Ultrashort PFAS in Swedish and Norwegian Drinking Water

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Abbreviations:

AFFF = Aqueous film forming foam; DWD = Drinking water directive (EU); FTCA = Fluorotelomer carboxylic acids; FTS = Fluortelomer sulphonates; GWD = Groundwater directive (EU); HCFC = Hydrochlorofluorocarbon; HFC = Hydrofluorocarbons; HFC-134a = 1,1,1,2-tetrafluoroethane; HFO = hydrofluoroolefin; HFO-1234yf = 2,3,3,3-tetrafluoropropene; MLR = Multiple linear regression; NrM = Non-relevant metabolite; PBT = Persistent, bioaccumulative, toxic; PFAS = Poly- and perfluoroalkyl substances; PFBS = Perfluorobutane sulphonate; PFBSA = Perfluorobutane sulphonamide; PFCA = Perflourinated carboxylic acids; PFEtS = Perfluoroethane sulfonate; PFHxS = Perfluorohexane sulfonate; PFHxSA = Perfluorohexane sulfonamide; PFPrA = Perfluoropropanoate; PFOA = Perfluorooctanoate; PFOS = Perfluorooctane sulfonate; PFOSA = Perfluorooctane sulfonamide; PFPrS = Perfluoropropane sulfonate; PFSA = Perfluoroalkyl sulfonic acids; PreFOS = PFOS precursors; RPF = Relative potency factor; TFA = trifluoroacetate; TFMS = trifluoromethane sulphonic acid; vPvB = Very persistent, very bioaccumulative; WFD = Water framework directive (EU); WWTP = Waste water treatment plant

Introduction

PFAS, per- and polyfluorinated substances are a broad group of chemicals that have been used for various purposes since the 1950's. Examples of application areas and products are polymer manufacturing, surface coating, firefighting foams, cosmetics and paints. The widespread contamination as well as human and environmental exposure of PFAS has been paid much attention to over the last 20 years. This concerns not at least the more long-chained PFAS with >6-7 carbons. As the historically most used PFAS substances, especially the C8 substances PFOS and PFOA, have been banned and/or phased out there has been a shift in production to shorter perfluorinated (e.g. C4 or C6) carboxylic acids (PFCA) and sulphonates (PFSA) as well as telomers (e.g. 6:2 and 8:2).

As the field of PFAS develops more substances and classes are being considered. Ultrashort PFAS are typically characterized as having one, two or three carbon atoms. Taking the two most common types of PFAS structures, PFCA and PFSA, this means that there are five ultrashort compounds; trifluoroacetic acid (TFA), perfluoro-propionic acid (PFPrA), trifluoromethane sulphonic acid (TFMS; triflic acid), perfluoroethane sulphonic acid (PFEtS) and perfluoropropane sulphonic acid (PFPrS). These substances may not always be directly used as PFAS products, but rather occur as impurities, degradation products or manufactured for other purposes. Ultrashort PFAS are starting to receive more attention and a growing number of reports demonstrate their presence in the environment, especially in water.

Among the ultrashort PFAS, TFA has been most extensively studied to date. In precipitation, one source can be contamination in, and phototransformation of the refrigerants HFC-134a, HFO-1234yf and possibly other HFC/HCFC. TFA may also be formed at degradation of pesticides (e.g. Fluazinam) and pharmaceuticals having trifluoromethyl (CF_3) moieties, and at combustion of F-polymers (UBA, 2021; Miljødirektoratet, 2017). At present there are 45 active pesticide substances containing a CF_3 group approved in the EU (UBA, 2021). Moreover, TFA is employed as a reagent in different chemical processes. TFMS is a "super acid" used in organic synthesis and can be included as an additive in lithium ion battery (LIB) electrolytes (Neuwald et al., 2022).

