STICKY BUSINESS

”Background concentrations of PFAS in Swedish environment and lessons learned from 10 years of sampling and analysis of lakes and biota within the City of Stockholm”

MARKO FILIPOVIC

ATV JORD OG GRUNDVAND 2021

OUTLOOK

- ❑ Background concentrations of PFAS in Swedish environment

I. Surface water

II. Ground water

III. Potable water

IV. Soil

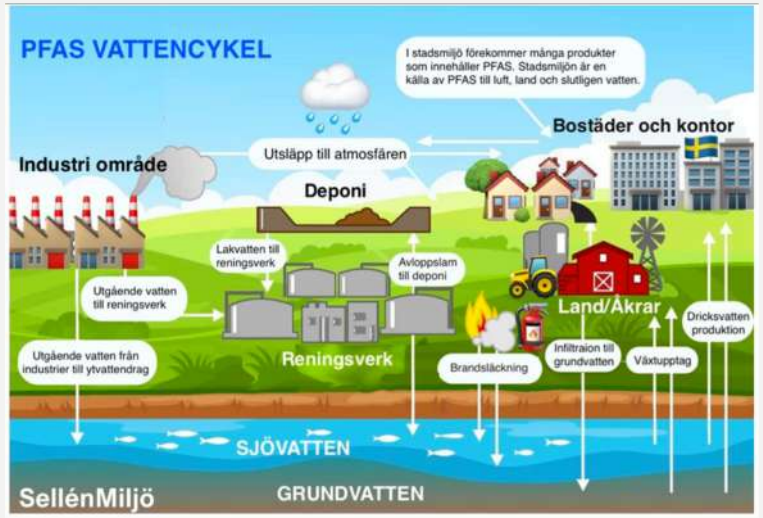
V. Sediment (inland lake)

VI. Atmospheric deposition (air and rain/snow)

VII. Waste water treatment plants (effluent and sludge)

VIII. Landfill leachates

IV. Summary



- ❑ Case study: 10 years of sampling and analyis of PFAS in lakes and biota within the City of Stockholm

- ❑ Lessons learned and take home message

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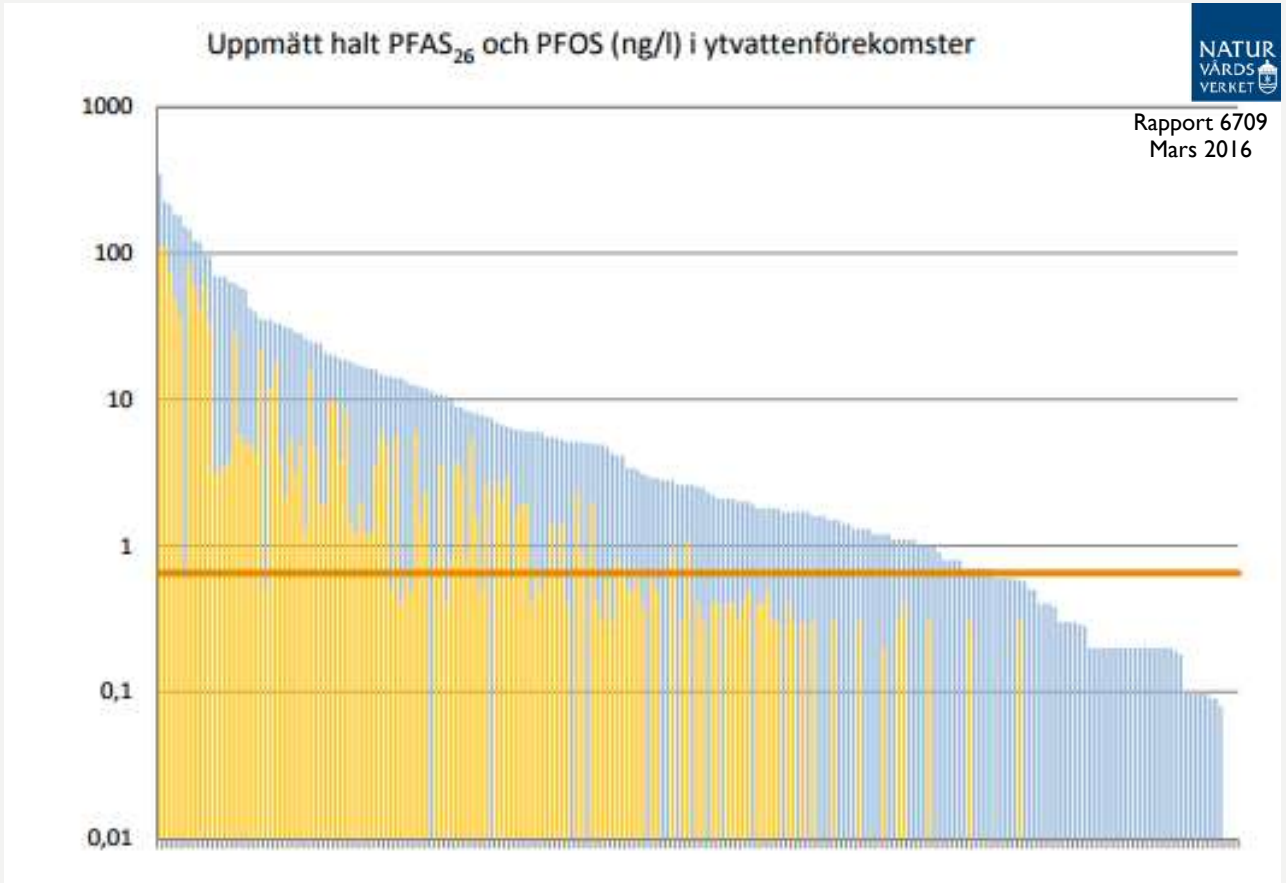
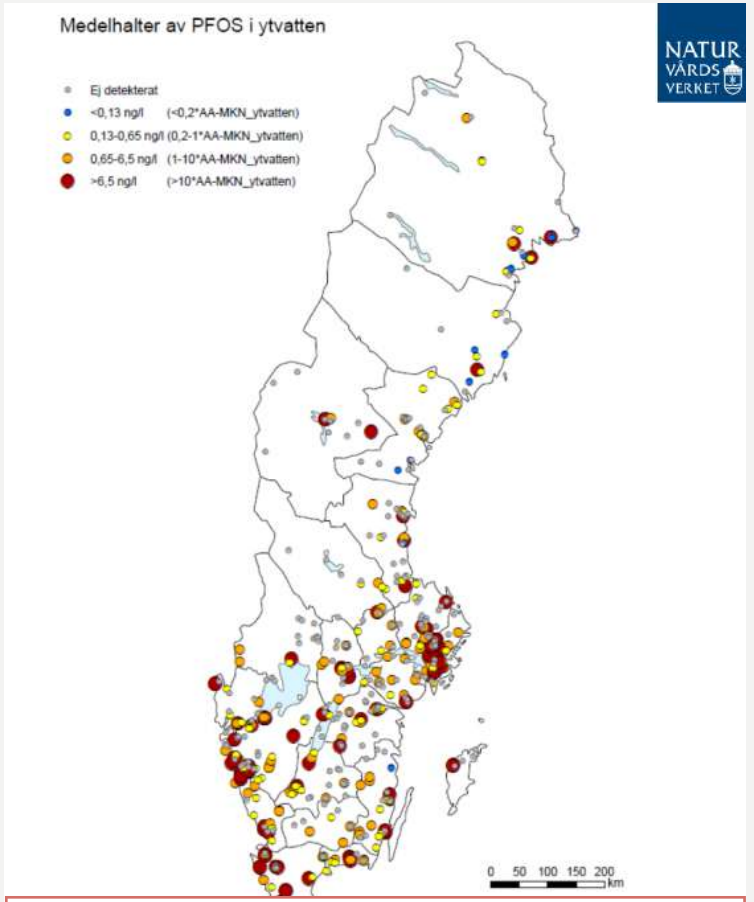
BACKGROUND CONC. SURFACE WATER



Measurement of $PFAS_{26}$ and PFOS (ng/L) content in **215 surface water samples** included in the Water Framework Directive (screening 2015). The height of the blue stack is sum concentrations of PFAS-26, yellow-colored stack indicates the level of PFOS. Orange vertical line indicates **EU EQS for PFOS, 0.65 ng/l.** Note that the scale is logarithmic.



Geographic distribution of PFOS concentrations in surface water. Dots with orange and red color illustrate concentrations above European EQS for PFOS, 0.65 ng/l.

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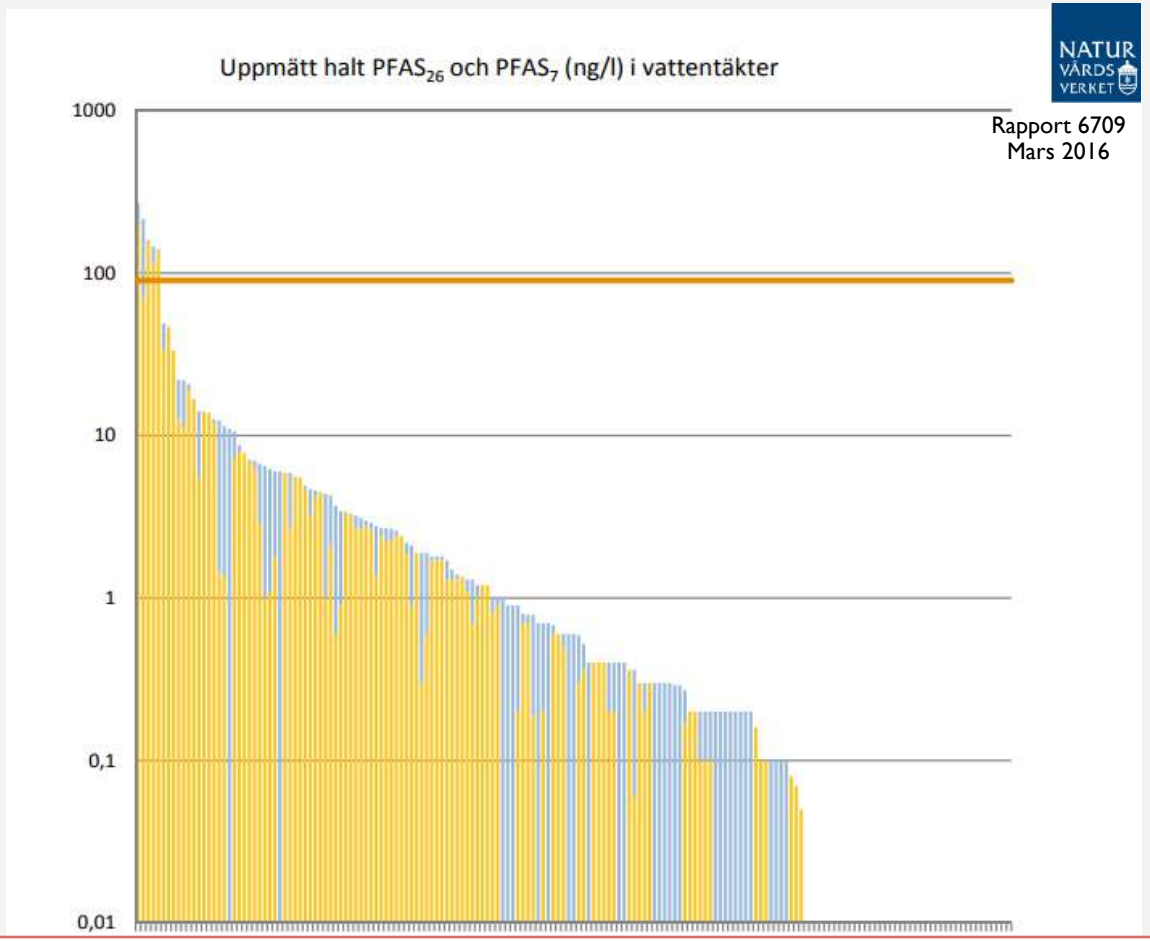
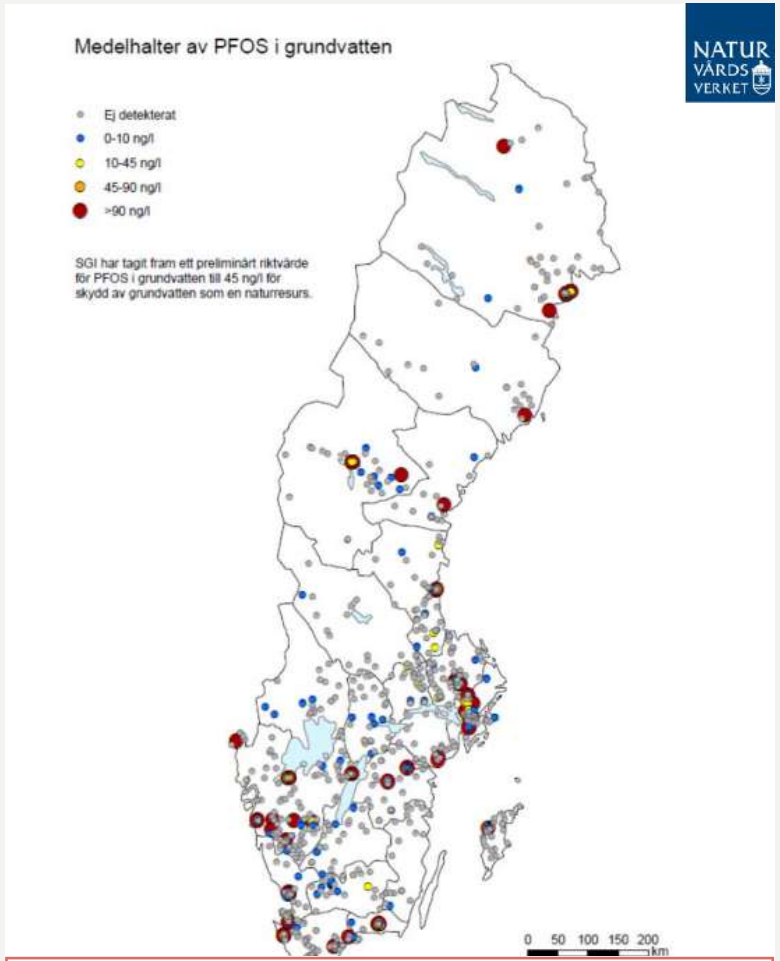
BACKGROUND CONC. GROUNDWATER



Measurement of $PFAS_{26}$ and $PFAS_7$ (ng/L) in **N=173** samples from water supplies. The height of the blue stack is sum concentrations of PFAS-26 , yellow-colored part indicates the level of PFOS. Orange line indicates the National food agancy, Swedem guideline values f or $PFAS_7$ 90 ng/l. Note that the scale is logarithmic.



