wissen schafft nutzen

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Long-range Transport and Spatial Distribution of Organophosphate Flame Retardants and plasticizers in the Marine and Polar Environment

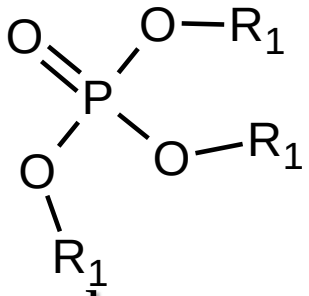
Xie Zhiyong Jing Li, Jianhui Tang, Wenying Mi, Weihai Xu, Senchao Lai, Ralf Ebinghaus

Helmholtz-Zentrum Geesthacht, Zentrum for Materials and Coastal Research, Institute of Coastal Research

Geesthacht , Germany

ICCE 2017 Oslo 20.06.2017

What are OPEs?



organophosphate esters **(OPEs)**

Flame retardant

Plasticizer

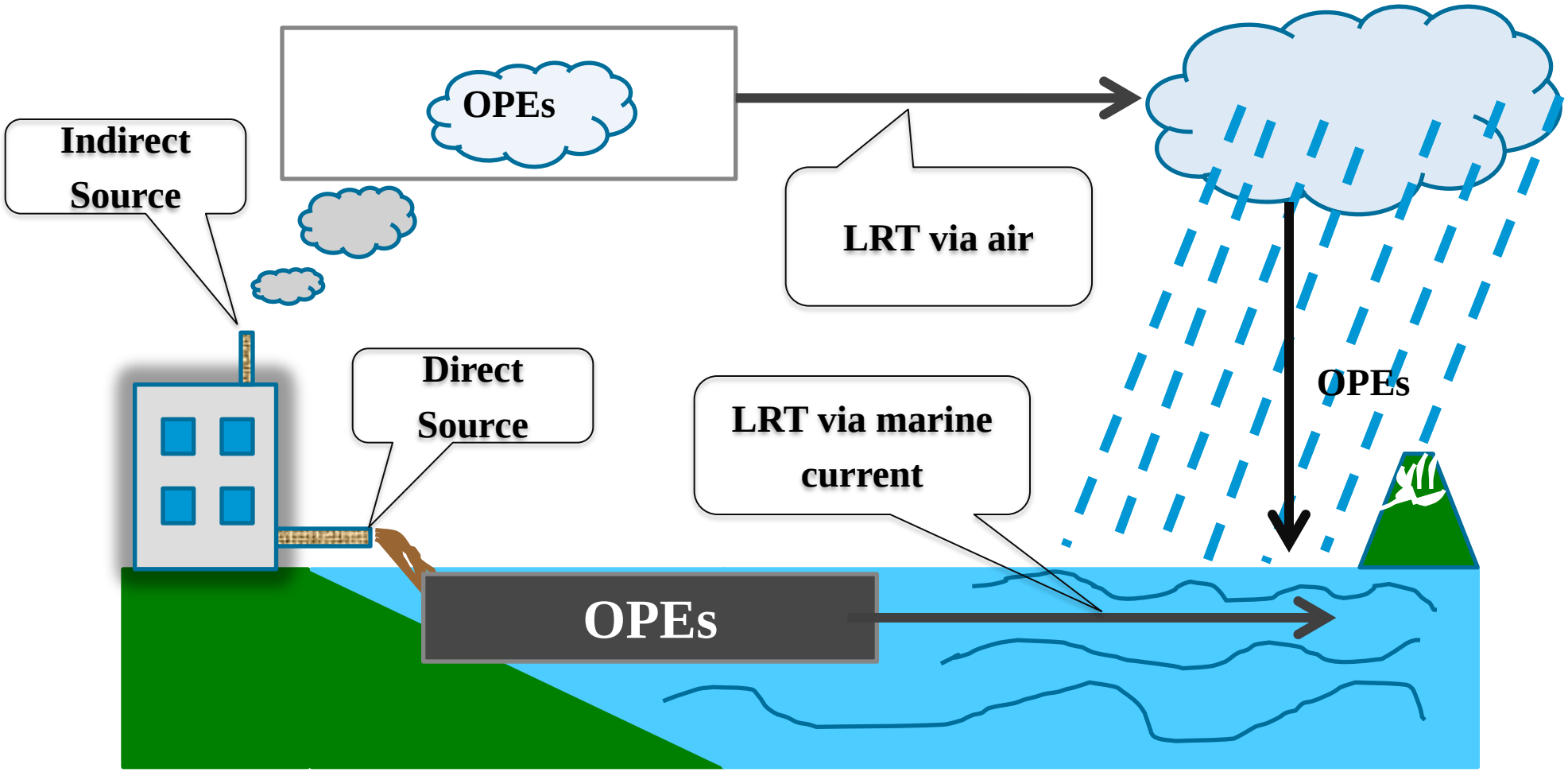
- The annual European consumption of OPEs as FRs was 91.000 tons in 2006
- The global consumption of OPEs amounted to 500.000 tons in 2011, and is expected to reach 680.000 tons in 2015

European Flame Retardant Association (www.cefic-efra)

Van der Veen et al.,2012

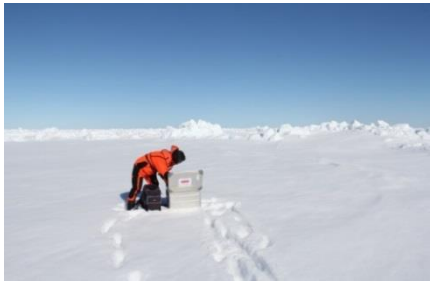
The sources and long-range transport of OPEs

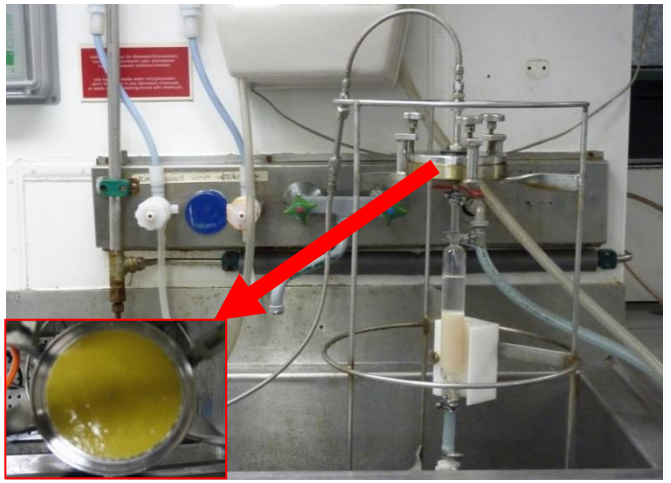
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research



Sampling on board RV Polarstern

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

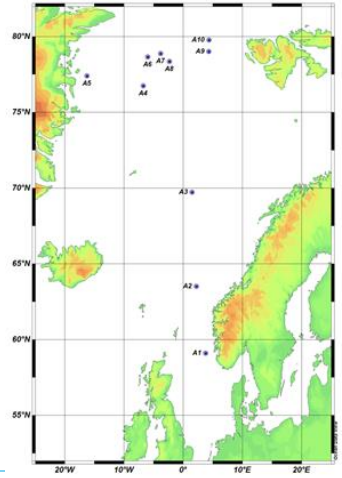




Water sampling:
Glass fiber filter (pore size 0.7 µm)
1-L seawater samples were collected in PP bottles

