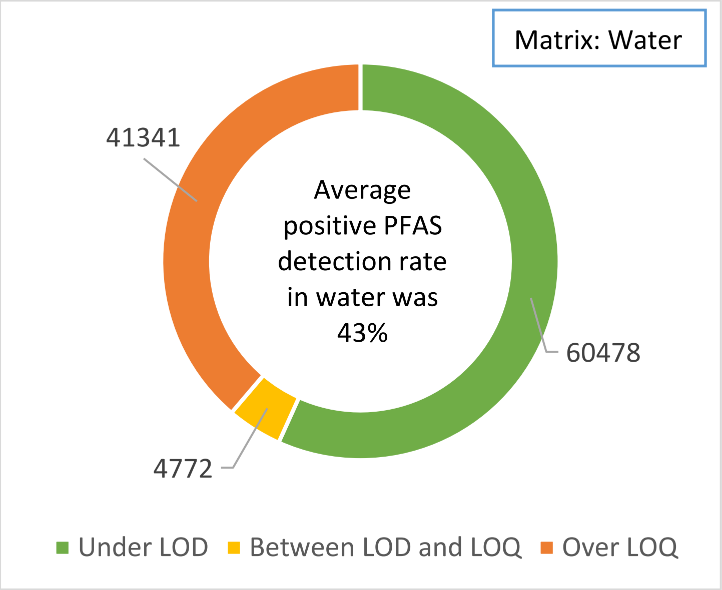

Figure 34 – Detection rates of PFAS in water samples, n=106 591

As part of the Zero Pollution action plan unveiled by the EC in October 2022, the current PFOS-specific entry in the Water Framework Directive priority substances list (Annex X) was proposed to be changed to a sum of 24 PFAS entry, including a new EQS for the sum value, based on PFOA toxicity. Each of the proposed 24 PFAS were given a relative potency factor (RPF) to PFOA, allowing the concentrations of different substances to be summed up. The new proposed EQS value for the sum of 24 PFAS is 0.0044 µg/l for water and 0.0077 µg/kg for biota.

Using these RPF together with the proposed EQS value for the sum, it is possible to estimated “thresholds” for each of the 24 PFAS – although in actual monitoring and assessment practices these thresholds would be unapplicable, they should be sufficient enough to be used with the current monitoring data collection. The 24 PFAS on the EU list, their relative potency factors and the derived “thresholds” are presented in Table 19. For this approach, the threshold of PFOS will also be calculated the same way, although the resulting threshold of 2.2 ng/l is significantly higher than the previous threshold of 0.65 ng/l for inland waters and 0.13 ng/l for marine waters.

Table 19 – Derived “threshold” values for the 24 PFAS outlined in the based on the PFOA equivalent threshold for the sum of 24 PFAS and the relative potency factors of each substance proposed in the Zero Pollution action plan.

Substance	RPF	EU water “threshold” (ng/l PFOA eq)	Substance	RPF	EU water “threshold” (ng/l PFOA eq)
PFOA	1	**4.4**	PFHpA	0.505	8.71
PFOS	2	2.2	PFTrDA	1.65	2.67
PFHxS	0.6	7.33	PFHpS	1.3	3.38
PFNA	10	0.44	PFDS	2	2.2
PFBS	0.001	4400	PFTeDA	0.3	14.67
PFHxA	0.01	440	PFHxDA	0.02	220
PFBA	0.05	88	PFOcDA	0.02	220
PFPeA	0.03	146.67	HFPO-DA (Gen X)	0.06	73.33
PFPeS	0.3005	14.64	ADONA	0.03	146.67
PFDA	7	0.63	6:2 FTOH	0.02	220
PFDoDA	3	1.47	8:2 FTOH	0.04	110
PFUnDA	4	1.1	C6O4	0.06	73.33

Using these “thresholds”, it is possible to estimate the exceedances for all 24 PFAS on the EU list. Out of the around 100 000 datapoints in the EMPEREST database, 74 000 are for the PFAS included in the list. As two PFAS from the list (Gen X and C6O4) do not have any measurements in any matrices included in the dataset, and two PFAS (6:2 FTOH and 8:2 FTOH) did not have any measurements in the water matrix; in practice only 20 of 51 PFAS reported in the dataset are included in the evaluation presented on Figure 35.

Out of the analysed data, about 63 400 samples or 85.7% showed measurement results in proposed safe levels, with 4536 samples or 6.1% of the total amount were clearly over the threshold proposed in Table 19. 6077 datapoints or 8.2% of all analysis was considered “inconclusive”, as although the measurements were reported to be under LOD, the applied LOD itself was over the proposed thresholds. It is also worth mentioning that 19 of the 22 substances (around 23 000 datapoints) had some data represented with isomer-specific analysis (either linear or branched isomers analysed separately). As different isomer data was not summed for this part of the analysis (the summing was done later for the overall assessment presented in the respective chapter, the exceedance of these results over the threshold might be slightly underestimated.

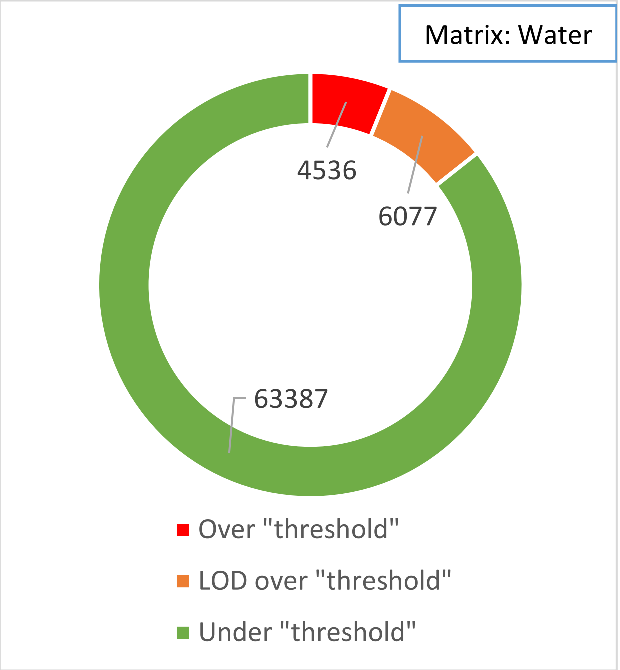

Figure 35 – Breaches of the proposed PFAS 24 threshold by single substance concentrations (n=74000)

Matrix: Water

Table 20 – A summary of all the monitoring data of the 24 PFAS on the EU list in the water matrix

		Measurements					Over threshold			LOD problems	
	Substance	Total	Under LOD	Between LOD/LOQ	Over LOQ	Over LOD %	#	% of total	% of over LOD	#	% of total
CARBOXYLIC ACIDS Chain length increase ↓	PFBA	4864	1631	14	3219	66.5	30	0.62	0.93	8	0.16
	PFPeA	4036	1669	76	2291	58.6	23	0.57	0.97	4	0.10
	PFHxA	5171	1757	64	3350	66.0	10	0.19	0.29	1	0.02
	PFHpA	4482	1084	51	3347	75.8	231	5.15	6.80	162	3.61
	PFOA	7020	2051	44	4925	70.8	865	12.32	17.41	233	3.32
	PFNA	4413	2653	142	1618	39.9	929	21.05	52.78	1200	27.19
	PFDA	4215	3328	188	699	21.0	265	6.29	29.88	1121	26.60
	PFUnDA	3611	3139	194	278	13.1	188	5.21	39.83	992	27.47
	PFDoDA	3436	3169	194	73	7.8	22	0.64	8.24	856	24.91
	PFTrDA	2468	2247	174	47	9.0	10	0.41	4.52	84	3.40
	PFTeDA	1985	1779	194	12	10.4	1	0.05	0.49	55	2.77
	PFHxDA	1810	1651	153	6	8.8	0	0.00	0.00	0	0.00
	PFOcDA	1795	1631	151	13	9.1	0	0.00	0.00	0	0.00
SULFONIC ACIDS Chain length increase ↓	PFBS	4476	1554	88	2834	65.3	0	0.00	0.00	0	0.00
	PFPeS	2122	1467	122	533	30.9	41	1.93	6.26	0	0.00
	PFHxS	4218	1957	76	2185	53.6	321	7.61	14.20	167	3.96
	PFHpS	2663	2152	163	348	19.2	85	3.19	16.63	160	6.01
	PFOS	8437	3114	70	5253	63.1	1507	17.86	28.31	855	10.13
	PFDS	2770	2548	174	48	8.0	8	0.29	3.60	179	6.46
	6:2 FTOH	0	0	0	0		0			0	
	8:2 FTOH	0	0	0	0		0			0	
	HFPO-DA	0	0	0	0		0			0	
	ADONA	8	8	0	0	0.0	0	0.00		0	0.00
	C6O4	0	0	0	0		0			0	

Table 21– A summary of all the monitoring data of other PFAS in the water matrix

	Measurements				
Substance	Total	Under LOD	Between LOD/LOQ	Over LOQ	Over LOD %
4:2 diPAP	8	8	0	0	0.0
6:2 diPAP	8	6	0	2	25.0
8:2 diPAP	39	39	0	0	0.0
10:2 diPAP	8	8	0	0	0.0
4:2 FTS	1409	1215	172	22	13.8
6:2 FTS	2414	1762	152	500	27.0
8:2 FTS	1459	1267	173	19	13.2
10:2 FTS	81	81	0	0	0.0
6:2 Cl-PFESA	8	8	0	0	0.0
8:2 Cl-PFESA	8	8	0	0	0.0
PF-3,7-DMOA	1159	985	174	0	15.0
PFECHS	0	0	0	0	
FOSA	2492	1968	170	354	21.0
FOSAA	1203	1001	193	9	16.8
FOSE	0	0	0	0	
N-EtFOSA	1166	992	29	145	14.9
N-EtFOSAA	1319	1124	173	22	14.8
N-EtFOSE	1166	989	173	4	15.2
N-MeFOSA	1197	1022	174	1	14.6
N-MeFOSAA	1213	1029	173	11	15.2
N-MeFOSE	1166	987	174	5	15.4
PFNS	1872	1644	166	62	12.2
PFDoDS	1505	1331	166	8	11.6
3:3 FTA	8	8	0	0	0.0
5:3 FTA	8	6	0	2	25.0
7:3 FTA	8	8	0	0	0.0
FHxSA	15	0	0	15	100.0
FBSA	3	0	0	3	100.0
HPFHpA	1244	1062	174	8	14.6
H2PFDA	0	0	0	0	
H4PFUnDA	85	85	0	0	0.0
PFPeDA	0	0	0	0	
PFUnDS	431	431	0	0	0.0
PFTrDS	331	330	0	1	0.3
TFA	104	76	0	28	26.9

Part 2 - Biota matrix

Biota, as the second most populated matrix in the dataset, had samples reported from all countries (Figure 36). For Poland, the database includes only data reported to ICES, while for the rest of the countries national databases or other sources of data have been included as well. The biota database includes around 36 000 individual datapoints and results from a total of 40 different PFAS substances, 22 of which also had some specific isomeric data reported. A total of 9 different sum parameters were also reported, from two different sums of PFOS and PFOA to a larger sum of 22 PFAS. For this round of the results summary, the sum parameters were not included in the analysis.

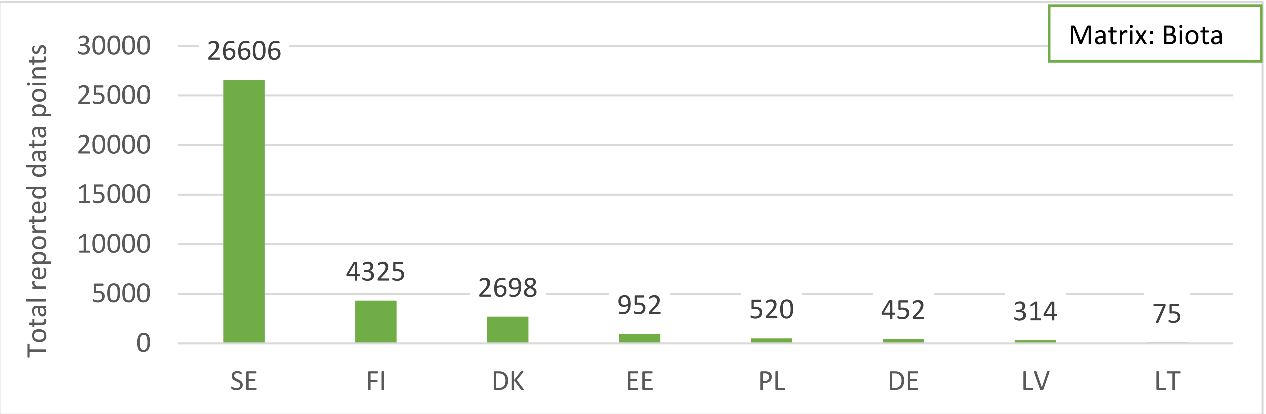

Figure 36 – Biota matrix data points reported by country.