Geographic distribution of PFOS concentrations in groundwater. Dots with orange and red color illustrate concentrations above European EQS for PFOS, 0.65 ng/l.

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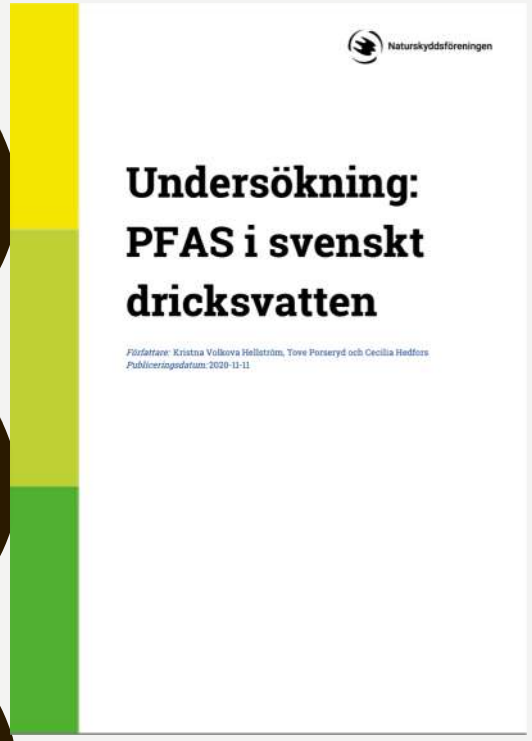
BACKGROUND CONC. POTABLE WATER



Område	Lägst uppmätt halt PFAS 4	Högst uppmätt halt PFAS 4	Personer med vatten över 3,77 ng/L
Halmstad	1,3	47,4	13 000
Gävle	<1	44,83	83 000
Sundsvall	<1	29,3	1 500
Uppsala	<1,1	20,48	86 000
Jönköping	<1,4	19	*okänt*
Karlskrona	<1,4	13,1	<500
Båstad	<7	11,2	<500
Ockelbo	<1	10,5	*okänt*
Ljungby	8,6	8,6	19 000
Västerås	4,27	8,28	140 000
Östhammar	<1,4	8,27	2 800
Västra Skåne (inkl.Malmö, Lund)	<1,14	7,72	500 000
Stor-Stockholm	3,32	5,91	1 300 000
Östersund	<1,4	5,47	<500
Bräcke	<1,4	5,3	<500
Södertälje	2,99	5,1	96 000
Gotland	<1,29	2,95	
Eskilstuna/Strängnäs	<1,4	3,82	
Norrköping	<1,4	2,64	
Lidköping	2,4	2,4	
Hjo	2,35	2,35	
Göteborg	1,98	2,3	
Linköping	<1,59	2,3	
Skövde	2,2	2,2	
Karlstad	<1,4	1,77	
Ängelholm	<1,64	<1,64	
Ronneby	<1,4	<1,54	
Luleå	<1,4	<1,4	
Alingsås	<1,4	<1,4	
Borlänge	<1,4	<1,4	
Umeå	<1,4	<1,4	
Hofors	<1,1	<1,1	
Älvkarleby	<1	<1,1	
Öland	<1	<1,1	
Kalmar	<0,9	<1	
Nordvästra Skåne (inkl. Helsingborg)	<7	<7	
Ludvika kommun	<7	<7	
Boden	<4	<40	
Skellefteå	<4	<4,1	
Eksjö	<1,1	<4	
Örebro kommun	<22,5	<22,6	
Söderhamn	2,45	<22,5	
Gislaved	ej svarat	ej svarat	
Nyköping	ej svarat	ej svarat	

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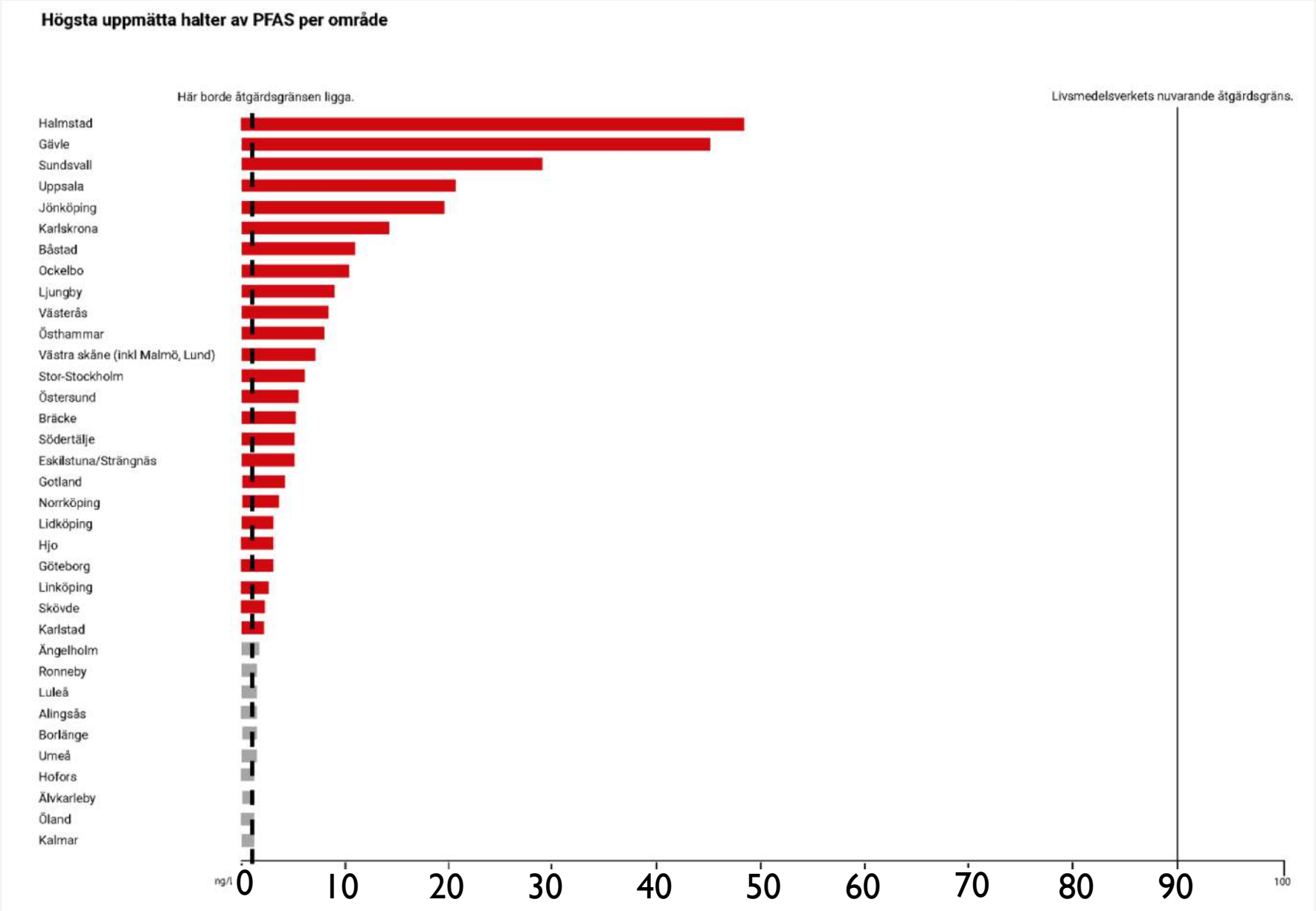
BACKGROUND CONC. POTABLE WATER



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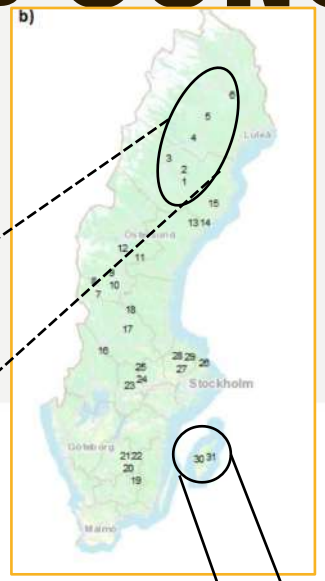
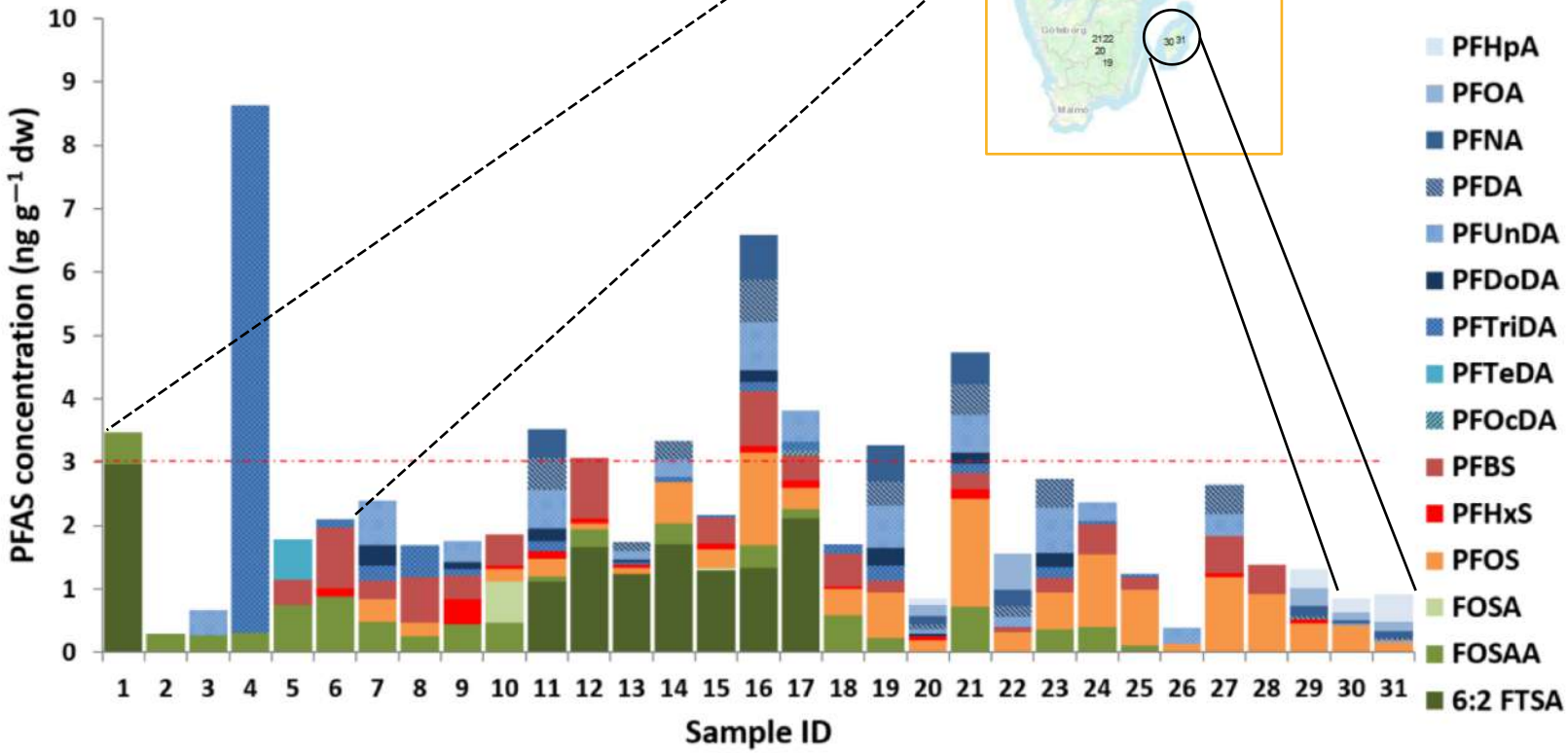
BACKGROUND CONC. IN SOIL


Analysis of per- and polyfluoroalkyl substances (PFASs) in soil from Swedish background sites

Analys av PFAS i mark från bakgrundsområden





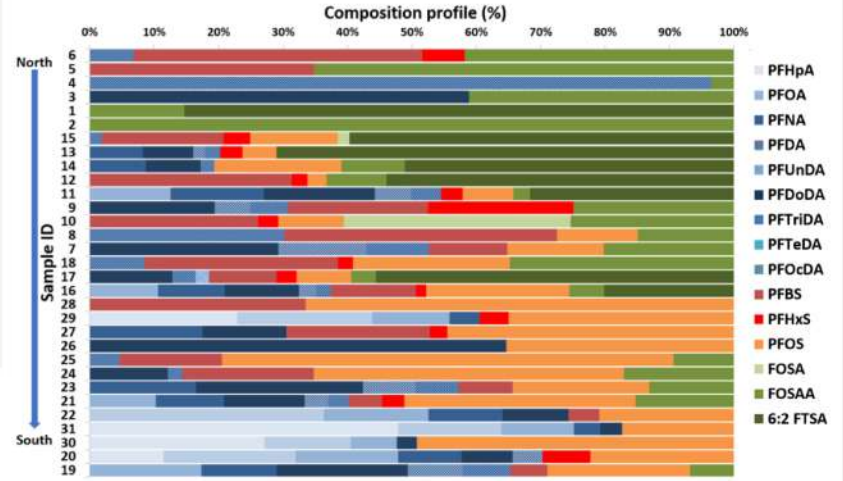


Figure 4. Composition profiles (%) for individual PFASs for soil samples ordered latitudinally from north to south.

