Norwegian Geotechnical Institute

The paper industry as a source of precursors to Perfluorinated Alkyl Acids (PFAA) in a Norwegian lake

Lake Tyrifjorden case study site

Norsk institutt for vannforskning
Norwegian Institute for Water Research

School of Mines 1874 Colorado

VU University Amsterdam

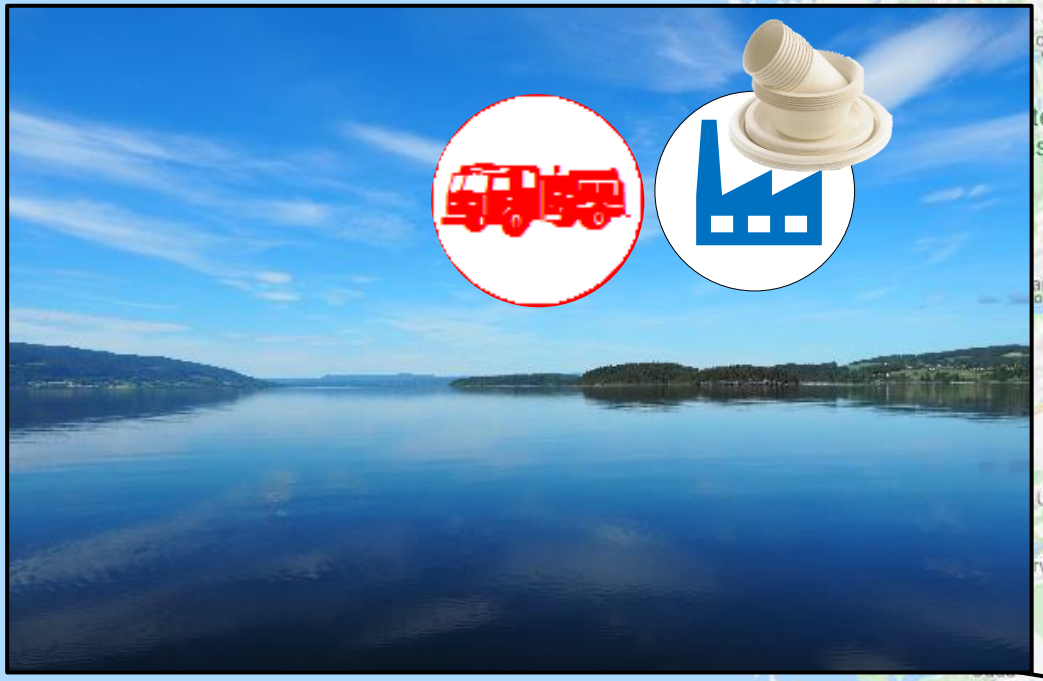
NMBU Norwegian University of Life Sciences

UNIS

NTNU
Norwegian University of Science and Technology

Lake Tyrifjorden

- Elevated PFOS concentrations in perch livers (183 µg kg^{-1}) were reported in 2015



Lake Tyrifjorden

- Unknown source
- Fire station since the 1980s
- Produced PFAS coated paper products since the 1970s. Factory shut down in 2013.

PFAS history

1960

- **PFAS-firefighting foam (AFFF) (ca. 1950)**
- **Teflon frying pans (ca. 1960)**

1970

- **PFCA based AFFF used by U.S. Military (until ca. 1975)**
- **SAmPAP in paper products (1974)**

1980

1990

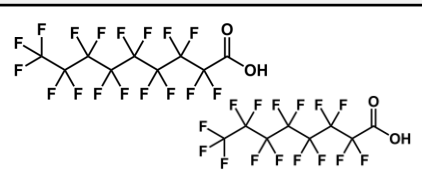
- **FTMAP in paper products (1995)**
- **3M phase out PFOS production (2001)**

2000

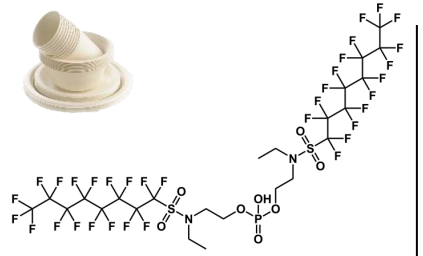
- **PFOS based foam phased out in Norway. Replaced by 6:2 FTS based foam (2007)**
- **PFOS included in the Stockholm convention (2009)**

2010

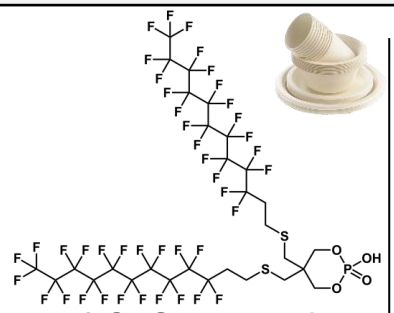
- **Phase out of all PFAS based foam in Norway (2012-2013)**
- **PFOA included in the Stockholm convention (2019)**



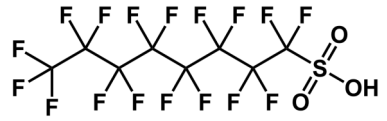
Perfluoroalkyl carboxylates (PFCA)



SAmPAP diester

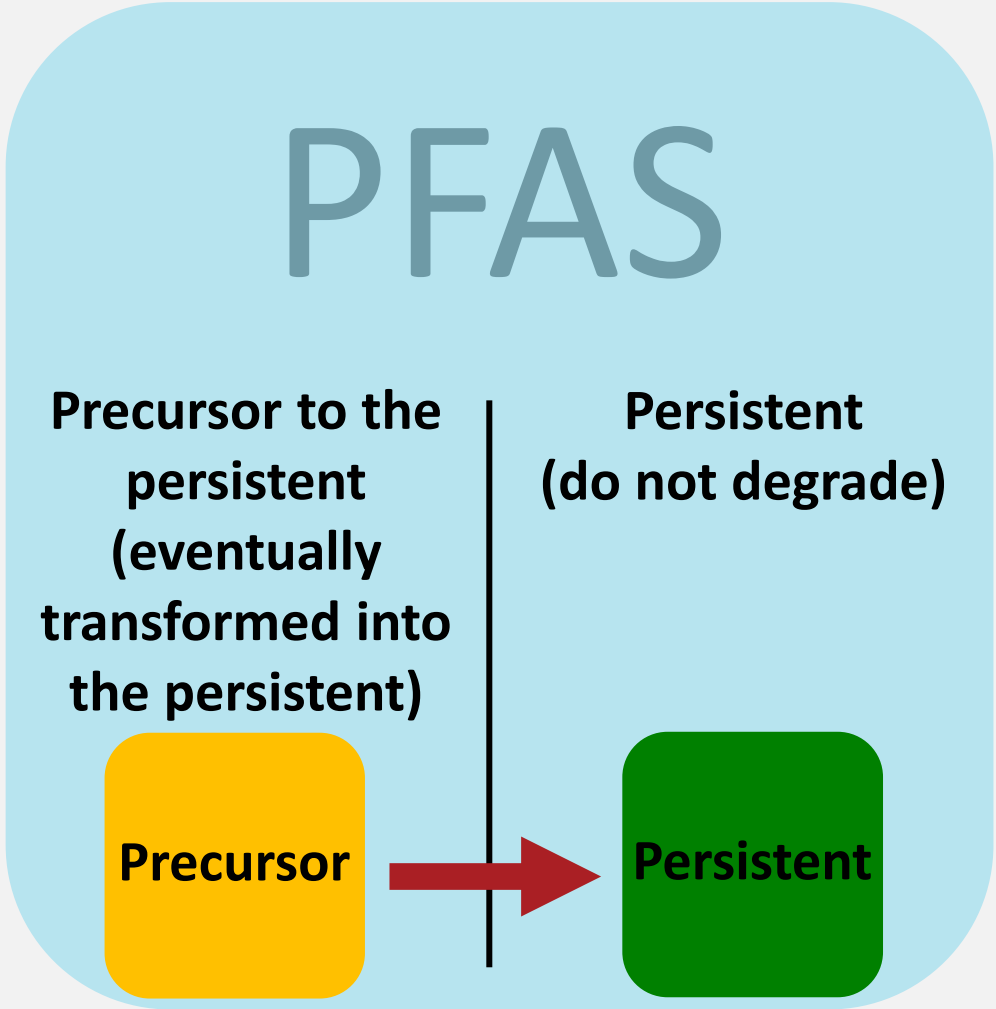


10:2 FTMAP



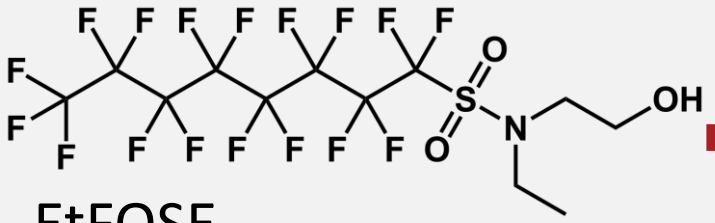
Perfluorooctane-sulfonic acid (PFOS)

PFAS - Persistence



- Thousands of different PFAS
- All PFAS are either persistent in the environment or precursors to the persistent PFAS
- PFAS in the environment do not disappear

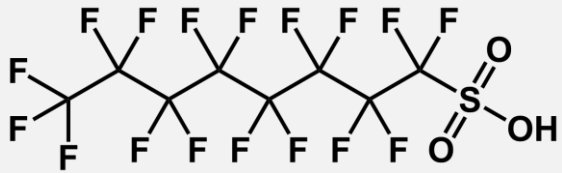
Precursor



EtFOSE

N-ethyl perfluorooctane sulfonamidoethanol

Persistent



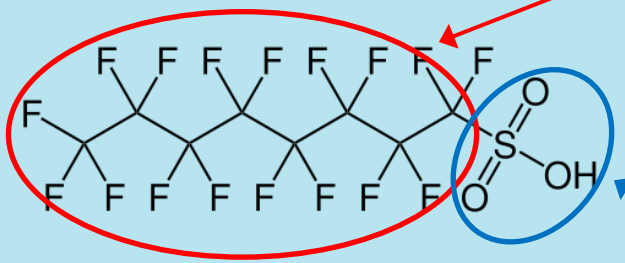
PFOS

Perfluorooctanesulfonic acid

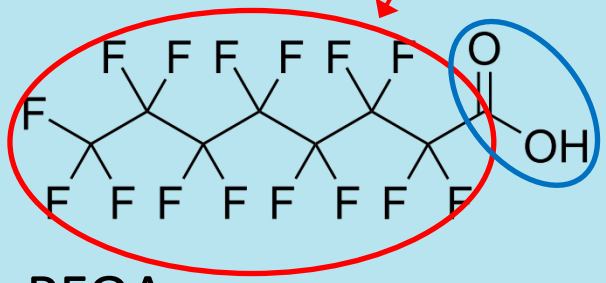
NGI NTNU Norwegian University of Science and Technology

Perfluorinated Alkyl Acids (PFAA)

PFAS



PFOS (Perfluorooctanesulfonic acid)



PFOA (Perfluorooctanoic acid)

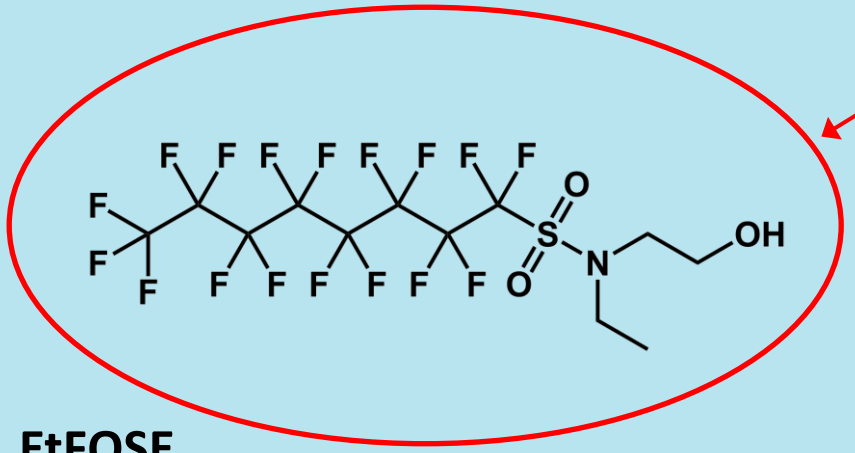
Fluorinated "tail" (hydrophobic and lipophobic)

Functional group (hydrophilic)