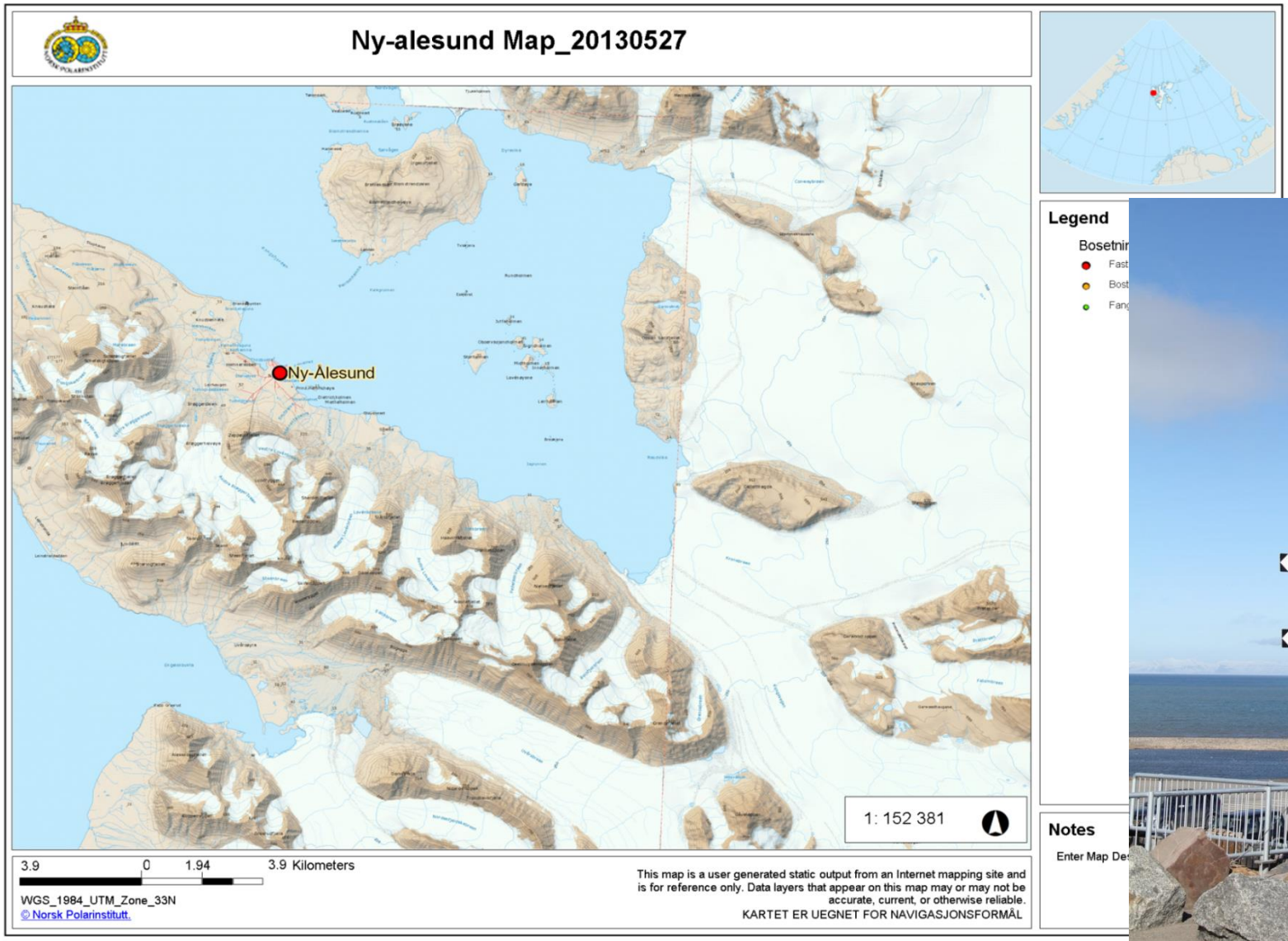
Snow sampling:
on the Arctic sea ice
10-L stainless steel barrels

Air sampling:
PUF/XAD-2 column for vapor phase
Glass fiber filter (Ø150 mm, pore size 0.7 µm)
Air sample volume: 300-500 m^3



Arctic Research Station Ny-Alesund, Svalbard

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research



Northwestern of Svalbard
(78°55'24"N, 11°55'15"E**)**

Ny-Alesund: AWIPEV Research Station

Bayelva ~ 2.5km West

Corbel ~ 6km East

New Hall Storage

UWO

High-volume air sampling at German Observatory

KB Marine Lab

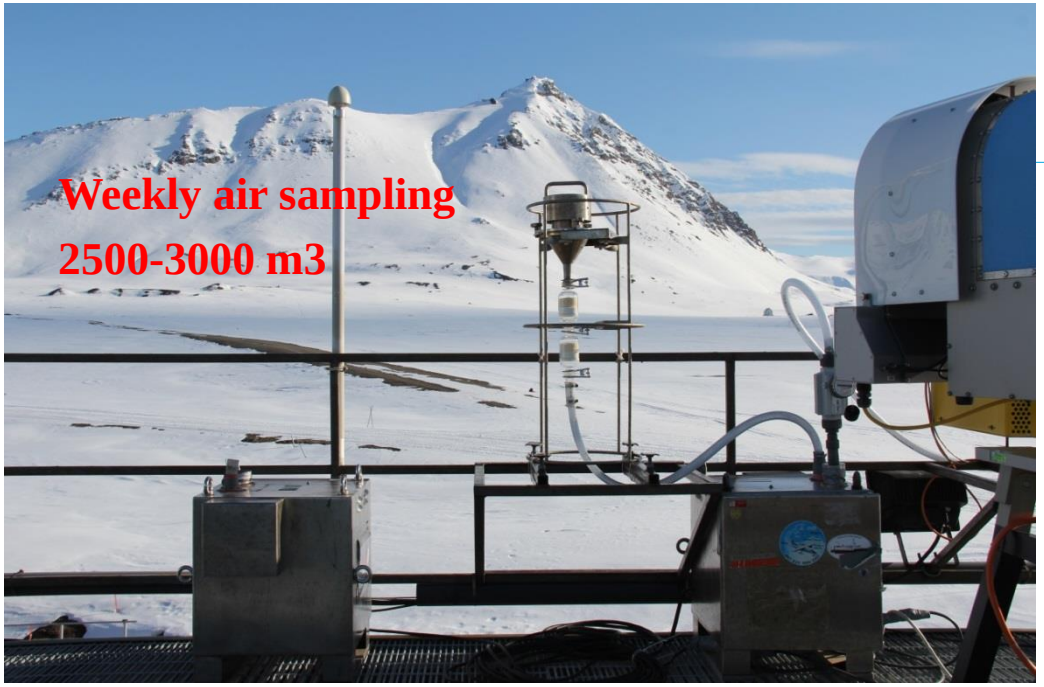
Vaskeriet Lab

Scooter garage

NDACC Observatory

Blue House

Rabot


Weekly air sampling
2500-3000 m3

Analytical method for OPEs

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

OPEs

air

GFF | PUF/XAD-2

surface snow

0-10 cm | 1 L

surface seawater

-11m | 1 L

Soxhlet extraction
DCM 16 hours

Liquid-Liquid extraction
with 3 x 50 ml DCM

GC-MS/MS
HP-5ms column
30 m × 0.25 mm
i.d. × 0.25 µm

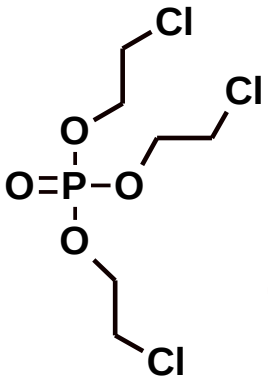
Clean lab in Helmholtz-Zentrum Geesthacht