Contrary to the water matrix, most biota samples were taken from the marine environment, representing a total of 54% of all datapoints (a). Interestingly, an important amount of data, around 900 datapoints or 2.5% of the total dataset was also reported for PFAS in terrestrial animals e.g. in otters or reindeer. This can be seen as an indication on the danger and spread of PFAS, as due to the different mobility and bioaccumulation capacity of the substances they can be found in very different sources and matrices.

The second largest subset in the biota data was samples taken from lakes, which in comparison to the marine data should give an overall indication about the spread of newer PFAS substances due to their proximity to potential pollution sources.

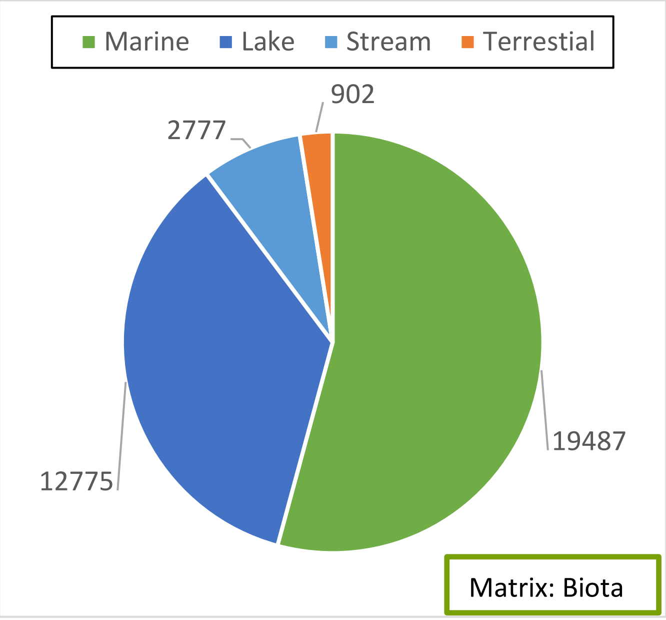

Figure 37 – Biota datapoints by sample source.

When looking at the time-profile of submitted data, it is clear that the PFAS analysis from biota has been done for a longer period of time than from water, as data until back to 2000 was able to be collected from supplied national databases (Figure 38). As some countries have a biota sample archive, some of these results might have also come from analysing older archived samples after the PFAS problem was brought to light. Another visible difference between water and biota samples, is that although a download from national databases was done at the end of 2023, most of the latest biota results only include data from 2022, which itself seems also underpopulated compared to previous years. There is still a visible trend of biota analysis getting more focus since 2007, with a bigger uptick between 2013 and 2014. As some countries do parts of their environmental monitoring biannually or with even a longer frequency, the data amounts year to year might differ considerably.

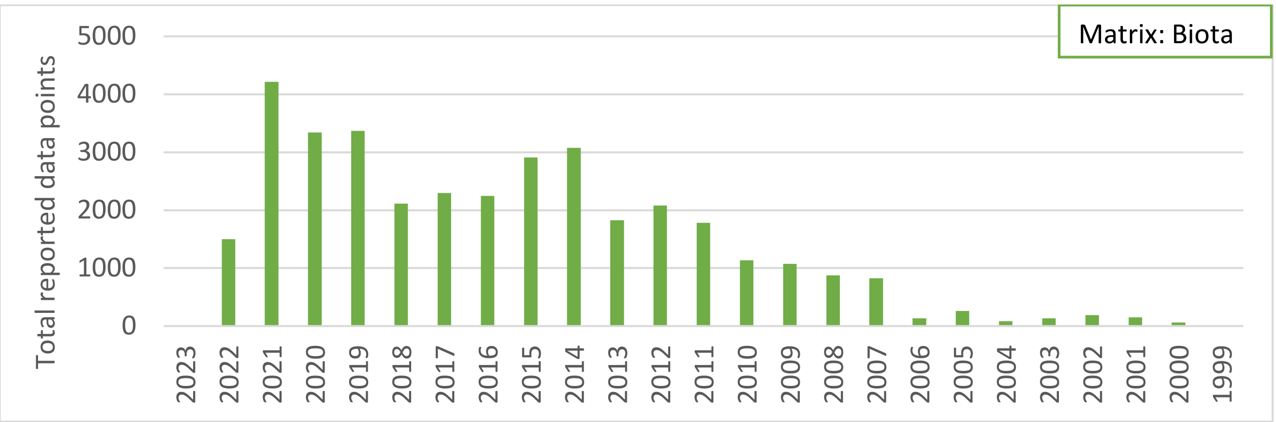

Figure 38 – Yearly distribution of biota data

The distribution of biota samples based on the sample fraction/tissue is highlighted on Figure 39. Samples that were labelled as "fillet" were consolidated into "muscle". The different use of tissues in environmental monitoring was also discussed with monitoring experts. Liver tissue for example generally has higher concentrations of substances, which allows for better detection of different micropollutants, while muscle tissue has much more volume, allowing for a larger total sample size and more opportunities for analysis. It was also said that in some cases, the preferred tissue type is because of historic reasons, as conversion factors between different tissue types are complicated to come by and the change might interfere with long-running timeseries. For the current analysis of the larger dataset, no conversion factors between liver and muscle samples were used (though they are included in the later PFOS-specific analysis)

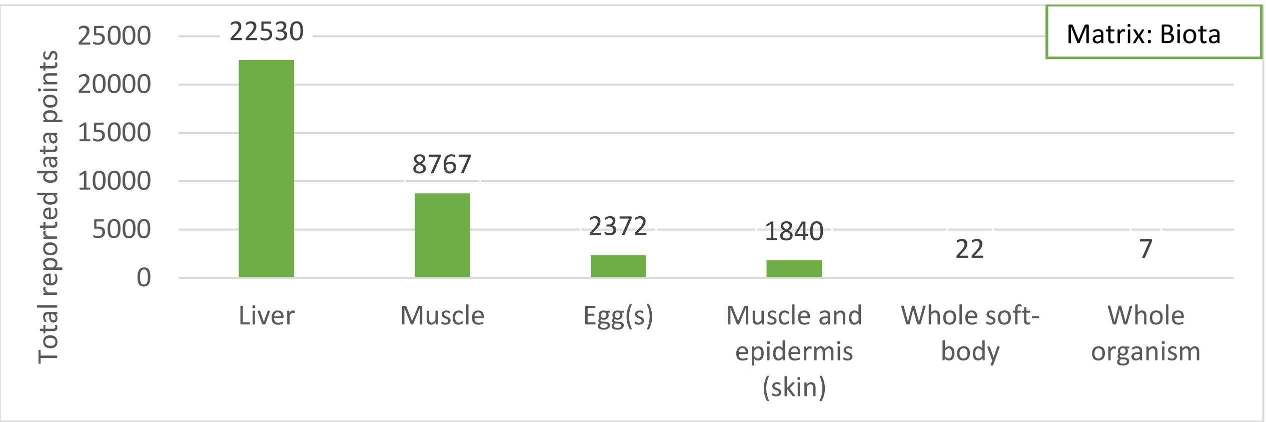

Figure 39 – Distribution of biota data based on the sample fraction

Without surprise, the largest subsets of biota analysis were reported for the herring (*Clupea harengus*) and perch (*Perca fluviatilis*) (Figure 40), with larger (around 1000 datapoints) also for pike (*Esox Lucius*), white-tailed eagle (*Heliaeetus albicilla*), flounder (*Platichthys flesus*), char (*Savelinus alpinus*) and eelpout (*Zoarces vivparus*). For the further analysis, the two subspecies of herring (*Clupea harengus* and *Clupea harengus membras*) were summed together and the same with the two subspecies of salmon (*Salmo trutta* and *Salmo trutta morfa fario*). In larger terms, the herring data has been used in HELCOM holistic assessments (HOLAS) to assess the open sea areas and the perch data for coastal waters, while for the first evaluation of the data, the all species will be used in a single dataset.

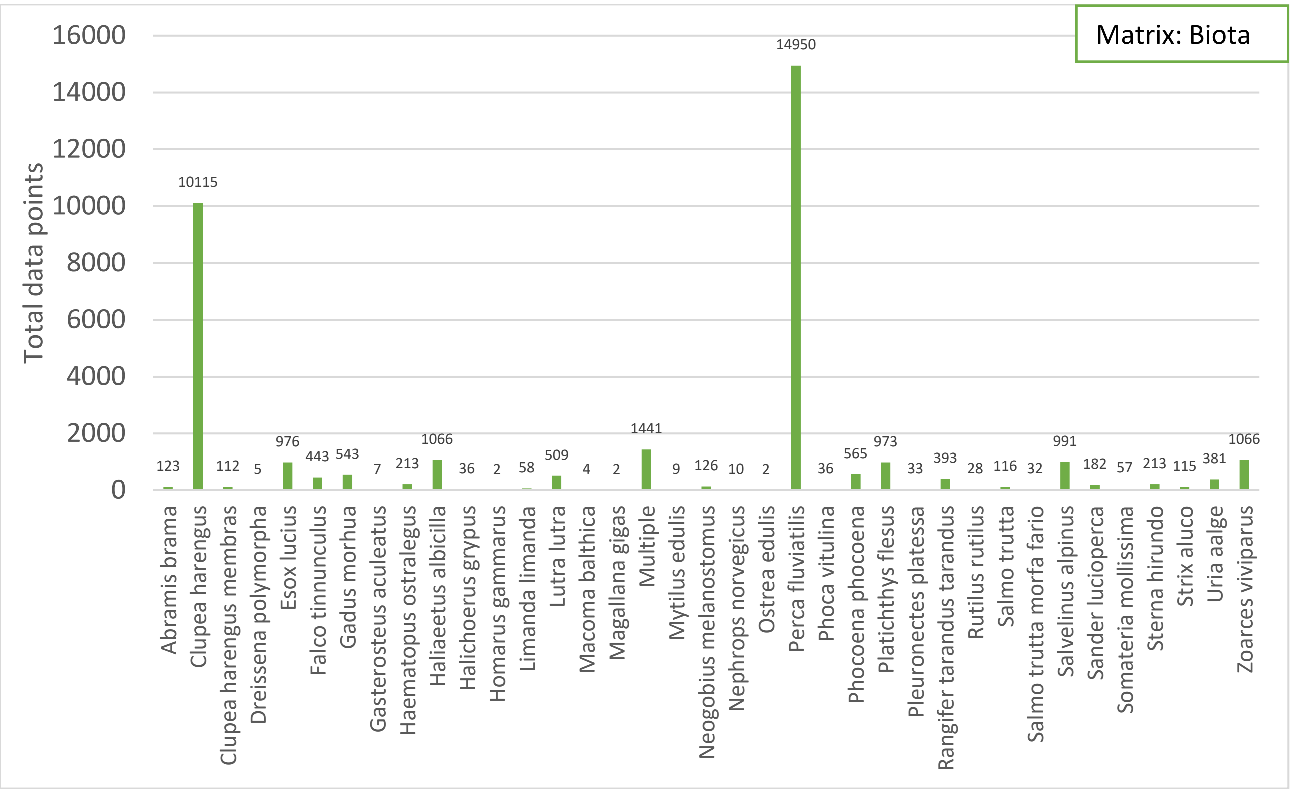

Figure 40 – Species distribution of the biota dataset

When looking at all of the different biota samples together, without any differentiation between the sample source, the species or the analysis tissue, the average PFAS positive detection rate was 70% (Figure 41). This is significantly higher than the same detection rate in water samples (43%) and indicates generally a higher success rate in analysing biota than water. At the same time, both taking and analysing water samples is generally significantly cheaper than biota samples. When looking more in-depth into detection rates of specific substances, the difference between newer and older PFAS should also be apparent, as the water matrix should represent the PFAS usage today, with biota representing the PFAS usage in the near past.