- C-F bond = Extremely stable
- Hydrophobic and lipophobic
- Bind to specific proteins in the body
- Some bioaccumulate and biomagnify

Precursors to perfluorinated Alkyl Acids (PFAA)

PFAS

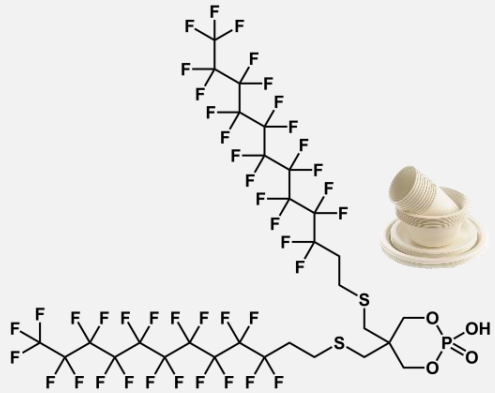


Hydrophobic

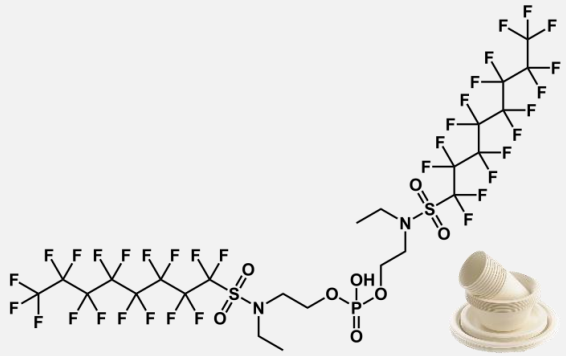
EtFOSE

N-ethyl perfluorooctane sulfonamidoethanol

- Can be (bio)transformed to PFAA in the environment
- Some are neutral and hydrophobic



FTMAP



SAmPAP diester

NTNU
Norwegian University of Science and Technology

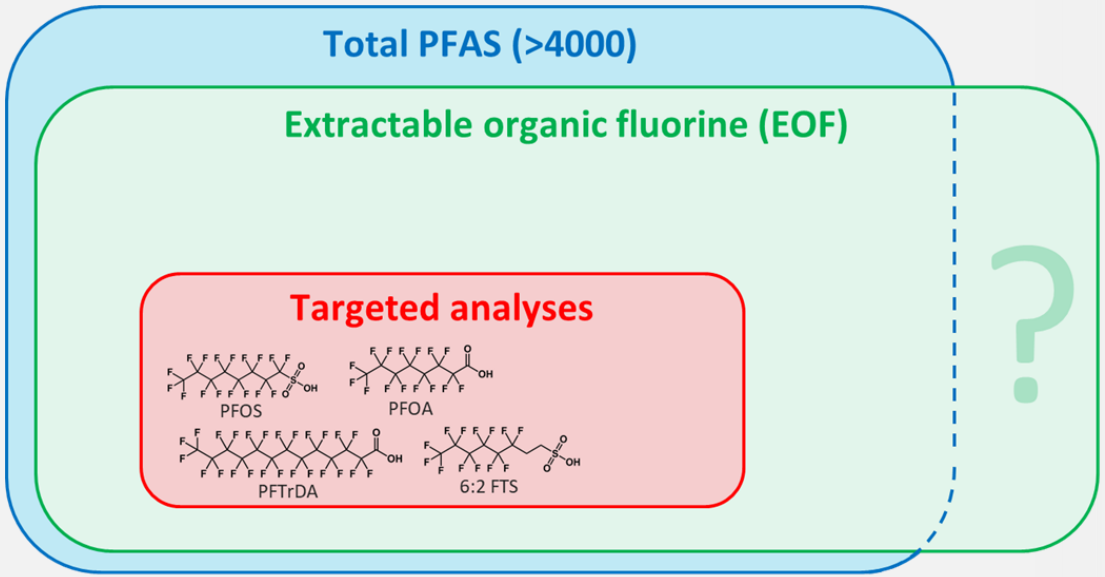
Fieldwork and analyses

Sampled media

- Sediment
- Water
- Biota:
  - Crayfish
  - Fish

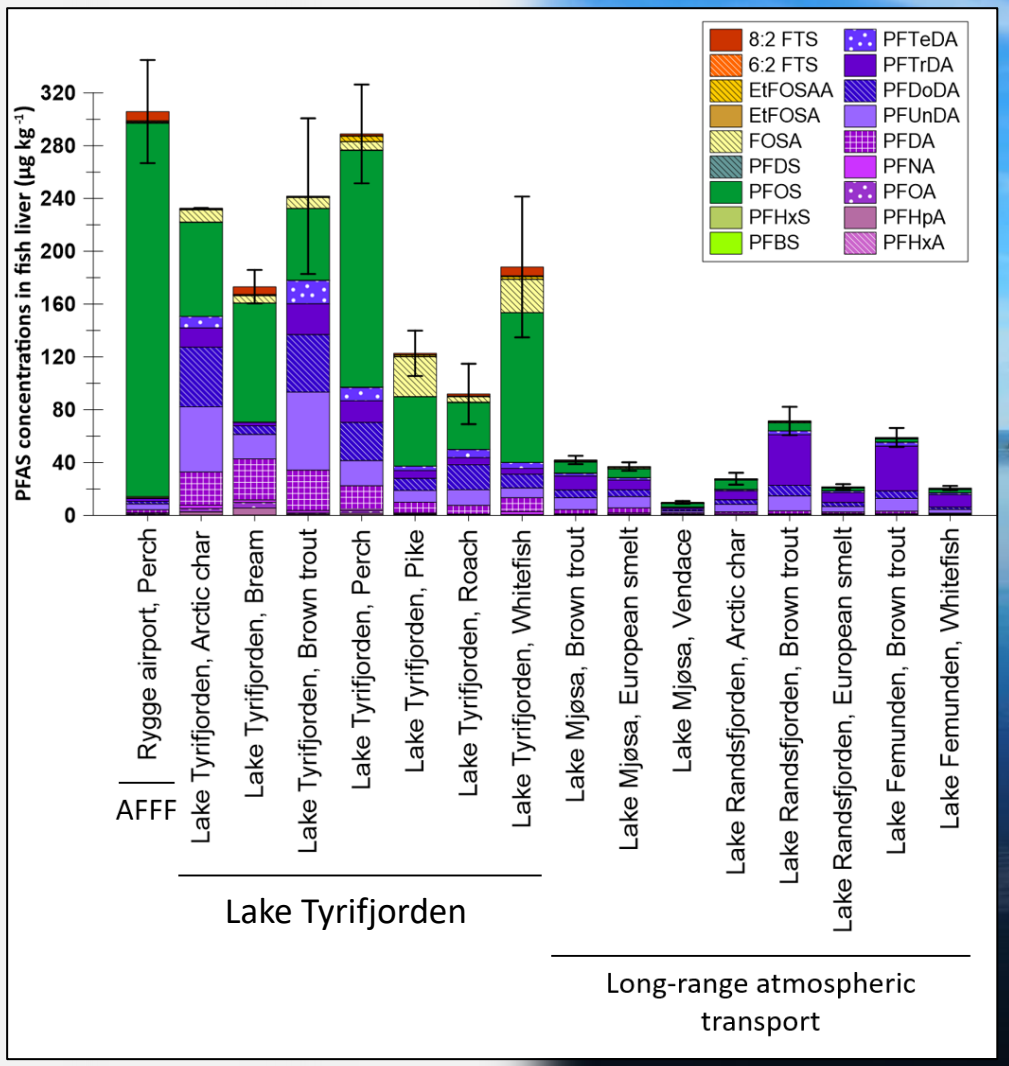
Analyses

- Targeted analyses
- Extractable organic fluorine (EOF)
- Biota: Stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$)



Lake Tyrifjorden versus other Norwegian lakes

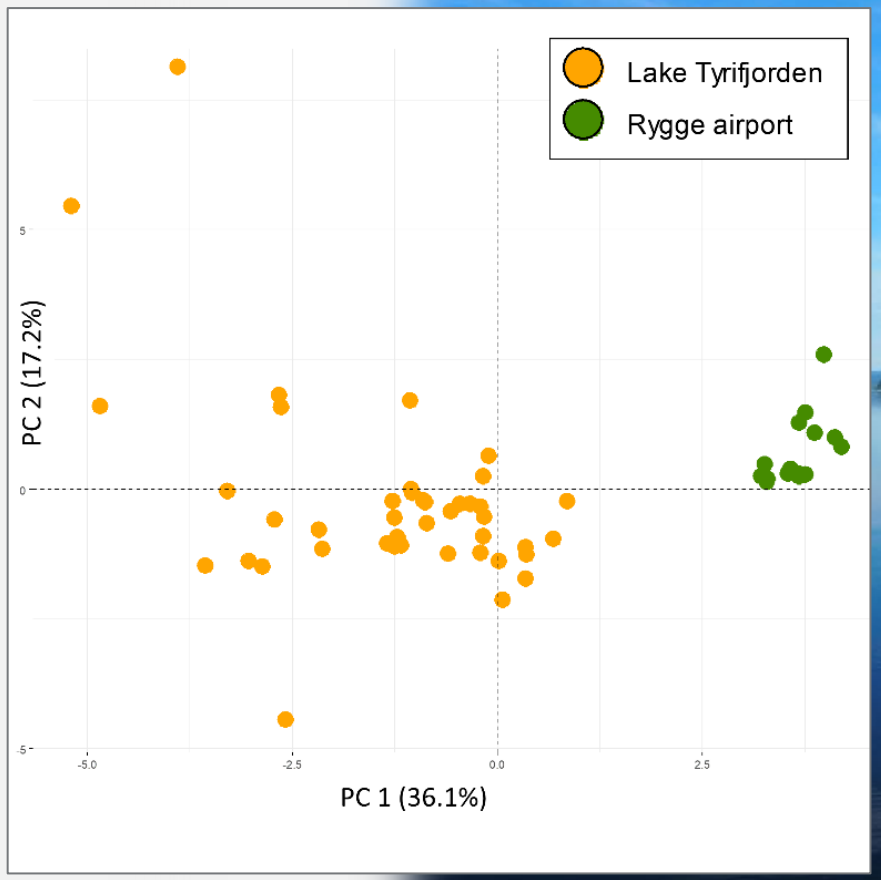
- Water: low concentrations, 0.2 – 0.3 ng L^{-1} PFOS (Br + L)
- Fish: Comparable concentrations of sum PFAS to fish sampled near Rygge airport
- Fish: More long chained PFCA in biota from lake Tyrifjorden
- Fish: More PFOS precursors (preFOS) chained PFCA in biota from lake Tyrifjorden



NGI NTNU Norwegian University of Science and Technology

PFAS profiles in biota

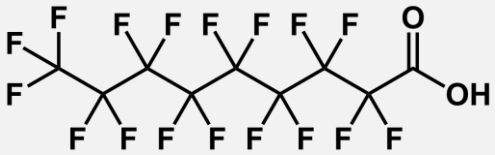
- Comparable concentrations of sum PFAS to fish sampled near Rygge airport
- More long chained PFCA in biota from lake Tyrifjorden
- More PFOS precursors (preFOS) chained PFCA in biota from lake Tyrifjorden
- Different PFAS profiles in fish from lake Tyrifjorden compared to fish affected by AFFF sources



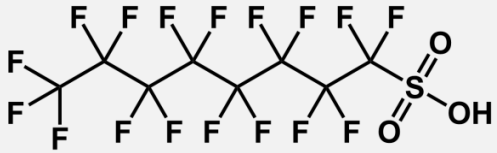
NGI NTNU Norwegian University of Science and Technology

PFAS-levels in sediments

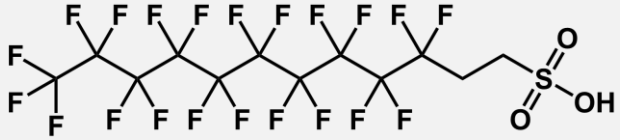
- Low levels at fire station
- Levels of FTS and preFOS high compared to fluorinated sulfonic and carboxylic acids
- Lake levels highest at river mouth



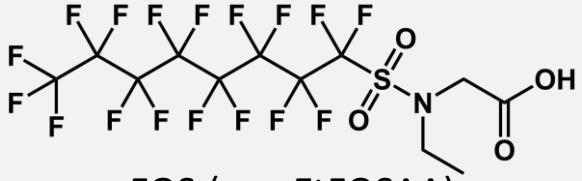
PFCA (Perfluoroalkyl carboxylates)
(max 25 µg/kg)



