A note on PFAS in Wastewater, Sludge, and Groundwater from Bornholm

By Torben Jørgensen, Bornholms Energy & Forsyning, May 2020

Introduction:

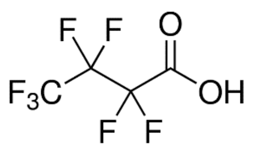
PFAS is a very large group of polyfluoroalkyl substances that is widespread in the aquatic environment, as a result from a broad range of uses in different products. PFAS range from small molecules to large plastic polymers as Teflon, and the carbon-fluoride bond makes these substances slowly degradable in nature, so most of the compounds can be characterized as Persistant Organic Pollutants (POPs). The knowledge of the fate and dispersion of these compounds is still incomplete, and this is the background for the findings presented here, as a little contribution from the STEP project on the matter, also pointing out what further work will be relevant to do with regard to sludge.

In this note the results from a few analysis from Bornholm is presented and discussed. The analysis from wastewater and sludge was made as an extension of the ordinarily analysis-program from the routine control of wastewater and sludge quality. Analysis of PFAS in drinking water is already included in the Danish standard program. New analysis of Trifluoroacetic acid (TFA) in drinking water and wells is also presented, even though it is not a proper PFAS, but related to the problem and found in relatively high concentrations.

PFAS in wastewater from Rønne Waste Water Treatment Plant (WWTP) 2020

During the summer 2020 twelve different "standard" PFAS compounds was analyzed in samples from in- and out-let from the WWTP – see table 1. Generally the concentrations of these PFAS was low, as expected at a WWTP receiving mainly wastewater from households. The highest concentration of the analyzed species was 7.5 ng/l of PFBA (Perfluorobutanoic acid) in inlet from 01.07.2020; the outlet concentration was reduced til 2.9 ng/l, indicating either degradation in the waste water treatment process, or binding to sludge, or both – the detection limit was 1 ng/l. Samples was taken flow-proportional over 24 hours,

The sum of the 12 analyzed PFAS was 15-22 ng/l in inlet, and 6.3-14 ng/l in outlet, corresponding to a max load of app. 0.15 g/day in inlet, and 0.1 g/day in outlet; the average flow through the WWTP was app. 6,000 m3/day.