Xie et al., 2008

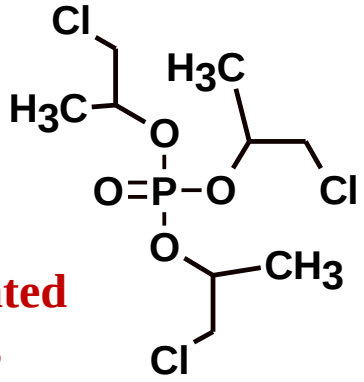
Target compounds

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

TCEP

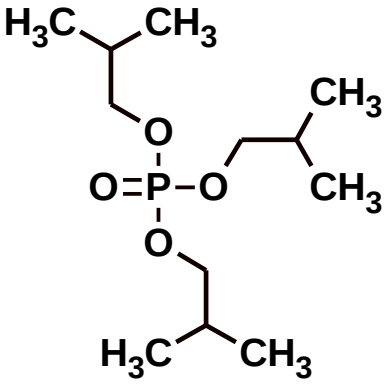


TCPP

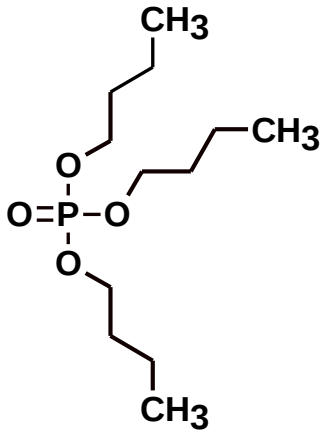


Chlorinated OPEs

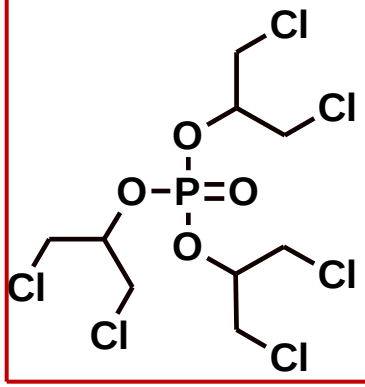
TiBP



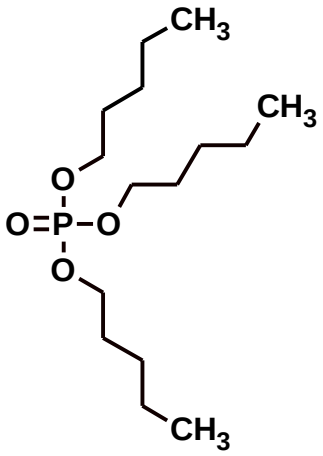
TnBP



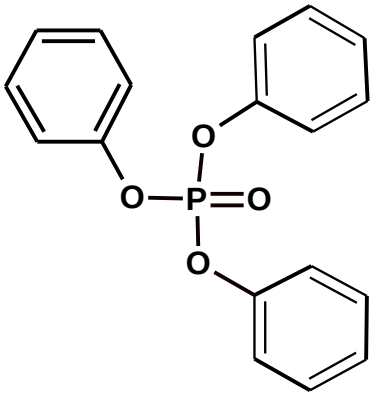
TDCP



TPeP

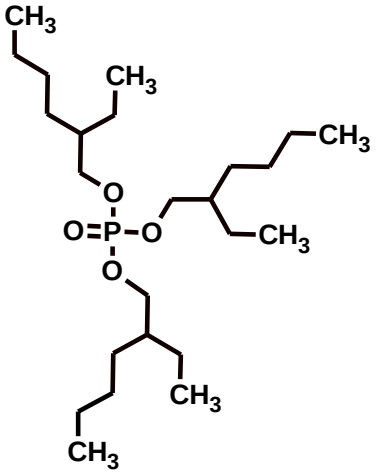


TPhP



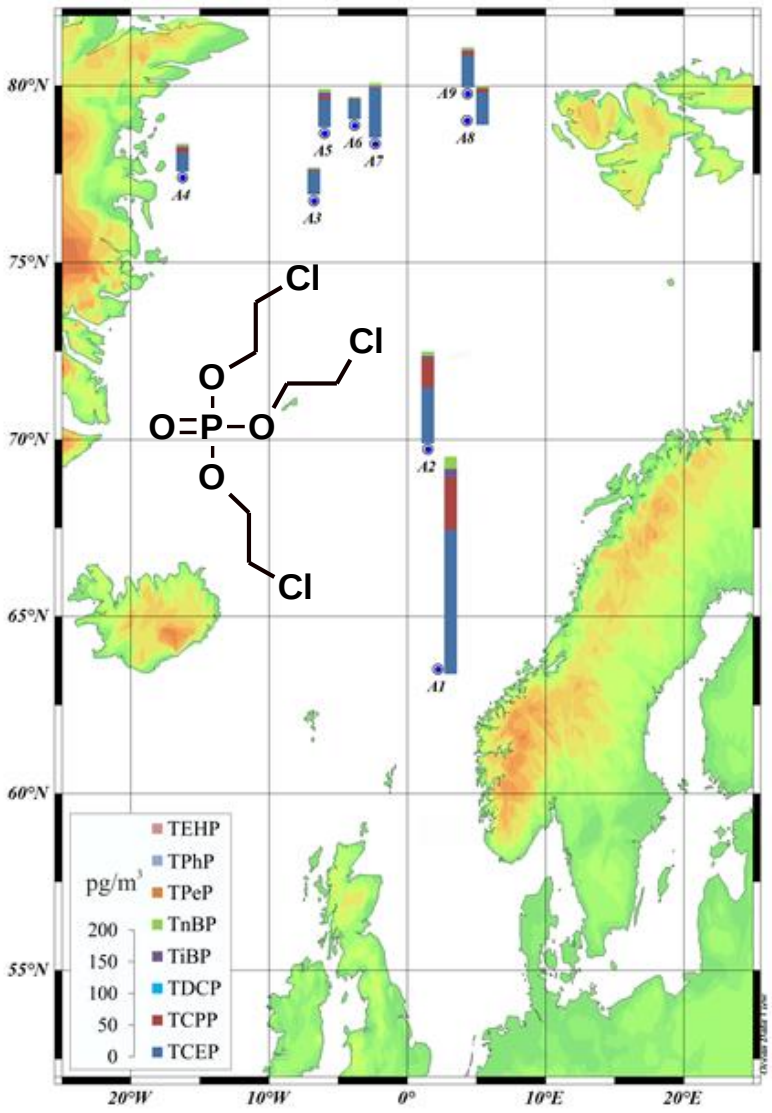
Non-chlorinated OPEs