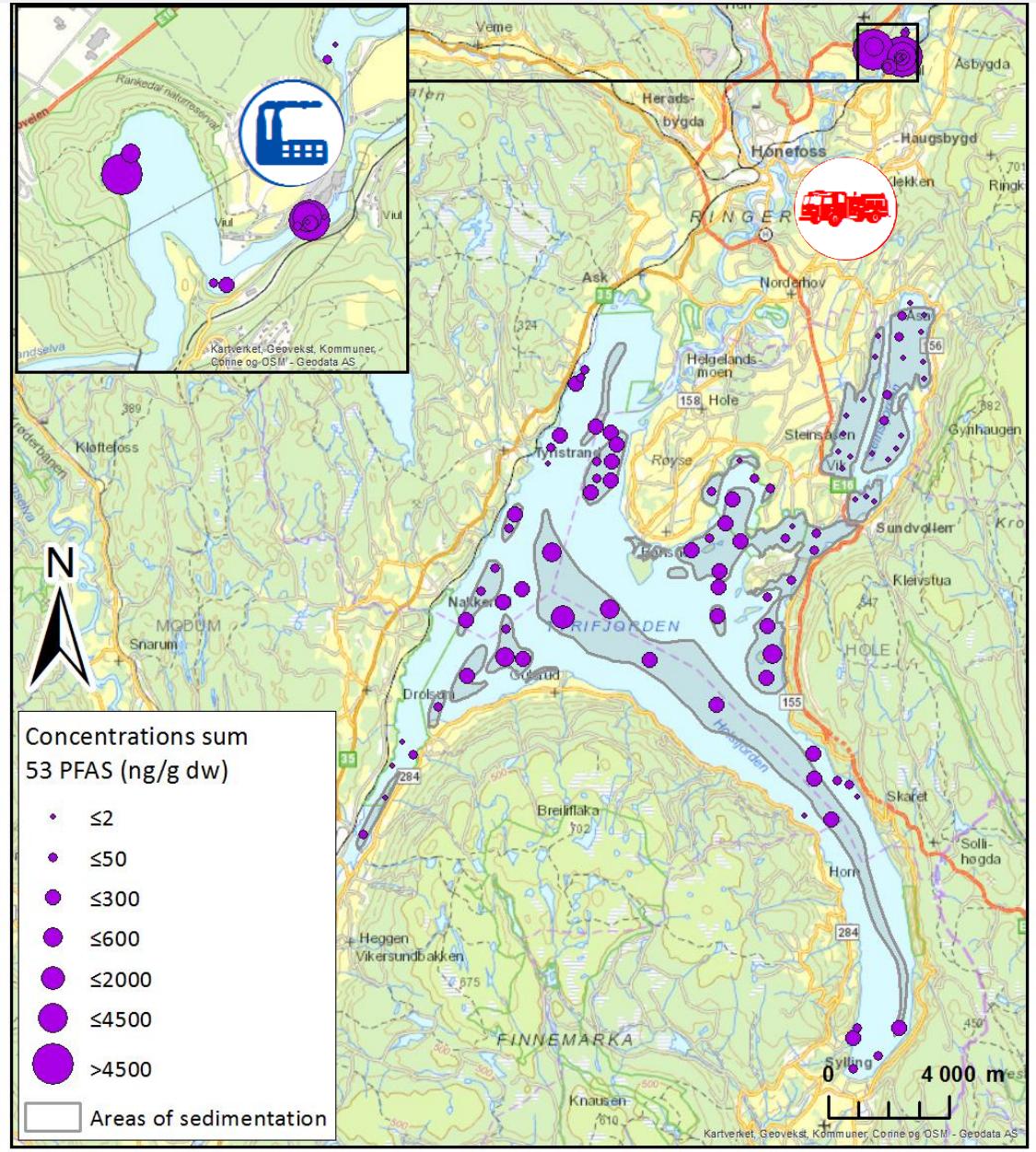
PFSA (Perfluoroalkyl sulfonates)
(max 25 µg/kg)



FTS (Fluorotelomer sulfonates)
(max 509 µg/kg)

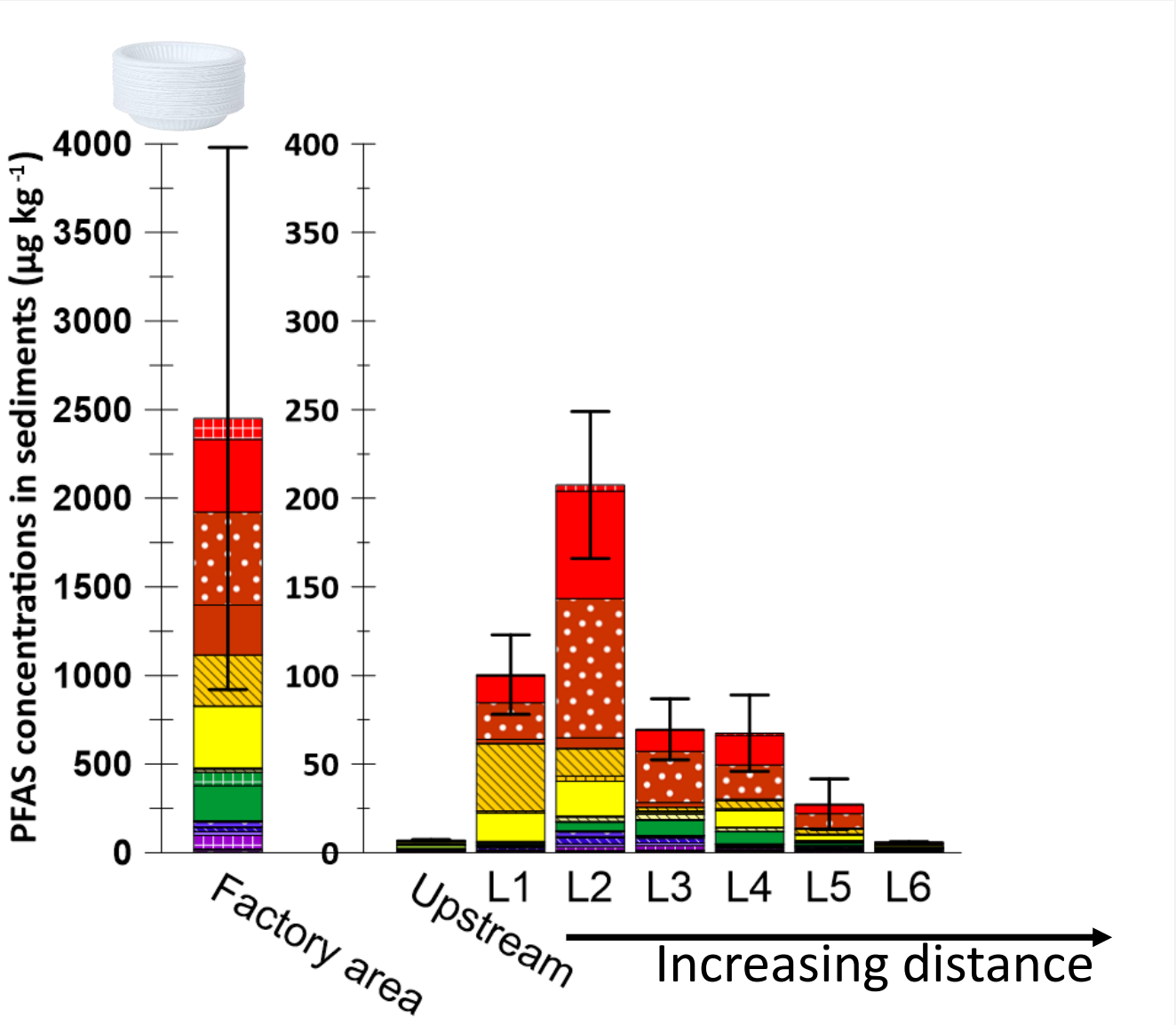


preFOS (e.g. EtFOSAA)
(max 178 µg/kg)



PFAS in sediment and water

Sediments:



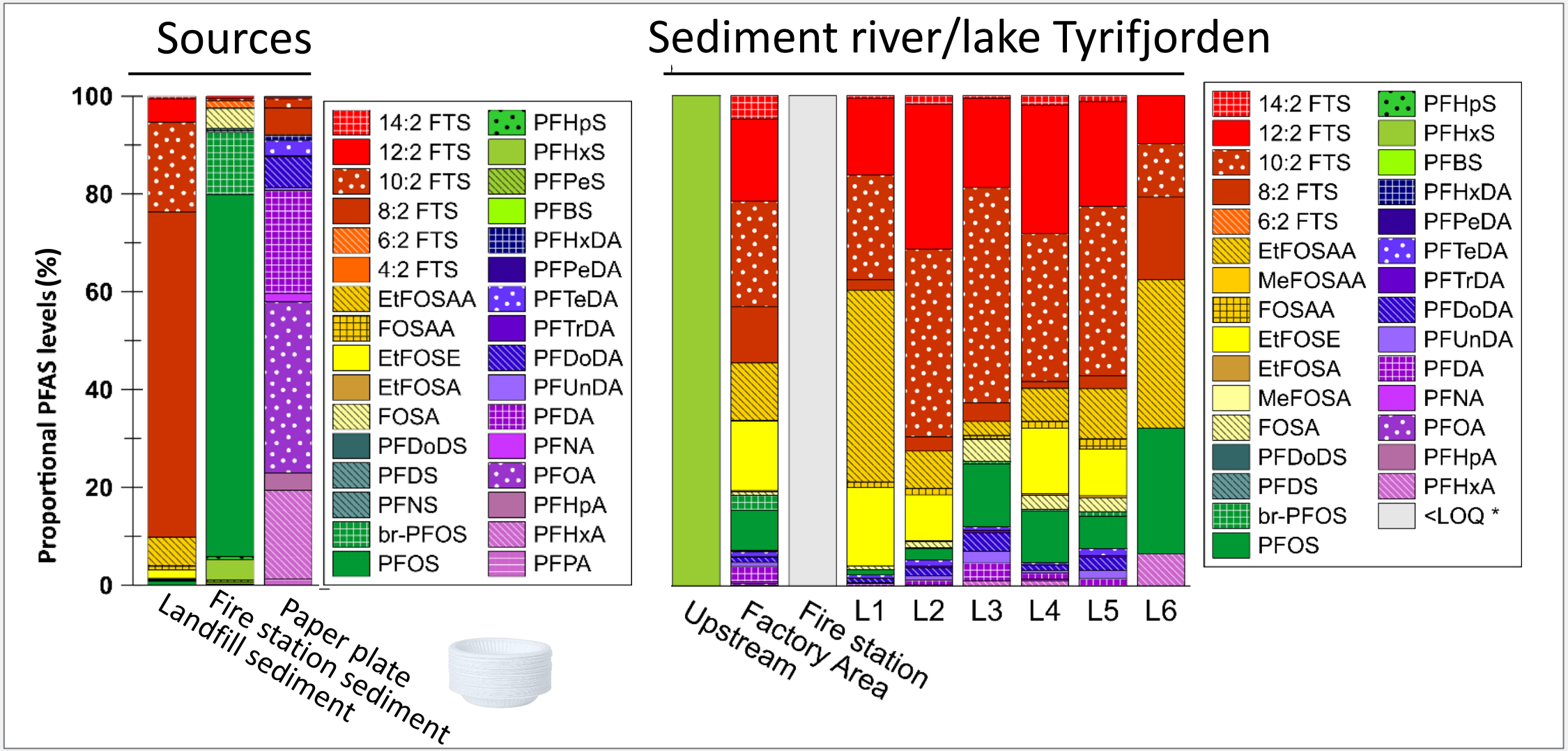
Sediments:

- Highest levels near the factory
- Concentrations at the fire station was below detection limit
- Dominated by preFOS and fluorotelomer sulfonates (FTS)
- PFAS distribution similar downstream

Fluorinated sulfonates (PFSA)
Carboxylic acids (PFCA)
Fluorotelomer sulfonates (FTS)
Perfluoroalkane sulfonamides (PFASA, preFOS)