PFBA = Perfluorobutanoic acid

Waste Water analysis	Rønne WWTP inlet				Rønne WWTP outlet				
Komponent	26.05.20	15.06.20	01.07.20	mean	26.05.20	15.06.20	01.07.20	mean	unit
Flow	**5,436**	**4,949**	**6,876**	**5,754**	**5,365**	**5,080**	**7,457**	**5,967**	**m3/day**
Total Nitrogen	**62**	**76**	**96**	**78**	**4.9**	**2.9**	**5.5**	**4.4**	**mg/l**
Total Phosphor	**8.7**	**10**	**12**	**10.2**	**0.49**	**0.29**	**0.37**	**0.4**	**mg/l**
BI5 (uden ATU)	**440**	**590**	**620**	**550**	**2.8**	**1.7**	**2.8**	**2.4**	**mg/l**
COD, kemisk iltforbrug	**1200**	**1300**	**1400**	**1300**	**37**	**15**	**33**	**28**	**mg/l**
LAS	**280**	**650**	**730**	**553**	**< 5**	**< 5**	**< 5**	**-**	**µg/l**
Acenaphthen	**< 0.02**	**0.69**	**< 0.2**	**-**	**< 0.01**	**< 0.01**	**0.015**	**-**	**µg/l**
Fluoren	**< 0.04**	**0.3**	**< 0.5**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Phenanthren	**0.11**	**0.94**	**0.19**	**0.41**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Fluoranthen	**0.21**	**< 0.1**	**< 0.1**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Pyren	**0.27**	**0.47**	**< 0.2**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Benzo(b+j+k)fluoranthen	**0.075**	**< 0.1**	**< 0.1**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Benzo(a)pyren	**0.022**	**< 0.1**	**< 0.1**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Indeno(1,2,3-cd)pyren	**< 0.15**	**0.21**	**< 0.1**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Benzo(g,h,i)perylen	**< 0.08**	**0.12**	**< 0.1**	**-**	**< 0.01**	**< 0.01**	**< 0.01**	**-**	**µg/l**
Sum af PAH'er	**0.69**	**2.7**	**0.19**	**1.19**	**#**	**#**	**0.015**	**-**	**µg/l**
Diethylhexylphthalat (DEHP)	**10**	**23**	**16**	**16**	**0.86**	**0.63**	**1.4**	**0.96**	**µg/l**
Nonylphenoler	**0.66**	**0.45**	**0.56**	**0.56**	**< 0.05**	**< 0.05**	**< 0.05**	**-**	**µg/l**
PFBA (Perfluorobutanoic acid)	**3.7**	**4.1**	**7.5**	**5.1**	**3.4**	**2.4**	**2.9**	**2.9**	**ng/l**
PFBS (perfluorobutane sulfonic acid)	**<1**	**<1**	**<1**	**-**	**<1**	**<1**	**<1**	**-**	**ng/l**
PFPeA (Perfluoropentanoic acid)	**2.3**	**2.9**	**2.3**	**2.5**	**1.6**	**<1**	**1.6**	**1.6**	**ng/l**
PFHxA (Perfluorohexanoic acid)	**3.1**	**1.9**	**<1**	**2.5**	**2.8**	**1.3**	**2.6**	**2.2**	**ng/l**
PFHxS (Perfluorohexane sulfonic acid)	**<1**	**<1**	**<1**	**-**	**<1**	**<1**	**<1**	**-**	**ng/l**
PFHpA (Perfluoroheptanoic acid)	**1.9**	**1.0**	**1.9**	**1.6**	**1.3**	**<1**	**1.1**	**1.2**	**ng/l**
PFOA (Perfluorooctanoic acid)	**5.5**	**3.7**	**6.6**	**5.3**	**3.7**	**2.6**	**3.3**	**3.2**	**ng/l**
PFOS (Perfluoroctane sulfonic acid)	**1.2**	**<1**	**2.6**	**1.9**	**1.6**	**<1**	**1.2**	**1.4**	**ng/l**
6:2 FTS (Fluorotelomer sulfonate)	**<1**	**1.6**	**<1**	**1.6**	**<1**	**<1**	**<1**	**-**	**ng/l**
PFOSA (Perfluorooctane sulfonamide)	**<1**	**<1**	**<1**	**-**	**<1**	**<1**	**<1**	**-**	**ng/l**
PFNA (Perfluorononanaoic acid)	**<1**	**<1**	**1.0**	**1**	**<1**	**<1**	**<1**	**-**	**ng/l**
PFDA (Perfluorodecanoic acid)	**<1**	**<1**	**<1**	**-**	**<1**	**<1**	**<1**	**-**	**ng/l**
Sum PFAS	**18.0**	**15.0**	**22.0**	**18.3**	**14.0**	**6.3**	**13.0**	**11.1**	**ng/l**

Table 1: Waste water analysis from Rønne WWTP 2020.

Waste Water analysis
(min – max)

