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Closing the gap between small and smaller:

Towards an analytical protocol for the detection of Micro- and Nanoplastic in freshwater systems

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BACKGROUND

Nowadays microplastic (MP) can be found in almost all environmental habitats. Degradation and fragmentation lead to smaller particles. Recently the actual fragmentation of polystyrene into nanoplastic (NP) was proven experimentally (Lambert & Wagner 2016).

However, sampling and identification methods are still under development, consequently information on quantity, quality and fate of especially small NMP are limited.

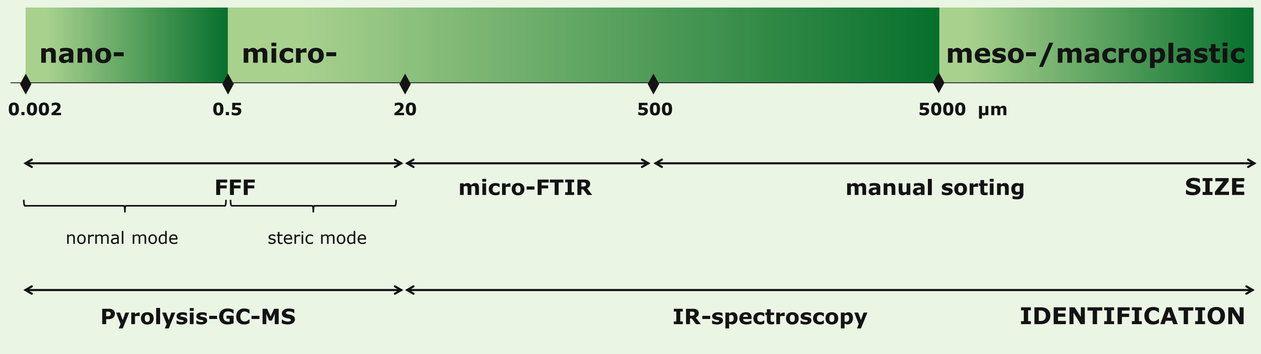
RESEARCH GAPS

- Unharmonized sampling, extraction and identification methods generate data of different quality and resolution
- Numerous studies perform visual sorting of MP, with a size limitation of 300 µm. Often no spectroscopic or thermo-chemical polymer identification is conducted
- Actual occurence of NP in environmental samples has not been proven yet

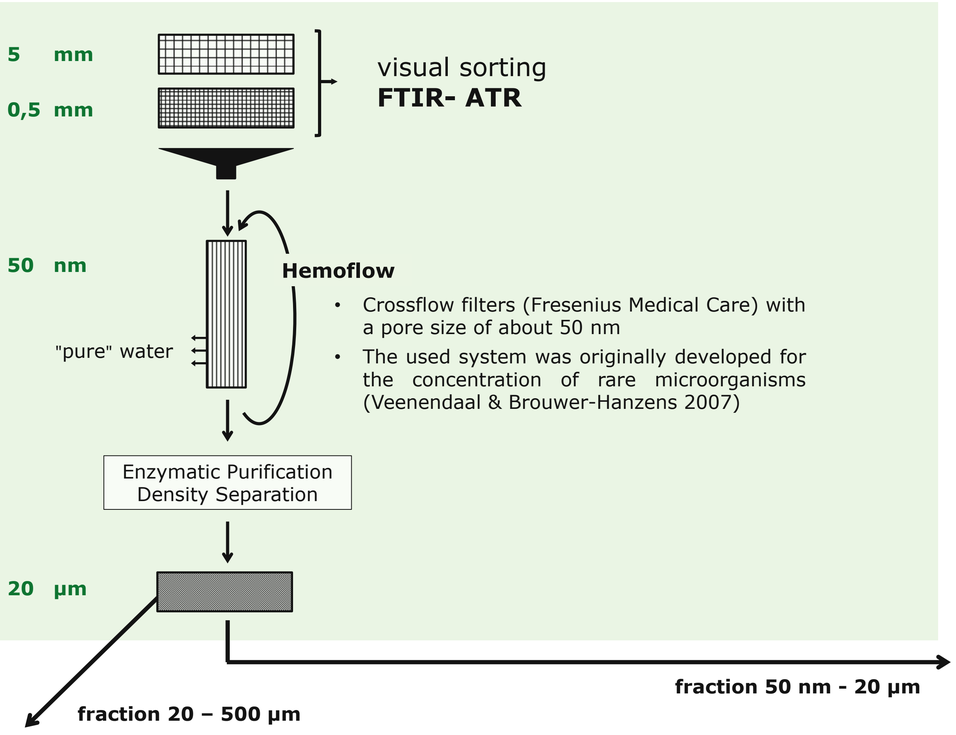
STUDY OBJECTIVE

Development of an analytical protocol, consistently determining sizes and polymer types of all plastics from environmental samples.

