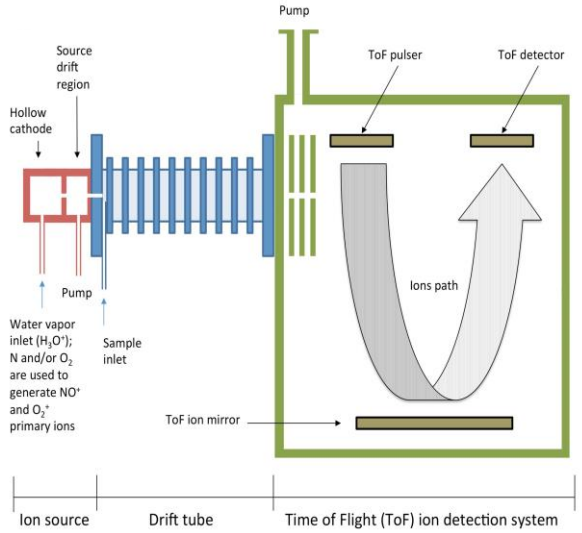
Measuring environmental nanoplastics with TD-PTR-MS

Dr. Dušan Materić (Matt)



IMAU Institute for Marine and Atmospheric research Utrecht

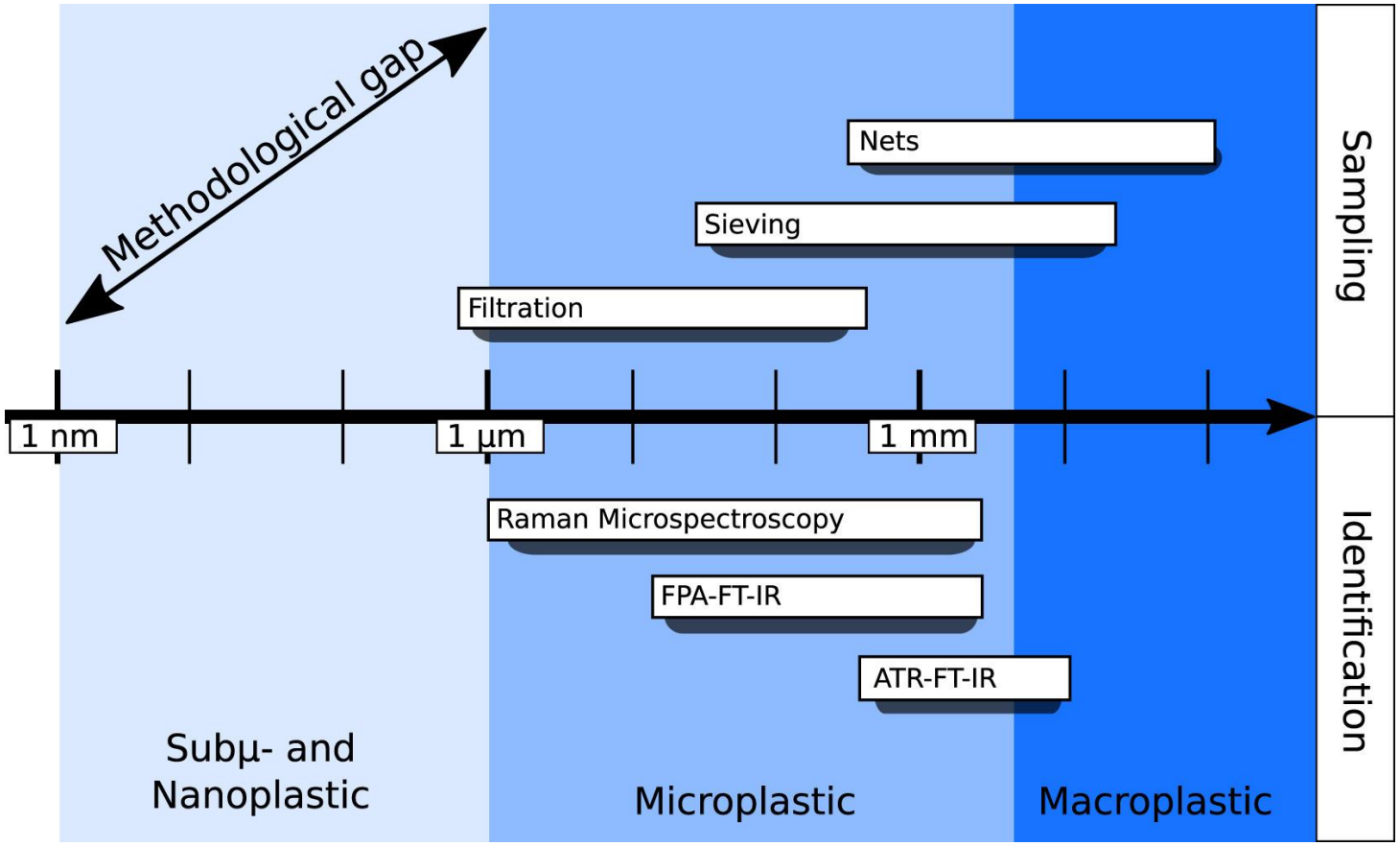
ZAMG Zentralanstalt für Meteorologie und Geodynamik

NIOZ Royal Netherlands Institute for Sea Research

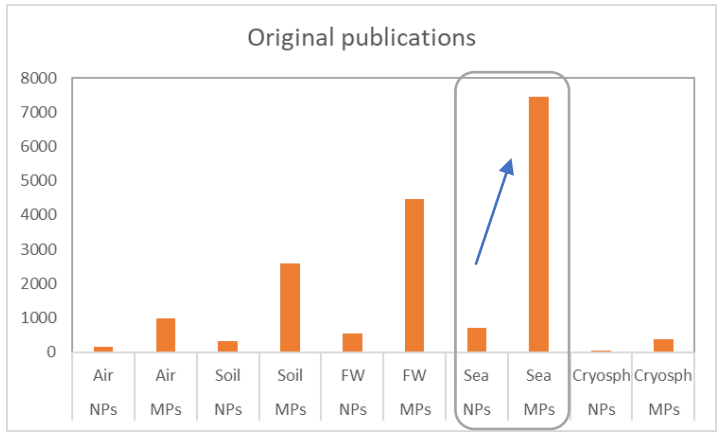
UFZ HELMHOLTZ Zentrum für Umweltforschung

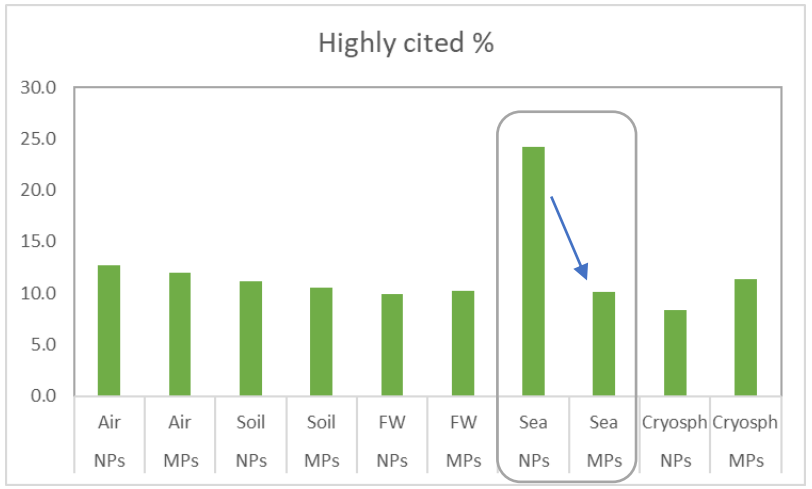
Methods and more

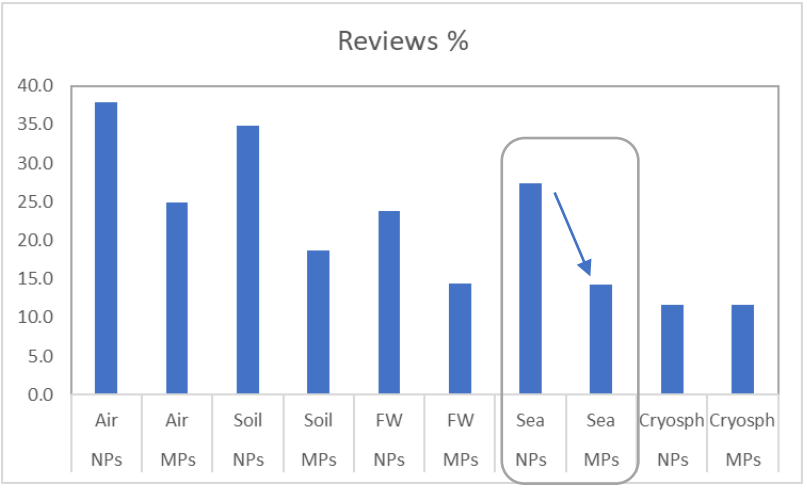
Schwaferts, C., Niessner, R., Elsner, M. & Ivleva, N. P. Methods for the analysis of submicrometer- and nanoplastic particles in the environment. TrAC Trends Anal. Chem. 112, 52–65 (2019).

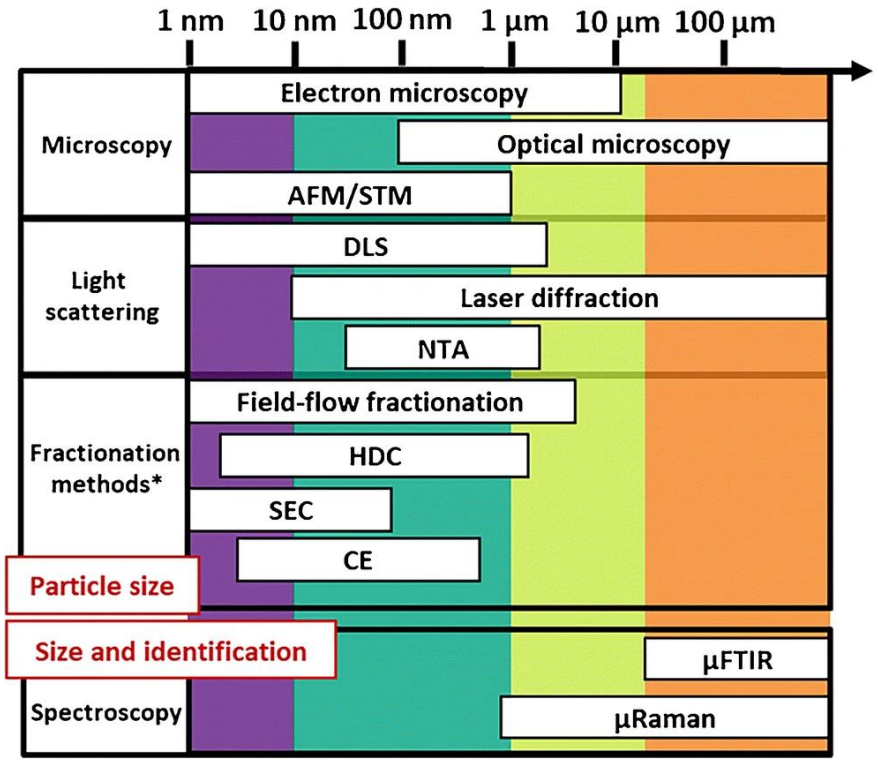


How hot is nanoplastics topic?