Komponent	WWTP inlet: Rønne WWTP 2020	WWTP inlet: Eriksson et al. 2017	WWTP inlet: Strand et al. 2007	WWTP outlet: Rønne WWTP 2020	WWTP outlet: Eriksson et al. 2017	WWTP outlet: Strand et al. 2007	unit	DL
Total Nitrogen	**62 – 96**			**2.9 – 5.5**			**mg/l**	0.05
Total Phosphorus	**8.7 – 12**			**0.29 – 0.49**			**mg/l**	0.01
BOD5	**440 – 620**			**1.7 – 2.8**			**mg/l**	0.5
COD	**1200 – 1300**			**15 – 37**			**mg/l**	5
LAS	**280 – 730**			**< 5**			**µg/l**	5
Acenaphthen	**<0.02 – 0.69**			**<0.01 –0.02**			**µg/l**	0.01
Fluoren	**< 0.04 – 0.3**			**< 0.01**			**µg/l**	0.01
Phenanthren	**0.11 – 0.94**			**< 0.01**			**µg/l**	0.01
Fluoranthen	**< 0.1 – 0.21**			**< 0.01**			**µg/l**	0.01
Pyren	**< 0.2 – 0.47**			**< 0.01**			**µg/l**	0.01
Benzo(b+j+k)fluoranthen	**< 0.1 – 0.075**			**< 0.01**			**µg/l**	0.01
Benzo(a)pyren	**<0,1 – 0.022**			**< 0.01**			**µg/l**	0.01
Indeno(1,2,3-cd)pyren	**< 0.1 – 0.21**			**< 0.01**			**µg/l**	0.01
Benzo(g,h,i)perylen	**< 0.1 – 0.12**			**< 0.01**			**µg/l**	0.01
Sum of PAH's	**0.19 – 2.7**			**#**	**#**		**µg/l**	
Diethylhexylphthalat (DEHP)	**10 – 23**			**1.4 – 0.86**			**µg/l**	0.1
Nonylphenoler	**0.45 – 0.66**			**< 0.05**			**µg/l**	0.05
PFBA (Perfluorobutanoic acid)	**3.7 – 7.5**	**< 3.4 – 5.5**		**2.4 – 3.4**	**8.2 – 30.1**		**ng/l**	1
PFBS (perfluorobutane sulfonic acid)	**< 1**			**< 1**			**ng/l**	1
PFPeA (Perfluoropentanoic acid)	**2.3 – 2.9**	**3.1 – 5.0**		**< 1 – 1.6**	**2.5 – 10.2**		**ng/l**	1
PFHxA (Perfluorohexanoic acid)	**< 1 – 3.1**	**3.1 – 7.1**		**1.3 – 2.8**	**5.0 – 16.8**		**ng/l**	1
PFHxS (Perfluorohexane sulfonic acid)	**< 1**	**0.8 – 1.8**	**< 0.2 – 33**	**< 1**	**1.4 – 1.9**	**< 0.2 – 2.7**	**ng/l**	1
PFHpA (Perfluoroheptanoic acid)	**1 – 1.9**	**1.2 – 2.5**		**< 1 – 1.3**	**1.4 – 2.8**		**ng/l**	1
PFOA (Perfluorooctanoic acid)	**3.7 – 6.6**	**3.0 – 5.2**	**< 2.0 – 24**	**2.6 – 3.7**	**4.1 – 5.2**	**< 2 – 24**	**ng/l**	1
PFOS (Perfluoroctane sulfonic acid)	**< 1 – 2.6**	**1.0 – 1.7**	**< 1.5 – 10**	**< 1 – 1.,6**	**< 0.7 – 1.,5**	**< 1.5 – 18**	**ng/l**	1
6:2 FTS (Fluorotelomer sulfonate)	**< 1 – 1.6**	**2.9 – 6.3**		**< 1**	**2.0 – 5.1**		**ng/l**	1
PFOSA (Perfluorooctane sulfonamide)	**< 1**	**-**	**<0.3 – 1.0**	**< 1**	**-**	**< 0.3 – 2.1**	**ng/l**	1
PFNA (Perfluorononanaoic acid)	**< 1**	**0.3 – 0.7**	**< 0.8 – 8**	**< 1**	**0.4 – 0.6**	**< 0.8 – 3.0**	**ng/l**	1
PFDA (Perfluorodecanoic acid)	**< 1**	**0.2 – 0.5**	**< 1.6**	**< 1**	**< 0.2 – 0.5**	**< 1.6 – 3.6**	**ng/l**	1

Table 2: Comparison of waste water analysis from Rønne WWTP, with other references:

J. Strand et al. 2007: Faglig rapport fra DMU nr. 608 - PFAS og organotinforbindelser i punktkilder og det akvatiske miljø, Table 6.1 *(https://www.dmu.dk/Pub/FR608.pdf)*

Eriksson et al. 2017: Screening of PFASs in sludge and water from waste water treatment plants. Örebro University. *(http://naturvardsverket.diva-portal.org/smash/get/diva2:1076658/FULLTEXT01.pdf)*

Comparison of levels of PFAS in wastewater:

The levels of the PFAS species from Rønne WWTP, inlet and outlet in 2020, corresponds very well to other Nordic studies, specially the study of Eriksson at al from smaller Swedish WWTPs in 2015; the data in Strand et al. is from 2004-2005, and comprises mostly WWTPs much larger than in Rønne, and the levels of PFOA and PFOS in some analysis is much higher than the analysis from Rønne. The outfasing of PFOS in EU from 2006, have presumably caused a general reduction of input to WWTPs over the years. The content of some PFAS species can increase from inlet to outlet, caused by degradation of precursors - this is also exemplified in a few of the analysis presented here.