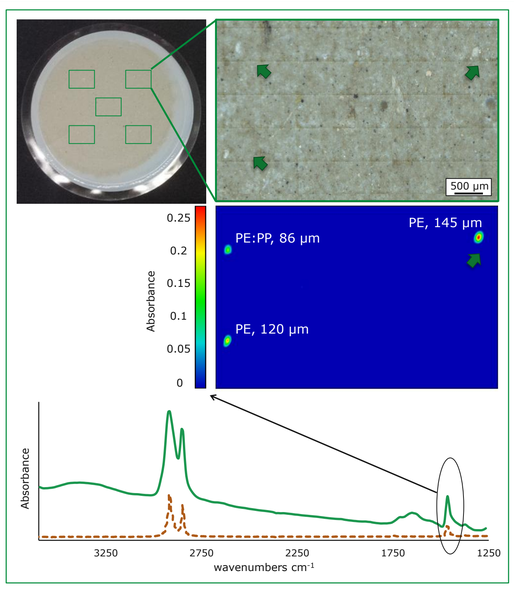
Thereby a special focus is on the unknown NP-fraction.



ANALYTICAL PROTOCOL



- Crossflow filters (Fresenius Medical Care) with a pore size of about 50 nm
- The used system was originally developed for the concentration of rare microorganisms (Veenendaal & Brouwer-Hanzens 2007)



Micro-FTIR
(Nicolet iN10, ThermoFisher)

- Fourier- Transform Infrared Microscopy
- MP enriched on aluminum oxide (Anodisc) filter are identified by chemical mapping
- Five fields (35 % of the filter area) are mapped with a spatial pixel resolution of 20 x 20 µm, resulting in a measuring time of 7 hours (Figure 1)

Fig. 1: Surfacewater sample from lake IJsselmeer (NL) enriched on Anodisc filter, the visual picture of one measuring field and the chemical map (integrated from 1480- 1430 cm^{-1}, Loeder et al 2015). Identification of polymers through library reconciliation

Field Flow Fractionation (FFF, Postnova)

- Separation of NP due to differences in size
- **2 working modes (normal and steric)**: Reversal of fractionation order for particles larger than 500 nm (Figure 2)

  → A prior filtration step is necessary to guarantee a sufficient separation
- Coupled detectors: Determination of sizes (MALS) and concentrations (UV-Vis)

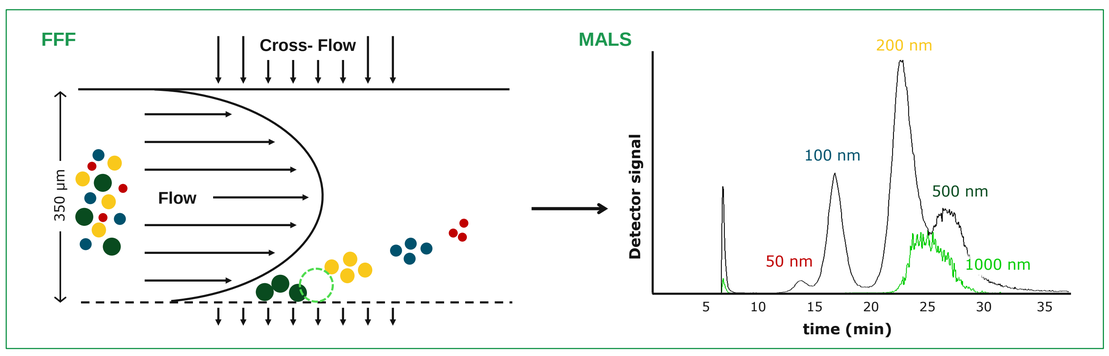
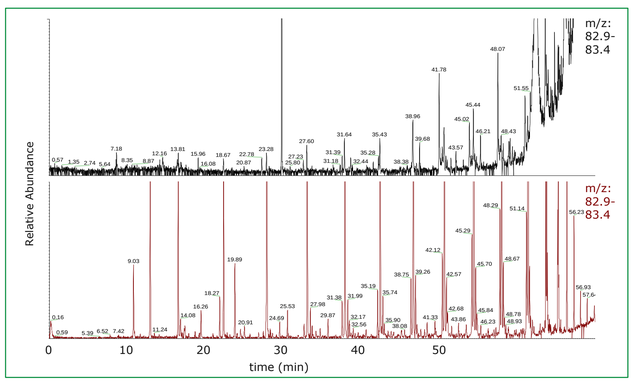


Fig. 2: Principle of the Asymmetrical Flow- FFF. Particles of a heterogeneous sample are fractionated according to size. A successful fractionation for PS particles of 50 – 500 nm size was conducted (black). A coupled MALS detector determines particles sizes, revealing a distortion if 1000 nm PS beads (green) would be injected simultaneously.

Pyrolysis GC- MS (GSG- Mess & Analysengeräte)



- Size fractions are identified by pyrolysis coupled to GC-MS
- Using the characteristic fingerprint of individual polymer types for their identification in environmental samples (Figure 3)
- A database, including 6 polymer types was created and needs to be extended

Fig. 3: The pyrogram (black) of the surfacewater sample from lake IJsselmeer **(50 nm – 500 µm)** showing the characteristic signals of polyethylene (PE, red) at a mass of 82.9 – 83.4.

CONCLUSION

- **MP (20- 500 µm) is identified by micro-FTIR without manual particle handling**
- **NP with a size of 25- 500 nm are successfully fractionated by FFF**
- **Single plastic types in an environmental matrix can be determined by Pyrolysis GC-MS**

OUTLOOK

- Further optimisation of settings for individual analytical techniques
- Protocol- validation for drinking, surface and treated waste water samples
- Usage of the FFF for the determination of nano- fragmentation for various plastics as a consequence of UV- exposure

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