Concerning PFEtS and PFPrS they have been used for applications such as ion conductive agents, photolithography processing and can be present in AFFF (Björnsdotter, 2021). For the latter matrix Barzen-Hanson and Field (2015) showed an average content of 0.22% and 3.5% for PFEtS and PFPrS, respectively, related to total PFSA content in old 3M foams (n=5) dominated by PFOS and PFHxS. Other sources that have been put forward are decomposition of precursors (e.g. 4:2 flourotelomers) and oxidative treatment of PFAS at remediation (Freeling and Björnsdotter, 2023). Regarding drinking water direct pollution from e.g. WWTP and landfills may be considered as well. The five ultrashort compounds are all associated with high water solubility and low pKa values, which besides small molecular sizes, suggests that in the long-term the aquatic environment becomes the eventual sink. Therefore, they have been highlighted as potential vPvM and possibly PMT substances.

The presence of ultrashort PFAS in drinking water has received growing attention. In a study of 46 German (DE) drinking waters TFA was found at a median concentration of 900 ng/l, PFPrA 13 ng/l and TFMS 8 ng/l. Overall ultrashort PFAS typically comprised 98% of all PFAS detected (Neuwald et al., 2022). In a similar work by Sadia et al (2023) TFA showed a mean value of approx. 310 ng/l and PFPrA 17 ng/l in Dutch (NL) drinking waters (n=18). TFA levels in precipitation has been shown to increase over time e.g. 4-5 times since the mid-90’s in Germany and 17 times in Beijing (2002-12) (UBA, 2021; ATMOsphere, 2022). The current precipitation weighted average in Germany was found to be 335 ng/l (Freeling et al., 2020). Björnsdotter (2021) reported TFA (6-270 ng/l), PFPrA (0.2-1.5 ng/l) and TFMS (0.2-3 ng/l) in snow from six sites in Spitsbergen, Svalbard (NO). Concentrations in rain from the island of Visingsö (Lake Vättern, SE) showed comparable ranges (TFA: 18-300 ng/l; PFPrA: 0.9-4 ng/l) while TFMS was occasionally found at lower levels (<1 ng/l). Also in Denmark (DK) ultrashort PFAS has been assessed. In a study by the DK EPA (Miljøstyrelsen, 2021) TFA was found in nearly 90% of the groundwaters sampled (n=247) in concentrations up to 2400 ng/l. Regarding surface water ultrashort PFAS were found in three lakes in the vicinity of Stockholm in significant concentrations with TFA ranging from 400-2200 ng/l, PFPrA 5-1900 ng/l and TFMS <1-35 ng/l (Filipovic, unpubl).

The objective of this study was to monitor ultrashort PFAS in Swedish (SE) and Norwegian (NO) drinking waters. As reference and for correlation assessment a number of “regular” PFAS were determined including the 20 PFAS covered by the EU drinking water directive (EU, 2020) and the SE and DK additions. Longtitude, latitude and the population of the urban area were also taken into account.

Material and Methods

Sampling was made from tap water at, in total, 32 sites covering 31 cities. Cold water was allowed to flow for 3-5 min before sampling was performed. Two, or in most cases three 100 ml PE bottles were rinsed three times with water to be sampled and then filled up. The bottles were the same as those normally used for PFAS at Eurofins and were in addition tested for any ultrashort PFAS contamination. Four samples were taken from Eurofins archive and were included after written permission from the client. Sampling was undertaken between Dec 2022 and July 2023.

Analysis of ultrashort PFAS was performed by an in-house method developed at Eurofins SE. The method is based on mixed mode (reversed phase/anion-exchange) separation using UPLC-MS/MS. The limit of quantification (LOQ) varies from 1 ng/l (TFMS), 3 ng/l (PFPrA, PFEtS, PFPrS) to 50 ng/l (TFA). In addition, 30 other PFAS (C4-C16) were analysed using an accredited UPLC-

MS/MS method. The range covered the DWD PFAS20, SE21 and DK22 lists together with a number of PFAS selected from experience and scientific literature e.g. PFBSA, PFHxSA, 4:2 and 8:2 FTS. LOQ ranged from 0.1-1 ng/l. PFPrS was determined with both methods with a LOQ for the latter of 0.3 ng/l.