From other work it is known that the "standard" PFAS analyzed here is just a fraction of the total organic fluorine in wastewater and sludge. This is very well illustrated in the study: PFASs in the Nordic environment:

Figure 25: Total dissolved concentration of EOF (ng F/g) in effluent divided into sum of targeted PFAS and unidentified organofluorine (UOF). b) composition of sum targeted PFASs and unidentified EOF in percentage of total EOF

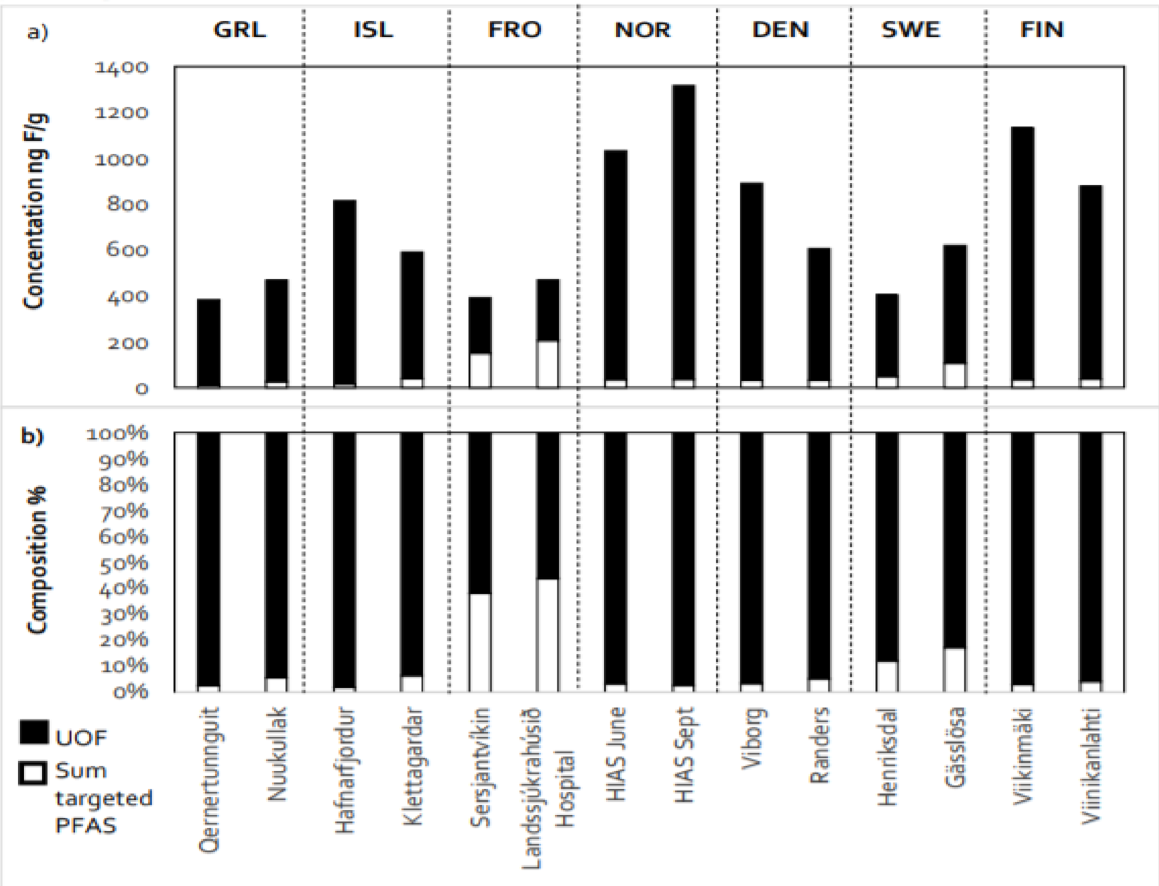


Figure from: Kallenborn et al.: PFASs in the Nordic environment. © Nordic Council of Ministers 2019 (https://norden.diva-portal.org/smash/get/diva2:1296387/FULLTEXT01.pdf)

The figure shows that the PFAS species we usually analyse, is only a fraction of the total unidentified organic fluorine, and what is the fate of this unidentified fraction in the environment?

