EURO CHARM

BASEMAN
MICROPLASTICS ANALYSES IN EUROPEAN WATERS

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

Lessons learned by the harmonization between spectroscopic and thermal degradation methods for the analysis of microplastics

Sebastian Primpke *et al.*

sebastian.primpke@awi.de

1. Alfred-Wegener-Institut, Biologische Anstalt Helgoland, Kurpromenade 201, 27498 Helgoland

HELMHOLTZ

Why it is important to analyze MP?

- Mandatory for monitoring[1] of microplastics < 500 µm
- May contain additional chemicals like plasticizers
- Risk assessment needs particle numbers, particle shape and polymer[2]

1. GESAMP. Guidelines for the Monitoring and Assessment of Plastic Litter in the Ocean 2019.
2. Kögel T, et al. Sci Total Environ. 2020;709:136050. doi:10.1016/j.scitotenv.2019.136050.

How can microplastics be analyzed?

FTIR spectroscopy

- Determines particle numbers
- Polymer type characterization via reference databases or other chemometric approaches
- Particles >10 µm can be measured in a rapid fashion.

1. Primpke S, et al., *Appl Spectrosc*. 2020, *74* ,1012-47. doi:10.1177/0003702820921465.

How can microplastics be analyzed?

FTIR spectroscopy

- Determines particle numbers
- Polymer type characterization via reference databases or other chemometric approaches
- Particles >10 µm can be measured in a rapid fashion.

Raman spectroscopy

- Determines particle numbers
- Polymer type characterization via reference databases or other chemometric approaches
- Particles <1 µm can be measured, but the analysis is time consuming

1. Primpke S, et al., *Appl Spectrosc*. 2020, *74* ,1012-47. doi:10.1177/0003702820921465.

How can microplastics be analyzed?

FTIR spectroscopy

- Determines particle numbers
- Polymer type characterization via reference databases or other chemometric approaches
- Particles >10 µm can be measured in a rapid fashion.

Raman spectroscopy

- Determines particle numbers
- Polymer type characterization via reference databases or other chemometric approaches
- Particles <1 µm can be measured, but the analysis is time consuming

Thermoanalysis-GC-MS

- Particle mass
- Using specific degradation products of the materials for quantification using signal to mass calibrations

1. Primpke S, et al., *Appl Spectrosc*. 2020, *74* ,1012-47. doi:10.1177/0003702820921465.

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

Can be analyzed by automated approaches

Example: Sediment sample

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

Harmonization by automated analysis

Automatization of microplastic analysis
based on FTIR imaging

- 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!

Primpke et. al., *Anal. Methods,* 2017*, 9,* 1499–1511
Primpke et. al., *Anal. Bioanal. Chem.,* 2018, *410*, 5131-5141.

Harmonization!

Water samples (surface etc.)

Cabernard et al,, 2018, ES&T
Lorenz et al., 2019, EP
Tekman et al., 2020, ES&T
Mintenig et al., 2020, WR
Primpke et al. 2020, ABC

Treated waste water

Primpke et al., 2017, CHIUZ
Primpke et al., 2019, Analytical Methods
Mintenig et al., 2020, WR
Primpke et al. 2020, ABC

siMPle

Primpke et al., 2020, Applied Spectroscopy

Automatization of microplastic analysis based on FTIR imaging

Sediments

Bergmann et al., 2017, ES&T
Haave et al., 2019, MBP
Lorenz et al., 2019, EP
Mani et al., 2019, ES&T
Abel et al. 2021, EP
Primpke et al. 2020, ABC

Biota

In progress

(Arctic) Sea Ice

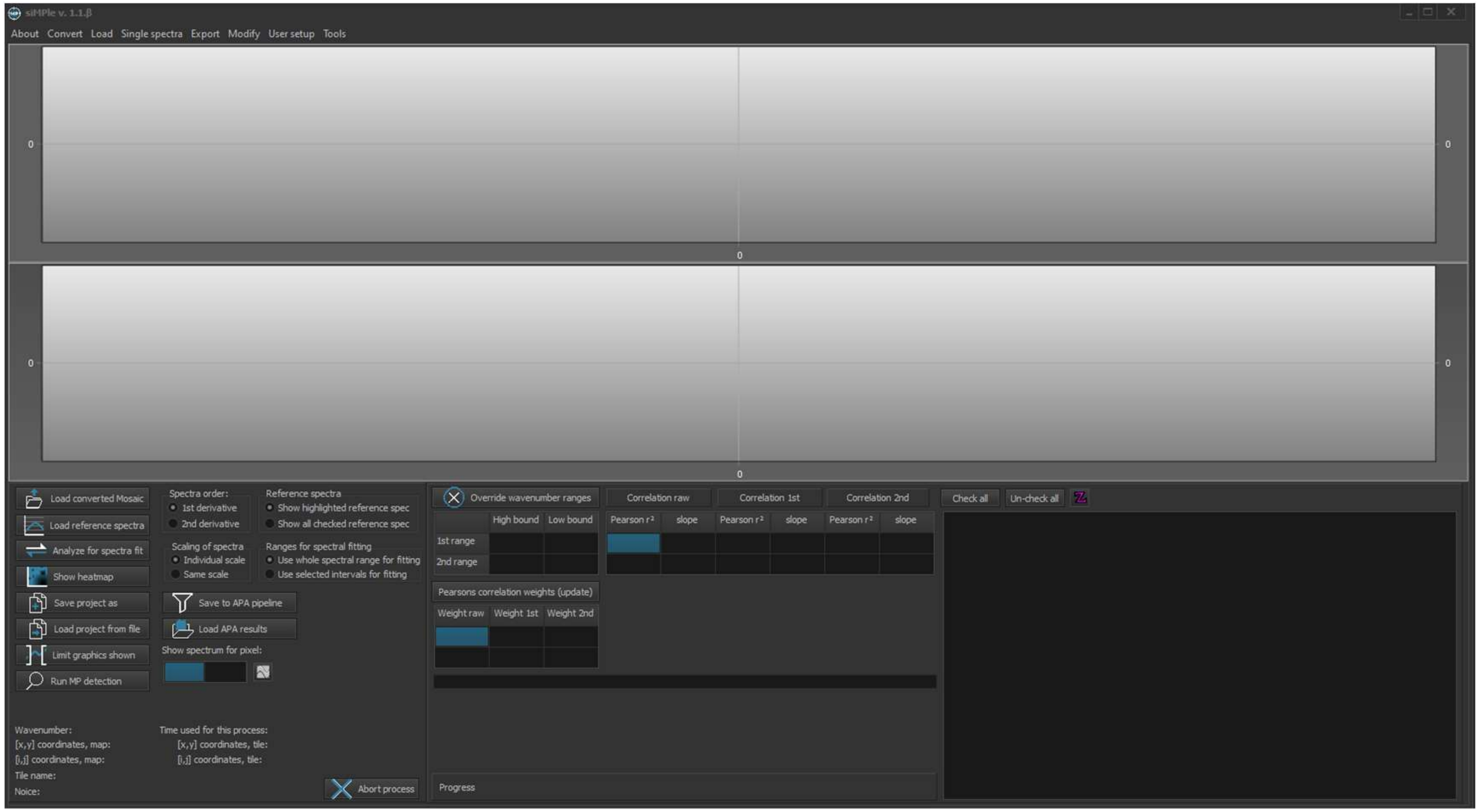
Peeken et al., 2018, Nature Communications