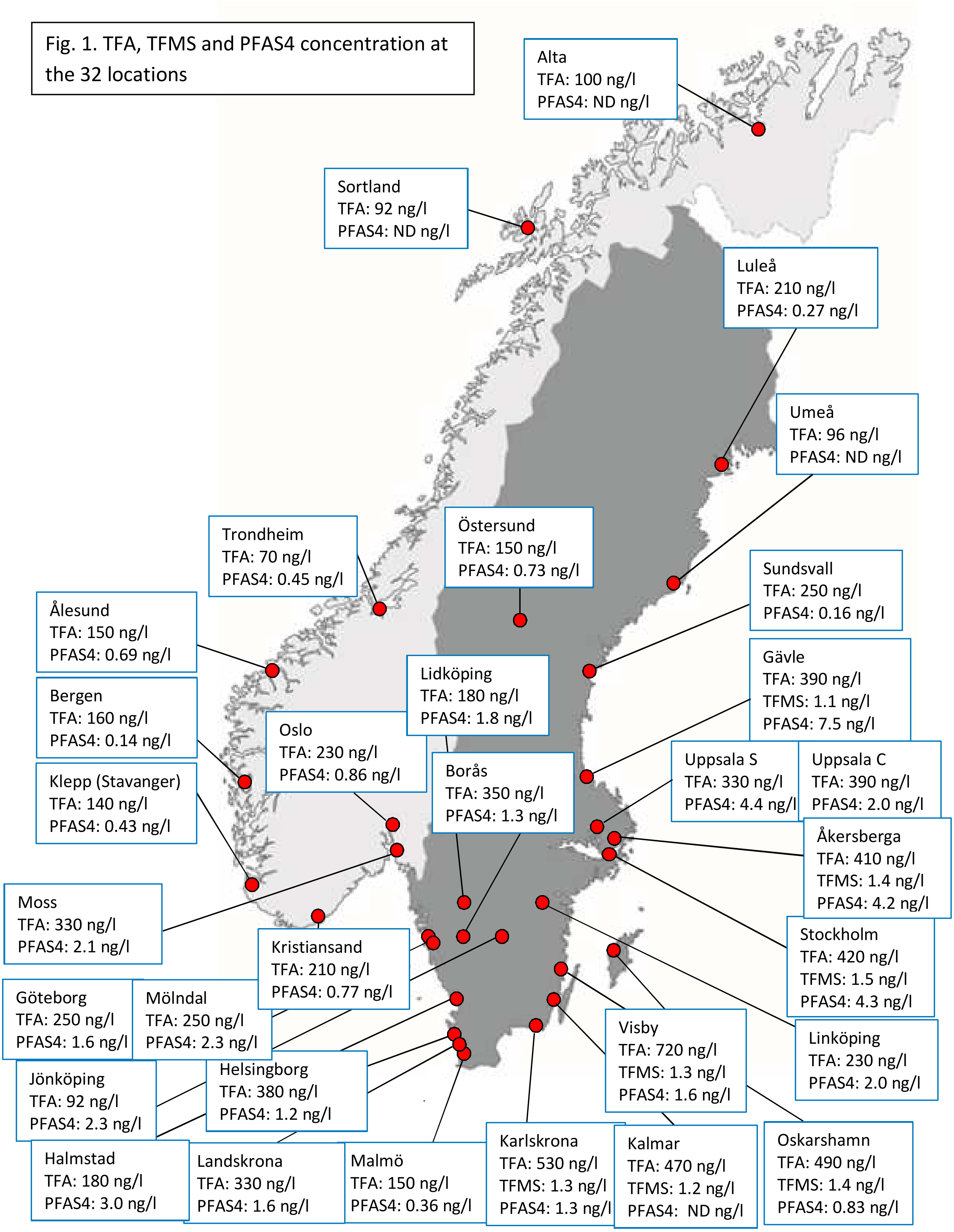
Statistical evaluation was performed using a stepwise (forward selection) multiple linear regression model (MLR; Tanagra 1.4.50, R. Rakotomalala, Lumière Univ Lyon 2). TFA was evaluated as dependent (y) variable with major ultrashort and “regular” PFAS plus longitude, latitude and population of the urban area as independent (x) variables. Only PFAS compounds with two or more detects (>LOQ) in the data set were included (n=16).