TEHP



OPEs in atmosphere

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

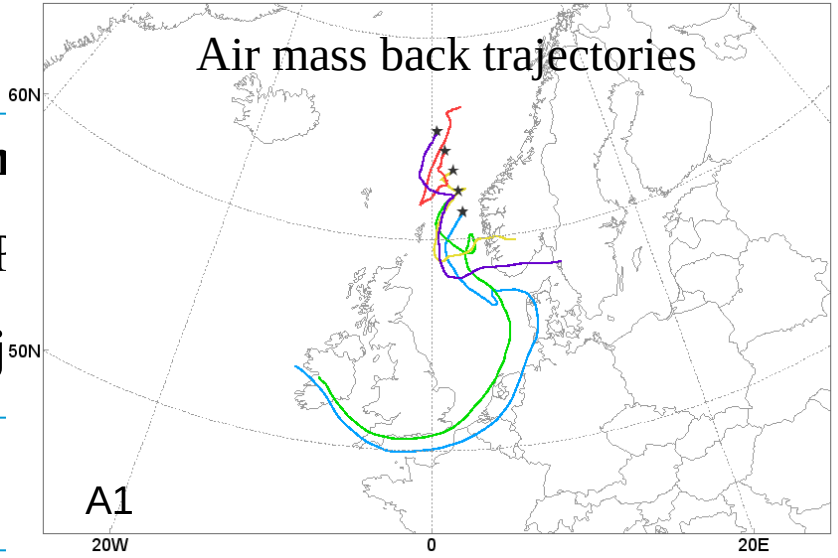


Sam

ΣOH

Maj

Air mass back trajectories



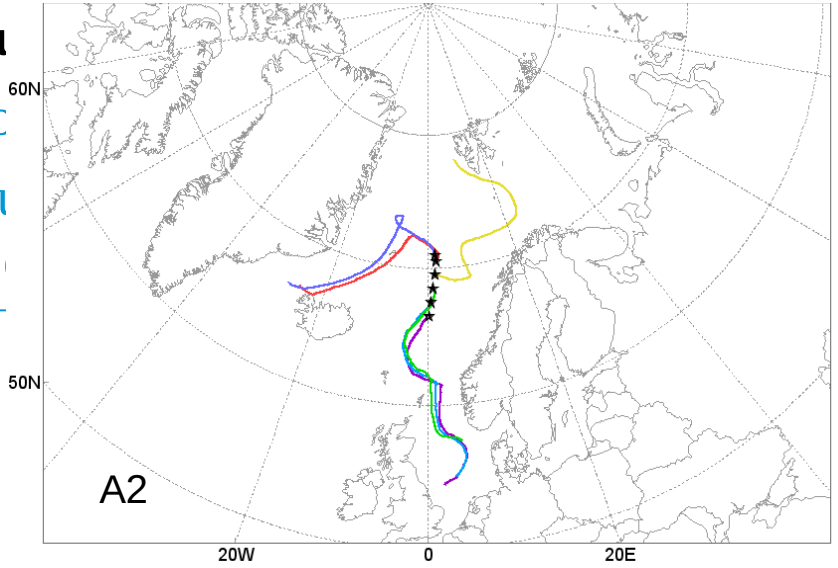
Resu

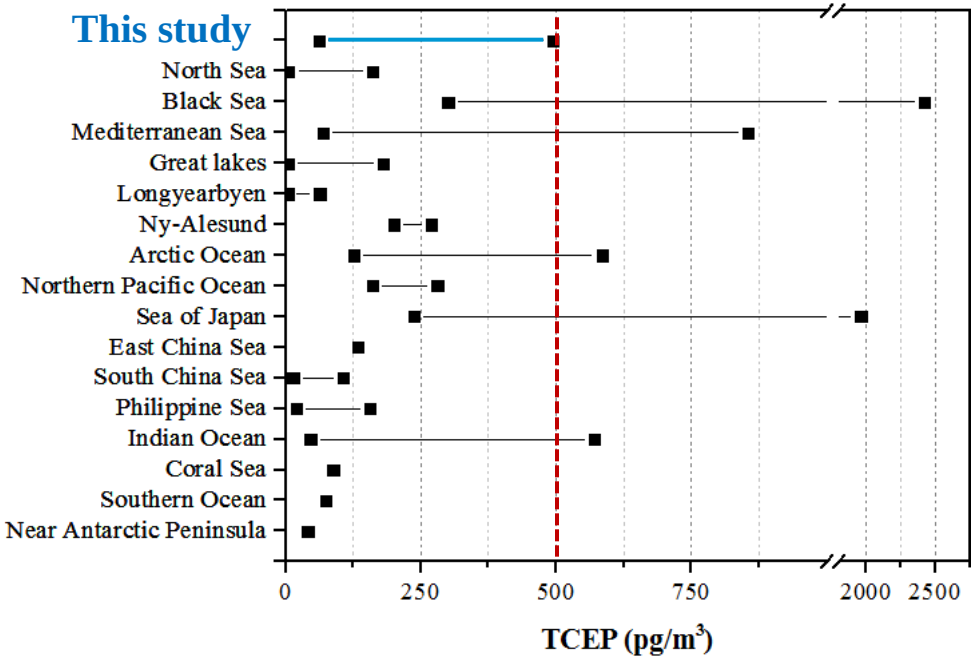
Euro

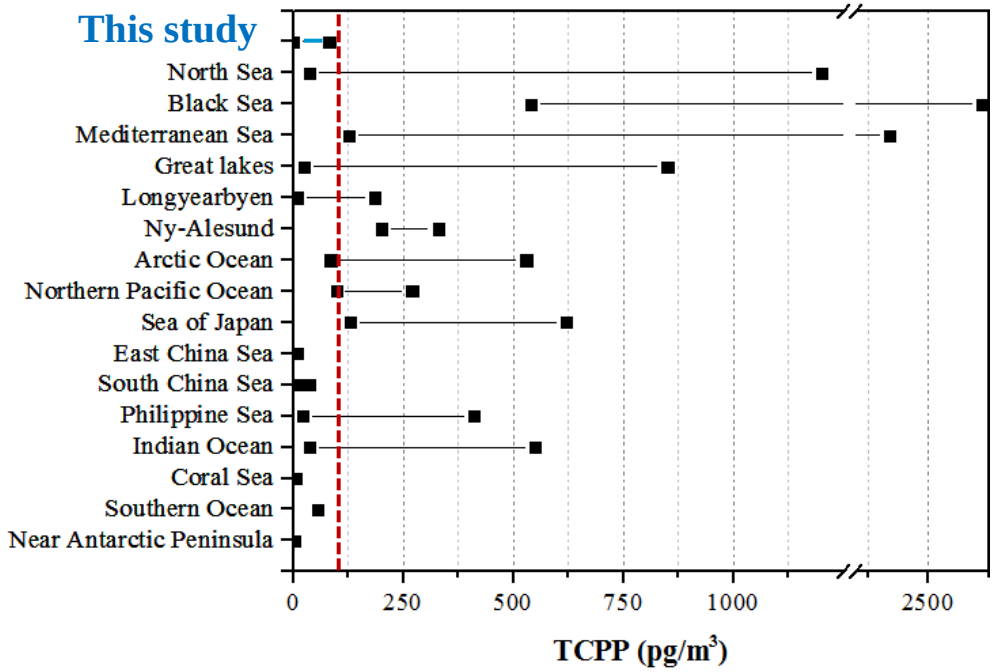
Thou

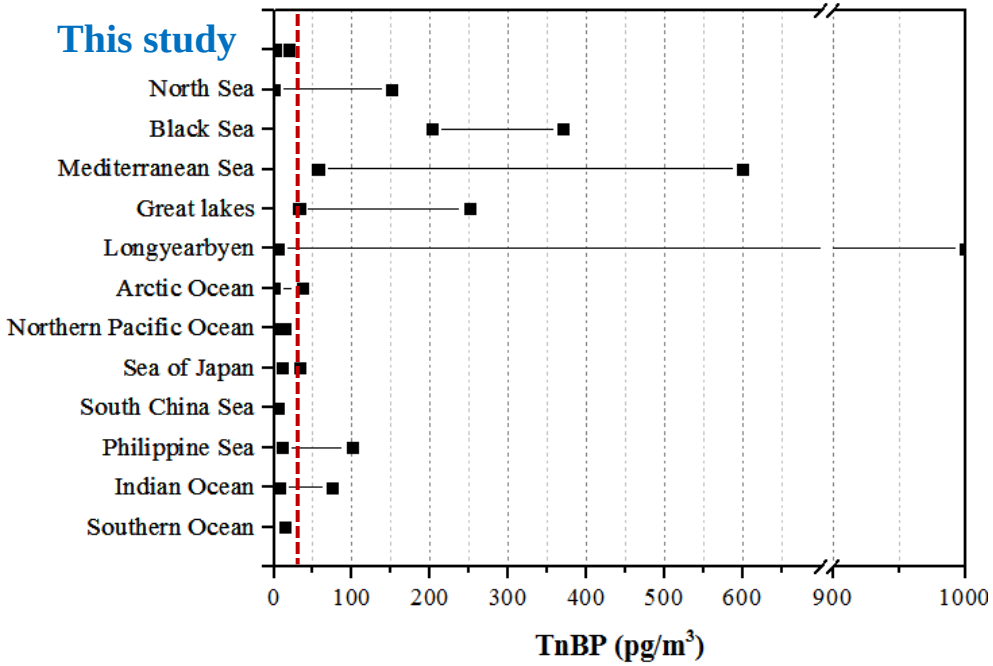
still

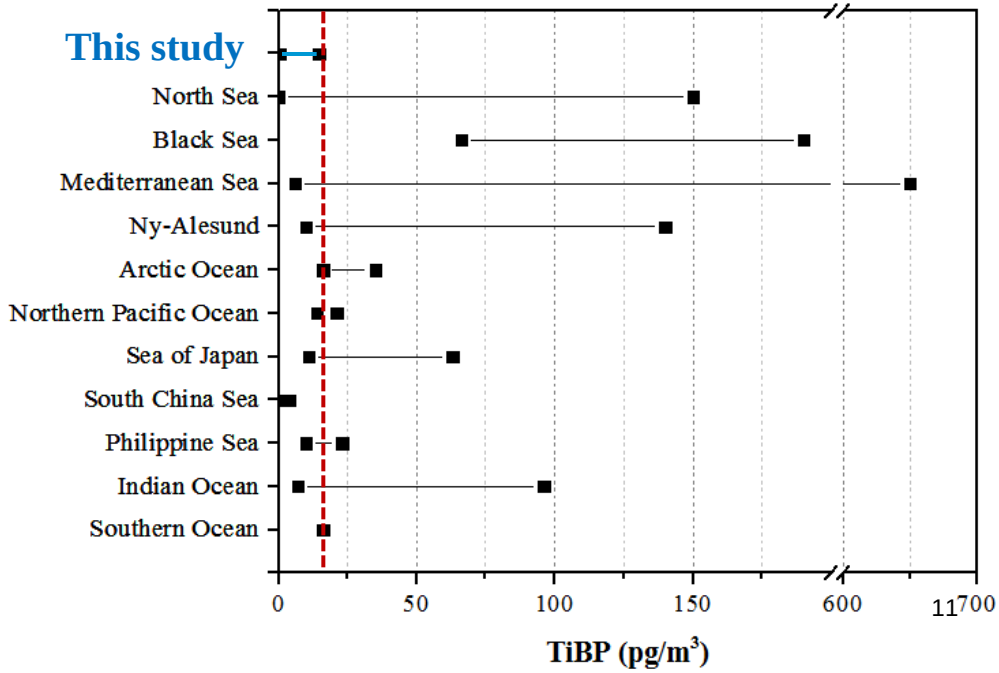
ission




This study
North Sea
Black Sea
Mediterranean Sea
Great lakes
Longyearbyen
Ny-Alesund
Arctic Ocean
