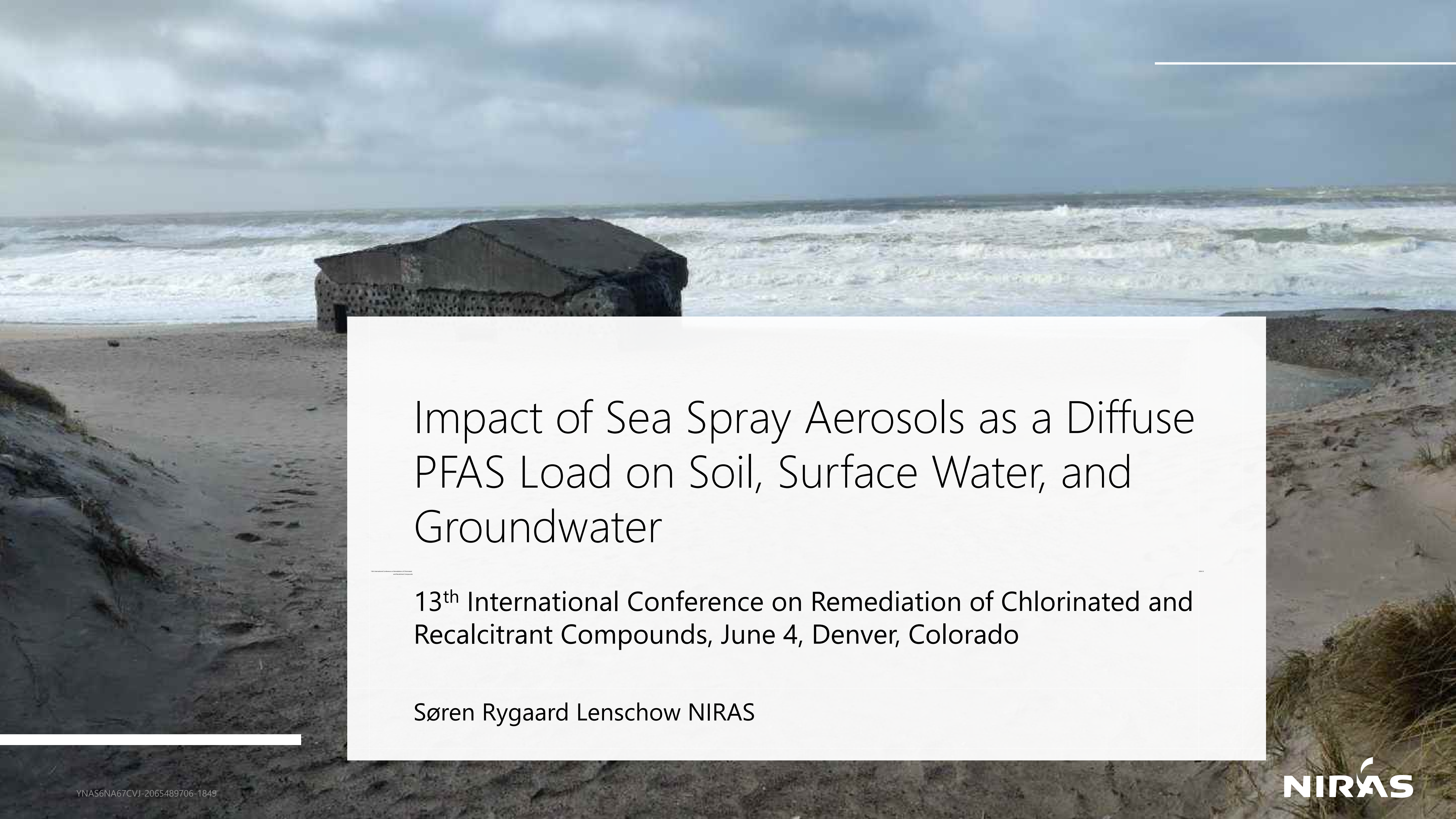


Impact of Sea Spray Aerosols as a Diffuse PFAS Load on Soil, Surface Water, and Groundwater

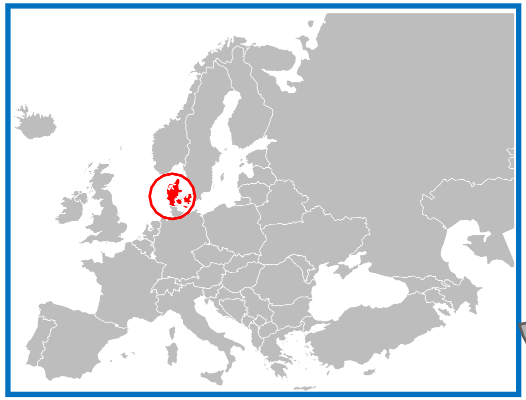
13th International Conference on Remediation of Chlorinated and Recalcitrant Compounds, June 4, Denver, Colorado

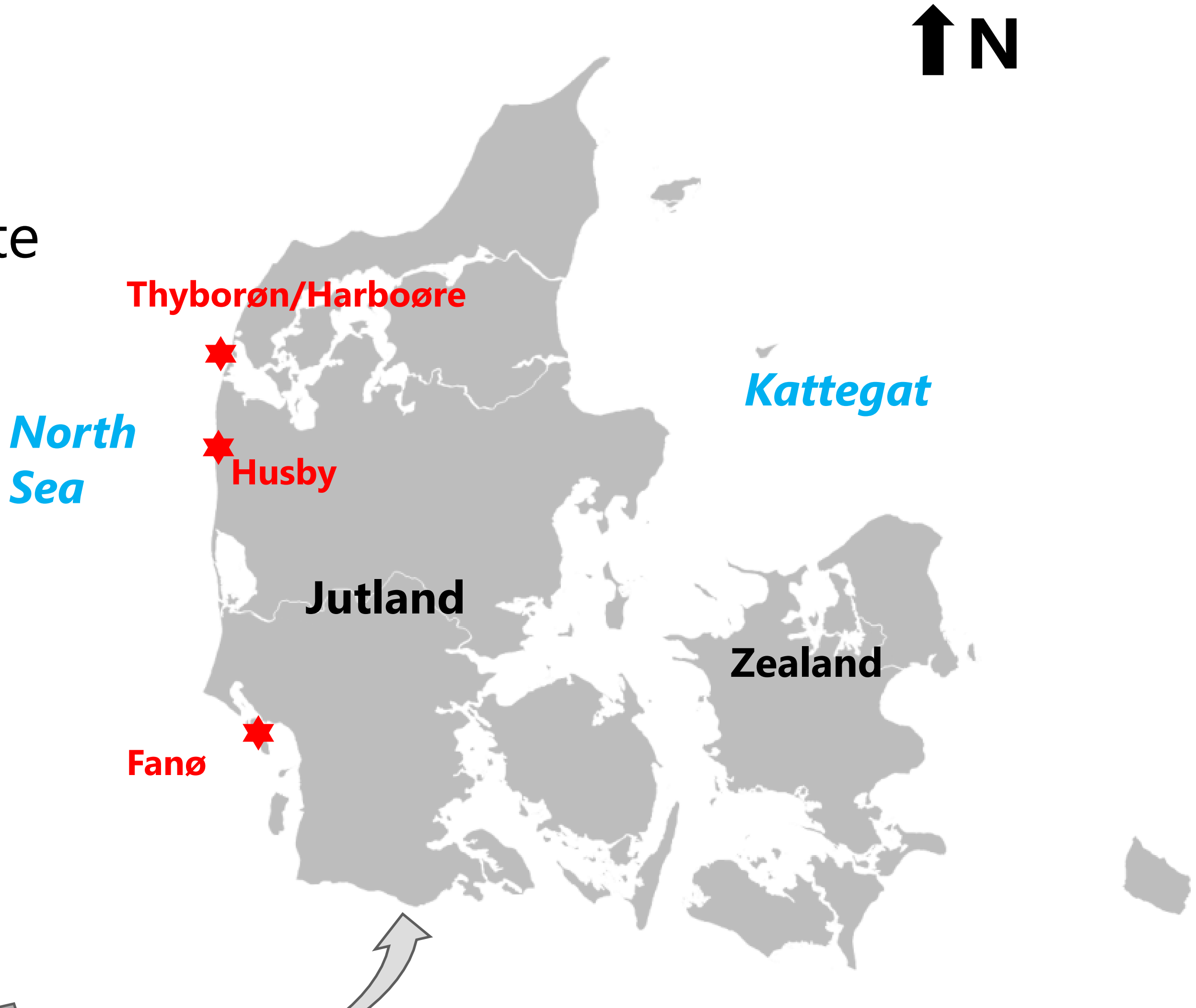
Søren Rygaard Lenschow NIRAS

NIRAS

Agenda

- PFAS criteria in Danmark
- Background - Thyborøn/Harboøre site
- Project at Fanø and Husby
- Perspectives and conclusions





Overview of criteria in Denmark

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

Soil ground-/ drinking water	Implemented 2021 **∑22 PFAS** Groundwater/drinking water: 100 ng/l Soil: 400 µg/kg dw	**∑PFOA, PFNA, PFHxS, PFOS** **2 ng/l** **10 µg/kg dw**
Surface water	EU quality criterium for **PFOS** in surface waters - Implemented 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**	
Surface water **Not used in these projects**	PFOA-equivalent (**PEQ**) Implemented November 2023 Fresh and marine water 4.4 ng/l **PEQ**	**PEQ** is the sum of 24 PFFAS and refer to a method of comparing the environmental and health impacts of different PFAS to those of perfluorooctanoic acid (PFOA). This is done by assigning a relative potency factor (RPF) to each PFAS.

Which PFAS?

Low criteria for ∑4 PFAS groundwater/ drinking water (2 ng/l)

Low criteria for PFOS for surface water (0.13/0.65 ng/l)

New criteria for surface water based on PEQ (4.4 ng/l)

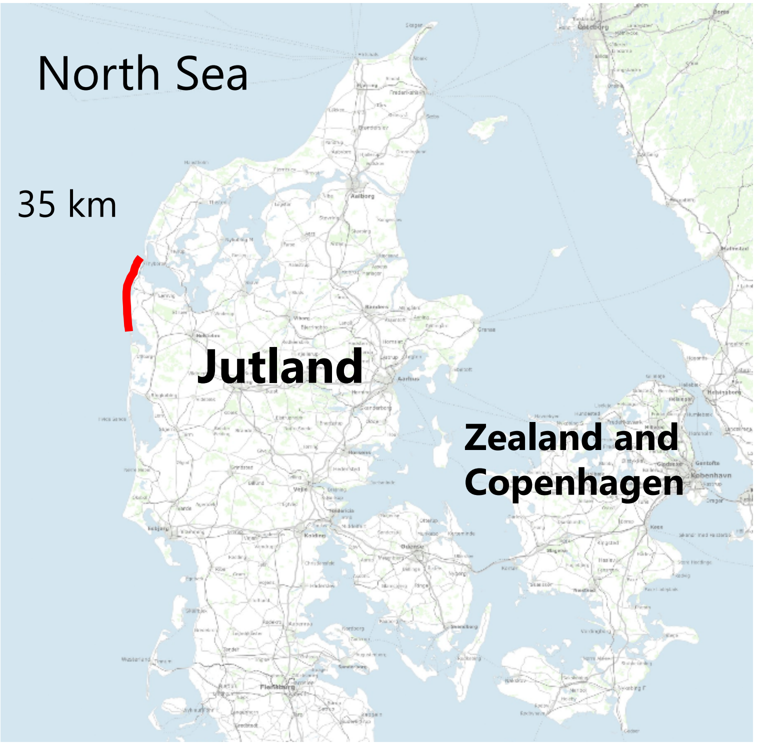
Relative potential factors (RPF) vary by several orders of magnitude