Results and Discussion

In this study 32 drinking water samples from S:th SE to N:th NO were analysed (Fig 1). The sources, taken from web-based information from the water authorities, were surface- (22), ground- (3), infiltrated ground- (6) and mixed surface/groundwater (1). TFA was present in all ranging from 70-720 ng/l (280±160 ng/l; mean ± s.d.) having the lowest values in West and N:th NO. The highest were measured along the South-Eastern Swedish coast and the island of Gotland (Visby). TFMS was found (1-1.5 ng/l) in seven waters coinciding with high TFA concentrations (>390 ng/l). PFPrA and PFPrS were seen in one sample taken at Uppsala South (S), a location with a known PFAS contamination and carbon filters installed at the waterworks. PFEtS was <LOQ for all samples. PFOS, PFOA and PFHxS were frequently detected >LOQ in more than half of the samples (18-25 of 32; range 0.1-5.4 ng/l). A further eight PFAS were identified on occasion (0.1-4.3 ng/l), most frequently short-chained (C4-C7) PFCA but also PFBS. No PFAS >C9 was identified. Among the water bodies, TFA levels were in ground- 190±50 (mean ± s.d.), surface- 240±130 and infiltrated groundwater 400±130 ng/l. The reason for the higher value of the latter is unclear but likely linked to local conditions. A pronounced difference is the lower TFA value in Malmö (150 ng/l) than in the neighbouring cities of Landskrona and Helsingborg (>300 ng/l). This is likely caused by the fact that the part of Malmö where the sample was taken is served by a waterworks extracting groundwater from the so called “Alnarp stream”, while remaining Malmö and the other two cities obtain their water mainly from the Lake Bolmen. It can also be noted that the PFAS profile was very similar between Stockholm and Åkersberga, both receiving water from relatively close extraction points in East Lake Mälaren. Another observation is the difference in TFA between water from the two largest Swedish lakes, Lake Vänern (Lidköping; 180 ng/l) and Lake Vättern (Jönköping; 92 ng/l). Although differences in inputs to the lakes is one possible explanation it can also be assumed that the much longer turnover time (76 vs 13y; SMHI, 2021) plays a role. Regarding Lake Vättern it was calculated that deposition corresponded to about 57% of the total input of TFA while surface water and effluents made up the rest (Björnsdotter, 2021). Given the net input of 120-170 kg/yr and the mean concentration of 34 ng/l in the water column it can be estimated that it would take 18 years for the TFA level to double in the lake.

Regarding limit values the range for PFAS4 was ND-4.4 ng/l with four locations exceeding the SE limit of 4 ng/l (Fig 1). If the DK limit of 2 ng/l was considered instead, ten samples would show sums higher than this figure. No sample would go beyond the DWD PFAS20 value of 100 ng/l (range ND-11 ng/l), or the SE/DK PFAS21/22 (Miljøministeriet, 2023; SLV, 2022). A calculation, based on the RPF (Relative potency factor) factors suggested in the WFD revision (EU, 2022) for the 10 out of 24 PFAS that were analysed and detected in this work, did not change the overall picture. If a comparison to the proposed EQS value of 4.4 ng/l PFOA equivalents was made,

Fig. 1. TFA, TFMS and PFAS4 concentration at the 32 locations



besides the four samples with PFAS4 >4 ng/l, two additional waters (Mölndal and Visby) summed up to more than 4.4 (with three sites just below).

To the best of our knowledge TFA guideline/limit values for drinking water exist in Denmark and Germany (UBA, 2020; Miljøministeriet, 2023) only. All TFA concentrations were below the DK drinking water quality criterion of 9000 ng/l, the lower of the two. If, hypothetically, ultrashort PFAS would be included in the DWD PFAS total value of 500 ng/l two waters would exceed, but some additional samples with high TFA levels approached the limit.

The TFA results were evaluated using a stepwise MLR with TFMS, PFBA and latitude found to be significant variables ($p<0.01$; not shown). It was interpreted that a more northern latitude mirrored possibly a lower atmospheric deposition and, in general, fewer agricultural and other anthropogenic activities. TFMS as well as PFBA could reflect more local pollution sources, but in the case of PFBA also deposition. If the sites Malmö and Jönköping were omitted due to the special conditions discussed above also longitude became significant possibly mirroring the higher TFA values along the SE East coast and lower in western NO.