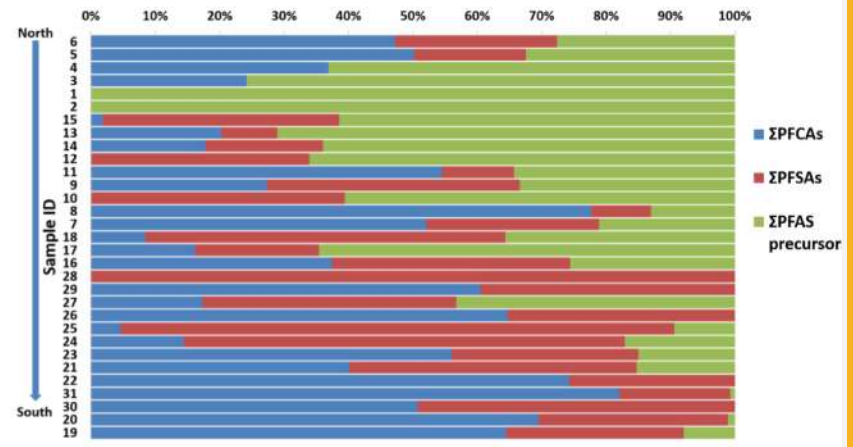


Figure 3. Composition profiles (%) for ∑PFCAs, ∑PFSAs and ∑PFAS precursors for soil samples ordered latitudinally from north to south.

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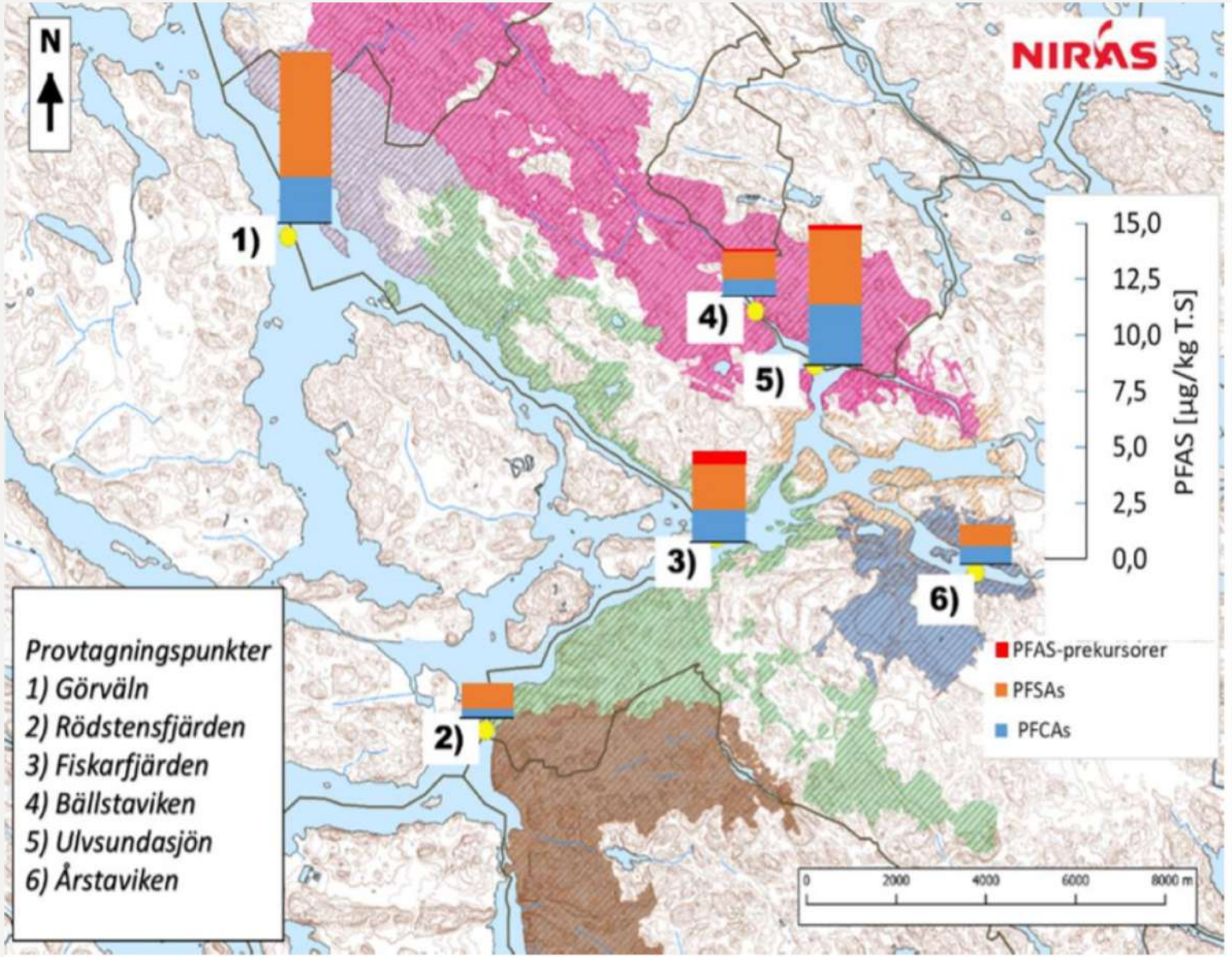
BACKGROUND CONC. IN SEDIMENT



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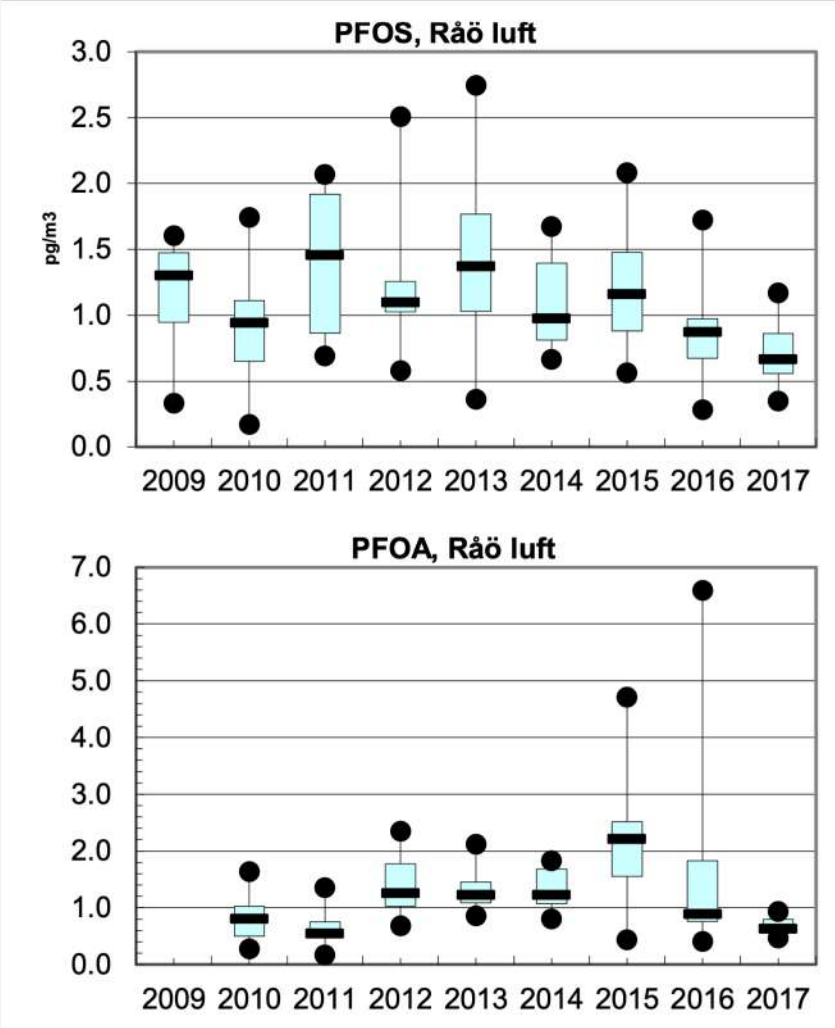
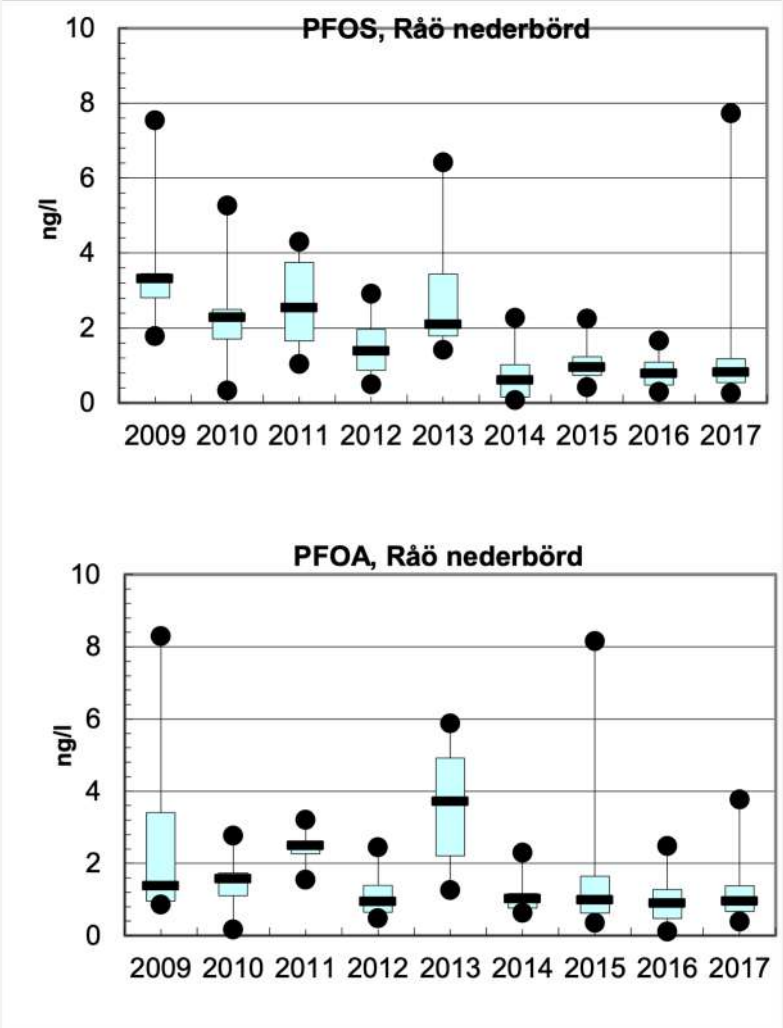
BACKGROUND CONC. IN AIR AND ATMOSPHERIC DEPOSITION





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BACKGROUND CONC. IN AIR AND ATMOSPHERIC DEPOSITION

	Concentration Min-max (mean, median)	Stockholm, Stockholms universitet (2015-2016)	Stockholm Kungsholmen (2018-2019)	Krycklan, Umeå (2011- 2012)	Råö, Göteborg (2015- 2016)
PFHxA	pg/L	0-3981 (498,246)	235-1077 (588,580)	228-1691 (826,731)	51-331 (165,168)
PFHpA	pg/L	59-5792 (732,371)	354-1354 (666,570)	107-654 (650,625)	152-461 (269,269)
PFOA	pg/L	168-1377 (469,373)	393-1396 (782,772)	217-1181 (650,625)	303-1297 (779,814)
PFNA	pg/L	102-6762 (961,543)	210-854 (501,524)	84-289 (179,176)	360-839 (460,392)
PFDA	pg/L	45-1812 (390,163)	139-780 (380,381)	35-211 (131,148)	64-171 (93,92)
PFUnDA	pg/L	0-1981 (830,831)	72-419 (197,188)	31-106 (63,57)	30-1731 (502,301)
PFHxS	pg/L	0-75 (22,9)	0-169 (27,0)	5-51 (17,13)	28-2373 (595,152)
L-PFOS	pg/L	0-391 (115,101)	0-404 (206,175)	16-110 (48,39)	284-1152 (716,611)
Reference		Johansson et al, 2018	Filipovic 2021, not published	Filipovic et al, 2015	Johansson et al, 2018