Northern Pacific Ocean
Sea of Japan
East China Sea
South China Sea
Philippine Sea
Indian Ocean
Coral Sea
Southern Ocean
Near Antarctic Peninsula
0
250
500
750
2000
2500
TCEP (pg/m3)

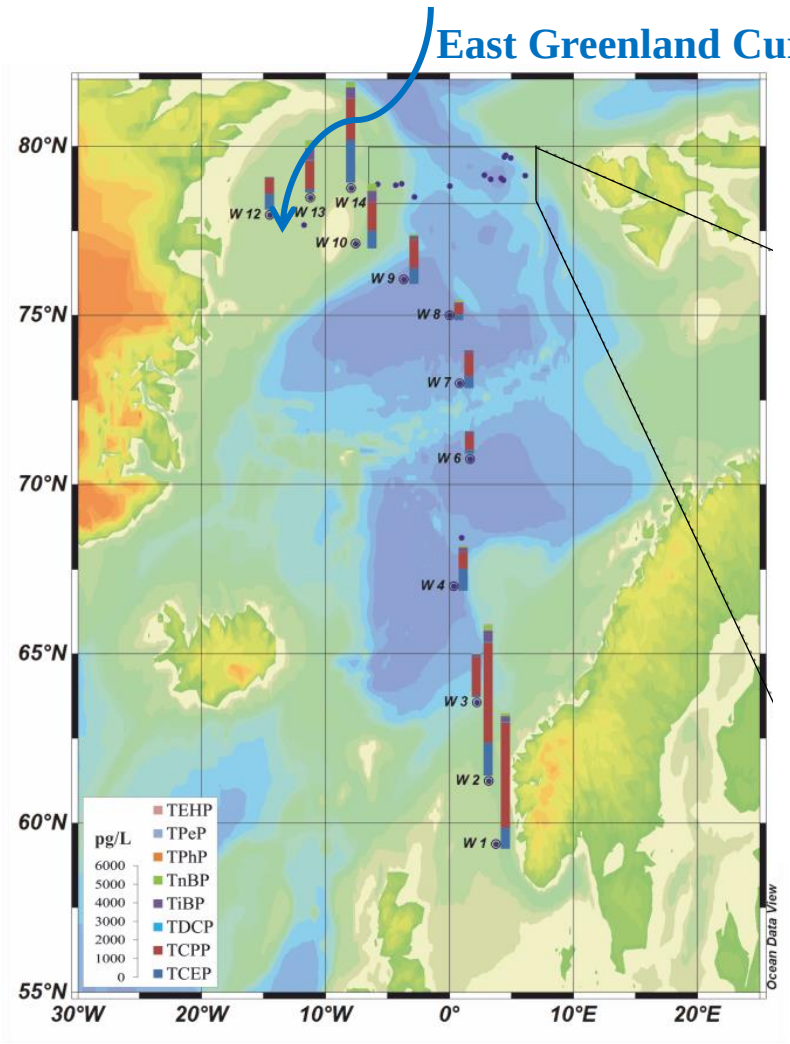

This study
North Sea
Black Sea
Mediterranean Sea
Great lakes
Longyearbyen
Ny-Alesund
Arctic Ocean
Northern Pacific Ocean
Sea of Japan
East China Sea
South China Sea
Philippine Sea
Indian Ocean
Coral Sea
Southern Ocean
Near Antarctic Peninsula
0
250
500
750
1000
2500
TCPP (pg/m3)