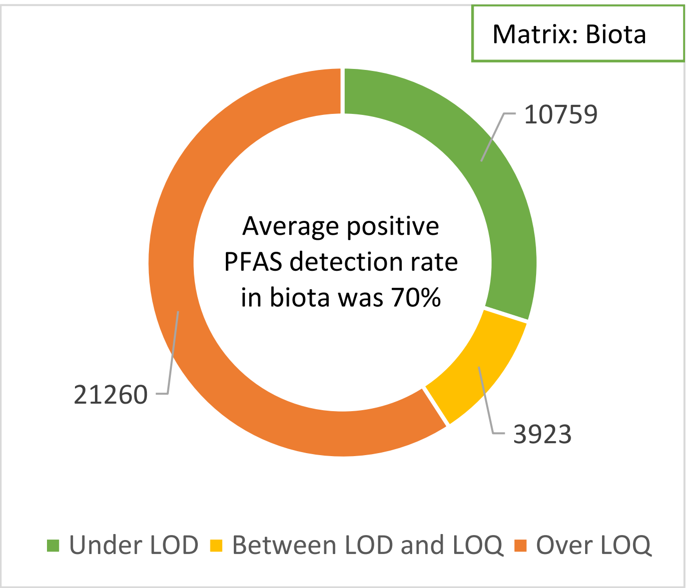

Figure 41 – Detection rates of PFAS in biota samples, n=35942

The look into the specific substances and whether the above LOQ results are of concern, threshold values are needed again. In the current HELCOM PFOS indictor, a human health EQS based on the current EU EQS dossier of 9.1 µg/kg ww is used, which as mentioned earlier is used on herring and cod data to evaluate the open sea areas and on flounder, sole, eelpout and perch data for the coastal waters. The EQS is mainly used for tissue types of muscle, muscle and epidermis or whole fish; for liver tissue, a conversion factor of 17.9 is applied due to a higher bioaccumulation of toxins in fish livers.

In order to look at a larger subset of PFAS again as in the water matrix subchapter, the recalculations based on the new EU Zero Pollution Action Plan proposal for a PFAS group approach are also applied for biota. As explained previously, each of the proposed 24 PFAS has been given a relative potency factor (RPF) to PFOA in that approach, allowing the concentrations of different substances to be summed up. The new proposed EQS value for the sum of 24 PFAS is 0.077 µg/kg ww for biota, which is multiple magnitudes lower than the previous PFOS limit. Using the EQS sum value together with the proposed RPF values, it is possible to estimated "thresholds" for each of the 24 PFAS, which are presented in Table 22.

Table 22 – Derived "threshold" values for the 24 PFAS outlined in the based on the PFOA equivalent threshold for the sum of 24 PFAS and the relative potency factors of each substance proposed in the Zero Pollution action plan.

Substance	RPF	EU biota threshold (µg/kg ww PFOA eq)	Substance	RPF	EU biota threshold (µg/kg ww PFOA eq)
PFOA	1	**0.077**	PFHpA	0.505	0.152
PFOS	2	0.039	PFTrDA	1.65	0.047
PFHxS	0.6	0.128	PFHpS	1.3	0.059
PFNA	10	0.008	PFDS	2	0.039
PFBS	0.001	77	PFTeDA	0.3	0.257
PFHxA	0.01	7.7	PFHxDA	0.02	3.85
PFBA	0.05	1.54	PFOcDA	0.02	3.85
PFPeA	0.03	2.567	HFPO-DA (Gen X)	0.06	1.283
PFPeS	0.3005	0.256	ADONA	0.03	2.567
PFDA	7	0.011	6:2 FTOH	0.02	3.850
PFDoDA	3	0.026	8:2 FTOH	0.04	1.925
PFUnDA	4	0.019	C6O4	0.06	1.283

These "thresholds" allow us to estimate the exceedances for all datapoints of the 24 PFAS on the EU list. Out of about 36 000 biota datapoints, 30 500 measurements were for one of the PFAS included in the list; in practice, only 19 of the 24 PFAS had any measurements included in the dataset, with 6:2 FTOH, 8:2 FTOH, GenX (HFPO-DA), ADONA and C6O4 not having a single reported measurement in biota. The evaluation of the 19 PFAS measurements are presented on Figure 14 and following tables Table 23, Table 24 and Table 25.

Out of the analysed data, 60% of measurements from biota samples showed single PFAS substance values over the new proposed PFAS sum EQS. A large proportion of results (14%) were also "inconclusive", as although the measurements were reported under LOD, the applied LOD was over the new proposed thresholds. Again, it is worth mentioning that all of the 19 PFAS had some data split by different isomers, therefore even more of the samples might be exceeding the threshold.

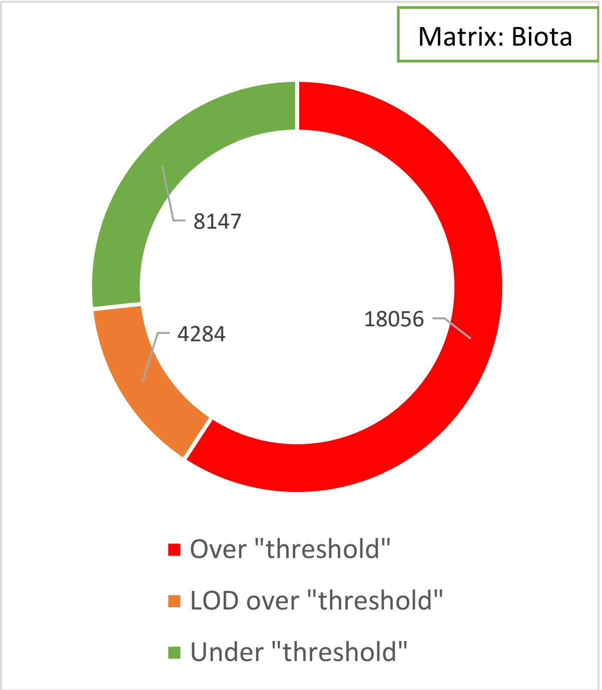

Figure 42 – Breaches of the proposed PFAS 24 threshold by single substance concentrations n=30487

Matrix: Biota

Table 23 – A summary of all the monitoring data of the 24 PFAS on the EU list in the biota samples

		Measurements					Over threshold			LOD problems	
	Substance	Total	Under LOD	Between LOD/LOQ	Over LOQ	Over LOD %	#	% of total	% of over LOD	#	% of total
CARBOXYLIC ACIDS Chain length increase	PFBA	414	319	59	36	22.9	24	5.80	25.26	0	0.00
	PFPeA	264	162	73	29	38.6	21	7.95	20.59	0	0.00
	PFHxA	1547	1080	355	112	30.2	3	0.19	0.64	0	0.00
	PFHpA	1442	965	350	127	33.1	145	10.06	30.40	430	29.82
	PFOA	2536	1333	267	936	47.4	986	38.88	81.96	1074	42.35
	PFNA	2477	442	120	1915	82.2	2035	82.16	100.00	442	17.84
	PFDA	2532	346	49	2137	86.3	2185	86.30	99.95	341	13.47
	PFUnDA	2528	325	69	2134	87.1	2201	87.06	99.91	325	12.86
	PFDoDA	2054	282	95	1677	86.3	1770	86.17	99.89	265	12.90
	PFTrDA	1837	143	59	1635	92.2	1672	91.02	98.70	122	6.64
	PFTeDA	1600	465	111	1024	70.9	563	35.19	49.60	111	6.94
	PFHxDA	210	186	18	6	11.4	0	0.00	0.00	0	0.00
	PFOcDA	201	185	15	1	8.0	0	0.00	0.00	0	0.00
SULFONIC ACIDS Chain length increase	PFBS	1257	870	297	90	30.8	0	0.00	0.00	0	0.00
	PFPeS	28	16	12	0	42.9	6	21.43	50.00	16	57.14
	PFHxS	2135	877	446	812	58.9	661	30.96	52.54	463	21.69
	PFHpS	338	184	32	122	45.6	98	28.99	63.64	44	13.02
	PFOS	4858	210	75	4573	95.7	4619	95.08	99.38	202	4.16
	PFDS	2229	1061	546	622	52.4	1067	47.87	91.35	449	20.14
	6:2 FTOH	0	0	0	0		0			0	
	8:2 FTOH	0	0	0	0		0			0	
	HFPO-DA	0	0	0	0		0			0	
	ADONA	0	0	0	0		0			0	
	C6O4	0	0	0	0		0			0	

Table 24 – Summary of 19 PFAS measurements and limit exceedances of all the biota data, split by sample environment. ***# - number of samples; >LOD % - percentage of samples over LOD; >TH % - percentage of samples over calculated threshold; !LOD % - percentage of samples with LOD values higher than thresholds***

	MARINE				STREAM				LAKE				TERRESTIAL			
	#	**>LOD %**	**>TH %**	**!LOD %**	**#**	**>LOD %**	**>TH %**	**!LOD %**	**#**	**>LOD %**	**>TH %**	**!LOD %**	**#**	**>LOD %**	**>TH %**	**!LOD %**
PFBA	159	13.8	11.9	0.0	85	14.1	5.9	0.0	170	35.9	0.0	0.0	0			
PFPeA	107	21.5	13.1	0.0	27	25.9	18.5	0.0	130	55.4	1.5	0.0	0			
PFHxA	823	28.7	0.4	0.0	92	14.1	0.0	0.0	582	35.2	0.0	0.0	50	26.0	0.0	0.0
PFHpA	766	33.7	10.4	32.2	44	31.8	25.0	18.2	601	32.9	8.5	29.1	31	22.6	9.7	0.0
PFOA	1308	64.8	56.2	25.5	374	14.4	13.6	76.7	819	33.2	20.8	54.8	35	85.7	85.7	14.3
PFNA	1292	91.7	91.7	8.3	287	35.5	35.5	64.5	811	81.5	81.5	18.5	87	100.0	100.0	0.0
PFDA	1309	90.5	90.4	9.2	279	48.0	48.0	52.0	857	91.1	91.1	8.9	87	100.0	100.0	0.0
PFUnDA	1310	92.6	92.4	7.4	287	43.2	43.2	56.8	846	92.3	92.3	7.7	85	100.0	100.0	0.0
PFDoDA	1124	85.6	85.5	13.0	95	46.3	46.3	53.7	757	91.5	91.4	8.3	78	93.6	93.6	6.4
PFTrDA	1055	90.6	88.8	7.4	41	82.9	82.9	17.1	676	95.4	95.0	4.6	65	90.8	90.8	9.2
PFTeDA	870	67.4	22.6	5.2	32	50.0	21.9	15.6	653	76.0	49.9	9.2	45	82.2	73.3	2.2
PFHxDA	100	0.0	0.0	0.0	20	0.0	0.0	0.0	90	26.7	0.0	0.0	0			
PFOcDA	100	0.0	0.0	0.0	20	0.0	0.0	0.0	81	19.8	0.0	0.0	0			
PFBS	689	29.5	0.0	0.0	36	22.2	0.0	0.0	501	29.5	0.0	0.0	31	90.3	0.0	0.0
PFPeS	10	0.0	0.0	100.0	6	0.0	0.0	100.0	12	100.0	50.0	0.0	0			
PFHxS	1215	73.6	42.3	13.3	235	20.4	15.7	72.3	617	40.2	11.5	21.4	68	100.0	57.4	0.0
PFHpS	182	42.3	25.3	20.9	28	28.6	7.1	21.4	101	43.6	31.7	0.0	27	92.6	66.7	0.0
PFOS	2946	97.2	96.8	2.7	394	86.5	86.5	13.5	1434	94.8	93.7	4.8	83	100.0	100.0	0.0
PFDS	1223	56.7	53.1	20.4	49	44.9	34.7	22.4	912	45.6	40.2	20.6	45	82.2	73.3	2.2

Table 25 – A summary of all the monitoring data of other PFAS in the biota samples

	Measurements				
Substance	Total	Under LOD	Between LOD/LOQ	Over LOQ	Over LOD %
4:2 diPAP	0	0	0	0	
6:2 diPAP	0	0	0	0	
8:2 diPAP	0	0	0	0	
10:2 diPAP	0	0	0	0	
4:2 FTS	102	37	46	19	63.7
6:2 FTS	200	98	73	29	51.0
8:2 FTS	152	82	47	23	46.1
10:2 FTS	14	5	8	1	64.3
6:2 Cl-PFESA	12	12	0	0	0.0
8:2 Cl-PFESA	12	11	0	1	8.3
PF-3,7-DMOA	33	6	27	0	81.8
PFECHS	15	4	0	11	73.3
FOSA	3278	599	328	2351	81.7
FOSAA	17	0	16	1	100.0
FOSE	0	0	0	0	
N-EtFOSA	27	6	21	0	77.8
N-EtFOSAA	59	28	29	2	52.5
N-EtFOSE	27	6	21	0	77.8
N-MeFOSA	28	5	22	1	82.1
N-MeFOSAA	37	6	29	2	83.8
N-MeFOSE	27	6	21	0	77.8
PFNS	0	0	0	0	
PFDoDS	0	0	0	0	
3:3 FTA	0	0	0	0	
5:3 FTA	0	0	0	0	
7:3 FTA	0	0	0	0	
FHxSA	0	0	0	0	
FBSA	18	0	0	18	100.0
HPFHpA	48	16	30	2	66.7
H2PFDA	23	6	17	0	73.9
H4PFUnDA	23	6	16	1	73.9
PFPeDA	1157	369	124	664	68.1
PFUnDS	0	0	0	0	
PFTrDS	0	0	0	0	
TFA	0	0	0	0	

Part 3 - Sediment matrix

The third matrix collected within the PFAS data call was sediment, which was reported with the lowest frequency, having only a small number of datapoints in the total set (about 3.4% of all reported datapoints). Sediment data was only received (either directly or through data in ICES) from Sweden, Estonia, Finland, Denmark and Lithuania (Figure 43). No sediment data from Latvia, Poland or Germany was reported.