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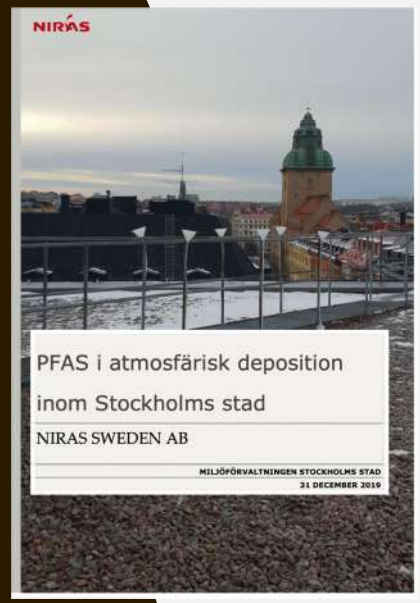
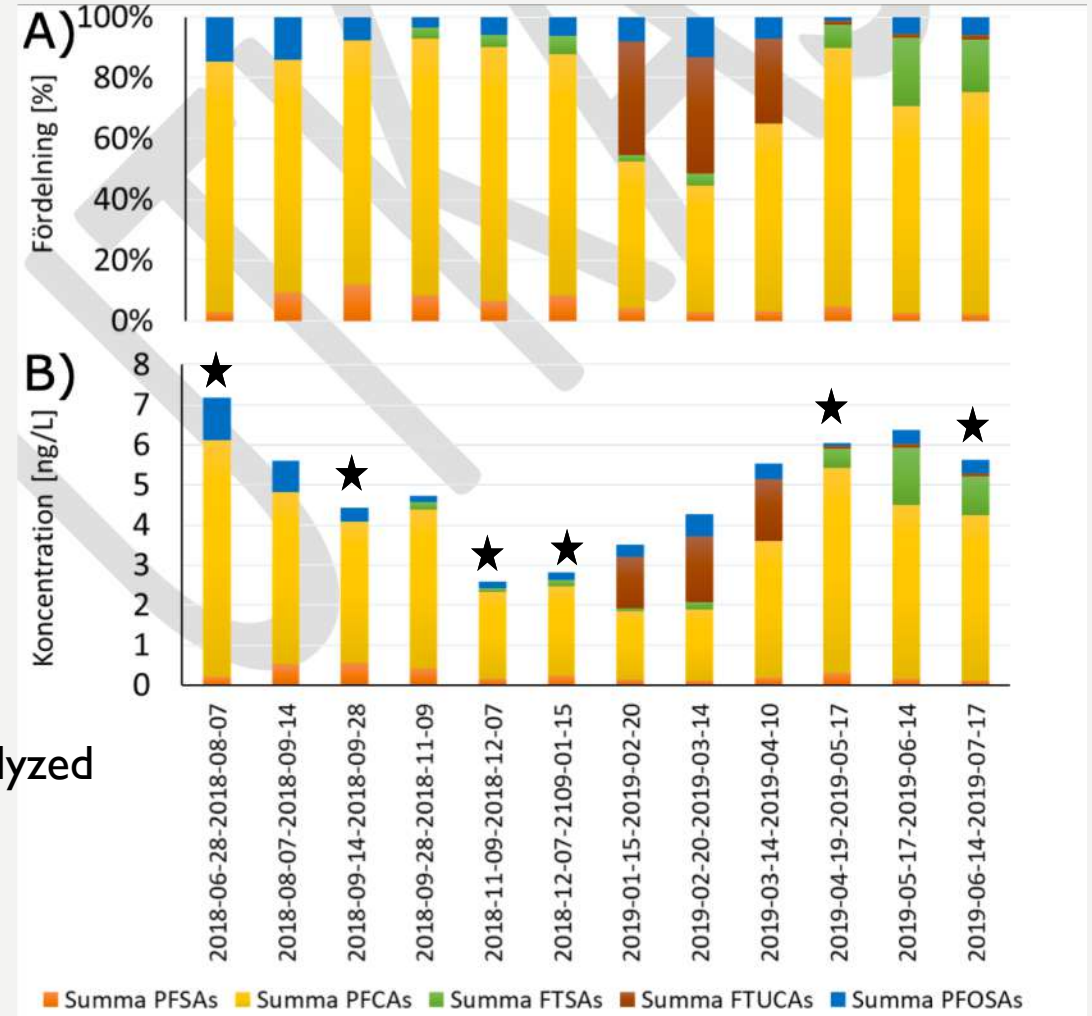
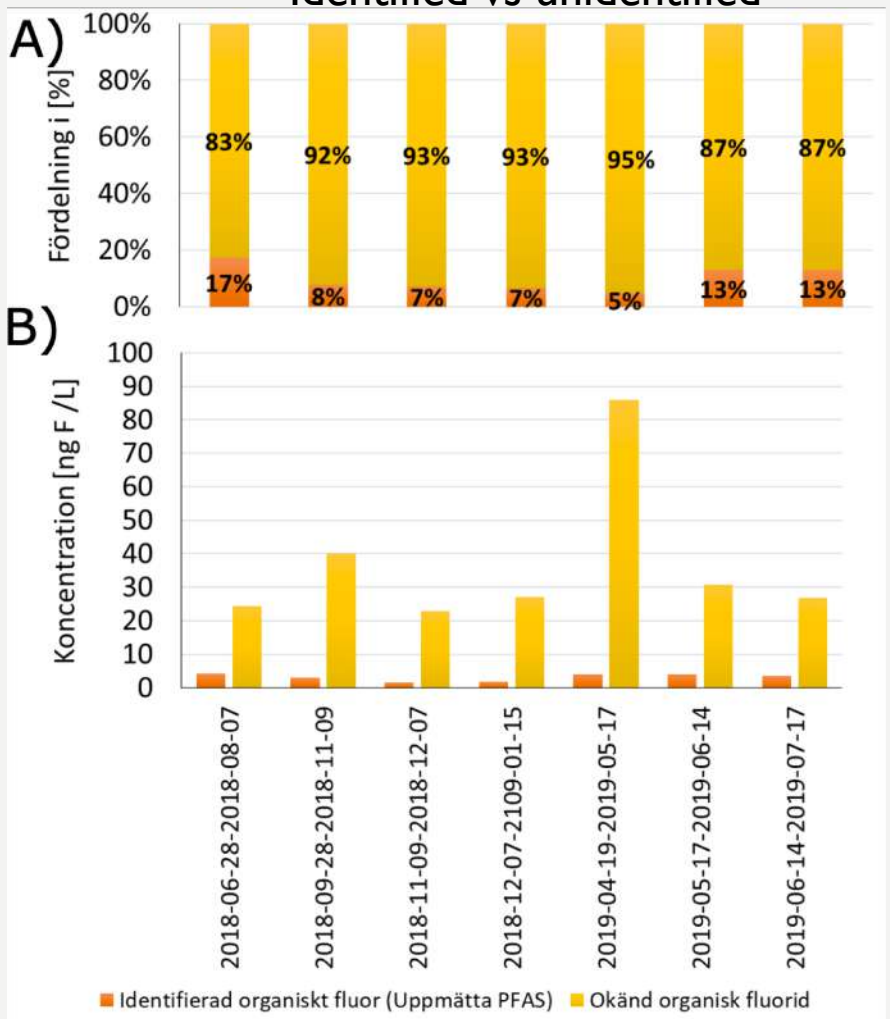
MASS BALANCE OF PFAS IN ATMOSPHERIC DEPOSITION



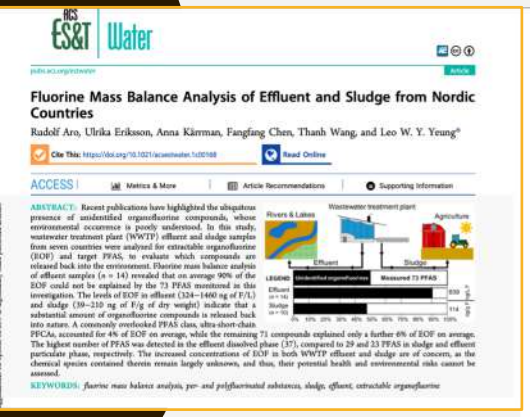
★ Sample analyzed with EOF



EOF mass balance
Identified vs unidentified



BACKGROUND CONC. IN EFFLUENT AND SLUDGE FROM WWTPS



ACS ES&T Water

Fluorine Mass Balance Analysis of Effluent and Sludge from Nordic Countries

Rudolf Aro, Ulrika Eriksson, Anna Kärrman, Fangfang Chen, Thanh Wang, and Leo W. Y. Yeung*

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ABSTRACT: Recent publications have highlighted the ubiquitous presence of unidentified organofluorine compounds, whose environmental occurrence is poorly understood. In this study, wastewater treatment plant (WWTP) effluent and sludge samples from seven countries were analyzed for extractable organofluorine (EOF) and target PFAS, to evaluate which compounds are released back into the environment. Fluorine mass balance analysis of effluent samples (n = 14) revealed that on average 90% of the EOF could not be explained by the 73 PFAS monitored in this investigation. The levels of EOF in effluent (324−1460 ng of F/L) and sludge (39−210 ng of F/g of dry weight) indicate that a substantial amount of organofluorine compounds is released back into nature. A commonly overlooked PFAS class, ultra-short-chain PFCAs, accounted for 4% of EOF on average, while the remaining 71 compounds explained only a further 6% of EOF on average. The highest number of PFAS was detected in the effluent dissolved phase (37), compared to 29 and 23 PFAS in sludge and effluent particulate phase, respectively. The increased concentrations of EOF in both WWTP effluent and sludge are of concern, as the chemical species contained therein remain largely unknown, and thus, their potential health and environmental risks cannot be assessed.

KEYWORDS: *fluorine mass balance analysis, per- and polyfluorinated substances, sludge, effluent, extractable organofluorine*

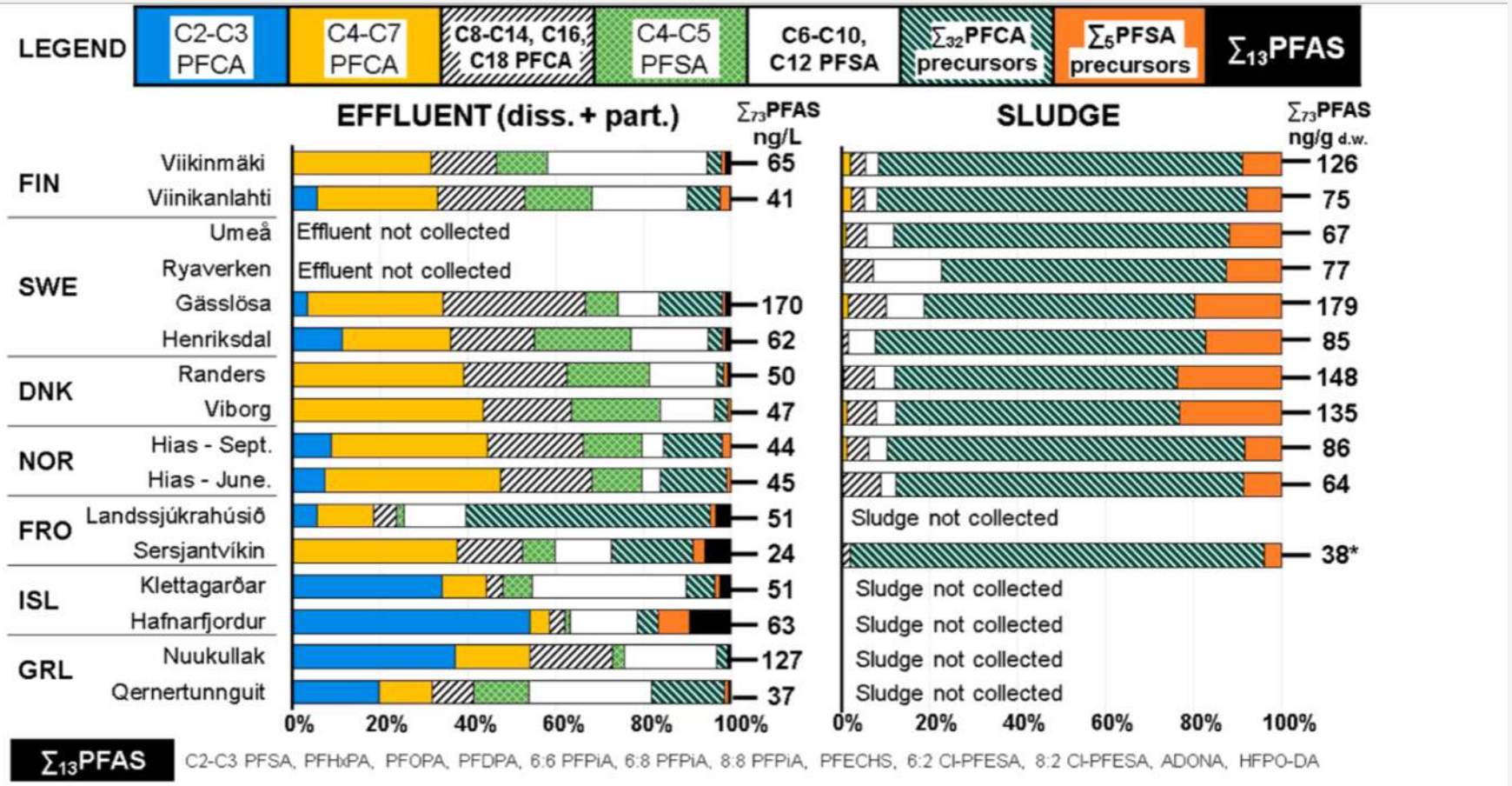

Figure 4. Profiles of the major PFAS classes and the 13 remaining PFAS present in WWTP effluent (combined dissolved and particulate phase) (left) and sludge samples (right) from the Nordic countries. $\sum_{73}$PFAS levels are given in nanograms per liter for effluent and nanograms per gram of dry weight for sludge. *Two sludge samples from Sersjantvikin were collected; the one collected together with effluent is shown here.

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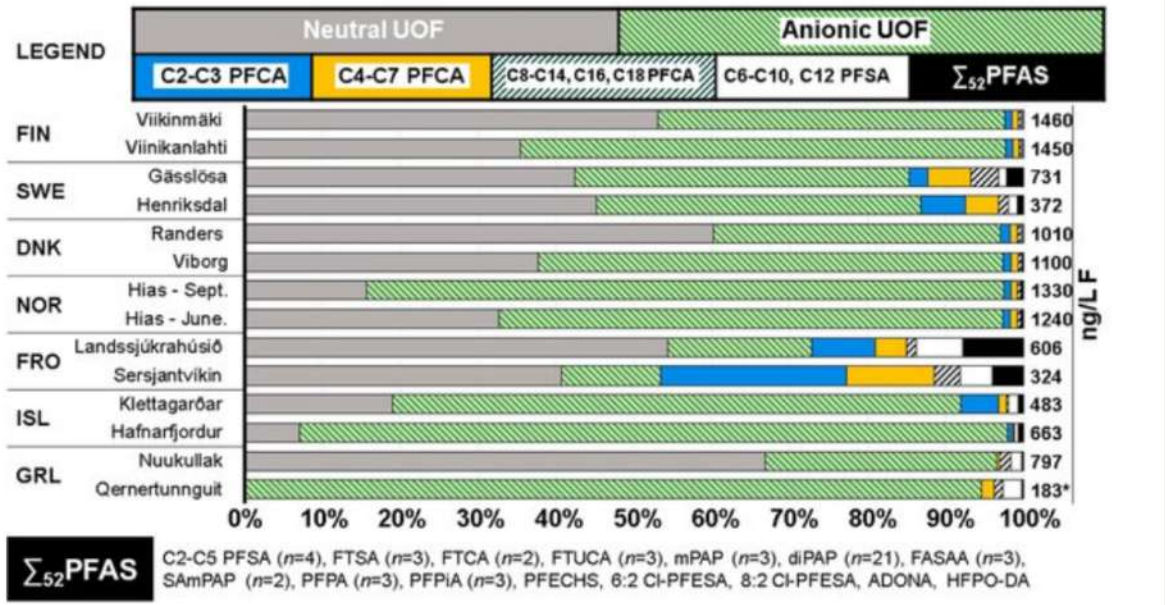
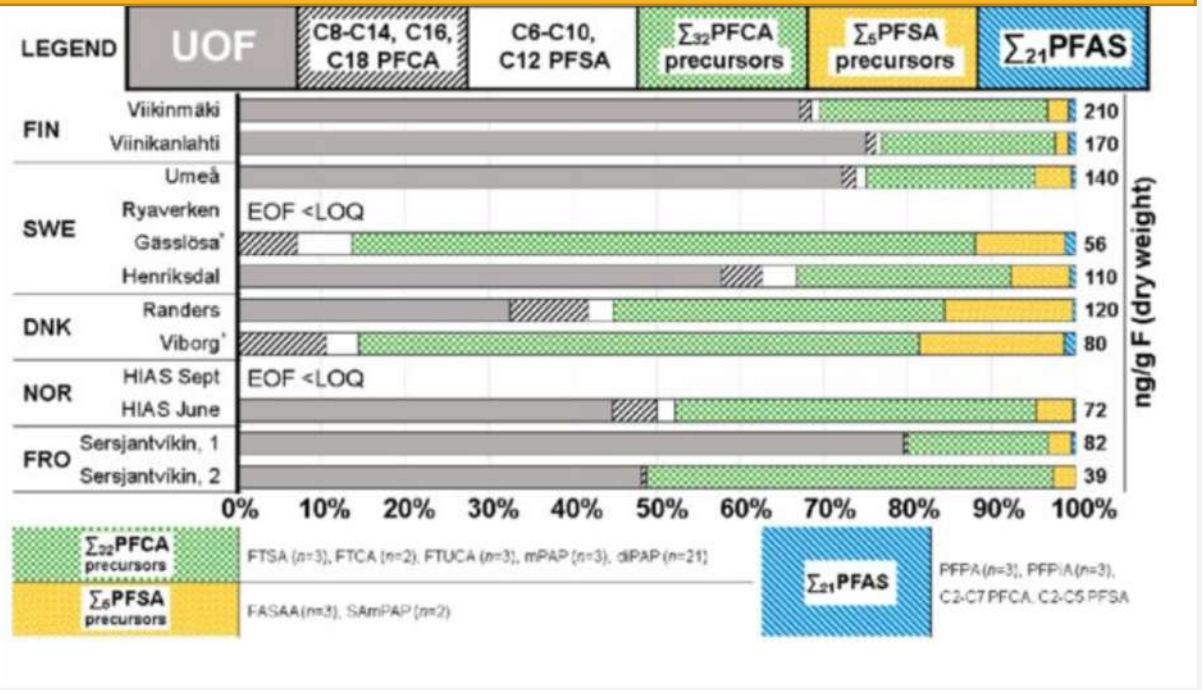
MASS BALANCE OF ORGANOFLUORINE IN EFFLUENTS AND SLUDGE