Sediment and potential sources

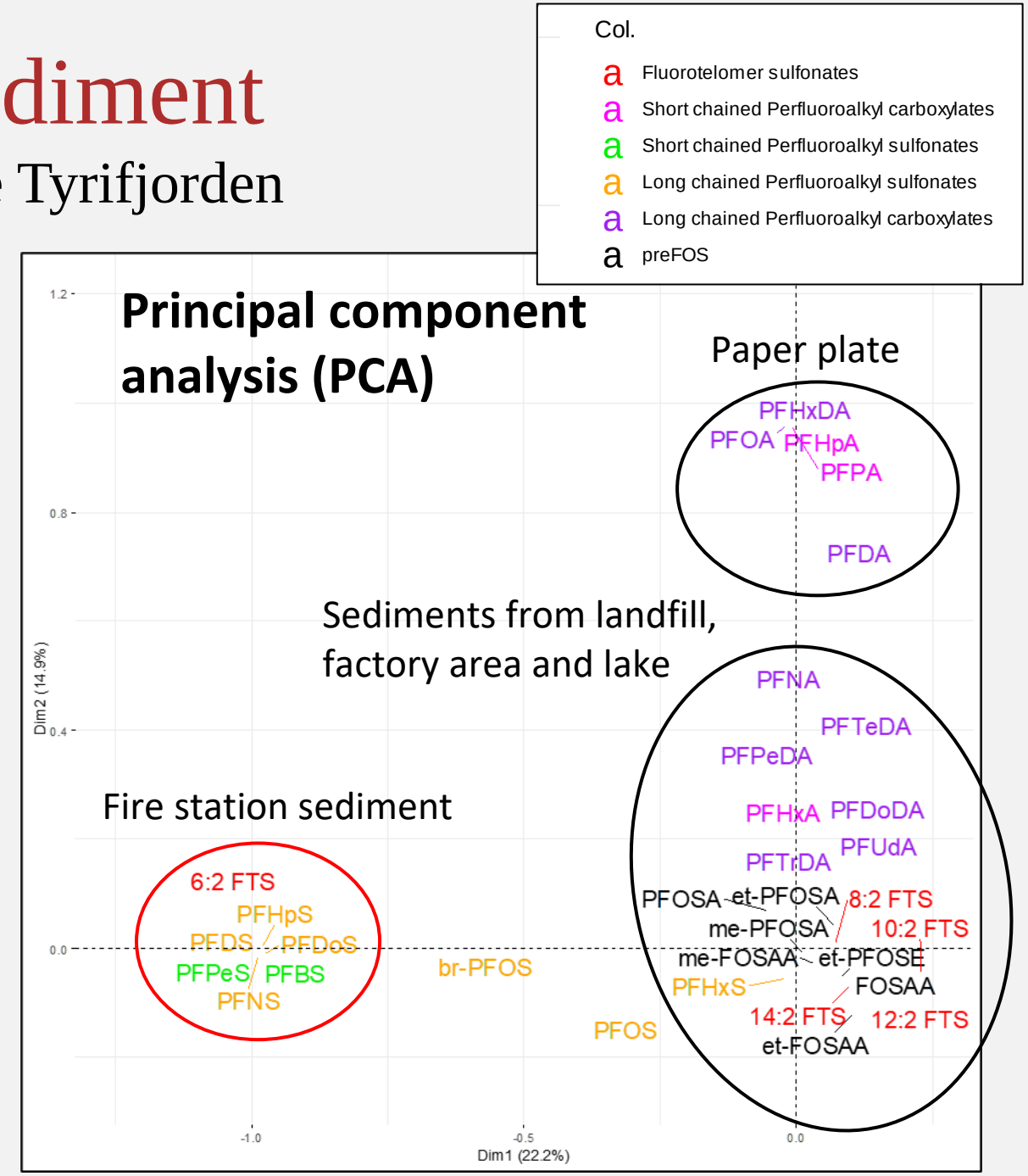
Lake Tyrifjorden

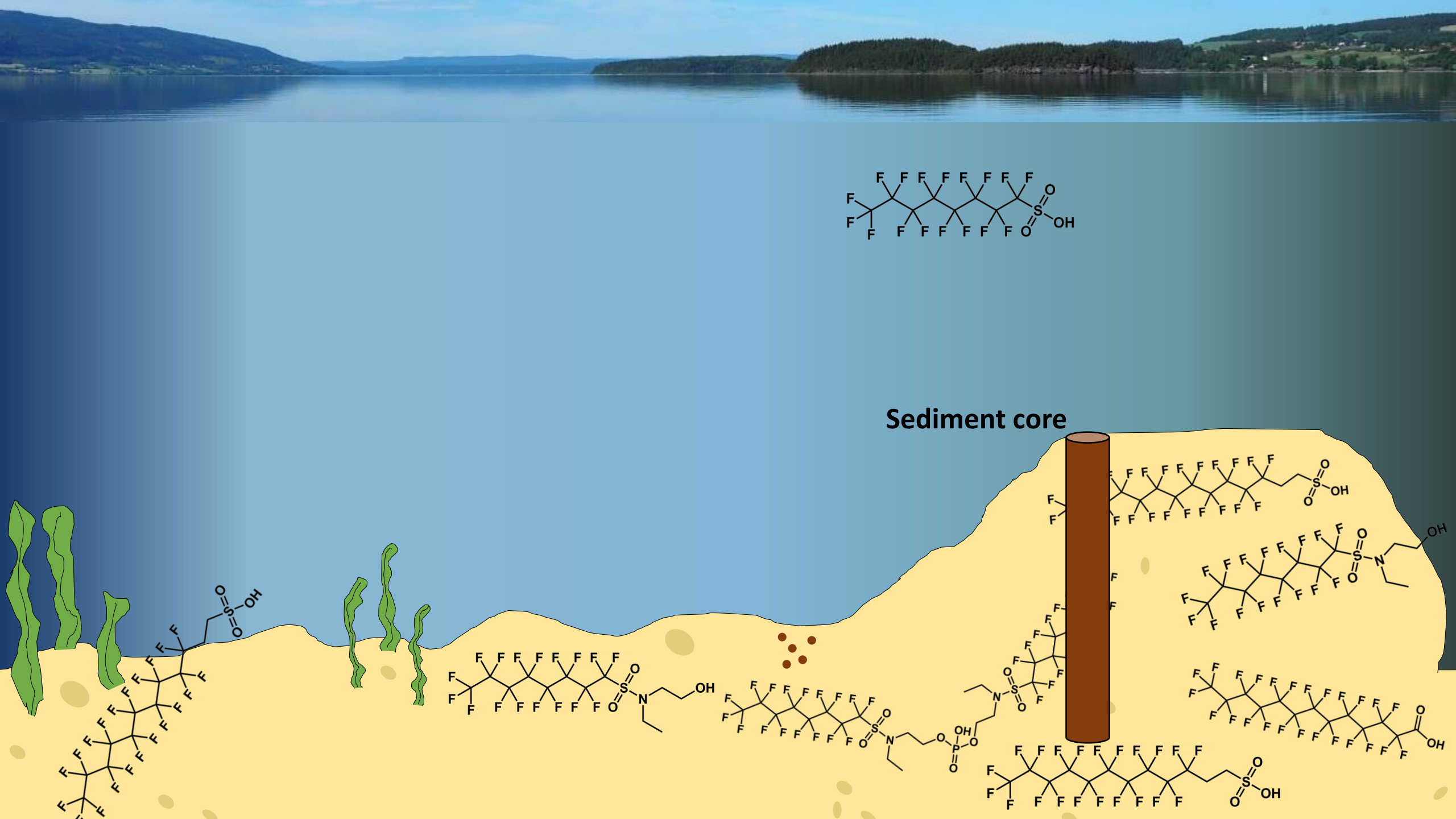


Sediment

Lake Tyrifjorden

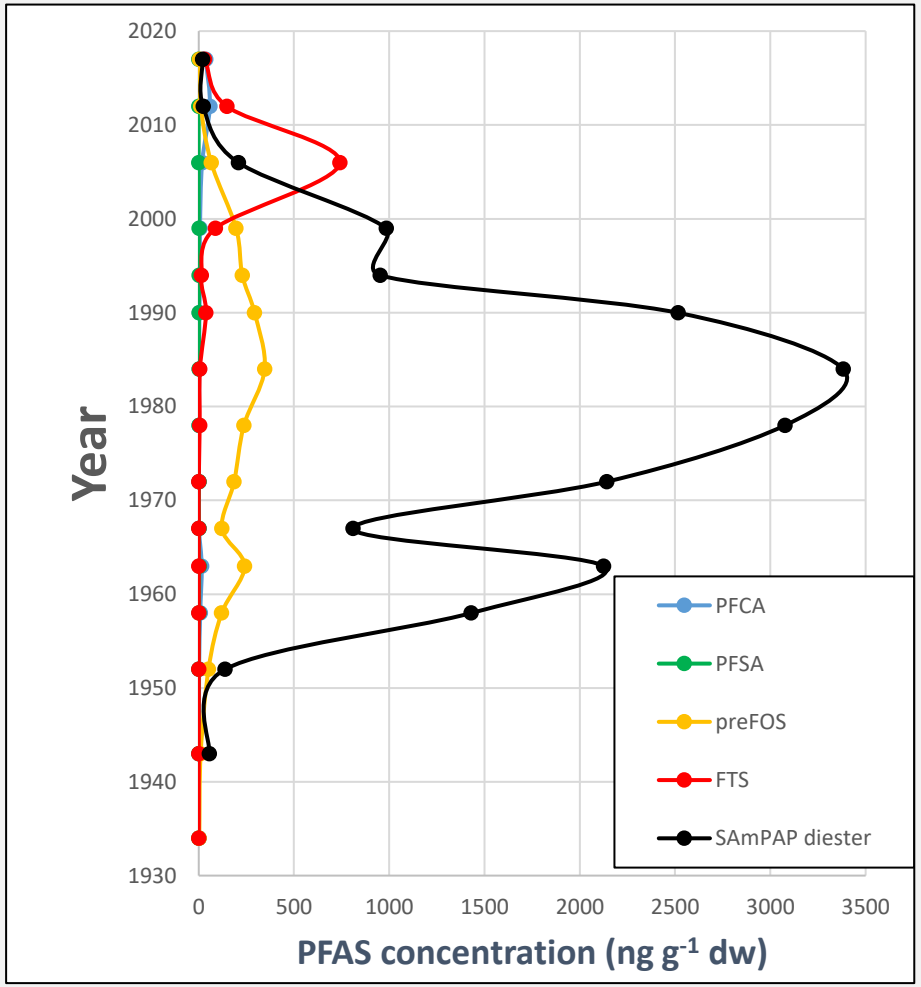
- PFAS profiles in fire station sediments differ to sediments from the river and the lake
- PFAS profiles in both biota and sediments in lake Tyrifjorden are different from AFFF sources

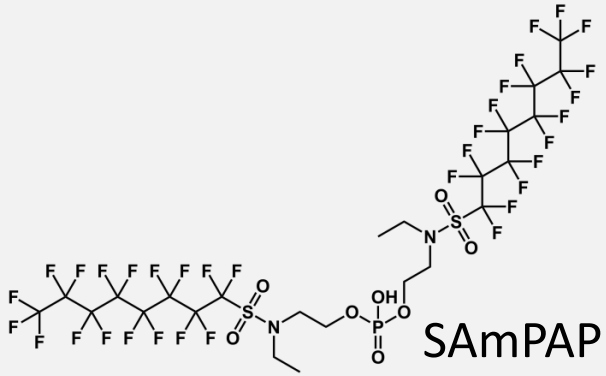



Sediment core

Lake Tyrifjorden - Dated sediment core

- Peak exposure with know compounds has passed
  - preFOS release highest in 1980's
  - preFOS phased out ca. 2002
  - FTS compounds dominant from 2000, peak reached ca. 2006.
  - Decrease coincides with closure of factory in 2013.



