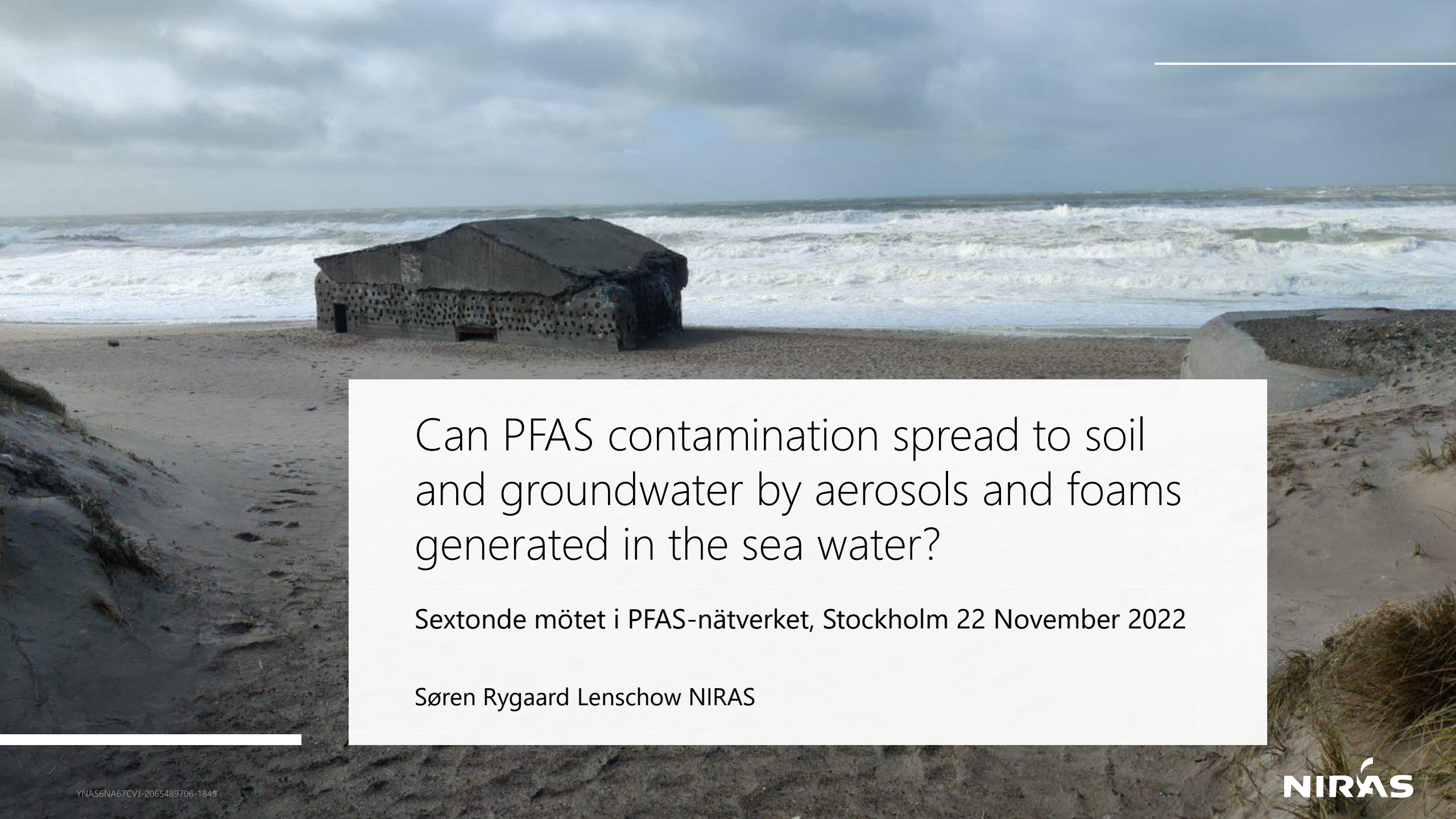


Can PFAS contamination spread to soil and groundwater by aerosols and foams generated in the sea water?

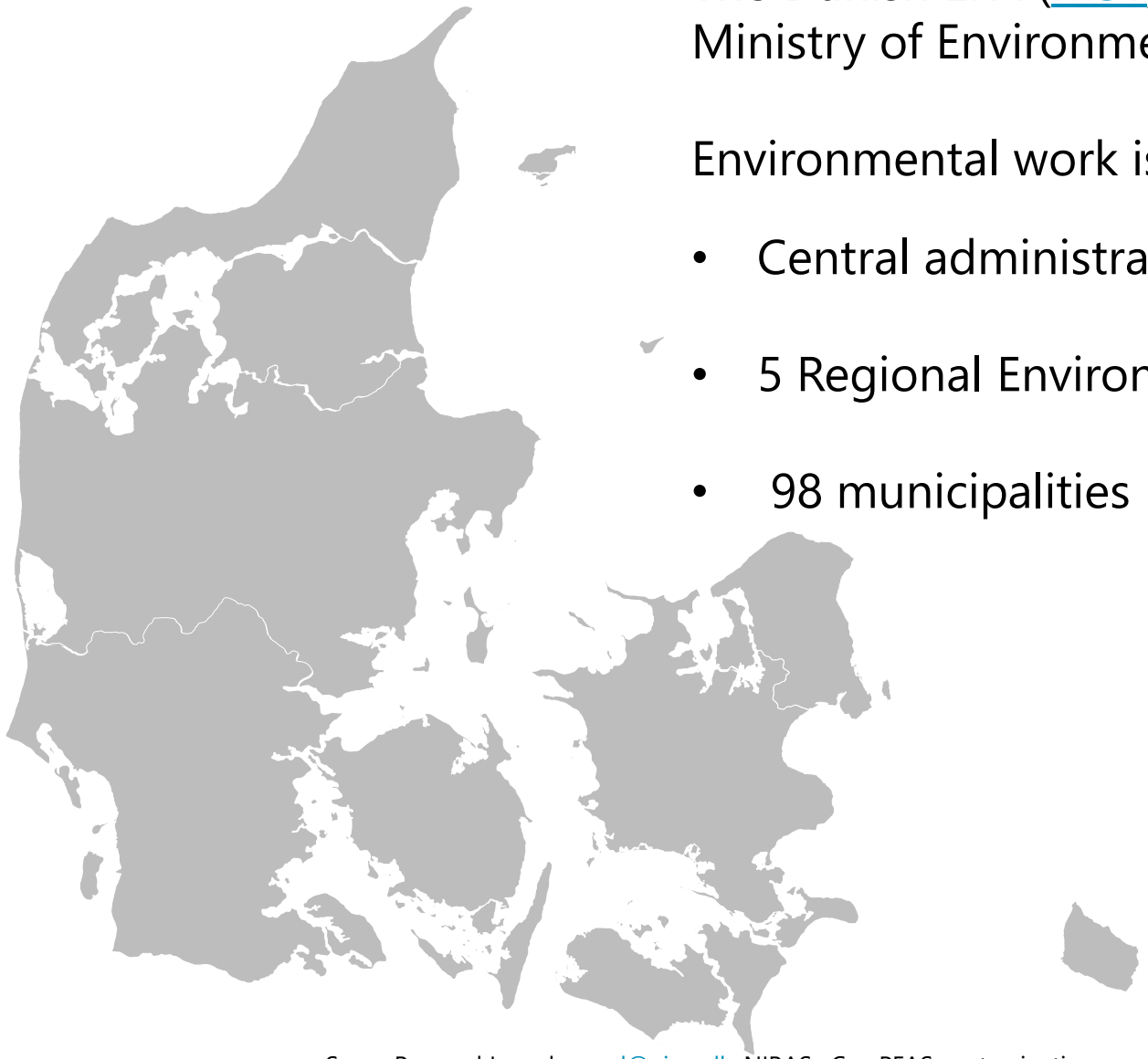
Sextonde mötet i PFAS-nätverket, Stockholm 22 November 2022

Søren Rygaard Lenschow NIRAS

Agenda

- PFAS state and criteria in Danmark
- Background Thyborøn/Harboøre site
- Methods
- Results
- New projects and results
- Future work

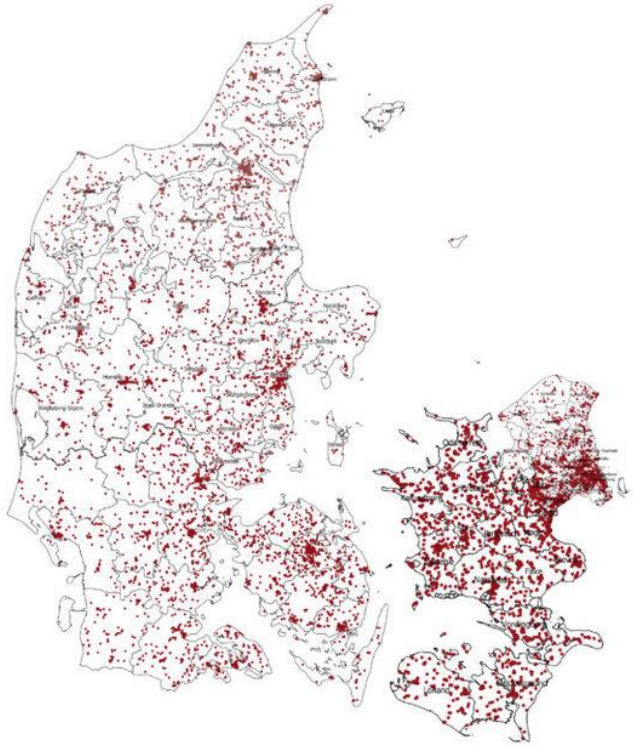
Denmark



The Danish EPA (MST) is under the Danish Ministry of Environment

Environmental work is divided between

- Central administration (MST)
- 5 Regional Environmental Authorities
- 98 municipalities



Up to 15,000 sites are potentially contaminated with PFAS
8% investigated
900 documented as contaminated

Historical overview of criteria in Denmark

2015	Quality criteria for		∑**12 PFAS**	
	Groundwater /drinking water:		100	ng/l
	Soil:		400	µg/kg dw
2018	EU quality criterium for **PFOS** in surface waters implemented from December 2018			
	Fresh waters:	annual av.	0.65	ng/l **PFOS**
		max.	36 000	ng/l **PFOS**
	Marine waters:	annual av.	0.13	ng/l **PFOS**
		max.	7 200	ng/l **PFOS**
2019	Additional supplementary criteria for		**PFOS**	**PFOA**
	Groundwater /drinking water:		6 ng/l	3 ng/l
	Soil:		30 µg/kg dw	10 µg/kg dw
2021	New quality criteria for		∑**22 PFAS**	∑**PFOA, PFNA, PFHxS, PFOS**
	Groundwater:		100 ng/l	**2 ng/l**
	Soil:		400 µg/kg dw	**10 µg/kg dw**
	Drinking water:		100 ng/l (pt. only ∑12 PFAS)	**2 ng/l**

2020 EFSA (European Food Safety Authority define TWI of 4,4 ng/kg bw for ∑4 PFAS

Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by Aerosols and foams generated in sea water?
Sextonde motet I PFAS-nätverket, 22th of November 2022, Stockholm

Which 22 PFAS?