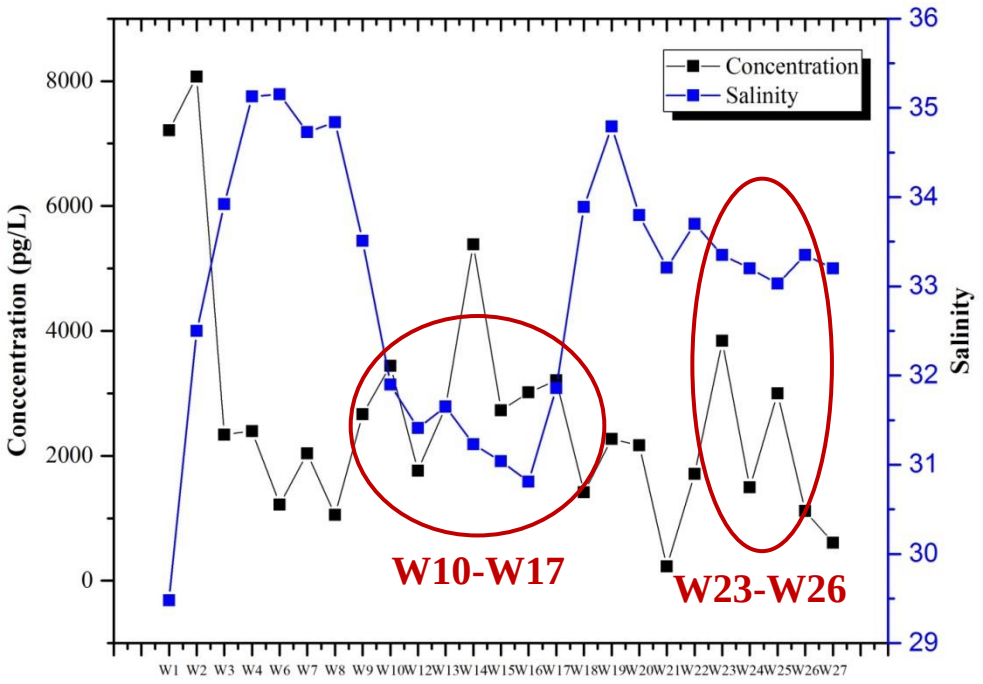

This study
North Sea
Black Sea
Mediterranean Sea
Great lakes
Longyearbyen
Arctic Ocean
Northern Pacific Ocean
Sea of Japan
South China Sea
Philippine Sea
Indian Ocean
Southern Ocean
0
100
200
300
400
500
600
900
1000
TnBP (pg/m3)


This study
North Sea
Black Sea
Mediterranean Sea
Ny-Alesund
Arctic Ocean
Northern Pacific Ocean
Sea of Japan
South China Sea
Philippine Sea
Indian Ocean
Southern Ocean
0
50
100
150
600
1700
TiBP (pg/m3)

OPEs in seawater

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research





Inverse , r^2 = 0.31, n = 25, p = 0.004

1) Gradient from the North Sea to the Arctic.
2) Increase of OPEs near Greenland and Svalbard.
3) Decrease of salinity near Greenland and Svalbard.

OPEs in snow

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Sampling date:

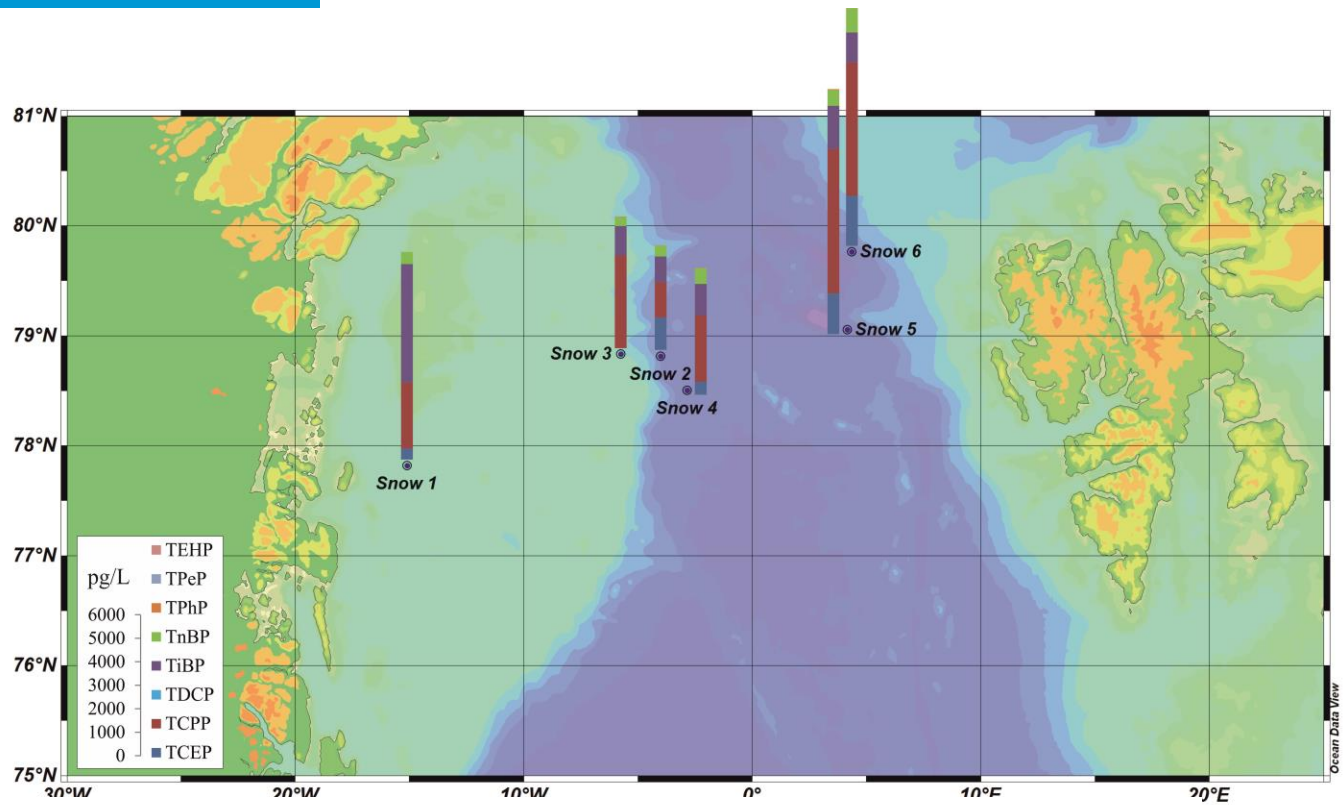
15.06.2014--25.06.2014

Major OPEs:

TCPP, TCEP, TiBP, TnBP

ΣOPEs concentration:

4530-10600 pg/L



Comparison: TCPP

[this study] mean 3.8 ng/L, 1-3 orders of magnitude lower than the urban areas

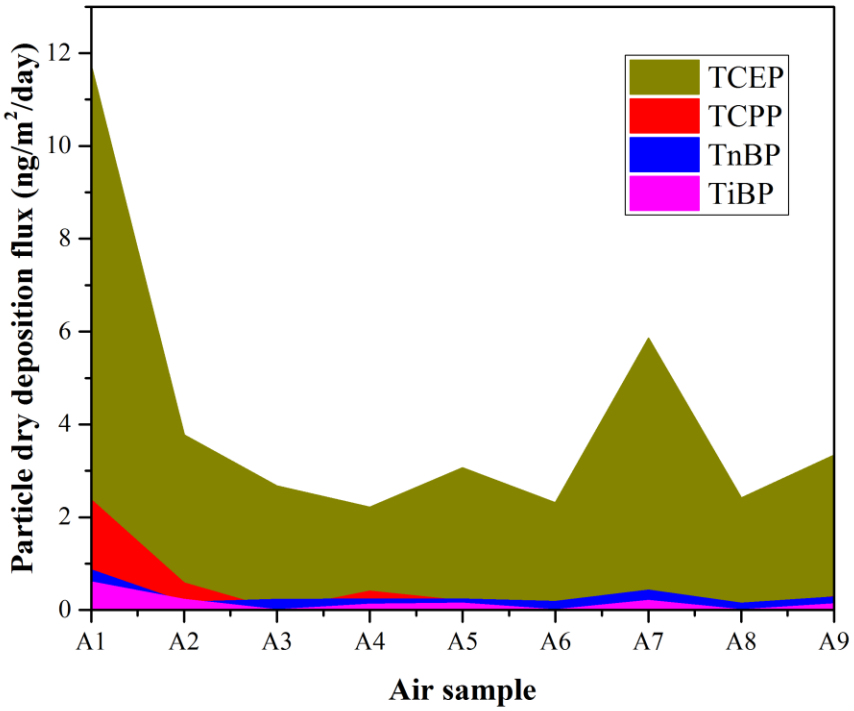
[1] northern Sweden: 100- 220 ng/kg, snow [Marklund et al., 2005]