Snow

Bergmann et al., 2019, Science Advances

Automatization via siMPle

- Systematic Identification of MicroPLastics in the Environment (siMPle)
- Software tool available by CC-BY-SA 4.0 on www.simple-plastics.eu. In collaboration with Aalborg University (Jes Vollertsen)



See also: Primpke, S., *et al*. 2020 Appl. Spectrosc. 74(9), 1127-1138. doi: 10.1177/0003702820917760

siMPle for various IR systems

Universal application of data analysis using the same database.

- ➢ Not limited to one manufacturer
- ➢ Database is free of charge available
- ➢ Software is free of charge available
- ➢ Currently imports for Agilent, Bruker, DRS Daylight Solutions, Perkin Elmer and ThermoFischer Scientific

– Please contact us if you manufacturer is not in the list yet to find a solution

See also: Primpke, S., *et al*. 2020 Appl. Spectrosc. 74(9), 1127-1138. doi: 10.1177/0003702820917760

siMPle for various IR systems

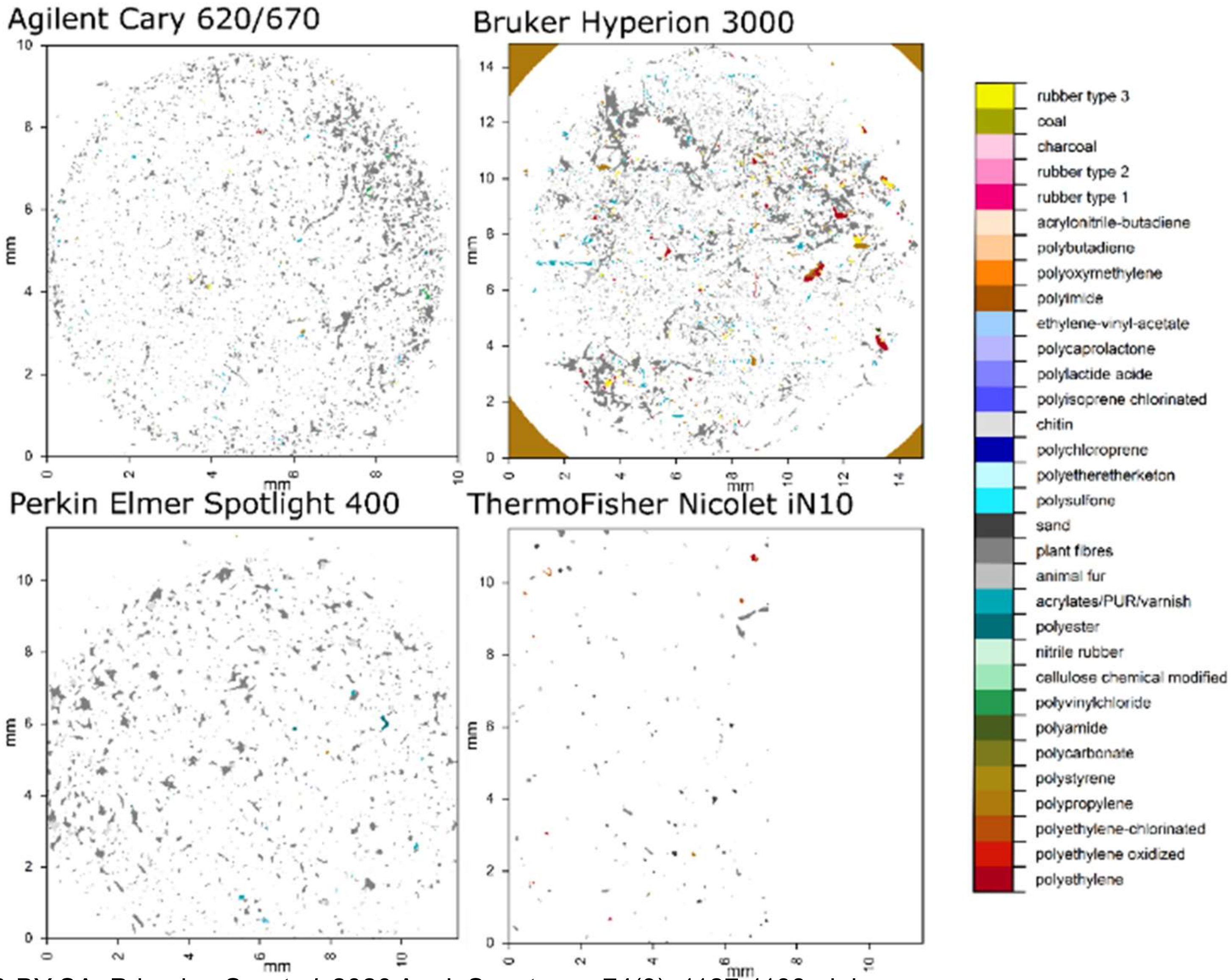
Testing the universal application of data analysis using the same database.