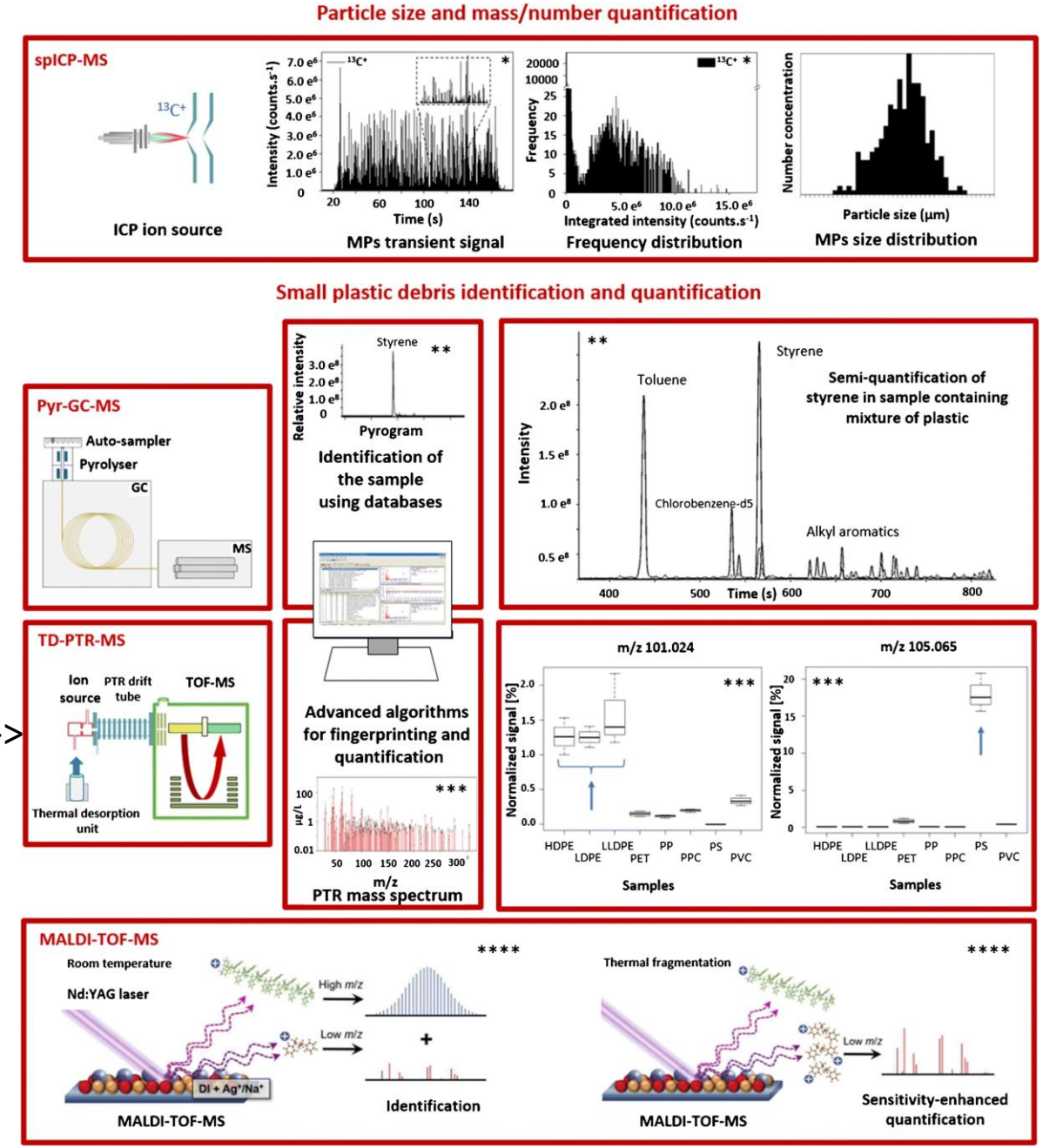






LoD ~50 ng ->

LoD ~0.12 ng ->



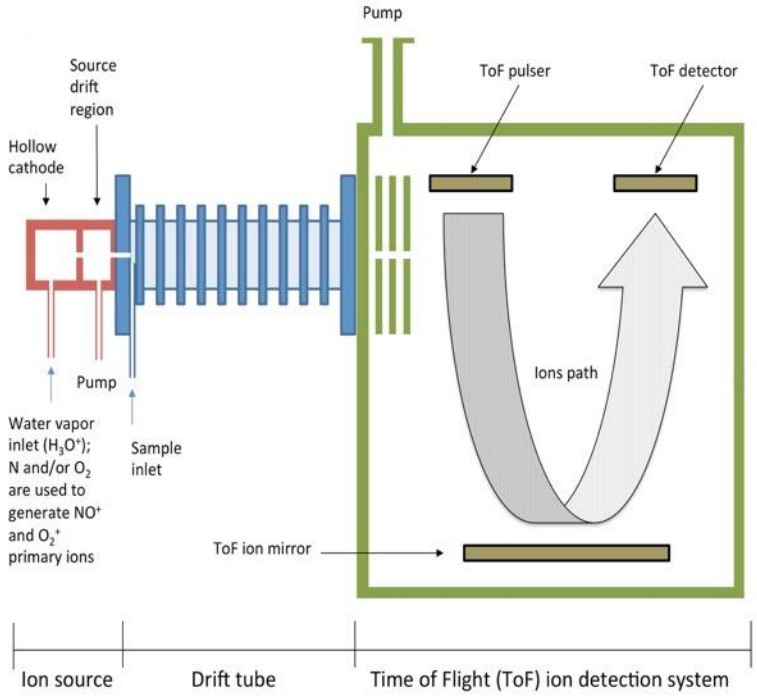
Velimirovic, M., Tirez, K., Voorspoels, S. & Vanhaecke, F. Recent developments in mass spectrometry for the characterization of micro- and nanoscale plastic debris in the environment. *Anal. Bioanal. Chem.* (2020).

Proton Transfer Reaction - Mass Spectrometry

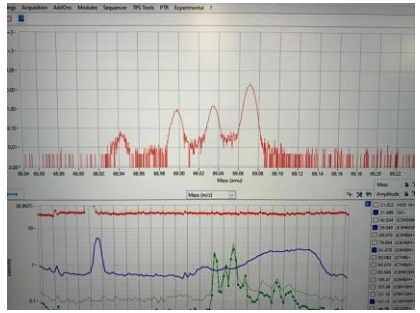
m/z	Formula:
99.008	$C_4H_2O_3H^+$
99.043	$C_5H_6O_2H^+$
99.079	$C_6H_{10}OH^+$

Key advantages:

- Sensitivity
- **Quantitative**
- Most organics detectable
- **High mass resolution**
- High time resolution
- Minimal fragmentation

