BASEMAN
MICROPLASTICS ANALYSES IN EUROPEAN WATERS

ALFRED-WEGENER-INSTITUT
HELMHOLTZ-ZENTRUM FÜR POLAR- UND MEERESFORSCHUNG

FTIR in microplastic research: Towards a harmonized and standardized analysis

Sebastian Primpke et al.

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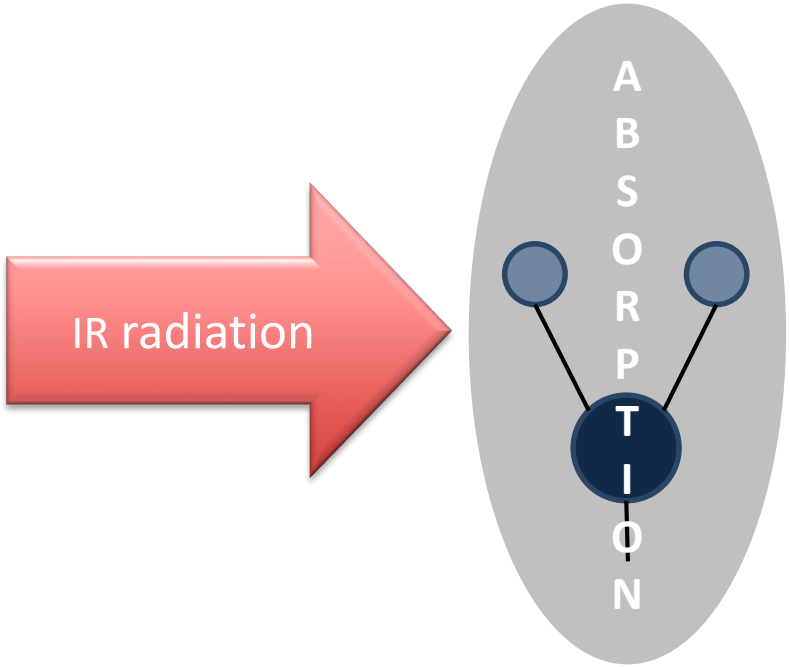
HELMHOLTZ

FTIR spectroscopy

Fourier transform infrared (FTIR)

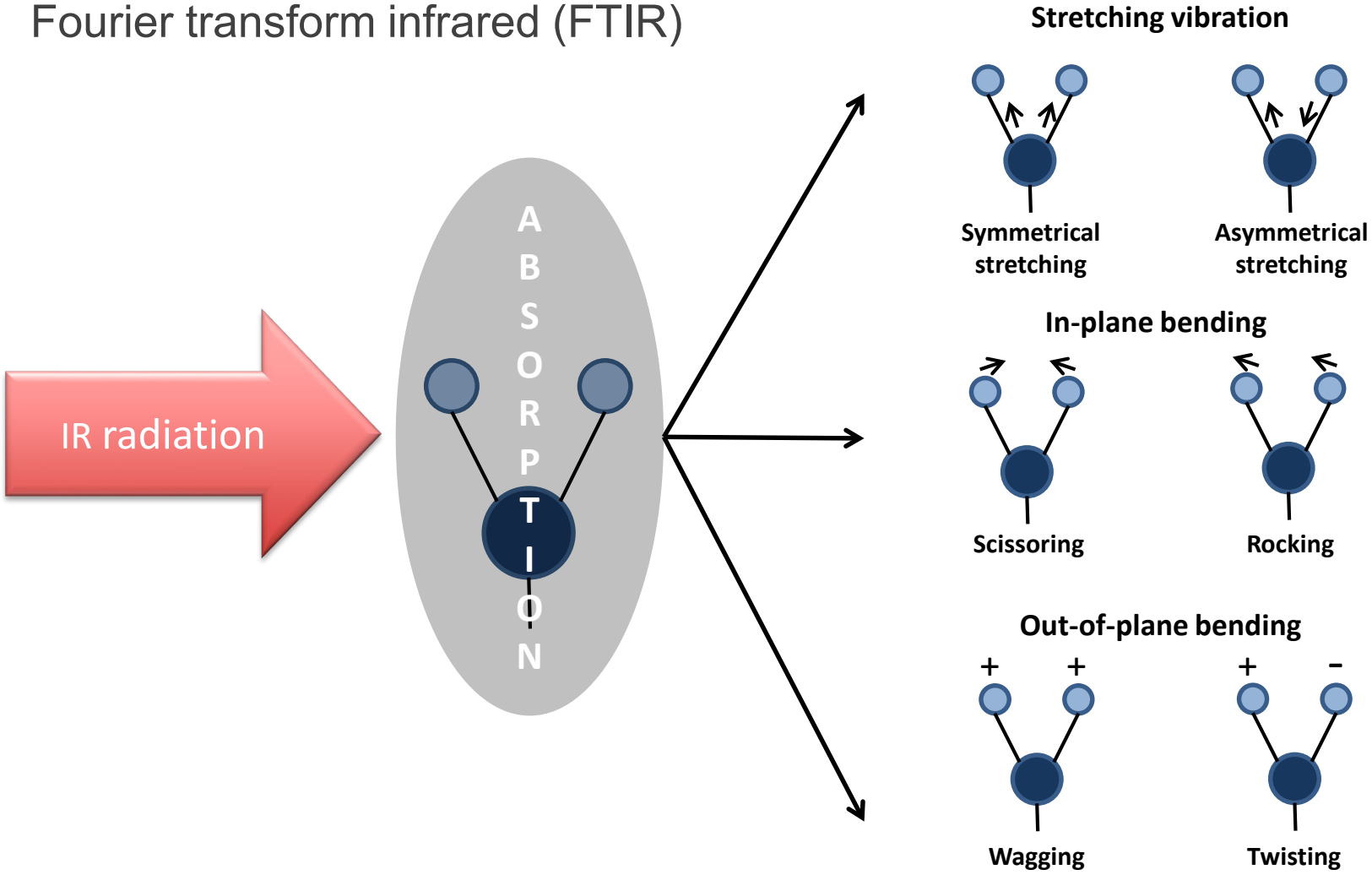
FTIR spectroscopy

Fourier transform infrared (FTIR)



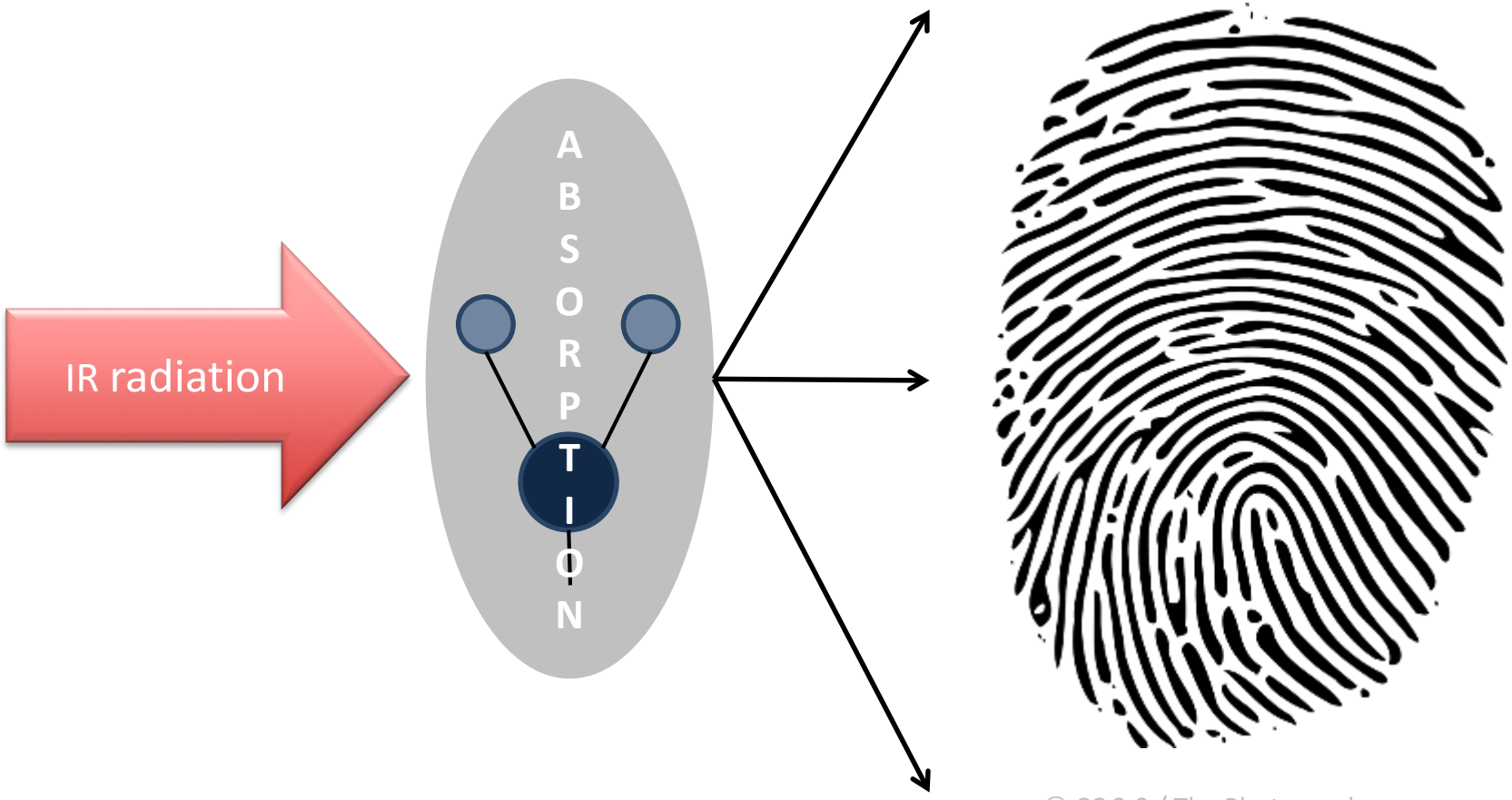
FTIR spectroscopy

Fourier transform infrared (FTIR)



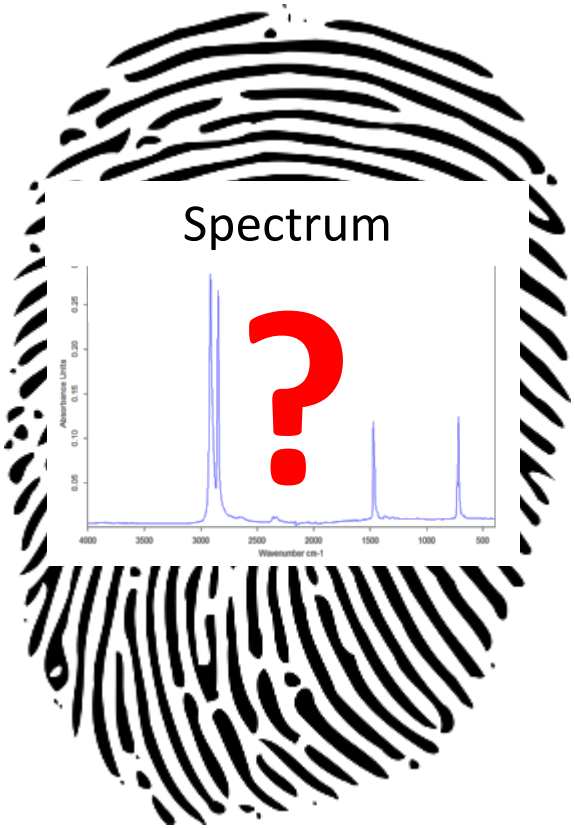
FTIR spectroscopy

Fourier transform infrared (FTIR)



Analysis via Library Search

Analysis via Library Search



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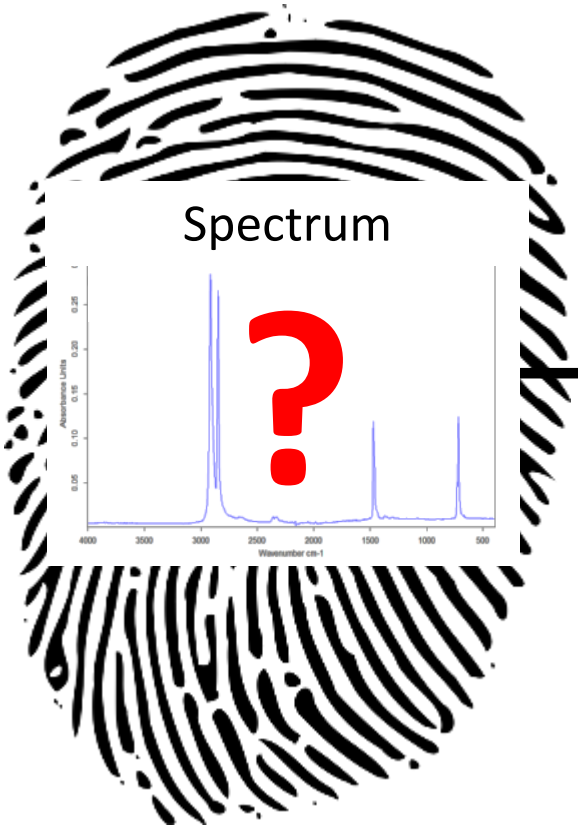
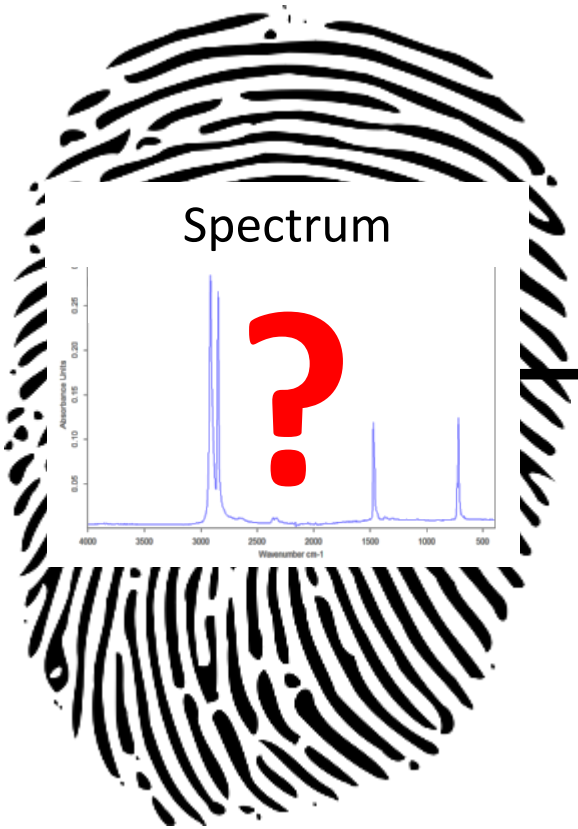
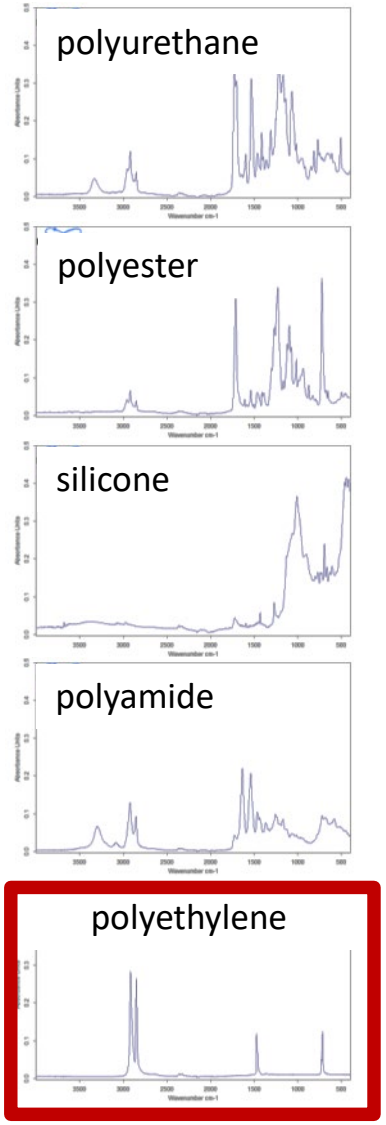