Carboxylic acids		Sulfonic acids	
PFBA	C_3F_7•COOH		
PFPeA	C_4F_9•COOH	PFBS	C_4F_9•SO_3H
PFHxA	C_5F_{11}•COOH	*PFPeS#*	C_5F_{11}•SO_3H
PFHpA	C_6F_{13}•COOH	PFHxS*	C_6F_{13}•SO_3H
PFOA*	C_7F_{15}•COOH	*PFHpS#*	C_7F_{15}•SO_3H
PFNA*	C_8F_{17}•COOH	PFOS*	C_8F_{17}•SO_3H
PFDA	C_9F_{19}•COOH	*PFNS#*	C_9F_{19}•SO_3H
PFUnDA#	$C_{10}F_{21}$•COOH	*PFDS#*	$C_{10}F_{21}$•SO_3H
PFDoDA#	$C_{11}F_{23}$•COOH	*PFUnDS#*	$C_{11}F_{23}$•SO_3H
PFTrDA#	$C_{12}F_{25}$•COOH	*PFDoDS#*	$C_{12}F_{25}$•SO_3H
		PFTrDS#	$C_{13}F_{27}$•SO_3H
Fluorotelomer		6:2 FTS	C_6F_{13}•C_2H_4•SO_3H
Sulfonamide		PFOSA	C_8F_{17}•SO_2NH_2

**∑4 PFAS with low criteria*

#the 2021 extra 10 PFAS for groundwater and soils - and for drinking water from 2023

Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by Aerosols and foams generated in sea water?
Sextonde motet I PFAS-nätverket, 22th of November 2022, Stockholm

2021: PFAS in the media – Korsør fire training site

PFOS I KORSØR

Trods oprensning - ny rapport fastslår omfattende PFOS-forurening ved Korsør Nor

KORSØR SEKTION 1 Sjællandske • LØRDAG 27. MARTS 2021 11

Toårig mystisk syg efter at have spist PFOS-forgiftet kalvekød

Rapport dokumen
Brandskole. Korsø
jordforureningen r

GIFTUDSLIP: De store mængder PFOS-gift på brandskolen har overrasket region og kommune. Der er allerede fundet PFOS i fisk i Korsør Nor.

Giftbombe kom bag på myndigheder

10 KORSØR SEKTION 1 Sjællandske • LØRDAG 6. FEBRUAR

Gigantiske giftmængder er fundet på brandskolen

UDSLIP: Kilden til forureningen fra

De gigantiske giftmængder oplyser kommunen om i

Akut giftigt

Tidligere har Jane Hansen

Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by aerosols and foams generated in the sea water?
Sextonde mötet i PFAS-nätverket, 22th of November 2022, Stockholm

Korsør Fire Training Site

- Discharge of surface and groundwater to meadows
- Meadows used for grazing cattle
- Cooperative where the meat is shared between a few members/families (less than 200 people)
- High concentration of PFAS (∑4 PFAS) in ditch water (up to 8.000 ng/l), soil (up to 3.000 µg/kg dw) and grass (up to 165 ng/g ww)
- High concentration of PFAS in meat from grazing livestock (up to 230 ng/g ww)
- High Concentration of PFAS in blood serum (up to 500 ng/ml) from people who have eaten meat from the grazing cattle.

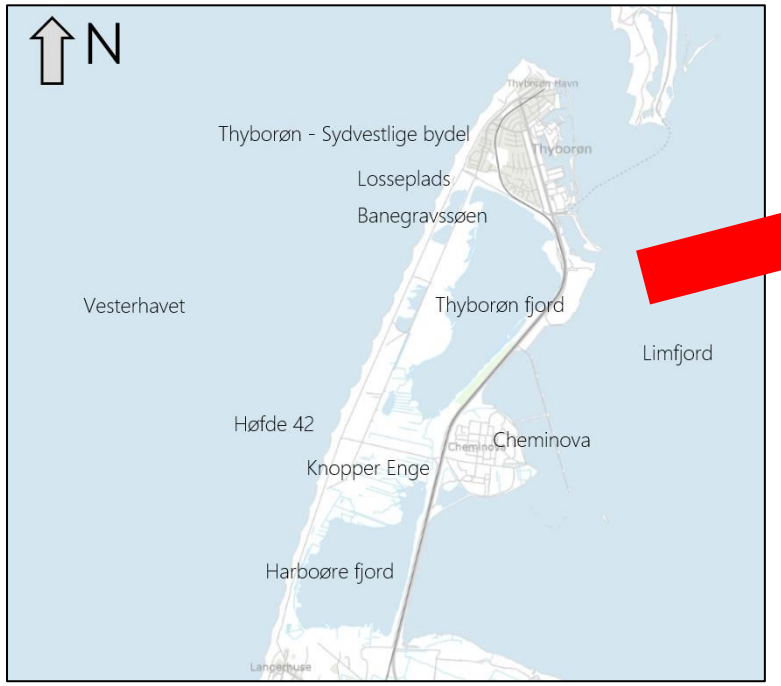
Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by aerosols and foams generated in the sea water?
Sextonde mötet i PFAS-nätverket, 22th of November 2022, Stockholm

West Coast Jutland

Surfactant chemistry leads to alarming consequences for the diffuse contamination of soils, surface water and groundwater

Thyborøn town and Harboøre Tange – Lemvig Municipality- Denmark

PFAS found in ground water, in drainage water under town, soil samples and surface waters



Working conceptual hypothesis

Initial results had a declining trend with distance to sea

Can PFAS contamination spread by aerosols and foams generated in the sea water?

(Sea water contamination can come from sources downstream along the coast)

Working conceptual hypothesis

PFAS are surfactants with air water interphase

Agitation by wind or waves creates bubbles

Aerosols

Air bubble

Foams contain numerous (SML) layers, so a massive PFAS enrichment occurs in foams compared to bulk sea water content

Enrichment of surfactants (PFAS) occurs in the SML at the air-water interface

Foams

Surface Micro Layer SML

1 mm

Air

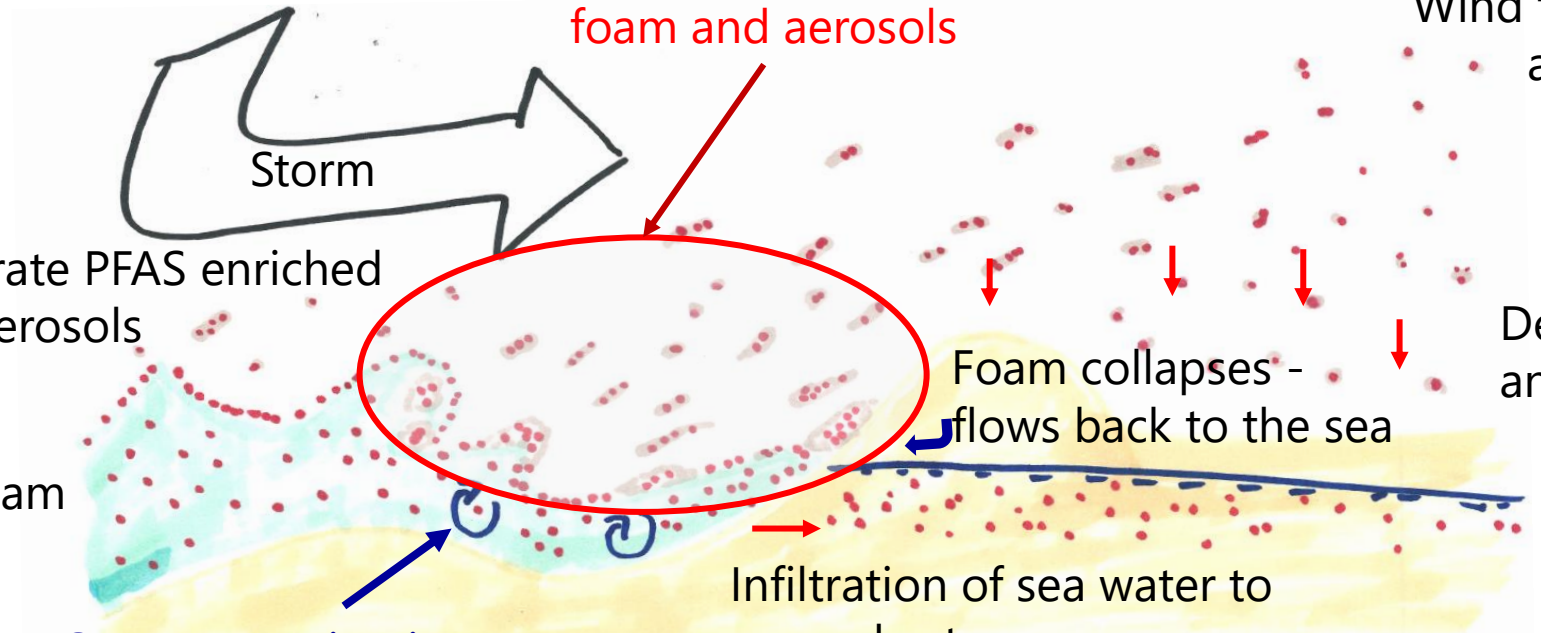
Air

water

Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by Aerosols and foams generated in sea water?
Sextonde motet I PFAS-nätverket, 22th of November 2022, Stockholm