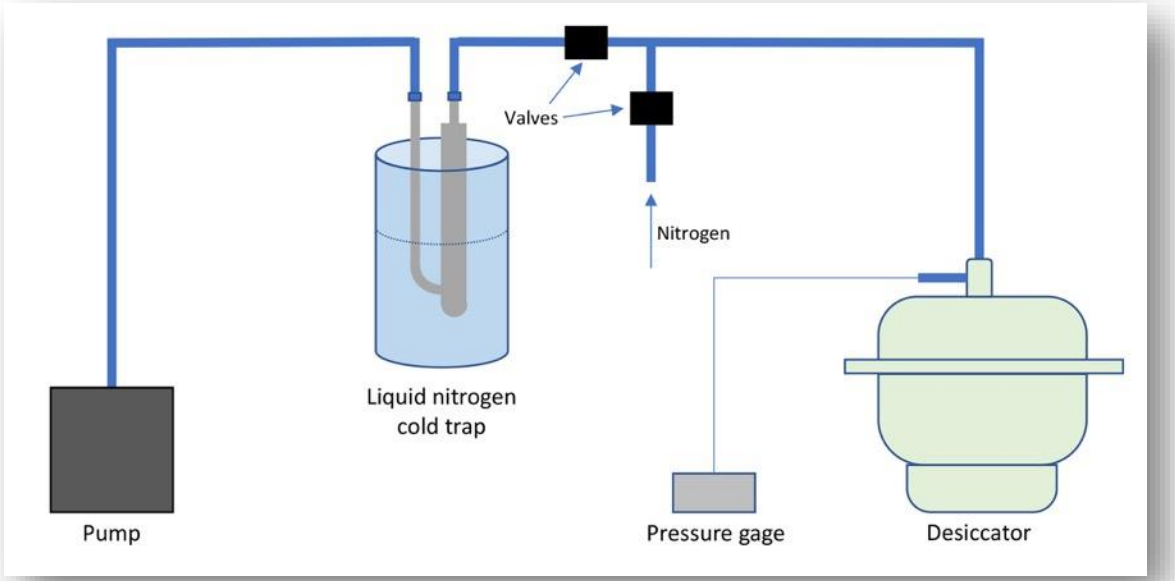


$H_3O^+ + VOC \rightarrow VOCH^+ + H_2O$

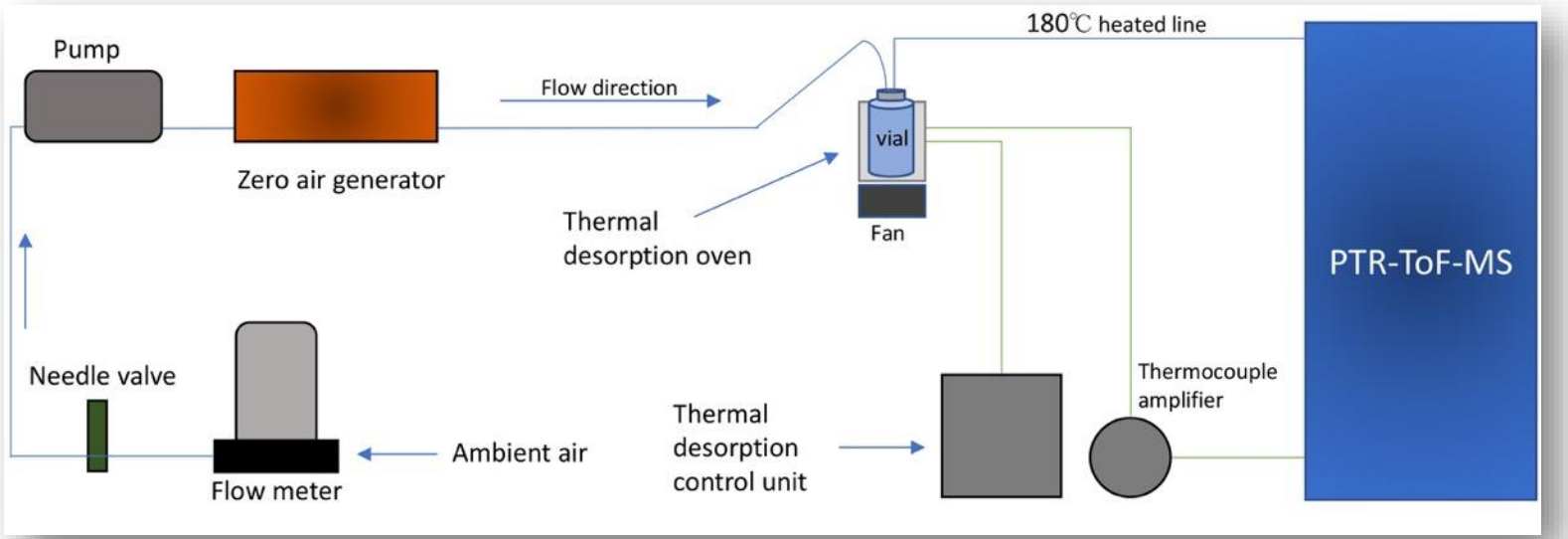


PTR-ToF-MS

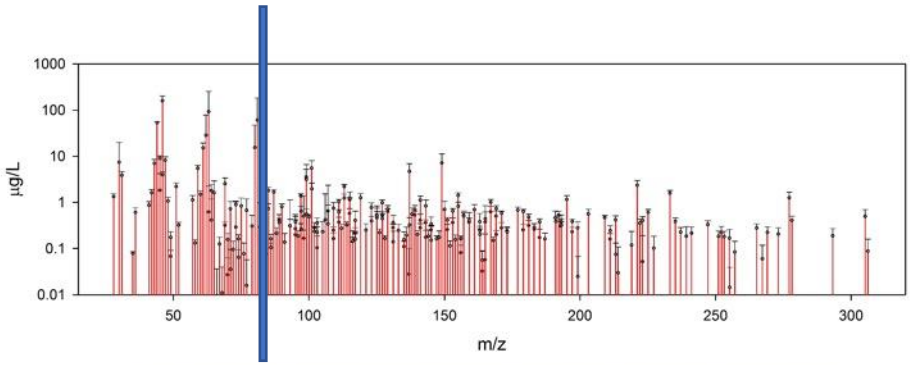
Water removal



TD inlet

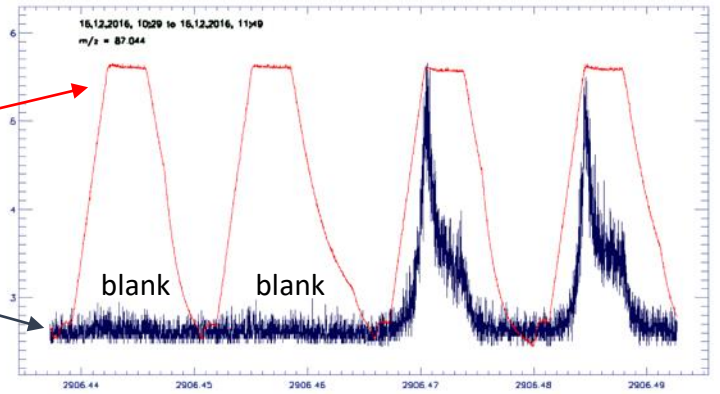


Every second one spectra



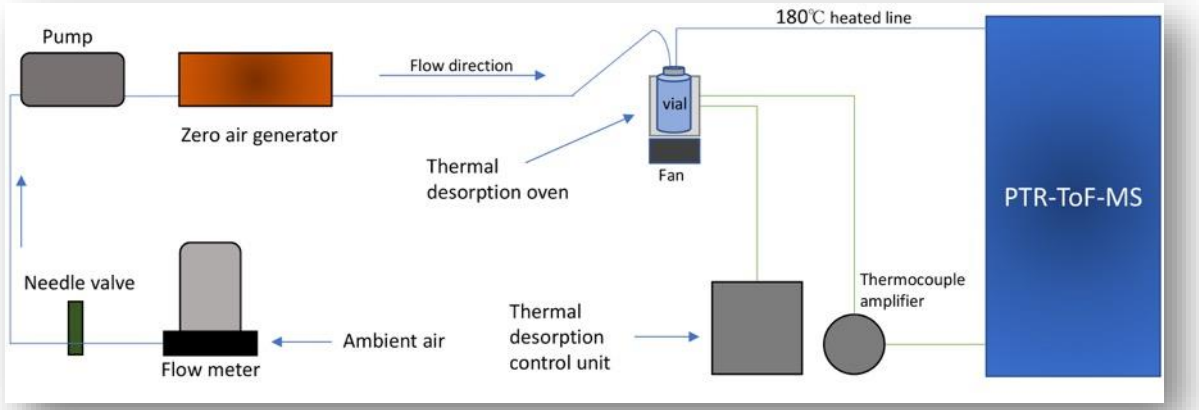
TD ramp [^{o}C]