Spectral database

Analysis via Library Search

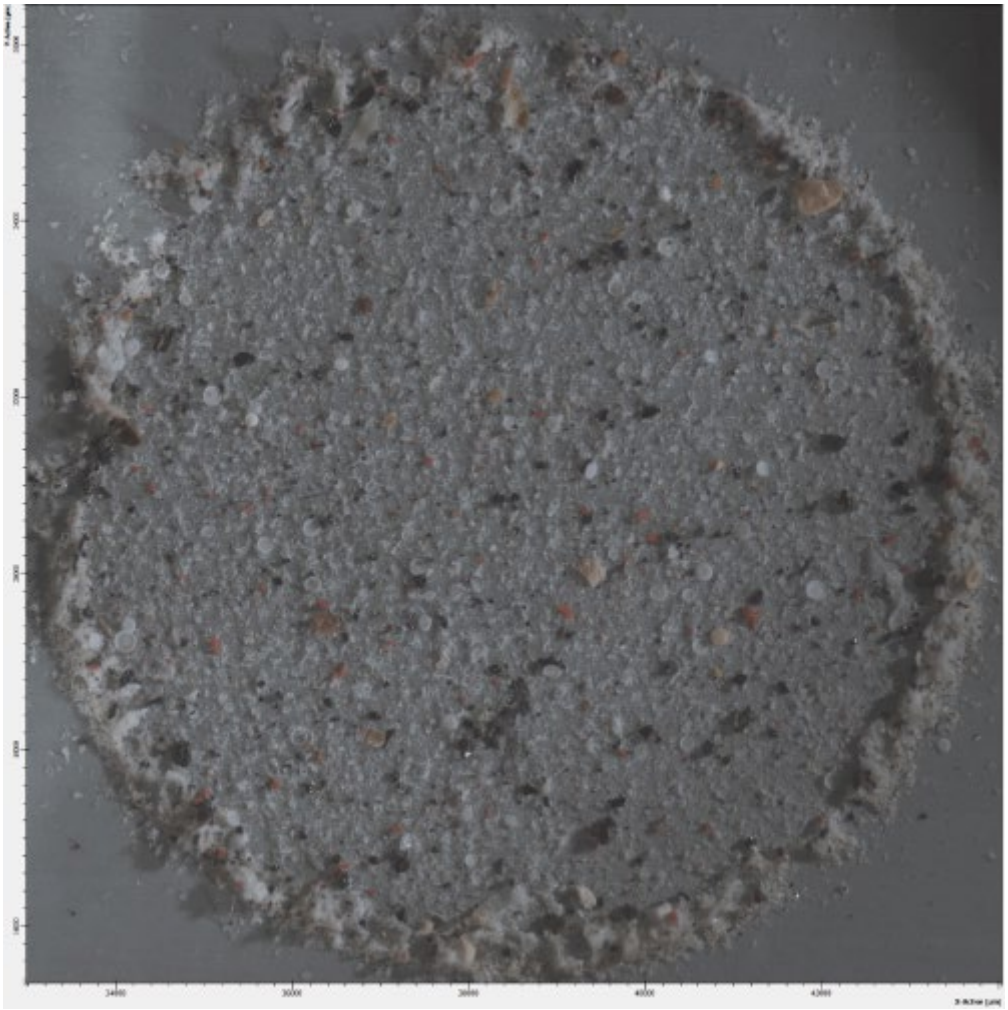


Spectral database



Why FTIR for MP analysis?

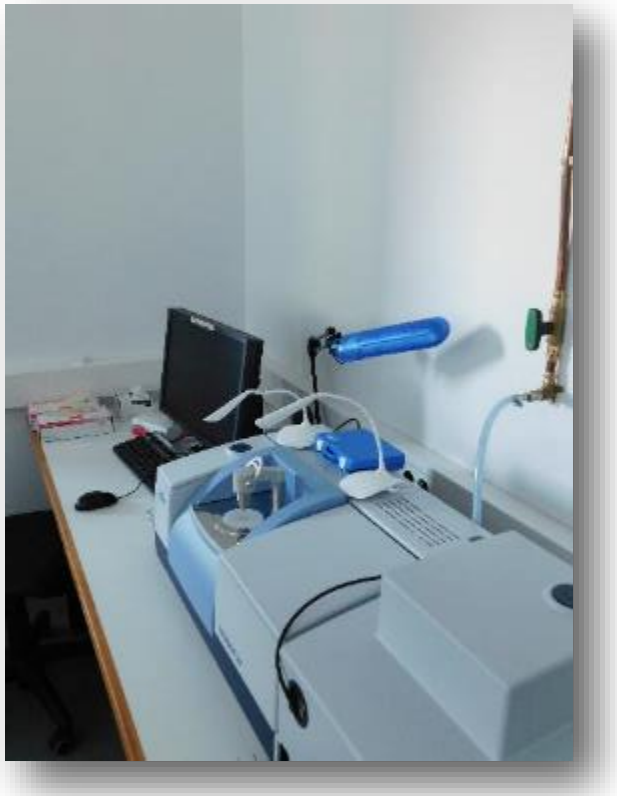
- Chemical imaging via a non destructive method.
- Sample preparation compared to RAMAN microscopy is less demanding.
- Complete mapping of membrane filters is possible.



Particles > 500 µm

If the particles can be sorted by hand:

- Filtration onto filter meshes with 500 µm pore size
- Optical sorting of the particles
- Attenuated total reflection (ATR)-FTIR-measurement



Particles > 500 µm

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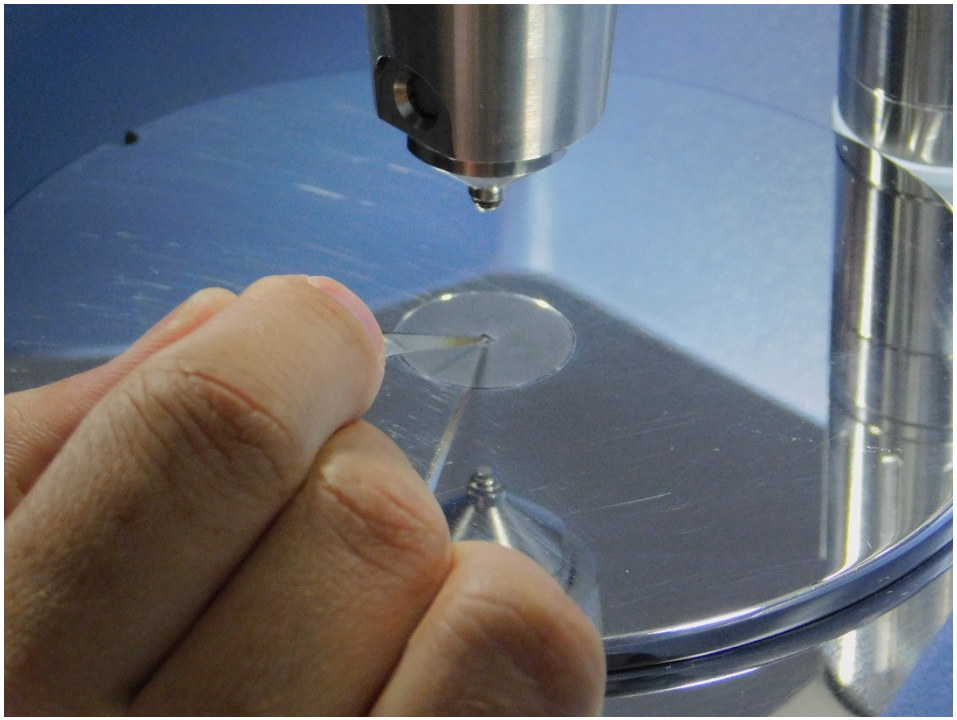

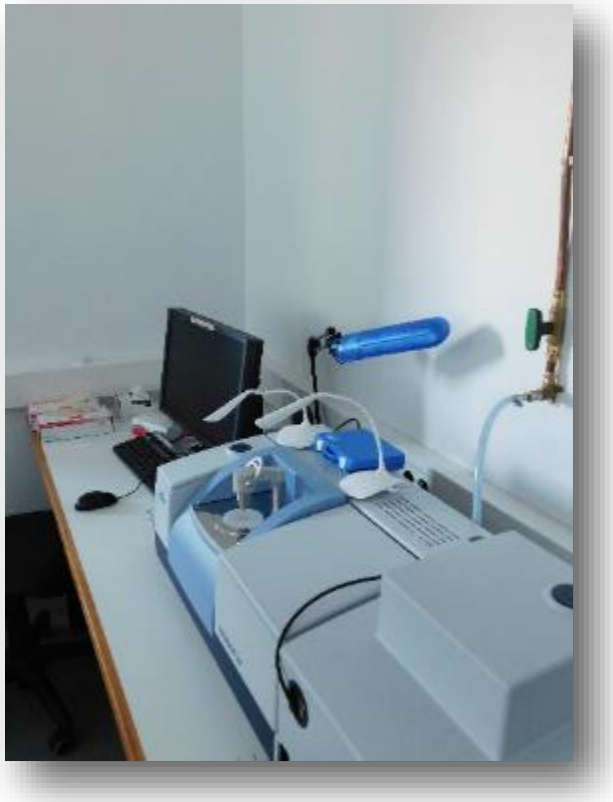

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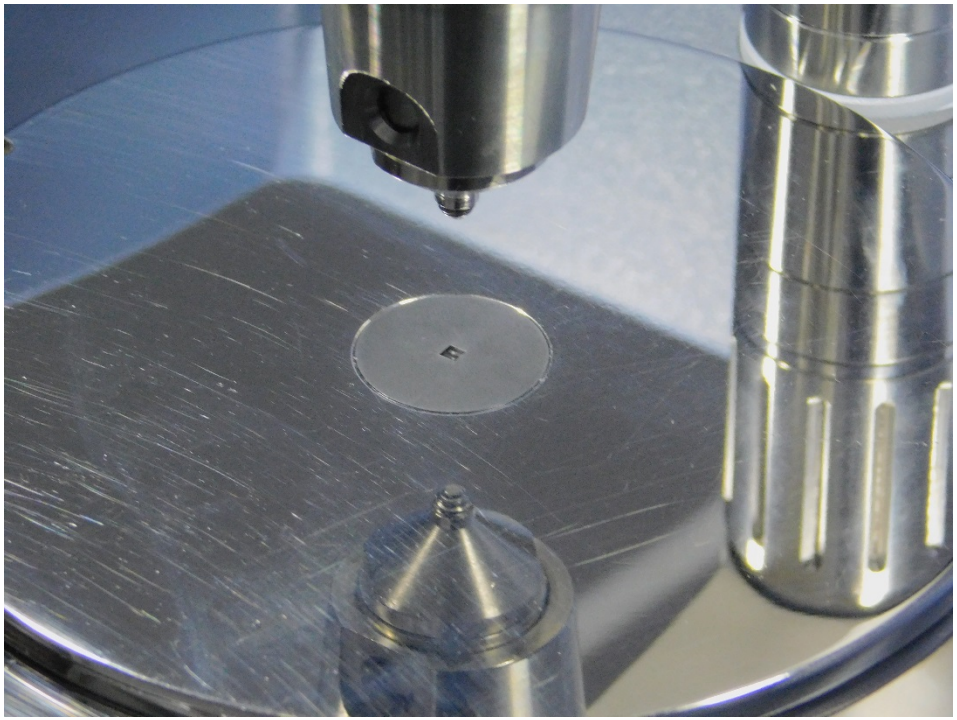
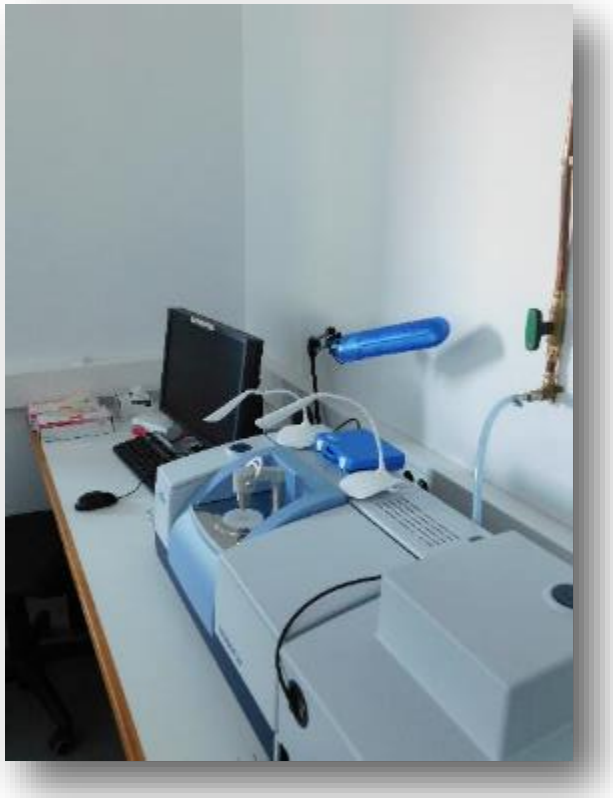
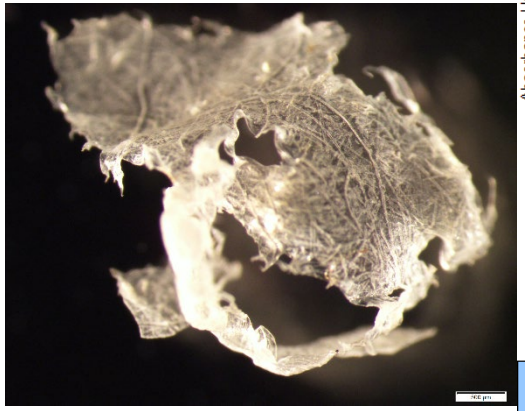
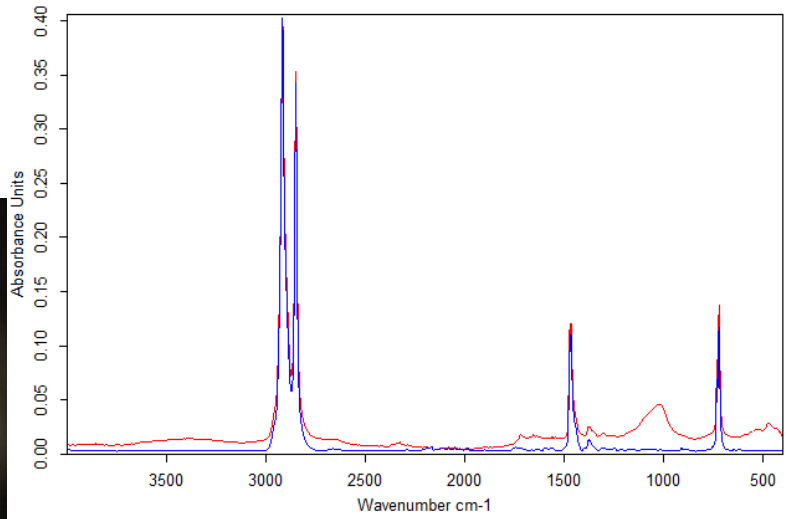