Working hypothesis seems likely

PFAS spread from the sea to land during storms in foams and aerosols



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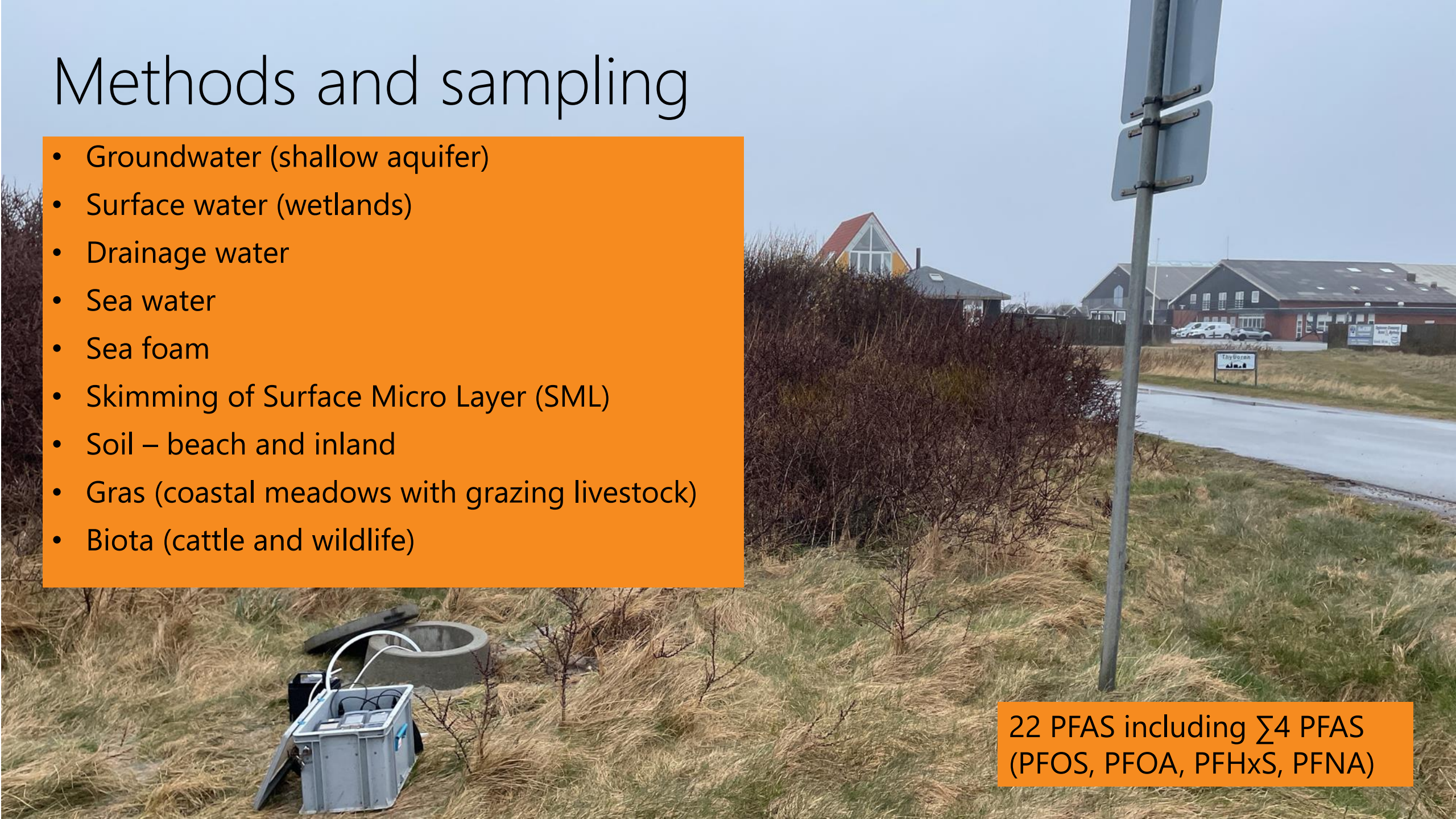
Methods and sampling

- Groundwater (shallow aquifer)
- Surface water (wetlands)
- Drainage water
- Sea water
- Sea foam
- Skimming of Surface Micro Layer (SML)
- Soil – beach and inland
- Gras (coastal meadows with grazing livestock)
- Biota (cattle and wildlife)



22 PFAS including ∑4 PFAS (PFOS, PFOA, PFHxS, PFNA)

Analysis af foam

Storm 4th. April 2022

Analyseperiode:	05.04.2022 - 19.04.2022	
Prøvemærke:	Havskum1	
Lab prøvenr:	835-2022-03850315	Enhed
PFAS-forbindelser		
PFBA (Perfluorbutansyre)	<20	ng/l
PFBS (Perfluorbutansulfonsyre)	<10	ng/l
PFPeA (Perfluorpentansyre)	<10	ng/l
PFPeS (Perfluorpentansulfonsyre)	25	ng/l
PFHxA (Perfluorhexansyre)	36	ng/l
PFHxS (Perfluorhexansulfonsyre)	3300	ng/l
PFHpA (Perfluorheptansyre)	1100	ng/l
PFHpS (Perfluorheptansulfonsyre)	590	ng/l
PFOA (Perfluoroktansyre)	21000	ng/l
PFOS (Perfluoroktansulfonsyre)	85000	ng/l
6:2 FTS (Fluortelomersulfonat)	170	ng/l
PFOSA (Perfluoroktansulfonamid)	200	ng/l
PFNA (Perfluornonansyre)	8900	ng/l
PFNS (Perfluornonansulfonsyre)	<10	ng/l
PFDA (Perfluordekansyre)	3300	ng/l
PFDS (Perflordekanesulfonsyre)	<10	ng/l
PFUnDA (Perfluorundekansyre)	550	ng/l
PFUnDS (Perfluorundekansulfonsyre)	<10	ng/l
PFDoDA (Perfluordodekansyre)	35	ng/l
PFDoDS (Perfluordodekansulfonsyre)	<10	ng/l
PFTrDA (Perfluortridekansyre)	22	ng/l
PFTrDS (Perfluortridekansulfonsyre)	<10	ng/l
Sum af PFAS 4 excl. LOQ	120000	ng/l
Sum af PFAS	120000	ng/l

Analysis of liquid phase of collapsed foam

Preliminary measurement of foam generated under a storm **120,000 ng/l for ∑4 PFAS**
(i.e. mainly PFOS 70% and PFOA 18%)

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More storms and foam Samples

The conditions have to be right for sampling – Storms help

Coastal wetland 10 km north of Thyborøn:

Foam:	1 700 000	ng/l ∑4 PFAS
Wetland water	1 300	ng/l ∑4 PFAS

Beach west coast 50 km south of Thyborøn:

Foam	1 900	ng/l ∑4 PFAS
Sea Water	9	ng/l ∑4 PFAS

Concentration will vary with wind, coastal structure etc.?

Skimming of SML – 10-1000 ng/l ∑4 PFAS - difficult to reproduce with waves.

Not a local contamination limited to Harboøre/Thyborøn area

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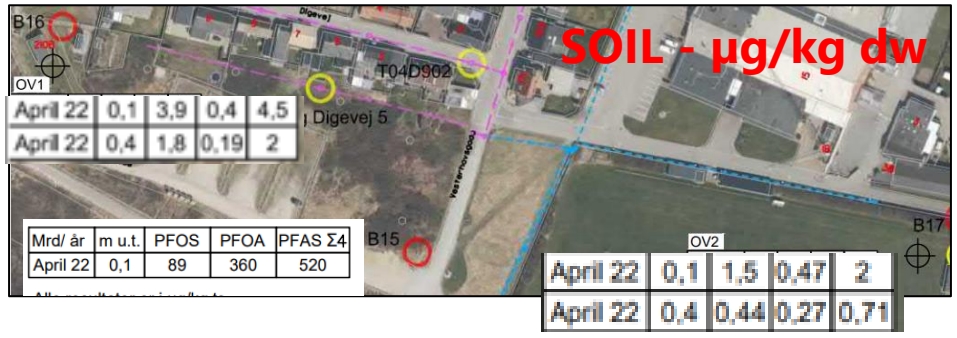
PFAS contamination in west coast coastal town

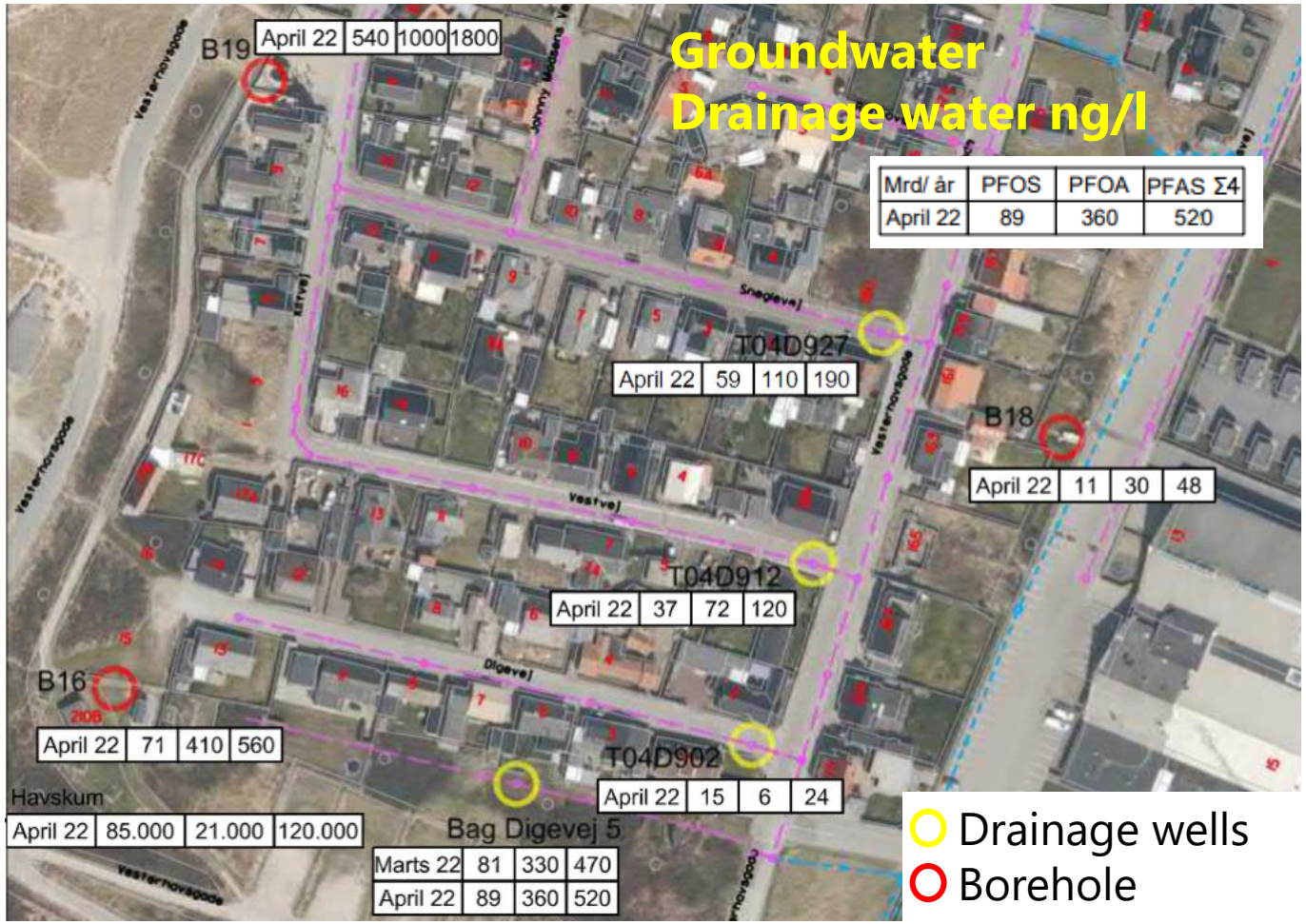
Thyborøn town

Groundwater – max. 1,800 ng/l ∑4 PFAS
Drainage water – max. 520 ng/l ∑4 PFAS

Soil – max. 4.5 µg/kg TS ∑4 PFAS

Overall trend for a decreasing content from west to east (away from the coast)





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Can distance to coast explain content