[2] Italy: 633-739 ng/L, rainwater [lessandro et al.,2008]

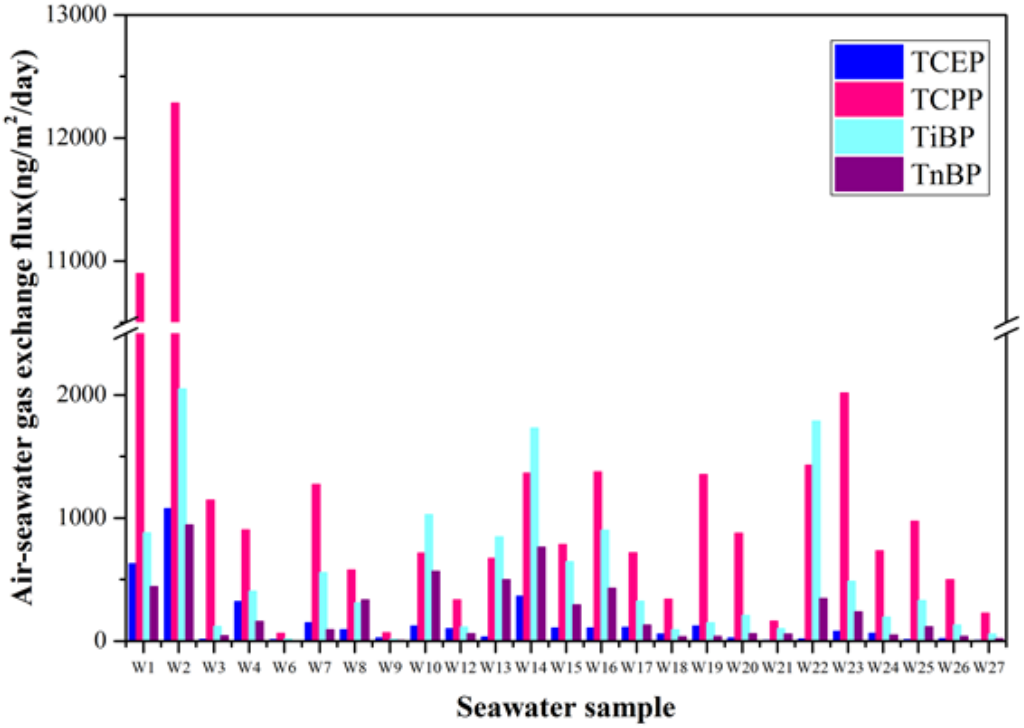
[3] central Germany:46-2659 ng/L, rainwater [Regnery et al., 2009]

Atmospheric particle-bound deposition and air-sea exchange flux:

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research



Atmospheric particle deposition fluxes of 4 OPEs

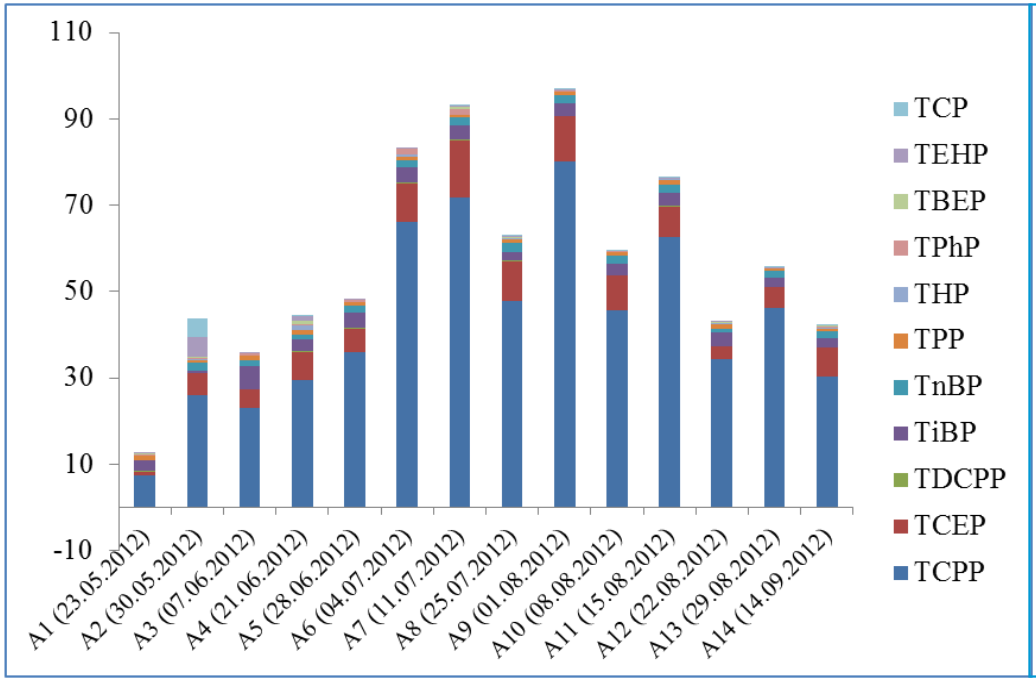


Air-water gas exchange fluxes of OPE

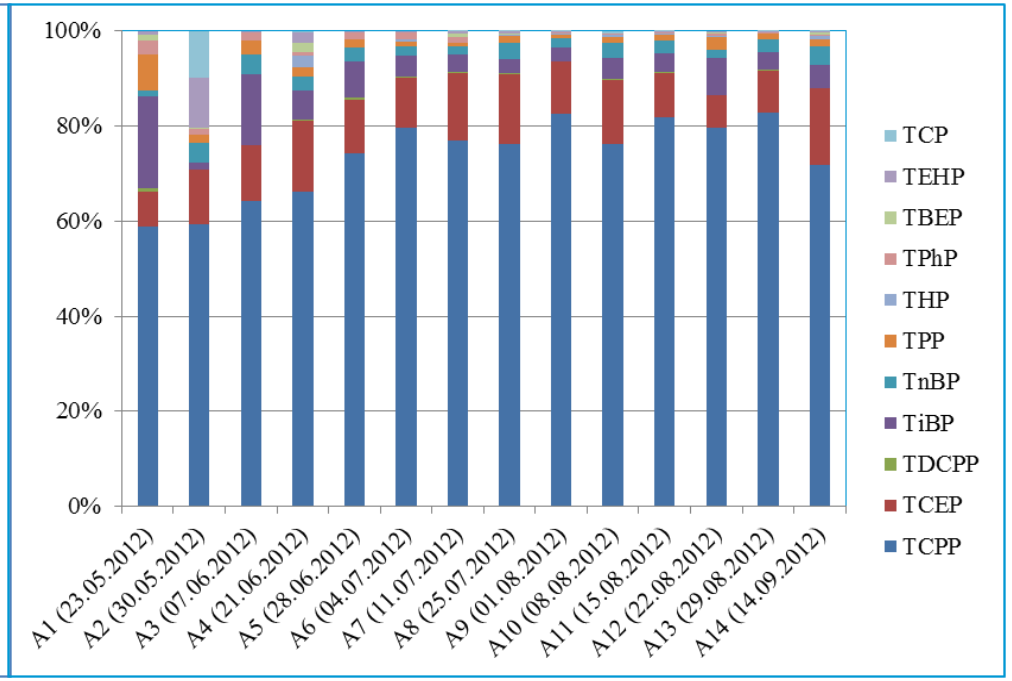
The Henry's law constants (HLCs) of OPEs were estimated by SPARC as suggested by Zhang et al. (*Chemosphere, 2016*), and corrected by the given temperature and salinity
Very strong water to air volatilization were estimated for TCPP and TiBP
Li et al., Envion Sci. Technol. 2017