Example – ATR-FTIR-spectroscopy



Bibliothekssuche **18.01.2018 14:55:16**



Substanz	polyethylene, low density
Kurzzeichen	LDPE
Hersteller	unknown
Form (Pulver, Pellet, Folie, Stü	foil
Farbe	red
Messmethode	ATR
Eintrag Nr.	211
Bibliotheksname	BASEMANN_POLYMER_REFERENCE_DATABA
Bibliotheksbeschreibung	Database containing spectra from polymers a
Copyright	Marisa Wirth, Sebastian Primpke, Gunnar Gerd

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	954	polyethylene, low density			

Color	File	Path	Spectrum Type
	St5_hexanephase_19b.0	L:\Daten für MELUND	Anfragespektrum

Seite 1 von 1

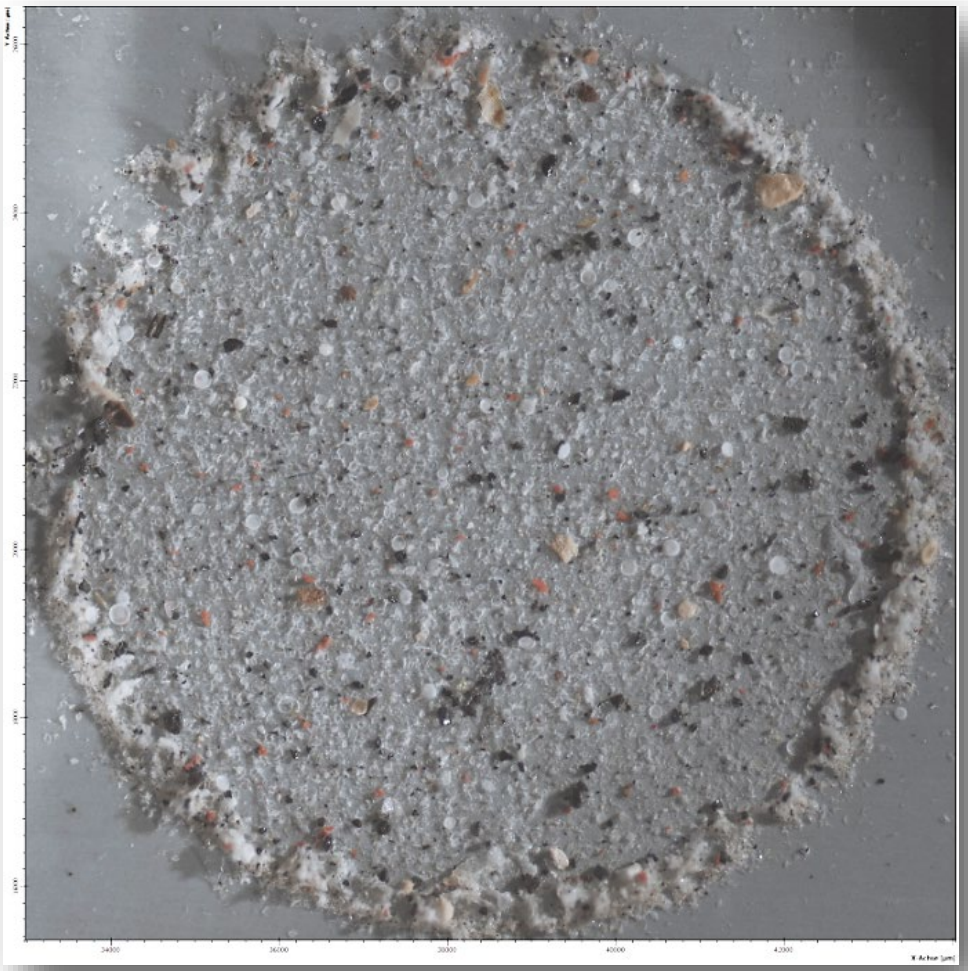
FTIR Imaging

Using the common Fourier-transform infrared (FTIR) spectroscopy

Allows the analysis of large filters (diameter usually 10 - 13 mm)

Applicable in transmission and reflection mode

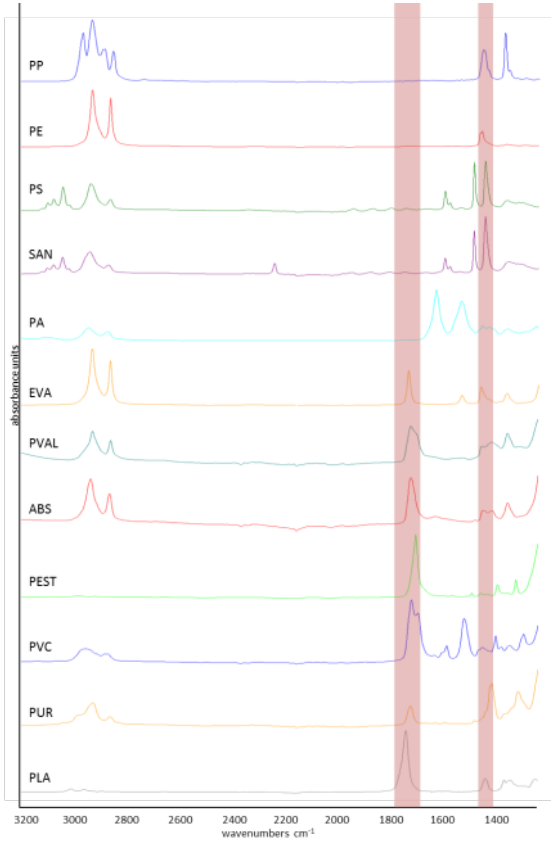
Example: Sediment sample

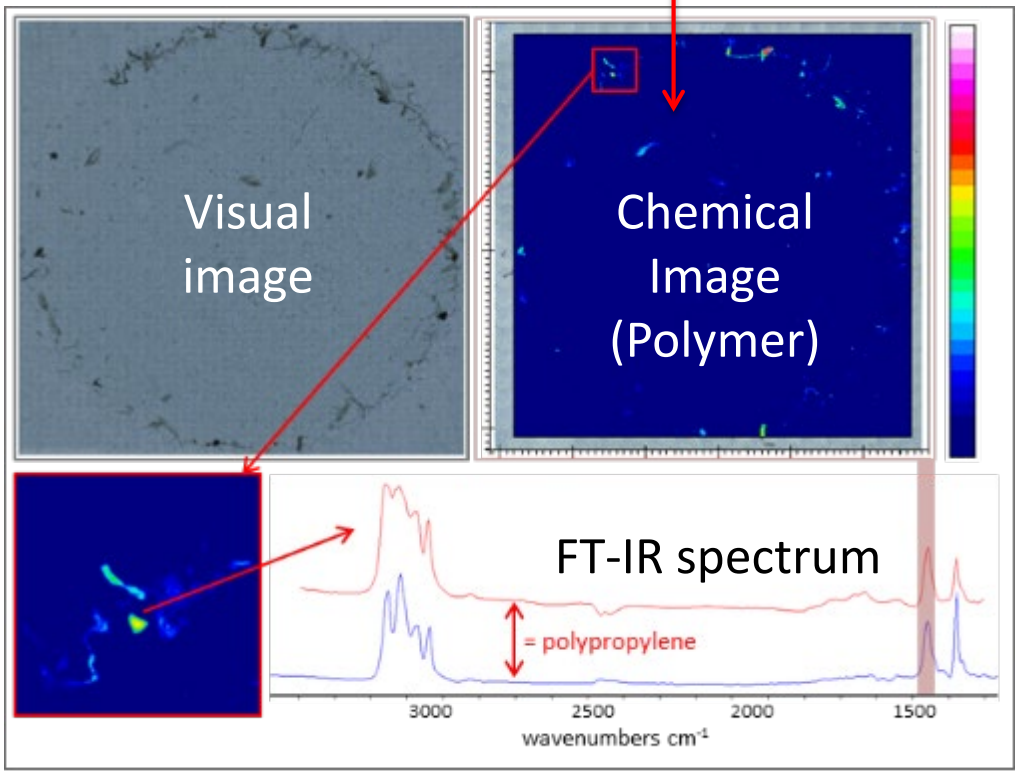


Chemical Imaging

Manual analysis based on false color images

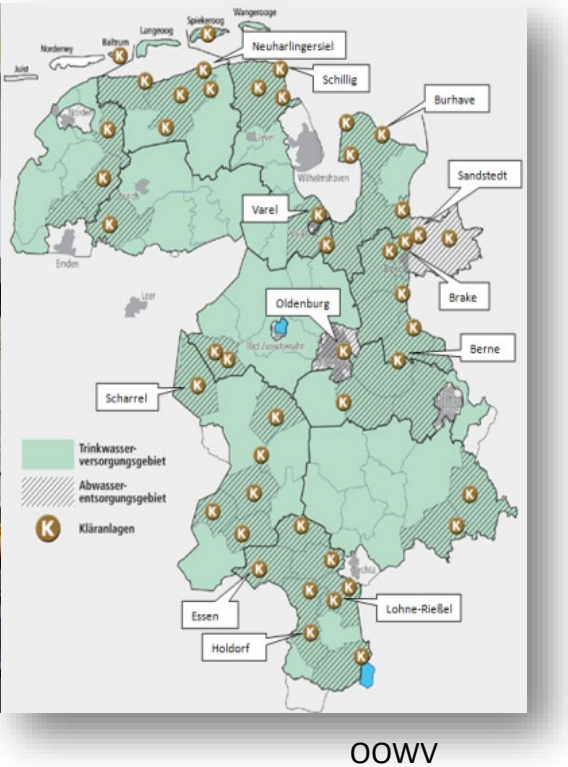
Polymer signatures





Example – Treated Waste Water

Sampling of several waste water treatment plants

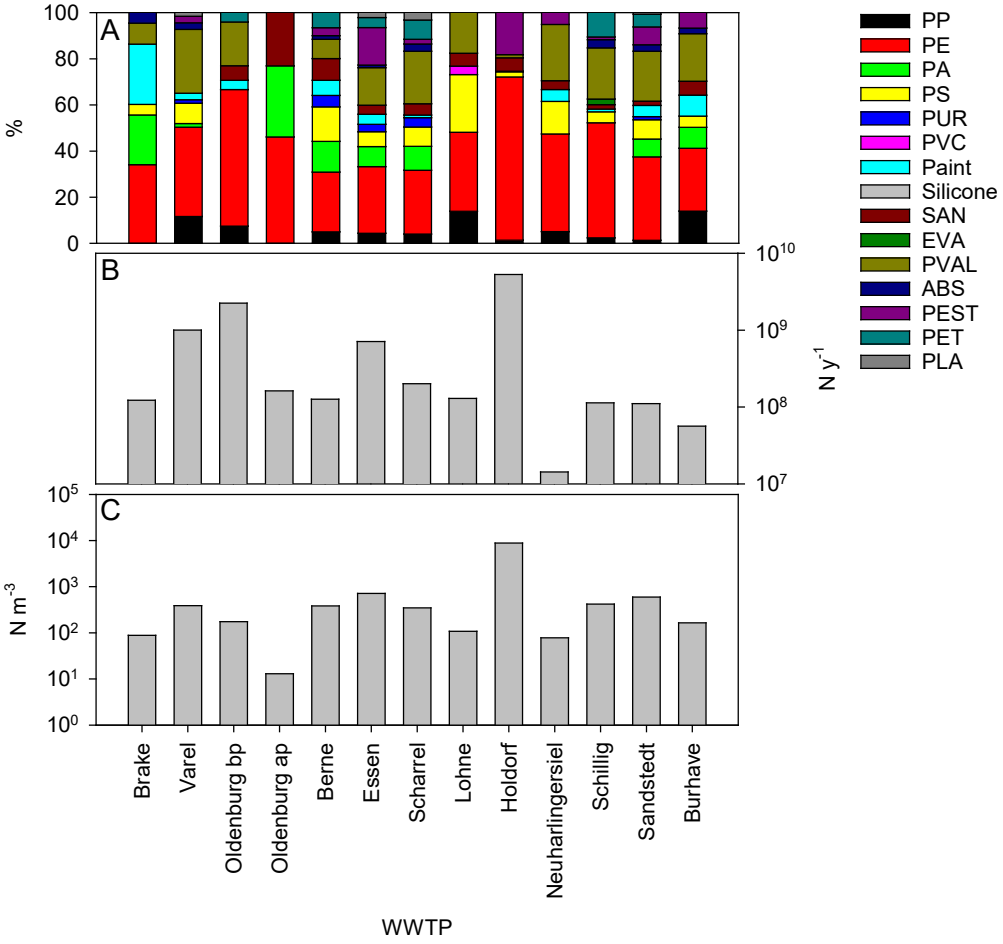


OOWV

Example – Treated Waste Water

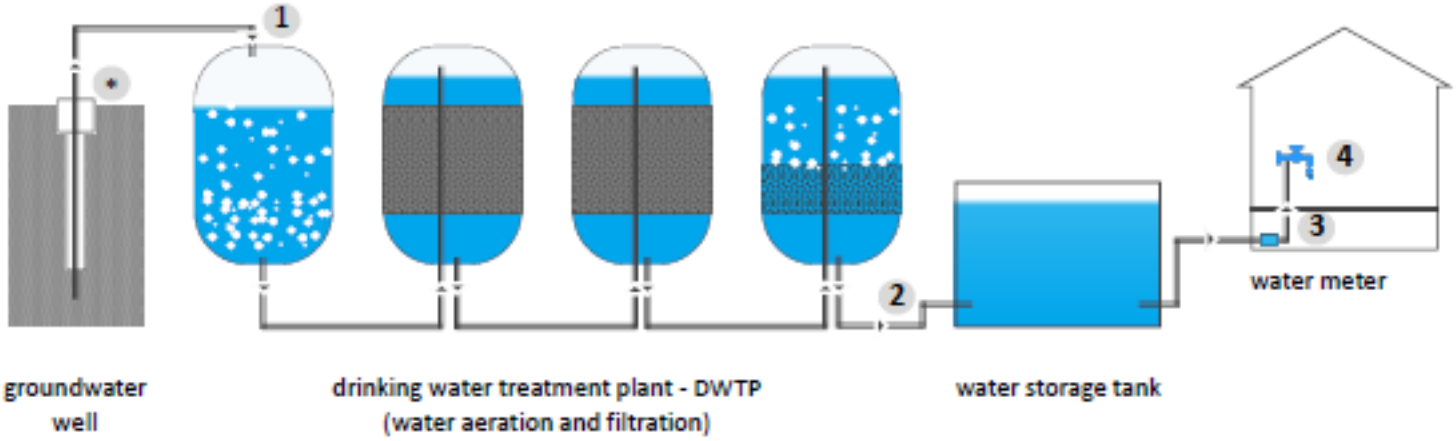
Sampled at the plant effluent

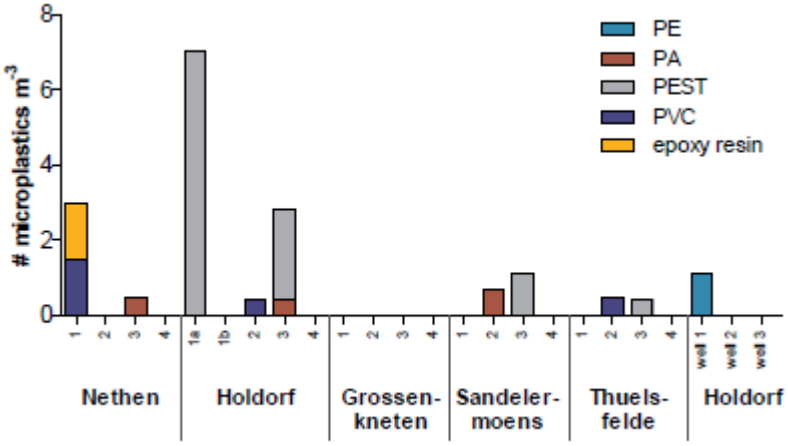
- Filtration on 10 µm stainless steel cartridges
- Sample volume ranged From 0.39 to 1 m^3
- Purified by enzymatic digestion



S. M. Mintenig et al., Water Research, 2017, 108, 365-372

Example – Drinking water





S. M. Mintenig et al., Science of The Total Environment 2019, 648, 631-635.

Manual Analysis via FTIR Imaging

High expenditure of time:

- Manual selection of possible particles
- Manual library search
- Size determination of the particles limited

Overall the process is prone to human bias!