The knowledge of ultrashort PFAS in drinking water is limited. The mapping in this work demonstrates the universal presence of especially TFA. Although some relationships were seen, there are still factors for individual samples that merit further investigations. In this work tap water was sampled “at the user”, with a few exceptions, and thus reflect the intake by the consumer. However, differences among the sites may depend not only on raw water quality but also treatment processes, chemicals employed etc. In the paper by Sadia et al (2023) increases of TFA and PFPrA (up to +700%) were seen in some treated surface waters employing GAC/PAC (carbon) with or without UV cleaning while reductions 0-80% were observed for other raw waters. Regarding sources of ultrashort PFAS, in particular TFA, these may include (urban) atmospheric deposition, industrial emissions and contributions from decomposition of pesticides in agricultural areas. In addition, a more detailed assessment of various raw water sources would be relevant. No major difference was found between surface- and groundwater in this work, and the same finding was made in the NL project mentioned (Sadia et al., 2023). However, this must be related to the fact that the groundwaters were taken in South SE where, on average, higher surface water TFA were recorded. Seasonal variation would also be of interest to evaluate closer. Repeated measurements of TFA were made at five sites during the sampling period with limited changes of 11-22% seen (not shown), but would need to be measured at more sites and at longer intervals.

The levels of TFA and TFMS were generally lower than what has been reported for German drinking waters (up to 12400 (TFA) and 2100 (TFMS) ng/l; Neuwald et al., 2022). The same was true for TFA in comparison to N Swiss water samples (510-1500 ng/l; n=10; SRF, 2022) while the Dutch TFA levels reported by Sadia et al (2023) were more comparable (30-1100 ng/l; n=18). TFMS was found in all DE samples (n=46), but <LOQ for most SE/NO waters. Moreover, PFPrA and PFPrS were only detected in one sample in our work. The fraction made up by ultrashort PFAS (dominated by TFA) of the total PFAS determined, corresponded to 99±1% (mean ± s.d.), a number similar to the one calculated by Neuwald et al. (2022), but higher than the fraction obtained by Sadia et al. (2023) (~90%). The concentrations of TFA from W and N NO and Umeå (SE) suggested that 70-100 ng/l (all surface waters) could be seen as some kind of “minimum” or “background”. Snow sampled at five locations in Spitsbergen (Svalbard, NO), believed only to be affected by long range atmospheric processes, showed comparable levels between 7−270 ng/l (mean 65 ng/l; n=15; Björnsdotter, 2021). The highest concentrations were recorded in late summer, likely caused by greater solar radiation and consequently a larger atmospheric oxidation.

Conclusions

This work gives, to our knowledge, the first overview of ultrashort PFAS in SE and NO drinking waters. The results show the prevalent presence of TFA and that TFMS can be found on occasions as well. The levels (70-720 ng/l) are still below present DK and DE guideline values but may increase over time given continued (and growing) inputs as well as mobility and persistence of the substance. An overall conclusion is thus that they can be considered relevant in quality and risk assessment of drinking water. Evaluation and identification of (ultrashort) PFAS and other PM/vPvM/PMT substances such as triazines are of growing concern and a field for intense research.

The TFA levels especially, are also of interest for the EU DWD with its PFAS total limit of 500 ng/l. Although just two samples exceeded this figure if TFA was included, other sites could be at risk over time. Moreover, in the light that waters from continental Europe frequently seem to have higher concentrations it can be speculated that if TFA was considered a very high number of drinking waters would pass the limit. The work on a recommendation for analysis of PFAS total according to DWD is ongoing. However, it can be discussed if TFA, on its own, should be viewed in the light of risk, policy and degree of inclusion/exclusion in the preferred analytical method(s). A separate limit value as in DK and DE can be a point for discussion. In addition, TFA can be regarded as a so called non-relevant metabolite (NrM; UBA, 2021). In the proposed GWD revision (EU, 2022) quality standards (QS; 0.5-12.5 µg/l) are suggested for this group of compounds. Given the purpose of GWD to protect groundwater as a drinking water source there is a link. NrM has already been included in the DK drinking water regulation (Miljøministeriet, 2023; TFA having a separate limit, see above) and in the SE regulation on groundwater classification as part of the pesticide group (SGU, 2022; 2023).

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