- Collaboration with Svenja Mintenig (Utrecht University), Richard Cross (Centre for Ecology and Hydrology/Wallingford), Alvise Vianello, Marta Simon and Jes Vollertsen (all Aalborg University)

- Dataset from Agilent, Bruker, Perkin Elmer and ThermoFischer Scientific systems

See also: Primpke, S., *et al*. 2020 Appl. Spectrosc. 74(9), 1127-1138. doi: 10.1177/0003702820917760

siMPle for various IR systems

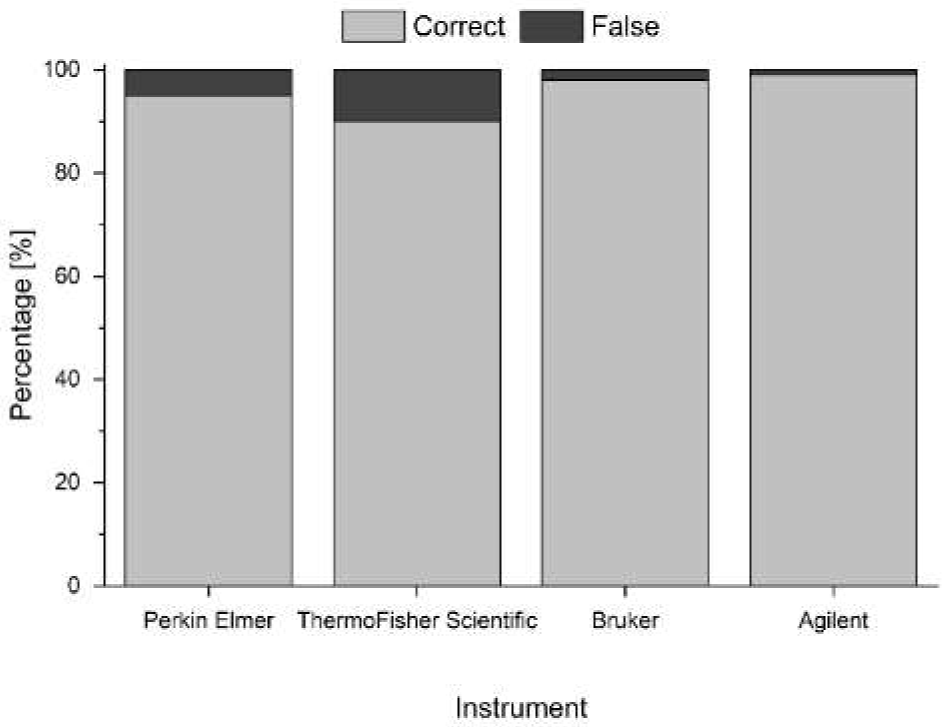


Graph: CC 4.0-BY-SA: Primpke, S., *et al*. 2020 Appl. Spectrosc. 74(9), 1127-1138. doi: 10.1177/0003702820917760

siMPle for various IR systems

Results of the intercomparsion

- All datasets yield identified particles
- Number of identified particles are dependent on the available pixel resolution
- All systems yielded mainly high ratios of correct assignments

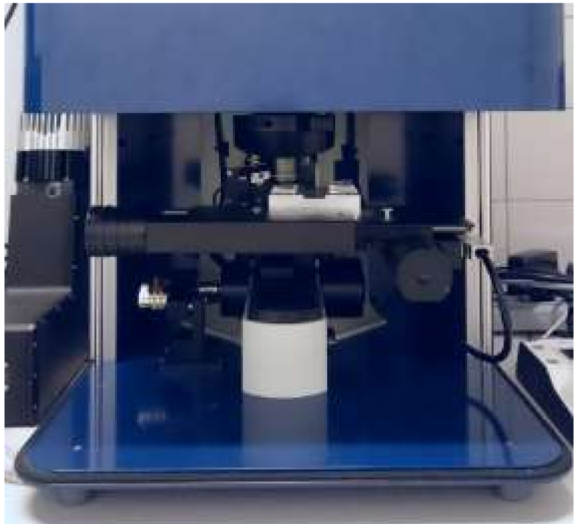


Graph: : Primpke, S., *et al*. 2020 Appl. Spectrosc. 74(9), 1127-1138. doi: 10.1177/0003702820917760

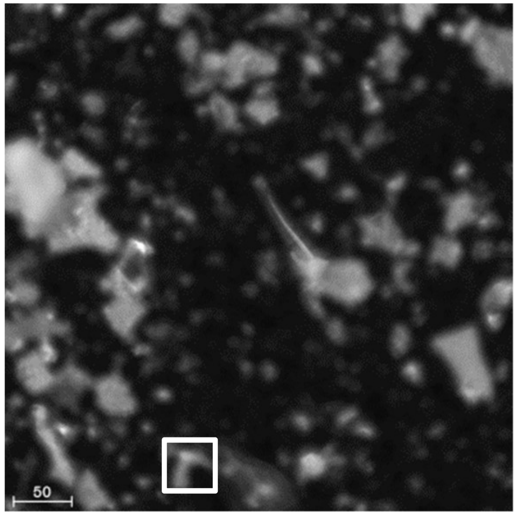
Raman for MP

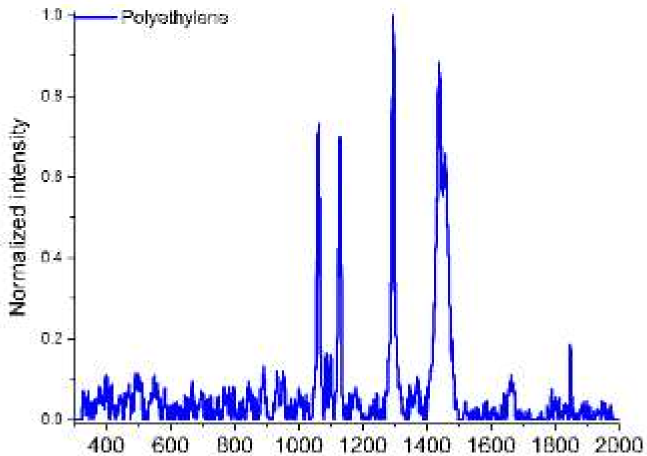
Automated single particle exploring (ASPE) Raman

- Together with Livia Cabernard (AWI, now ETH Zürich), Claudia Lorenz (AWI, now Aalborg University), Lisa Roscher and Gunnar Gerdts (all AWI)
- Combines Particle analysis and counting with Raman analysis
- Each identified particle is individually targeted by Raman



© Sophia Mützel





size = 33.8 µm

1. L. Cabernard, et al. , Environmental Science & Technology 2018, 52, 13279-13288.

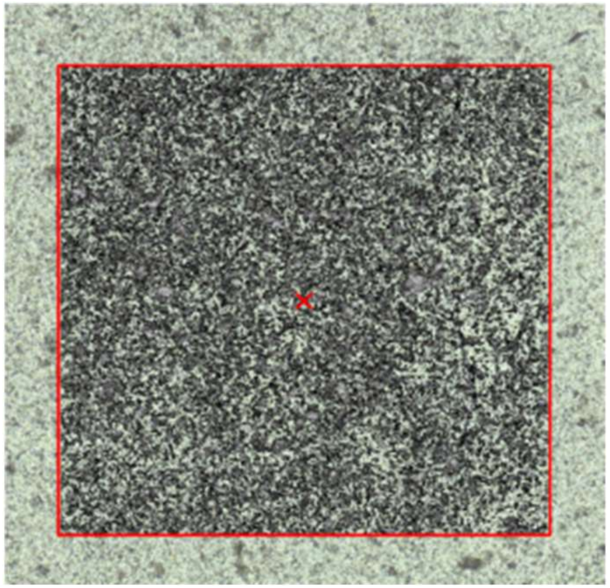
Comparison of FTIR and Raman

FTIR imaging and automated single particle exploring (ASPE) Raman microscopy

Seven environmental samples

Using gold coated polycarbonate filters

Measurement of FTIR (full image) and Raman (red square)