Additionally a high demand of personnel requirements

Manual Analysis via FTIR Imaging

High expenditure of time:

- Manual selection of possible particles

Unsuitable for standardization of microplastic analysis

Additionally a high demand of personnel requirements

Requirements for standardization

- Low expenditure of time
- Impartial analysis
- A minimum of personnel requirements
- Fast and reliable measurements

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Automatization of microplastic analysis based on FTIR imaging

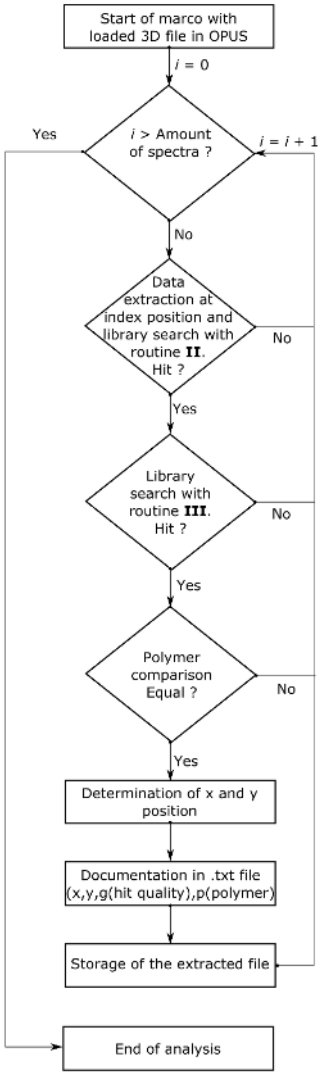
Automated Analysis

Combination of two library searches with different data handling

- Correlation of the original spectrum with vector normalization
- Correlation with the 1st derivative of the original spectrum with vector normalization

Successfully automated data generation with a 3% error value

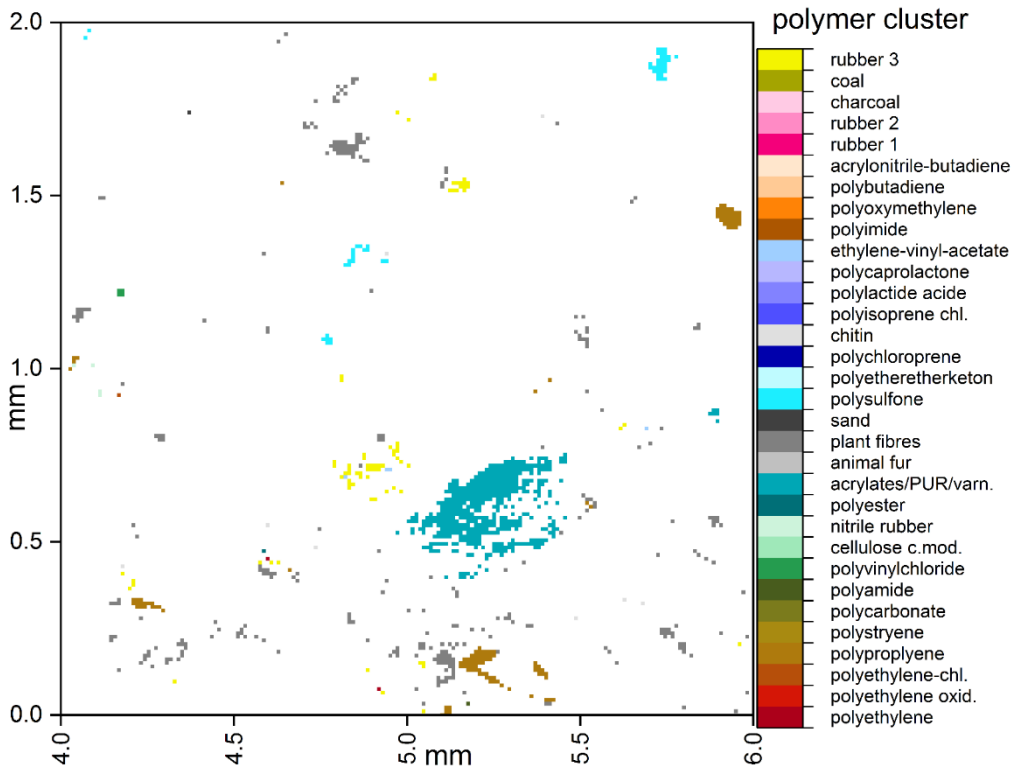
Transformation into images possible



1. Sebastian Primpke et. al., *Anal. Methods,* **2017**, *9,* 1499–1511

Image Analysis

Implementation of an analytical program based on Python and SimpleITK



1. Sebastian Primpke et. al., *Anal. Methods,* **2017**, *9,* 1499–1511

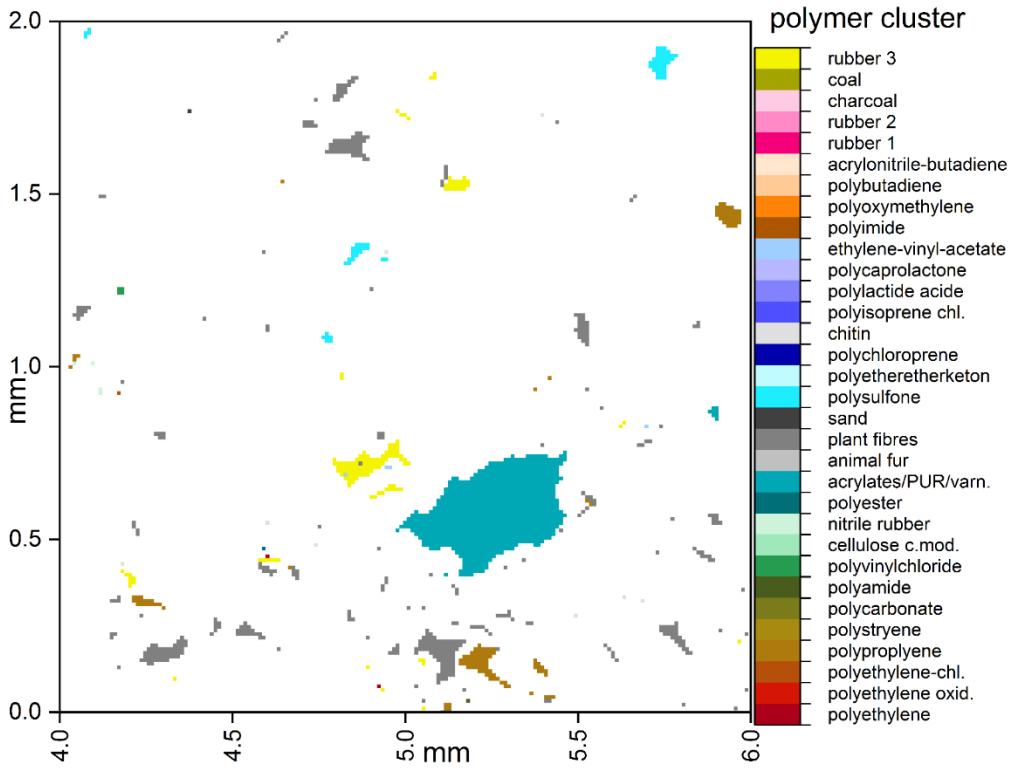
Image Analysis

Implementation of an analytical program based on Python and SimpleITK

Allows determination of particle sizes

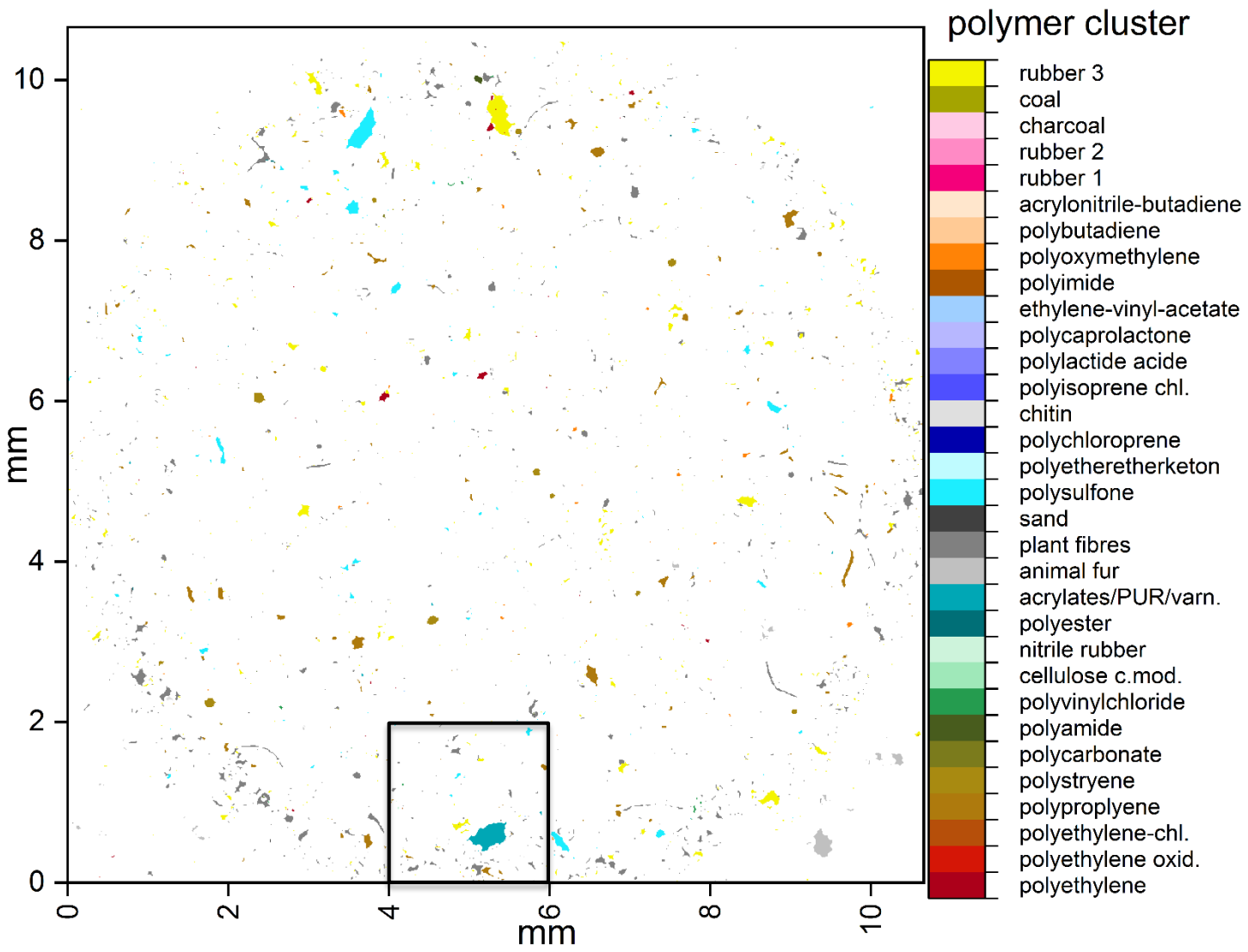
Resulting in high quality data within a short time

Sediment sample as example



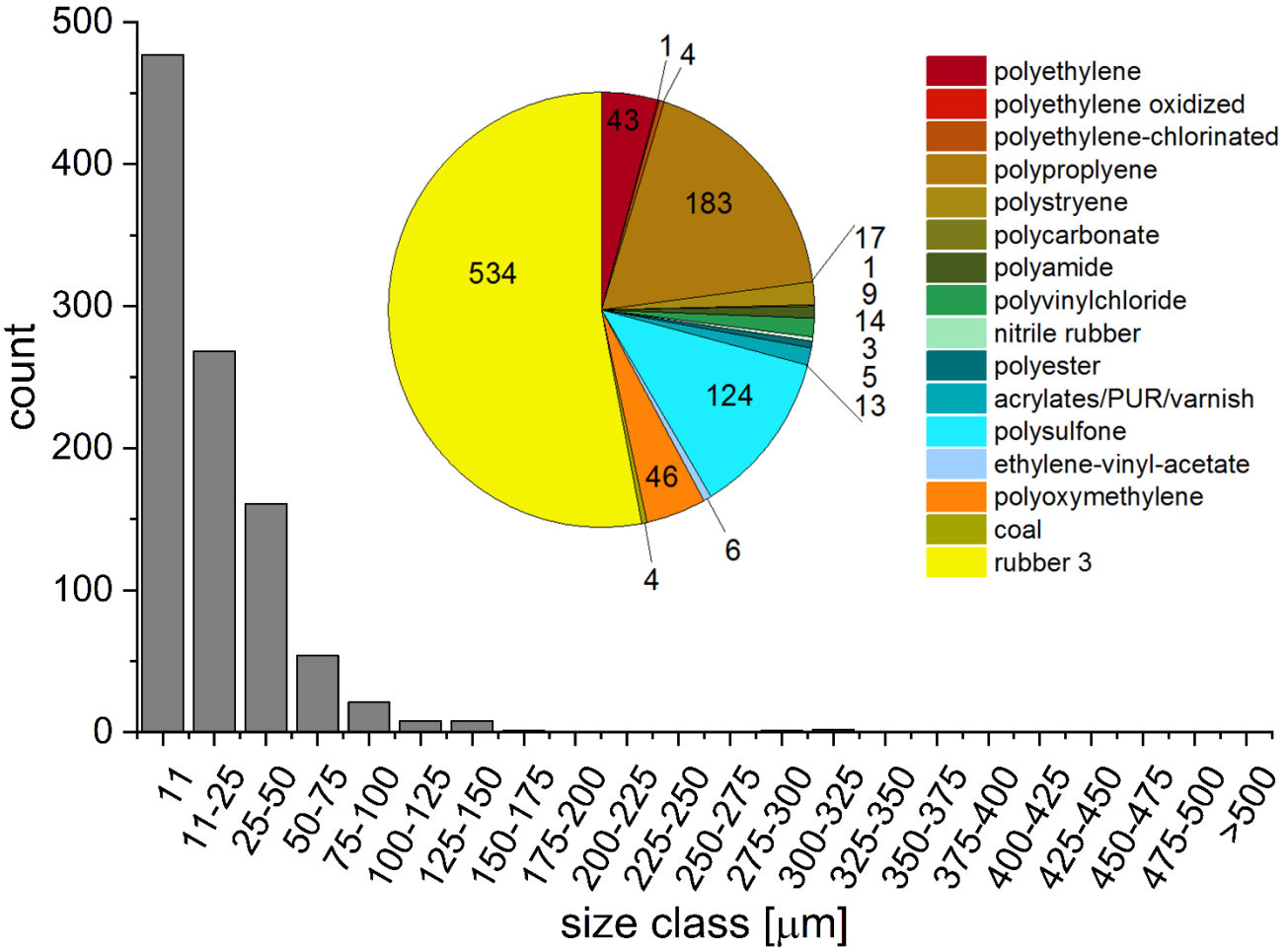
1. Sebastian Primpke et. al., *Anal. Methods,* **2017**, *9,* 1499–1511