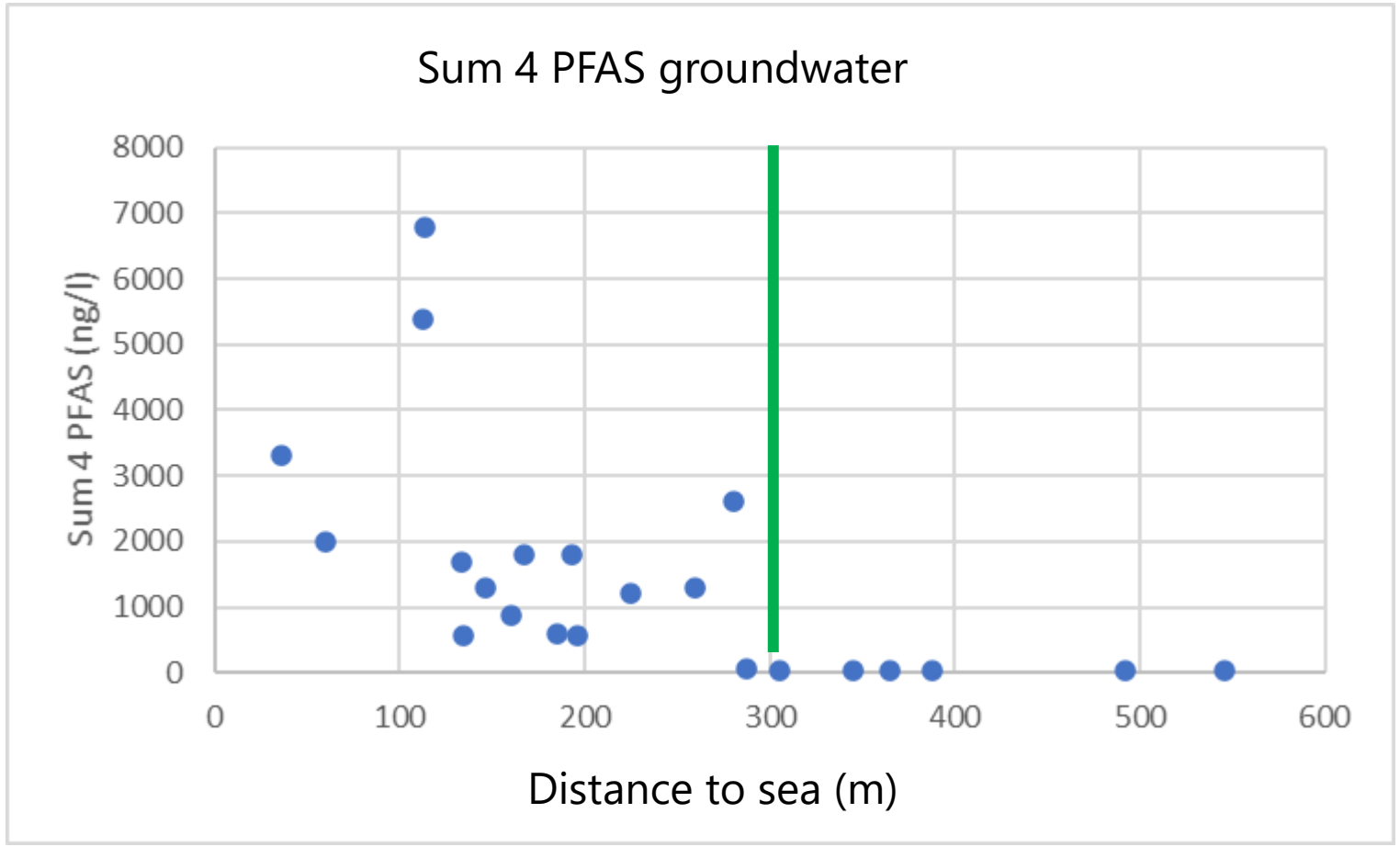
Groundwater:

Content highest within 300 m of coastline

>300 m: lower content

But up to ca. 50 ng/l for ∑4 PFAS

All samples 300-550 m exceed groundwater criterium of 2 ng/l) for ∑4 PFAS



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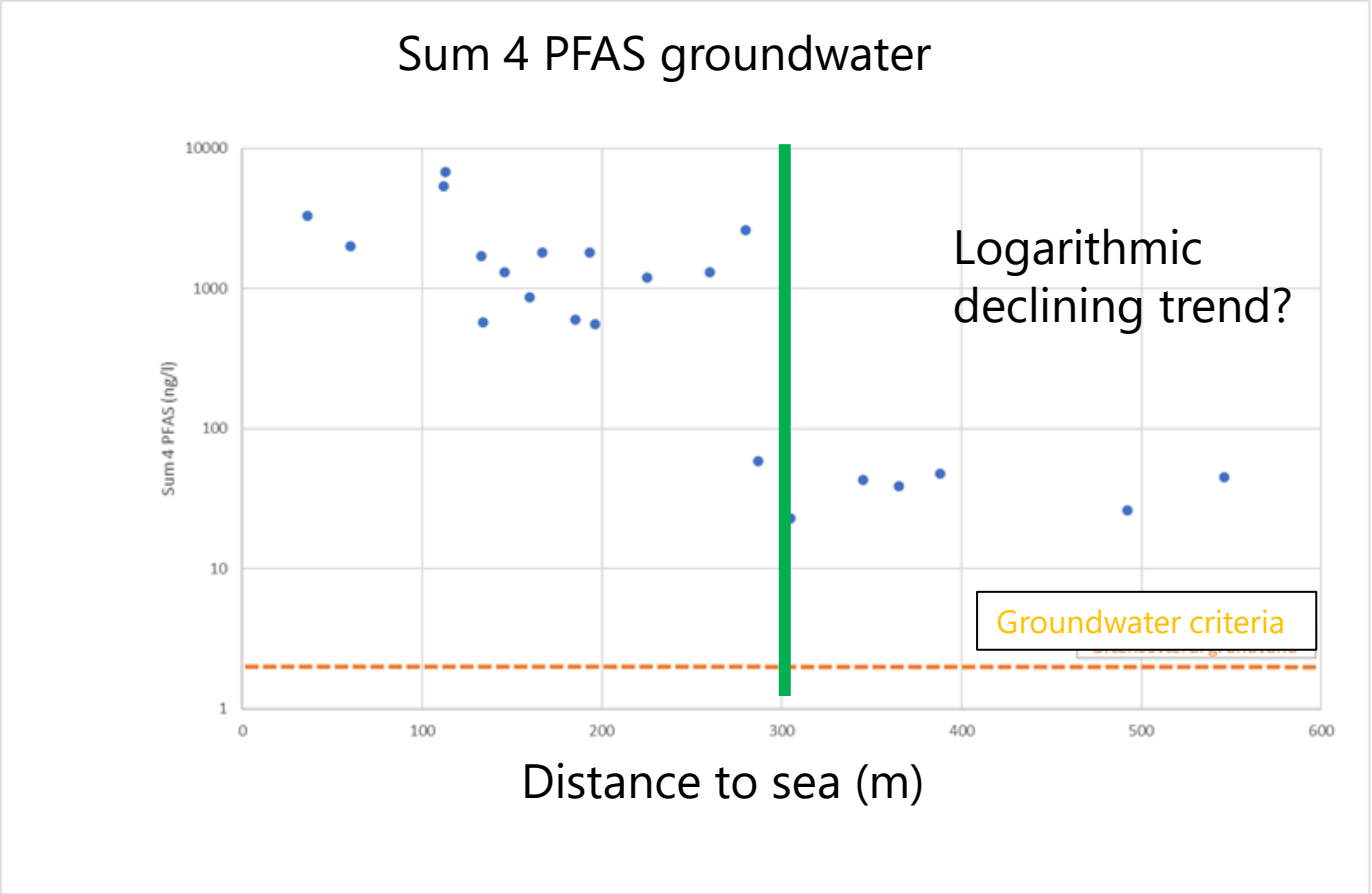
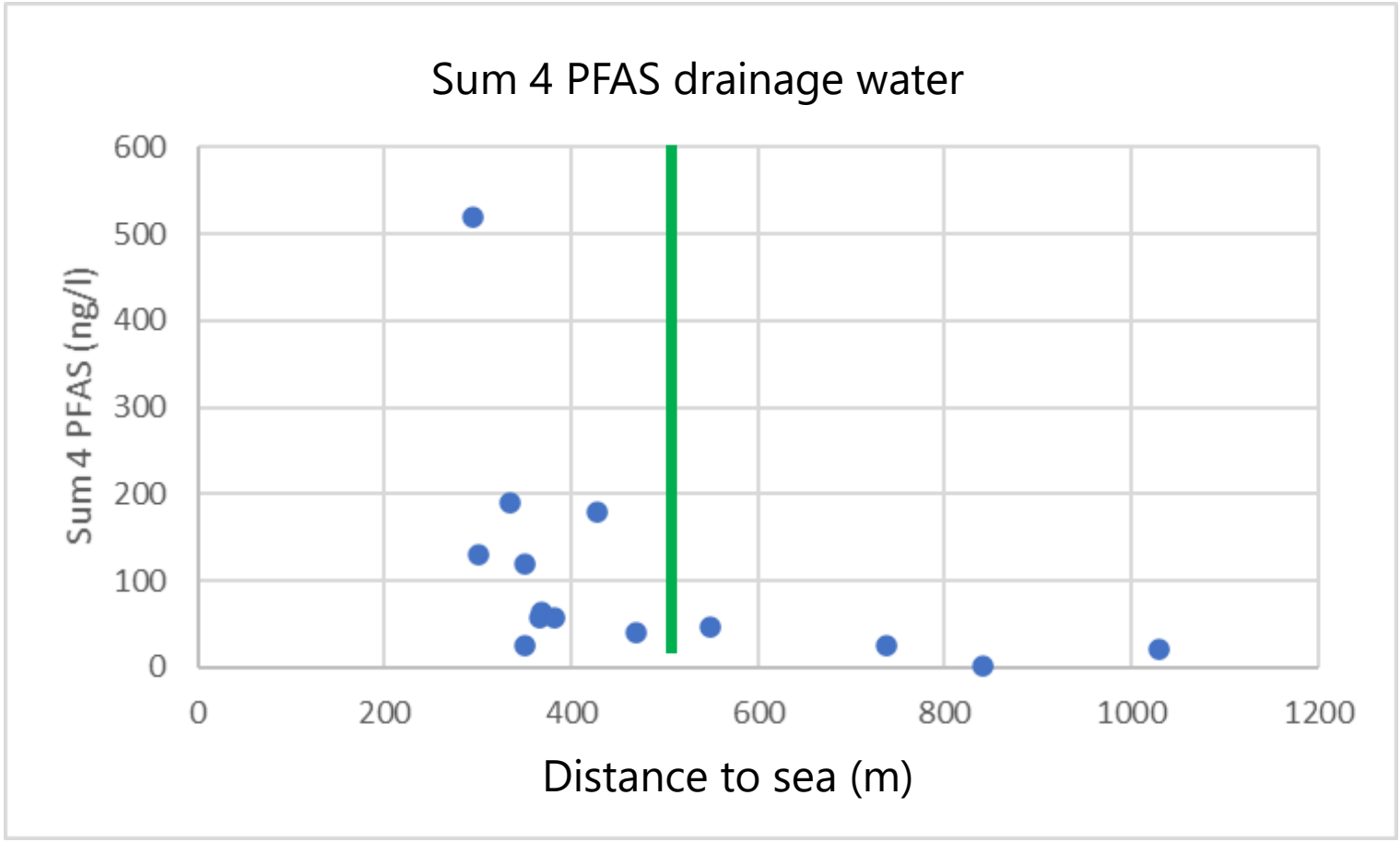