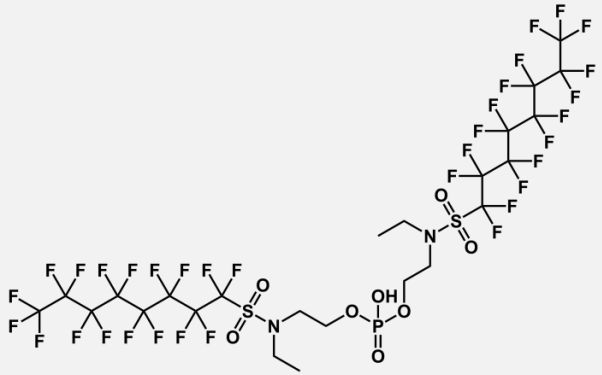


SAmPAP diester

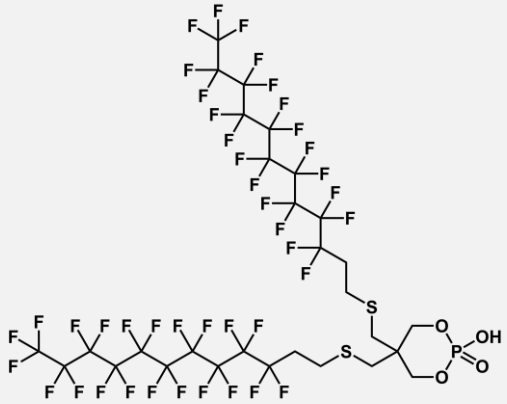
NTNU
Norwegian University of Science and Technology

NGI

Lake Tyrifjorden – Modelling of emission volumes based on the dated sediment core

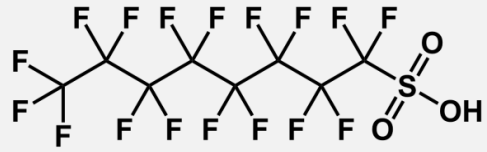


SAmPAP diester



FTMAP (likely precursor to

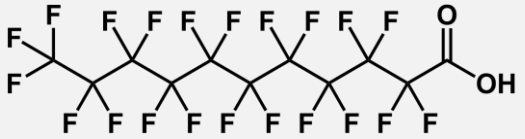
Scotchban ™



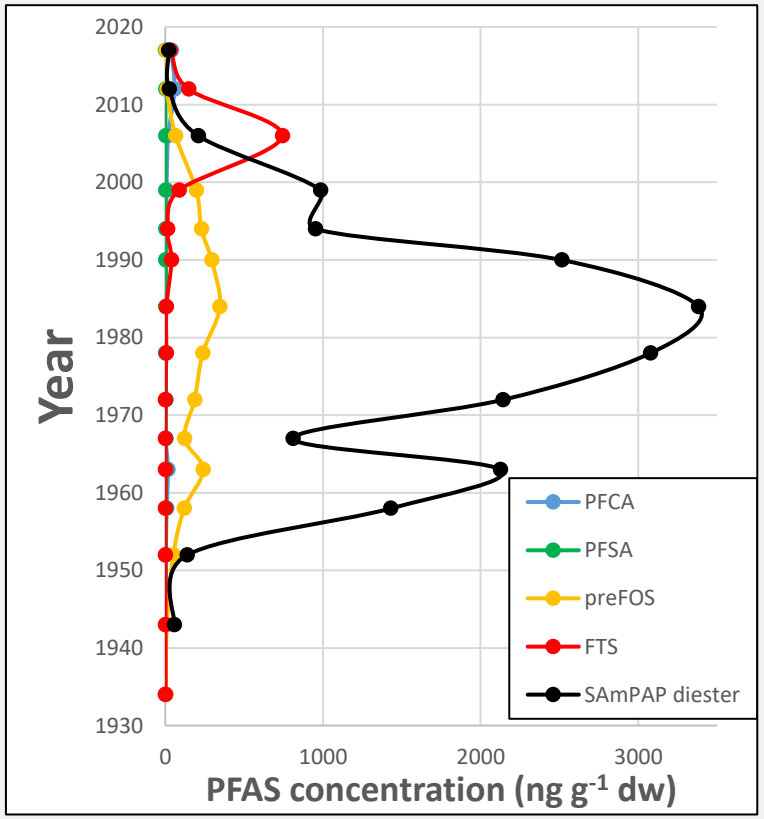
PFOS

FTS mixture

FTS



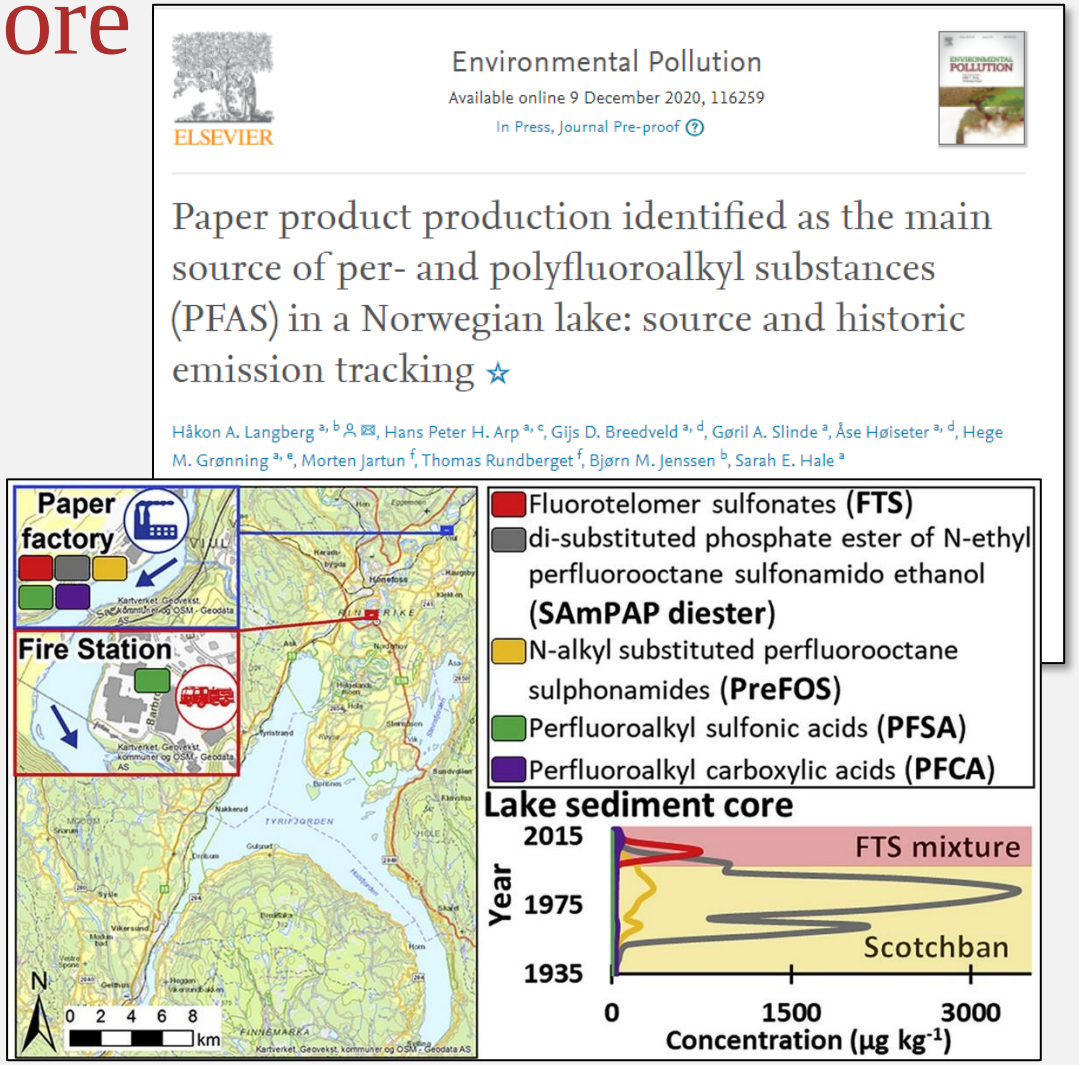
PFCA



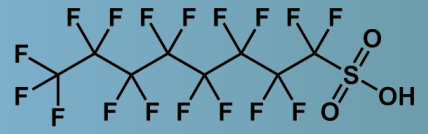
NTNU Norwegian University of Science and Technology

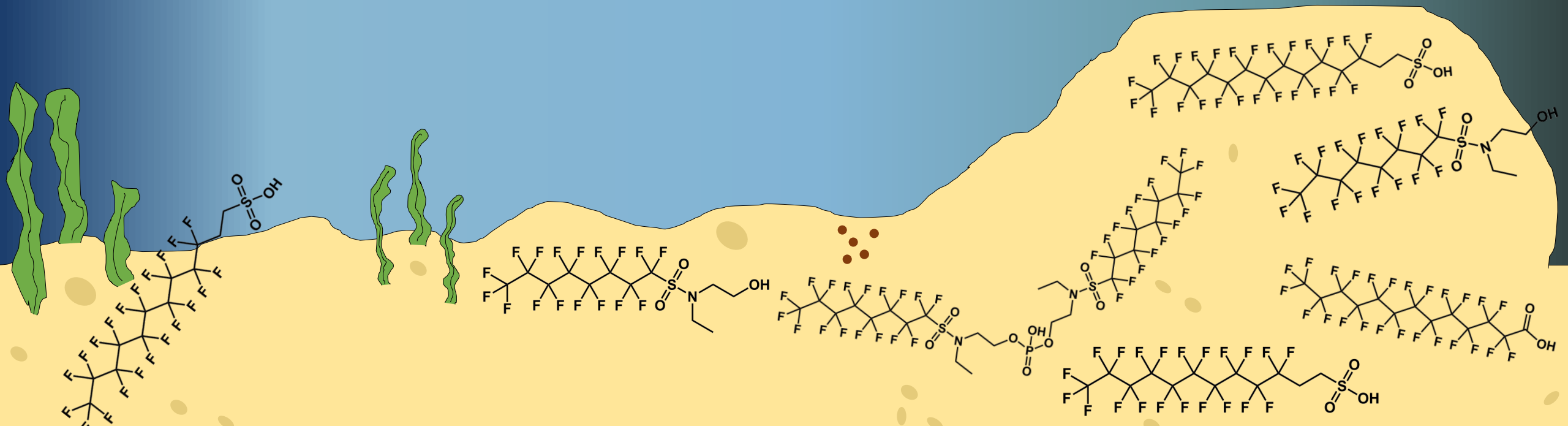
Lake Tyrifjorden – Modelling of emission volumes based on the dated sediment core

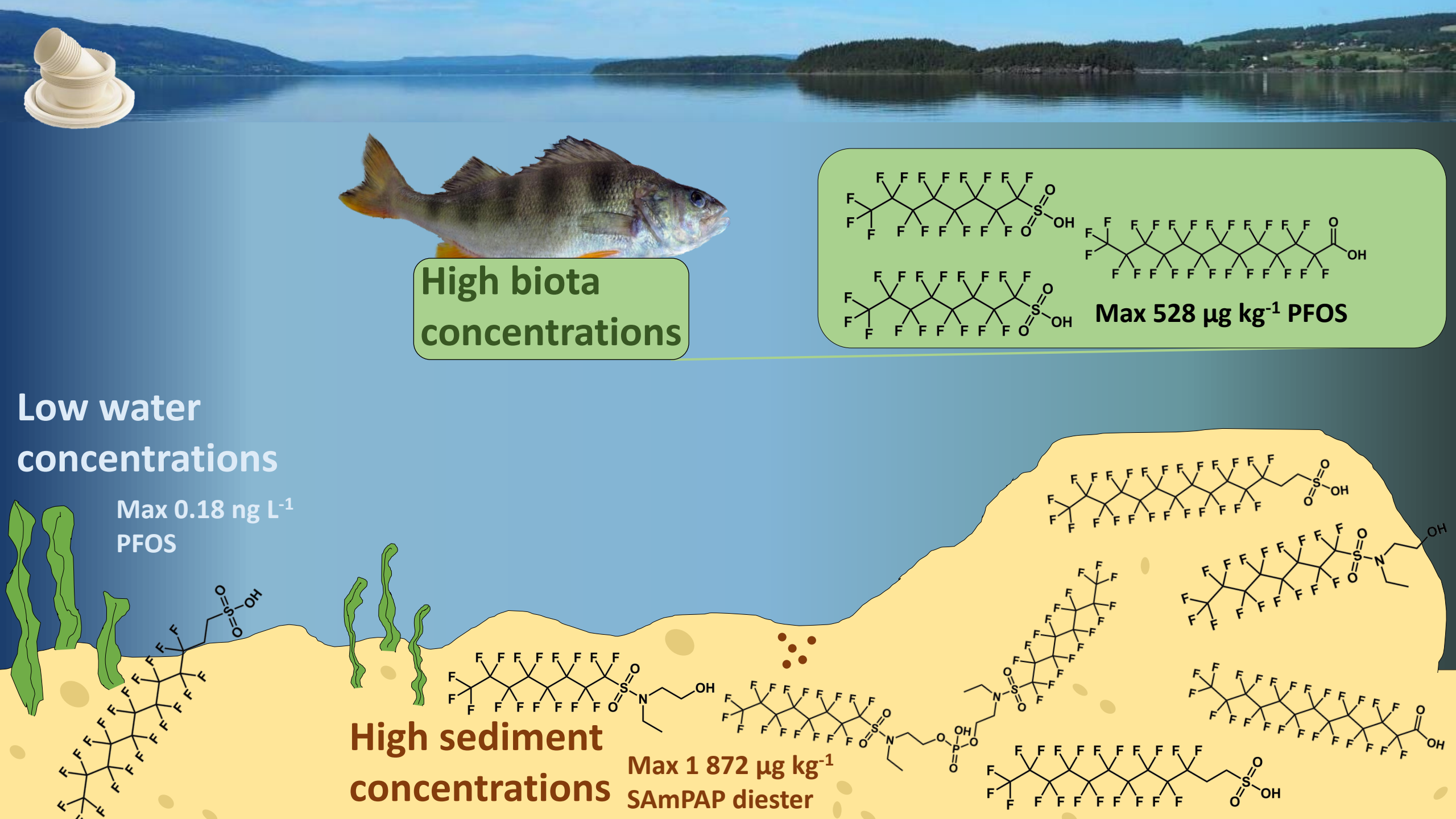
- Extrapolating the core: a total of 40.7 tons of Scotchban and 2.3 tons of the FTS mixture
- Modelling: 42-189 tons of Scotchban have been emitted
- Modelling: 2.4-15.6 tons FTS mixture were emitted
- Previously estimated global emissions of PFOS, preFOS, and POSF are 1228-4930, 1230-8738, and 670 tons, respectively (not included SAmPAP diester)
- Extremely high emission volumes in lake Tyrifjorden