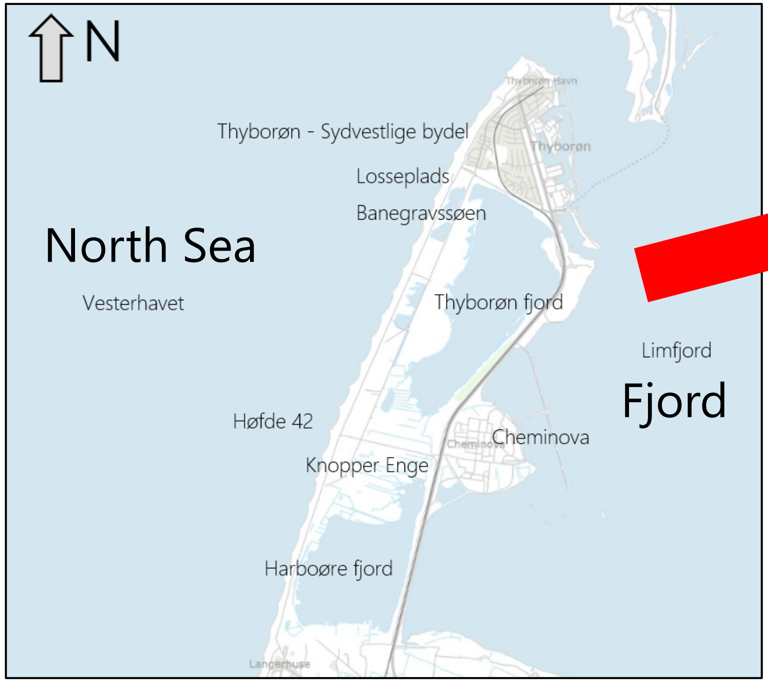
Soil and goundwater ∑4 and ∑22 PFAS		**Surface water** **PFOS** and PEQ – ∑24 (RPF)	
PFBA	PFBS	PFBA (0.05)	PFBS (0.001)
PFPeA	PFPeS	PFPeA (0.03)	PFPeS (0.3)
PFHxA	PFHxS*	PFHxA (0.01)	PFHxS (0.6)
PFHpA	PFHpS	PFHpA (0.5)	PFHpS (1.3)
PFOA*	PFOS*	PFOA (1)	**PFOS** (2)
PFNA*	PFNS	PFNA (10)	PFDS (2)
PFDA	PFDS	PFDA (7)	PFTeDA (0.3)
PFUnDA	PFUnDS	PFUnDA (4)	PFHxDA (0.02)
PFDoDA	PFDoDS	PFDoDA (3)	PFODA (0.02)
PFTrDA	PFTrDS	PFTrDA (1.65)	Gen X (0.06)
PFOSA	6:2 FTS	6:2 FTOH (0.02)	ADONA (0.03)
**∑4 PFAS with low criteria*		8:2 FTOH (0.04)	C604 (0.06)

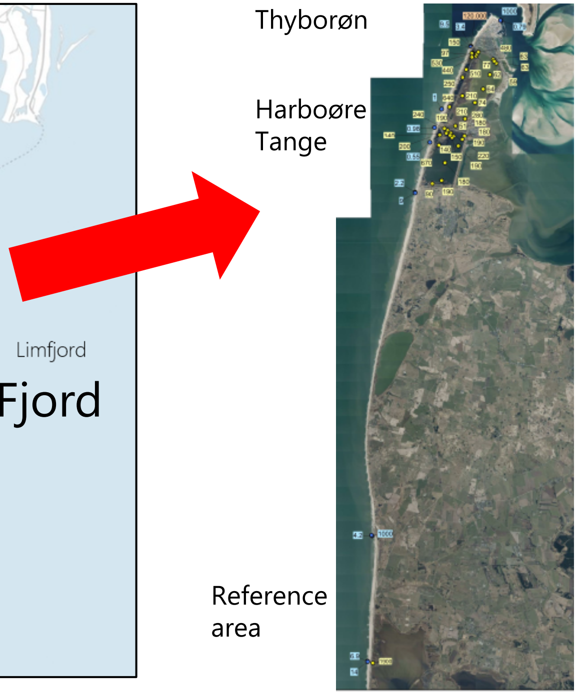
Start 2022 –West Coast Jutland

Thyborøn town and Harboøre Tange – Lemvig Municipality - Denmark

- PFAS found in groundwater, drainage water and surface waters
- Relations to point sources? (Cheminova – Høfde 42)







PFAS contamination in west coast coastal town

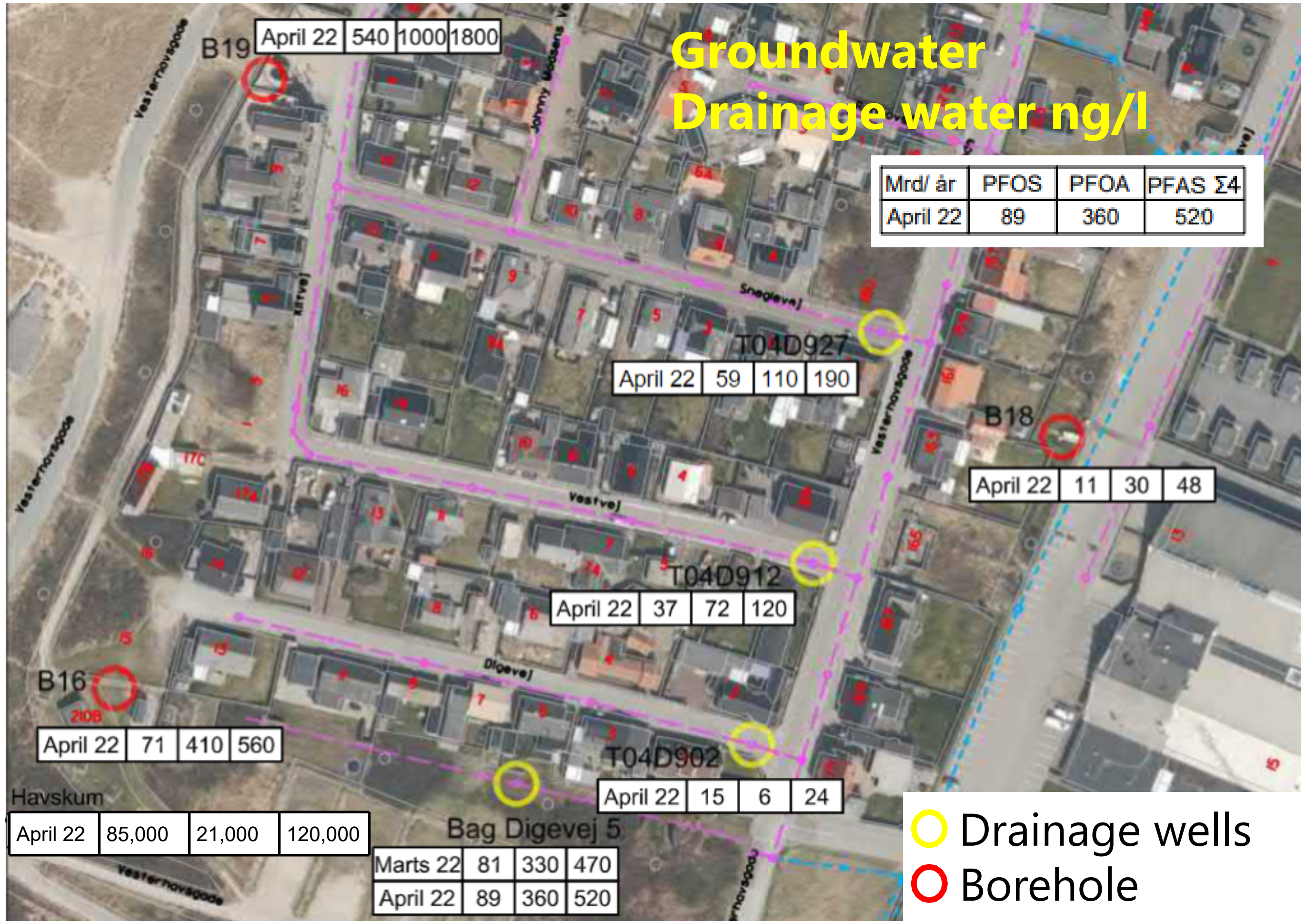
Thyborøn town

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

Soil – max. 4.5 µg/kg dw ∑4 PFAS

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

Sea foam



Søren Rygaard Lenschow srl@niras.dk, NIRAS: Impact of Sea Spray Aerosols as a Diffuse PFAS Load on Soil, Surface Water, and Groundwater

NIRAS

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%)

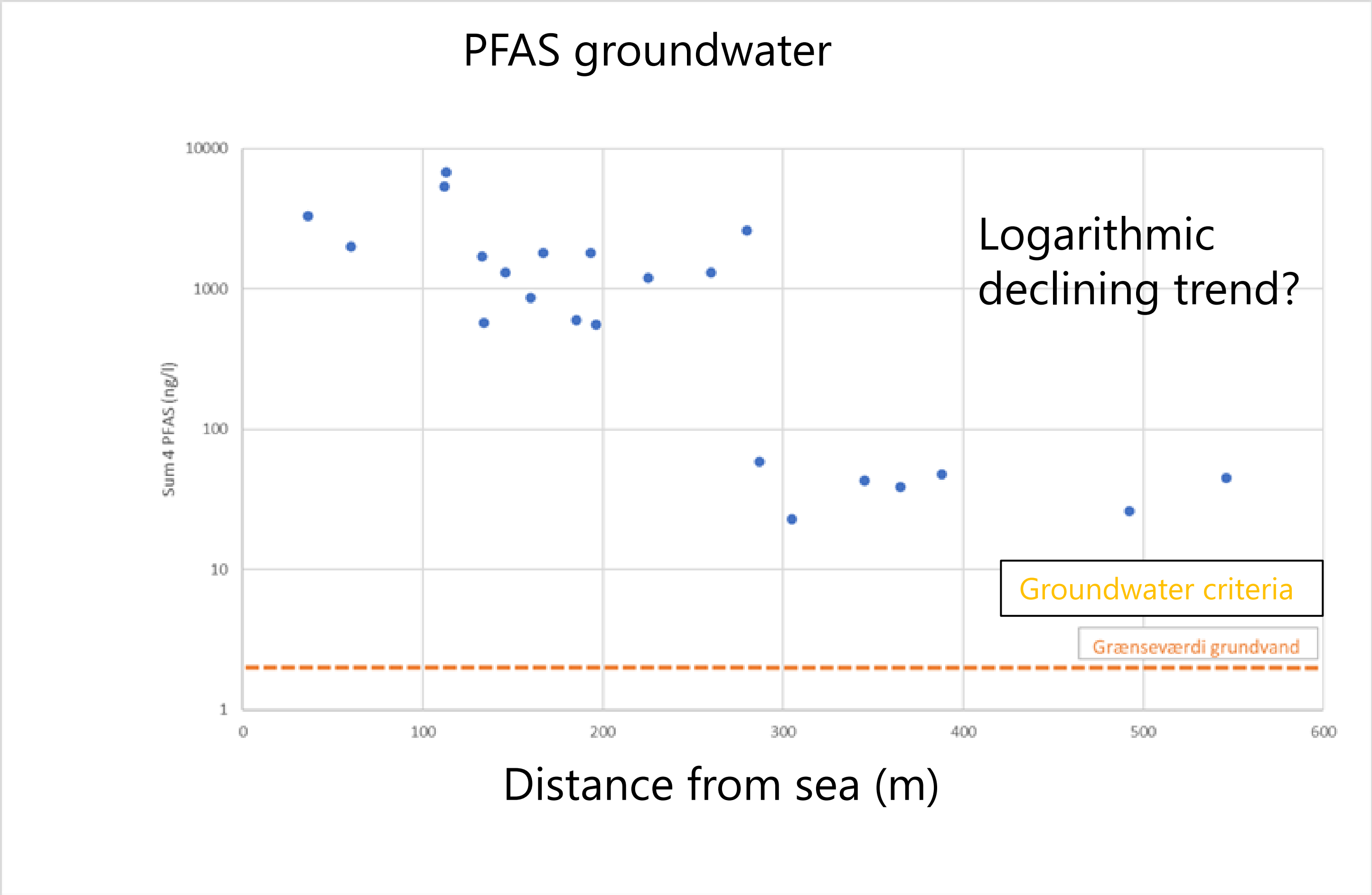
Can distance to sea explain content

Groundwater:

Content highest within 300 m of the sea (coastline)

Declining trend with distance from sea: 8,000 -> 50 ng/l for ∑4 PFAS

Similar results for surface water and drainage water.