Ion signal

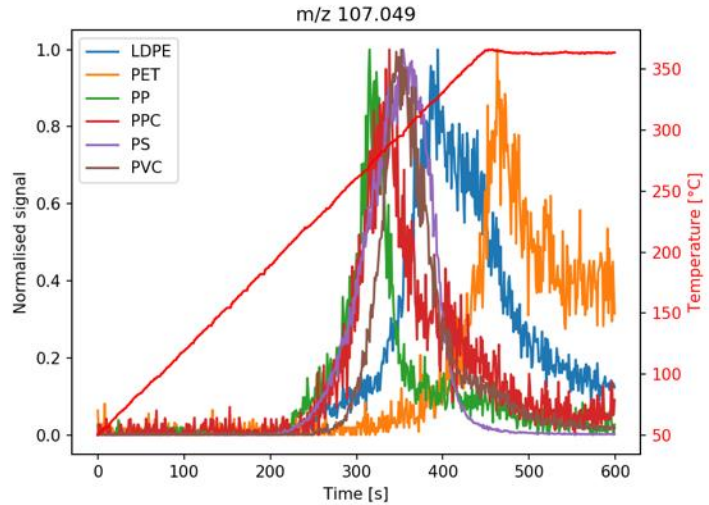


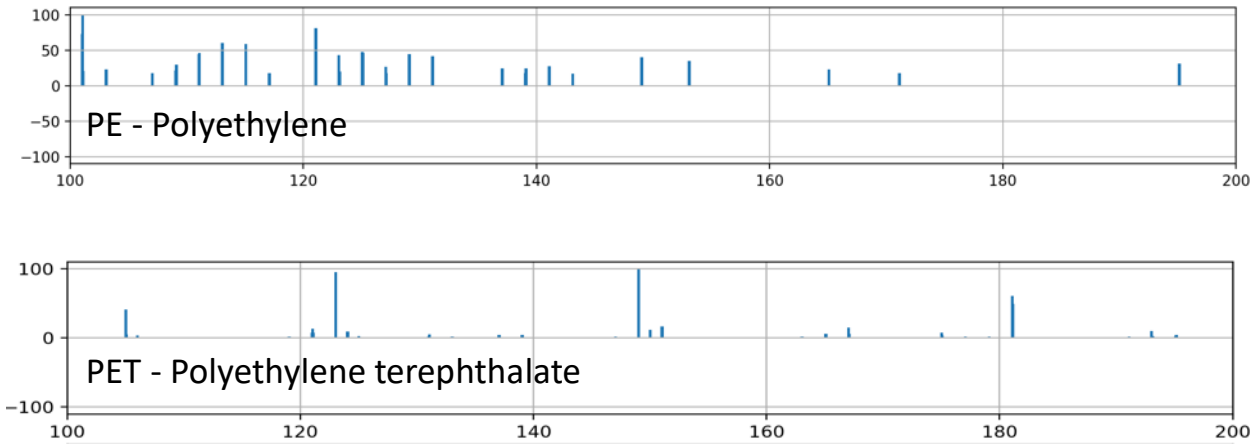
Time

TD-PTR-MS

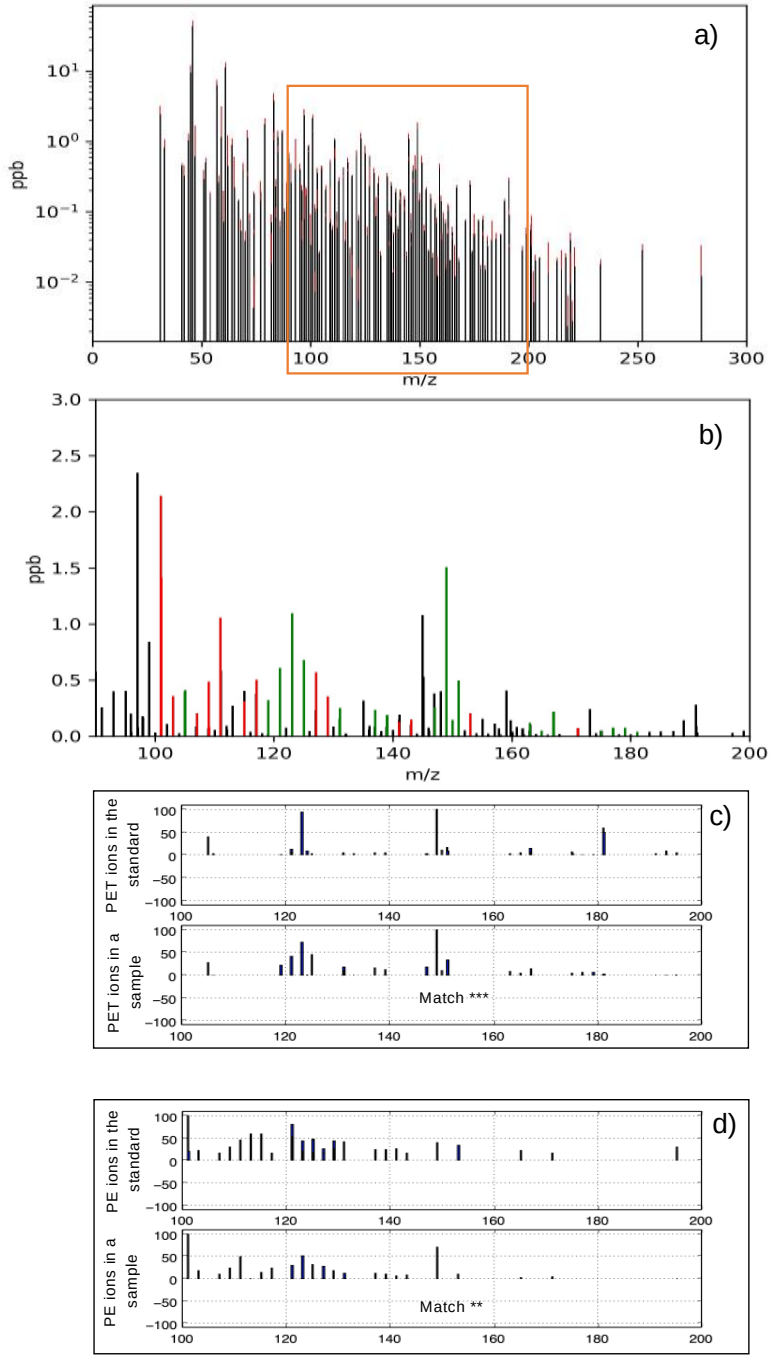


First level
data processing:
Reducing 20GB to 2MB



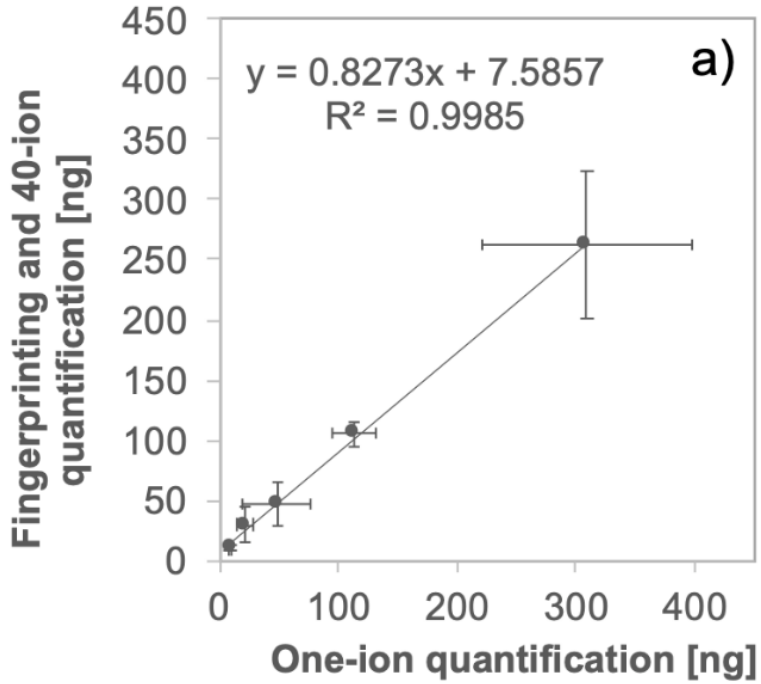


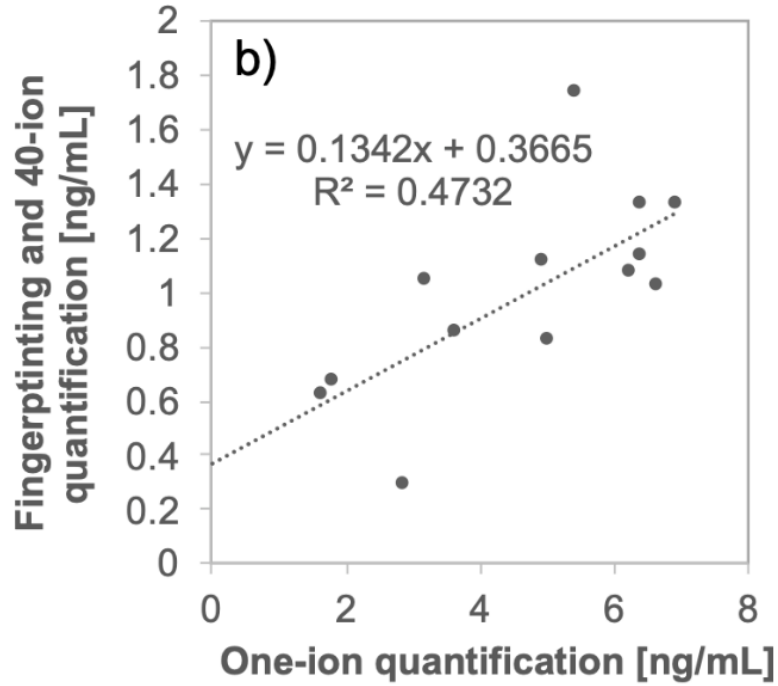
Algorithm for:
1) Identification of different types of polymer
2) Quantification – PTR-MS advantage

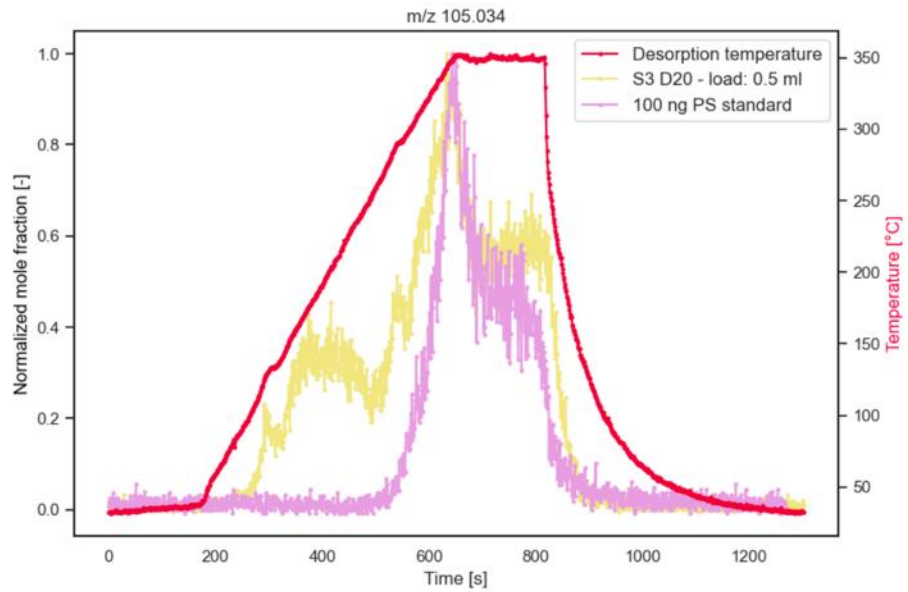


QC/QA, KPI

- Sensitivity of the instrument, m21.022
- Impurities in the ion source, e.g. m34, clusters
- OM load check (DOC analysis)
- Spiking of the samples (PS)
- Spiking of the blanks (PS)


a)
y = 0.8273x + 7.5857
R² = 0.9985
Fingerprinting and 40-ion quantification [ng]
One-ion quantification [ng]
0
50
100
150
200
250
300
350
400
450
0
100
200
300
400

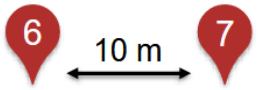

b)
y = 0.1342x + 0.3665
R² = 0.4732
Fingerptinting and 40-ion quantification [ng/mL]
One-ion quantification [ng/mL]
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
2
4
6
8


m/z 105.034
Desorption temperature
S3 D20 - load: 0.5 ml
100 ng PS standard
Normalized mole fraction [-]
Temperature [°C]
Time [s]
0.0
0.2
0.4
0.6
0.8
1.0
50
100
150
200
250
300
350
0
200
400
600
800
1000
1200

Quality Control (some examples)