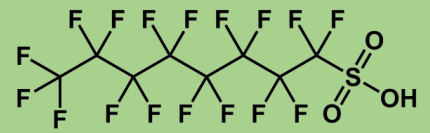
Lake Tyrifjorden

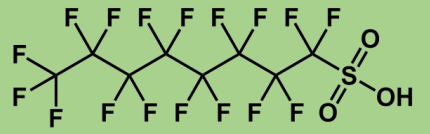


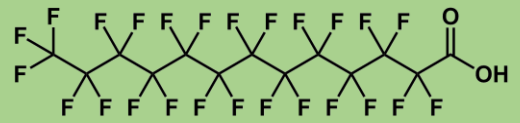



High biota concentrations
Max 528 µg kg-1 PFOS
Low water concentrations
Max 0.18 ng L-1 PFOS
High sediment concentrations
Max 1 872 µg kg-1 SAmPAP diester

High biota concentrations





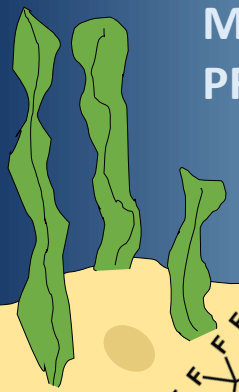


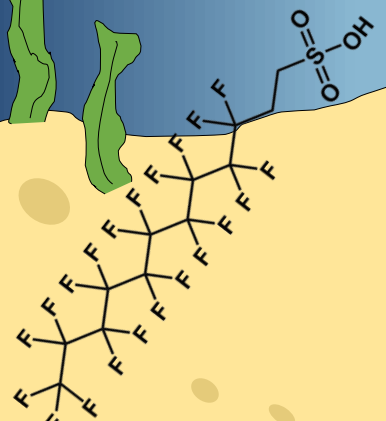
Max 528 µg kg^{-1} PFOS

Low water concentrations

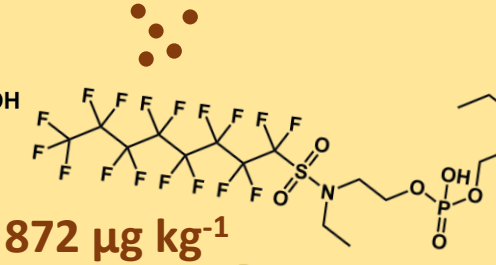
Max 0.18 ng L^{-1} PFOS

TMF

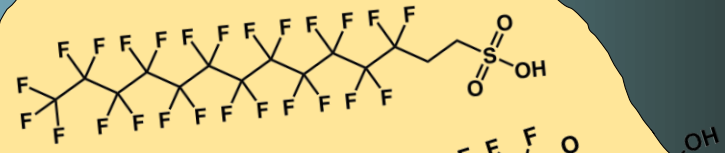


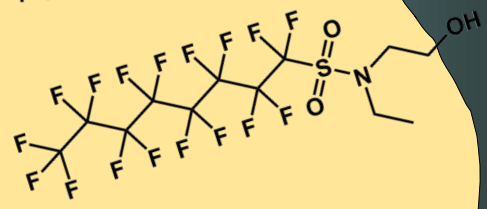


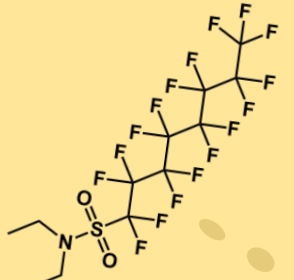
High sediment concentrations

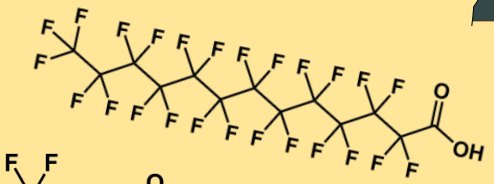


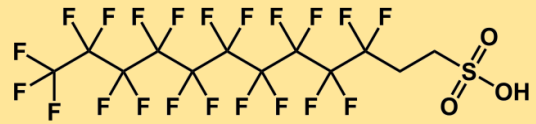
Max 1 872 µg kg^{-1} SAmPAP diester



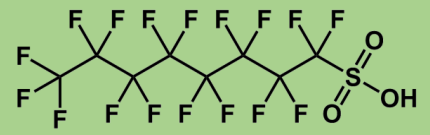


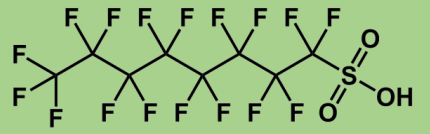


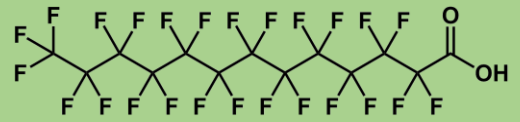




High biota concentrations







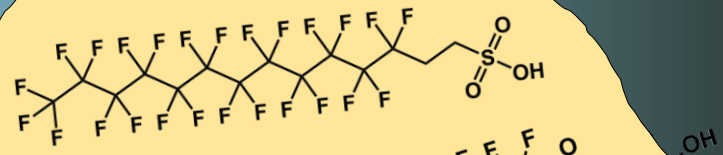
Max 528 µg kg^{-1} PFOS

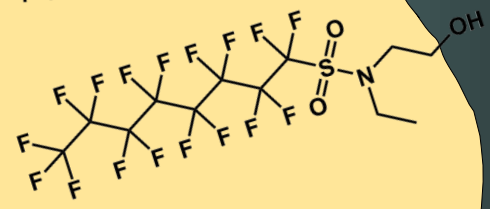
Low water concentrations

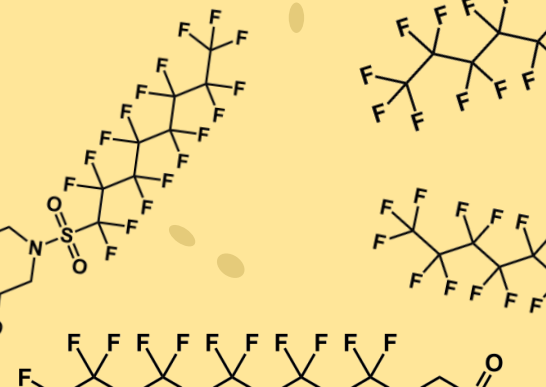
Max 0.18 ng L^{-1} PFOS

TMF

Pore water

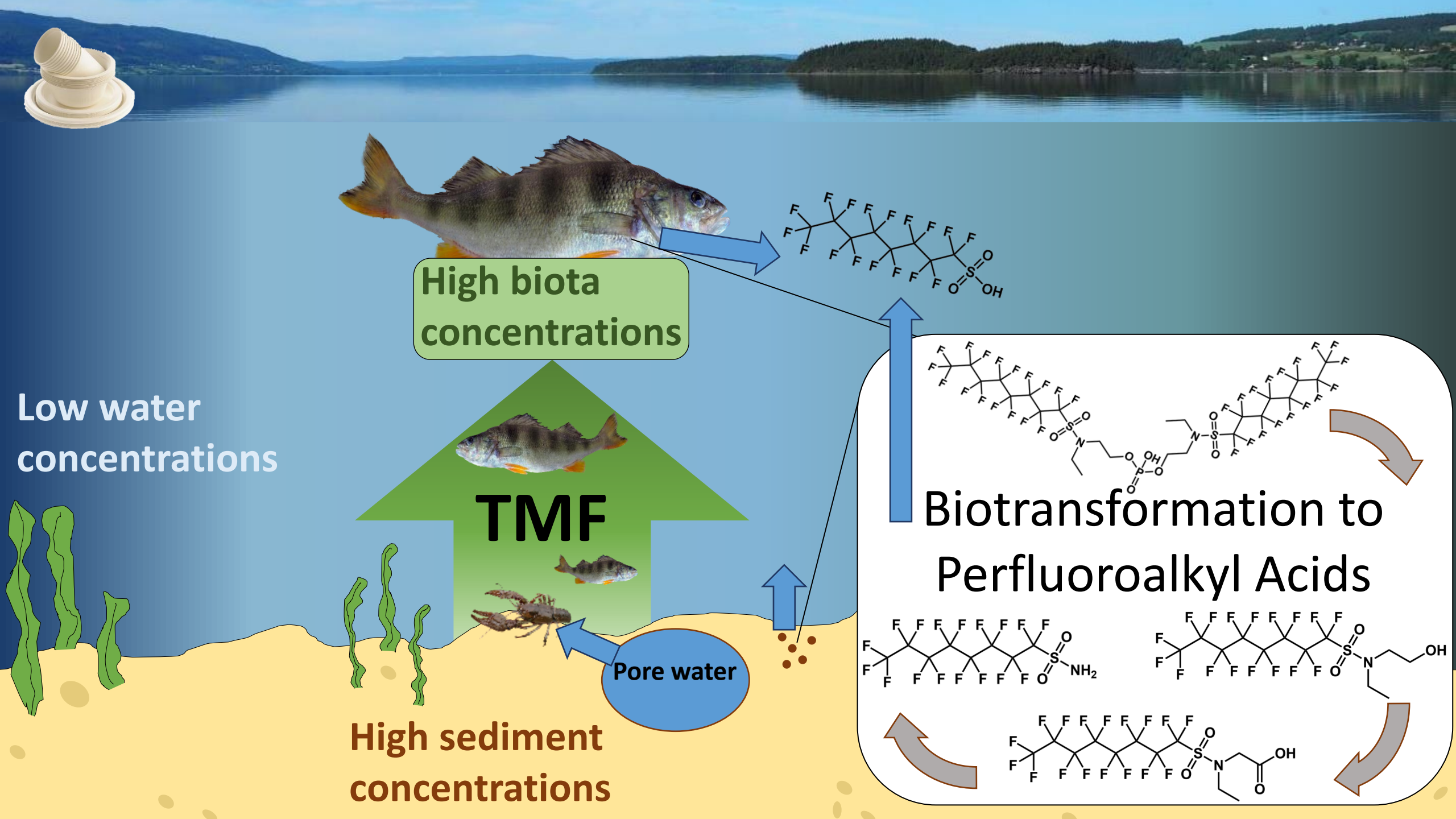






High sediment concentrations

Max 1 872 µg kg^{-1} SAmPAP diester


High biota concentrations
Low water concentrations
TMF
Pore water
High sediment concentrations
Biotransformation to Perfluoroalkyl Acids

Summary and key findings

- A factory producing paper products is concluded to be the main source of the PFAS pollution in lake Tyrifjorden
- PFAS profiles in environmental samples (biota and sediments) are different compared to other PFAS sources (AFFF and long-range atmospheric transport)
- Known and unknown hydrophobic Perfluoroalkyl Acids (PFAA) precursors (from paper industry) in sediments are the major source of PFAA to biota.
- Emitted volumes of PFAS from the factory are very high (tons)
- Paper industry likely represents major point sources elsewhere, and should be the focus of future studies