Søren Rygaard Lenschow srl@niras.dk, NIRAS: Impact of Sea Spray Aerosols as a Diffuse PFAS Load on Soil, Surface Water, and Groundwater

Working conceptual hypothesis

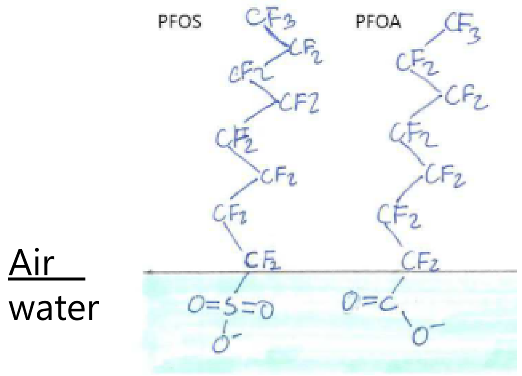
Initial results had a declining trend with distance from sea (coastline)

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



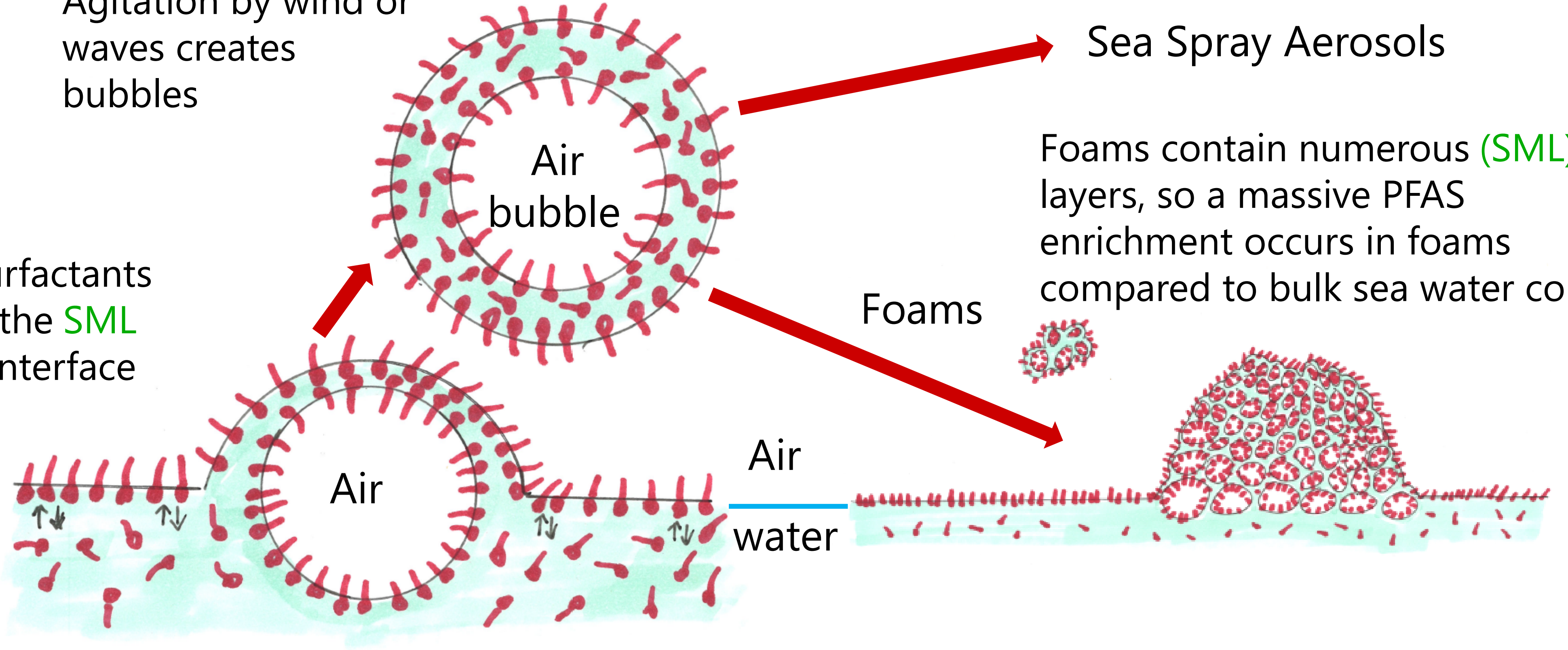
Agitation by wind or waves creates bubbles

Sea Spray Aerosols

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

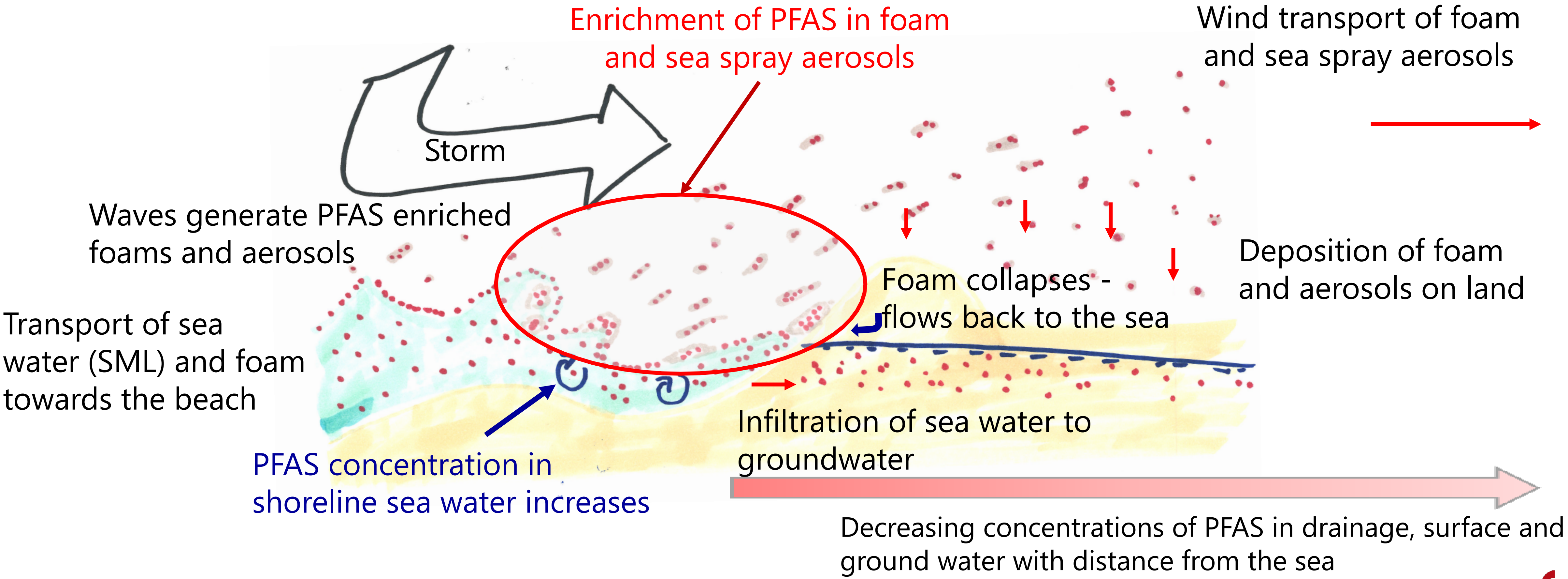
Enrichment of surfactants (PFAS) occurs in the SML at the air-water interface

Surface Micro Layer SML



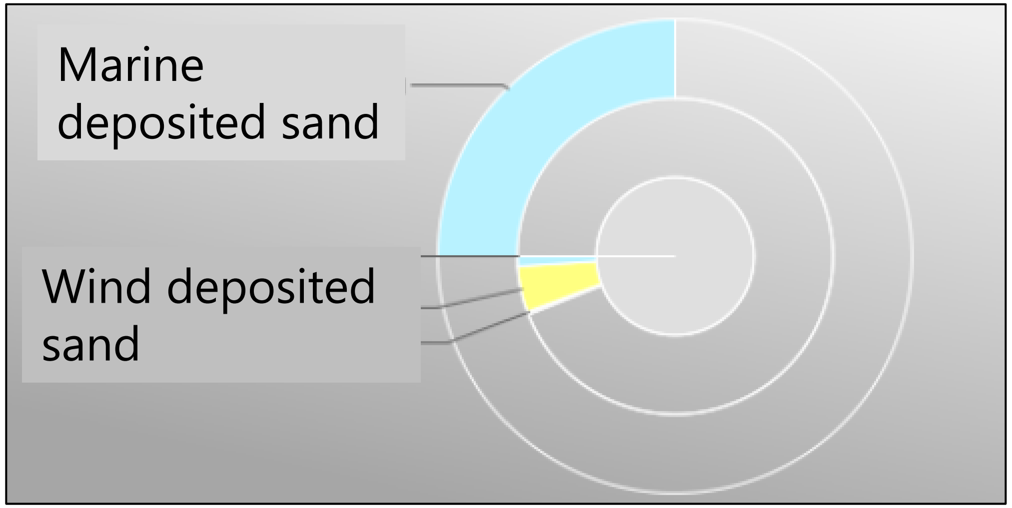
Working hypothesis seems likely

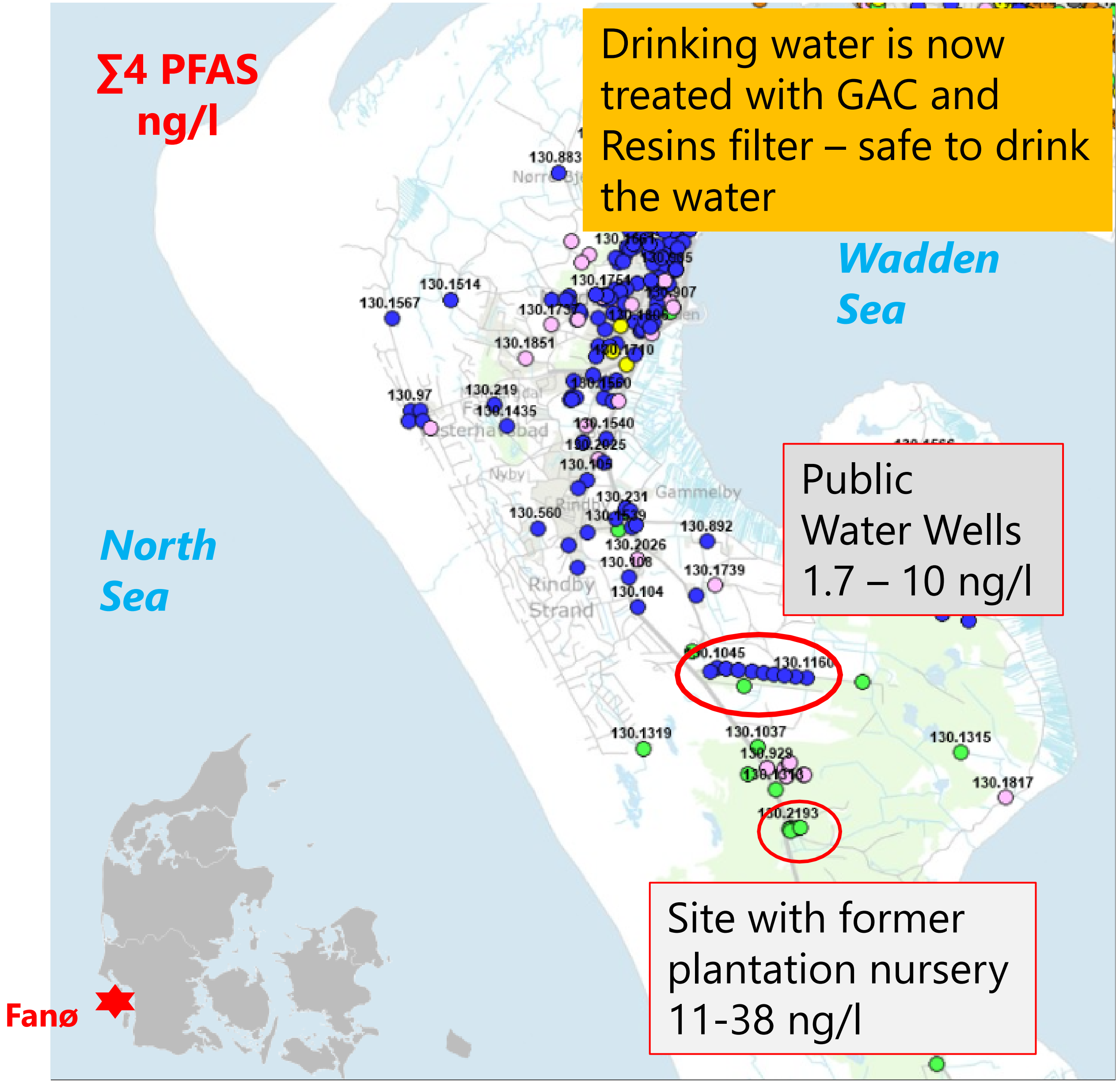
PFAS spread from the sea to land during storms in foams and aerosols



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 groundwater
- Geology – Sand