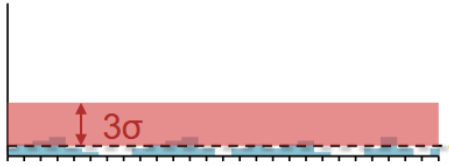
QUALITY CONTROL

3 samples + field blank

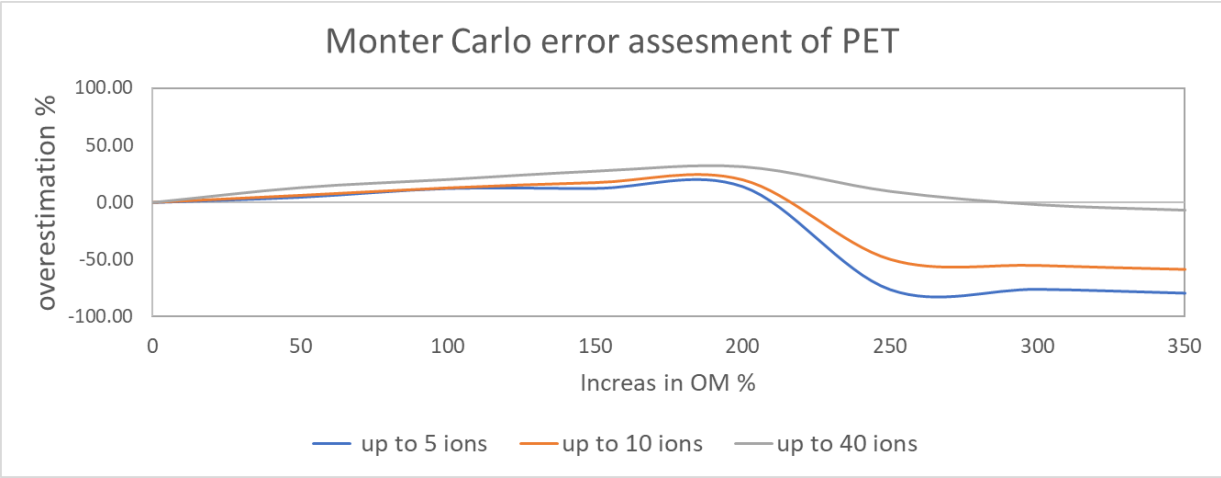


control sample

samples spiked with PS → ionisation efficiency estimated

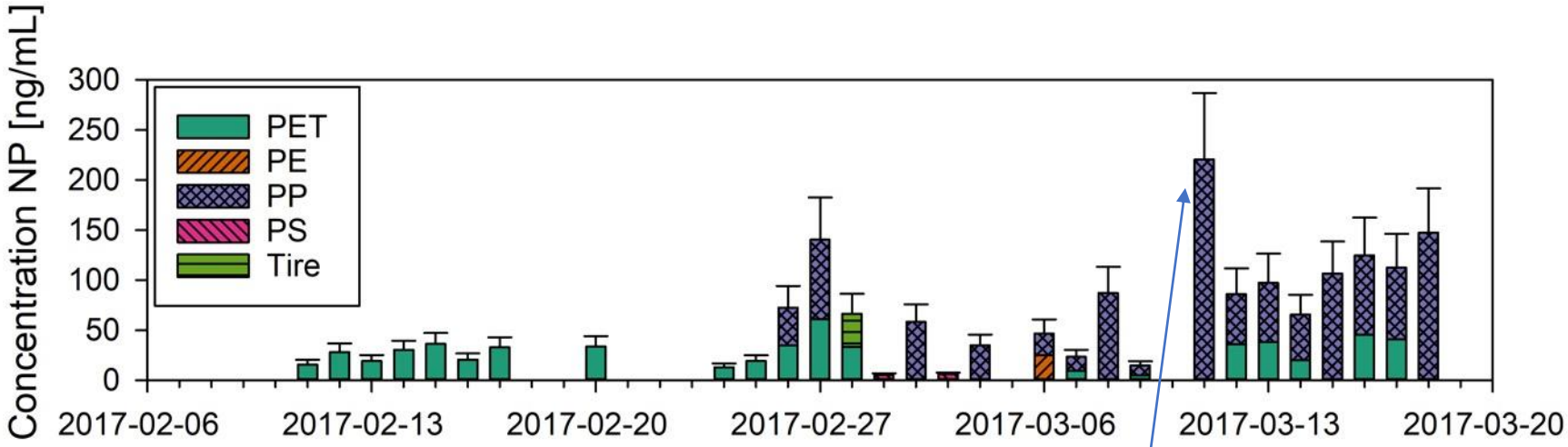


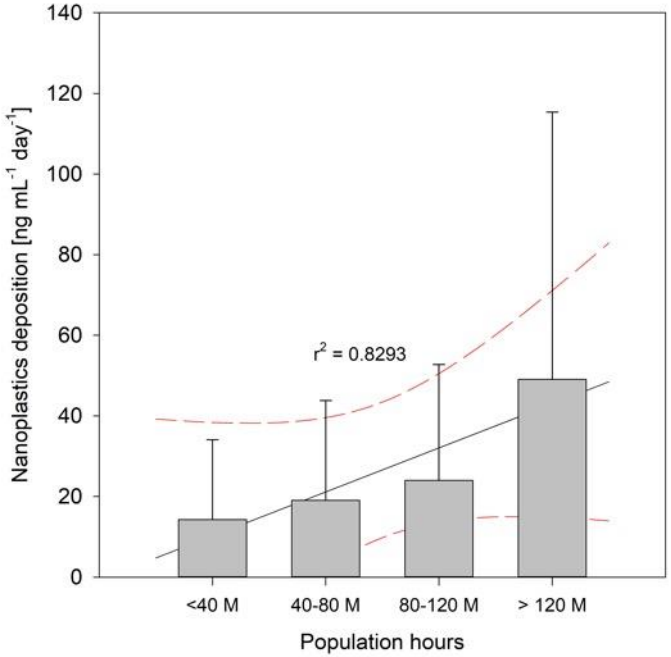
system blanks measured → background level subtracted + strict 3σ limit applied

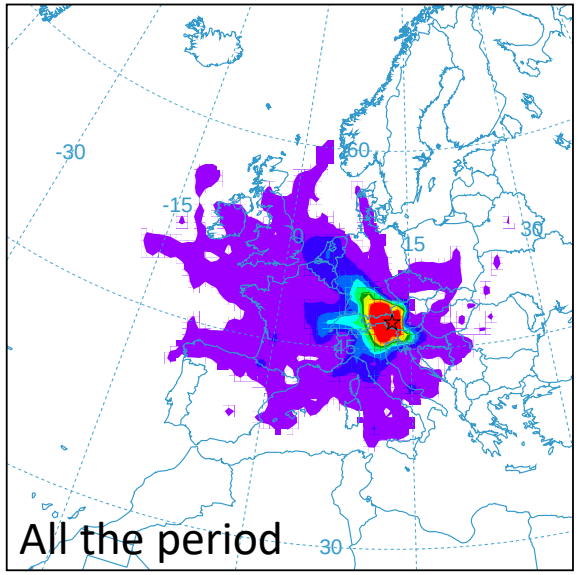


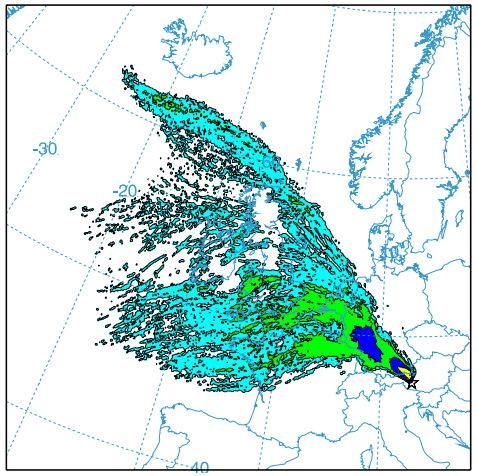
NanoEU a new INTERACESS project in progress

Austrian Alps 3100 m a.s.l.





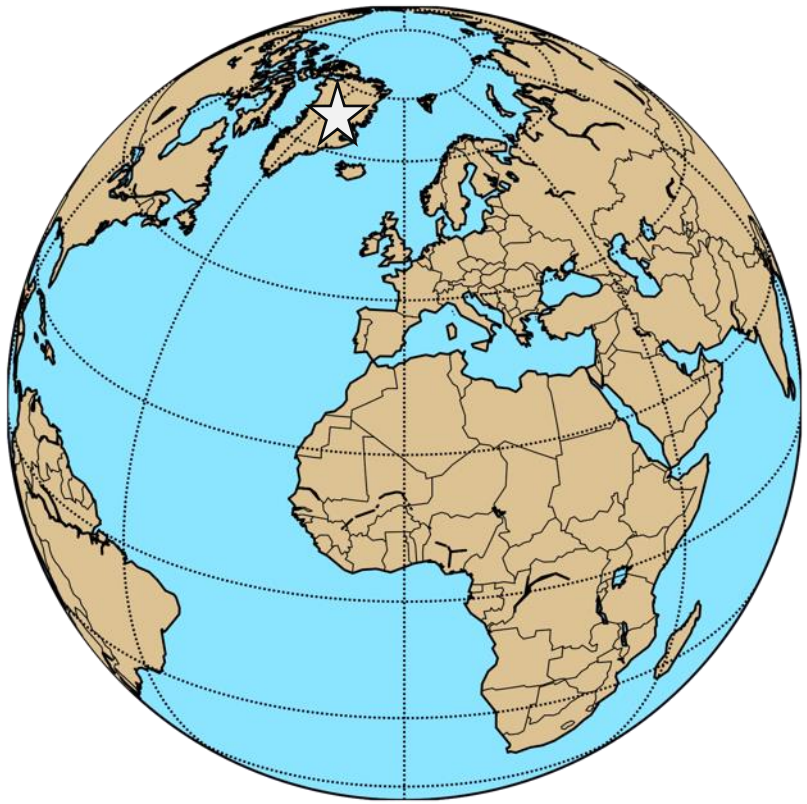


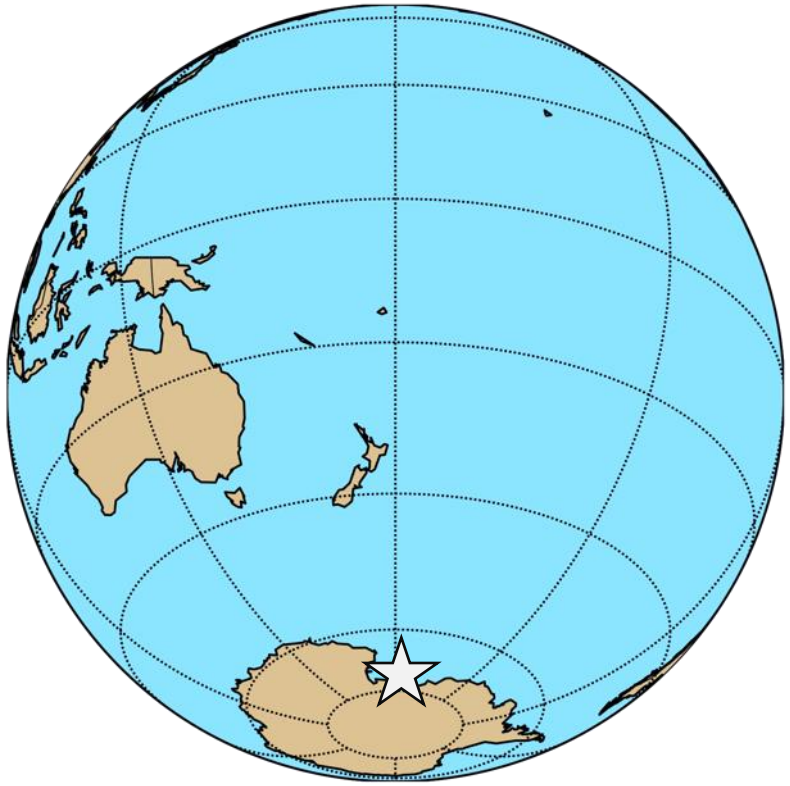


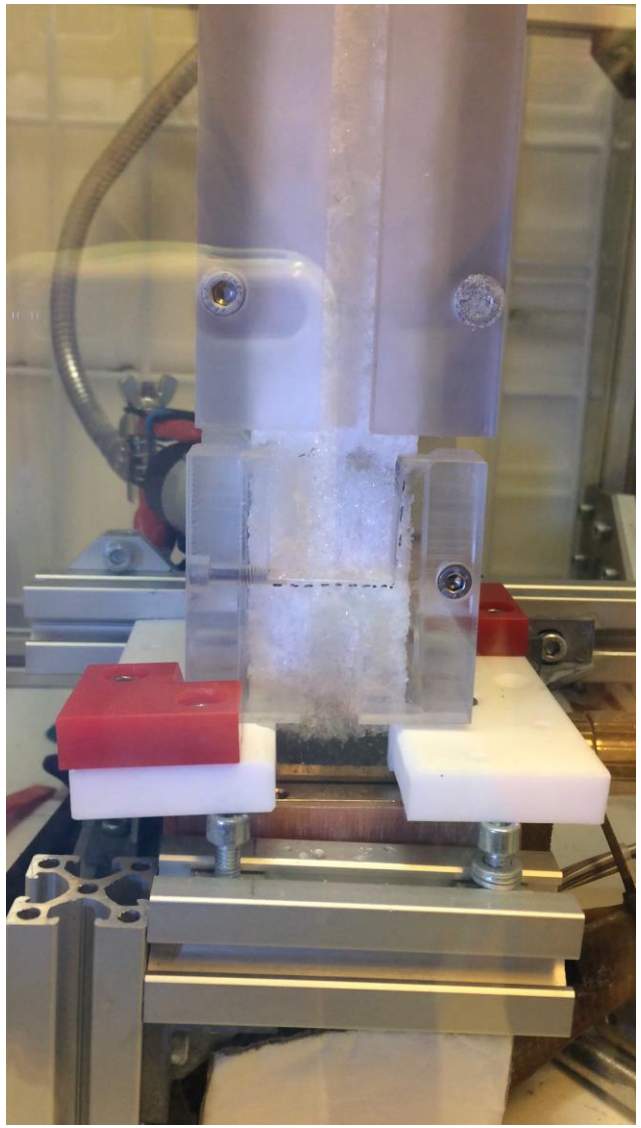
<u>Result:</u>
Population weighted surface area correlates with nanoplastics plastics deposition!

