





Measurements of CECs under the Norwegian air monitoring program

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The climate and environmental research institute NILU
A part of the research alliance NORIN



What does NILU do?

NILU performs air monitoring from pole to pole:

- Zeppelin in the Arctic
 - Birkenes in Norway
 - Troll in Antarctica
 - Sofienbergparken in Oslo (urban)
- time trends
 - long-range transport



Norwegian air monitoring

		Zeppelin		Birkenes		Sofienbergparken	
	Matrix	Start year	Sampling frequency	Start year	Sampling frequency	Start year	Sampling frequency
S/MCCPs	Gas+particle phase	2013	weekly	2017	monthly	2022	monthly
cVMS	Gas phase	2013	weekly	2017	monthly	2022	monthly
IVMS	Gas phase	2021	campaign			2022	monthly
iPFAS	Particle phase	2006	monthly*	2006	monthly*	2022	monthly
vPFAS	Gas phase	2017	monthly*	2017	monthly*	2022	monthly
nBFRs	Gas+particle phase	2017	monthly*			2022	monthly
OPFRs	Gas+particle phase	2017	monthly*			2022	monthly
Dechloranes	Gas+particle phase	2019	monthly			2022	monthly
Vol. F+Cl sub.	Gas phase	2020	campaign			2022	monthly

*Two samples per months



Background

- The Norwegian priority list:
 - Substances that represent a threat to health and the environment in Norway
 - 75 compounds/compound groups
- Screening programme:
 - Selection of substances based on e.g. physiochemical properties, usage, potential for long-range transport and lack of international regulations
 - Early identification of new environmental contaminants
- Non-target screening:
 - Allow for screening of a wide range of chemicals



Air sampling with GFF/PUF/XAD

- A pump draws air through the sampling media:
 - Glass fiber filter + PUF/PUF → POPs, CPs, dechloranes, nBFRs, OPFRs (aggregated sample)
 - Glass fiber filter + PUF/XAD/PUF → PFAS
- High-volume sampler → 25-30 m³/hour (600-2000 m³)

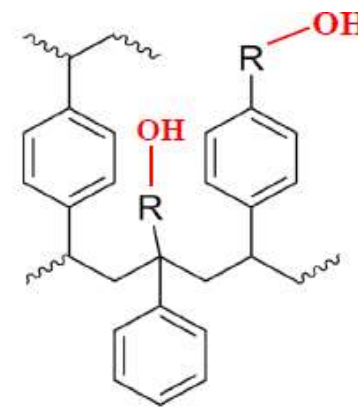


Alternatively with XAD (i.e. polystyrene-divinylbenzene polymer) for more volatile compounds → PFAS

Air sampling with ABN

- Evolute ABN 50 μm (Biotage)
- Low-volume sampler \rightarrow 0.7-1.0 m^3/hour (50-70 m^3)
- Sampling of volatile methyl siloxanes (VMS) and volatile fluorinated and chlorinated substances (vol. F+Cl. sub.)

Modified polystyrene-divinylbenzene polymer



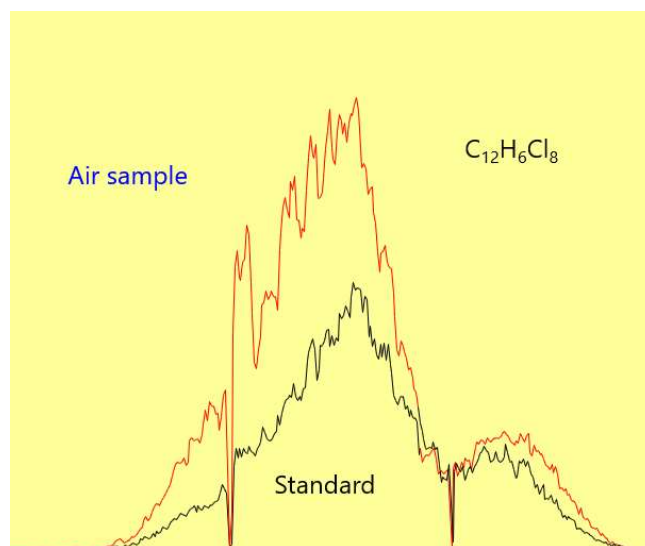
GFF + PUF/PUF

Chlorinated paraffins (CPs)

- Platicizers and fire retardants (e.g. rubber, PVC, consumer products and building materials)
- Both SCCP (since 1997) and MCCP (since 2002) on the Norwegian priority list;
 - SCCPs: C10-C13
 - MCCPs: C14-C17
- Conventional POP method: soxhlet extraction → sulphuric acid → SPE with silica