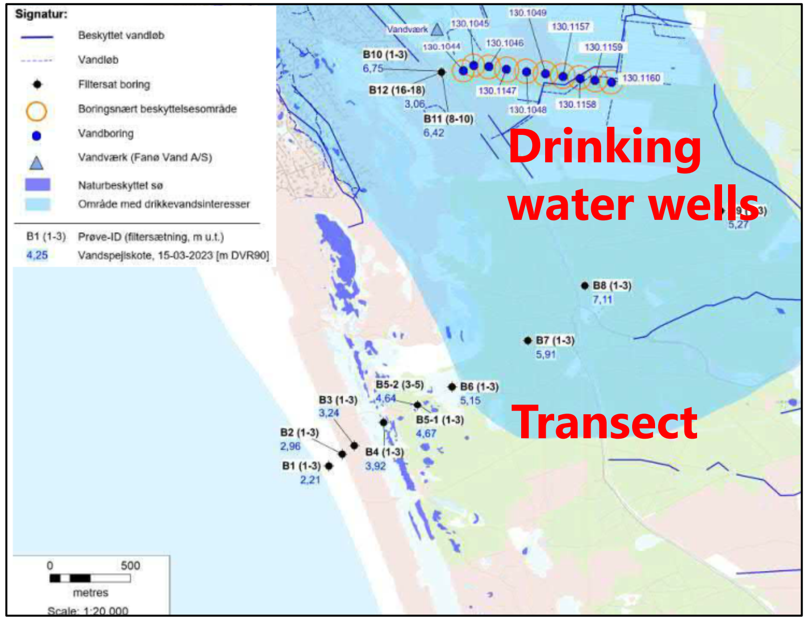


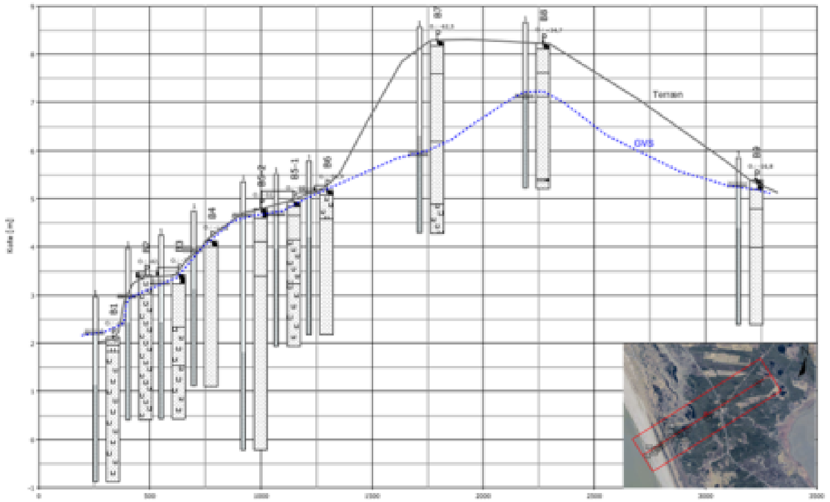
Investigations at Fanø

Funded by the Region of Southern Denmark

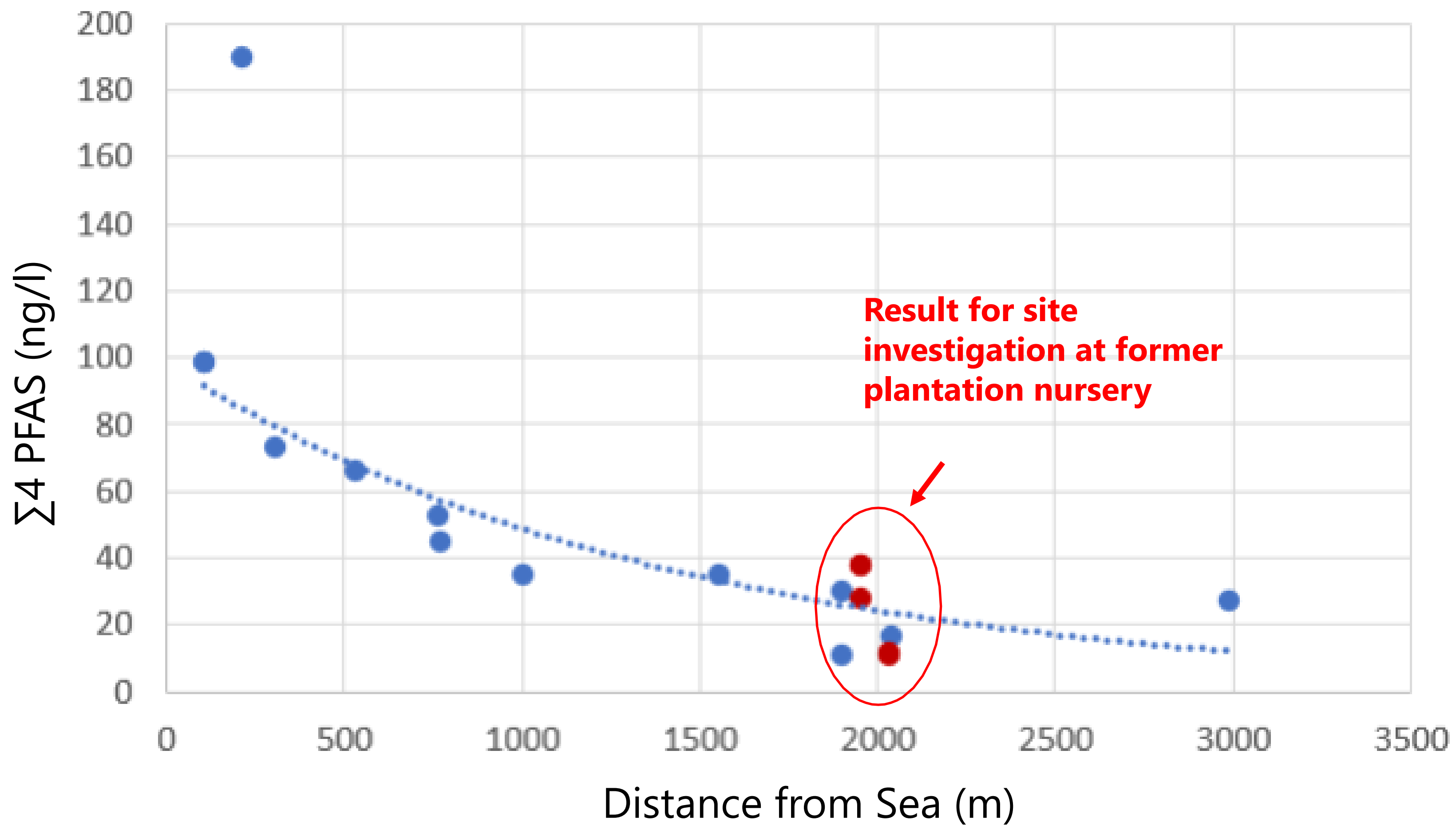
Transect approx.: 100 m; 200 m; 300 m; 500 m; 750 m; 1,000 m; 1,500 m; 2,000 m; 3,000 m: 4,000 m from sea (West Coast)

- Monitoring wells (shallow groundwater) along transect
- Sampling of soil (along transect)
- Sampling of surface water (small lakes/ponds) along transect
- Deeper monitoring wells at the public drinking water wells
- Analysis for 22 PFAS (ground-/surface water and soil)
- Analysis for Mg and Na (soil and surface water)





Results Fanø – groundwater

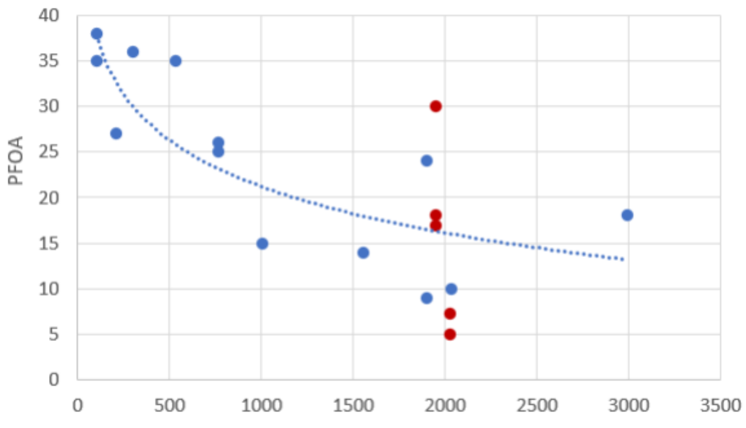


Declining trend with distance from sea

All results for sum of 4 PFAS in the groundwater (PFOA, PFOS, PFNA og PHxS) > 2 ng/l

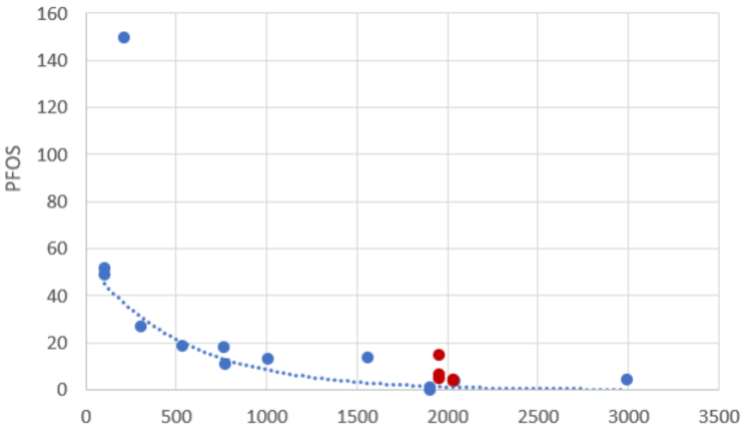
Results Fanø – groundwater

ng/l



Distance from Sea (m)

ng/l

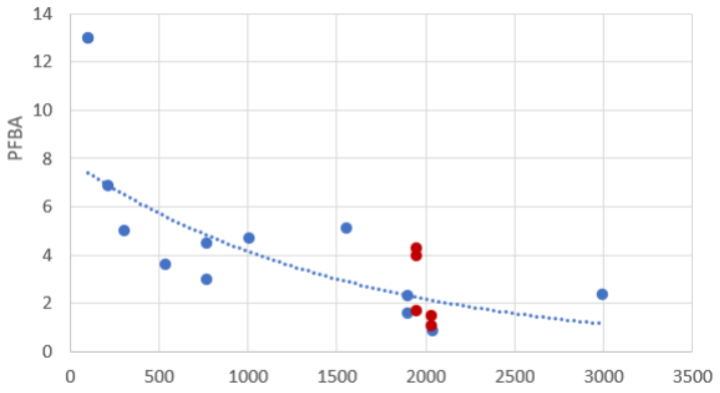


Distance from Sea (m)

Declining trends with distance from sea

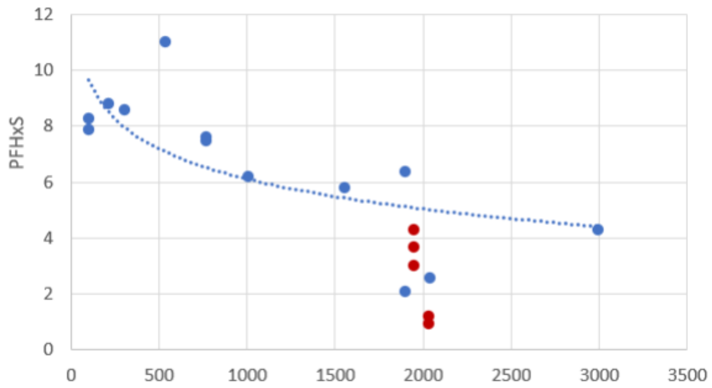
Main components: PFOS, PFOA and partly PFHxS and PFBA