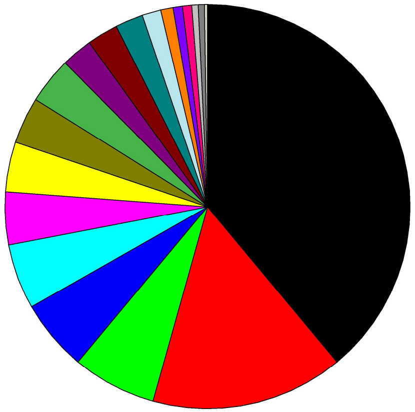


Only FTIR and Raman within the red square were compared

1. L. Cabernard, et al. , Environmental Science & Technology 2018, 52, 13279-13288.

Method intercalibration

SPE-μ-Raman

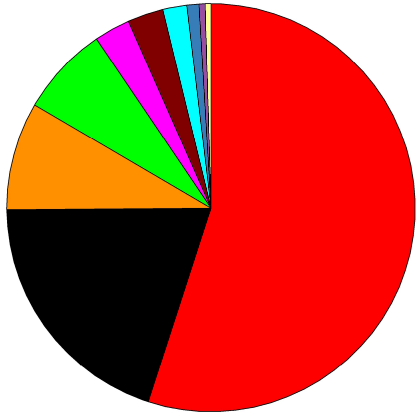


	n
polyethylene	157
rubber	62
polymethylmetharcylate	27
poly(vinyl stearate)	23
polypropylene	21
polyamide	17
varnish	16
polystyrene	15
acrylonitrile-styrene-butadiene	15
polytetrafoluroethylene	10
polyester	10
viscose	9
copolymer*	6
silicone	4
polyoxymethylene	3
polyhydroxybutyrate	3
polycarbonate	2
terpolymer**	2
polyphenyle sulfide	1
total	**403**

*styrene/allyl alcohol & vinyl chloride/vinylacetate

**vinylchloride/vinylacetat/maleic acid

FTIR imaging

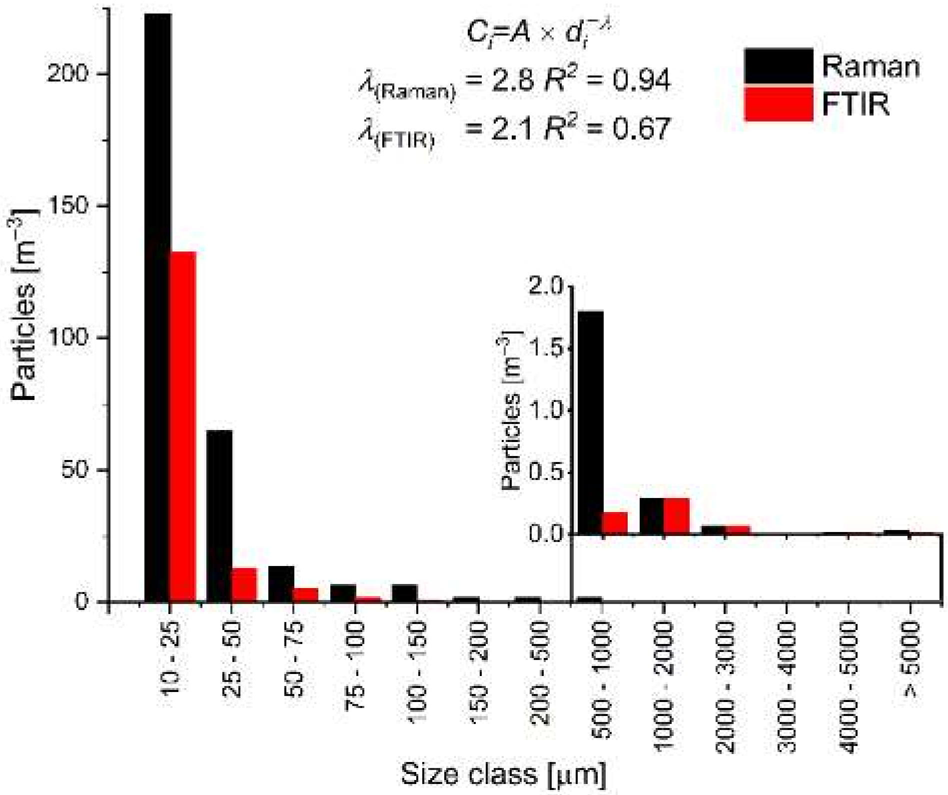


	n
rubber	116
polyethylene	42
ethylene-vinyl-acetate	18
acrylates/varnish	15
polyamide	6
polyester	6
polypropylene	4
polycaprolactone	2
polyetheretherketone	1
polyvinylchloride	1
total	**211**

Raman: average 43 hours per sample   FTIR: 8 hours per sample

1. L. Cabernard, et al. , Environmental Science & Technology 2018, 52, 13279-13288.

Method intercalibration

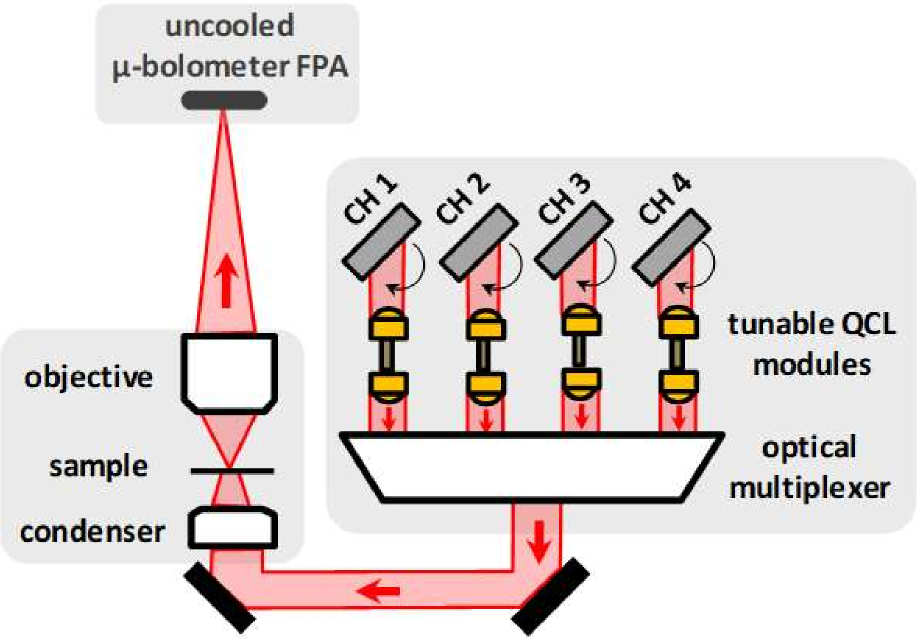


Raman: average 43 hours per sample FTIR: 8 hours per sample

1. Reprinted with permission from L. Cabernard, et al. , Environmental Science & Technology 2018, 52, 13279-13288. Copyright 2018 American Chemical Society.