Similar distribution between targeted and unidentified organic fluorine can be found in sludge, as the figure below shows. When sludge is used as fertilizer in agriculture what is the fate of these organic fluorinated compounds? can it pose a tread to future drinking water quality? These subjects needs further clarification, together with development of eg. biological methods to remove PFAS from sludge, so we can be able to maintain the values of using sludge as fertilizer and carbon storage in agriculture.

Figure 22: a) Total concentration of EOF (ng F/g) in sludge divided into sum of targeted PFASs and unidentified organofluorine (UOF). b) composition of sum targeted PFASs and unidentified EOF in percentage of total EOF. Empty column indicates sample concentration below the limits of detection (<556 ng F/g)

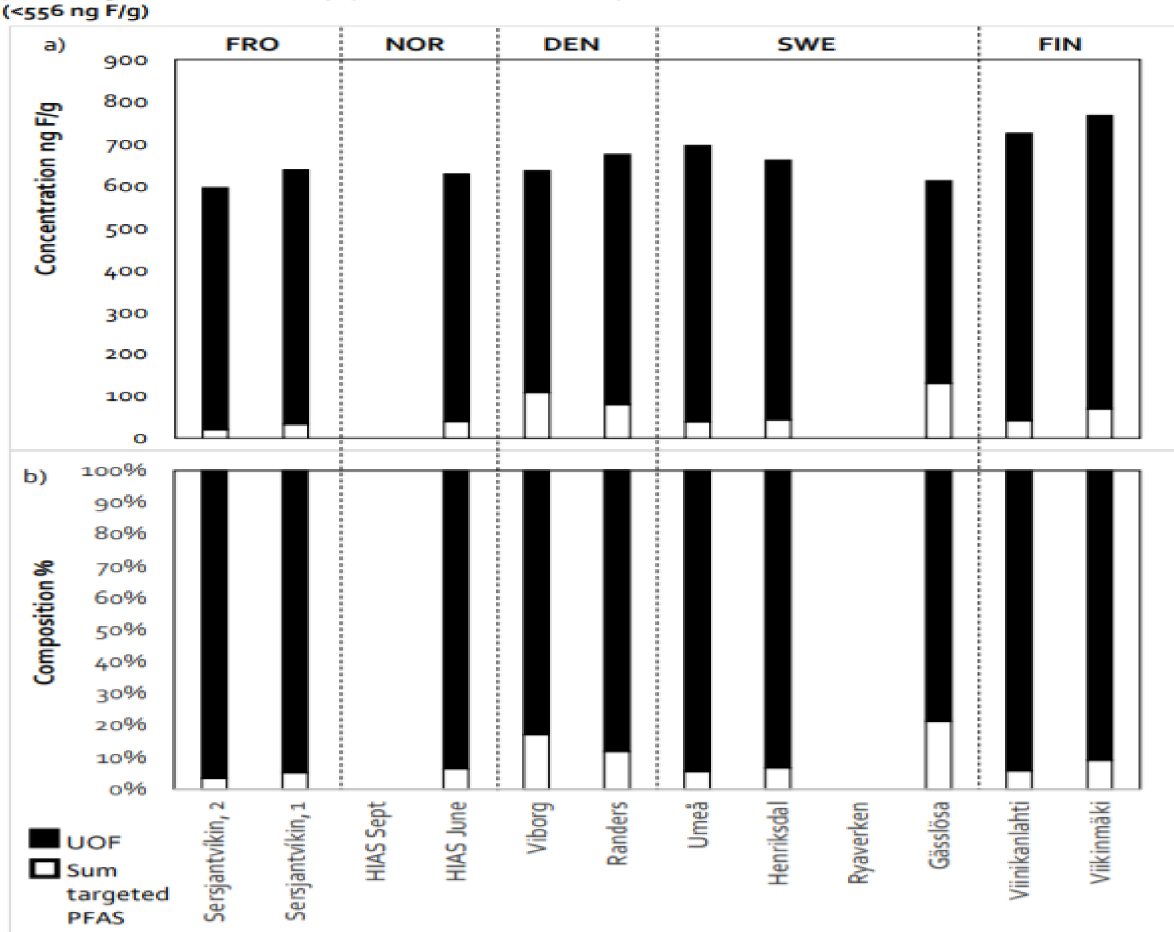


Figure from: Kallenborn et al.: PFASs in the Nordic environment. © Nordic Council of Ministers 2019(https://norden.diva-portal.org/smash/get/diva2:1296387/FULLTEXT01.pdf)