ng/l



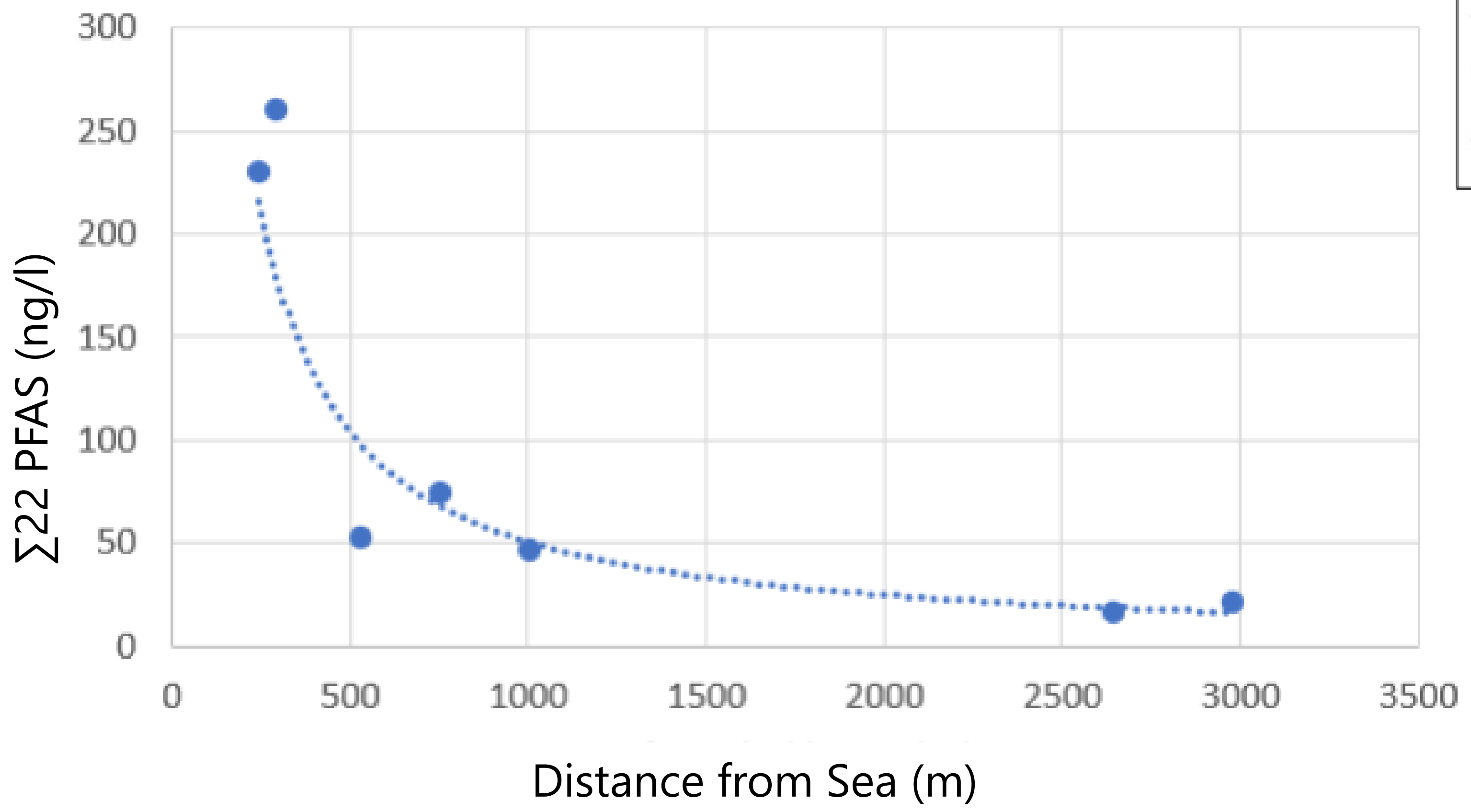
Distance from Sea (m)

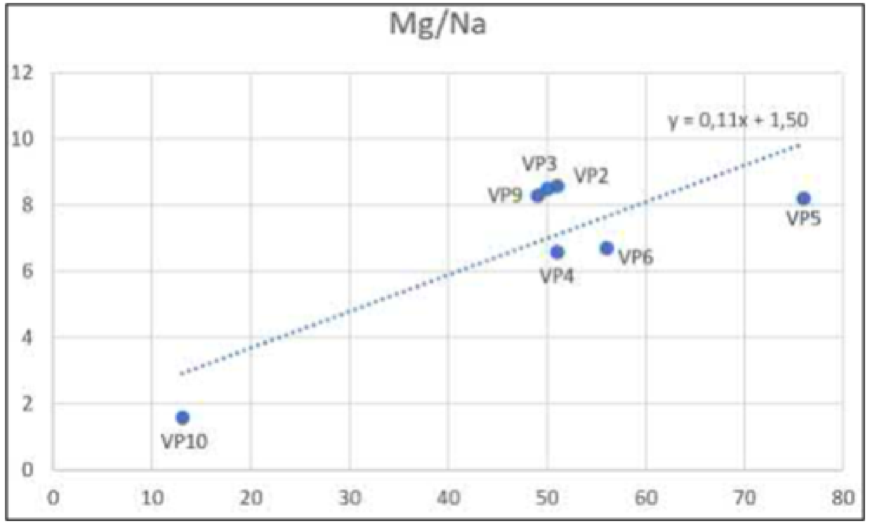
ng/l



Distance from Sea (m)

Results Fanø – surface water

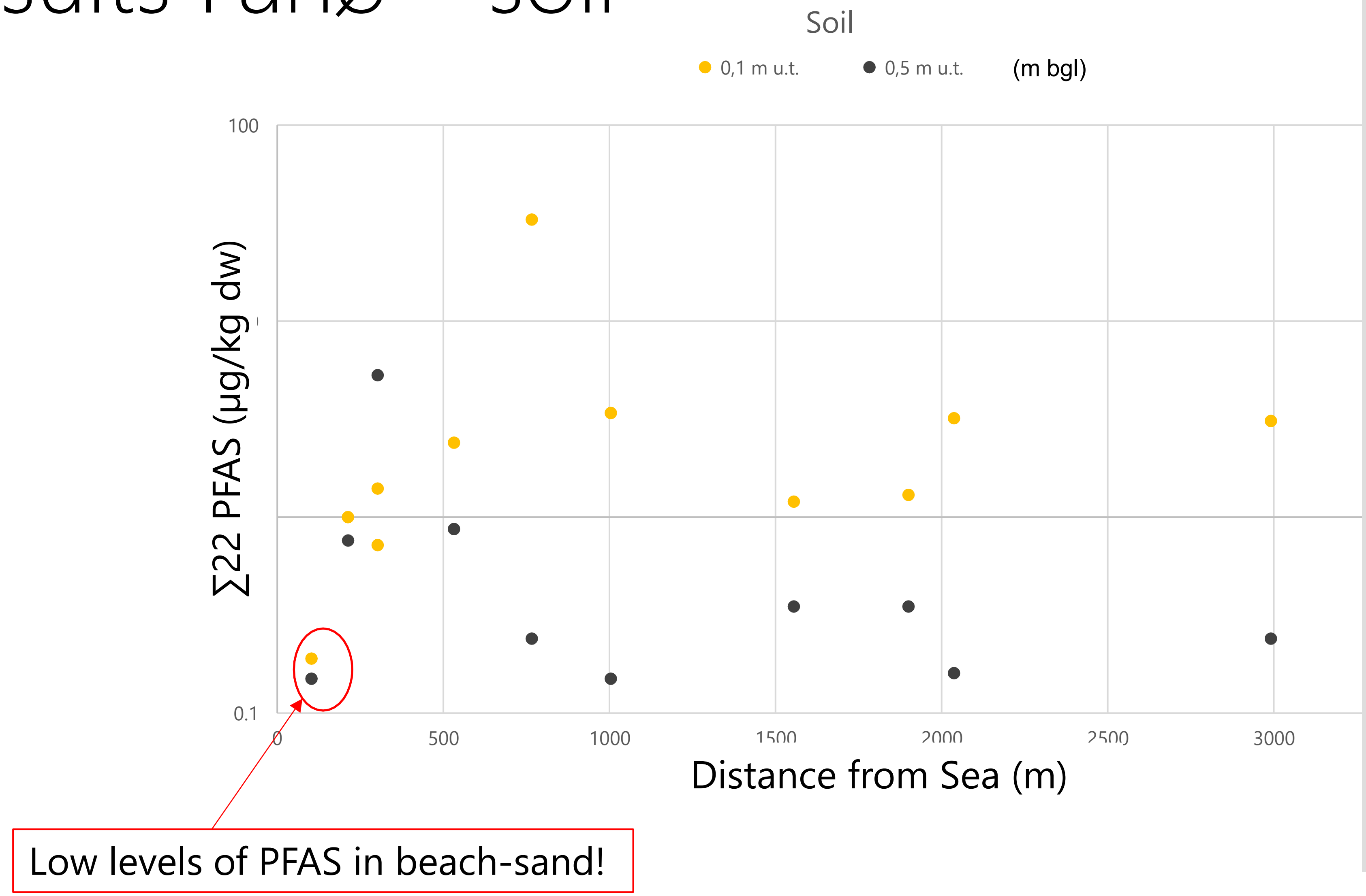




Linear relation for the ratio between Mg and Na. Relation of Mg/Na ratio of 0.12 for seawater.

All water samples exceed criteria for PFOS in fresh surface water (0.65 ng/l)

Results Fanø – soil



Higher concentrations in topsoil 0.1 m bgl than in lower samples from 0.5 m bgl.

Main components:
PFOS and partly PFOA

Low concentrations i beach sand

Concentration generally lower than soil criteria

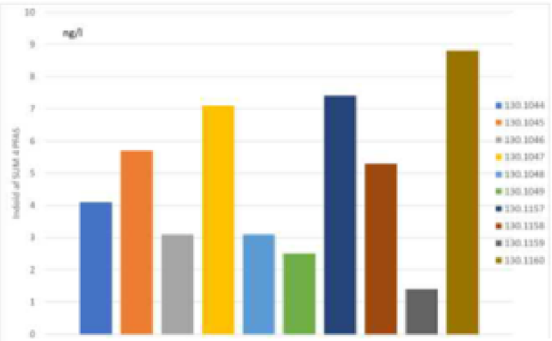
Soil parameters may be important for PFAS concentration (organic matter, particle size, water content etc.)?

Fanø – Public water wells

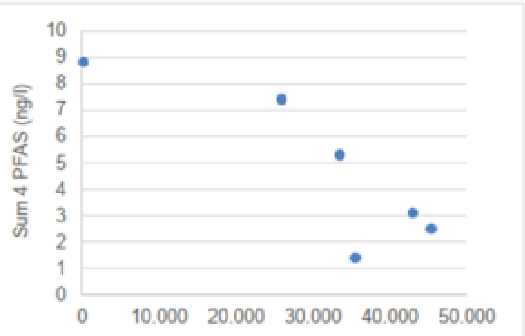
PFOA is most dominant in public wells – PFOS are not present (yet)

Conceptual model

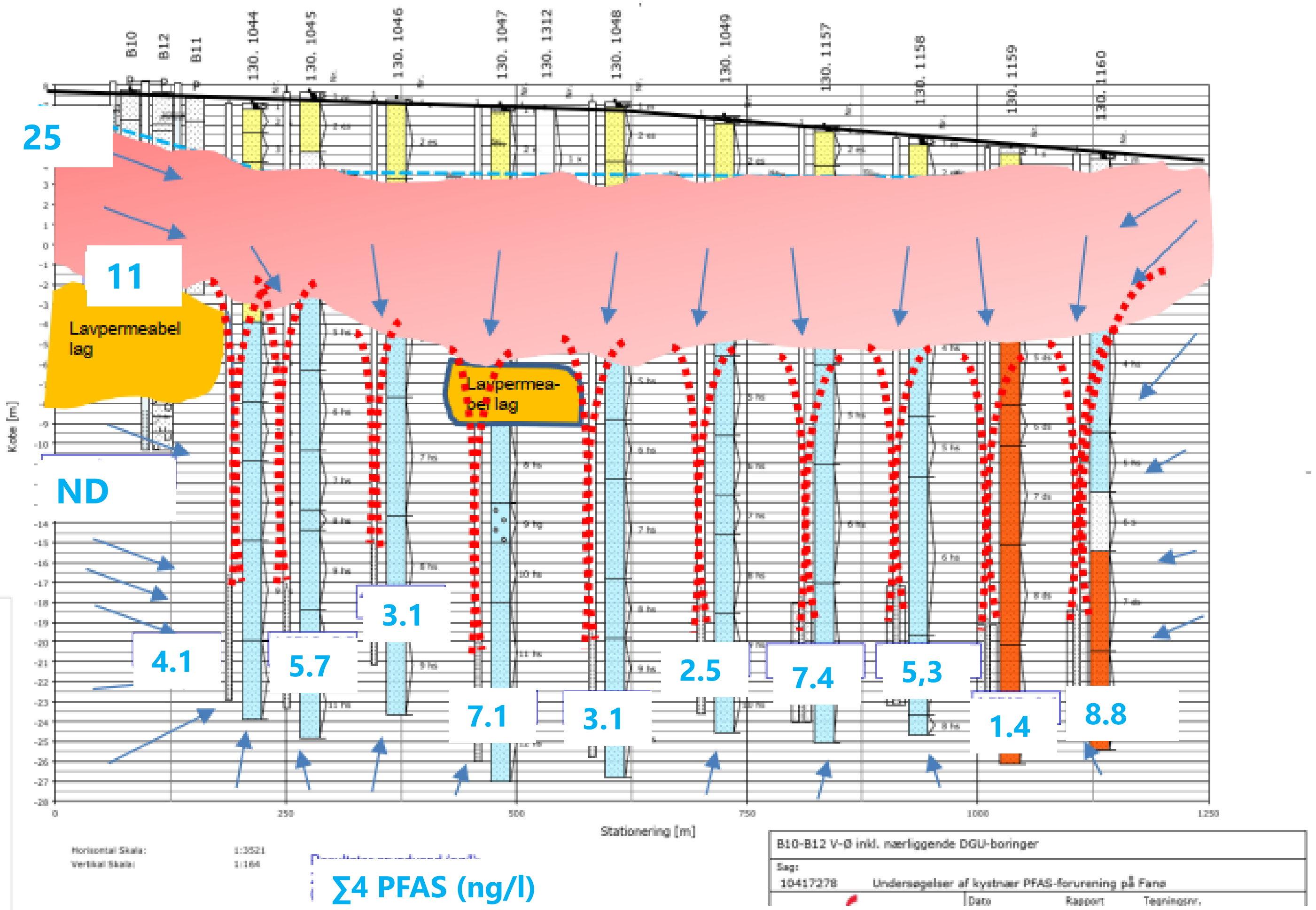
- 3 monitoring wells with screens in different depths
- PFAS-concentration declines with depth (monitoring wells)
- Public wells are extracting groundwater, which is a mixture of PFAS-contaminated groundwater from the upper aquifer and non-contaminated groundwater from the deeper aquifer.
- No "distance from sea" trend for public wells
- PFAS concentration in public wells is related to the volume of extracted ground water