Quantum Cascade Laser Imaging

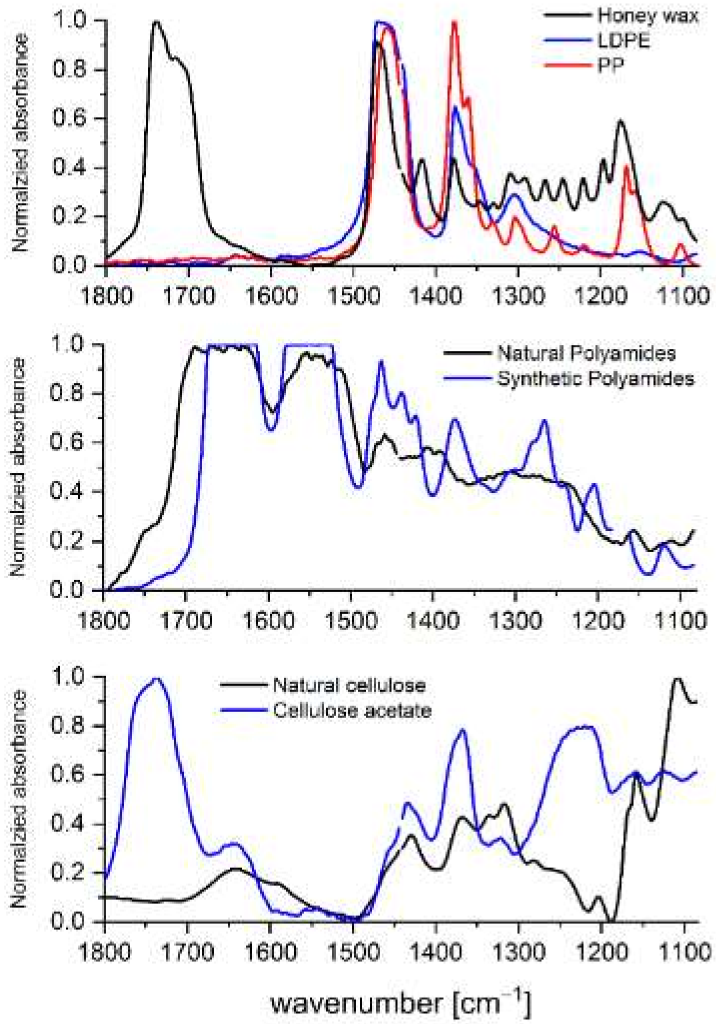
- DRS Daylight SperoQT: Setup similar to an infra red microscope
- Infra red source is a tunable laser
- No liquid nitrogen required
- Speed: 1 minute for a 2 × 2 mm field of view with a wavenumber range of 1800 – 950 cm^{-1}
- Resolution: 4.2 µm per pixel in the field of view



Graph: CC 4.0-BY Primpke S, et al. Environ Sci Technol. 2020;54(24):15893-903. doi:10.1021/acs.est.0c05722.

QCL based spectra on Anodisc

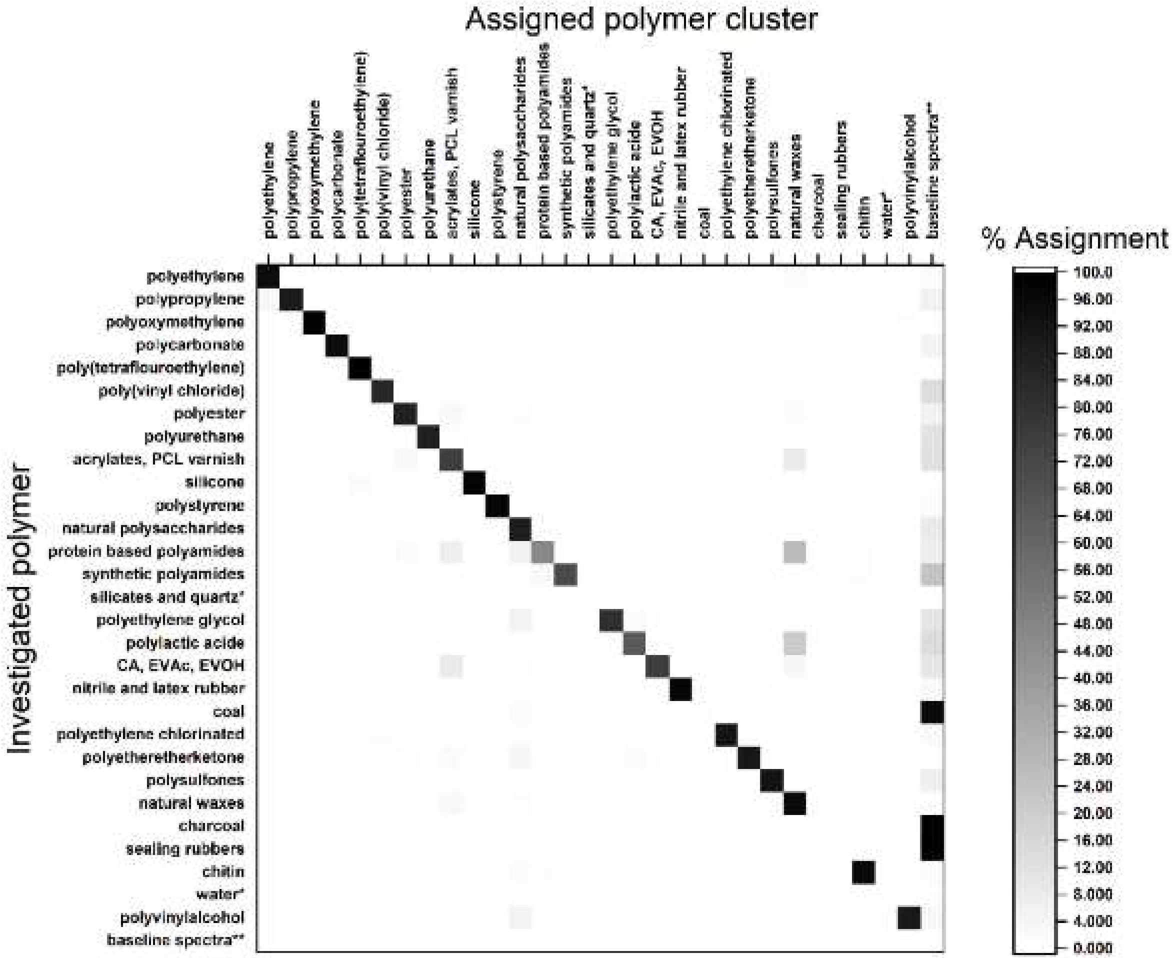
- Anodisc is one of the few suitable filters for IR
- Inexpensive, but limited in wavenumber range (>1250 cm^{-1})
- Using a QCL, measurements are possible until >1084 cm^{-1}
- Separation of natural and anthropogenic materials possible