And on larger scale



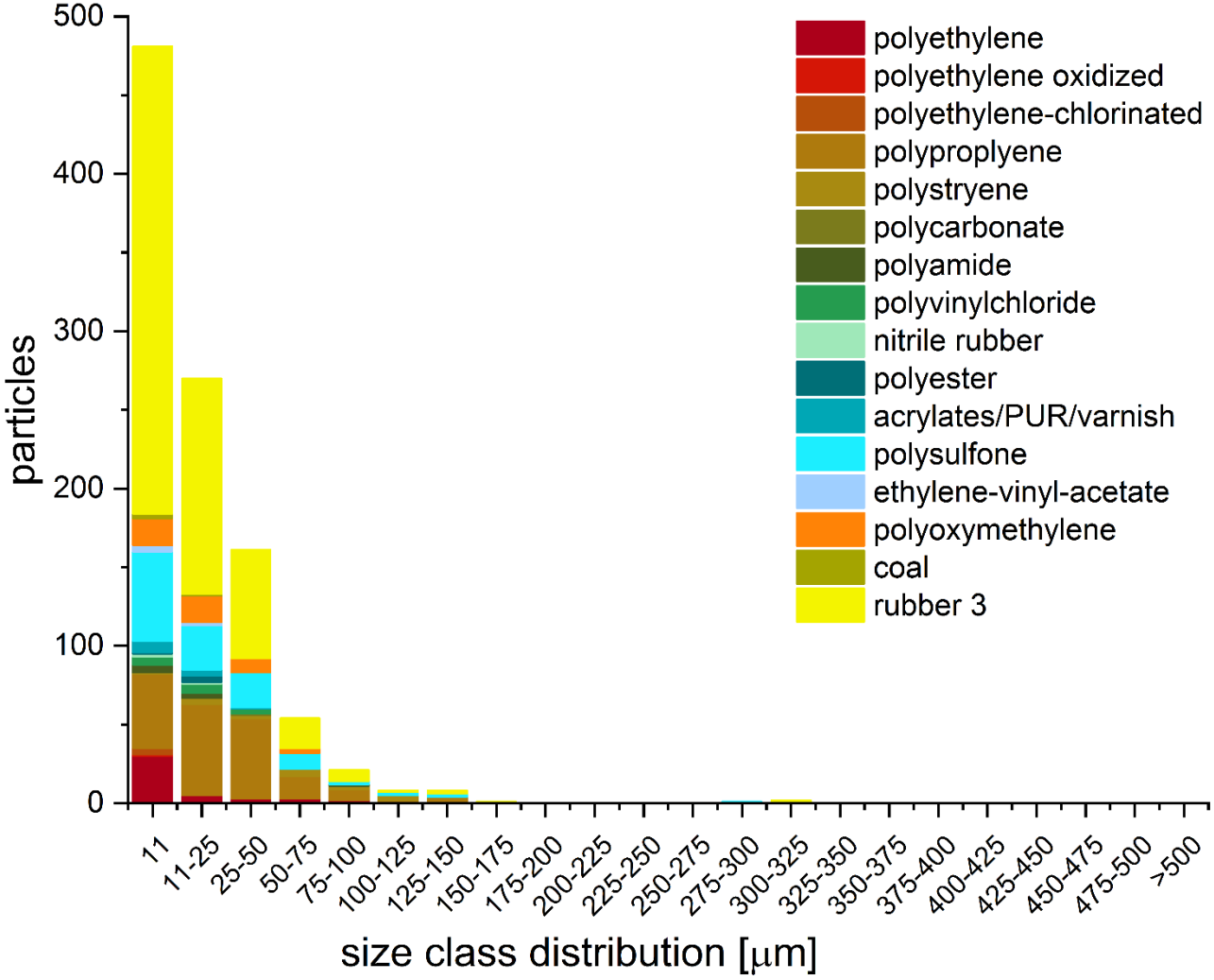
After Particle Analysis

Size distribution and polymer numbers accessible



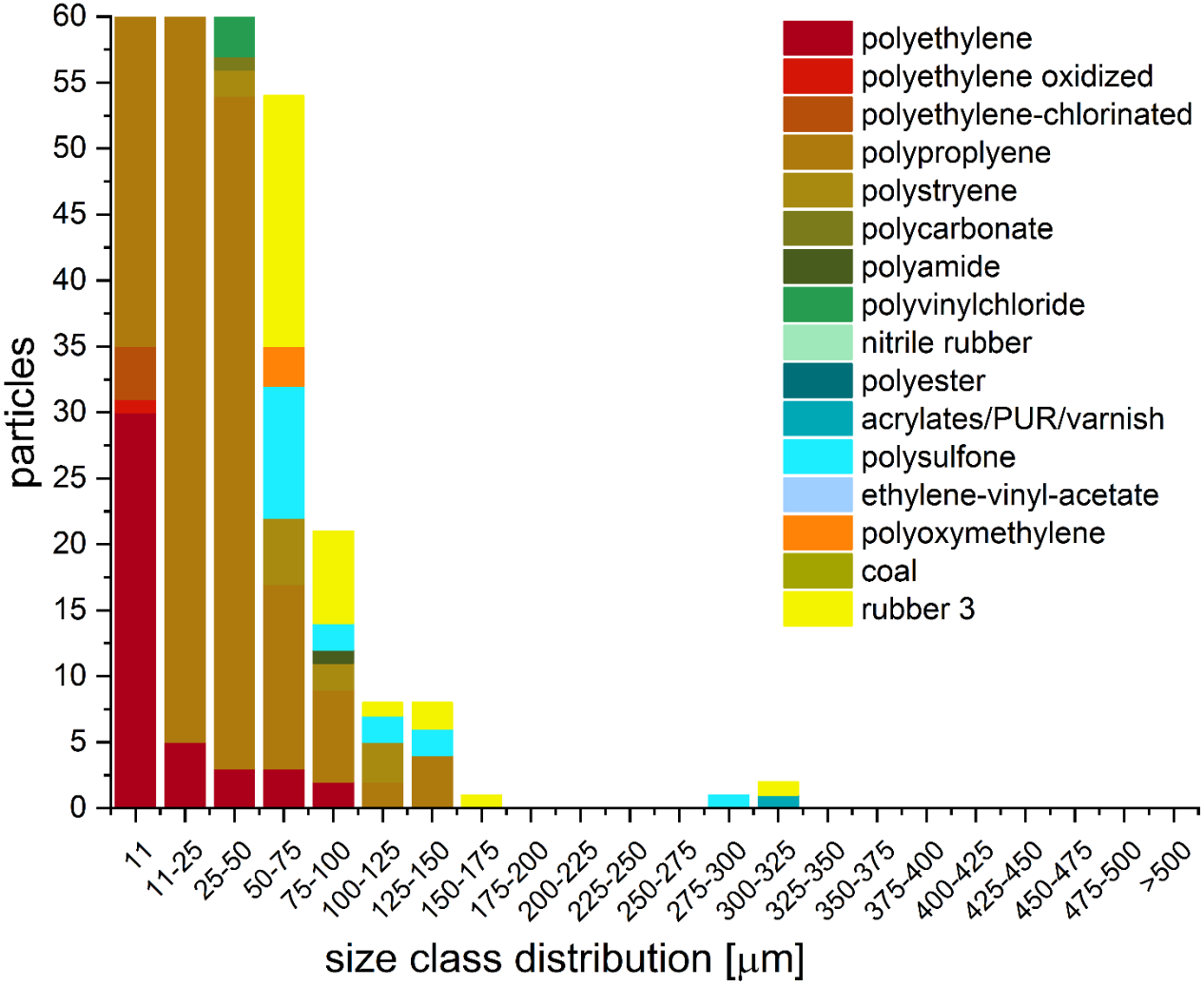
After Particle Analysis

Or even combined:



After Particle Analysis

And as zoom in:



Standardization

- Data analysis independent from human bias via automated analysis
- Identification and Quantification of MP already within this process
- Time saving due to parallelization
- High comparability of results!

Standardization!

Water samples (surface etc.)

Lorenz et al., submitted
Tekman et al., in preparation

Treated waste water

Primpke et al., 2017, CHIUZ
Primpke et al., 2019, Analytical Methods
Mintenig et al., 2019 in preparation

Time series

Song et al., in preparation

Automatization of microplastic analysis based on FTIR imaging

Sediments

Bergmann et al., 2017, ES&T
Haave et al., 2019, Marine Pollution Bulletin
Lorenz et al., submitted
Mani et al., submitted

Biota

Currently in progress

(Arctic) Sea Ice

Peeken et al., 2018, Nature Communications

Snow

Bergmann et al., submitted

Standardization!

Treated waste water

Primpke et al., 2017, CHIUZ
Primpke et al., 2019, Analytical Methods

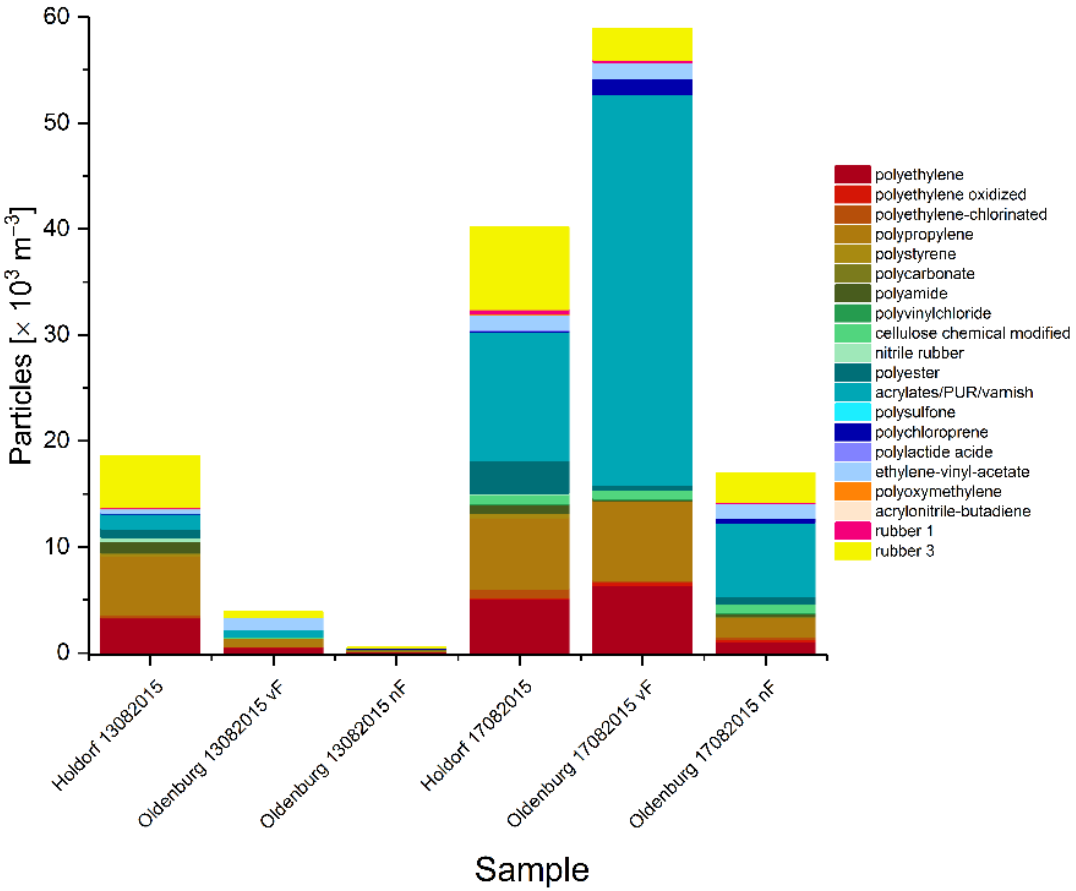
Automatization of microplastic analysis based on FTIR imaging

Treated Waste Water

Two sample sides, one with post filtration unit (Oldenburg)

Additional sampling prior to filtration unit

Sampling on two days

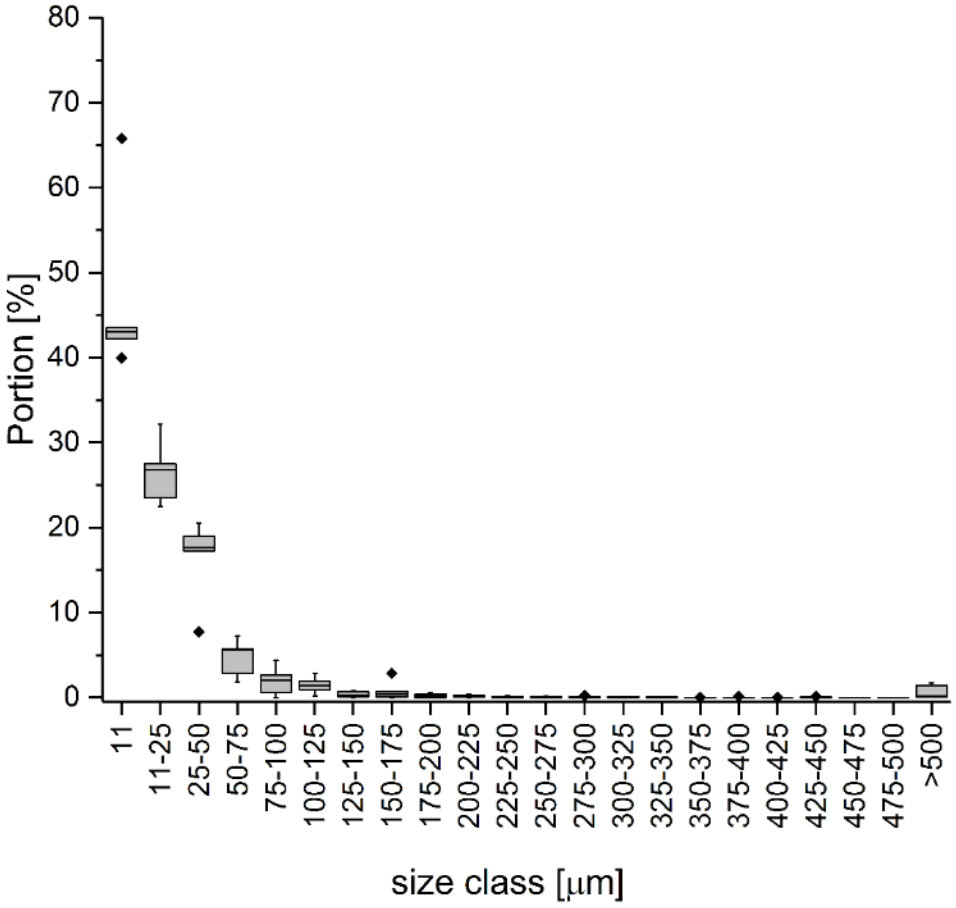


Collaboration with working group of Prof. Laforsch (Univ. Bayreuth) and OOWV (Water Board of Oldenburg and East Frisia)