EFFLUENTS

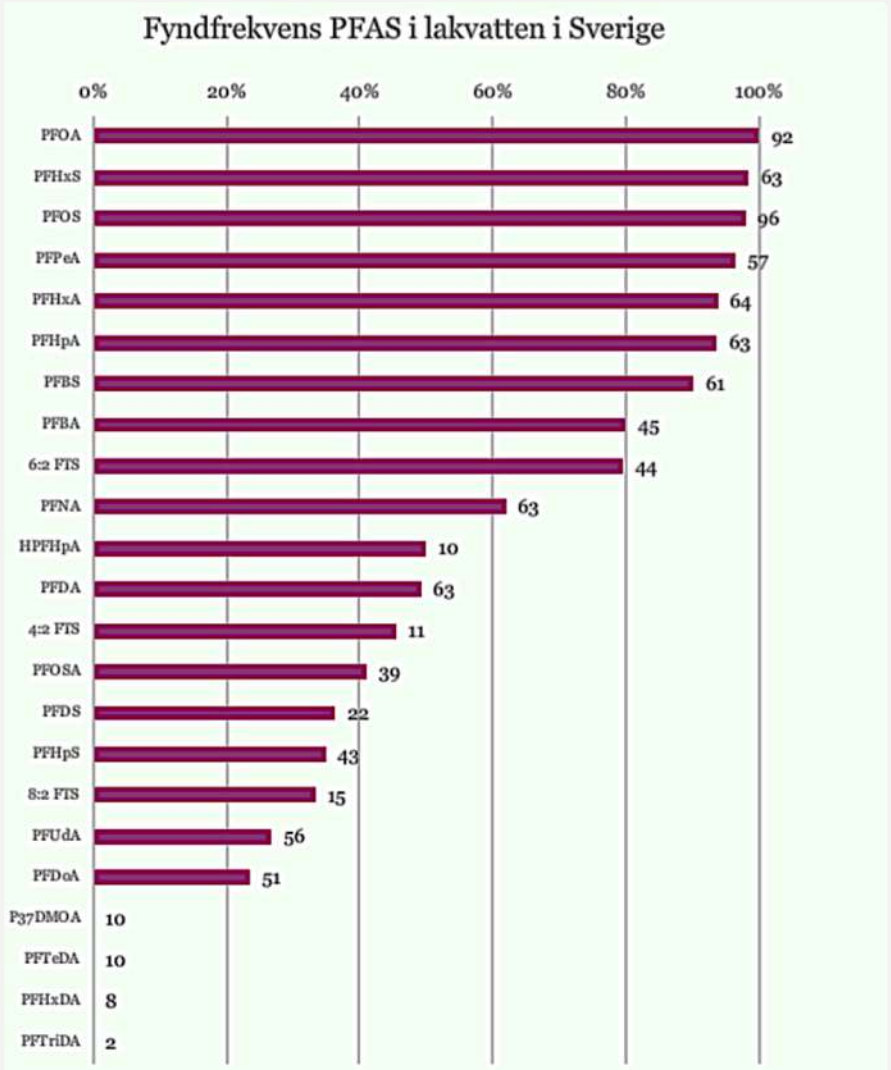


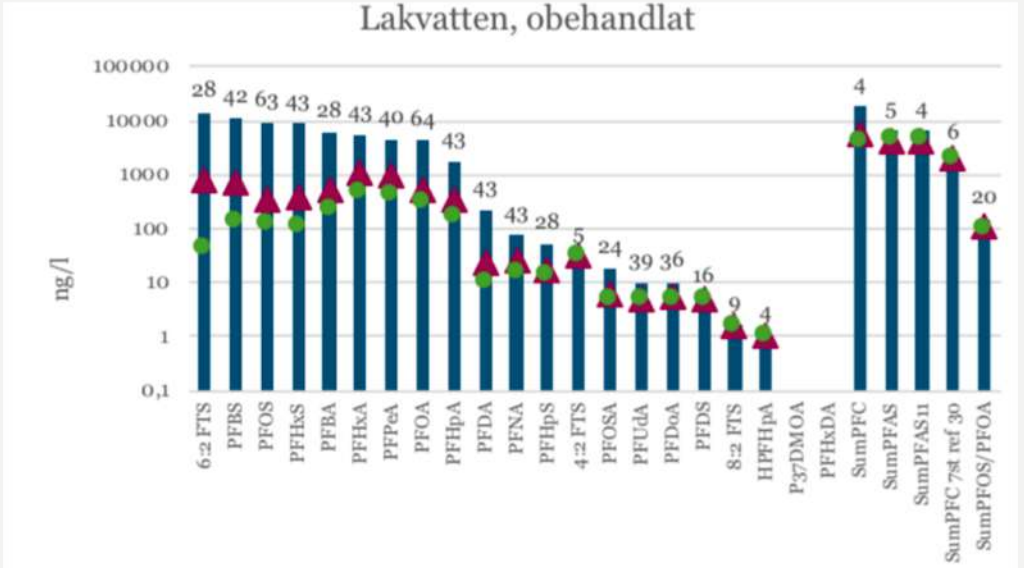
SLUDGE

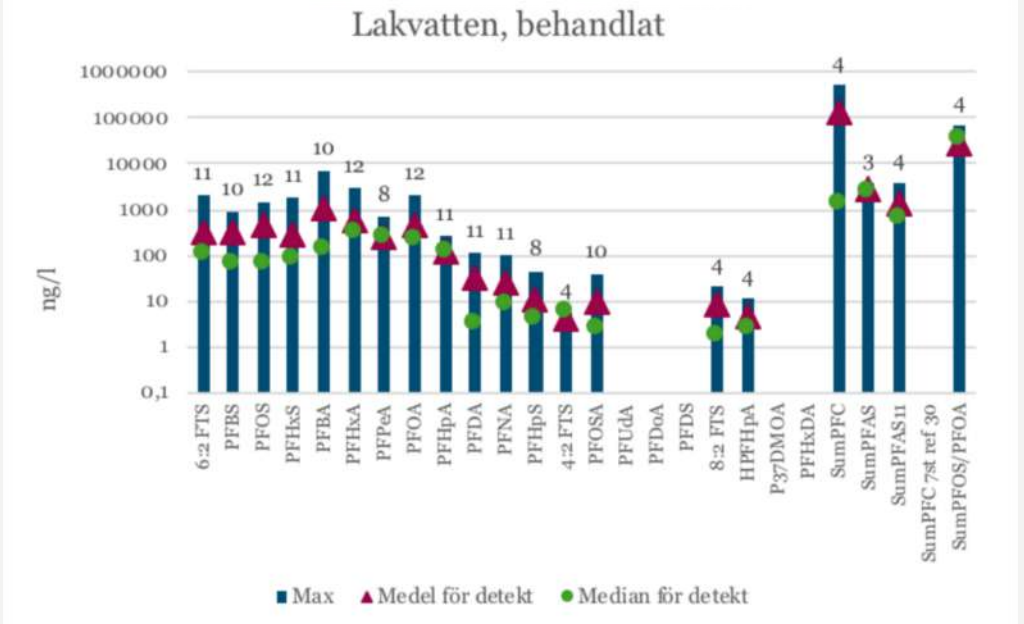


The proportion of Unidentified Organofluorine is very high in both effluents and sludge! New methods to identify the unknown PFAS are needed in order to make better riskassesments.

BACKGROUND CONC IN LANDFILL LEACHATES







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SUMMARY

Atmospheric depostition
Air: 0,3-2,7 pg m3
Rain/snow 2 to16 ng L-1

Landfil leachates >100 to >1000 ng L-1

Surface water
<LOD to >100ng L-1

Waste water treatement plant
Effluent: >60 ng L-1
Sludge: >10 ng g-1 d.w.

Groundwater
<LOD to >100ng L-1

Sediment
<1,0 to 10 ng g-1 d.w.

Potable water
<LOD to <50 ng L-1

Soil
0,3 to 8,5 ng g-1 d.w.

New mass balance approaches show that PFAS measured today only encompass a small fraction of total amount of organofluorine in the samples and thus what is present in the environment !

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Naturhistoriska riksmuseet

ivl SVENSKA MILJÖINSTITUTET

Stockholms stad

LESSONS LEARNED

From 10 years of sampling and analysis of lakes and biota within the City of Stockholm

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ENVIRONMENTAL MONITORING, SURFACE WATER AND BIOTA

- Since 2010, the City of Stockholm has been conducting monthly environmental monitoring of surface water, as well as annual sampling and analysis of biota (muscle and liver from perch), within the city's water bodies.
- The present study evaluates of all compiled data from environmental monitoring program of the City of Stockholm since 2010, which includes a dataset of a total of **1,369 samples and 17,678** measured values for surface water and **124 samples and 1,817** measured values for biota.
- PFAS that are detected in more than 80% of the samples are included in the evaluation and statistical analysis.
- For water: PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFNA and PFDA.
- For biota: PFOS, PFDS, PFOSA, PFDA and PFUnDA.

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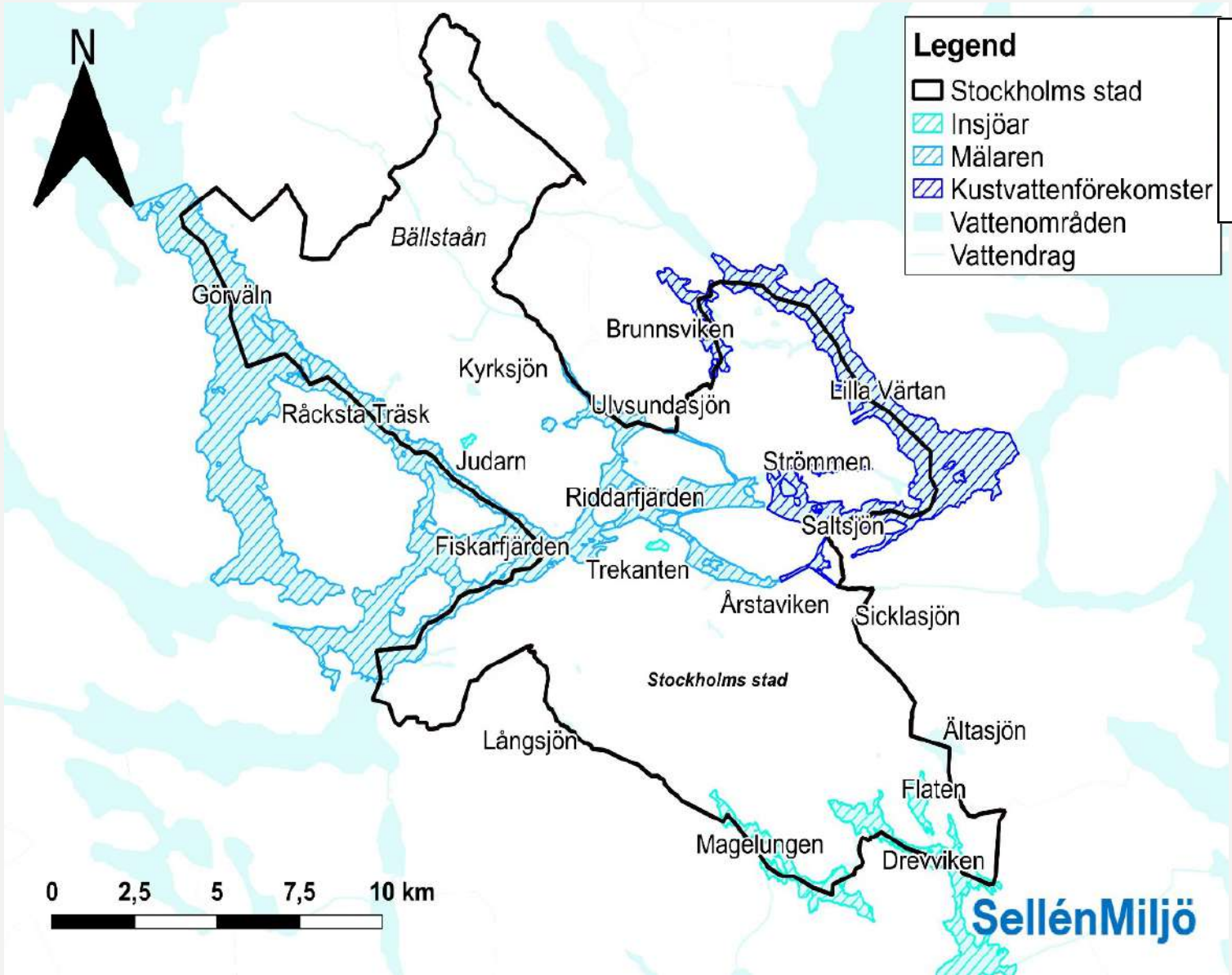
MAP CITY OF STOCKHOLM