W ***Distance from sea*** ***E***



Volume of extracted groundwater (m³)



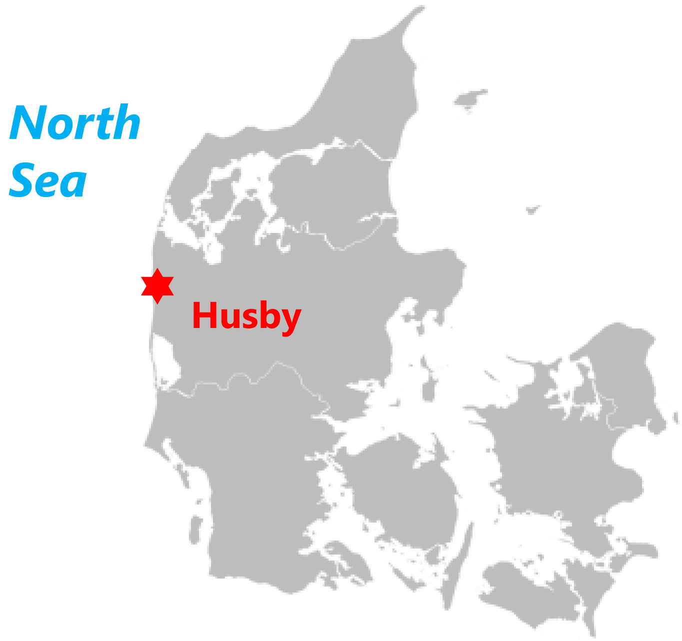
NIRAS

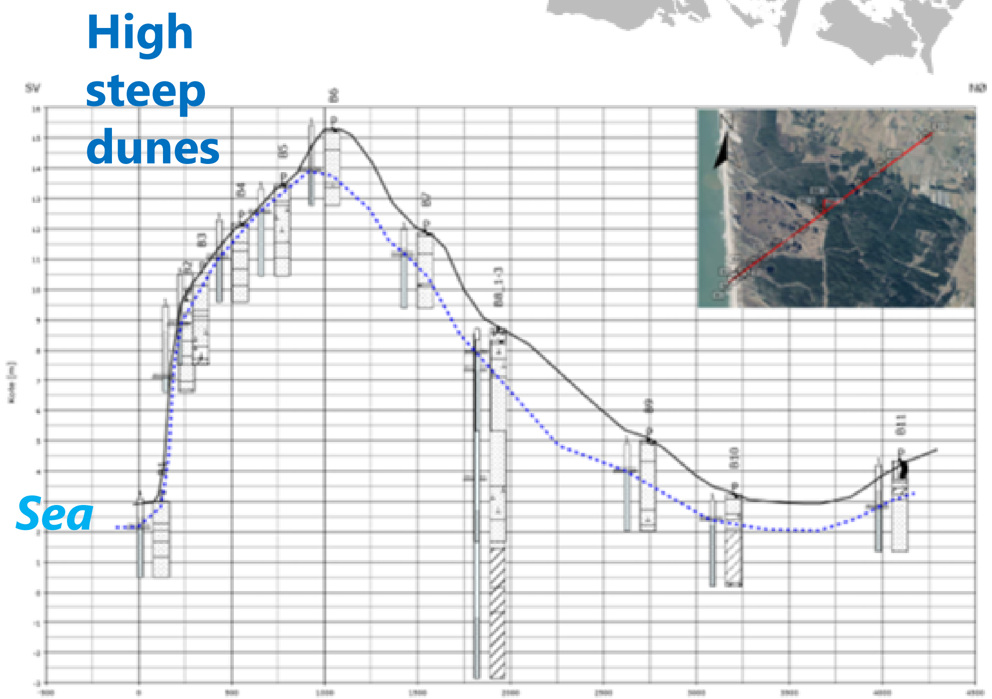
Husby plantage

Funded by the Central Denmark Region and Danish EPA

Transect approx.: 100 m; 200 m; 300 m; 500 m; 750 m; 1,000 m; 1,500 m; 2,000 m; 3,000 m: 4,000 m from sea (West Coast)

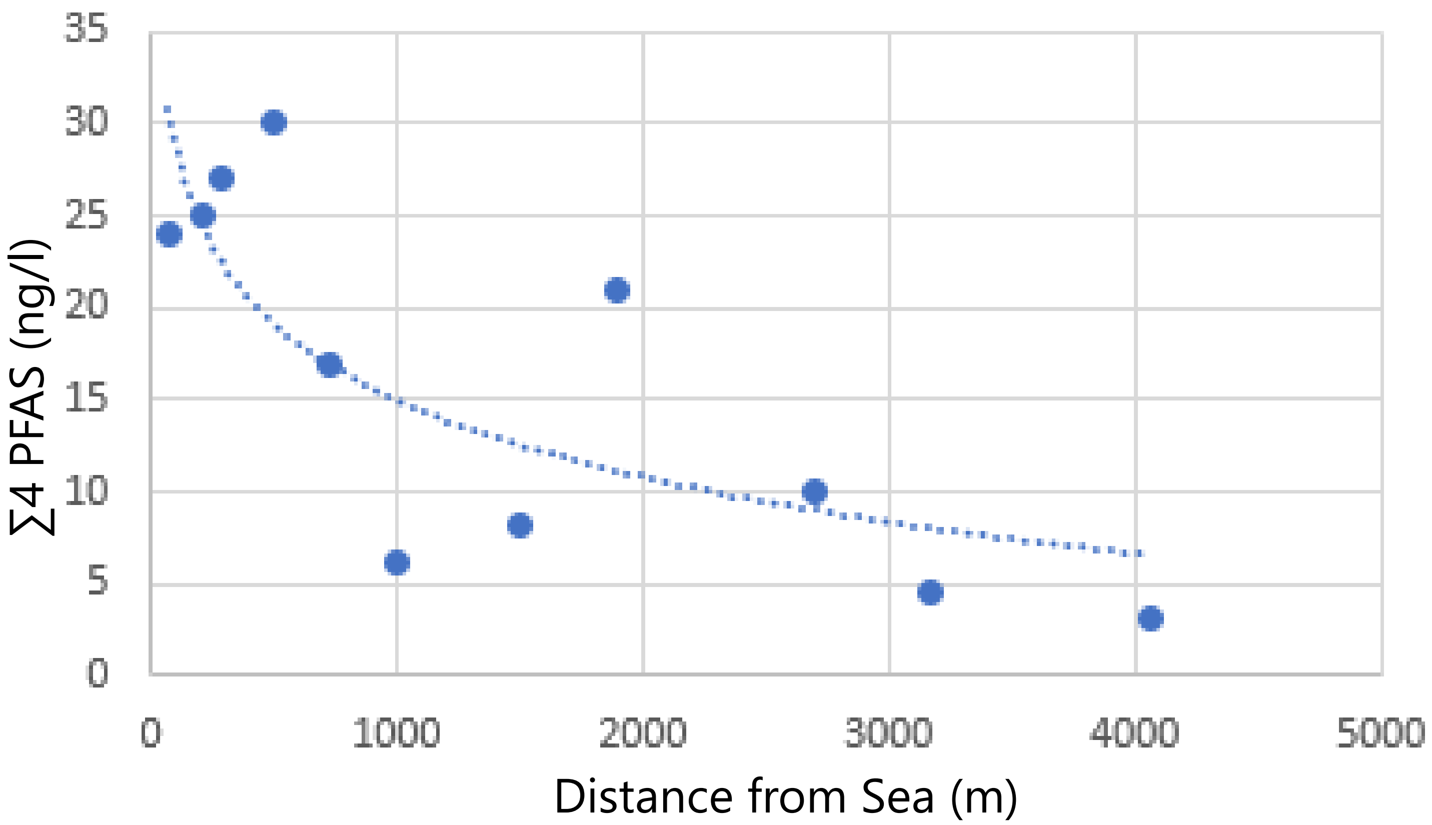
- Monitoring wells (shallow ground water) along transect
- Sampling of soil (along transect)
- Sampling of surface water (small lakes/ponds) along transect
- Samples of sea foam
- Analysis for 22 PFAS (ground-/surface water, soil)
- Analysis for 49 PFAS (Sea foam)
- Analysis for Mg and Na (soil and surface water)