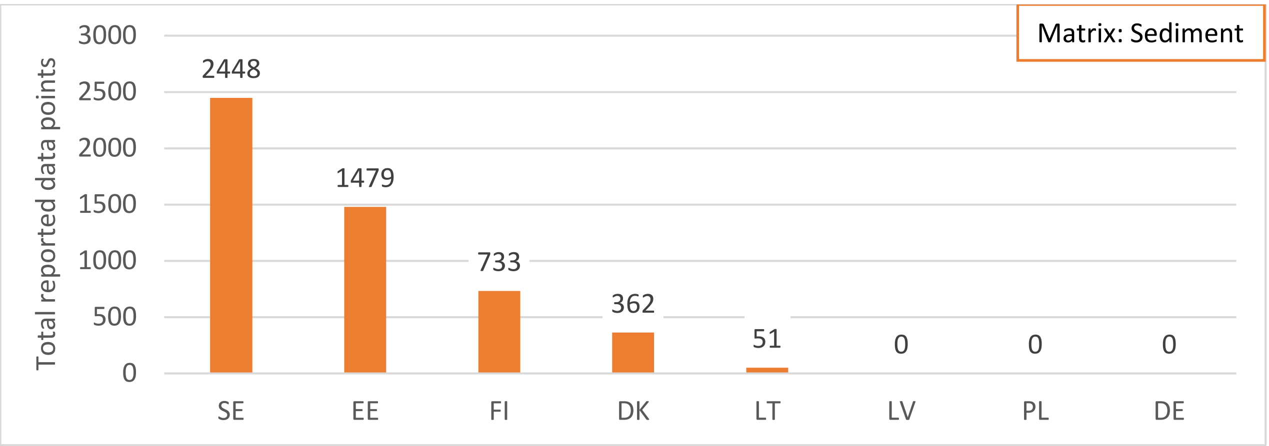

Figure 43 – Sediment matrix data points reported by country.

The sediment matrix included data of a total of 35 different PFAS substances, 23 of which had also some specific isomeric data reported. Only one sum parameter (Sum of 4 PFAS from Denmark) was included in the database, while the dataset had 17 different substance reports measured after TOP-assay.

The division of sediment samples based on the source (Figure 44) was quite equally distributed between marine environment, lakes and streams, with about 38%, 35% and 25% of total samples in each category, respectively. A small number of substances also indicated sediments collected right at the outlet of WWTPs, or other pollution sources (marinas).

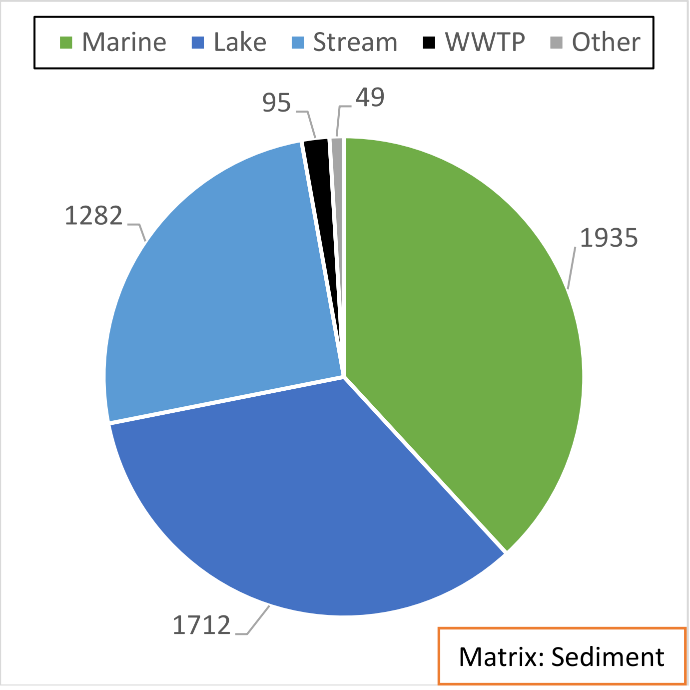

Figure 44 – Sediment datapoints divided by sample source.

As most of sediment data was downloaded directly from online databases, the earliest data acquired was from 2007 (Figure 45), with most earlier data being infrequent screenings or related to projects. Even after 2017, which is the year with the most sediment data reported, the numbers of annual datapoints differ from year to year, as similar to biota measurements, countries reported that sediment monitoring often follows a multi-year cycle, with 2–3-year gaps between consecutive samplings. No data from 2023 was yet available in the databases, as similar to biota data, the sampling, analysis and reporting are significantly more time-consuming than for water samples.

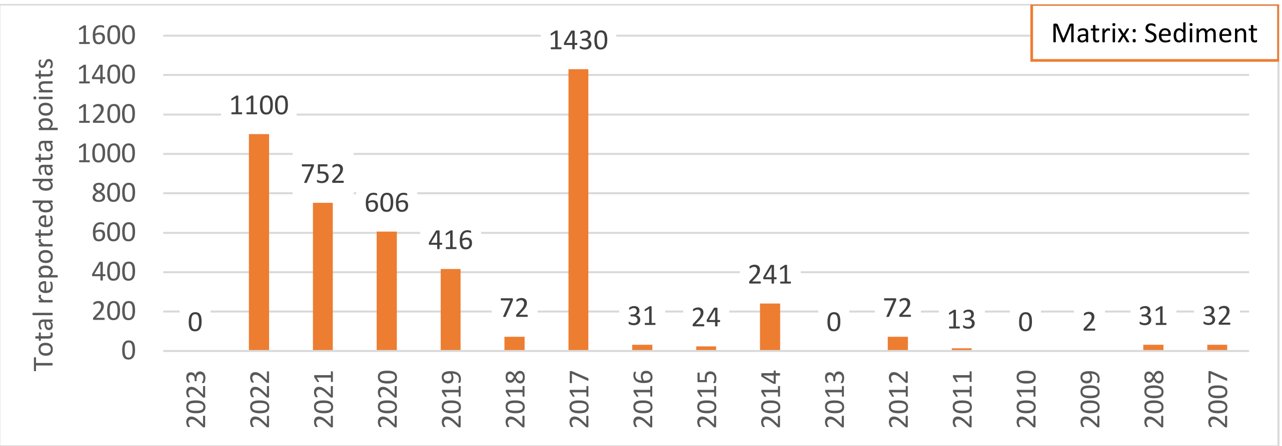

Figure 45 – Yearly distribution of sediment data.

The PFAS detection rates in sediment (Figure 46) were significantly lower than for water (43%) or biota (70%). As the PFAS analysis is usually done from the top layer of sediment, it should affirm PFAS still being fairly "new" micropollutants. As PFAS in general are non-degradable biotically, the accumulation into sediment is expected to increase as the PFAS are exiting the biotic cycle.

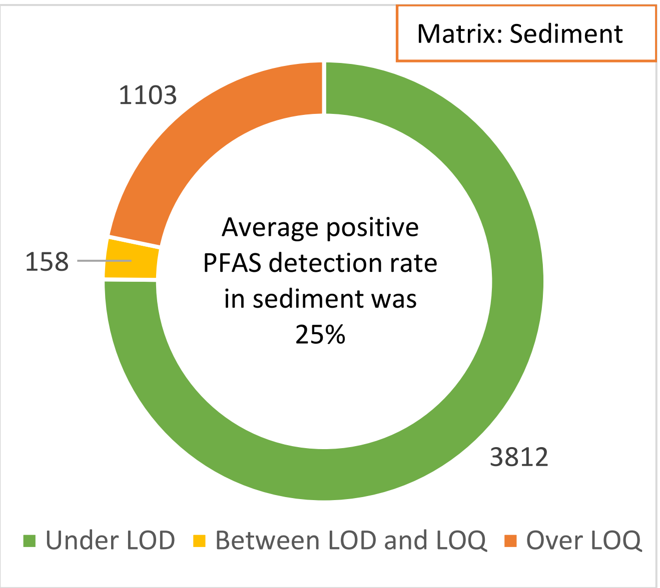

Figure 46 – Detection rates of PFAS in sediment, n=5073

Contrary to the PFAS in water or biota samples, there are currently no threshold values for either PFOS or other PFAS, which would be widely used at the HELCOM or EU level. Even the 2021 Zero Pollution action plan proposing new EQS values for the sum of 24 PFAS, that have been used for other sample matrices, does not include any threshold values for sediments. There have been some historic threshold values proposed by Norway in 2008, indicating non-effect concentrations for PFOS at 220 µg/kg dry weight, chronic toxicity at 220-630 µg/kg dry weight and acute short-term effects range from 630 µg/kg dry weight. However, from the whole dataset only 3 datapoints from the total of 5000 have reported concentrations of any PFAS above 220 µg/kg dry weight (and all three of these results were actually below LOD, as just the LOD together with the dilution effect was too high a value). Furthermore, only 17 datapoints show positive measurements (over LOD/LOQ) of above 10 µg/kg dry weight for any PFAS or their sums. Still, as these thresholds were proposed in 2008, the overall knowledge on PFAS has drastically increased in the last 15 years, and the threshold values would need to be checked again. Comparatively, the biota threshold values have been proposed to be changed from 9.1 µg/kg ww (PFOS) to 0.077 µg/kg ww (PFOA eq sum of 24 PFAS), which indicates how much new research has increased the danger levels of PFAS pollution.

As no threshold values can be used, the sediment data will be presented with simple statistics included, such as the minimum, maximum, mean and median values of all positive detections. The data for all included PFAS substances is presented in Table 26. Similarly to biota samples, from the EU list of 24 PFAS, no measurements in sediments were reported of the 6:2 FTOH, 8:2 FTOH, GenX (HFPO-DA), ADONA and C6O4. Table 27 also shows the data split by the three main sampling environments – marine, lake and stream.

Table 26 – Summary and statistics of all the monitoring data for the sediment matrix

	Measurements					Positive measurement statistics (all results µg/kg dry weight)			
Substance	Total	Under LOD	Between LOD/LOQ	Over LOQ	Over LOD %	Min	Max	Mean	Median
PFBA	297	270	10	17	9.1	0.05	3.80	0.96	0.50
PFPeA	133	110	12	11	17.3	0.03	1.64	0.51	0.53
PFHxA	348	300	10	38	13.8	0.02	2.50	0.43	0.21
PFHpA	160	110	2	48	31.3	0.02	2.40	0.51	0.21
PFOA	406	311	18	77	23.4	0.02	6.80	1.33	0.33
PFNA	348	239	26	83	31.3	0.03	8.20	1.86	0.48
PFDA	364	264	15	85	27.5	0.03	3.50	0.55	0.27
PFUnDA	356	229	10	117	35.7	0.11	1.80	0.57	0.54
PFDoDA	278	254	0	24	8.6	0.02	0.19	0.07	0.07
PFTrDA	104	65	0	39	37.5	0.05	0.59	0.16	0.12
PFTeDA	95	91	0	4	4.2	0.55	0.91	0.75	0.78
PFHxDA	36	36	0	0	0				
PFOcDA	36	36	0	0	0				
PFBS	144	136	6	2	5.6	0.03	0.15	0.09	0.09
PFPeS	5	5	0	0	0				
PFHxS	160	119	13	28	25.6	0.02	1.20	0.16	0.07
PFHpS	99	94	0	5	5.1	0.02	0.05	0.03	0.03
PFOS	532	309	4	219	41.9	0.00	72.00	2.28	0.97
PFDS	151	140	10	1	7.3	0.51	0.51	0.51	0.51
6:2 FTS	92	91	0	1	1.1	0.56	0.56	0.56	0.56
8:2 FTS	57	57	0	0	0				
10:2 FTS	4	4	0	0	0				
PF-3,7-DMOA	4	4	0	0	0				
FOSA	108	103	0	5	4.6	0.06	0.50	0.31	0.36
FOSAA	4	4	0	0	0				
N-EtFOSA	56	55	0	1	1.8	2.75	2.75	2.75	2.75
N-EtFOSAA	4	4	0	0	0				
N-EtFOSE	60	53	0	7	11.7	0.61	1.62	1.11	1.01
N-MeFOSA	56	56	0	0	0				
N-MeFOSAA	4	4	0	0	0				
N-MeFOSE	56	56	0	0	0				
PFNS	4	4	0	0	0				
PFDoDS	4	4	0	0	0				
HPFHpA	5	5	0	0	0				

Table 27 – Summary of the PFAS measured in sediment data, split by the sampling environment.

