# Ultrashort PFAS – A New Challenge In PFAS Assessment

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PFAS, per- and polyfluorinated substances are a broad group and as risk assessment develops more PFAS compounds need to be be considered. Ultrashort PFAS are characterized as having one, two or three carbon atoms. Taking the two most common types of PFAS, PFCA and PFSA, this implies that there are five ultrashort compounds; trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), trifluoromethane sulphonic acid (TFMS; triflic acid), perfluoroethane sulphonic acid (PFEtS) and perfluoropropane sulphonic acid (PFPrS). These have so far been largely overlooked in both contaminated land risk assessment (CLM) and environmental monitoring. The picture is changing, e.g. through the drinking water directive's (DWD) "PFAS total", so-called "non-relevant metabolites" (NrM) in the revised groundwater directive (GWD) and limit values for drinking water (DE, NL and DK). Here two projects are presented for (1) drinking water and (2) a field study in Stockholm, with the objective to highlight levels and mass flows.

## Background

A growing number of reports show that ultrashort PFAS are present in the environment. TFA has so far been most studied. In precipitation, one source is photo-transformation of "new" refrigerants e.g. HFC-134a and HFO-1234yf, and TFA has increased 4-5x since the mid-90s in Germany (DE). TFA can also be formed during the breakdown of pesticides and drugs with CF3 groups (UBA, 2021). TFMS is a "super acid" used in organic synthesis and can be included in lithium-ion batteries (Neuwald et al., 2022). PFEtS/PFPrS can be found in firefighting foams. Moreover, ultrashort can be formed at degradation of precursors and oxidative remediation techniques (Björnsdotter, 2021). All compounds have high water solubility and low pKa values, implying that the water environment will be the final sink. They have been highlighted as vPvM and possibly PMT substances.

## Discussion

*Project 1:* PFAS4 was between ND-10 ng/l with five above the SE limit of 4 and 12 the DK limit of 2 ng/l. No sample would exceed the DWD (drinking water directive) PFAS20 (or SE21, DK22) value of 100 ng/l. A calculation, based on the RPF (Relative potency factor) in the WFD revision (EU, 2022) for the 10 out of 24 PFAS that were detected showed that 7 samples would exceed the proposed EQS value of 4.4 ng/l PFOA eqv. If TFA was taken into account (RPF=0.002; RIVM, 2023a) then 14 waters would sum up to >4.4 (Fig 4), and TFA would correspond to on ave 14%. TFA guideline values for drinking water exist in DK, NL and DE (UBA, 2020; Miljøministeriet, 2023, RIVM 2023b). All samples but one were below the NL (2200 ng/l). If ultrashort would be incl. in the DWD PFAS total value of 500 ng/l, four waters would be above, but some samples would come close.

*Project 2:* Three of five ultrashort PFAS were identified at levels generally higher than in drinking waters, and PFPrA/TFMS were much more common. PFOS exceeded the current EQS of 0.65 ng/l at all sites and PFAS24 at all but one (4.3-110 ng/l PFOA eqv) based on the 12 of 24 detected. TFA would add a further 0.75-4.4 ng/l PFOA eqv. The study shows there is a need to further quantify the inputs of ultrashort PFAS (e.g. the high PFPrA near and downstream an old landfill. For TFA more detailed data on sources e.g. precipitation, pesticide decomposition (affecting surface and groundwater) and other anthropogenic activities.