Can distance to sea explain content

Drainage water - Town:

Content up to 520 ng/l for ∑4 PFAS

BUT content decreases for drain wells that are more than 500 m from the coast,



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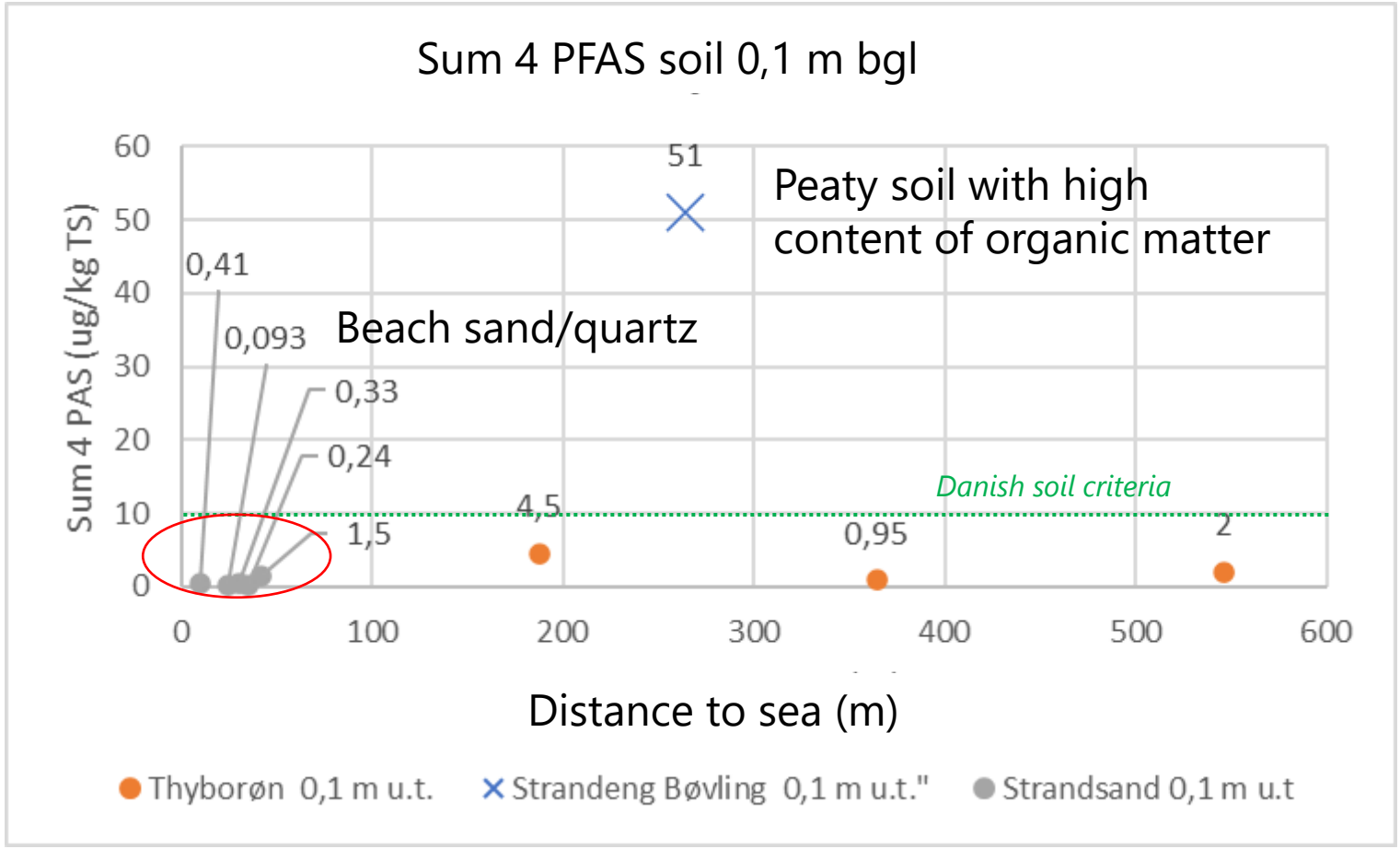
Can distance to sea explain content

Soils : Relatively small data set

Soil type (Humus, Peat, Beach sand /quartz sand), organic and mineral content, water content and particle size distribution etc. can affect the binding capacity of PFAS to soils

Highest concentration found at reference area 35 km to the south

Most soil samples do not exceed the soil criterium for 10 µg/kg dw for ∑4 PFAS



Low content in beach sand

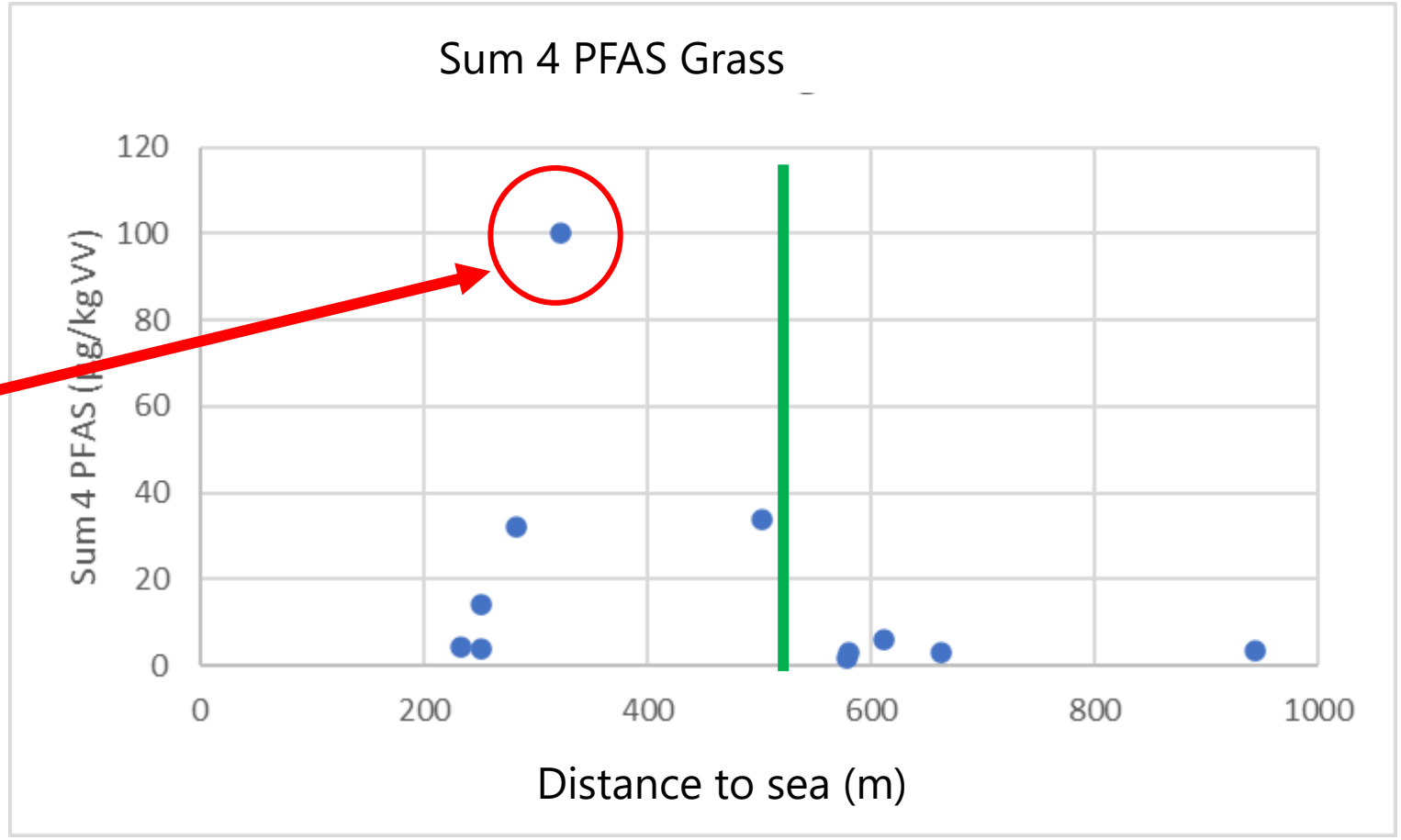
Can distance to sea explain content

Vegetation (grass):

Samples from coastal meadows with livestock (cattle)

Highest PFAS content in vegetation (grass) is found within 500 m of the coast.

Deposition of aerosols/foam in connection with the storm on the 5th. April can explain the highest content?



PFAS can bioaccumulate in livestock

Grazing cattle and game at Harboøre tange

Sample no	PFOS in plasma µg/kg ww	Animal	Comment
1	20	Cow	Grazed summer 2021 on contaminated area
1a	15	Calf of no. 1	Grazed summer 2021 on contaminated area
2	20	Cow	Grazed summer 2021 on contaminated area
2a	11	Calf of no. 2	Grazed summer 2021 on contaminated area
3	11	Cow	Grazed summer 2021 on contaminated area
3a	8	Calf of no 3	Grazed summer 2021 on contaminated area
4	2.1	Calf	Grazed on other areas
5	1.8	Calf	Grazed on other areas

Livestock (cattle) grazing on coastal meadows

Level of concern: 3.3 µg/kg ww

Data from Danish Veterinary and Food Administration (Fødevarestyrelsen)

Ministry of Food, Agriculture and Fisheries of Denmark
Danish Veterinary and Food Administration

Analysis of wild ducks show high Concentration of PFAS so hunting are now banned on Harboøre Tange