Environmental Science & Technology

pubs.acs.org/est

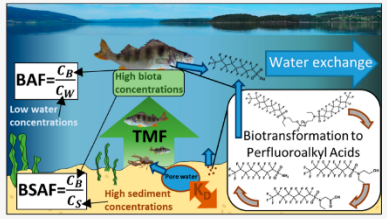
Article

Fluorinated Precursor Compounds in Sediments as a Source of Perfluorinated Alkyl Acids (PFAA) to Biota

Håkon A. Langberg,* Gijs D. Breedveld, Gøril Aa. Slinde, Hege M. Grønning, Åse Høisæter, Morten Jartun, Thomas Rundberget, Bjørn M. Jenssen, and Sarah E. Hale

Read Online

Recommendations | Supporting Information



Environmental Pollution 273 (2021) 116259

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking☆

Håkon A. Langberg [a, b, *], Hans Peter H. Arp [a, c], Gijs D. Breedveld [a, d], Gøril A. Slinde [a], Åse Høiseter [a, d], Hege M. Grønning [a, e], Morten Jartun [f], Thomas Rundberget [f], Bjørn M. Jenssen [b], Sarah E. Hale [a]

[a] Geotechnics and Environment, Norwegian Geotechnical Institute (NGI), Oslo, Norway
[b] Department of Biology, Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[c] Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[d] Department of Geosciences, University of Oslo (UiO), Oslo, Norway
[e] DMR Miljø Og Geoteknikk, Trondheim, Norway
[f] Norwegian Institute for Water Research (NIVA), Oslo, Norway

ARTICLE INFO

Article history:

ABSTRACT

The entirety of the sediment bed in lake Tyrifjorden, Norway, is contaminated by per- and polyfluoroalkyl

Norwegian Geotechnical Institute

NTNU
Norwegian University of Science and Technology

Key references

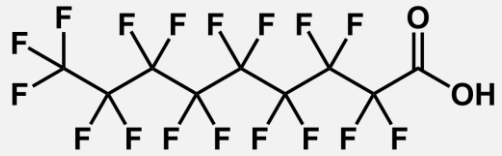
Benskin, J. P.; Ikonomou, M. G.; Gobas, F. A. P. C.; Woudneh, M. B. and Cosgrove, J. R. (2012) 'Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments', Environmental Science & Technology, 46(12), pp. 6505–6514. doi: 10.1021/es300823m.

Trier, X.; Granby, K. and Christensen, J. H. (2011) 'Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging', Environmental Science and Pollution Research, 18(7), pp. 1108–1120. doi: 10.1007/s11356-010-0439-3.

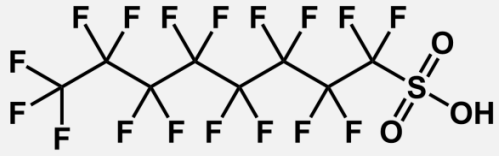
Zhang, S.; Peng, H.; Mu, D.; Zhao, H. and Hu, J. (2018) 'Simultaneous determination of (N-ethyl perfluorooctanesulfonamido ethanol)-based phosphate diester and triester and their biotransformation to perfluorooctanesulfonate in freshwater sediments', Environmental Pollution, 234, pp. 821–829. doi: 10.1016/j.envpol.2017.12.021.

PFAS-levels in sediments

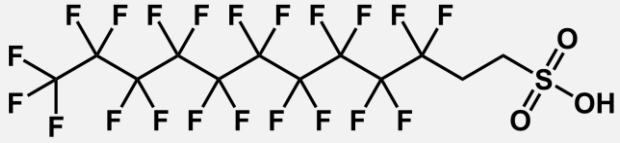
- Low levels at fire station
- Levels of FTS and preFOS high compared to fluorinated sulfonic and carboxylic acids
- Lake levels highest at river mouth



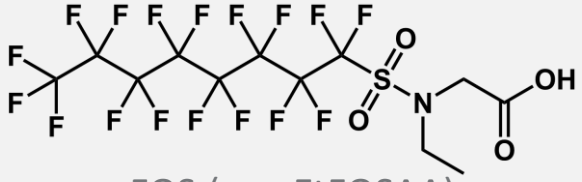
PFCA (Perfluoroalkyl carboxylates)



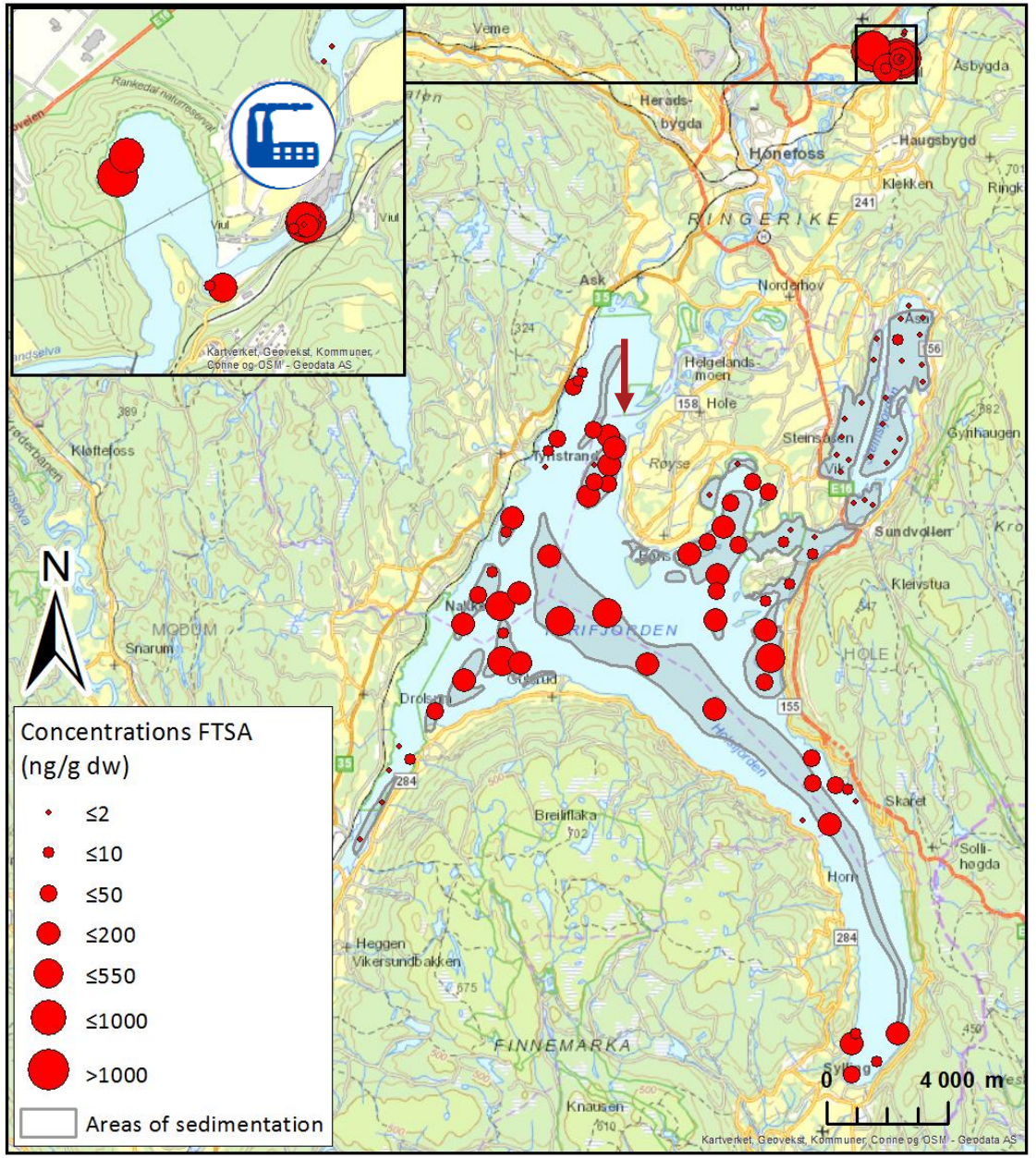
PFSA (Perfluoroalkyl sulfonates)



FTS (Fluorotelomer sulfonates)



preFOS (e.g. EtFOSAA)

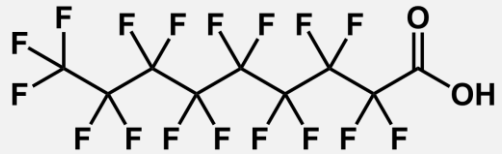


NTNU
Norwegian University of Science and Technology

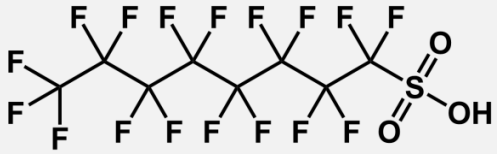
NGI

PFAS-levels in sediments

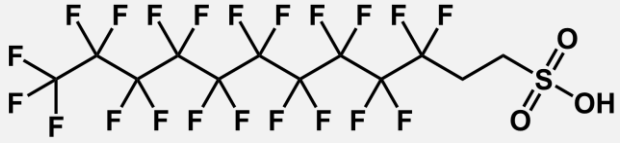
- Low levels at fire station
- Levels of FTS and preFOS high compared to fluorinated sulfonic and carboxylic acids
- Lake levels highest at river mouth



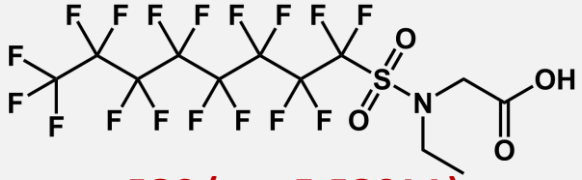
PFCA (Perfluoroalkyl carboxylates)



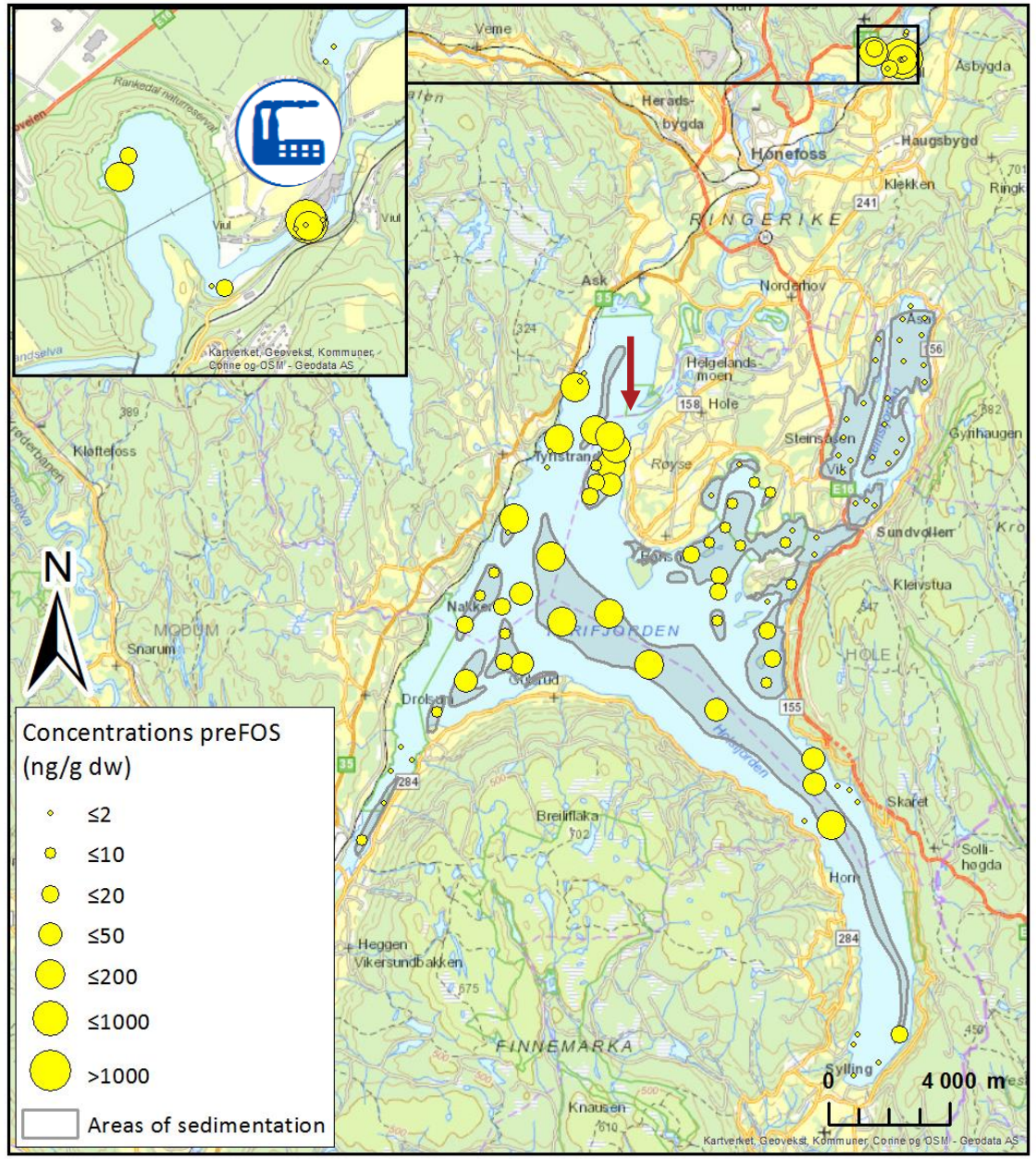
PFSA (Perfluoroalkyl sulfonates)