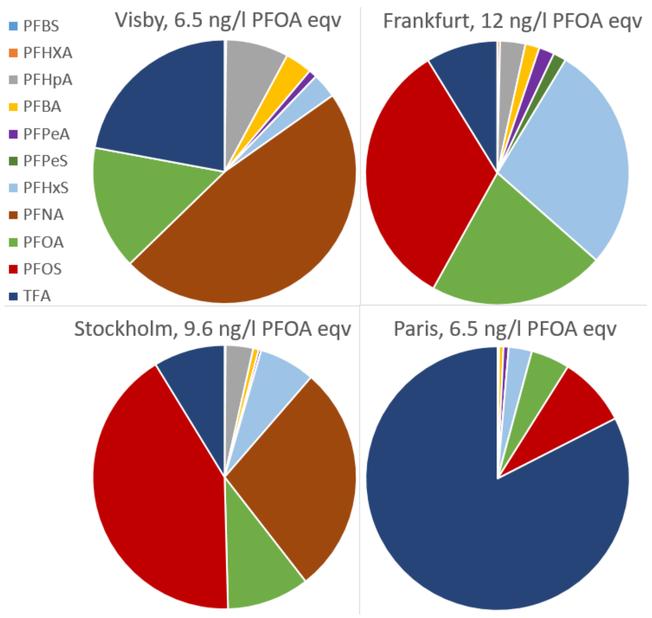


**Fig 4.** RPF weighted relative contributions to sum of PFOA eqv in water from Visby, Frankfurt, Stockholm, Paris

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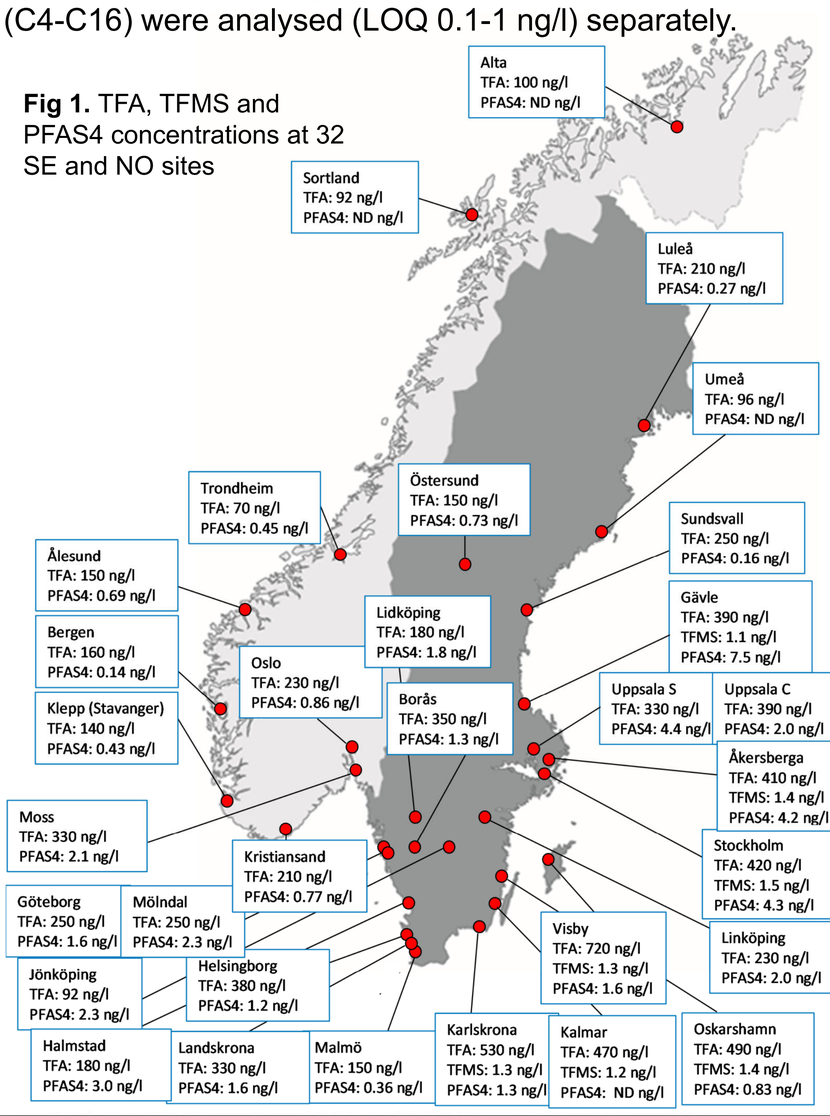
## Sampling and Analysis

*Project 1:* Sampling of tap water was made at 9 Norwegian (NO), 23 Swedish (SE), 6 Danish (DK), 4 German (DE) sites plus Vienna (AU) and Paris (FR). Sampling was undertaken between Dec 22 and Oct 23. More info on the sampling and NO/SE results can be found in the report by van Hees et al (2023).

*Project 2:* To quantify flows of PFAS within the catchment areas of lakes Flaten (2), Drevviken (6) and Magelungen (7) (no = sampling points) Stockholm and create mass balances. The lakes are in turn part of the Tyresån lake system. Furthermore to identify and rank transport routes and sources. Data are from two sampling occasions, Oct and Nov 22. The project is funded by Stockholms stad and presented in Filipovic et al (2023).