Graph: CC 4.0-BY Primpke S, et al. Environ Sci Technol. 2020;54(24):15893-903. doi:10.1021/acs.est.0c05722.

Polymer types detectable

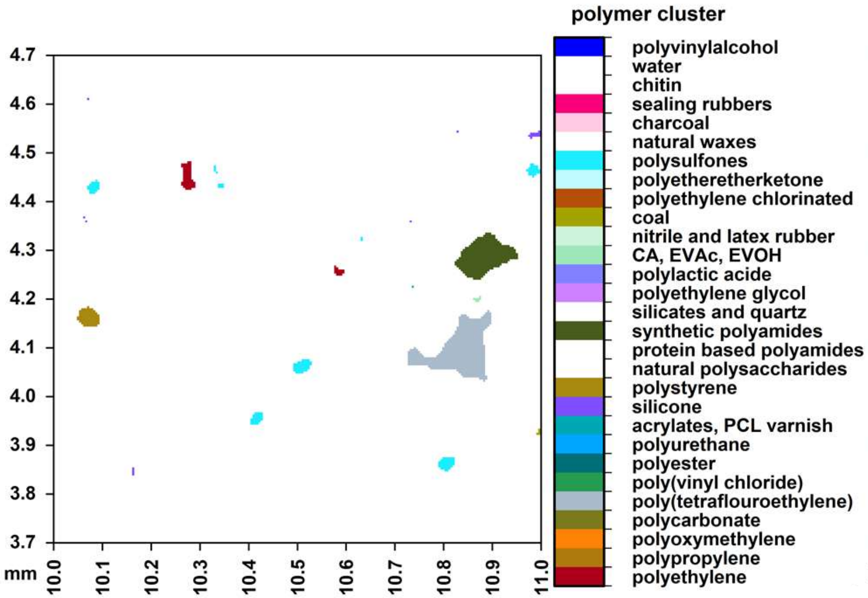
- Aiming for automated analysis
- Based on hierarchical cluster analysis
- Cluster generation based ATR-FTIR spectra
- Afterwards addition of QCL measured spectra

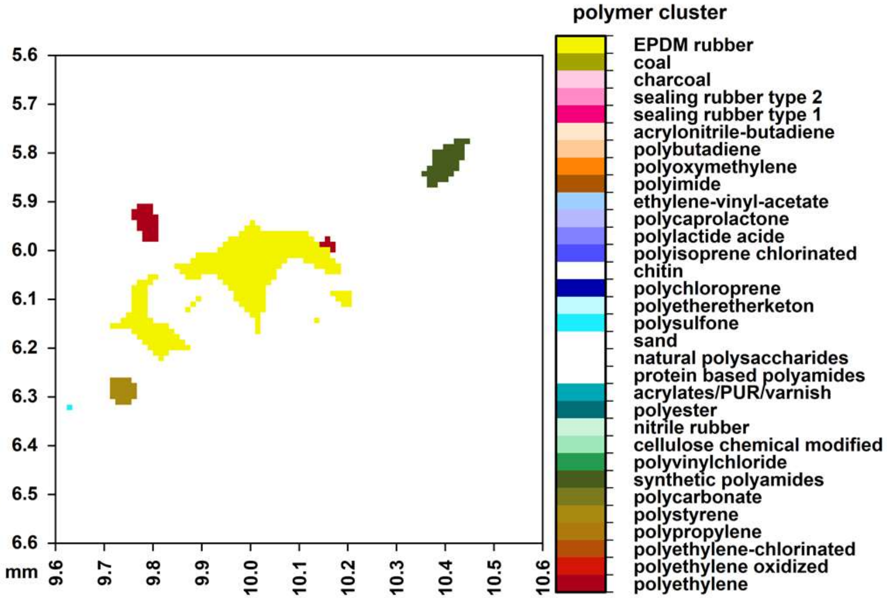


Graph: CC 4.0-BY Primpke S, et al. Environ Sci Technol. 2020;54(24):15893-903. doi:10.1021/acs.est.0c05722.

Comparsion with FTIR imaging

- Similar particles for main polymer types were found.
- In addition more polysulphones and also PTFE were detected.
- The large EPDM assigned particles were not detected.