	MARINE				LAKE				STREAM			
Substance	Total	>LOD %	Max	Mean	Total	>LOD %	Max	Mean	Total	>LOD %	Max	Mean
PFBA	107	14.95	0.57	0.18	88	6.82	3.70	1.05	99	4.04	3.80	2.02
PFPeA	65	29.23	1.64	0.62	59	6.78	0.53	0.32	6	0		
PFHxA	132	21.97	0.83	0.22	95	7.37	2.50	0.81	100	11.00	1.50	0.39
PFHpA	90	53.33	2.40	0.53	61	3.28	0.15	0.15	6	0		
PFOA	163	46.01	6.80	1.67	123	14.63	2.60	0.28	99	2.02	1.10	0.91
PFNA	154	62.99	8.20	2.04	92	5.43	0.28	0.11	99	7.07	4.50	1.20
PFDA	151	60.26	3.50	0.57	93	8.60	0.58	0.14	99	1.01	2.80	2.80
PFUnDA	157	64.97	1.80	0.59	97	24.74	0.90	0.48	99	1.01	0.61	0.61
PFDoDA	85	21.18	0.19	0.08	91	6.59	0.12	0.07	99	0		
PFTrDA	39	79.49	0.37	0.13	59	13.56	0.59	0.31	3	0		
PFTeDA	30	3.33	0.91	0.91	59	5.08	0.88	0.70	3	0		
PFHxDA	26	0			8	0			2	0		
PFOcDA	26	0			8	0			2	0		
PFBS	79	7.59			56	3.57	0.15	0.09	6	0		
PFPeS	-	-	-	-	3	0			2	0		
PFHxS	87	42.53	1.20	0.16	64	6.25	0.50	0.16	6	0		
PFHpS	30	16.67	0.05	0.03	60	0			6	0		
PFOS	192	60.42	11.00	1.99	177	54.80	72.00	2.42	139	4.32	2.70	1.48
PFDS	84	11.90			61	1.64	0.51	0.51	3	0		
6:2 FTS	34	2.94	0.56	0.56	49	0			6	0		
8:2 FTS	3	0			48	0			3	0		
10:2 FTS	-	-	-	-	2	0			2	0		
PF-3,7-DMOA	-	-	-	-	2	0			2	0		
FOSA	53	0			49	8.16	0.50	0.27	3	0		
FOSAA	-	-	-	-	2	0			2	0		
N-EtFOSA	3	0			47	0			3	0		
N-EtFOSAA	-	-	-	-	2	0			2	0		
N-EtFOSE	3	0			51	13.73	1.62	1.11	3	0		
N-MeFOSA	3	0			47	0			3	0		
N-MeFOSAA	-	-	-	-	2	0			2	0		
N-MeFOSE	3	0			47	0			3	0		
PFNS	-	-	-	-	2	0			2	0		
PFDoDS	-	-	-	-	2	0			2	0		
HPFHpA	-	-	-	-	3	0			2	0		

ANNEX II – Additional maps, figures and tables

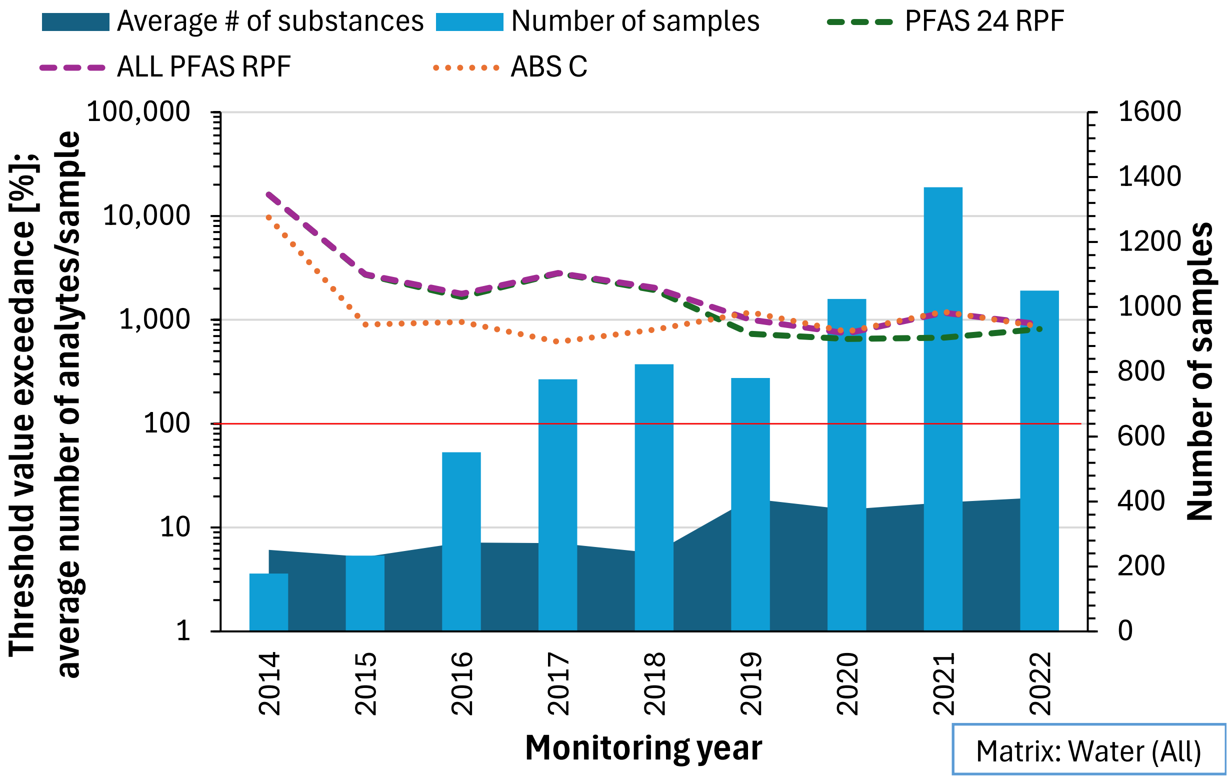

Figure 47 – Time-trends for different PFAS sum parameters in all water samples (including a few wastewater and groundwater samples). Three different sum parameters are represented with different lines, showing the yearly average on how much samples exceeded the new proposed thresholds (0.0044 µg/l PFOA equivalent). Blue area on the background indicates the number of different PFAS compounds on average included in samples each year.

Table 28 – Ranking of all PFAS measured from all surface water samples (rivers, lakes, marine) based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentrations (ng/L PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFNA	3381	965	244.32	5358487.15	44.88	44.88
PFOS	5644	2999	50.06	3411748.23	28.58	73.46
6:2 FTS	2252	556	81.71	1032574.22	8.65	82.11
PFOA	4338	2677	11.10	675554.91	5.66	87.77
PFUnDA	2950	191	106.38	461767.36	3.87	91.63
PFHxS	2747	1194	14.10	382492.96	3.20	94.84
PFDA	3398	370	21.09	177389.02	1.49	96.32
PFHpA	2788	1966	3.08	137714.10	1.15	97.48
N-EtFOSA	1054	150	40.00	136363.64	1.14	98.62
PFHpS	2037	221	4.77	23980.02	0.20	98.82
N-MeFOSE	1054	5	207.92	23627.27	0.20	99.02
PFBA	3098	1823	0.42	17467.39	0.15	99.16
PFDS	2136	12	62.73	17108.12	0.14	99.31
PFTrDA	1986	25	21.02	11943.08	0.10	99.41
PFPeA	2620	1468	0.35	11550.04	0.10	99.50
FOSA	1924	131	3.56	10596.20	0.09	99.59
PFDoDA	2822	23	19.47	10178.80	0.09	99.68
PFPeS	1474	282	1.50	9610.10	0.08	99.76
8:2 FTS	1257	35	10.15	8076.36	0.07	99.83
FHxSA	15	15	16.67	5681.82	0.05	99.87
PFHxA	3271	1960	0.13	5611.63	0.05	99.92
N-EtFOSE	1054	4	24.35	2213.64	0.02	99.94
4:2 FTS	1171	7	12.73	2025.91	0.02	99.96
TFA	104	28	1.50	955.64	0.01	99.96
PFNS	1467	8	5.04	915.73	0.01	99.97
N-EtFOSAA	1156	6	5.30	723.18	0.01	99.98
PFTeDA	1704	2	15.39	699.55	0.01	99.98
FBSA	3	3	10.00	681.82	0.01	99.99
PFDoDS	1355	8	3.55	645.45	0.01	99.99
FOSAA	1066	4	2.69	244.55	0.00	100.00
PFBS	2777	1350	0.01	210.71	0.00	100.00
N-MeFOSAA	1054	3	1.71	116.82	0.00	100.00
PFTrDS	269	1	2.13	48.35	0.00	100.00
N-MeFOSA	1054	1	1.98	45.00	0.00	100.00
HPFHpA	1067	3	0.48	32.95	0.00	100.00
PFOcDA	1617	7	0.02	3.18	0.00	100.00
PFHxDA	1631	5	0.02	2.09	0.00	100.00
PF-3,7-DMOA	1060	0				
PFUnDS	350	0				
H4PFUnDA	7	0				

Table 29 - Ranking of all PFAS measured from marine water samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentrations (ng/L PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	346	193	3.65	15998.65	66.10	66.10
PFOA	215	122	0.96	2669.34	11.03	77.13
PFNA	115	17	6.76	2611.74	10.79	87.92
TFA	104	28	1.50	955.64	3.95	91.87
PFBA	109	43	0.93	904.92	3.74	95.61
PFHpA	76	42	0.49	463.57	1.92	97.52
PFUnDA	115	1	16.40	372.73	1.54	99.06
FOSA	77	5	0.95	107.73	0.45	99.51
6:2 FTS	58	2	0.78	35.45	0.15	99.66
PFHxS	76	3	0.47	32.11	0.13	99.79
PFHxA	125	25	0.05	28.03	0.12	99.90
PFHpS	71	1	0.39	8.86	0.04	99.94
4:2 FTS	7	1	0.36	8.18	0.03	99.98
PFPeA	75	17	0.01	4.50	0.02	99.99
PFPeS	56	1	0.06	1.43	0.01	100.00
PFBS	75	4	0.00	0.03	0.00	100.00
PFDA	125	0				
PFDoDA	115	0				
PFDS	71	0				
PFTrDA	52	0				
PFNS	51	0				
PFDoDS	51	0				
PFUnDS	51	0				
PFTrDS	51	0				
PFTeDA	8	0				
8:2 FTS	6	0				
HPFHpA	6	0				
H4PFUnDA	5	0				
FOSAA	3	0				
PFHxDA	2	0				
PFOcDA	2	0				
N-EtFOSA	2	0				
N-EtFOSAA	2	0				
N-EtFOSE	2	0				
N-MeFOSA	2	0				
N-MeFOSAA	2	0				
N-MeFOSE	2	0				
PF-3,7-DMOA	1	0				

Table 30 - Ranking of all PFAS measured from all surface water samples (rivers, lakes, marine) based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (ng/l PFOA eq)	Average TH exceedance amount (%)	Rank
PFNA	3381	497	15	244	5553	1
6:2 FTS	2252	346	15	82	1857	2
PFOS	5644	867	15	50	1138	3
FHxSA	15	15	100	17	379	4
N-EtFOSA	1054	150	14	40	909	5
PFUnDA	2950	122	4	106	2418	6
FBSA	3	3	100	10	227	7
PFDA	3398	167	5	21	479	8
N-MeFOSE	1054	4	0	208	4725	9
PFHxS	2747	216	8	14	320	10
PFOA	4338	391	9	11	252	11
N-EtFOSE	1054	4	0	24	553	12
PFDS	2136	5	0	63	1426	13
PFDoDA	2822	12	0	19	443	14
PFTrDA	1986	6	0	21	478	15
8:2 FTS	1257	22	2	10	231	15
TFA	104	28	27	2	34	15
PFHpA	2788	204	7	3	70	18
PFHpS	2037	61	3	5	109	18
FOSA	1924	24	1	4	81	20
4:2 FTS	1171	3	0	13	289	20
PFTeDA	1704	1	0	15	350	22
PFPeS	1474	27	2	1	34	23
N-EtFOSAA	1156	2	0	5	121	23
PFNS	1467	2	0	5	114	25
PFBA	3098	19	1	0	10	26
PFPeA	2620	12	0	0	8	27
PFDoDS	1355	1	0	4	81	28
FOSAA	1066	1	0	3	61	29
PFTrDS	269	0	0	2	48	30
N-MeFOSA	1054	0	0	2	45	31
N-MeFOSAA	1054	0	0	2	39	32
PFHxA	3271	4	0	0	3	33
HPFHpA	1067	0	0	0	11	34
PFOcDA	1617	0	0	0	0	35
PFHxDA	1631	0	0	0	0	36
PFBS	2777	0	0	0	0	37
PF-3,7-DMOA	1060	0	0			
PFUnDS	350	0	0			
H4PFUnDA	7	0	0			