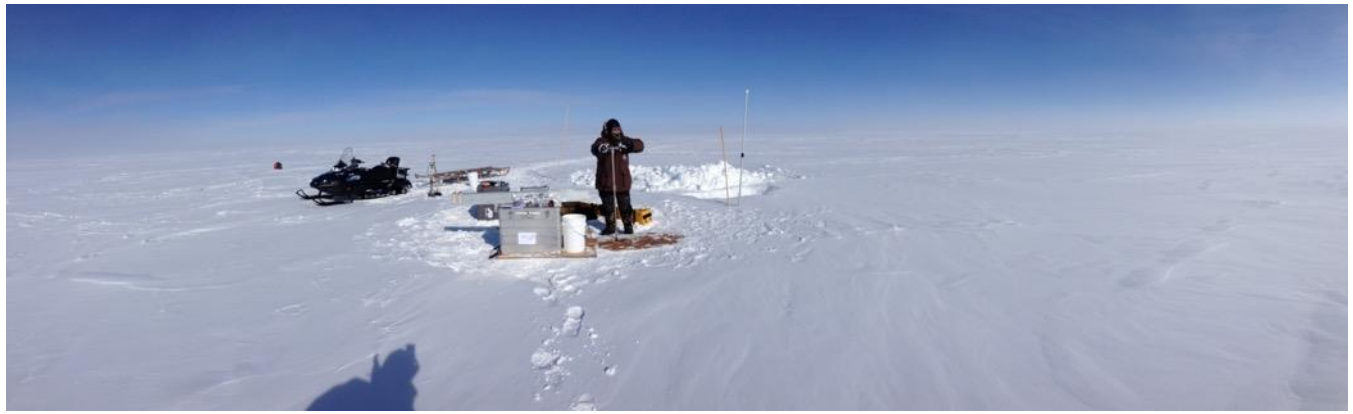
Published in EP

Nanoplastics presence in Northern and Southern Polar Regions

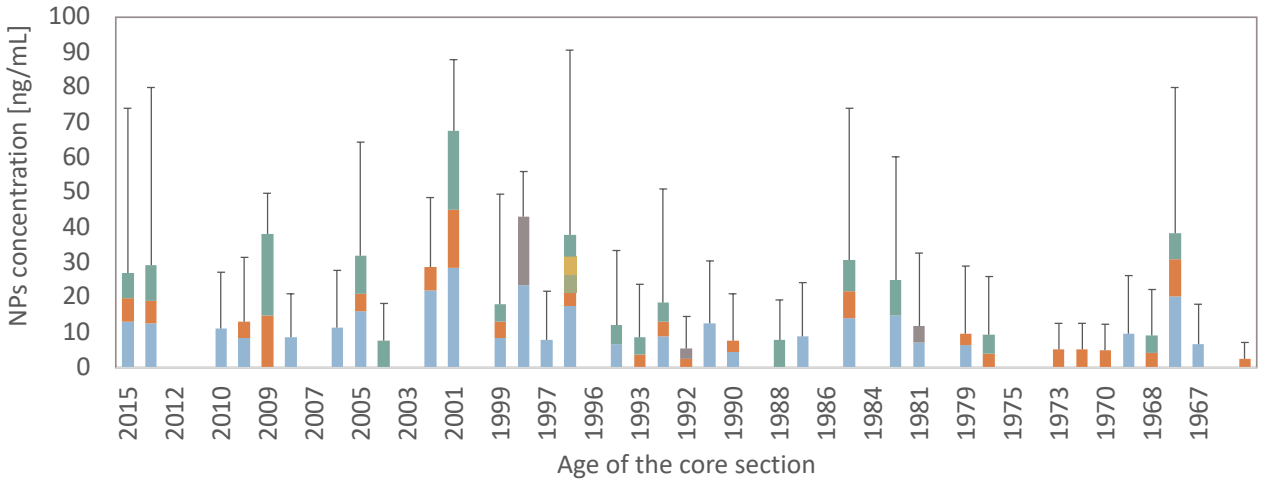


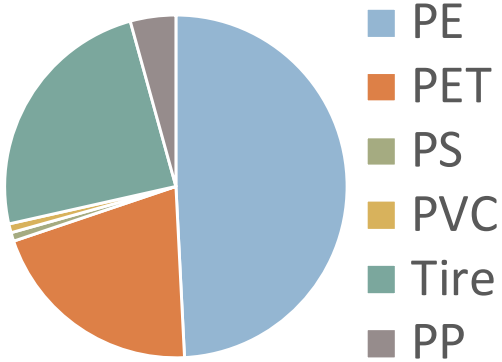




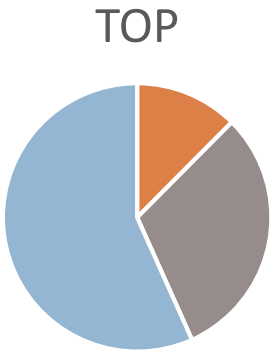


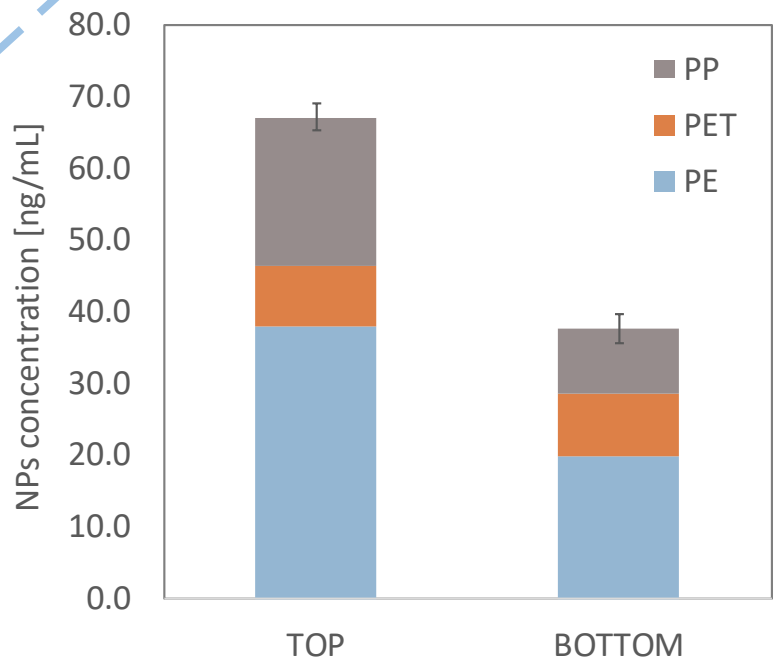
Greenland ice core 14 m (~1966)