Sampling:
10 Inland lakes
6 Basins of Lake Mälaren
4 Costal close water bodies

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SAMPLING 2010-2020

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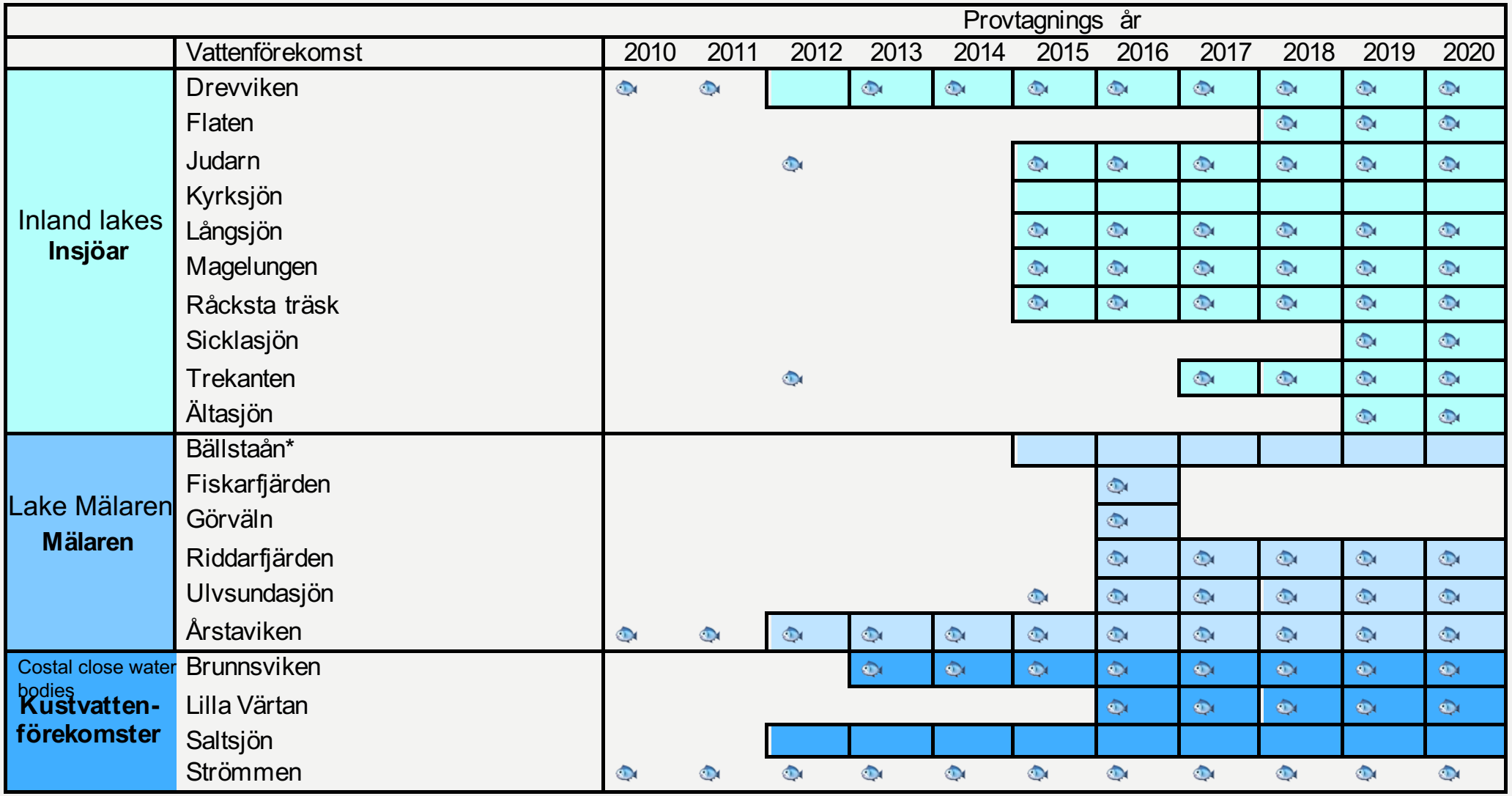

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PFAS ANALYSIS 2010-2020

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	2010			2011			2012			2013			2014			2015			2016			2017			2018			2019			2020		
	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL
PFBA																												0,63	0,2		0,6		
PFPeA																												0,1	0,2		0,1		
PFHxA						2,0–10			2,0–5,0				0,8–2,5			0,1–0,5	0,1	0,1	0,4	0,2	0,1	0,4	0,2	0,1	0,4	0,2	0,1	0,1	0,1		0,1		
PFHpA						5			5,0–35				0,3–1,0			0,01–0,1	0,1	0,1	0,2	0,1	0,2	0,2	0,1	0,2	0,2	0,1	0,2	0,1	0,2		0,1	0,2	
PFOA						1,0–2,0	0,8–2,0		1,0–10				0,8–1,5			0,1–0,3	0,1	0,1	0,2	0,5	0,3	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2		0,2	0,2	
PFNA						1,0–10			1,0–10				0,3–1,2			0,03–0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,3	0,3	0,1	0,3		0,1	0,3	
PFDA													0,4–1,0			0,02–0,3	0,1	0,1		0,1	0,1		0,1	0,1		0,1	0,1	0,1	0,2		0,1	0,2	
PFUnDA													0,2–0,6			0,03–0,1	0,1	0,1		0,1	0,1		0,05	0,1		0,1	0,1		0,2		0,2	0,2	
PFDoDA																															0,5	0,5	
PFTrDA																															0,5	0,5	
PFTeDA																															0,5	0,5	
PFBS						10			10				0,4			0,03–0,9	0,01	0,01	0,1	0,05	0,05	0,1	0,05	0,05	0,2	0,2	0,2	0,1	0,2		0,1		
PFHxS						1			1							0,004–0,9	0,02	0,02	0,1	0,02	0,02	0,1	0,02	0,02	0,1	0,2	0,2	0,1	0,2		0,1		
PFOS							1,4									0,1–0,7	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1		0,1	0,1	
PFDS									1				0,01–0,3			0,2–0,3			0,4		0,5	0,4	0,02	0,5	0,4	0,2	0,2	0,4	0,3		0,4	0,3	
6:2 FTS																									0,4			0,1	0,1		0,1	0,1	
8:2 FTS																												2			2,0	0,3	
PFOSA									2				1				0,02	0,02		0,05	0,05		0,05	0,05	0,4	0,05	0,05		0,1		0,1	0,1	
N-MeFOSA																															2,0		
N-EtFOSA																															2,0		
FOSAA																															2,0		
N-MeFOSAA																															1,0		
N-EtFOSAA																															1,5		
6:2 FTUCA																															2,0		
8:2 FTUCA																															2,0		
10:2 FTUCA																															2,0		
5:3 FTCA																															2,0		
7:3 FTCA																															2,0		

Increased number of matrixes and analytes over time

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PFAS ANALYSIS 2010-2020

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Vi kan miljöföroreningar

	2010			2011			2012			2013			2014			2015			2016			2017			2018			2019			2020		
	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL	YV	BM	BL
PFBA																												0,63	0,2		0,6		
PFPeA																												0,1	0,2		0,1		
PFHxA						2,0–10			2,0–5,0				0,8–2,5			0,1–0,5	0,1	0,1	0,4	0,2	0,1	0,4	0,2	0,1	0,4	0,2	0,1	0,1	0,1		0,1		
PFHpA						5			5,0–35				0,3–1,0			0,01–0,1	0,1	0,1	0,2	0,1	0,2	0,2	0,1	0,2	0,2	0,1	0,2	0,1	0,2		0,1	0,2	
PFOA						1,0–2,0	0,8–2,0		1,0–10				0,8–1,5			0,1–0,3	0,1	0,1	0,2	0,5	0,3	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2		0,2	0,2	
PFNA						1,0–10			1,0–10				0,3–1,2			0,03–0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,3	0,3	0,1	0,3		0,1	0,3	
PFDA													0,4–1,0			0,02–0,3	0,1	0,1		0,1	0,1		0,1	0,1		0,1	0,1	0,1	0,2		0,1	0,2	
PFUnDA													0,2–0,6			0,03–0,1	0,1	0,1		0,1	0,1		0,05	0,1		0,1	0,1		0,2		0,2	0,2	
PFDoDA																															0,5	0,5	
PFTrDA																															0,5	0,5	
PFTeDA																															0,5	0,5	
PFBS						10			10				0,4			0,03–0,9	0,01	0,01	0,1	0,05	0,05	0,1	0,05	0,05	0,2	0,2	0,2	0,1	0,2		0,1		
PFHxS						1			1							0,004–0,9	0,02	0,02	0,1	0,02	0,02	0,1	0,02	0,02	0,1	0,2	0,2	0,1	0,2		0,1		
PFOS							1,4									0,1–0,7	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1		0,1	0,1	
PFDS									1				0,01–0,3			0,2–0,3			0,4		0,5	0,4	0,02	0,5	0,4	0,2	0,2	0,4	0,3		0,4	0,3	
6:2 FTS																									0,4			0,1	0,1		0,1	0,1	
8:2 FTS																												2			2,0	0,3	
PFOSA									2				1				0,02	0,02		0,05	0,05		0,05	0,05	0,4	0,05	0,05		0,1		0,1	0,1	
N-MeFOSA																															2,0		
N-EtFOSA																															2,0		
FOSAA																															2,0		
N-MeFOSAA																															1,0		
N-EtFOSAA																															1,5		
6:2 FTUCA																															2,0		
8:2 FTUCA																															2,0		
10:2 FTUCA																															2,0		
5:3 FTCA																															2,0		
7:3 FTCA																															2,0		

Increased number of matrixes and analytes over time

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TEMPORAL TRENDS IN WATER

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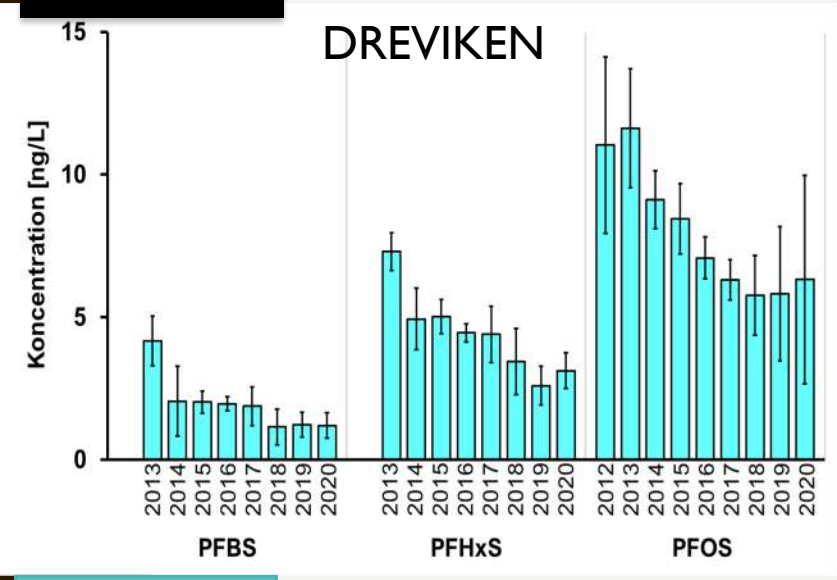
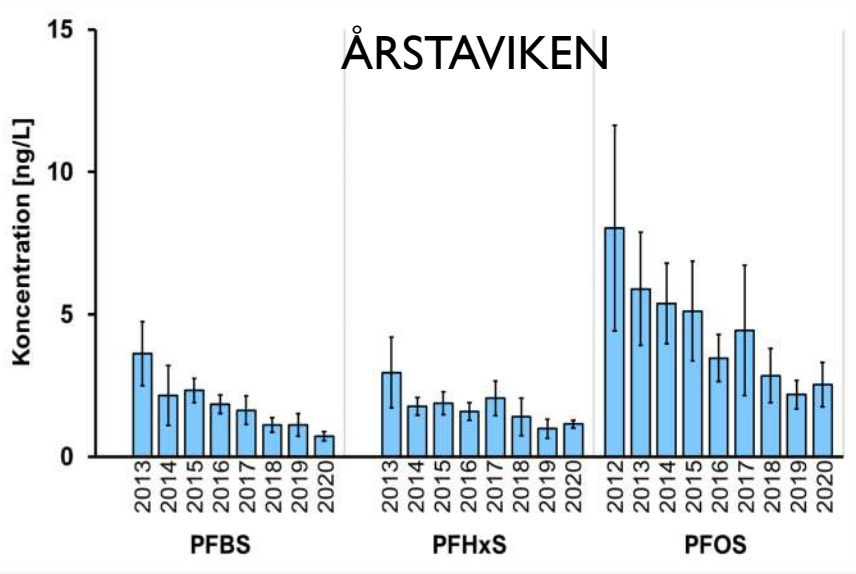
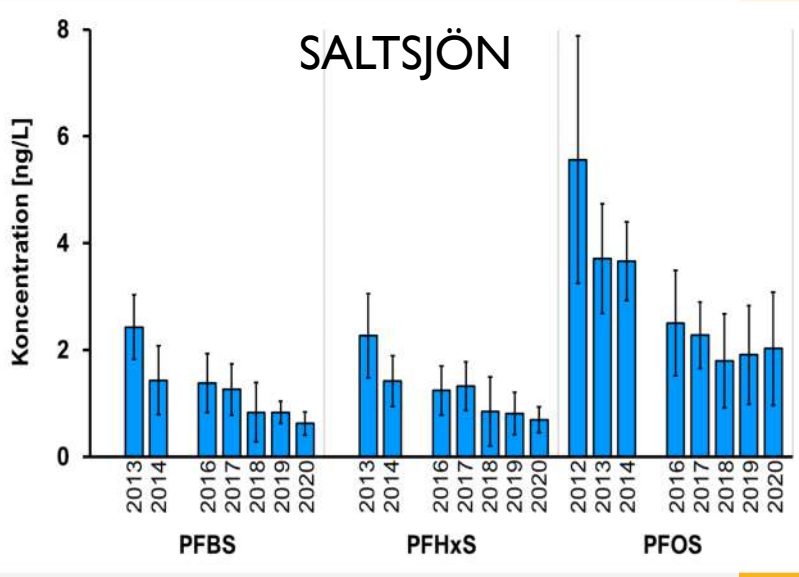
Vi kan miljöföroreningar