Table 31 - Ranking of all PFAS measured from marine water samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (ng/l PFOA eq)	Average TH exceedance amount (%)	Rank
PFNA	115	8	6.956522	6.759804	153.6319	1
TFA	104	28	26.92308	1.501714	34.12987	2
PFOS	346	13	3.757225	3.647361	82.89457	3
PFUnDA	115	1	0.869565	16.4	372.7273	4
PFOA	215	5	2.325581	0.962713	21.87984	5
PFBA	109	1	0.917431	0.925967	21.04471	6
FOSA	77	0	0	0.948	21.54545	7
PFHpA	76	1	1.315789	0.485642	11.03731	7
6:2 FTS	58	0	0	0.78	17.72727	9
PFHxS	76	0	0	0.471	10.70455	10
PFHpS	71	0	0	0.39	8.863636	11
4:2 FTS	7	0	0	0.36	8.181818	12
PFPeS	56	0	0	0.063105	1.434205	13
PFHxA	125	0	0	0.049336	1.121273	14
PFPeA	75	0	0	0.011647	0.264706	15
PFBS	75	0	0	0.000353	0.008011	16
PFDA	125	0	0			
PFDoDA	115	0	0			
PFDS	71	0	0			
PFTrDA	52	0	0			
PFNS	51	0	0			
PFDoDS	51	0	0			
PFUnDS	51	0	0			
PFTrDS	51	0	0			
PFTeDA	8	0	0			
8:2 FTS	6	0	0			
HPFHpA	6	0	0			
H4PFUnDA	5	0	0			
FOSAA	3	0	0			
PFHxDA	2	0	0			
PFOcDA	2	0	0			
N-EtFOSA	2	0	0			
N-EtFOSAA	2	0	0			
N-EtFOSE	2	0	0			
N-MeFOSA	2	0	0			
N-MeFOSAA	2	0	0			
N-MeFOSE	2	0	0			
PF-3,7-DMOA	1	0	0			

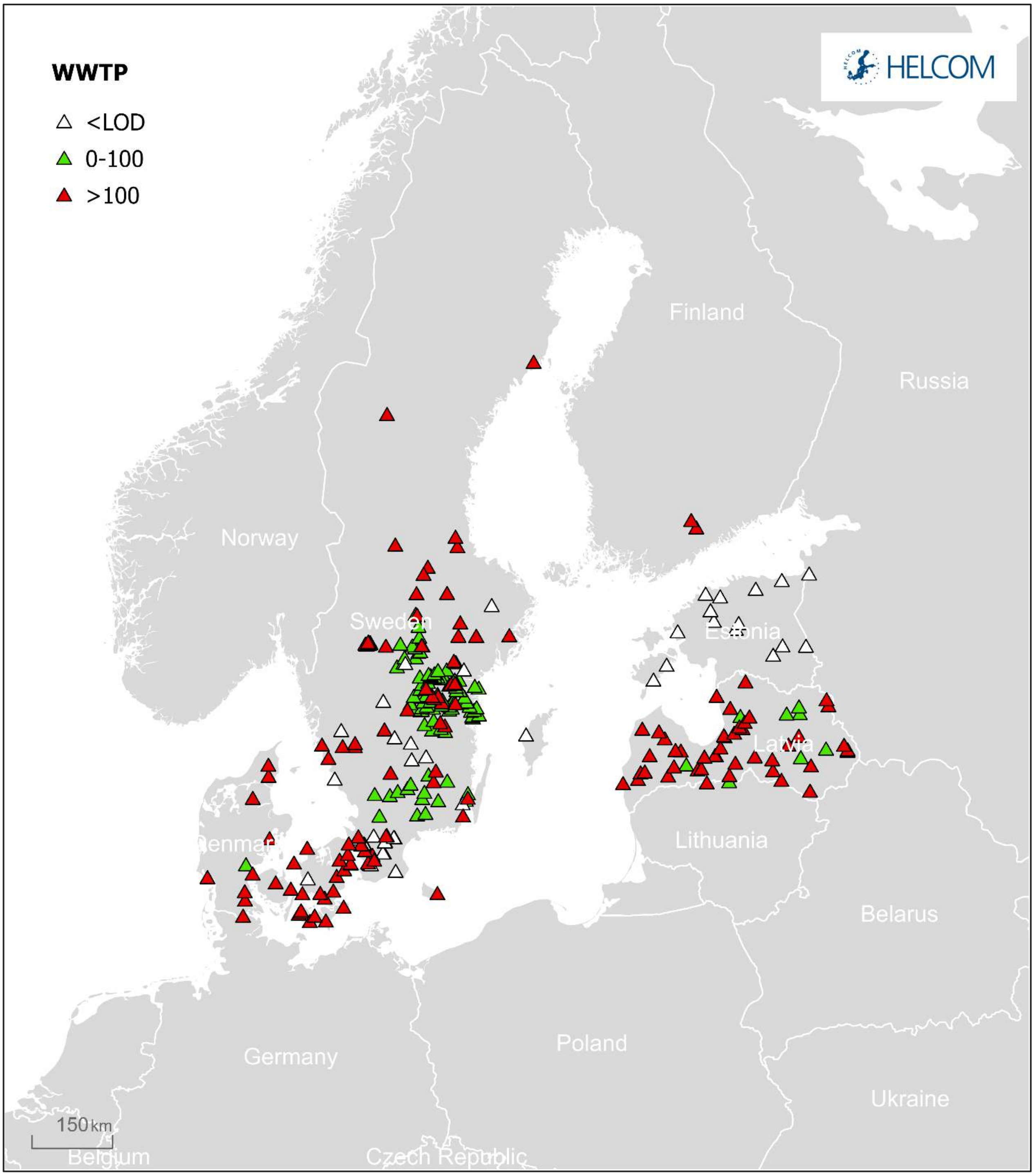

Figure 48 - Geographic distribution of the summed results of all measured PFAS from WWTP effluents and recipient waterbodies. Only the latest sample from each location is shown. The colours correspond to the new proposed threshold of 4.4 ng/L PFOA equivalents, with red samples over the threshold value. Samples marked <LOD are not necessarily under the threshold value, as in same water samples the applied LOD values were not sensitive enough to provide representative data according to the new thresholds and RPF system, an issue often further enhanced by wastewater matrix creating extra noise.

Table 32 - Ranking of all PFAS measured from all biota samples based on the total amount of “threshold exceedance”, calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg ww)	“Total” TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	3788	3534	4.82	22102519.76	62.13	62.13
PFNA	1992	1444	2.00	3753102.25	10.55	72.68
PFDA	1994	1613	1.66	3487578.50	9.80	82.48
PFUnDA	1976	1589	1.48	3056724.01	8.59	91.07
PFDoDA	1584	1227	0.68	1079192.83	3.03	94.10
PFTrDA	1336	1166	0.47	710735.83	2.00	96.10
PFDS	2165	563	0.51	375401.34	1.06	97.16
FOSA	2356	1510	0.18	357367.56	1.00	98.16
PFOA	2393	733	0.14	131321.68	0.37	98.53
PFHpS	424	126	0.79	129881.34	0.37	98.90
PFHpA	1470	131	0.41	69145.97	0.19	99.09
PFHxS	1925	615	0.08	67065.48	0.19	99.28
6:2 FTS	231	45	1.04	60648.68	0.17	99.45
FBSA	18	18	2.07	48494.52	0.14	99.58
10:2 FTS	14	1	22.60	29350.65	0.08	99.67
PFPeDA	901	494	0.04	27893.98	0.08	99.75
4:2 FTS	122	20	0.87	22572.44	0.06	99.81
PFTeDA	1320	786	0.02	20551.78	0.06	99.87
8:2 FTS	162	23	0.56	16845.06	0.05	99.91
HPFHpA	55	2	4.59	11922.08	0.03	99.95
PFBA	520	53	0.09	6266.89	0.02	99.97
PFPeA	344	47	0.07	4024.23	0.01	99.98
N-MeFOSA	36	1	2.00	2597.40	0.01	99.98
N-MeFOSAA	43	2	0.75	1948.05	0.01	99.99
PFECHS	23	11	0.10	1466.28	0.00	99.99
PFHxA	1621	117	0.01	1232.69	0.00	100.00
FOSAA	20	1	0.32	412.99	0.00	100.00
N-EtFOSAA	81	2	0.13	334.18	0.00	100.00
H4PFUnDA	23	1	0.20	259.74	0.00	100.00
PFBS	1300	100	0.00	65.83	0.00	100.00
8:2 Cl-PFESA	20	1	0.01	10.39	0.00	100.00
PFHxDA	273	6	0.00	2.30	0.00	100.00
PFOcDA	267	1	0.00	0.80	0.00	100.00
PF-3,7-DMOA	32	0				
PFPeS	30	0				
N-EtFOSA	30	0				
N-EtFOSE	27	0				
N-MeFOSE	27	0				
H2PFDA	25	0				
6:2 Cl-PFESA	20	0				

HFPO-DA	8	0				
ADONA	8	0				
6:2 diPAP	8	0				
8:2 diPAP	8	0				
PFPrA	5	0				
6:2/8:2 diPAP	3	0				
PFNS	2	0				
PFMOPrA	2	0				
10:2 diPAP	1	0				
Cl-PFHxPA	1	0				
8:2/10:2 diPAP	1	0				
6:2 monoPAP	1	0				
8:2 monoPAP	1	0				

Matrix: Biota (Marine)

Table 33 - Ranking of all PFAS measured from marine biota samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg ww)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	2237	2135	5.31	14730250.07	62.18	62.18
PFNA	971	830	2.98	3208644.27	13.54	75.72
PFUnDA	962	833	1.73	1874118.19	7.91	83.63
PFDA	982	844	1.65	1810315.01	7.64	91.27
PFDoDA	837	627	0.71	580622.91	2.45	93.72
PFTrDA	713	588	0.52	396589.98	1.67	95.40
PFDS	1226	391	0.58	295684.67	1.25	96.64
FOSA	1212	1009	0.22	287357.91	1.21	97.86
PFHpS	262	101	0.99	129288.56	0.55	98.40
PFOA	1190	595	0.15	115474.16	0.49	98.89
PFHxS	1042	486	0.09	59512.92	0.25	99.14
PFHpA	791	100	0.38	49658.80	0.21	99.35
FBSA	18	18	2.07	48494.52	0.20	99.55
6:2 FTS	105	35	1.01	46061.77	0.19	99.75
4:2 FTS	65	17	1.02	22533.48	0.10	99.84
PFPeDA	501	273	0.05	17510.45	0.07	99.92
PFTeDA	701	369	0.02	8469.33	0.04	99.95
PFBA	240	40	0.10	5158.77	0.02	99.98
PFPeA	162	37	0.06	3007.39	0.01	99.99
PFECHS	23	11	0.10	1466.28	0.01	99.99
PFHxA	910	85	0.01	1026.92	0.00	100.00
8:2 FTS	57	2	0.08	195.67	0.00	100.00
PFBS	736	47	0.00	52.11	0.00	100.00
8:2 Cl-PFESA	20	1	0.01	10.39	0.00	100.00
PFHxDA	135	0				
PFOcDA	135	0				
N-EtFOSAA	39	0				

6:2 Cl-PFESA	20	0				
HPFHpA	18	0				
PFPeS	12	0				
HFPO-DA	8	0				
ADONA	8	0				
6:2 diPAP	8	0				
8:2 diPAP	8	0				
N-MeFOSA	8	0				
N-MeFOSAA	8	0				
PFPrA	5	0				
FOSAA	3	0				
N-EtFOSA	3	0				
6:2/8:2 diPAP	3	0				
PFNS	2	0				
H2PFDA	2	0				
PFMOPrA	2	0				
10:2 diPAP	1	0				
Cl-PFHxPA	1	0				
8:2/10:2 diPAP	1	0				
6:2 monoPAP	1	0				
8:2 monoPAP	1	0				

Matrix: Biota (all)