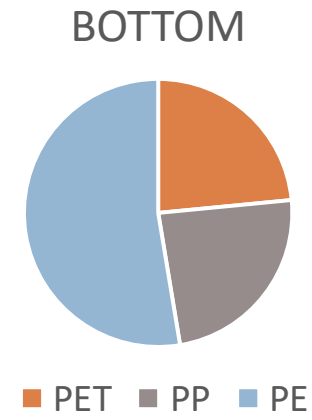


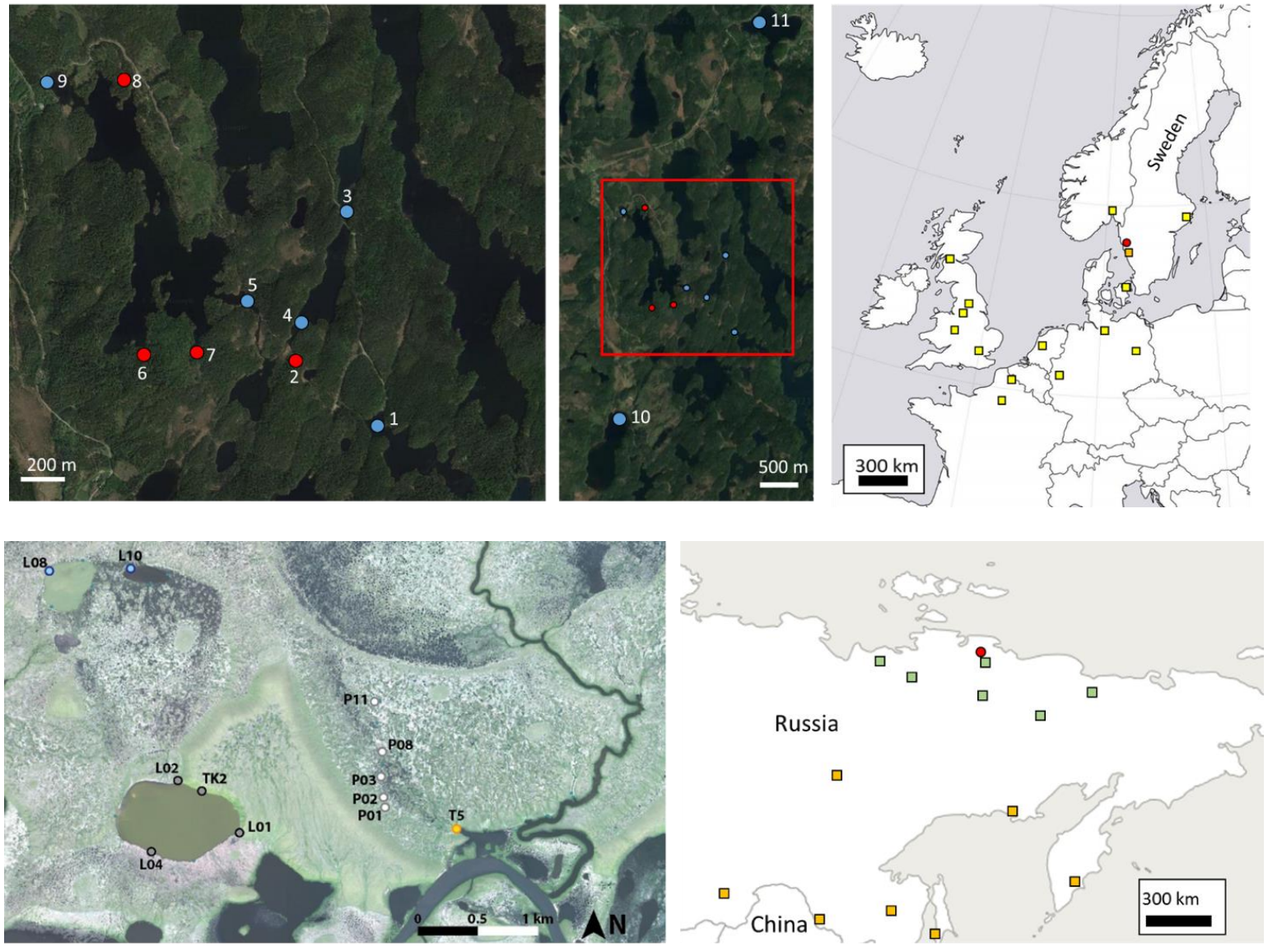


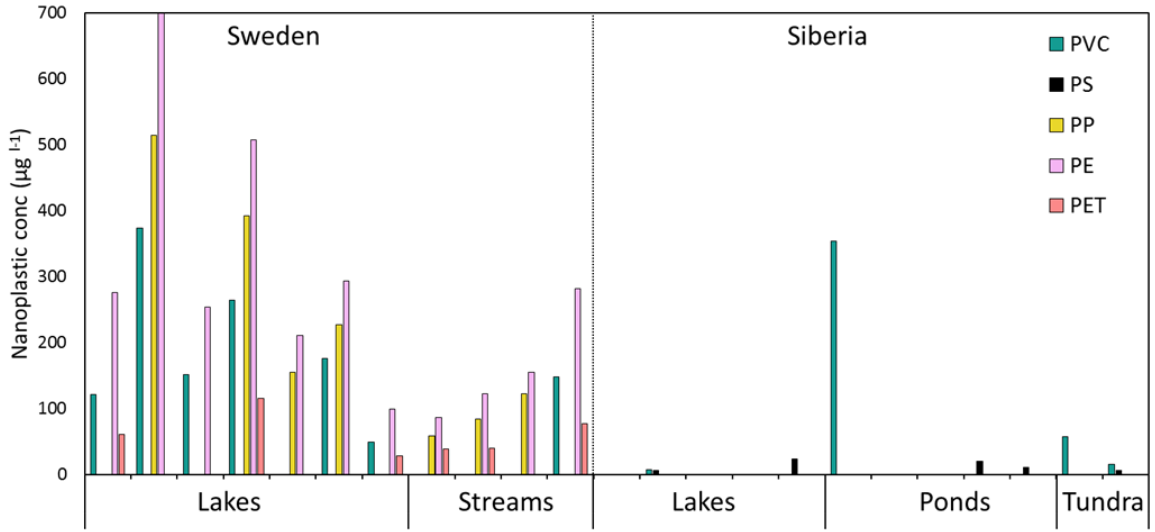
Sea ice Antarctic

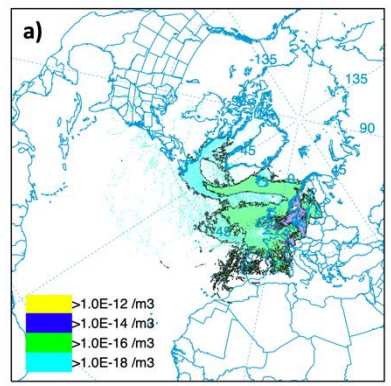


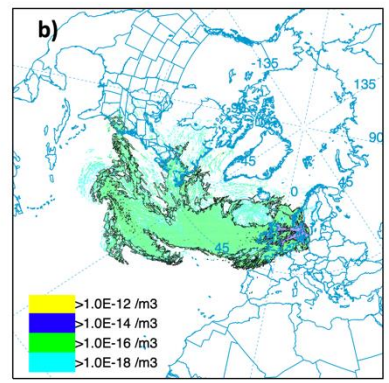


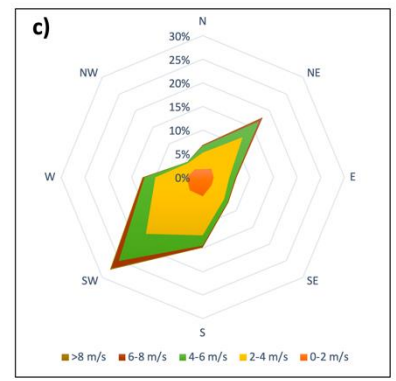


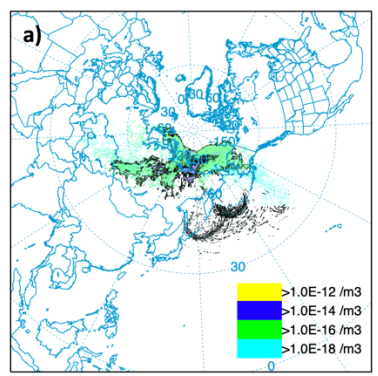

9
8
3
5
4
6
7
2
1
200 m
11
10
500 m
Sweden
300 km
L08
L10
P11
P08
L02
TK2
P03
P02
P01
T5
L01
L04
0
0.5
1 km
N
Russia
China
300 km

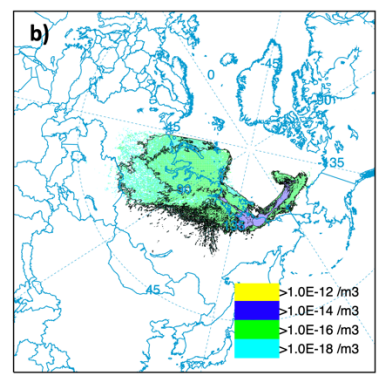

Sweden
Siberia
PVC
PS
PP
PE
PET
Nanoplastic conc (µg l-1)
700
600
500
400
300
200
100
0
Lakes
Streams
Lakes
Ponds
Tundra

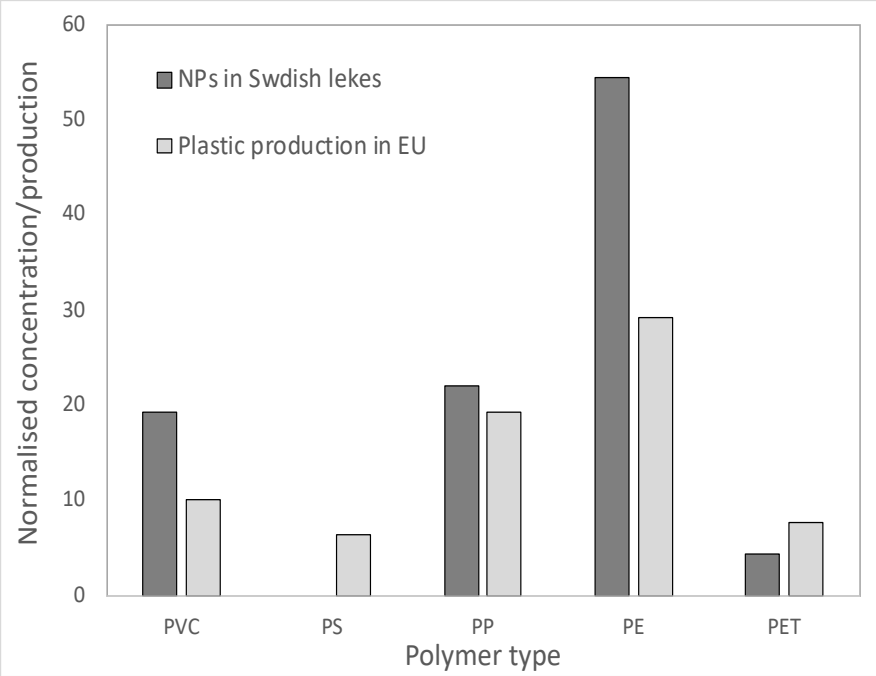

a)
>1.0E-12 /m3
>1.0E-14 /m3
>1.0E-16 /m3
>1.0E-18 /m3

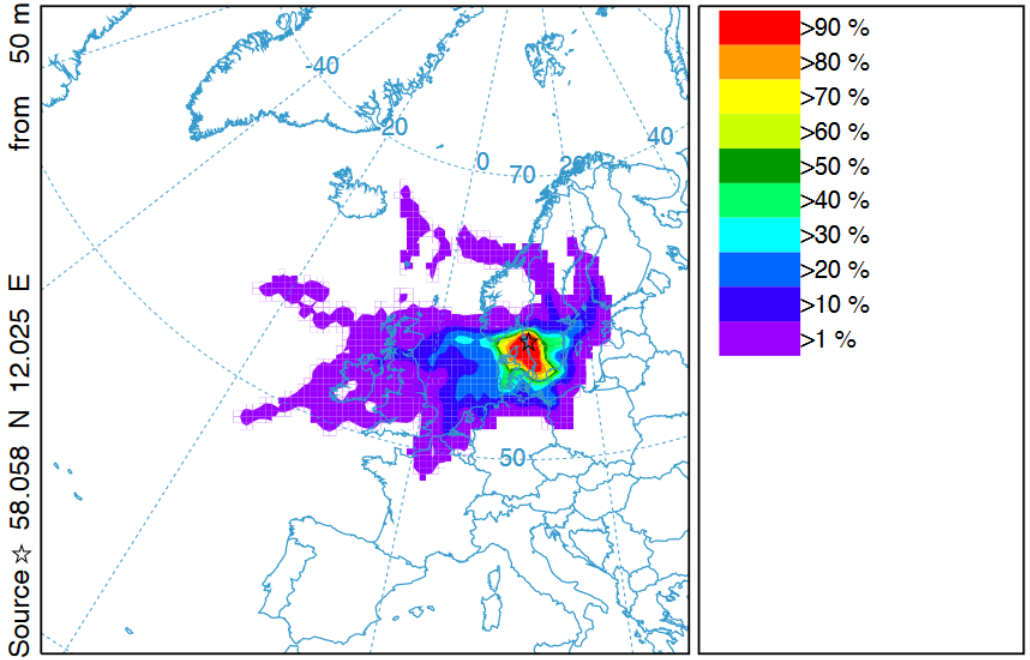

b)
>1.0E-12 /m3
>1.0E-14 /m3
>1.0E-16 /m3
>1.0E-18 /m3

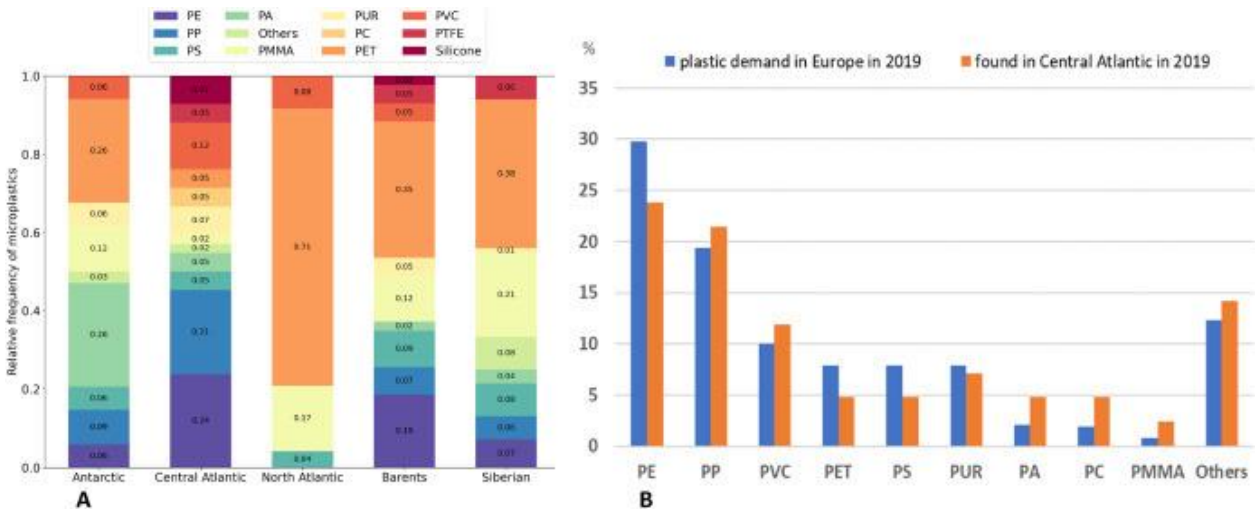

c)
N
NE
E
SE
S
SW
W
NW
30%
25%
20%
15%
10%
5%
0%
>8 m/s
6-8 m/s
4-6 m/s
2-4 m/s
0-2 m/s


a)
>1.0E-12 /m3
>1.0E-14 /m3
>1.0E-16 /m3
>1.0E-18 /m3


b)
>1.0E-12 /m3
>1.0E-14 /m3
>1.0E-16 /m3
>1.0E-18 /m3







Pakhomova, S., et al., 2022. Microplastic variability in subsurface water from the Arctic to Antarctica. Environmental Pollution 298, 118808. https://doi.org/10.1016/j.envpol.2022.118808

True Open Access and open access Data

All data needed to evaluate the conclusions in the paper (including raw files, the scripts and processing stages of the data analysis) are available at https://doi.org/10.24416/UU01-A9A28C↗.