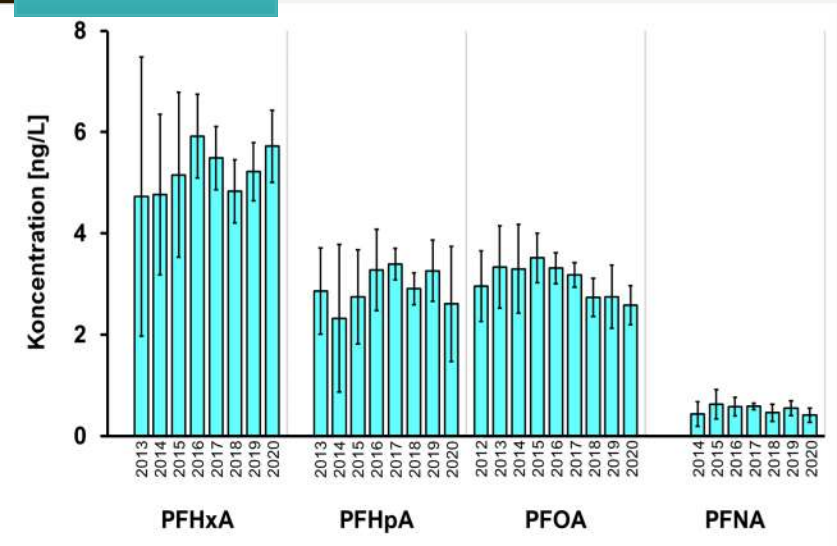
PFSAs

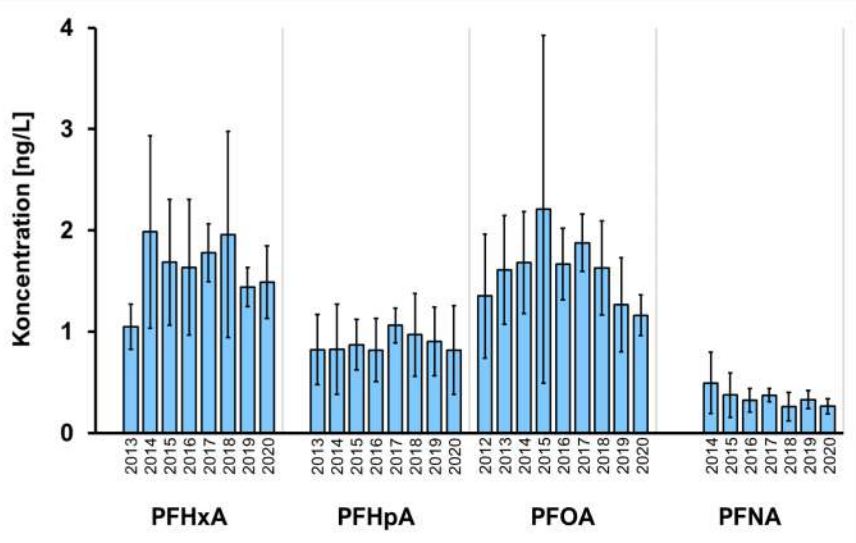


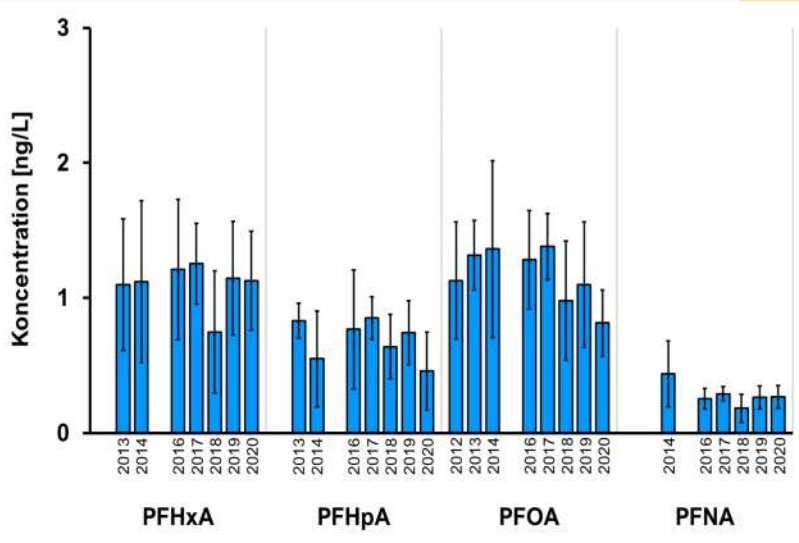




PFCAs







STATISTICAL ANALYSIS

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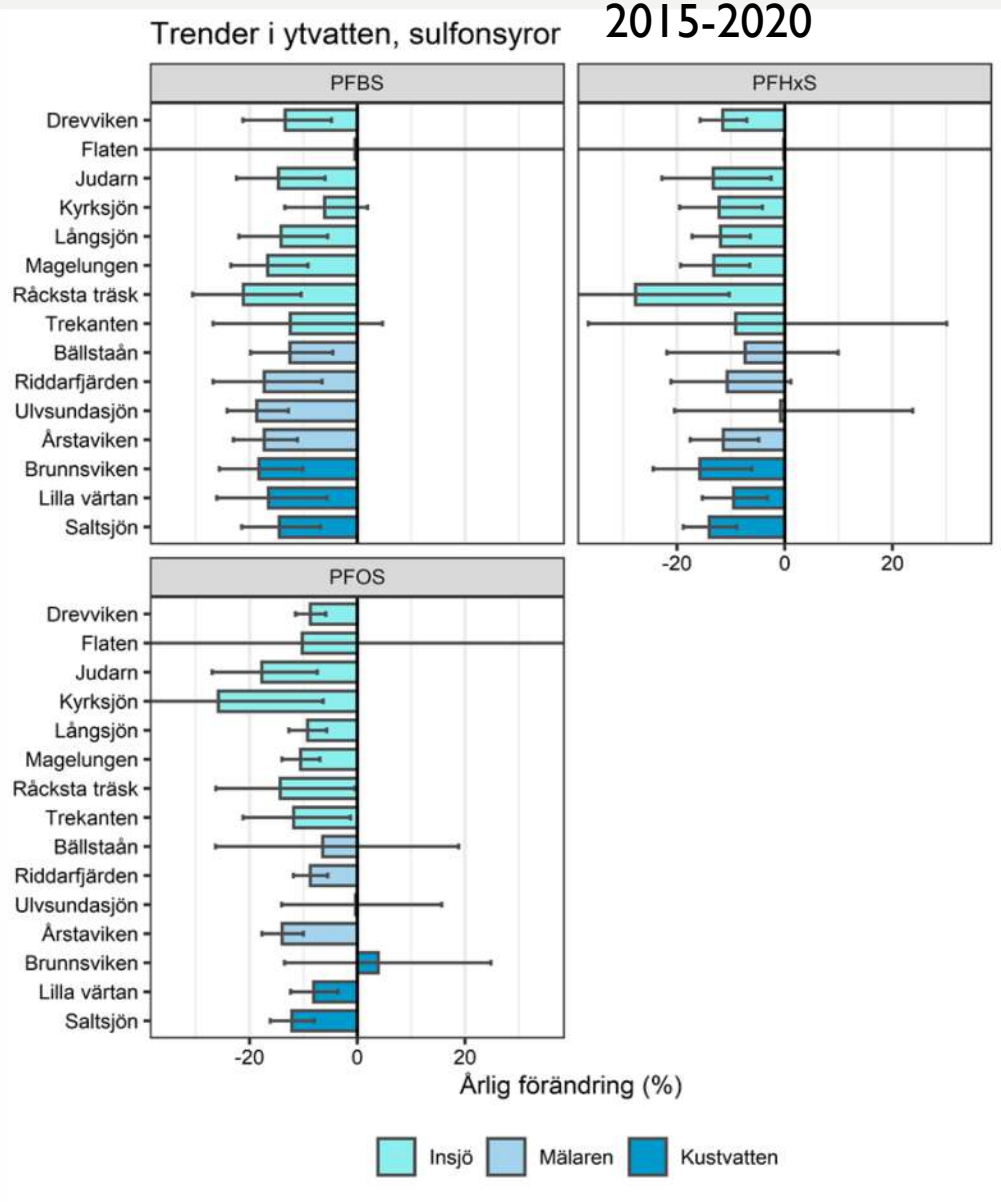
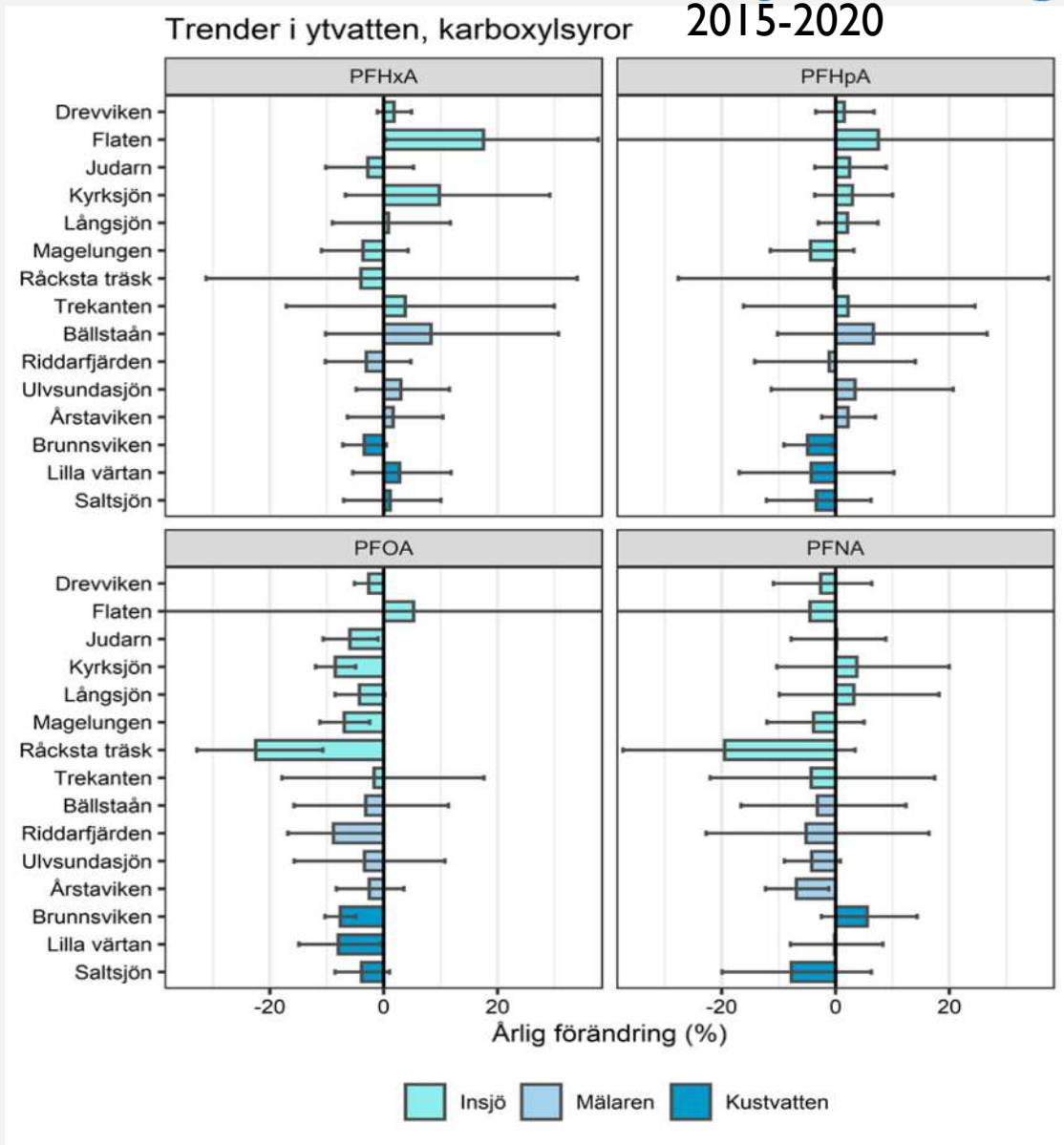
Vi kan miljöföroreningar