FTS (Fluorotelomer sulfonates)



preFOS (e.g. EtFOSAA)

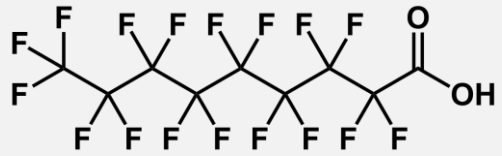


NTNU
Norwegian University of Science and Technology

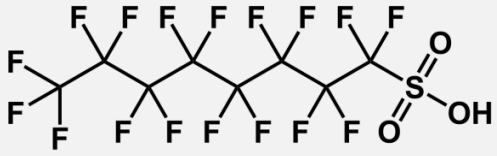
NGI

PFAS-levels in sediments

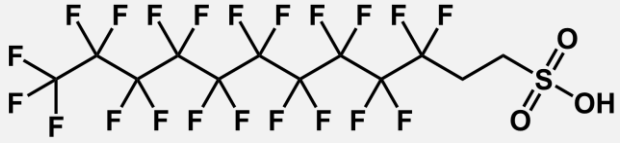
- Low levels at fire station
- Levels of FTS and preFOS high compared to fluorinated sulfonic and carboxylic acids
- Lake levels highest at river mouth



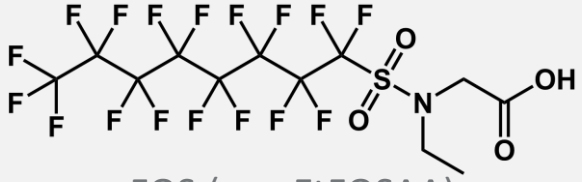
PFCA (Perfluoroalkyl carboxylates)



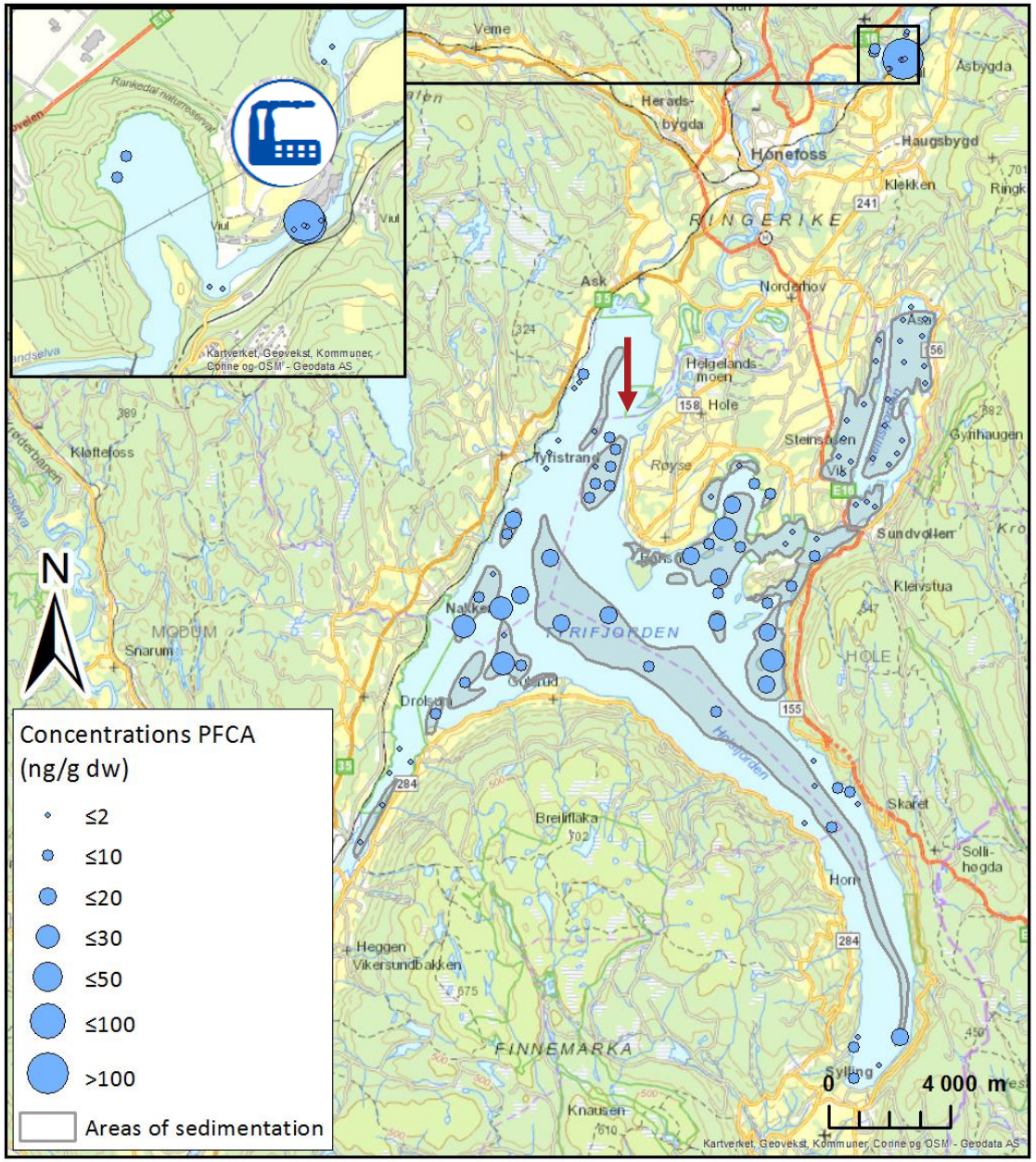
PFSA (Perfluoroalkyl sulfonates)



FTS (Fluorotelomer sulfonates)



preFOS (e.g. EtFOSAA)

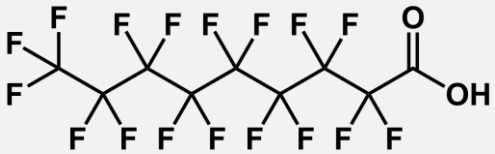


NTNU
Norwegian University of Science and Technology

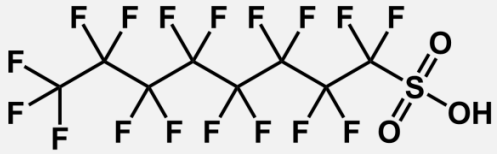
NGI

PFAS-levels in sediments

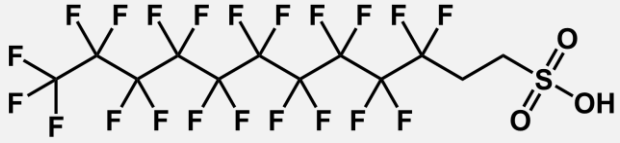
- Low levels at fire station
- Levels of FTS and preFOS high compared to fluorinated sulfonic and carboxylic acids
- Lake levels highest at river mouth



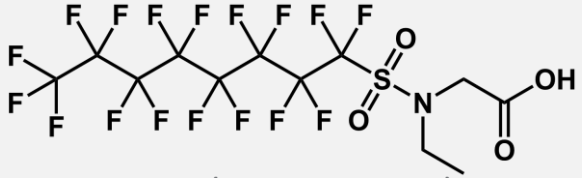
PFCA (Perfluoroalkyl carboxylates)



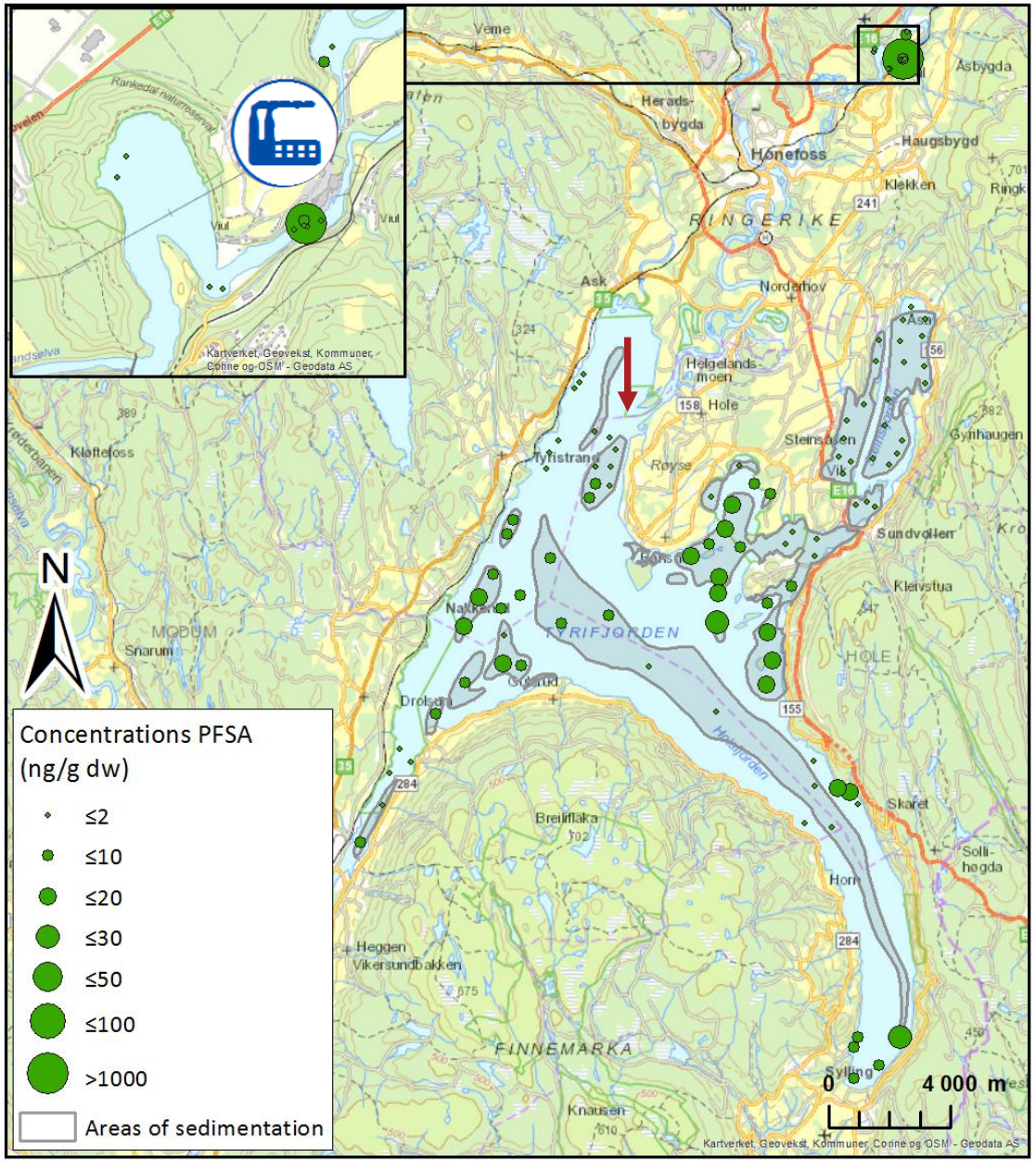
PFSA (Perfluoroalkyl sulfonates)



FTS (Fluorotelomer sulfonates)



preFOS (e.g. EtFOSAA)



NTNU
Norwegian University of Science and Technology

NGI

Totale extractable organic fluorine