NIRAS

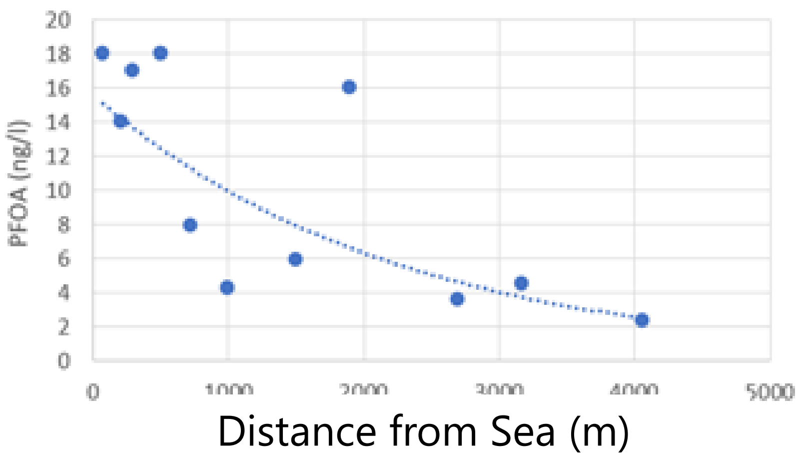
Results Husby – groundwater

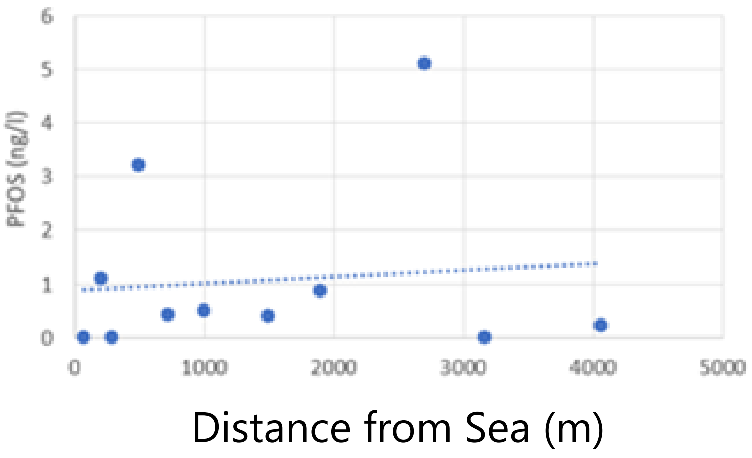


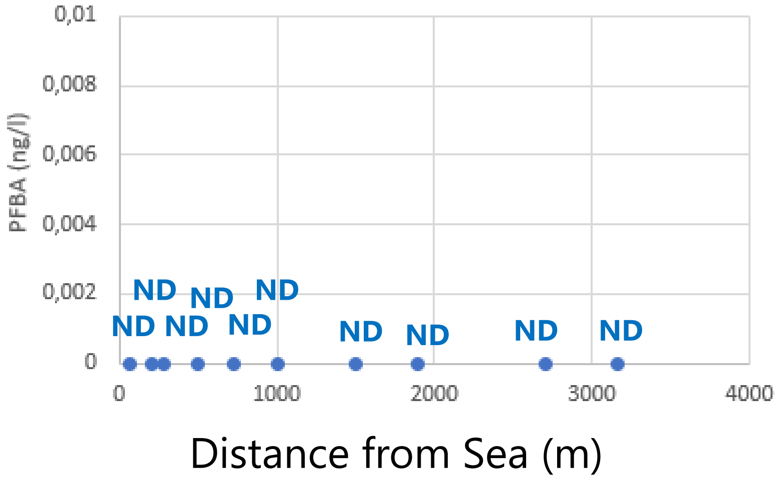
Declining trend with distance from sea

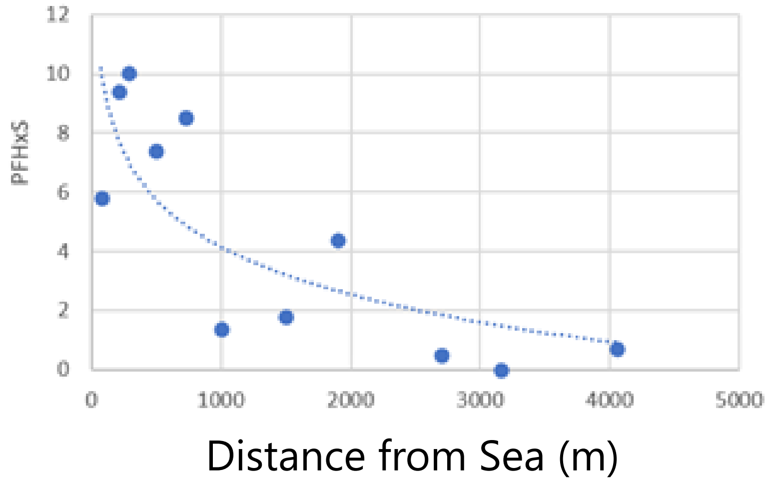
All results for sum of 4 PFAS in the groundwater (PFOA, PFOS, PFNA og PHxS) > 2 ng/l

Results Husby – groundwater









Main components: PFOA and partly PFHxS and PFOS

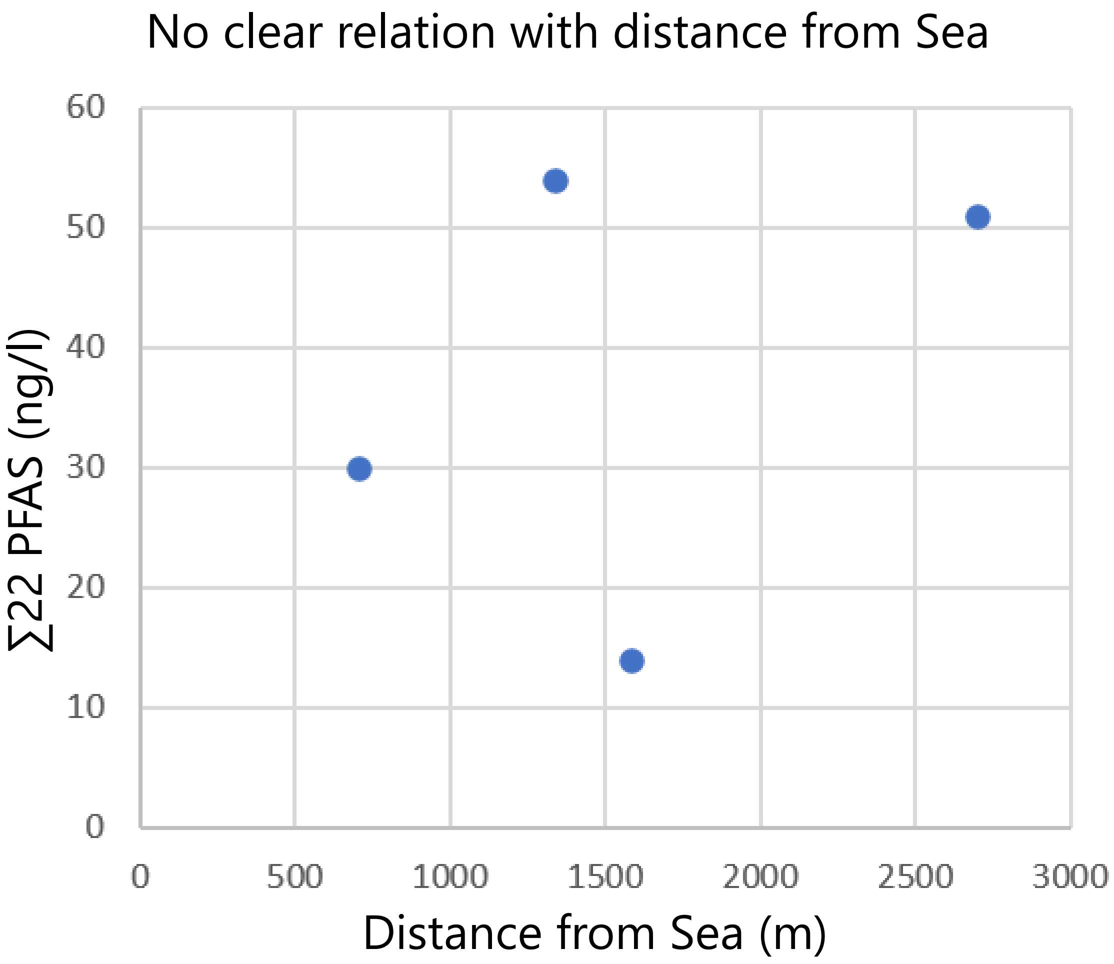
No decline for PFOS ?

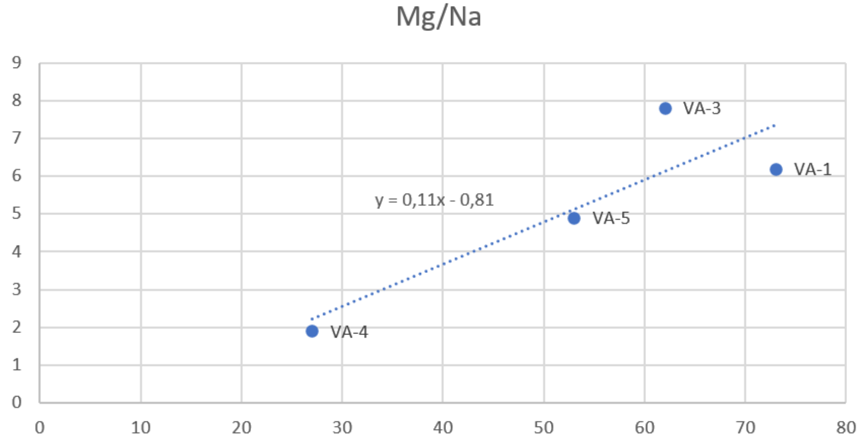
PFBA not detected

Site differences compared with Fanø ?

- ➢ High dunes
- ➢ Unsaturated zone
- ➢ Sorption

Results Husby – surface water

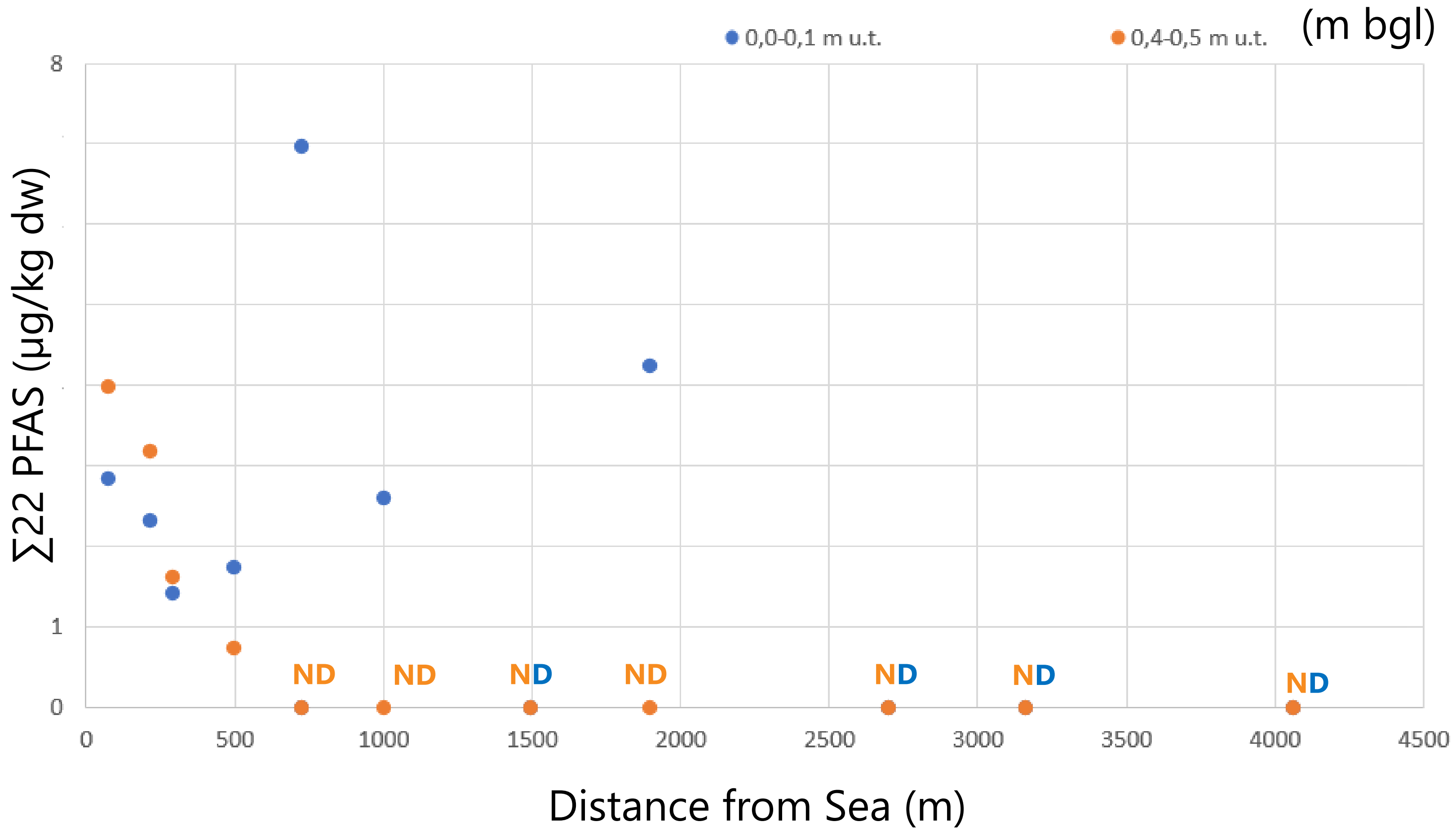




Linear relation for the ratio between Mg and Na. Relation of Mg/Na ratio of 0.12 for seawater

All water samples exceed criteria for PFOS in fresh surface water (0.65 ng/l)

Results Husby – soil



Generally low concentrations (below soil criteria)

Not detected (ND) 1500 m from the sea (Distance from Sea)

Main components:
PFOS and partly PFOA

Decline with distance from sea for samples 0.4-0.5 m bgl ?

Soil parameters may be important for concentration distribution (organic matter, particle size, water content etc.)?

High dunes near sea ?