OPE in atmospheric particles in the Arctic (Ny-Alesund)

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research



OPE concentration (pg/m3) in atmospheric particle

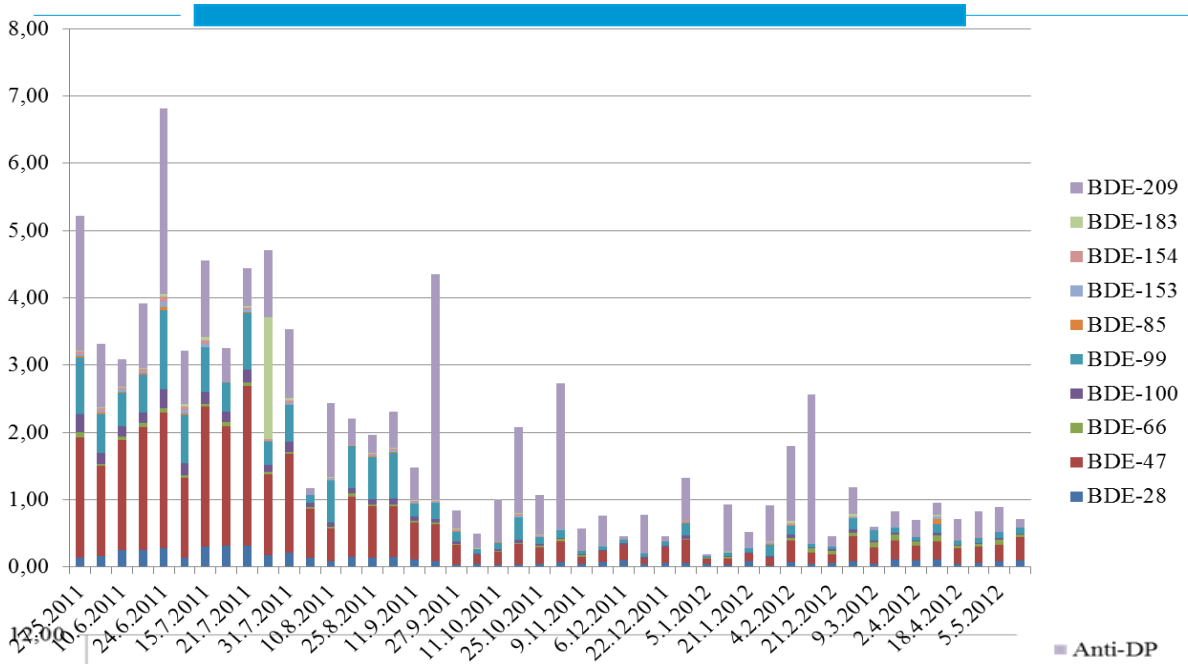


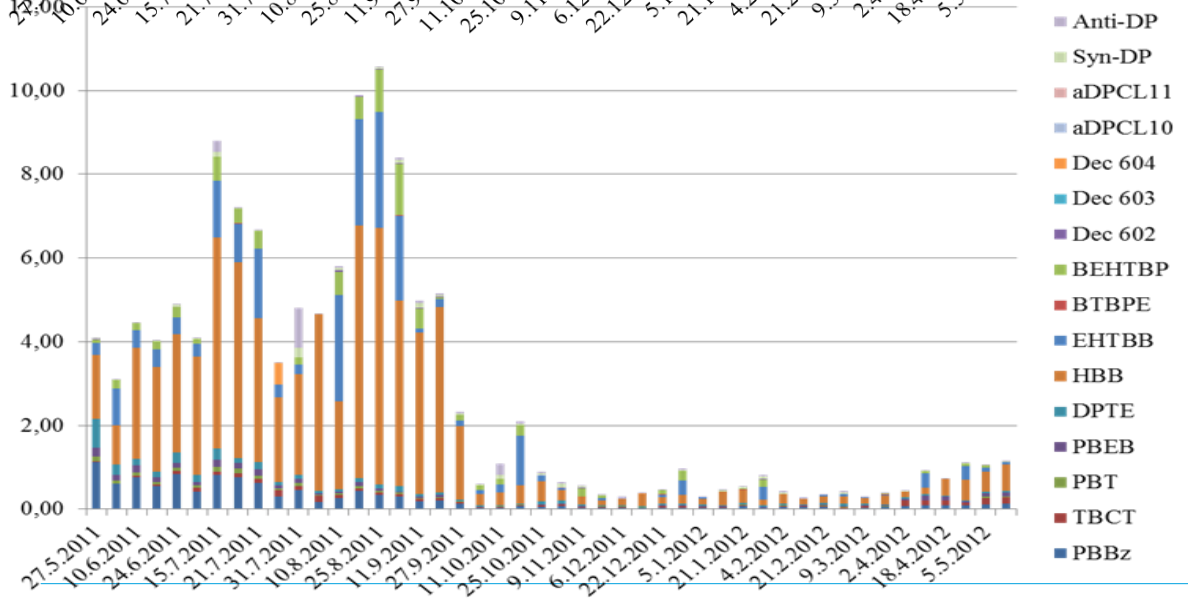
Profile of OPE in atmospheric particle

- ΣOPEs concentrations: 38 to 150 pg/m3
- TCPP: 7−80 pg/m3 >TCEP: 0.9-13 pg/m3 > TiBP:1.9-6.0 pg/m3 > TnBP: 1.3-4.1 pg/m3
- Chlorinated OPEs (TCPP, TCEP, TDCCP) account for 65-90%
- Nonchlorinated OPEs <10-35%

Comparison with BFR in the Arctic (Ny-Alesund)

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research





Chalange for determination of OPEs at the Arctic station

Local sources in arctic summer can be

- **Reemissions from snow melting**
- **Research scientists living at station and tourists …??**

Conclution

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

- **Occurrence,** Organophosphate flame retardants and plasticizers have been determined in air, seawater and snow in the North Atlantic and Arctic,and in other marine environment.
- **Spatial distribution,** Decreasing trend presented from the North Atlantic to the Arctic in both atmosphere and seawater.
- **Secondary source in the Arctic,** melting snow and ice in summer can discharge OPEs in air and seawater
- **Air-sea exchange,** Atmospheric particle dry deposition and air-seawater gas exchange may drive the remobilization of OPEs in the Arctic
- **Suggestion,** TCEP, TCPP, TiBP, TnBP might be new candidates for POPs or Semi-POPs, and require further attention and research for their bioaccumulation and toxicity in the Arctic ecosystem.

Thank you!

E-mail: zhiyong.xie@hzg.de