Analysis of ultrashort PFAS was performed by an in-house method developed at Eurofins SE based on mixed mode separation using UPLC-MS/MS. 30-49 other PFAS (C4-C16) were analysed (LOQ 0.1-1 ng/l) separately.

**Fig 1.** TFA, TFMS and PFAS4 concentrations at 32 SE and NO sites

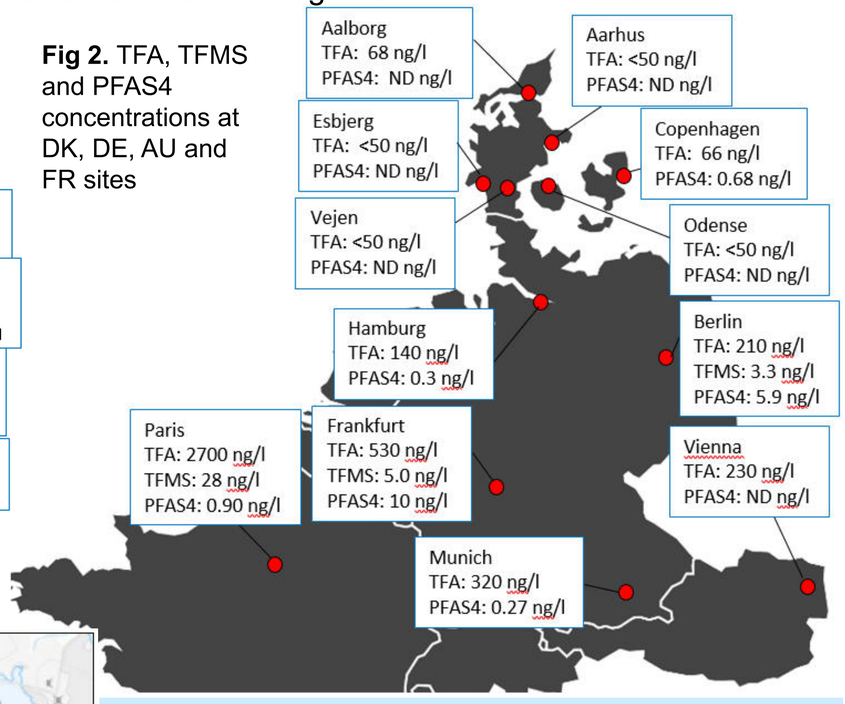



## Results

*Project 1:* The sources for the waters sampled (Fig 1-2), taken from web information, were surface- (23), ground- (13), infiltrated ground- (7) and mixed surface/ groundwater (1). TFA ranged from <50-2700 ng/l (295±405 ng/l; mean ± s.d.). The highest TFA was measured along the S-E SE coast and in Paris. TFMS was found (1-28 ng/l) in nine waters coinciding with high TFA expect for Berlin. PFPrA was seen in one sample and PFPrS in three (<1 ng/l). TFA levels were the lowest in groundwater as in e.g. DK, DE sites and Vienna. Surface and infiltrated groundwater showed a general S to N decrease. Over SE/NO an increasing gradient from W to E was observed. PFOS, PFOA and PFHxS were detected in a majority of samples and PFNA frequently (0.03-5.6 ng/l). A further nine PFAS were identified on occasion (0.3-7.6 ng/l), mostly short-chained (<C7) PFCA but also PFBS and PFBSA.

*Project 2:* 15 streams were selected for PFAS and water flow determinations, representing major in and outflows in the catchments. Water flows in these locations were either measured or modelled. TFA (370-2200), TFMS (<1-35) and PFPrA (6-1900 ng/l) were found. TFA was dominant (>90%) among the ultrashort at all sites but three. At Högdalsdiket PFPrA made up 60-75%, a site draining an old landfill. Levels were comparable (~2x) between the two occasions except for TFA at one site. Of the 49 “regular” PFAS analysed 17 were detected with concentrations between <0.3-150 ng/l. Short-chain PFCA (<7C) comprised a major part at all sites (60-75%) with few exceptions. Estimates of mass flows at the sampling points for Oct/Nov 22 showed a range between 17-1300g (Fig. 3). These flows were ~5-800x higher those of PFOS and PFAS17.