Supplementary data to: Nanoplastics and ultrafine microplastic in the Dutch Wadden Sea – the hidden plastics debris?

Publication Date: **2022-07-12T11:52:02.468220** Accessibility: **Open - freely retrievable**

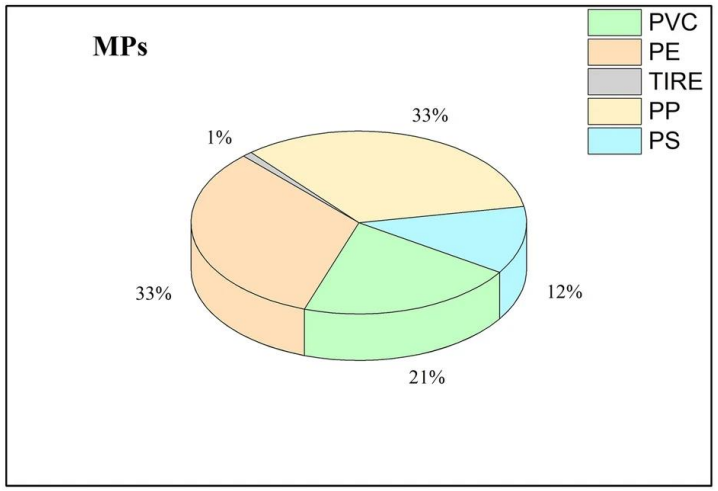
Dušan Materić 1,*, Rupert Holzinger1, Helge Niemann2,3 1 Institute for Marine and Atmospheric Research Utrecht, Utrecht University, Princetonplein 5, 3584CC Utrecht, the Netherlands 2 NIOZ Royal Netherlands Institute for Sea Research, Landsdiep 4, 1797 SZ 't Horntje (Texel), the Netherlands 3Department of Earth Sciences, Utrecht University, Princetonplein 5, 3584CC Utrecht, the Netherlands *Correspondence: d.materic@uu.nl This is the repository of the supplementary, data and it contains: 1. Raw .h5 data files as the original output of TD-PTR-MS for the direct measurement (Site A); 2. Raw .h5 data files as the original output of TD-PTR-MS for the cascade filtering measurements (Site B); 3. Raw .h5 data files as the original output of TD-PTR-MS for the calibration measurements (PS and PET); The folder also contains processing files as the output of PTRwid software used; 4. PTRwid version of software we used for mass spectra and molar ratio extraction; 5. PTRwid associated parameters file that contains the parameters for mass spectra extraction (including the ToF transmissions) 6. Nanoplastics Fingerprint scripts used for the experiments; All "massLibr*" files contain the mass spectra of virgin plastics with molar ratio (ppb) value for each ion detected in the plastics vapours (3 decimal point precision of m/z). The script files were written in PYTHON (compatible with PYTHON 2 and 3 - all versions). "DataFlip.py" is used for formatting the data into the matrix acceptable for the fingerprinting script. "FngClass.py" and "funFunctions.py" are supporting classes used for the main scripts. matchingTest.py is a main script used for comparing a sample mass spectrum to the one from the plastics library (e.g. for PET use "massLibrPET.csv"). matchingLoopQ3.py is a main script used for comparing all the samples with all the plastics from the library ("massLibr*" files). 7. Data analysis of mass spectra: subtraction and limit of detection calculation for "Direct WS*" measurement (Site A)

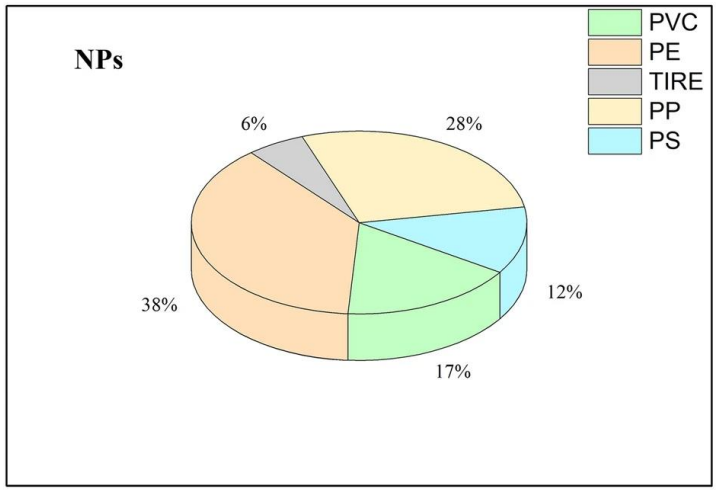
Tags

nanoplastics | microplastics | TD-PTR-MS | polystyrene | Wadden Sea

VIEW CONTENTS

NPs in biota samples





communications earth & environment Article

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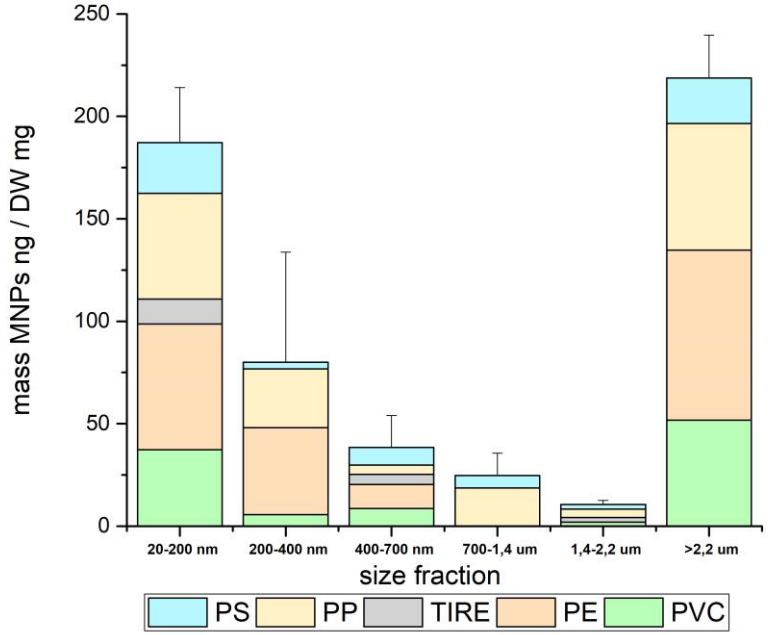
Microplastics and nanoplastics size distribution in farmed mussel tissues

Check for updates

Silvia Fraissinet[1], Giuseppe E. De Benedetto[2], Cosimino Malitesta[1], Rupert Holzinger[3] & Dusan Materić[3,4]

Microplastics and nanoplastics are hazardous to ecosystems, wildlife, and through seafood, also for human health. Due to biological, chemical, and physical characteristics, nanoplastics can slip through cell membranes, being even more toxicologically important than microplastics. Thermal Desorption - Proton Transfer Reaction - Mass Spectrometry was used to analyze mussels from the Apulian region, Italy. All the analyzed organisms have plastics (values ranging from 10 to 187 ng of microplastics and nanoplastics per dry weight mg). The highest mass of plastics was detected in the size groups >2.2 µm (218 ng per dry weight mg) and 20–200 nm (187 ng per dry weight mg). Upscaling data we estimated that people in Europe could ingest more than 2 mg of nanoplastics per year through seafood consumption. The detected presence of nanoplastics in farmed mussels here presented contributes to establishing a baseline for monitoring these pollutants.



https://www.nature.com/articles/s43247-024-01300-2/figures/5

Stayed tuned for more work:

Is there really that much nanoplastics in bottled water?

Nanoplastics measurements must have appropriate blanks

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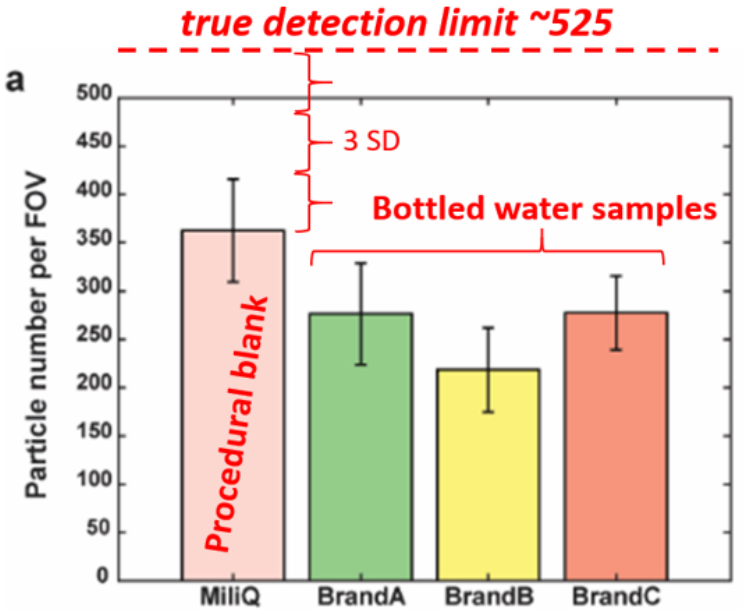

Fig.1. Estimating the true detection limit for particle number concentration based on the procedural blank sample reported by Qian et al.[1]. Note that the measured concentration of micro/nanoplastics in every bottled water sample is below that of the procedural blank and far below the theoretical detection limit of +3 standard deviations (or "3-sigma")[2]

A students' project