1. Primpke, S., et al., Chemie in unserer Zeit, 2017. 51(6): p. 402-412.

Treated Waste Water

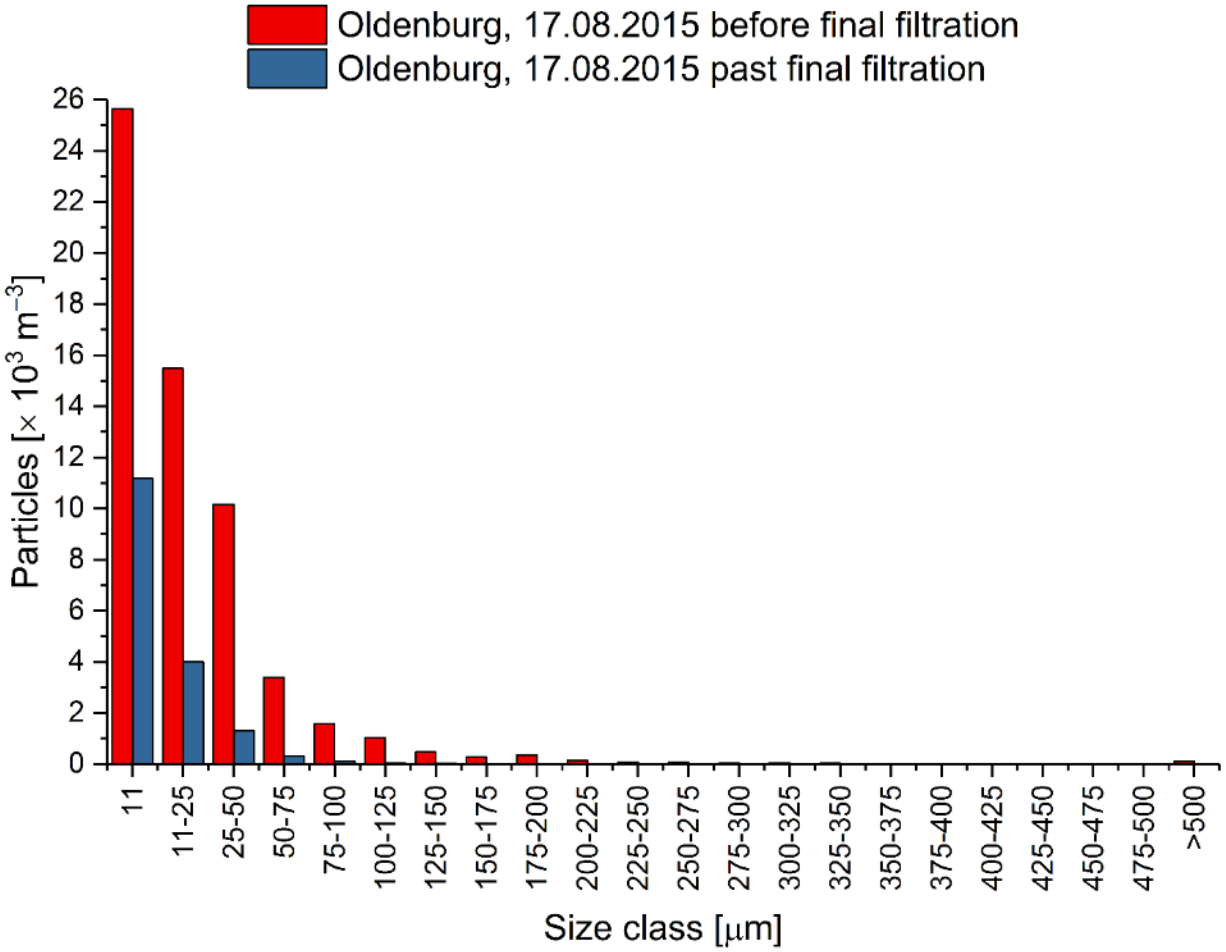
Particle sizes in general



1. Primpke, S., et al., Chemie in unserer Zeit, 2017. 51(6): p. 402-412.

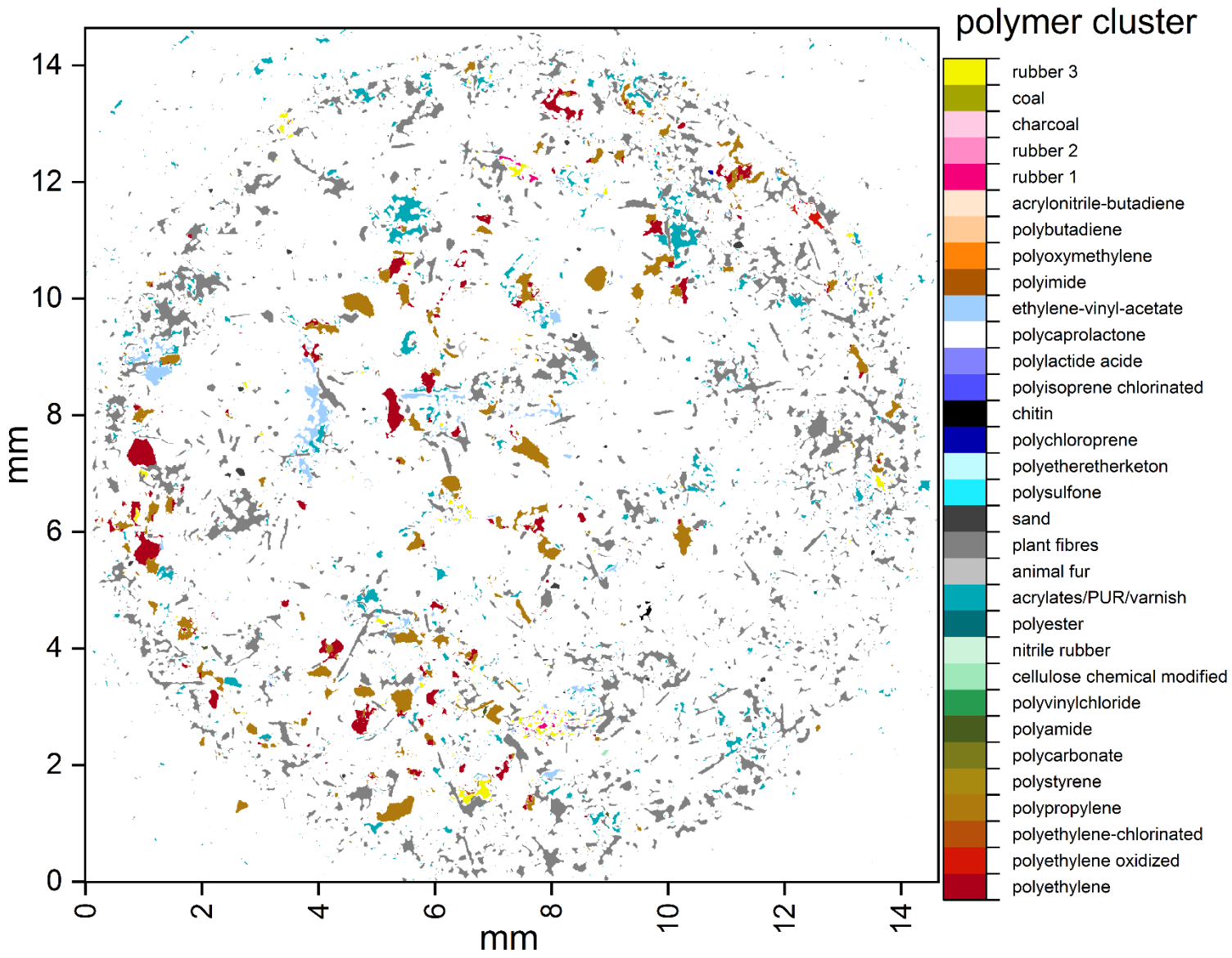
Treated Waste Water

Efficiency tests for filtration unit in Oldenburg:



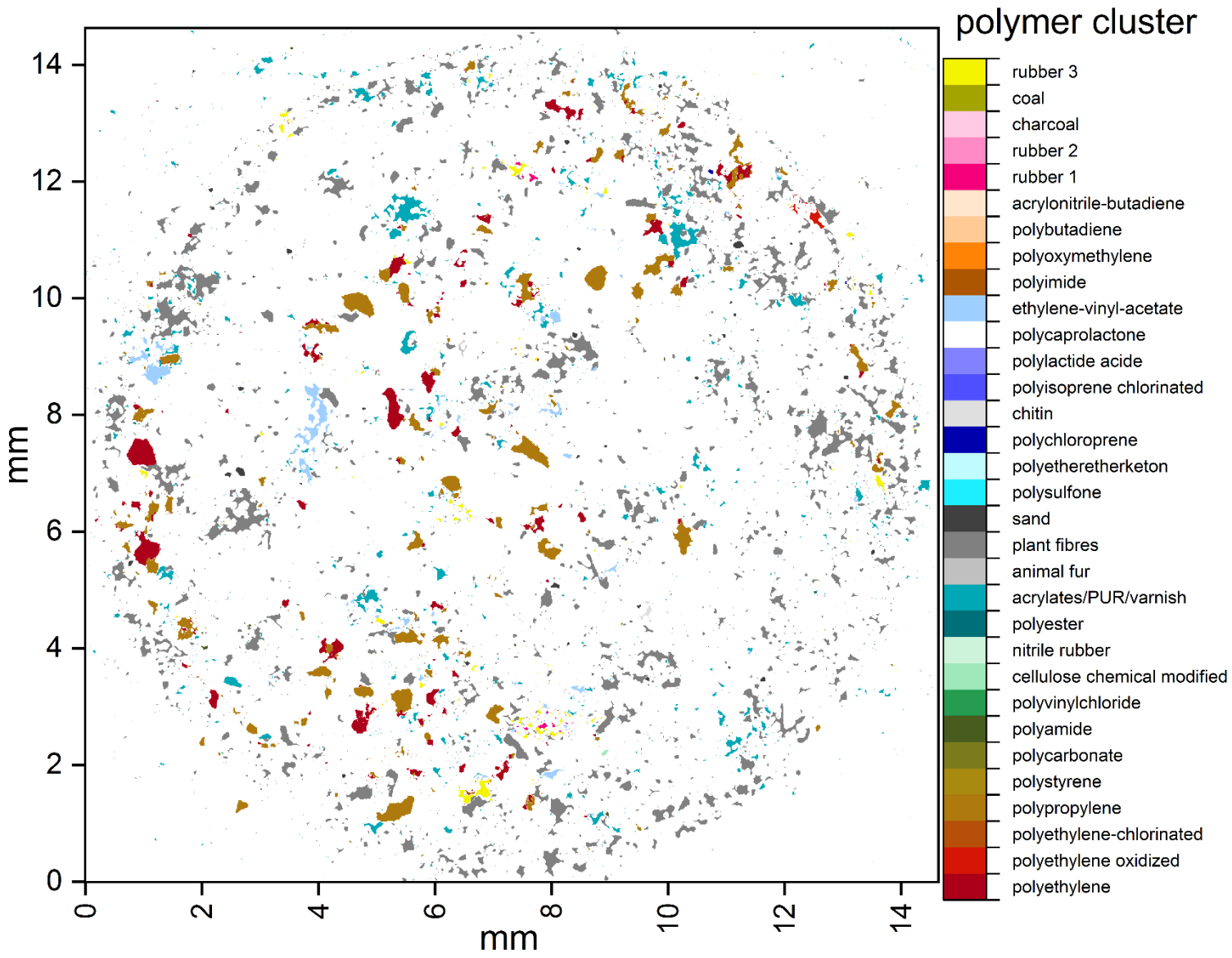
1. Primpke, S., et al., Chemie in unserer Zeit, 2017. 51(6): p. 402-412.

Lets go for fibers in waste water!



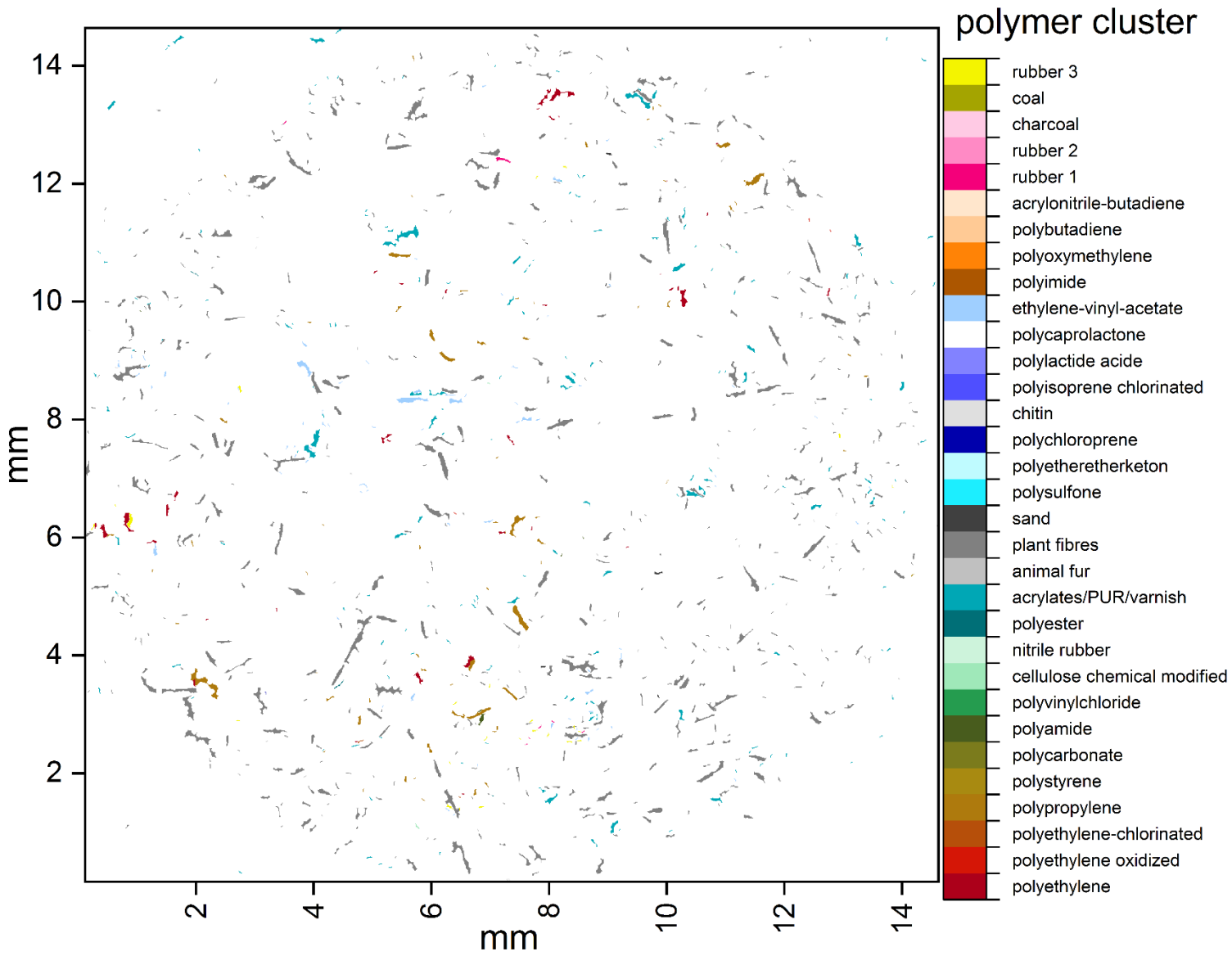
1. Primpke, S., et al., Analytical Methods, 2019. DOI: 10.1039/C9AY00126C