GC-QTOF (ECNI)

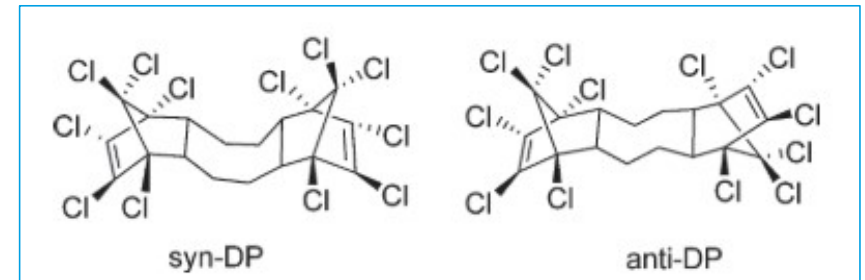


Recent implementation of deconvolution quantification method

GFF + PUF/PUF

Dechloranes

- Chlorinated flame retardants
- On the Norwegian priority list:
 - Dechlorane plus since 2019
 - Dechlorane 602 added 2023
- Conventional POP method: soxhlet extraction → sulphuric acid → SPE with silica → GC-QTOF



Brominated flame retardants (BFRs)

*Uncertain due to possible degradation when treated with acid

Geens et al., Talanta 81 (2010) 1865–1869

On the Norwegian priority list:

- Polybrominated diphenyl ethers (PBDEs) since 1997
- Hexabromocyclododecane (HBCDD) since 1997
- Of the novel BFRs (nBFRs):

Bis(2-ethylhexyl)tetrabromophthalate (TBPH) since 2022

- Conventional POP method: soxhlet extraction → sulphuric acid → SPE with silica
- PBDEs and nBFRs: HRGC/HRMS operating in EI mode
- HBCDD: HPLC/MS-TOF

Allyl 2,4,6-tribromophenyl ether	ATE (TBP- AF)*
α-Tetrabromoethylcyclohexane	α-TBECH (DBE-DBCH)
β-Tetrabromoethylcyclohexane	β-TBECH (DBE-DBCH)
γ/δ-Tetrabromoethylcyclohexane	γ/δ-TBECH (DBE-DBCH)
2-Bromoallyl-2,4,6-tribromophenyl ether	BATE (TBP- BAF)*
Pentabromotoluene	PBT
Pentabromoethylbenzene	PBEb
1,2,3,4,5-pentabromobenzene	PBBZ
Tetrabromo-p-xylene	DTBX
Hexabromobenzene	HBB
2,3-dibromopropyl-2,4,6-tribromophenyl ether	DPTE (TBP-DBPE)
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	EHTBB
1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE
Bis(2-ethylhexyl)tetrabromophthalate	TBPH (BEH-TBP)
Decabromodiphenylethane	DBDPE
Tetrabromobisphenol A	TBBPA

GFF + PUF/PUF

Organophosphorous flame retardants (OPFRs)

Acid labile compounds!

On the Norwegian priority list:

- Tri(2-chloroethyl)phosphate (TCEP) since 2013 (and listed in REACH)
- soxhlet extraction → SPE with EZ-POP (Supelclean) → UPLC-MSMS
- EZ-POP: Zr-silica/C18 + Florisil
- Sample preparation in clean cabinet



Triethyl phosphate	TEP
Tri (2-chloroethyl)phosphate	TCEP
Tri propyl phosphate	TPrP (TPP)
Tris(2-chloroisopropyl)phosphate	TCPP (TCIPP)
Tri isobutyl phosphate	TBP (TiBP)
Butyl diphenyl phosphate	BdBP
Triphenyl phosphate	TPP (TPhP)
Dibutyl phenyl phosphate	DBBP
Tri-n-butyl phosphate	TnBP
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP (TDCIPP)
Tris(2-butoxyethyl)phosphate	TBEP (TBOEP)
Tri resyl phosphate	TCP
2-ethylhexyldiphenyl phosphate	EHDP (EHDPP)
Tri xylyl phosphate	TXP
Tris(4-isopropylphenyl)phosphate	TIPPP
Tris(2-ethylhexyl)phosphate	TEHP
Tris(4-tert-butylphenyl)phosphate	TTBPP
Tris(2,3-dibromopropyl) phosphate	TDBPP
Tris(2-bromo-4-methylphenyl) phosphate	T2B4MP
Tris(4-bromo-3-methylphenyl) phosphate	T4B3MP
Tris(3-bromo-4-methylphenyl) phosphate	T3B4MP
2,2-bis(chloromethyl propane-1,3-diyl tetrakis(2-chloroethyl)bis(phosphate))	V6