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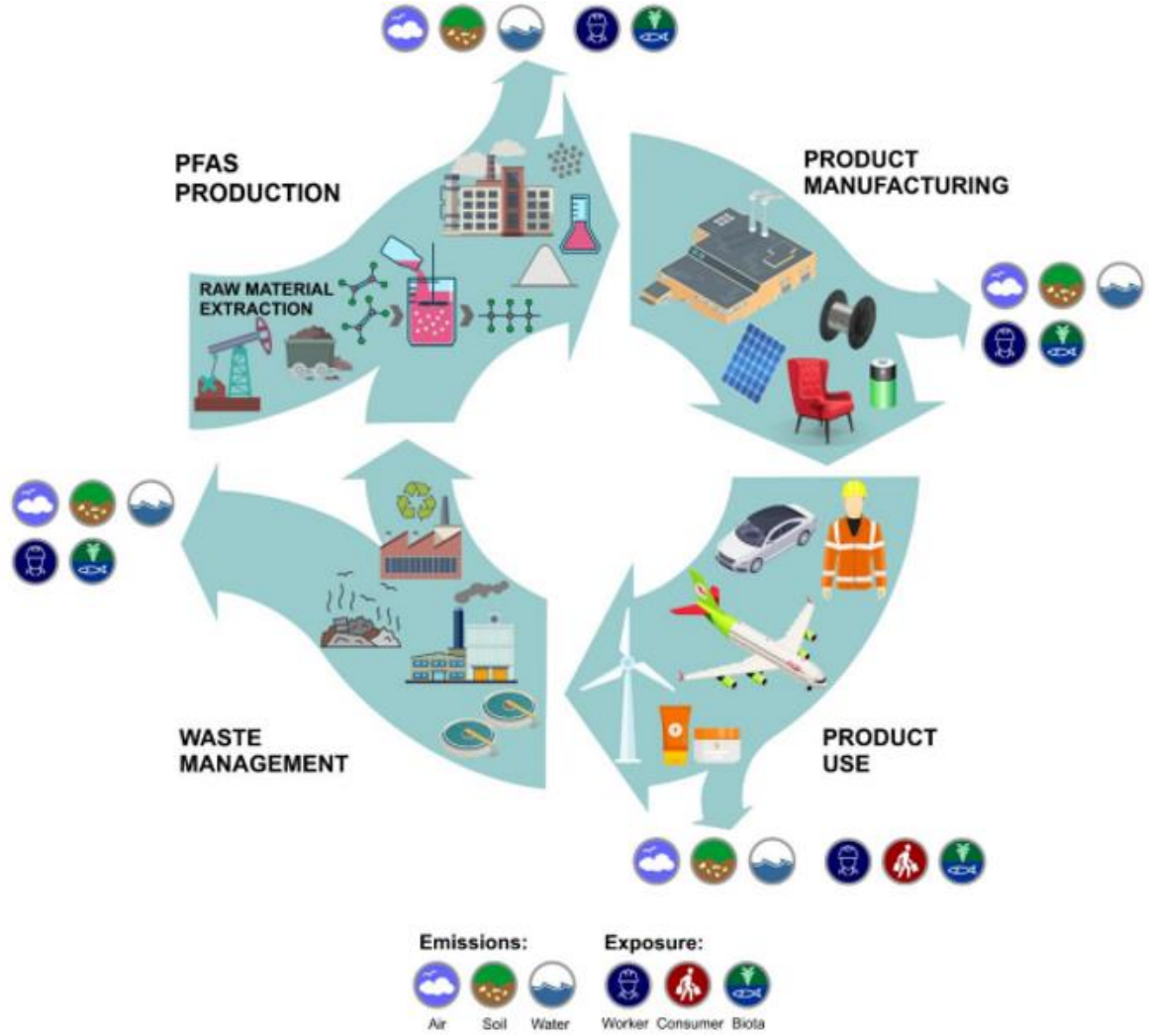
NIRAS

Origen of PFAS in sea water?



Commosion Staff Working Document – Poly- and perfluoroalkyl Substances (PPFAS). SWD(2020) 249 final, European Commission, 2020

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Possible Sources in Sea Water

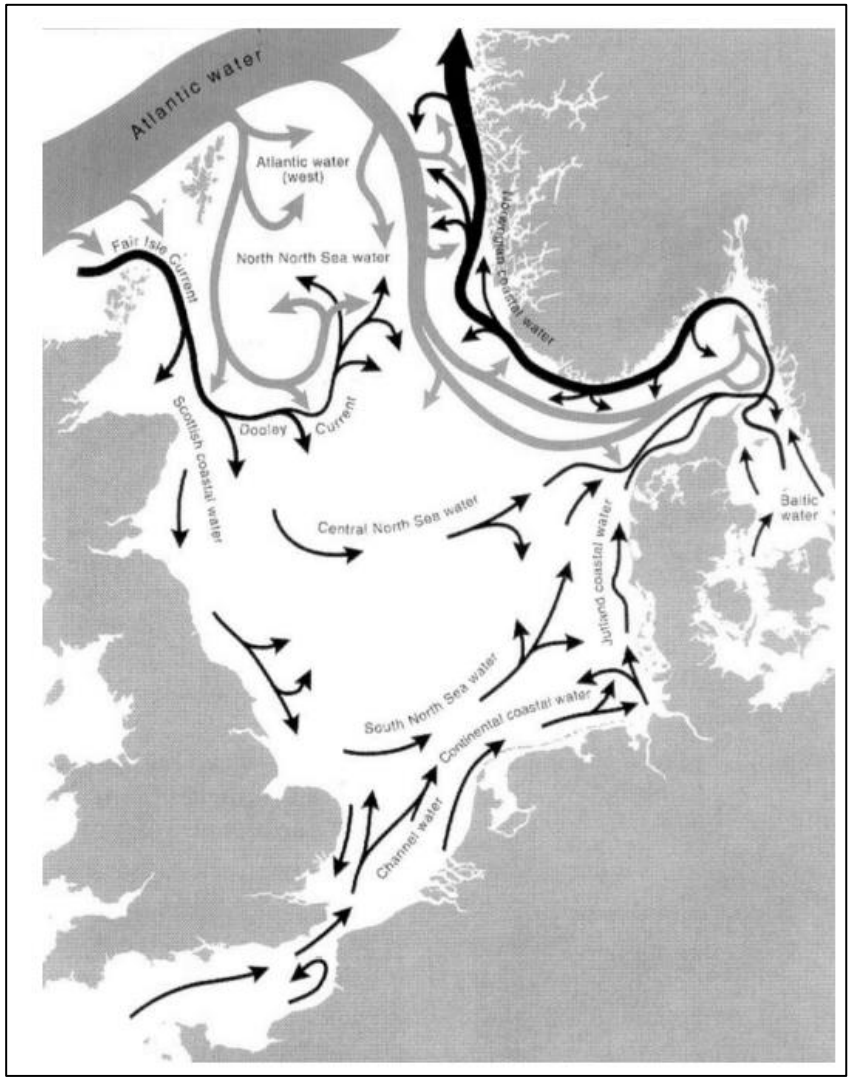
PFAS sources in sea water at Thyborøn ?

Local sources

- Contaminated sites –> industrial/waste dumps, firefighting training sites etc.
- Effluent from industry and wastewater treatment plants, storm water/road and roof drainage water

Regional sources via North Sea

- Wastewater treatment plants
- Emissions from incineration of waste
- PFAS sites and landfills with discharge to sea
- Offshore Oil Industry (platforms etc.)
- PFAS-production in Holland or Belgium
- Rainwater deposition? or rainwater impacted from seawater?



Hvas et al, 1998

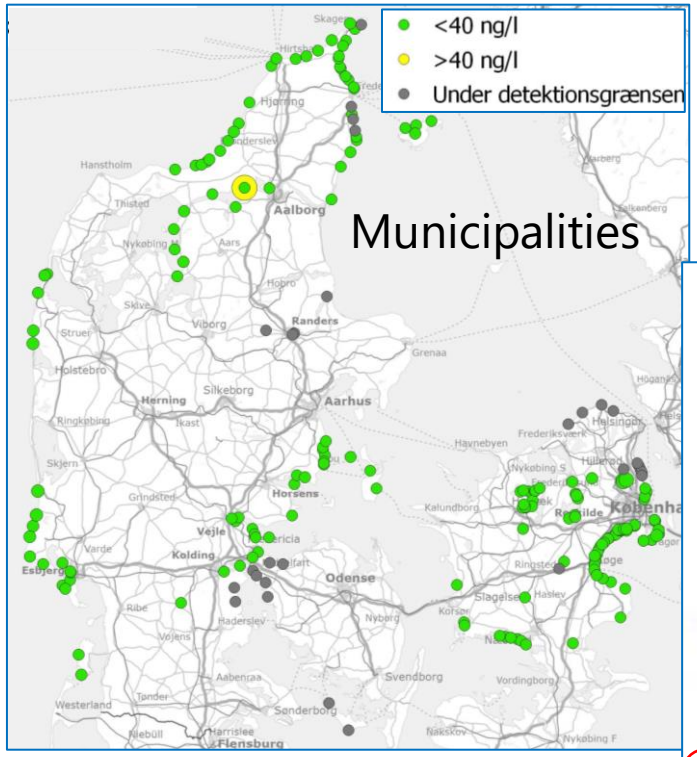
Other project and result

Are there PFAS in bathing waters?

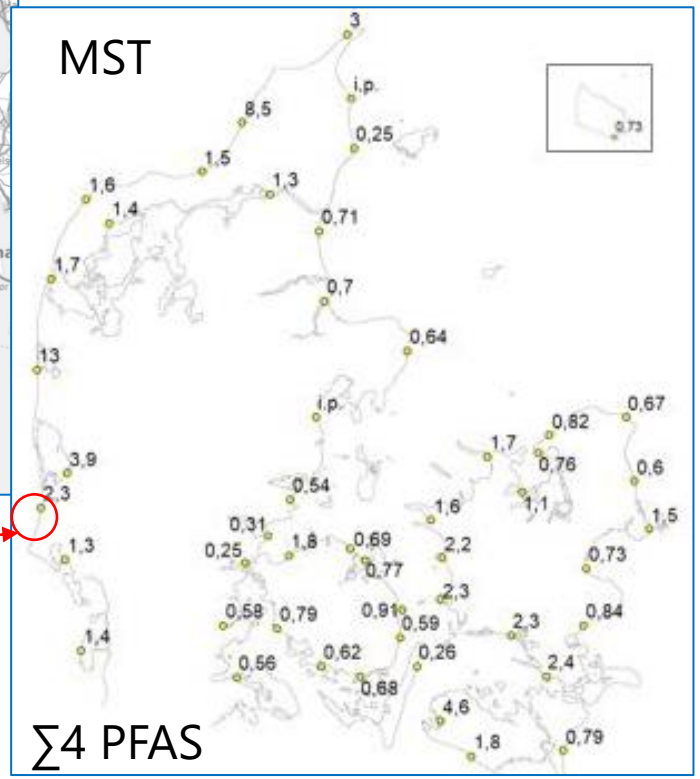
Concern about public health (July 2022)

The Danish EPA (MST) have instigated:

- 50 samples of bathing water (in 30 cm's depth) and SML from 50 sites around the coast
- Instructed relevant municipalities to sample bathing waters – 216 samples
- Defined a *provisional advisory guideline* of 40 ng/l for ∑PFOA, PFNA, PFHxS, PFOS (WHO)
- No samples exceed advisory guideline (except one sample, but not confirmed by control)
- 2 samples of SML in a coastal lagoon had elevated content of 1000 and 270 ng/l for ∑4PFAS
- Highest content is generally seen along the west coast (North Sea)



All Samples exced EU based cirtiera for marine surface water (0,13 ng/l)