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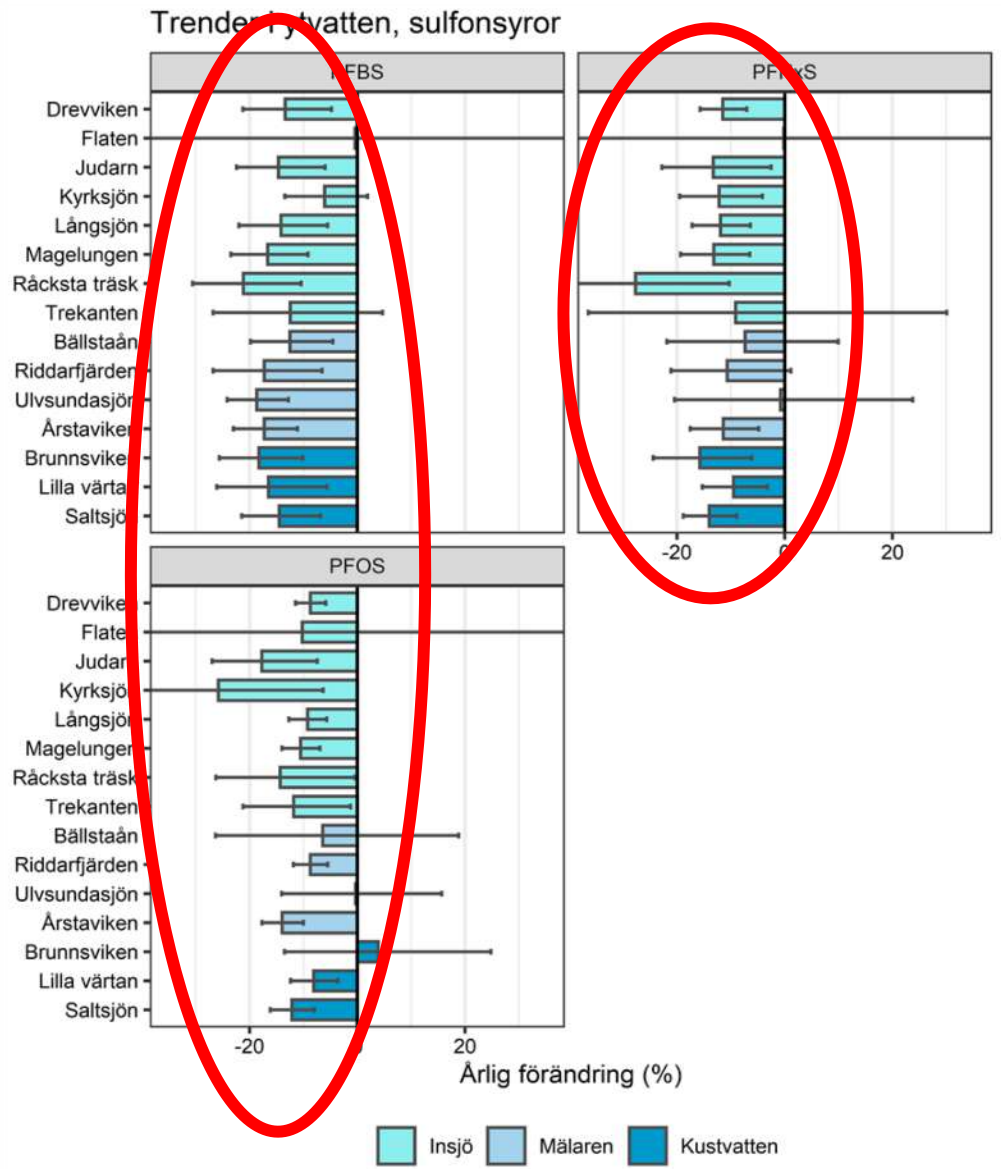
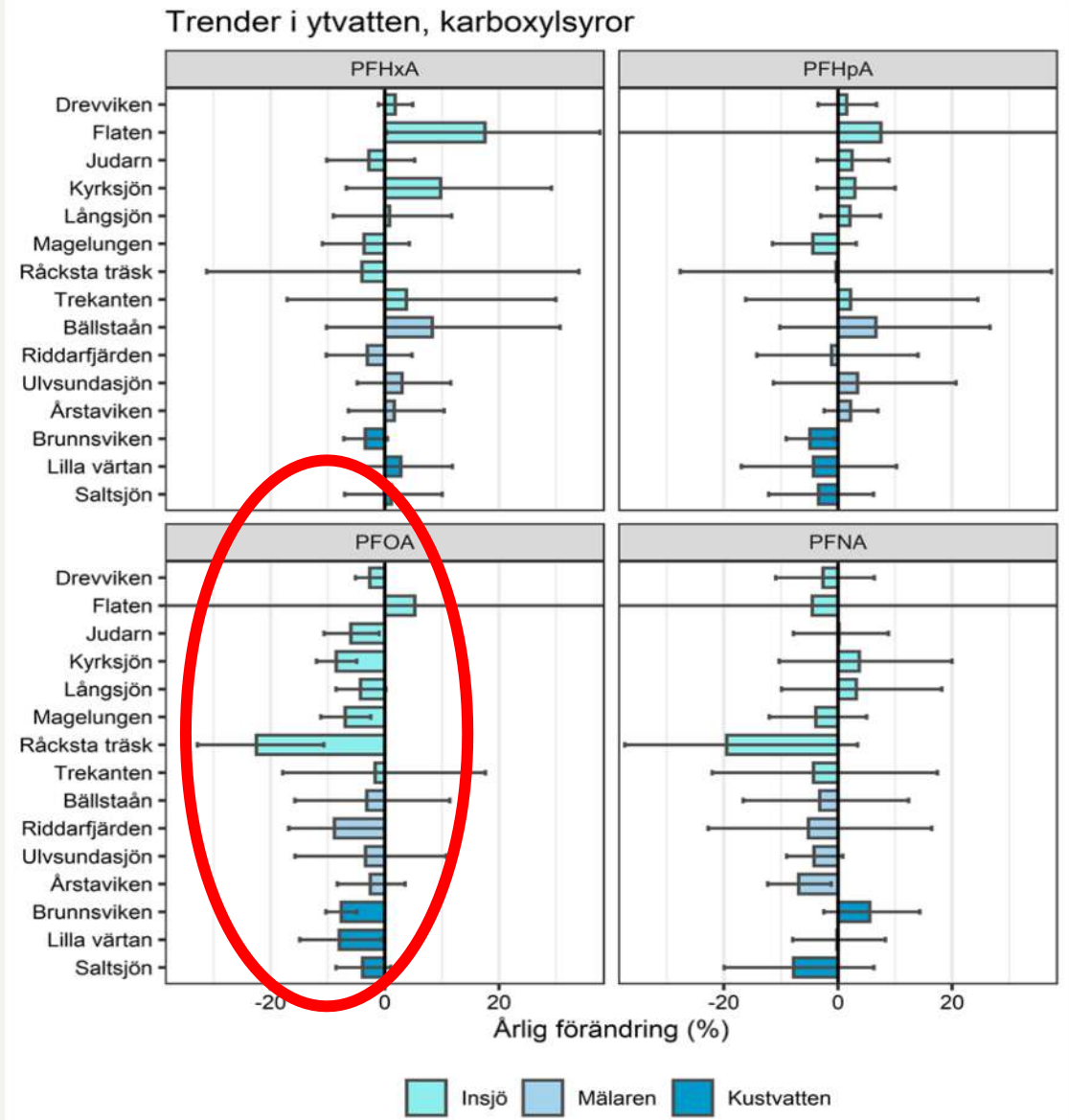
STATISTICAL ANALYSIS

SellénMiljö
Vi kan miljöföroreningar





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PFAS IN LIVER AND MUSCLE

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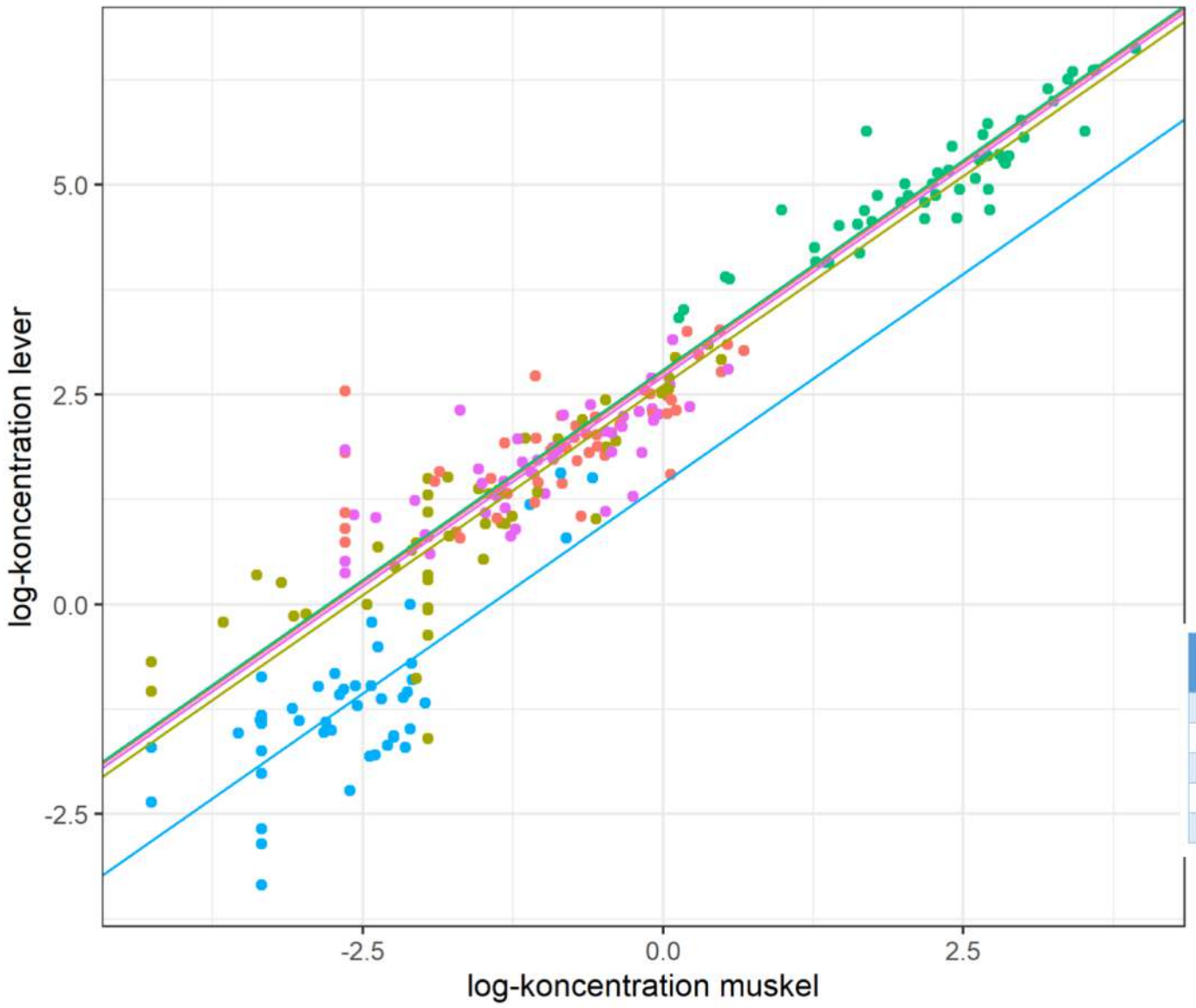

Ämne	Faktor	Konfidensintervall (Undre; Övre)
PFDA	15,8	(13,1; 19,1)
PFDS	13,6	(11,3; 16,3)
PFOS	16,3	(14,7; 18,1)
PFOSA	4,2	(3,5; 5,1)
PFUnDA	15,1	(12,8; 17,7)

NEW DATA!

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LESSONS LEARNED, TAKE HOME MESSAGES

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1) In 2010 the environmental monitoring program included annual sampling of biota in three water bodies and only analysis of PFOS. Ten years later in 2020 the environment monitoring program expanded to monthly sampling of surface water in 17 water bodies including analysis of 28 different PFAS substances, as well as annual sampling of biota in 15 water bodies and analysis of 13 PFAS substances. **= EXPANSION OVER TIME**
2) The design of the environmental monitoring, but above all the scope, has developed during the years since it was initiated. **NOT STATIC**
3) A continuous monitoring of the environment is essential in order to identify changes of concentrations and chemical pattern over time. One measurement is only informative data, multiple measurements could be used for trend analysis and fingerprinting. **BIG VALUE**
4) Are all compounds or matrixes necessary to measure? **RETHINK**
5) After some (years) of monitoring, evaluate the data and change analytical parameters/scope if needed. **REDISGN**
6) Use the accumulated data and make something out of it. Time trends or models? **USE THE DATA WISELY, EXCEL**
7) Strive for the future problems as well. Test new analytical methods they might give new insights. **PIONEER**

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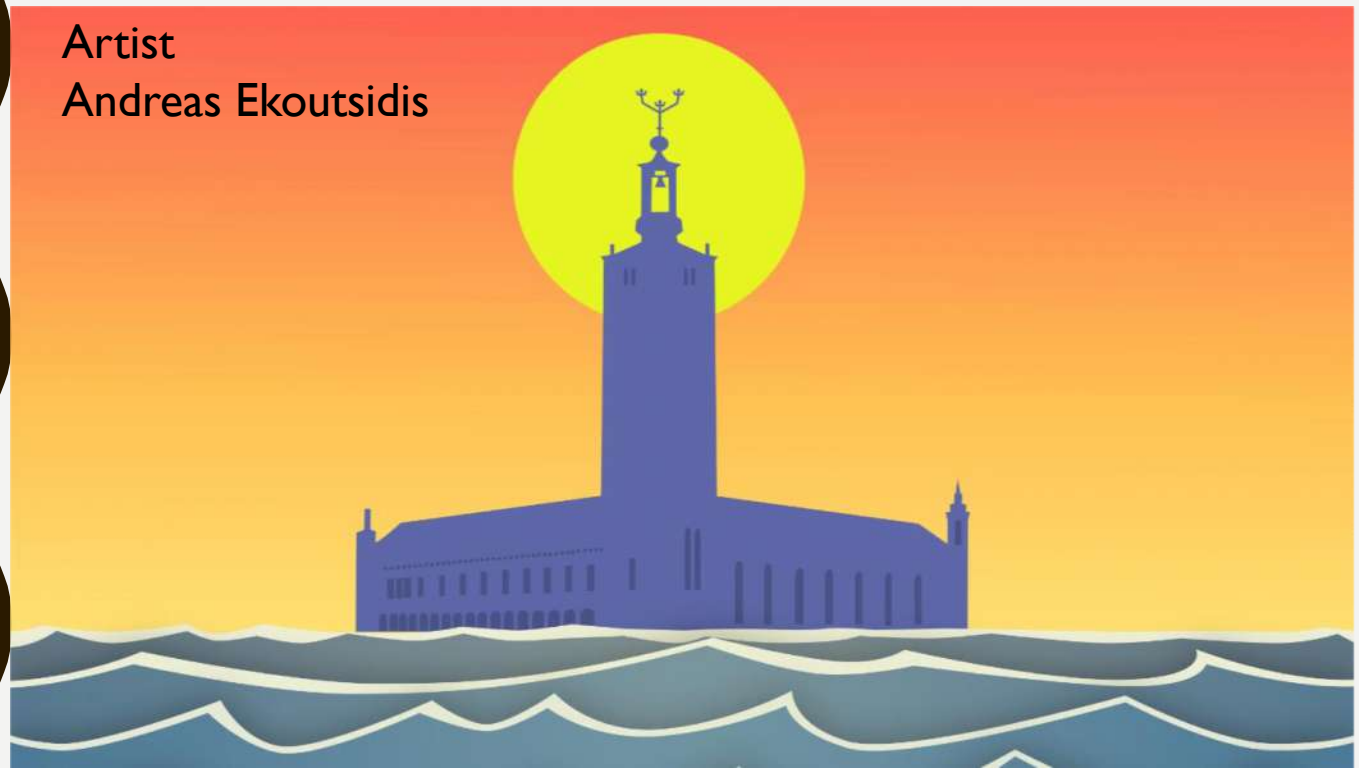
THANK YOU FOR YOUR ATTENTION

- ATV Jord og Grundvand for the invitation
- Ebba Sellén at SellénMiljö for preparing the PPT



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