Particles



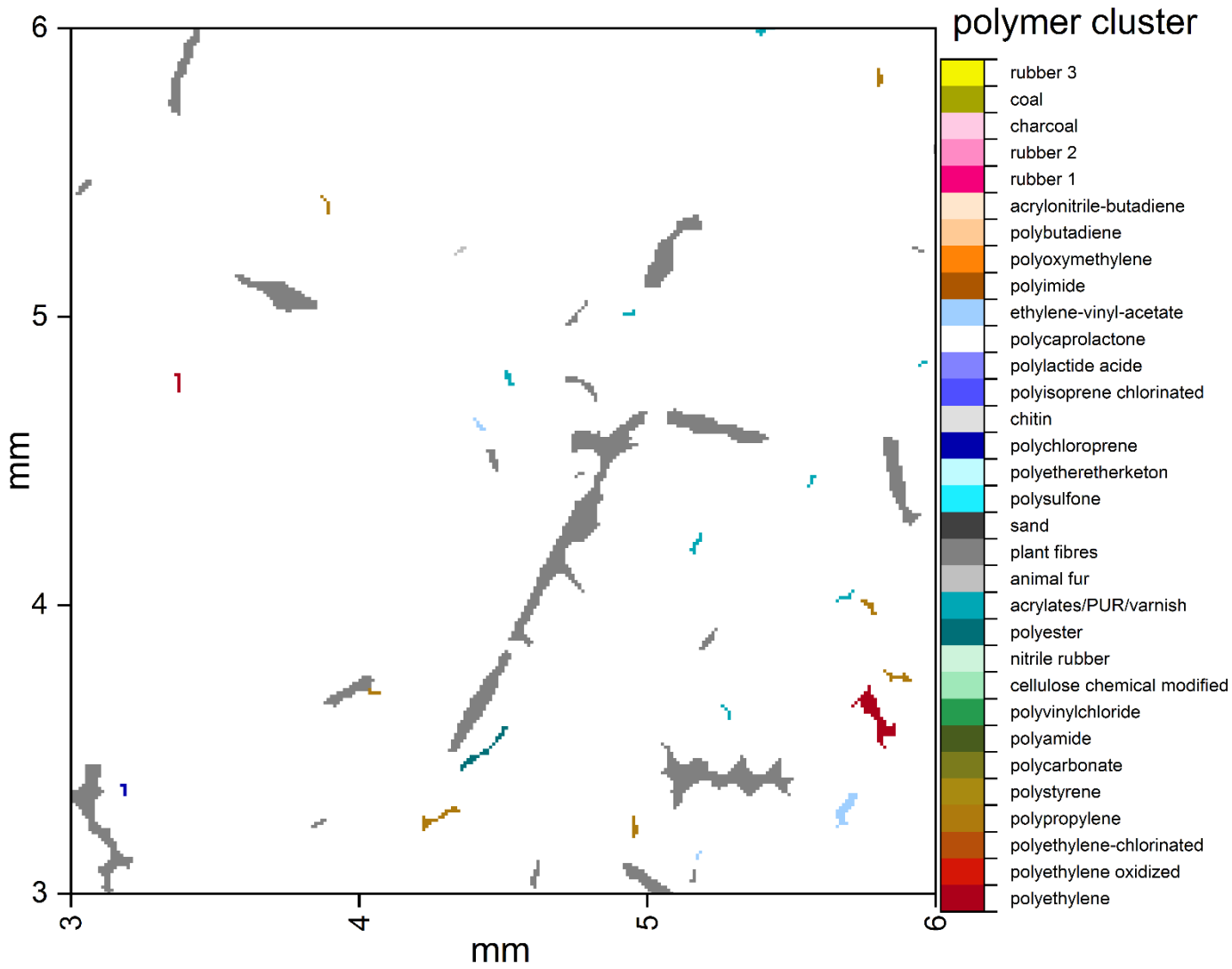
1. Primpke, S., et al., Analytical Methods, 2019. DOI: 10.1039/C9AY00126C

Fibers



1. Primpke, S., et al., Analytical Methods, 2019. DOI: 10.1039/C9AY00126C

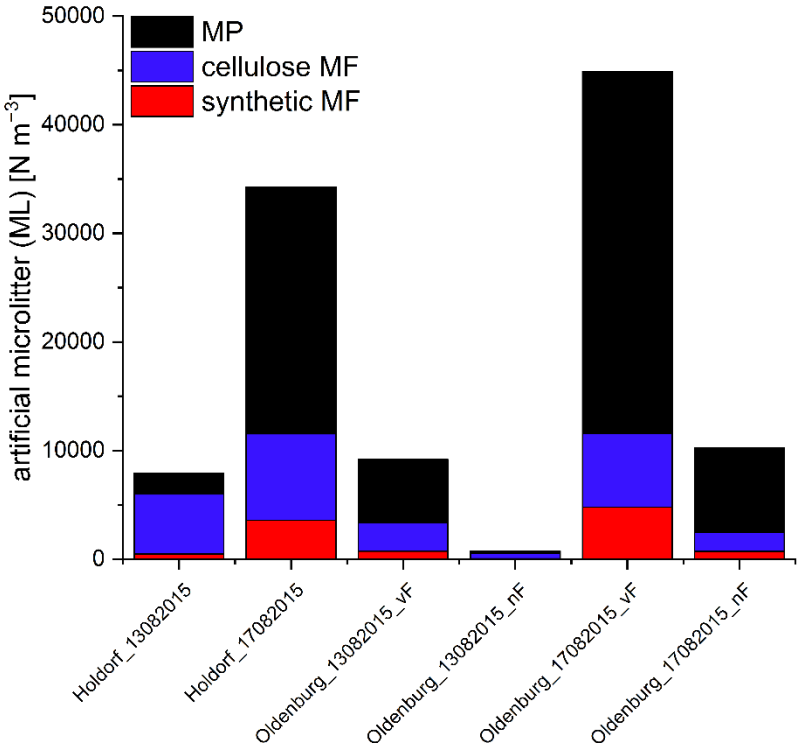
Fibers



1. Primpke, S., et al., Analytical Methods, 2019. DOI: 10.1039/C9AY00126C

Fibers

- MP dominated most of the samples
- Cellulosic fibers dominated
- MP was removed by ~ 86% during filtration
- Synthectic MF was removed by ~ 89% during filtration
- Cellulosic MF was removed by ~ 78% during filtration

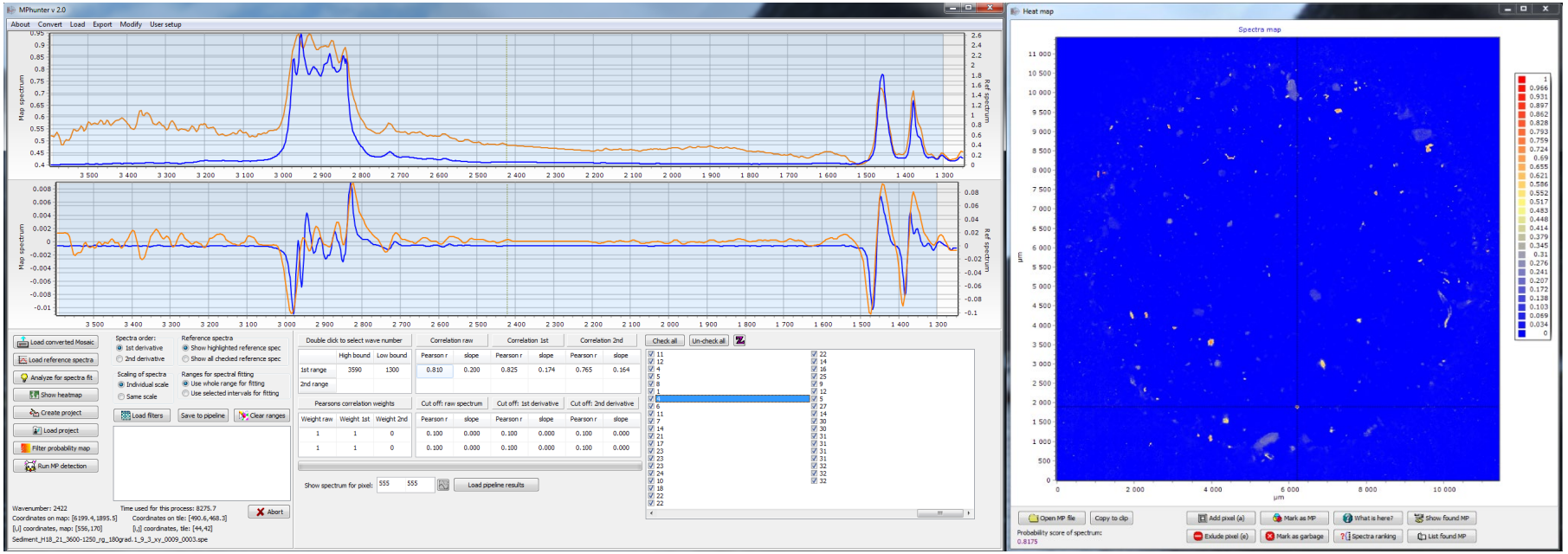


1. Primpke, S., et al., Analytical Methods, 2019. DOI: 10.1039/C9AY00126C

Towards Harmonization of Analysis

Manufacturer independent software including automated analysis and link to the available scripts (former MPhunter)

siMPle: Standardized Identification of MicroPLastics in the Environment



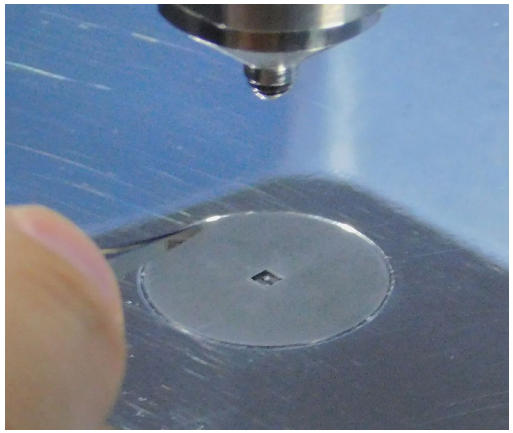
In collaboration with Jes Vollertsen of Aalborg University

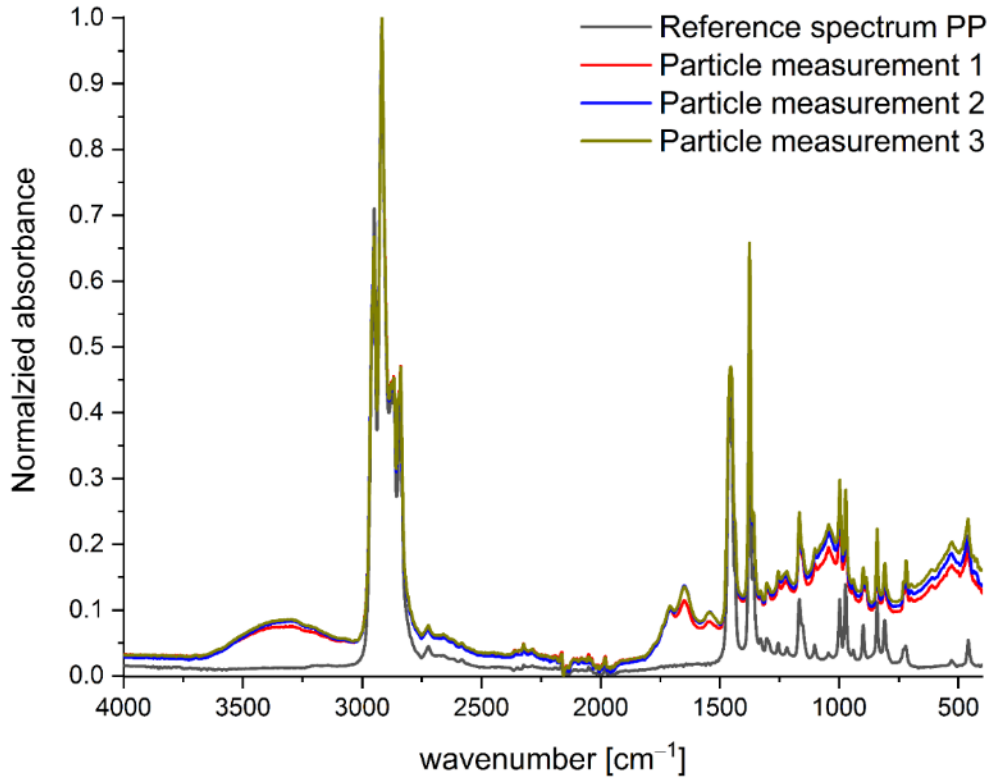
(Available on www.simple-plastics.eu from 1st of May 2019)

Towards Harmonization of Analysis

Single particles via attenuated total reflection (ATR) – FTIR:

Reference database available via Open Access in Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141