Per- and polyfluoralkyl substances (PFAS)

- Large group of synthetic compounds (>10 000) used in industrial processes and consumer products
- PFHxS, PFOS and PFOA are internationally regulated as POPs
- Neutral/volatile PFAS from PUF/XAD/PUF: cold extraction technique (Dreyer et al. 2008) → SPE with Envi-Carb (Supelclean) → GC/LRMS
- Other/ionic PFAS from filter: extraction by sonication bath → SPE with acidified Envi-Carb (Supelclean) → UHPLC/MS-MS

On the Norwegian priority list:

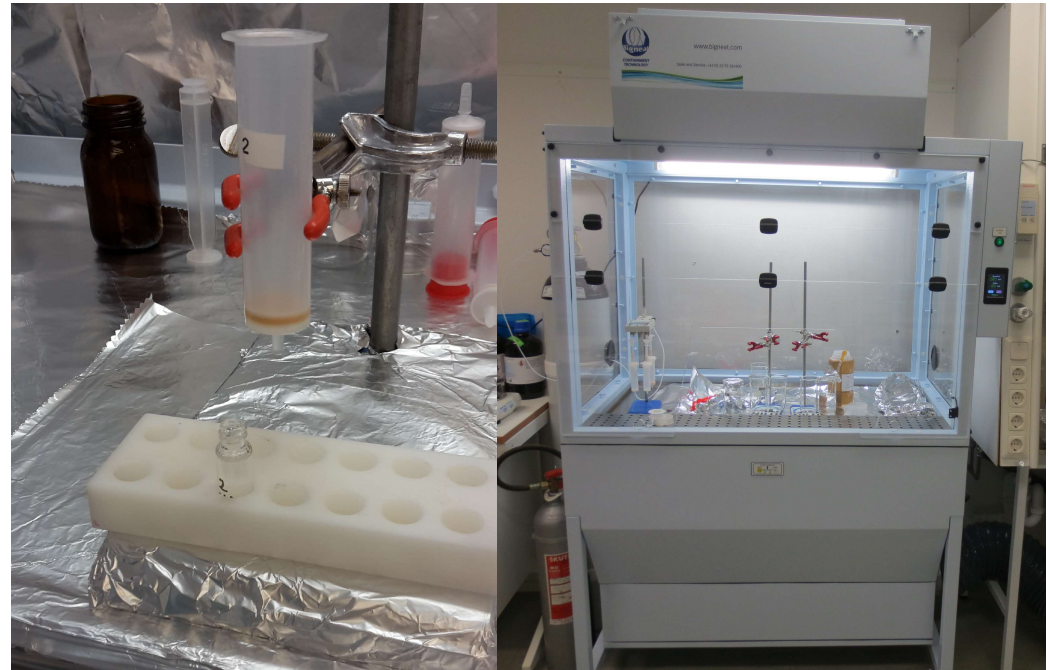
PFOS (2002)
 PFOA (2007)
 C9-PFCA–C14-PFCA (2014)
 PFHxS (2017)
 PFBS (2019)
 PHxA (2020)
 HFPO-DA (GenX) (2020)

Volatile PFAS	
4:2 fluorotelomer alcohol	4:2 FTOH
6:2 fluorotelomer alcohol	6:2 FTOH
8:2 fluorotelomer alcohol	8:2 FTOH
10:2 fluorotelomer alcohol	10:2 FTOH
12:2 fluorotelomer alcohol	12:2 FTOH
N-ethyl perfluorooctanesulfonamide	N-EtFOSA
N-ethyl perfluorooctane sulfonamido-ethanol	N-EtFOSE
N-methylperfluoro-1-octansulfonamide	N-MeFOSA
N-Methyl perfluorooctanesulfon-amido-ethanol	N-MeFOSE