PFAS in sludge from Rønne Waste Water Treatment Plant (WWTP)

A single standard analysis of sludge in 2020 was extended with analysis of 12 PFAS species, but only one was above the detection limit: PFPeA (Perfluoropentanoic acid) - 18,6 µg/kg Dry Matter (see table 3). The detection limit of PFAS in this analysis is rather high: 5 µg/kg DM.

Sludge analysis Rønne WWTP
pooled samples from 13.05.2020 – 1.07.2020

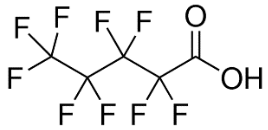
Komponent	Rønne WWTP 2020	Strand et al. 2007	Eriksson et al. 2017	unit	Limit
Total Nitrogen	**42**			**g/kg DM**	
Total Phosphorus	**19**			**g/kg DM**	
Cadmium	**1.1**			**mg/kg DM**	0.8
Cadmium	**57.9**			**mg/kg P**	100
Mercury	**0.23**			**mg/kg DM**	0,8
Mercury	**12,1**			**mg/kg P**	200
Lead	**11**			**mg/kg DM**	120
Nikkel	**10**			**mg/kg DM**	30
Chromium	**9.7**			**mg/kg DM**	100
Kobber	**120**			**mg/kg DM**	1000
Zink	**390**			**mg/kg DM**	4000
Kalium	**6.6**			**g/kg DM**	
Sulfur	**0.16**			**g/kg DM**	
LAS	**< 50**			**mg/kg DM**	1300
Sum of PAH's	**0.57**			**mg/kg DM**	3
Diethylhexylphthalat (DEHP)	**4.4**			**mg/kg DM**	50
Nonylphenoler	**< 0.6**			**mg/kg DM**	10
PFBA (Perfluorobutanoic acid)	**<.20**	**-**	**-**	**µg/kg DM**	
PFBS (perfluorobutane sulfonic acid)	**<.5**	**-**	**< 0.08 – 0.28**	**µg/kg DM**	
PFPeA (Perfluoropentanoic acid)	**18.6**	**-**	**-**	**µg/kg DM**	
PFHxA (Perfluorohexanoic acid)	**<.5**	**-**	**0.54 – 6.37**	**µg/kg DM**	
PFHxS (Perfluorohexane sulfonic acid)	**<.20**	**0.4 – 10.7**	**< 0.09 – 0.07**	**µg/kg DM**	
PFHpA (Perfluoroheptanoic acid)	**<.5**	**-**	**0.07 – 0.18**	**µg/kg DM**	
PFOA (Perfluorooctanoic acid)	**<.5**	**0.7 – 19.7**	**< 0.41 – 2.88**	**µg/kg DM**	
PFOS (Perfluoroctane sulfonic acid)	**<.5**	**4.8 – 74.1**	**1.06 – 8.10**	**µg/kg DM**	
6:2 FTS (Fluorotelomer sulfonate)	**<.5**	**-**	**< 0.23 – 0.94**	**µg/kg DM**	
PFOSA (Perfluorooctane sulfonamide)	**<.5**	**< 0.9 – 3.6**	**-**	**µg/kg DM**	
PFNA (Perfluorononanaoic acid)	**<.5**	**0.4 – 8.0**	**< 0.02 – 0.40**	**µg/kg DM**	
PFDA (Perfluorodecanoic acid)	**< 5**	**1.2 – 32.0**	**0.34 – 3.2**	**µg/kg DM**	
Sum PFAS	**18.6**			**µg/kg DM**	