Results Husby – sea foam

Sea water sample 1 0.35 ng/l

Foam sample 1 240,000 ng/l

Foam sample 2 18,000 ng/l

Main components in sea foam are PFOS, PFOA and partly PFNA, PFDA and PFHxS

Detection of long chain PFCA's (PFNA ->PFDoDA)

Detection of PFAS in sea foam that are non-detected in sea water

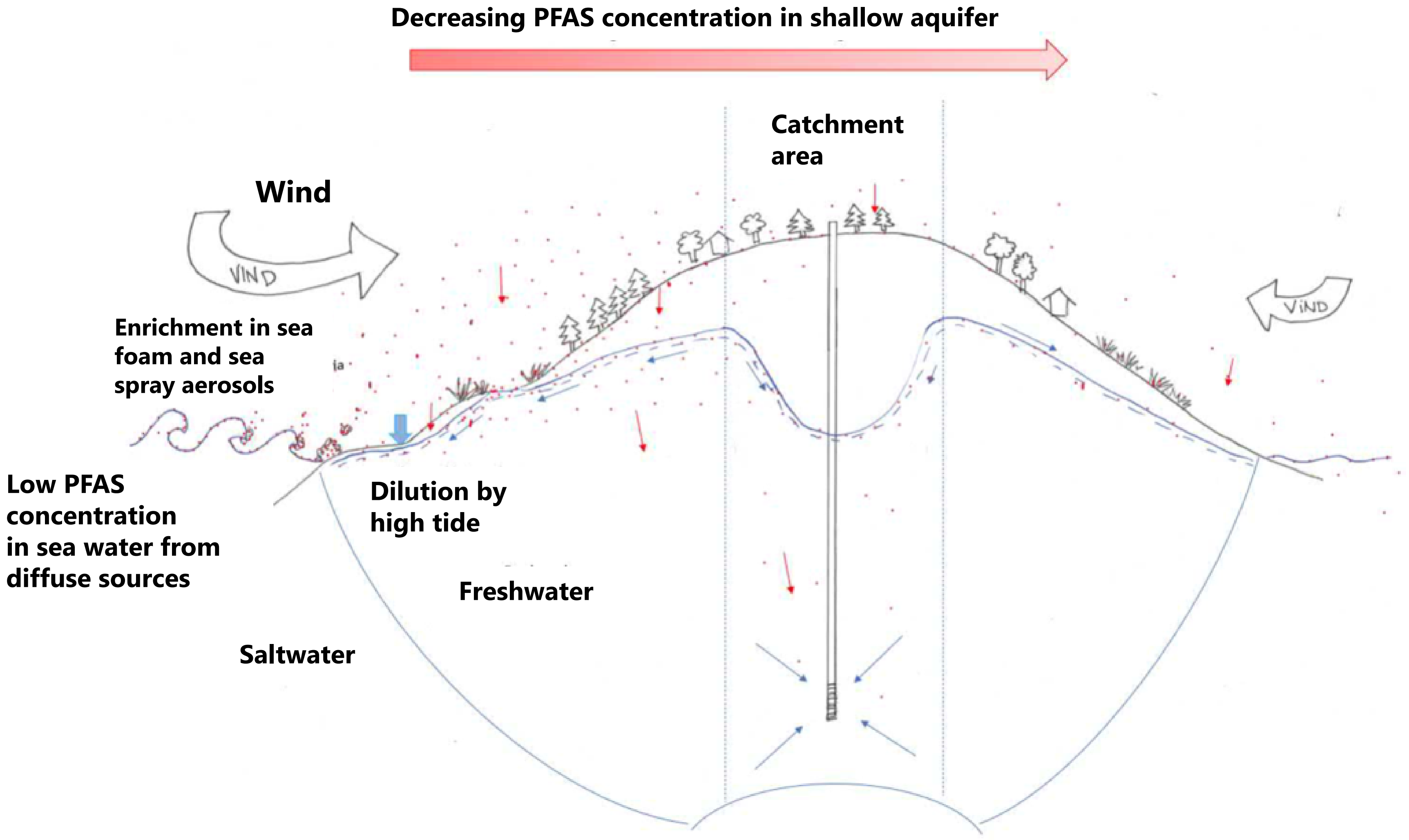
Analysis for 49 PFAS did not give significant change in PFAS composition compared to analysis for 22 PFAS

PFAS concentration in sea water and sea foam may vary in time (including days with no sea foam)

Conceptual model

Fanø site

Link to report (Fanø):
https://regionsyddanmark.dk/media/2jhjpev5/clean_unders%C3%B8gelser-af-kystn%C3%A6r-pfas-forurening_syddanske-udviklingspulje-22-52316_rapport-03-10_2023_optimized.pdf



Ministry of Environment of Denmark
Environmental Protection Agency

Perspectives

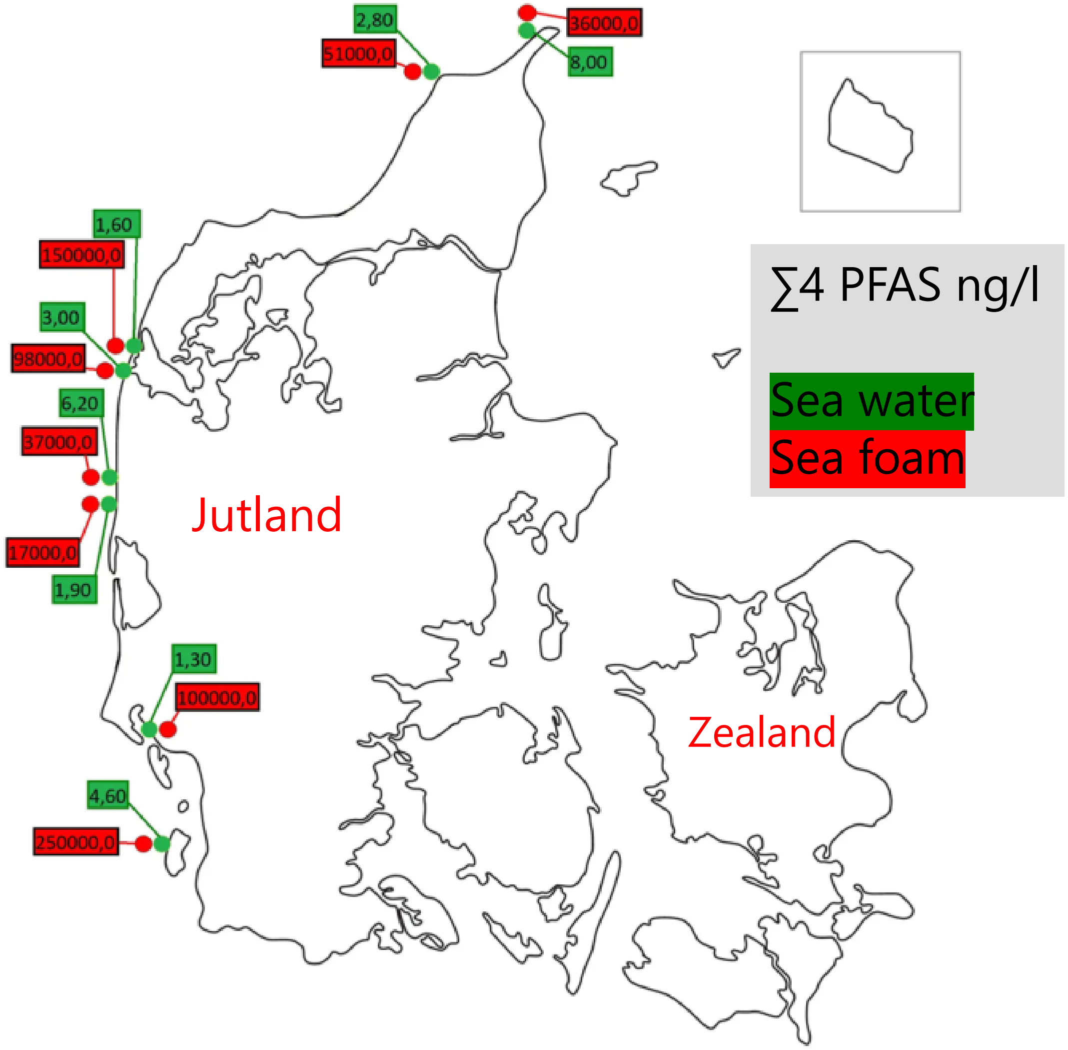
Other Projects/upcoming projects

Other projects

- Sampling sea water and sea foam along west Coast (Danish Environmental Protection Agency EPA)
- Impact on coastal meadows - 60 sites 0-10 km from sea along the coast of Jutland and Zealand (Danish Environmental Protection Agency EPA)
- Impact on humans using the sea for recreational activity by surfing (waiting to be published).

Upcoming

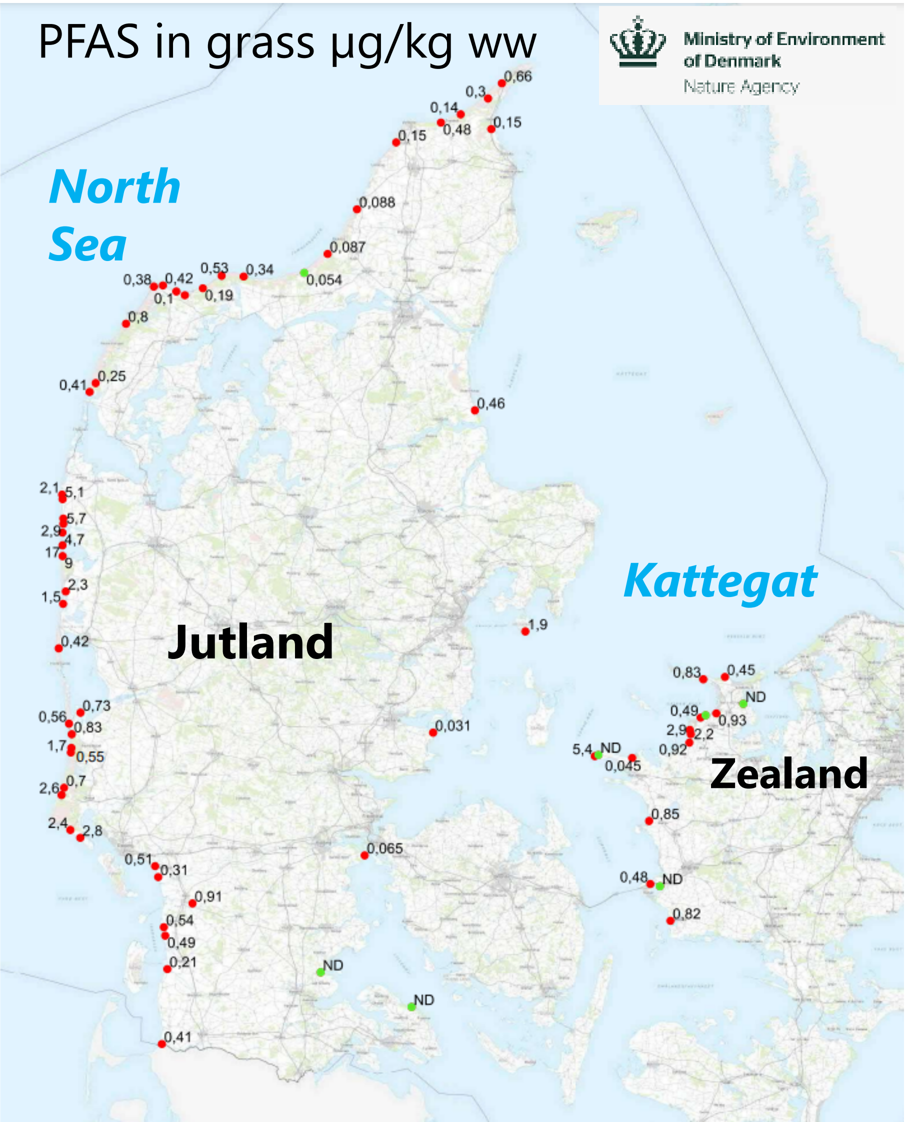
- More sampling at Fanø (seasonal changes)
- Second phase includes sampling of aerosols and deposition of PFAS in cooperation with Stockholm University
- More detailed studies on coastal meadows



Perspectives

PFAS can affect coastal meadows with grazing livestock

- Samling at 60 sites 0-10 km from sea at the coast of Jutland and Zealand by the Danish Nature Agency. Sampling includes grass and surface water. All sites are meadows leased out for grazing livestock.
- Not only the West Coast of Jutland – also impact on East Coast and western part of Zealand.
- Tests show that PFAS can be washed off since PFAS deposition occurs on the surface of vegetation (grasses)
- Impact on meadows with grazing livestock
- Impact on wildlife (hunting for ducks have been banned in some areas)



Conclusion

- **Low concentrations of PFAS in sea water can contaminate coastal surface water and groundwater due to enrichment in sea foam and sea spray aerosols which then spread to coastal areas**
- **Decreasing concentrations with distance from sea**
- **Morphology and geology including magnitude of unsaturated zone may have impact on distribution**
- **Impact on soil – soil parameters are controlling factors for concentrations level of PFAS in soil**
- **PFOS, PFOA, PFHxS and PFBA er most dominant PFAS in soil, groundwater and surface water**
- **Impact on vegetation (grass) in coastal areas**
- **Potential enrichment and spreading is driven by wind, wave energy and salinity?**
- **Risk to groundwater in coastal areas – risk to public water wells and private water wells (often shallow)**
- **Risk to wildlife and livestock in coastal areas**

Thank you for Attention

Acknowledgements

- Halfdan Sckerl - Central Denmark Region
- Anette Hansen, Region of Southern Denmark
- Lemvig municipality, Denmark
- Danish Ministry of Environment –
  Danish Environmental Protection Agency and Nature Agency
- Anne Henriksen and Anders G. Christensen - NIRAS