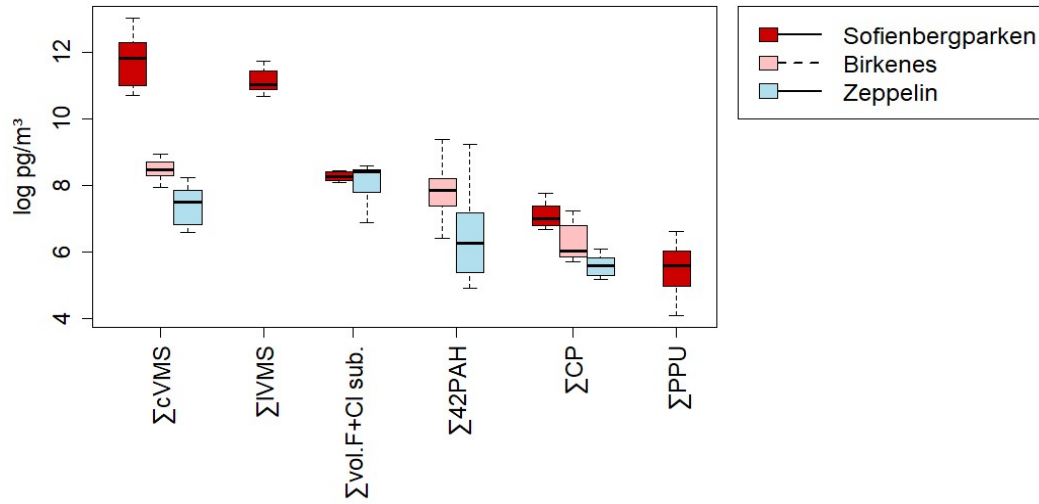
ABN

Volatile methyl siloxanes (VMS)

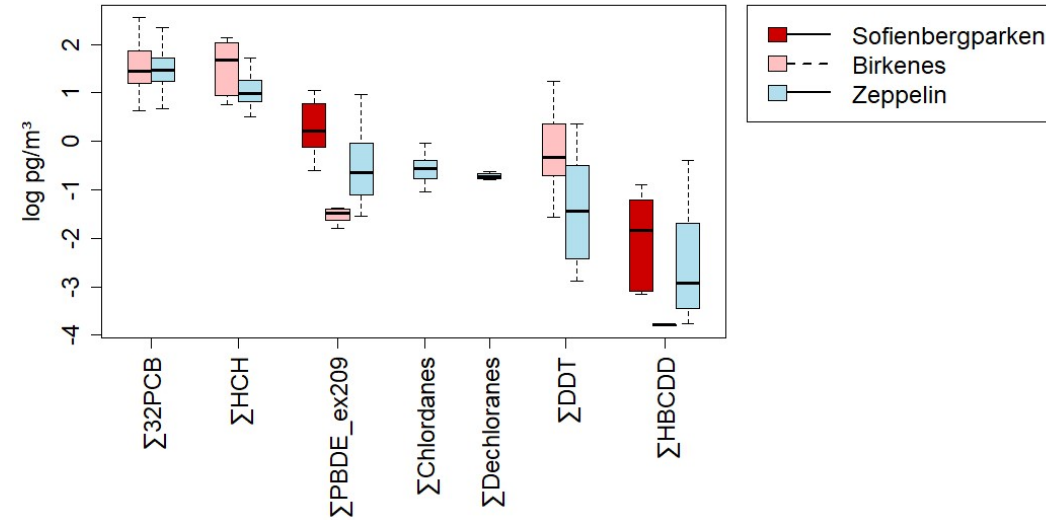
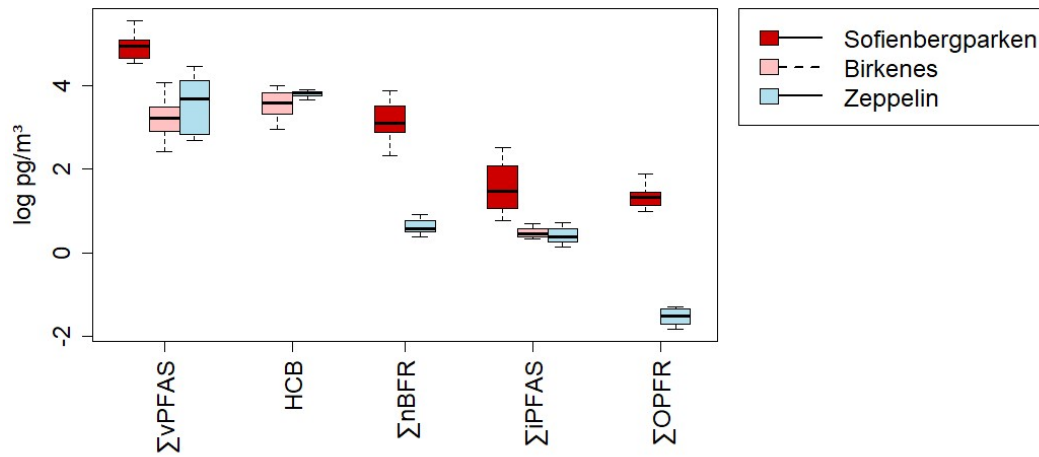
- Minimal sample treatment → elution only
- Clean cabinet and no use of personal-care products
- Analysis with GC-LRMS



Results from Norwegian air monitoring 2022



- Concentrations ranging over eight orders of magnitude
- Highest concentrations for the CECs





Thank you!

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