Table 3: Comparison of sludge analysis from Rønne WWTP, with other references

J. Strand et al. 2007: Faglig rapport fra DMU nr. 608 - PFAS og organotinforbindelser i punktkilder og det akvatiske miljø *(https://www.dmu.dk/Pub/FR608.pdf)*
Eriksson et al.2017: Screening of PFASs in sludge and water from waste water treatment plants *(http://naturvardsverket.diva-portal.org/smash/get/diva2:1076658/FULLTEXT01.pdf)*

Compared to other Scandinavian studies, the level of < 5 µg/kg DM for most of the analyzed species, is in good compliance except for PFOS, where the levels in other and older studies are typically higher than for Rønne WWTP. A possible explanation is, that Rønne WWTP only receives wastewater from few and small industries.

The sludge production from Rønne WWTP in 2020 was app. 933 t Dry Matter. If the level of PFPeA (Perfluoropentanoic acid) in this sludge analysis – 18.6 µg/kg Dry Matter - is representative, then the total amount of PFPeA in sludge from Rønne WWTP is app. 17 g/year



PFPeA = Perfluoropentanoic acid

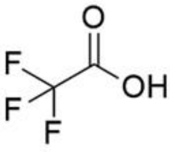
PFAS analysis of drinking water on Bornholm

Since 2018 analysis of 12 PFAS species in drinking water has been included in the Danish standard analysis program: PFBA, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, 6:2 FTS, PFOSA, PFNA and PFDA.

On Bornholm the PFAS-analysis from the four waterworks owned by the municipal water company has so far all been below the detection limit (1 ng/l).

Triflouroacetic acid (TFA) in drinking water on Bornholm

In 2020 the Danish EPA made a screening of TFA in Danish ground water; this was the first time an extensive screening of TFA has been carried out in Denmark, and TFA was found in 219 of 247 samples.



trifluoroacetic acid

TFA is formed in the atmosphere by degradation of hydrofluorocarbons, eg. from cooling gases, but can also be formed by degradation and incineration of PFAS, fluoropolymers and related substances. According to the Danish EPA, a newer German study showed that average rainwater in Germany had a concentration of 0.335 µg/l TFA. The highest concentration measured was 38.0 µg/l. Compared with older German studies, from1994-1996, this was a significant increase in the atmospheric deposition of TFA in Germany over the last decades.

Recent analysis from wells and drinking water on Bornholm, shows concentrations of TFA in the same levels as reported in the German study of rainwater, about 0.3 µg/l. In 8 out 28 wells on Bornholm, TFA was below the detection limit, and these wells are typically containing older water from deeper layers.

Smålyng Waterwork

well nr.	produced m3	TFA µg/l
DGU-nr.	**2020**	**2021**
247,435	103,495	0.51
247,664	57,033	<0.05
247,323	98,270	<0.05
247,322	109,821	0.37
247,330	65,132	<0.1
247,349	87,788	0.37
247,503	96,706	0.59
247,662	125,965	0.30
247,249	23,102	0.59
247,326	42,459	0.48
247,459	8,893	0.54
247,604	90,730	<0.05
tapwater	**805,899**	0.25

Hasle Waterwork

well nr.	produced m3	TFA µg/l
DGU-nr.	**2020**	**2021**
244,442	25,670	<0.05
244,463	34,751	0.35
244,461	90,802	0.37
244,565	52,668	0.62
246,779	48,459	<0.05
246,798	9,733	<0.05
246,760	68,935	<0.05
tapwater	**331,018**	0.38

Rø Waterwork

well nr.	produced m3	TFA µg/l
DGU-nr.	**2020**	**2021**
244,359	22,634	<0.05
244,569	84,698	0.20
tapwater	**109,352**	0.15

Brogård Waterwork

well nr.	produced m3	TFA µg/l
DGU-nr.	**2020**	**2021**
244,510	30,286	0.65
244,465	34,278	0.39
244,641	16,259	0.41
244,642	38,595	0.47
244,577	29,079	0.42
244,398	10,619	0.54
244,512	17,050	0.45
tapwater	**176,166**	0.40

Fortunately TFA toxicity seems to be low, and do not have a potential for bioaccumulation. However, the persistence will likely result in continuously increasing concentrations in the environment, essentially in the aquatic environment and in ground water.