**Fig 2.** TFA, TFMS and PFAS4 concentrations at DK, DE, AU and FR sites



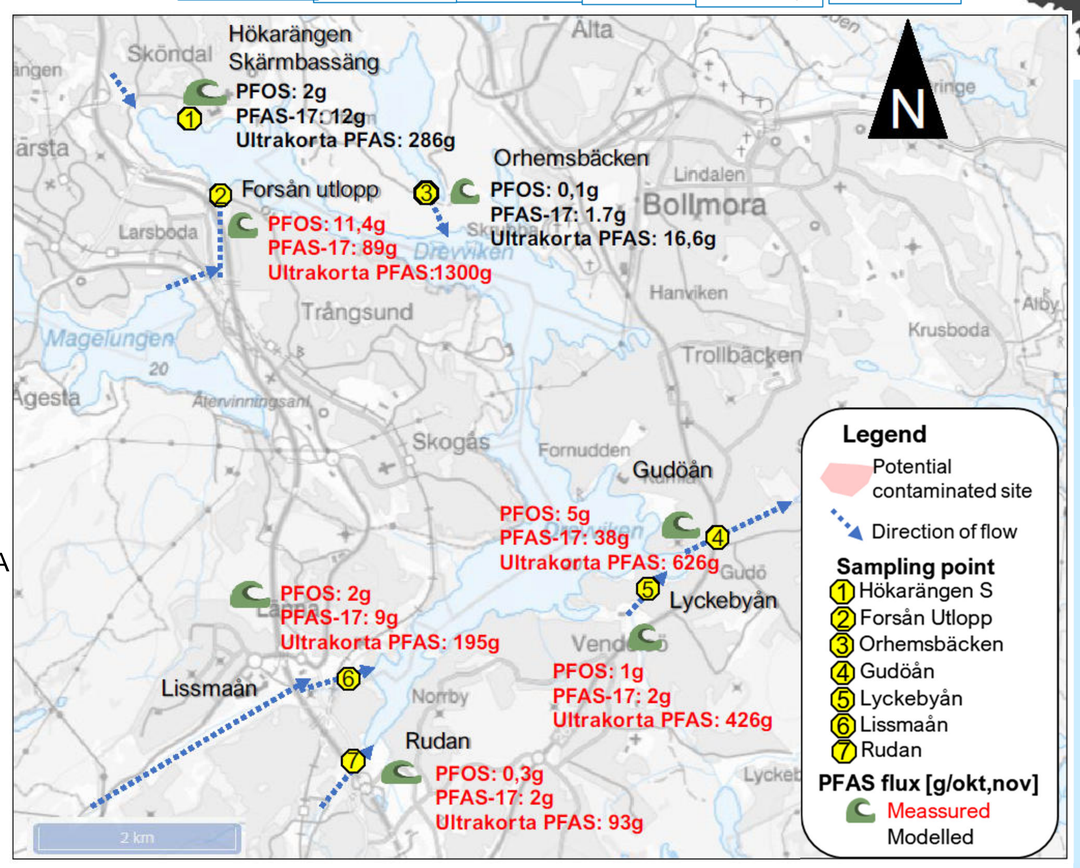




**Fig 3.** Mass flows of PFOS, PFAS-17 and ultrashort PFAS (Oct/Nov) in Drevviken

## Conclusions

*Project 1*

- Ultrashort PFAS were determined in two projects, one with focus on drinking water (44) and one quantifying flows in a catchment area
- TFA was found in nearly all drinking waters (ave 295 ng/l). TFMS in 5, PFPrA in 1 and PFPrS in 3
- PFAS4 exceeded the SE limit value of 4 ng/l at 5 sites and the DK value of 2 ng/l at 12 sites. An RPF based calculation showed >4.4 ng/l PFOA eqv for 7 samples and if TFA was included 14
- If ultrashort PFAS were included four sites would exceed the DWD PFAS total limit of 500 ng/l

*Project 2*

- In the catchment study both concentrations and mass flows of ultrashort were many times higher than for ”regular” PFAS (and PFOS)
- Current EQS for PFOS (0.65 ng/l) was exceeded for all and proposed PFAS24 for all but one site
- Local sources affecting levels and composition must be considered as seen for PFPrA close to an old landfill

**”Both projects call for further studies on identity and quantification of sources. For drinking water also treatment effects and seasonal variation”**

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