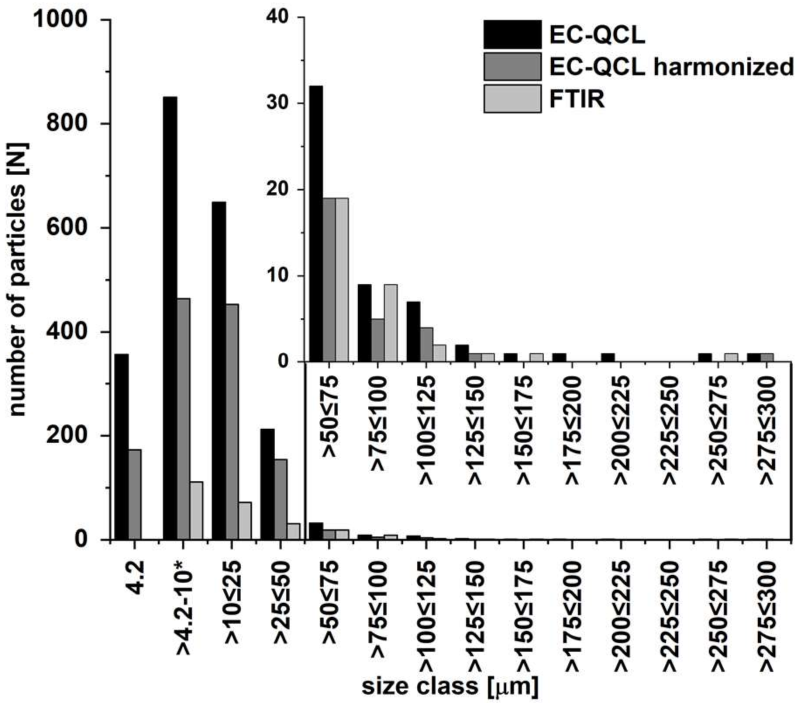


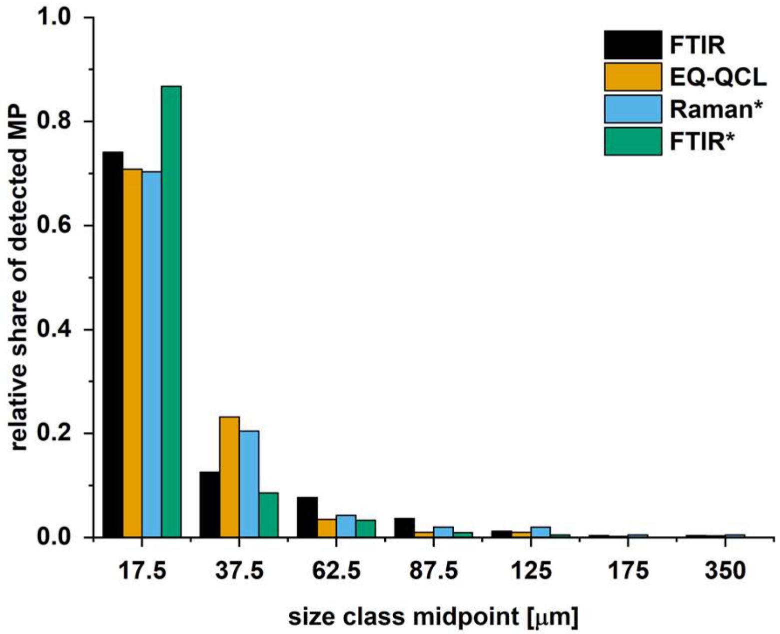
Graphs: CC 4.0-BY Primpke S, et al. Environ Sci Technol. 2020;54(24):15893-903.
doi:10.1021/acs.est.0c05722.

Comparsion with FTIR imaging

- More particles detected compared to FTIR imaging

- Similar relative particle shares like for Raman microscopy (Cabernard et al. 2018)





Graphs: CC 4.0-BY Primpke S, et al. Environ Sci Technol. 2020;54(24):15893-903. doi:10.1021/acs.est.0c05722.

Comparsion with py-GC/MS

Together with Marten Fischer, Barbara Scholz-Böttcher (ICBM), Claudia Lorenz (AWI, now Aalborg University) and Gunnar Gerdts (AWI)

Direct measurement of particle data for numbers and polymer types followed by mass data for polymer types

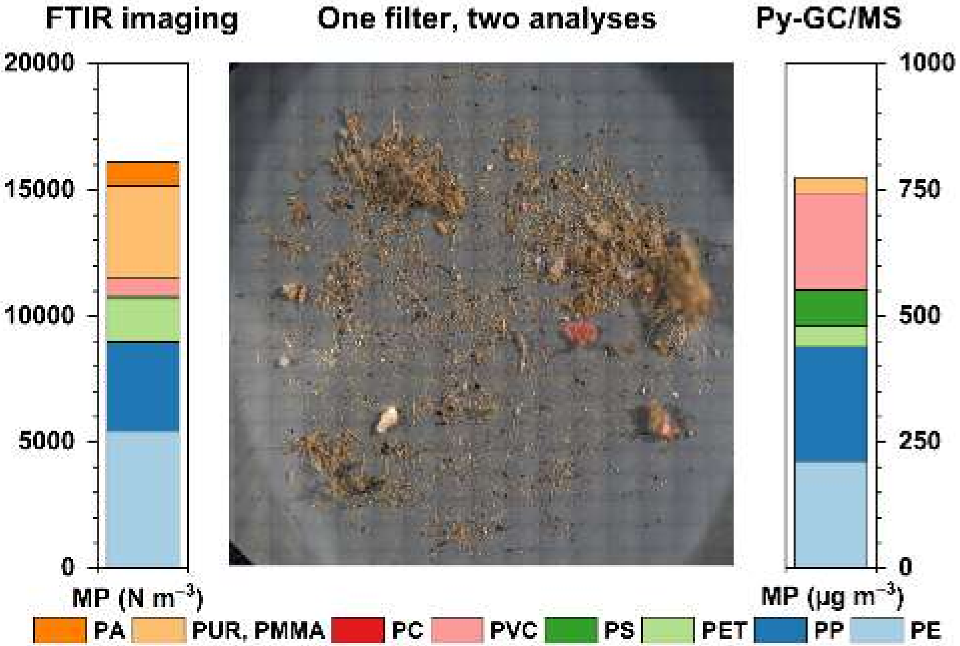
1. S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