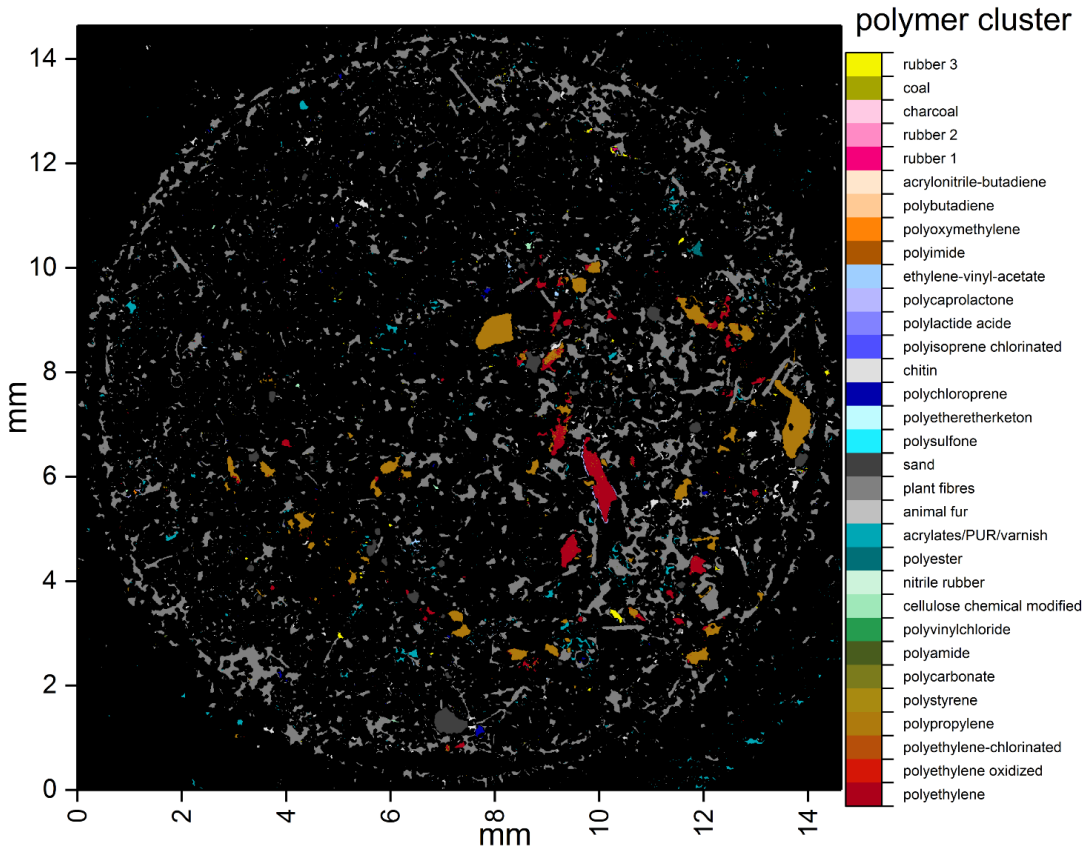


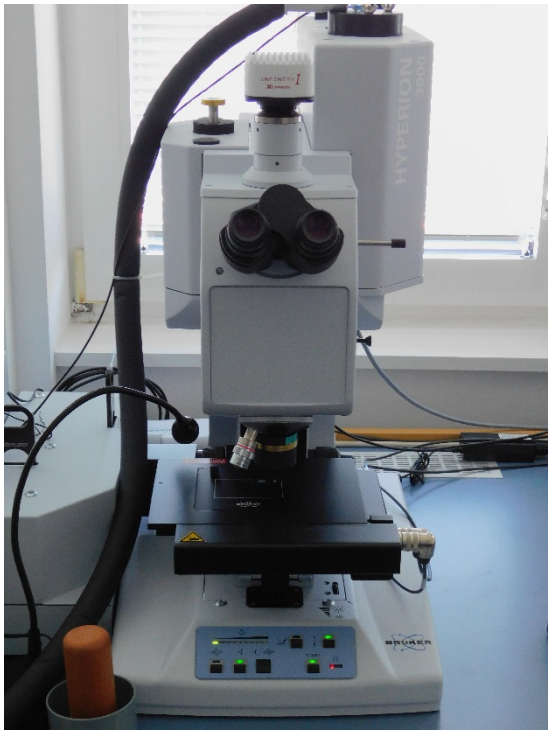
1. Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141

Towards Harmonization of Analysis

FTIR microscopy and imaging:

Automated analysis and reference database published via Open Access





1. Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141

Summary

- Low expenditure of time:
  - Data analysis time currently reduced from 24 hours to 3 hours by MPhunter for the automated analysis.
  - Depending on FTIR system 1 hours or less of manual labor per sample
- Impartial analysis
  - Evaluation within a fixed confidential interval
- Minimum of personnel requirements
  - One person can perform and analyze several samples in parallel
  - Data analysis can be parallelized
- Fast and reliable measurements
  - Measurement time 4 hours to 16 hours for the same region depending on lenses used.

Conclusion

Standardization by automatization of microplastic analysis based on FTIR imaging

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- Impartial analysis
- Minimum of personnel requirements
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Acknowledgements

Gunnar Gerdts (Leader WG)
Antje Wichels (Co-leader WG)
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Former PhD students: Inga Kirstein
Current Master students: Laura Stutzinger and Mathilde Falcou-Préfol

Aalborg University, Denmark: Jes Vollertsen (Professor), Alvise Vianello (Postdoc), PhD students: Nikki van Alst, Márta Simon, Kristina B Olesen

Melanie Bergmann (AWI researcher, Deep Sea Ecology and Technology)
Mine Tekman (PhD Student, Deep Sea Ecology and Technology)
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BASEMAN JPI OCEANS
MICROPLASTICS ANALYSES IN EUROPEAN WATERS

Bundesministerium für Bildung und Forschung


Questions ?
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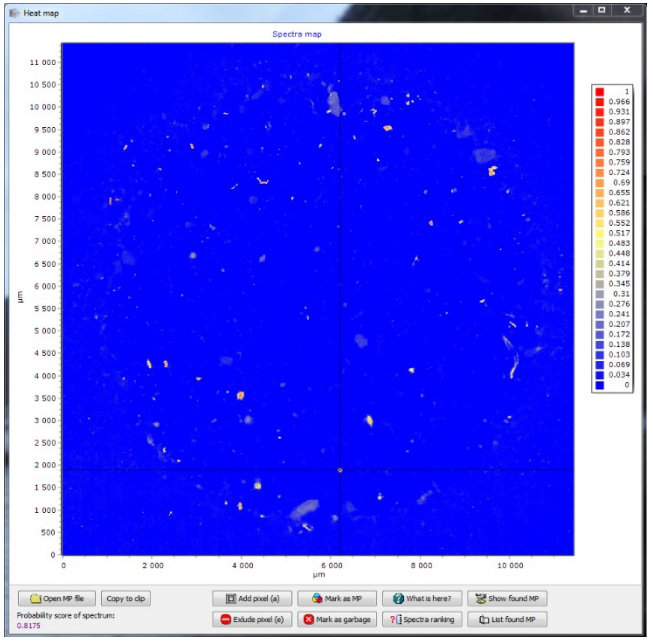
Towards Harmonization of Analysis

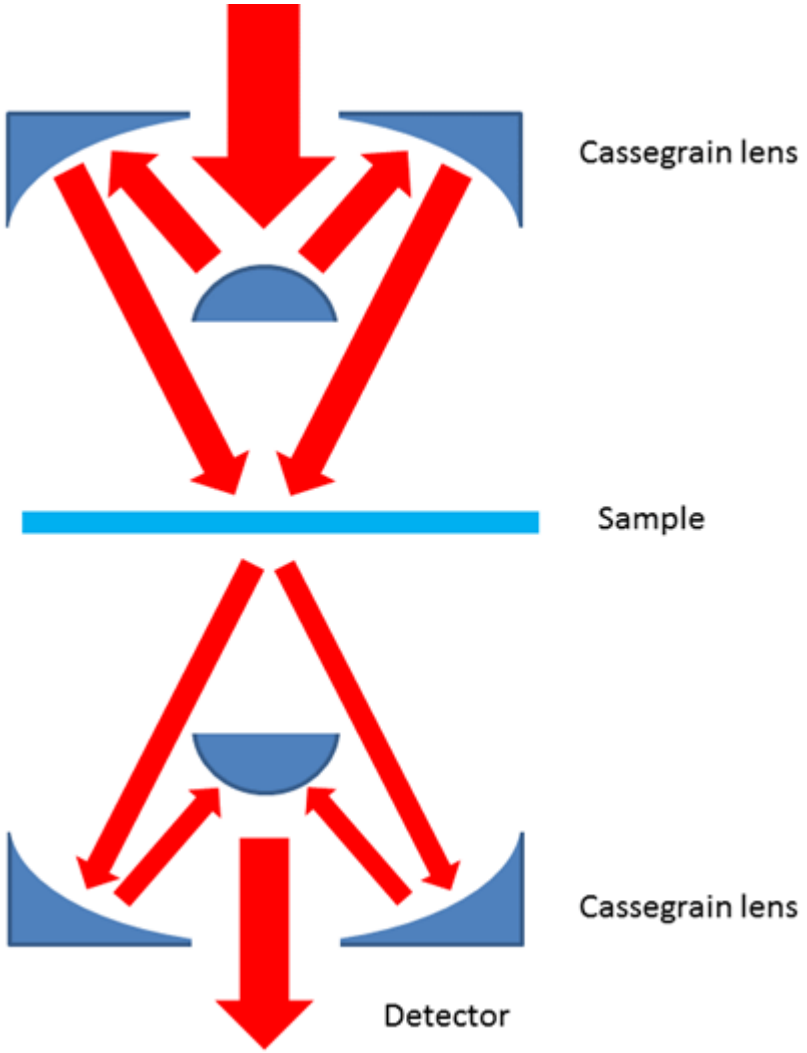
- Agilent
  - By import of the native Agilent .dmd file
- Bruker
  - Data export from OPUS into smaller fields in JCAMP-dx file format and import into MPhunter
  - Available as OPUS macro
- ThermoFisher
  - Export into JCAMP-dx
- PerkinElmer
  - Import via PerkinElmer files



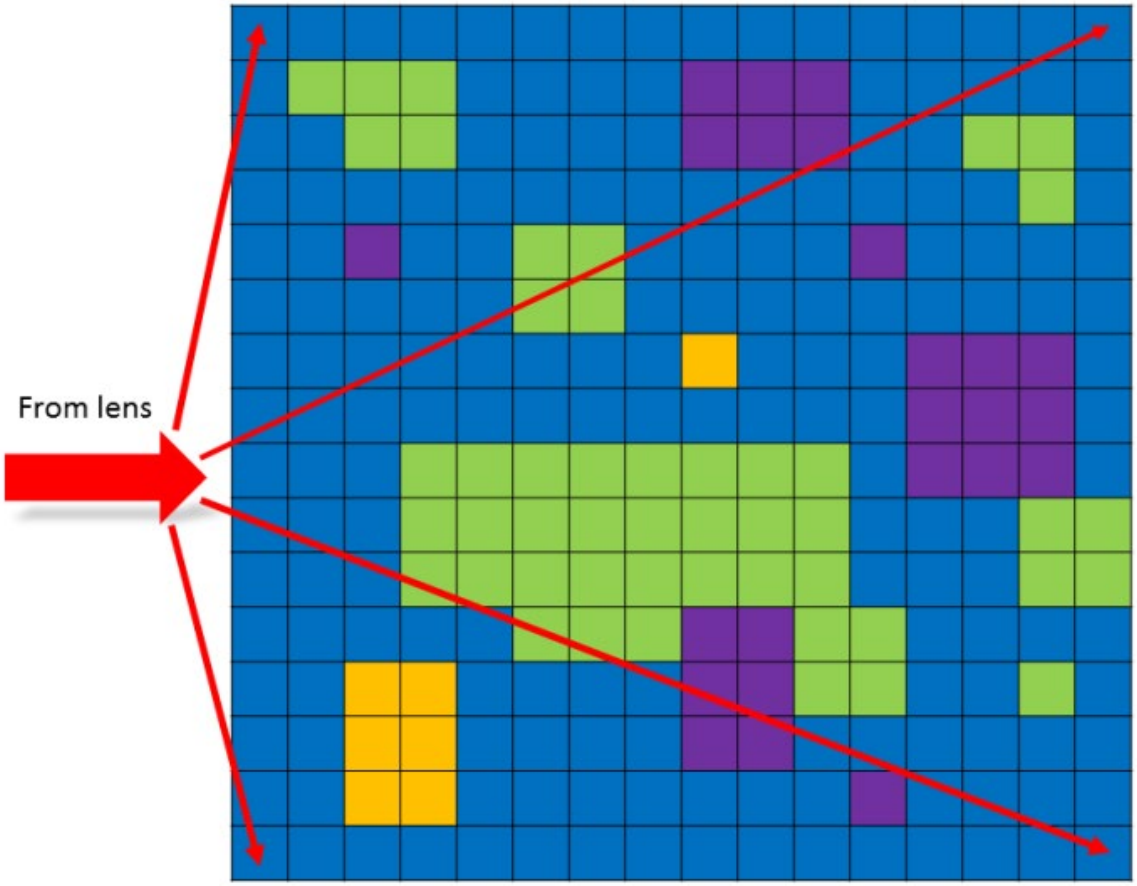
FTIR Imaging

Samples are collected on 0.2 µm Anodisc filters

Imaging via focal plane array (FPA) detector with a resolution of 11 µm

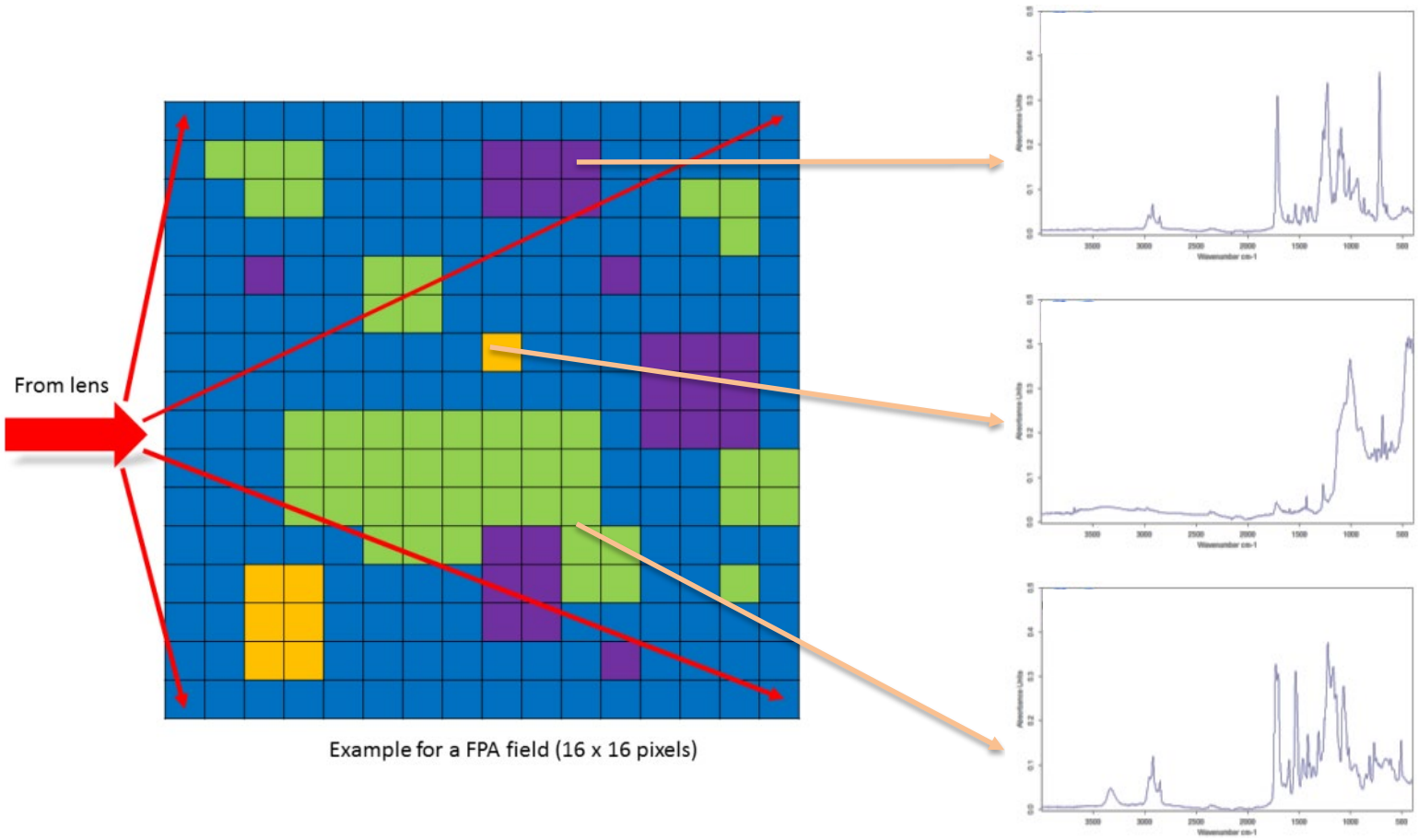


FTIR Imaging



Example for a FPA field (16 x 16 pixels)

FTIR Imaging



Example for a FPA field (16 x 16 pixels)