Table 34 - Ranking of all PFAS measured from all biota samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (µg/kg ww)	Average TH exceedance amount (%)	Rank
PFOS	3788	3302	87.17	4.82	6254.25	1
FBSA	18	18	100.00	2.07	2694.14	2
PFDA	1994	1543	77.38	1.66	2162.17	3
PFNA	1992	1420	71.29	2.00	2599.10	3
PFUnDA	1976	1517	76.77	1.48	1923.68	5
6:2 FTS	231	42	18.18	1.04	1347.75	6
PFDoDA	1584	933	58.90	0.68	879.54	7
10:2 FTS	14	1	7.14	22.60	29350.65	7
PFTrDA	1336	853	63.85	0.47	609.55	9
4:2 FTS	122	16	13.11	0.87	1128.62	9
PFHpS	424	49	11.56	0.79	1030.80	11
PFDS	2165	338	15.61	0.51	666.79	12
HPFHpA	55	2	3.64	4.59	5961.04	13
FOSA	2356	611	25.93	0.18	236.67	14
8:2 FTS	162	17	10.49	0.56	732.39	15
PFECHS	23	10	43.48	0.10	133.30	16
N-MeFOSA	36	1	2.78	2.00	2597.40	17
PFOA	2393	272	11.37	0.14	179.16	18
N-MeFOSAA	43	2	4.65	0.75	974.03	18

FOSAA	20	1	5.00	0.32	412.99	20
PFPeDA	901	98	10.88	0.04	56.47	21
PFHxS	1925	167	8.68	0.08	109.05	22
H4PFUnDA	23	1	4.35	0.20	259.74	22
PFBA	520	26	5.00	0.09	118.24	24
PFHpA	1470	38	2.59	0.41	527.83	25
PFTeDA	1320	128	9.70	0.02	26.15	25
8:2 Cl-PFESA	20	1	5.00	0.01	10.39	27
N-EtFOSAA	81	1	1.23	0.13	167.09	28
PFPeA	344	9	2.62	0.07	85.62	29
PFHxA	1621	4	0.25	0.01	10.54	30
PFOcDA	267	0	0	0.00	0.80	31
PFBS	1300	0	0	0.00	0.66	32
PFHxDA	273	0	0	0.00	0.38	33
PF-3,7-DMOA	32	0	0			
PFPeS	30	0	0			
N-EtFOSA	30	0	0			
N-EtFOSE	27	0	0			
N-MeFOSE	27	0	0			
H2PFDA	25	0	0			
6:2 Cl-PFESA	20	0	0			
HFPO-DA	8	0	0			
ADONA	8	0	0			
6:2 diPAP	8	0	0			
8:2 diPAP	8	0	0			
PFPrA	5	0	0			
6:2/8:2 diPAP	3	0	0			
PFNS	2	0	0			
PFMOPrA	2	0	0			
10:2 diPAP	1	0	0			
Cl-PFHxPA	1	0	0			
8:2/10:2 diPAP	1	0	0			
6:2 monoPAP	1	0	0			
8:2 monoPAP	1	0	0			

Matrix: Biota (Marine)

Table 35 - Ranking of all PFAS measured from marine biota samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (µg/kg ww)	Average TH exceedance amount (%)	Rank
PFOS	2237	2027	90.61	5.31	6899.41	1
FBSA	18	18	100.00	2.07	2694.14	2
PFNA	971	817	84.14	2.98	3865.84	3
PFUnDA	962	792	82.33	1.73	2249.84	4
PFDA	982	802	81.67	1.65	2144.92	5

PFDoDA	837	372	44.44	0.71	926.03	6
PFTrDA	713	335	46.98	0.52	674.47	7
6:2 FTS	105	35	33.33	1.01	1316.05	7
4:2 FTS	65	16	24.62	1.02	1325.50	7
PFHpS	262	48	18.32	0.99	1280.08	10
PFDS	1226	251	20.47	0.58	756.23	11
FOSA	1212	492	40.59	0.22	284.79	11
PFECHS	23	10	43.48	0.10	133.30	13
PFOA	1190	210	17.65	0.15	194.07	14
PFHpA	791	28	3.54	0.38	496.59	15
PFHxS	1042	142	13.63	0.09	122.45	16
PFBA	240	21	8.75	0.10	128.97	16
PFPeDA	501	86	17.17	0.05	64.14	18
PFTeDA	701	104	14.84	0.02	22.95	19
PFPeA	162	4	2.47	0.06	81.28	20
8:2 FTS	57	1	1.75	0.08	97.84	20
8:2 Cl-PFESA	20	1	5.00	0.01	10.39	22
PFHxA	910	4	0.44	0.01	12.08	23
PFBS	736	0	0	0.00	1.11	24
PFHxDA	135	0	0			
PFOcDA	135	0	0			
N-EtFOSAA	39	0	0			
6:2 Cl-PFESA	20	0	0			
HPFHpA	18	0	0			
PFPeS	12	0	0			
HFPO-DA	8	0	0			
ADONA	8	0	0			
6:2 diPAP	8	0	0			
8:2 diPAP	8	0	0			
N-MeFOSA	8	0	0			
N-MeFOSAA	8	0	0			
PFPrA	5	0	0			
FOSAA	3	0	0			
N-EtFOSA	3	0	0			
6:2/8:2 diPAP	3	0	0			
PFNS	2	0	0			
H2PFDA	2	0	0			
PFMOPrA	2	0	0			
10:2 diPAP	1	0	0			
Cl-PFHxPA	1	0	0			
8:2/10:2 diPAP	1	0	0			
6:2 monoPAP	1	0	0			
8:2 monoPAP	1	0	0			

Table 36 – Difference in PFAS detection, threshold (TH) exceedance and LOD issues in all measured fish samples according to the analysed tissue.

	MUSCLE			LIVER			L>M	L>M
Compound	Samples measured	Samples >LOQ %	Samples >TH %	Samples measured	Samples >LOQ %	Samples >TH %	Change >LOQ %	Change >TH %
ALL PFAS	10,846	38.30	32.72	16,279	57.20	34.36	**18.90**	**1.64**
PFOS	1,620	89.20	88.58	1,768	97.62	85.18	**8.43**	**-3.40**
PFNA	581	56.97	56.97	1,170	76.50	74.44	**19.52**	**17.47**
PFUnDA	571	64.80	64.80	1,169	85.29	79.13	**20.49**	**14.33**
PFDA	589	64.52	64.35	1,164	87.03	81.10	**22.51**	**16.75**
PFTrDA	360	73.89	68.89	754	92.04	53.71	**18.15**	**-15.18**
PFDoDA	558	53.23	52.87	785	91.08	54.27	**37.86**	**1.40**
PFDS	532	19.17	18.23	1,282	17.00	4.84	**-2.17**	**-13.40**
FOSA	274	32.85	24.82	1,763	66.82	19.17	**33.97**	**-5.65**
PFOA	974	20.23	11.29	1,174	35.09	3.75	**14.87**	**-7.55**
PFHxS	462	19.48	6.71	1,158	28.93	0.69	**9.45**	**-6.02**
PFPeDA	6	100.00	66.67	709	49.08	0.99	**-50.92**	**-65.68**
PFHpS	325	19.38	7.08	51	78.43	31.37	**59.05**	**24.30**
PFTeDA	363	30.85	5.23	748	65.51	0.27	**34.65**	**-4.97**
PFHpA	468	9.40	6.41	789	8.75	1.01	**-0.66**	**-5.40**
6:2 FTS	196	14.80	13.27	27	59.26	59.26	**44.46**	**45.99**
FBSA	10	100.00	100.00	8	100.00	100.00	**0.00**	**0.00**
10:2 FTS	14	7.14	7.14	-				
4:2 FTS	104	11.54	7.69	13	61.54	61.54	**50.00**	**53.85**
8:2 FTS	156	14.74	10.90	5	-	-	**-14.74**	**-10.90**
PFECHS	2	-	-	3	-	-	**0.00**	**0.00**
HPFHpA	49	4.08	4.08	1	-	-	**-4.08**	**-4.08**
PFBA	438	7.76	5.94	54	35.19	-	**27.42**	**-5.94**
PFPeA	309	10.03	2.91	30	53.33	-	**43.30**	**-2.91**
N-	29	3.45	3.45	2	-	-	**-3.45**	**-3.45**
N-	34	5.88	5.88	4	-	-	**-5.88**	**-5.88**
PFHxA	566	10.78	0.71	821	5.24	-	**-5.54**	**-0.71**
FOSAA	17	5.88	5.88	2	-	-	**-5.88**	**-5.88**
N-	71	1.41	1.41	5	20.00	-	**18.59**	**-1.41**
H4PFUnD	23	4.35	4.35	-				
8:2 Cl-	2	-	-	3	-	-	**0.00**	**0.00**
PFBS	354	5.08	-	728	7.14	-	**2.06**	**0.00**
PFHxDA	242	2.07	-	30	3.33	-	**1.27**	**0.00**
PFOcDA	238	-	-	28	3.57	-	**3.57**	**0.00**

Table 37 – Difference in PFAS detection, threshold (TH) exceedance and LOD issues in marine fish samples according to the analysed tissue.

	MUSCLE			LIVER			L>M	L>M
Compound	**Samples measured**	**Samples >LOQ %**	**Samples >TH %**	**Samples measured**	**Samples >LOQ %**	**Samples >TH %**	**Change >LOQ %**	**Change >TH %**
ALL PFAS	4,945	45.76	39.51	8,050	63.40	33.93	**17.64**	**-5.59**
PFOS	1,041	95.00	94.62	850	97.65	85.65	**2.64**	**-8.97**
PFNA	235	74.04	74.04	538	89.41	86.99	**15.36**	**12.95**
PFUnDA	232	65.09	65.09	537	93.67	86.03	**28.58**	**20.95**
PFDA	245	65.71	65.31	539	93.88	86.27	**28.16**	**20.96**
PFTrDA	163	63.80	53.99	371	85.98	22.37	**22.18**	**-31.62**
PFDoDA	243	47.74	47.33	396	85.35	21.46	**37.62**	**-25.86**
PFDS	239	18.83	17.99	678	20.65	6.64	**1.82**	**-11.35**
FOSA	81	46.91	35.80	854	89.93	34.19	**43.02**	**-1.61**
PFOA	439	35.76	18.00	542	63.28	7.56	**27.52**	**-10.43**
PFHxS	214	31.78	9.81	566	47.70	0.53	**15.93**	**-9.28**
PFPeDA	2	100.00	-	348	47.70	0.86	**-52.30**	**0.86**
PFHpS	183	27.87	12.02	38	84.21	42.11	**56.34**	**30.08**
PFTeDA	163	14.72	-	371	53.37	-	**38.65**	**0.00**
PFHpA	213	14.55	9.39	398	14.57	2.01	**0.02**	**-7.38**
6:2 FTS	73	26.03	26.03	24	66.67	66.67	**40.64**	**40.64**
FBSA	10	100.00	100.00	8	100.00	100.00	**0.00**	**0.00**
10:2 FTS	-			-				
4:2 FTS	50	18.00	16.00	10	80.00	80.00	**62.00**	**64.00**
8:2 FTS	54	3.70	1.85	2	-	-	**-3.70**	**-1.85**
PFECHS	2	-	-	3	-	-	**0.00**	**0.00**
HPFHpA	12	-	-	1	-	-	**0.00**	**0.00**
PFBA	182	13.19	11.54	30	53.33	-	**40.15**	**-11.54**
PFPeA	130	16.15	3.08	27	59.26	-	**43.11**	**-3.08**
N-	2	-	-	1	-	-	**0.00**	**0.00**
N-	2	-	-	1	-	-	**0.00**	**0.00**
PFHxA	253	14.23	1.58	463	8.42	-	**-5.81**	**-1.58**
FOSAA	1	-	-	1	-	-	**0.00**	**0.00**
N-	32	-	-	2	-	-	**0.00**	**0.00**
H4PFUnD	-			-				
8:2 Cl-	2	-	-	3	-	-	**0.00**	**0.00**
PFBS	162	7.41	-	389	8.48	-	**1.08**	**0.00**
PFHxDA	120	-	-	14	-	-	**0.00**	**0.00**
PFOcDA	120	-	-	14	-	-	**0.00**	**0.00**