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Drinking water

Concern about public drinking water

Denmark – 100 % supply by ground water

All tap water have drinking water quality

Concern for drinking water supply near the West Coast

Public waterworks have mostly their wells further inland

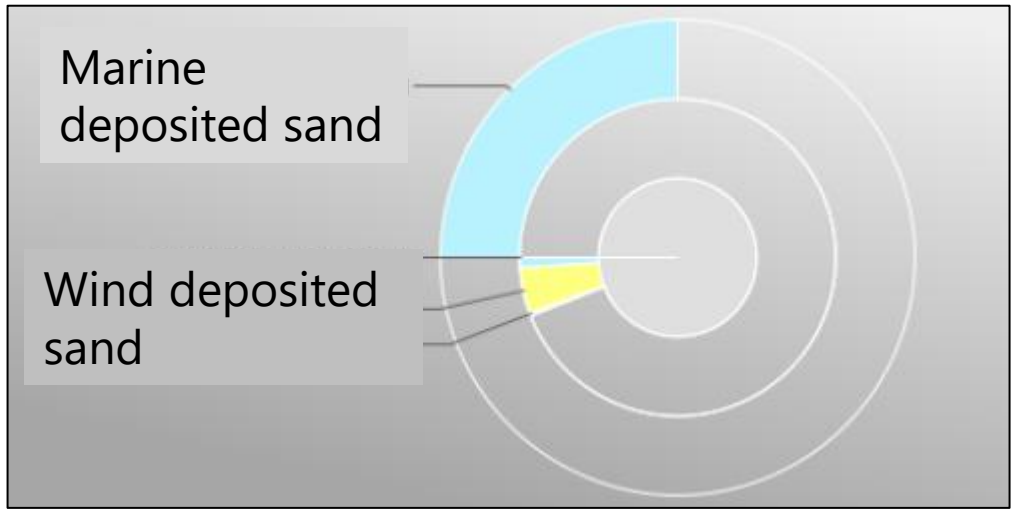
PFAS at Fanø Island, Hanstholm and Skagen

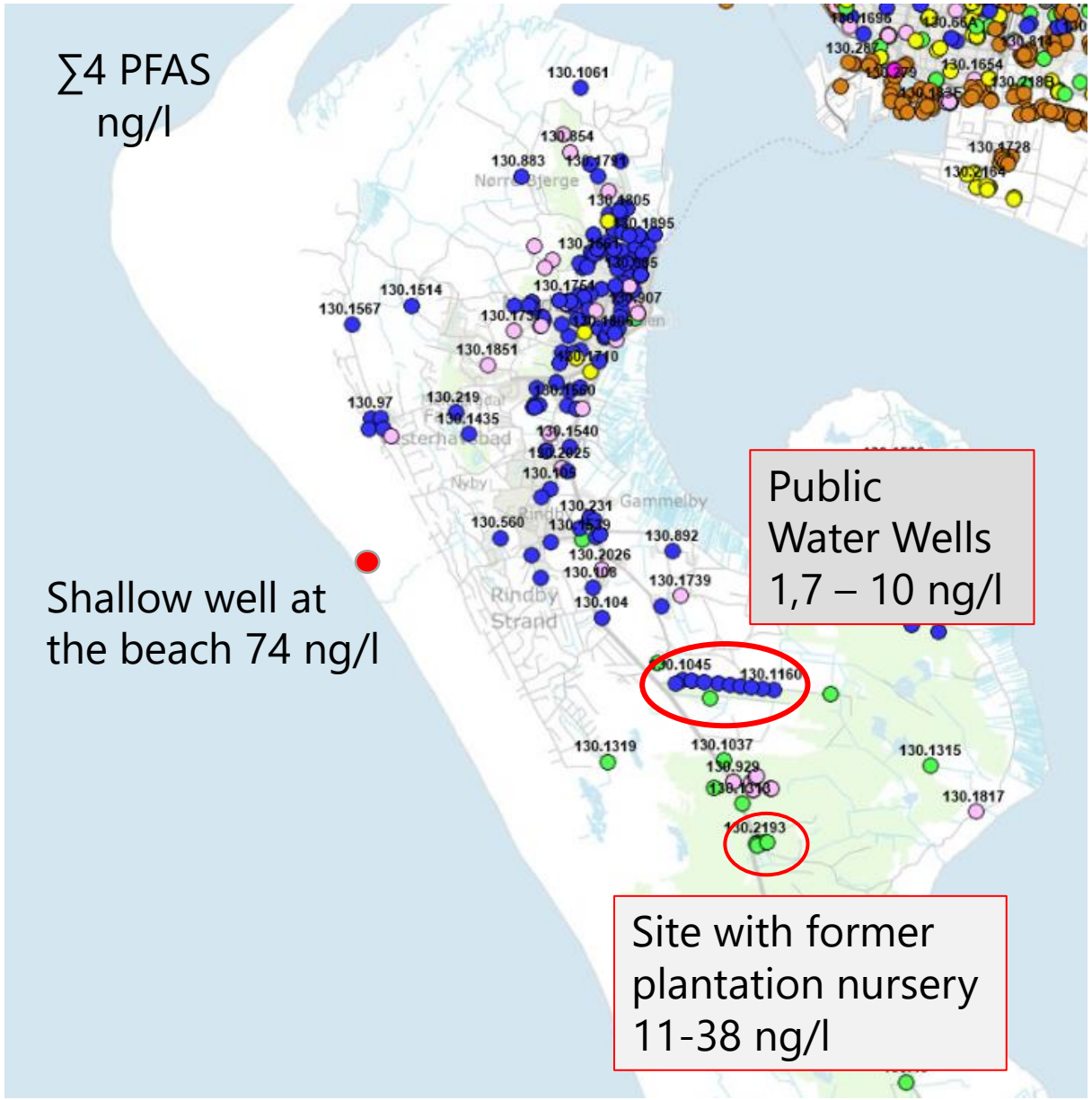
Aware of 3 public water works with PFAS contaminated wells placed close to the west coast of Jutland (2-5 km from sea) – suspicion of PFAS contamination from sea

- Fanø Island in the Wadden Sea
- Hanstholm
- Skagen

Fanø Island

- Public water wells contaminated: 1,7-10 ng/l (∑4 PFAS)
- Water wells are screened 22-33 m bgl
- Public water wells are surrounded by nature
- Site investigation at former plantation nursery: 11-38 ng/l (∑4 PFAS) in shallow ground water
- Geology – Sand





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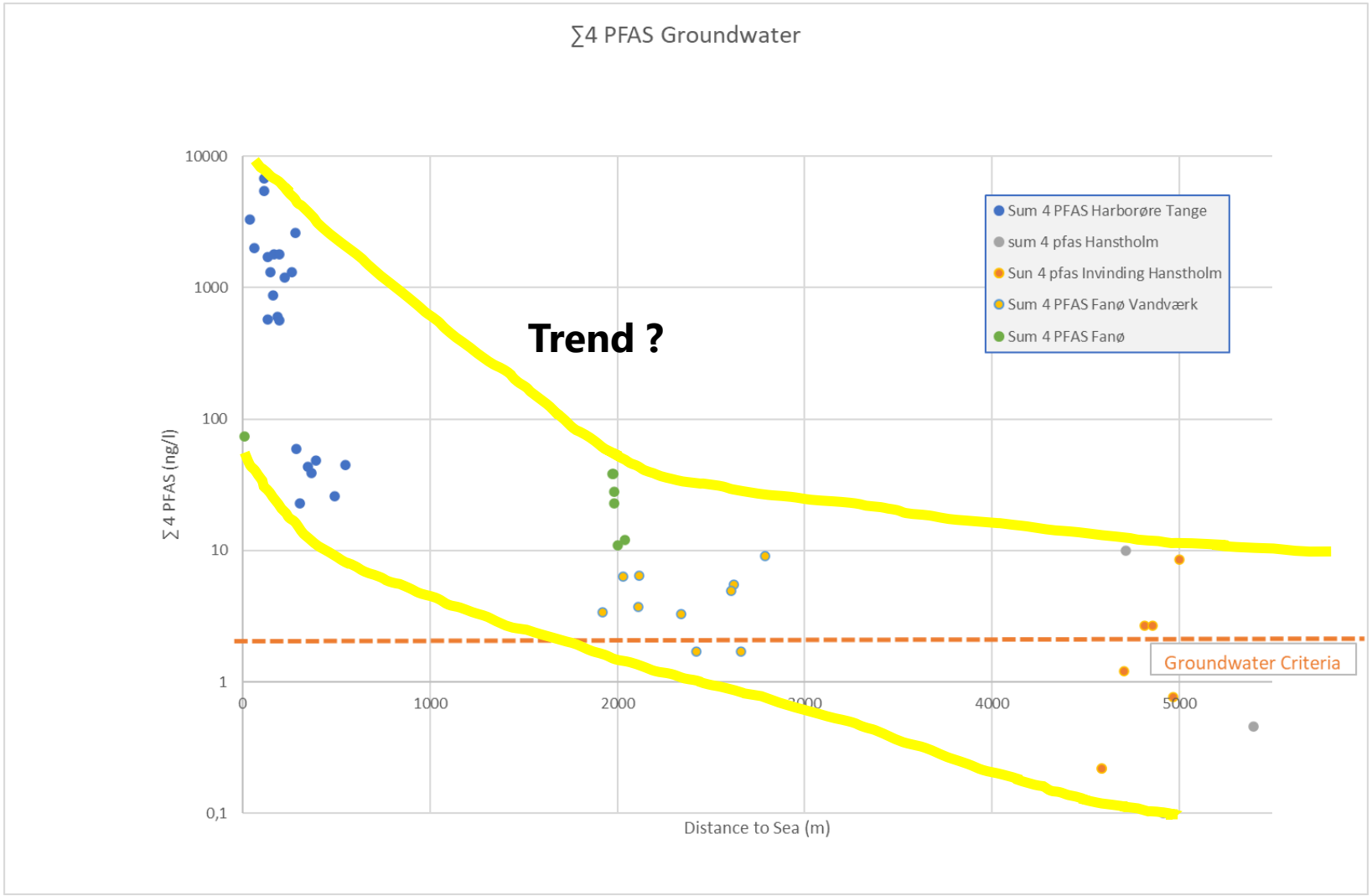
Data from several sites ∑4 PFAS



Data from Harboøre, Hanstholm and Fanø

- Impact up to 5 km from sea ?
- Different sites
- Monitoring and water wells
- Shallow/deeper aquifer
- Unsaturated/Vadose zone

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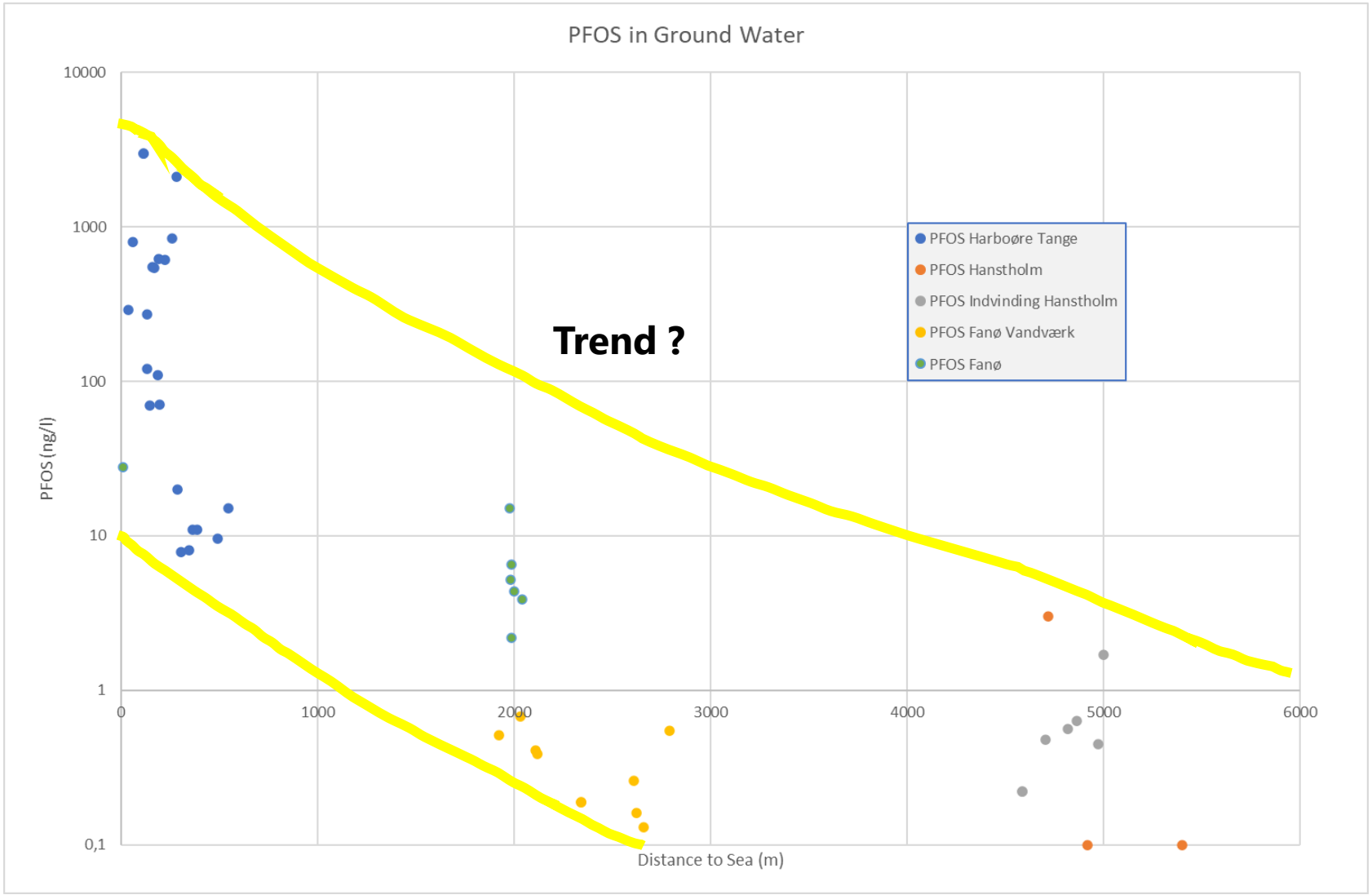
Data from several sites PFOS



Data from Harboøre, Hanstholm and Fanø

- PFOS is the main PFAS in sea foam (50-75 %)
- High concentration near sea
- Rapid decline with distance to sea
- Transport by foam and aerosols?

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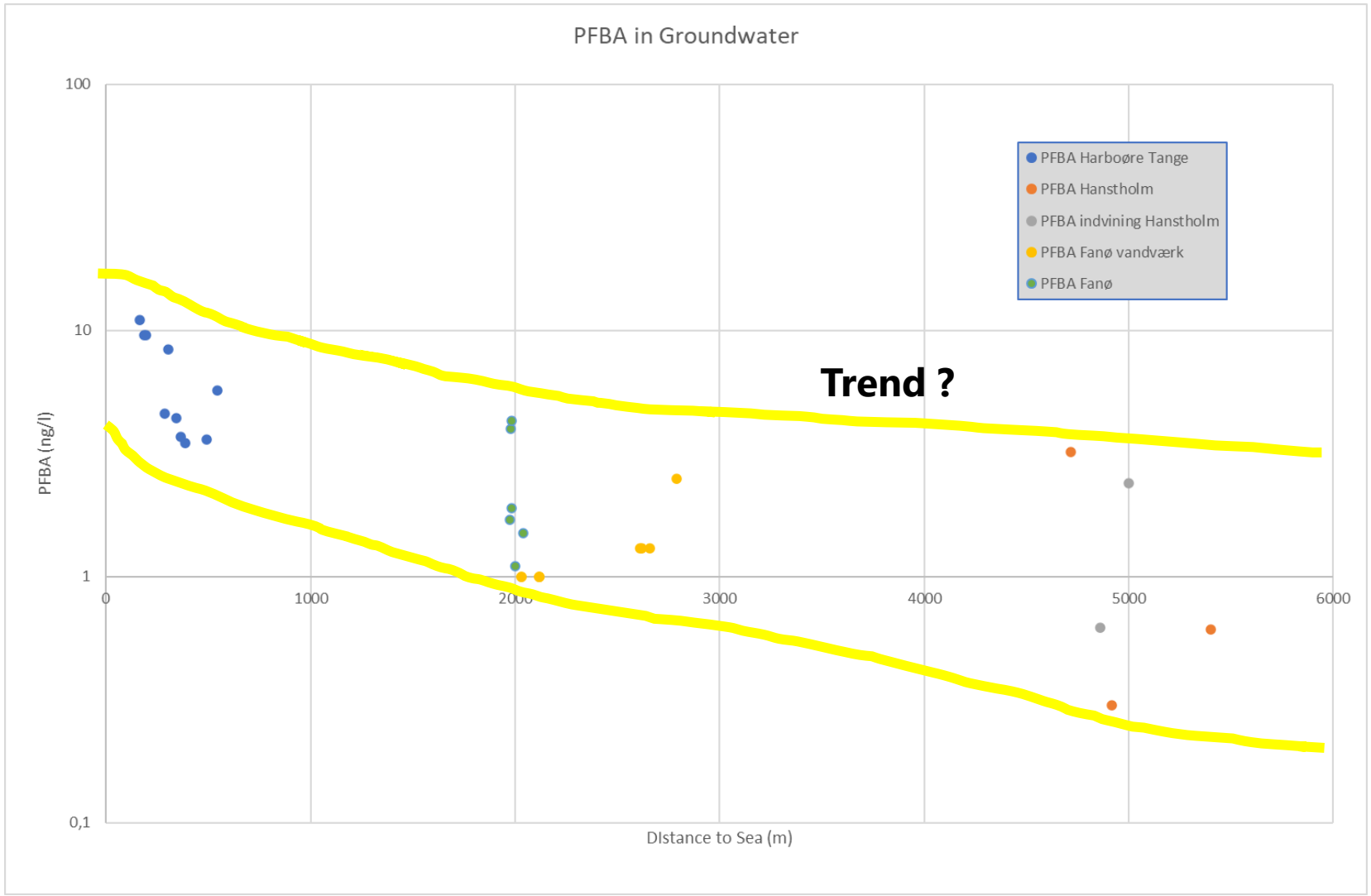
Data from several sites PFBA



Data from Harboøre, Hanstholm and Fanø

- PFBA not detected in sea foam
- Lower levels at sea
- Less decline with distance to sea
- Different transport – aerosols?

Future Projects

- Samling at 60 sites 0-10 km from sea at the west coast of Jutland and Seeland for the Nature Agency. Sampling include grass and surface water. All sites are meadows leased out for grazing livestock. Data will be "mined" for overall trends.
- Site investigation at Fanø Island to document PFAS contamination from sea – will include sampling af sea foam, shallow ground water and soil. Founded by Region of Southern Denmark
- More site investigations at the west coast of Jutland - will include sampling af sea foam, shallow ground water, surface water and soil. Founded by Central Region of Denmark, Lemvig Municipality, and Danish EPA. Second phase may include sampling of aerosols and deposition of PFAS in cooperation with Stockholm University
- NIRAS are working as a consultant for the water works in Hanstholm and Skagen

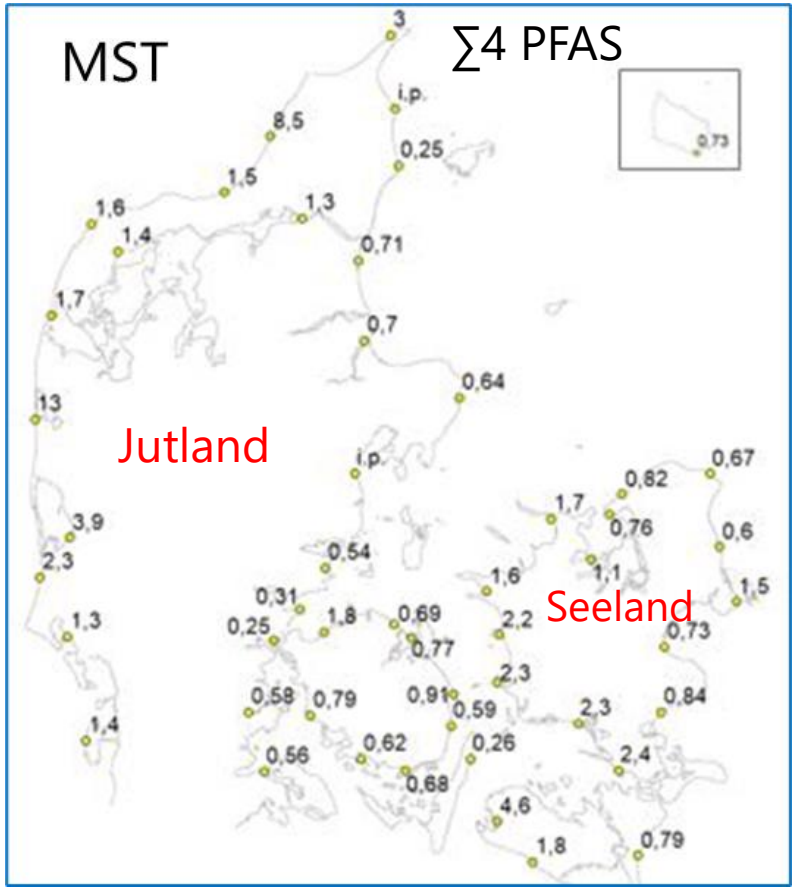
Ministry of Environment of Denmark
Nature Agency

Region Syddanmark

midt
Central Denmark Region

Ministry of Environment of Denmark
Environmental Protection Agency

Lemvig Kommune



Søren Rygaard Lenschow srl@niras.dk, NIRAS : Can PFAS contamination spread to soil and groundwater by aerosols and foams generated in the sea water?
Sextonde mötet i PFAS-nätverket, 22th of November 2022, Stockholm

NIRAS

Thank you for Attention

Acknowledgements
Morten Corneliusen - Lemvig municipality, Denmark
Halfdan R. Sckerl - Central Denmark Region, Denmark
Anne Bomann Henriksen, NIRAS
Anders G. Christensen - NIRAS, Denmark