Table 38 – Ranking of all PFAS measured from sediment samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFNA	621	133	12.74	6273.33	38.81	38.81
PFOS	861	424	3.80	5972.67	36.95	75.76
PFDA	620	160	2.61	1549.62	9.59	85.34
PFUnDA	511	214	1.61	1278.81	7.91	93.25
PFOA	738	154	0.76	431.01	2.67	95.92
N-EtFOSAA	137	10	4.30	159.31	0.99	96.91
PFDoDA	440	88	0.30	96.73	0.60	97.50
PFTrDA	256	125	0.20	90.57	0.56	98.06
N-EtFOSE	194	15	1.53	85.25	0.53	98.59
PFHpA	447	53	0.25	48.49	0.30	98.89
N-MeFOSAA	137	3	3.17	35.27	0.22	99.11
PFHxS	336	52	0.18	33.84	0.21	99.32
FOSA	265	26	0.33	32.08	0.20	99.52
6:2 FTS	352	18	0.33	21.97	0.14	99.65
N-EtFOSA	191	1	5.50	20.37	0.13	99.78
N-MeFOSE	191	1	2.22	8.22	0.05	99.83
10:2 FTS	137	1	2.10	7.78	0.05	99.88
PFTeDA	256	37	0.05	6.88	0.04	99.92
PFDS	329	3	0.43	4.79	0.03	99.95
PFBA	572	21	0.04	3.25	0.02	99.97
N-MeFOSA	191	2	0.24	1.76	0.01	99.98
PFHpS	256	6	0.06	1.43	0.01	99.99
PFPeA	403	14	0.01	0.74	0.00	99.99
PFHxA	620	57	0.00	0.73	0.00	100.00
PFBS	433	11	0.00	0.07	0.00	100.00
PFPeS	138	1	0.02	0.07	0.00	100.00
8:2 FTS	192	0				
PFHxDA	184	0				
PFOcDA	184	0				
4:2 FTS	138	0				
HPFHpA	138	0				
FOSAA	137	0				
PFNS	137	0				
PFDoDS	137	0				
PF-3,7-DMOA	4	0				

Table 39 - Ranking of all PFAS measured from marine sediment samples based on the total amount of "threshold exceedance", calculated based on the number of measurements and average concentrations using the RPF approach. This method heavily favours PFAS compounds that are measured more often.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFNA	246	109	14.52	5862.30	54.11	54.11
PFOS	293	199	2.79	2057.60	18.99	73.10
PFDA	245	113	3.12	1306.46	12.06	85.16
PFUnDA	245	149	1.80	994.47	9.18	94.34
PFOA	264	108	0.97	388.46	3.59	97.92
PFTrDA	126	83	0.17	52.80	0.49	98.41
PFDoDA	179	48	0.27	47.93	0.44	98.85
PFHpA	197	46	0.27	45.28	0.42	99.27
PFHxS	199	38	0.19	26.72	0.25	99.52
N-EtFOSE	83	6	1.00	22.30	0.21	99.72
N-EtFOSAA	81	1	2.36	8.74	0.08	99.81
10:2 FTS	81	1	2.10	7.78	0.07	99.88
FOSA	156	4	0.41	6.13	0.06	99.93
6:2 FTS	125	3	0.26	2.87	0.03	99.96
PFTeDA	126	11	0.05	2.06	0.02	99.98
PFHpS	125	6	0.06	1.43	0.01	99.99
PFPeA	166	7	0.02	0.48	0.00	100.00
PFBA	212	6	0.01	0.20	0.00	100.00
PFHxA	243	19	0.00	0.16	0.00	100.00
PFBS	198	2	0.00	0.00	0.00	100.00
PFDS	197	0				
PFHxDA	122	0				
PFOcDA	122	0				
8:2 FTS	84	0				
N-EtFOSA	84	0				
N-MeFOSA	84	0				
N-MeFOSE	84	0				
PFPeS	81	0				
4:2 FTS	81	0				
FOSAA	81	0				
N-MeFOSAA	81	0				
PFNS	81	0				
PFDoDS	81	0				
HPFHpA	81	0				

Table 40 - Ranking of all PFAS measured from all sediment samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (ng/l PFOA eq)	Average TH exceedance amount (%)	Rank
PFNA	621	25	4.03	12.74	47.17	1
N-EtFOSA	191	0	0	5.50	20.37	2
PFOS	861	6	0.70	3.80	14.09	3
N-EtFOSAA	137	0	0	4.30	15.93	3
N-MeFOSAA	137	0	0	3.17	11.76	5
PFDA	620	0	0	2.61	9.69	6
N-MeFOSE	191	0	0	2.22	8.22	7
10:2 FTS	137	0	0	2.10	7.78	8
PFUnDA	511	0	0	1.61	5.98	9
N-EtFOSE	194	0	0	1.53	5.68	10
PFOA	738	0	0	0.76	2.80	11
PFDS	329	0	0	0.43	1.60	12
FOSA	265	0	0	0.33	1.23	13
6:2 FTS	352	0	0	0.33	1.22	14
PFDoDA	440	0	0	0.30	1.10	15
PFHpA	447	0	0	0.25	0.91	16
N-MeFOSA	191	0	0	0.24	0.88	17
PFTrDA	256	0	0	0.20	0.72	18
PFHxS	336	0	0	0.18	0.65	19
PFHpS	256	0	0	0.06	0.24	20
PFTeDA	256	0	0	0.05	0.19	21
PFBA	572	0	0	0.04	0.15	22
PFPeS	138	0	0	0.02	0.07	23
PFPeA	403	0	0	0.01	0.05	24
PFHxA	620	0	0	0.00	0.01	25
PFBS	433	0	0	0.00	0.01	26
8:2 FTS	192	0	0			
PFHxDA	184	0	0			
PFOcDA	184	0	0			
4:2 FTS	138	0	0			
HPFHpA	138	0	0			
FOSAA	137	0	0			
PFNS	137	0	0			
PFDoDS	137	0	0			
PF-3,7-DMOA	4	0	0			

Table 41 - Ranking of all PFAS measured from marine sediment samples based on the threshold exceedance frequency and the average exceedance amount using the RPF approach. This method does not take into the cumulative impact of the compounds in the environment.

Compound	Samples measured	Samples exceeded threshold	Exceedance frequency (%)	Average concentration (ng/l PFOA eq)	Average TH exceedance amount (%)	Rank
PFNA	246	24	9.76	14.52	53.78	1
PFDA	245	0	0	3.12	11.56	2
PFOS	293	0	0	2.79	10.34	3
N-EtFOSAA	81	0	0	2.36	8.74	4
10:2 FTS	81	0	0	2.10	7.78	5
PFUnDA	245	0	0	1.80	6.67	6
N-EtFOSE	83	0	0	1.00	3.72	7
PFOA	264	0	0	0.97	3.60	8
FOSA	156	0	0	0.41	1.53	9
PFDoDA	179	0	0	0.27	1.00	10
PFHpA	197	0	0	0.27	0.98	11
6:2 FTS	125	0	0	0.26	0.96	12
PFHxS	199	0	0	0.19	0.70	13
PFTrDA	126	0	0	0.17	0.64	14
PFHpS	125	0	0	0.06	0.24	15
PFTeDA	126	0	0	0.05	0.19	16
PFPeA	166	0	0	0.02	0.07	17
PFBA	212	0	0	0.01	0.03	18
PFHxA	243	0	0	0.00	0.01	19
PFBS	198	0	0	0.00	0.00	20
PFDS	197	0	0			
PFHxDA	122	0	0			
PFOcDA	122	0	0			
8:2 FTS	84	0	0			
N-EtFOSA	84	0	0			
N-MeFOSA	84	0	0			
N-MeFOSE	84	0	0			
PFPeS	81	0	0			
4:2 FTS	81	0	0			
FOSAA	81	0	0			
N-MeFOSAA	81	0	0			
PFNS	81	0	0			
PFDoDS	81	0	0			
HPFHpA	81	0	0			

Table 42 – Ranking of all PFAS measured from water samples collected by the EMPEREST project partners based on the total amount of "threshold exceedance", calculated based on the number of quantified measurements and average concentrations using the RPF approach.

Compound	Samples measured	Samples >LOQ	Average concentrations (ng/L PFOA)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	52	49	15.98	783.08	48.82	48.82
PFNA	52	34	7.91	269.10	16.78	65.60
PFOA	52	52	3.36	174.81	10.90	76.49
PFHxS	52	47	1.73	81.50	5.08	81.58
PFDA	52	10	6.75	67.48	4.21	85.78
6:2 FTS	52	18	3.06	55.09	3.43	89.22
PFHpA	52	52	1.02	53.14	3.31	92.53
TFA	19	19	1.20	22.80	1.42	93.95
FHxSA	52	12	1.35	16.15	1.01	94.96
10:2 FTS	52	1	12.00	12.00	0.75	95.71
8:2 FTS	52	3	3.17	9.52	0.59	96.30
FOSA	52	7	1.17	8.18	0.51	96.81
PFUnDA	52	3	2.68	8.04	0.50	97.31
FBSA	52	12	0.65	7.85	0.49	97.80
PFBA	52	51	0.14	6.91	0.43	98.23
PFPeA	52	45	0.14	6.26	0.39	98.62
PFPeS	52	14	0.32	4.43	0.28	98.90
N-MeFOSAA	52	2	2.11	4.22	0.26	99.16
PFHpS	52	5	0.84	4.20	0.26	99.42
PFDoDA	52	2	1.50	3.00	0.19	99.61
5:3 FTA	52	1	2.90	2.90	0.18	99.79
PFHxA	52	45	0.03	1.56	0.10	99.89
PFMPA	52	3	0.32	0.97	0.06	99.95
PFDS	52	1	0.60	0.60	0.04	99.99
ADONA	52	4	0.05	0.19	0.01	100.00
PFBS	52	28	0.00	0.04	0.00	100.00
6:2 FTOH	19	0				
8:2 FTOH	19	0				
C6O4	19	0				
HPFHpA	19	0				
H4PFUnDA	19	0				
PFTrDA	52	0				
PFTeDA	52	0				
PFHxDA	52	0				
PFOcDA	52	0				
HFPO-DA	52	0				
4:2 FTS	52	0				
6:2 Cl-PFESA	52	0				
8:2 Cl-PFESA	52	0				
PF-3,7-DMOA	52	0				
PFECHS	52	0				
FOSAA	52	0				

N-EtFOSA	52	0				
N-EtFOSAA	52	0				
N-EtFOSE	52	0				
N-MeFOSA	52	0				
N-MeFOSE	52	0				
PFNS	52	0				
PFDoDS	52	0				
3:3 FTA	52	0				
7:3 FTA	52	0				
PFUnDS	52	0				
PFTrDS	52	0				
NFDHA	52	0				
PFEESA	52	0				
PFMBA	52	0				
HFPO-TA	52	0				

Matrix: Biota (piloting)

Table 43 – Ranking of all PFAS measured from biota samples collected by the EMPEREST project partners based on the total amount of "threshold exceedance", calculated based on the number of quantified measurements and average concentrations using the RPF approach.

Compound	Samples measured	Samples >LOQ	Average concentration (µg/kg ww)	"Total" TH exceedance (% of TH)	Share from total (%)	Cumulative exceedance
PFOS	21	21	3.01	63.16	39.88	39.88
PFNA	21	21	2.56	53.74	33.93	73.80
PFDA	21	21	0.89	18.73	11.83	85.63
PFUnDA	21	21	0.76	16.05	10.13	95.77
PFDoDA	21	17	0.13	2.25	1.42	97.19
PFTrDA	21	19	0.10	1.87	1.18	98.37
PFOA	21	9	0.09	0.82	0.52	98.88
FBSA	21	18	0.04	0.77	0.49	99.37
FOSA	21	5	0.06	0.29	0.18	99.55
PFECHS	21	10	0.02	0.23	0.15	99.70
FHxSA	21	7	0.02	0.16	0.10	99.80
PFHpS	21	4	0.03	0.12	0.07	99.87
PFHxS	21	5	0.02	0.12	0.07	99.95
6:2 FTS	21	1	0.04	0.04	0.02	99.97
PFHpA	21	3	0.01	0.02	0.02	99.99
PFTeDA	21	5	0.00	0.02	0.01	100.00
10:2 FTS	21	0				
8:2 FTS	21	0				
PFBA	21	0				
PFPeA	21	0				
PFPeS	21	0				
N-MeFOSAA	21	0				
5:3 FTA	21	0				
PFHxA	21	0				

PFMPA	21	0				
PFDS	21	0				
ADONA	21	0				
PFBS	21	0				
HPFHpA	21	0				
PFHxDA	21	0				
PFOcDA	21	0				
HFPO-DA	21	0				
4:2 FTS	21	0				
6:2 Cl-PFESA	21	0				
8:2 Cl-PFESA	21	0				
N-EtFOSAA	21	0				
PFNS	21	0				
PFDoDS	21	0				
3:3 FTA	21	0				
7:3 FTA	21	0				
PFUnDS	21	0				
PFTrDS	21	0				
NFDHA	21	0				
PFEESA	21	0				
PFMBA	21	0				
PFPrS	21	0				
N-MeFOSA	20	0				
N-MeFOSE	20	0				
FOSAA	5	0				
N-EtFOSA	3	0				
N-EtFOSE	3	0				