Full filter analysis

Pyrolysis GC/MS and FTIR imaging

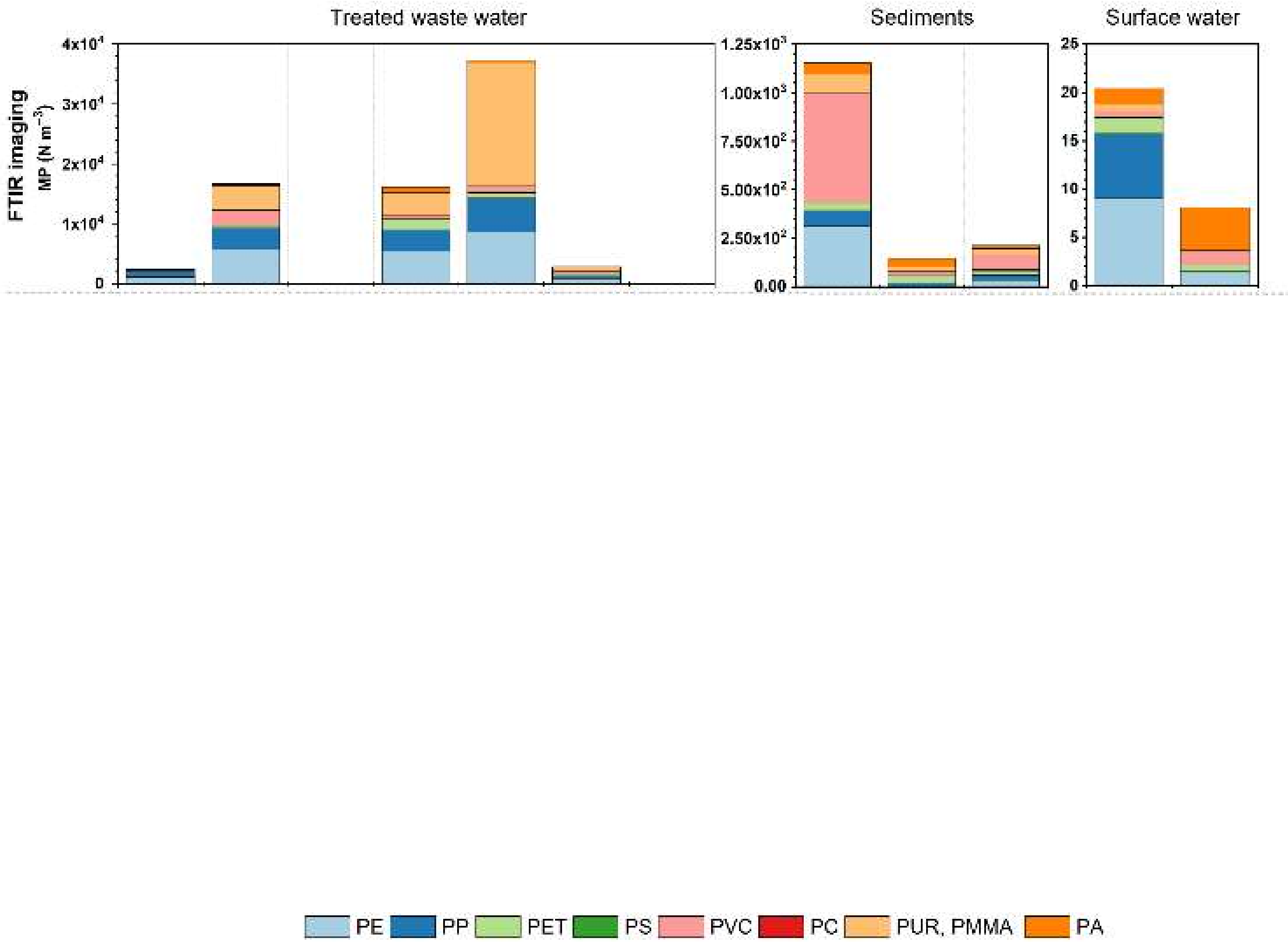
Prior to analysis: Sample preparation via enzymatic digestion

1. Measurement via FTIR imaging using 3.5x FTIR Objective on Anodisc
2. Measurement of same sample via Py-GC/MS at 590°C and on-line derivatization with TMAH



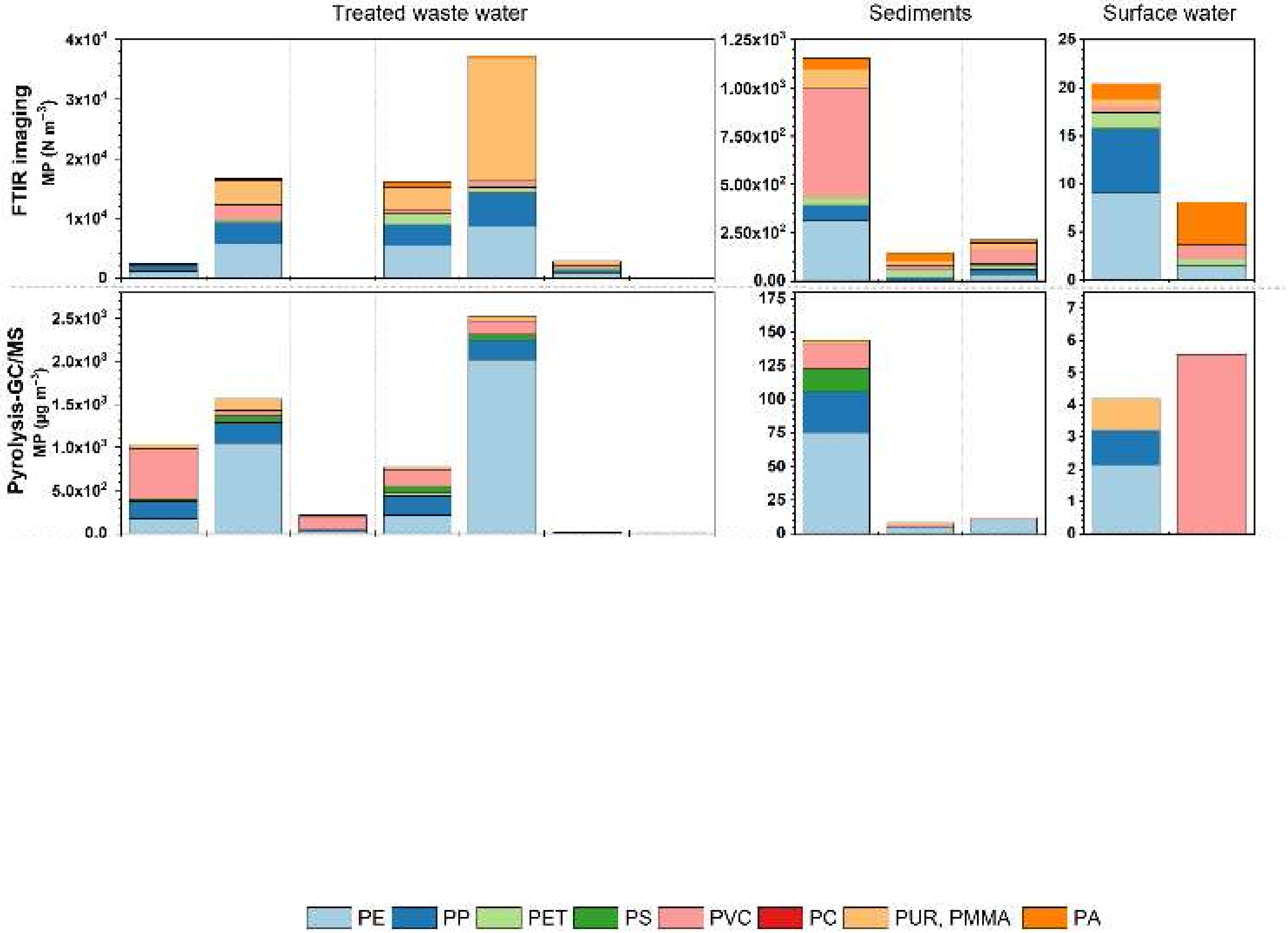
1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.*, 2020, *412*, 8283-8298

Results



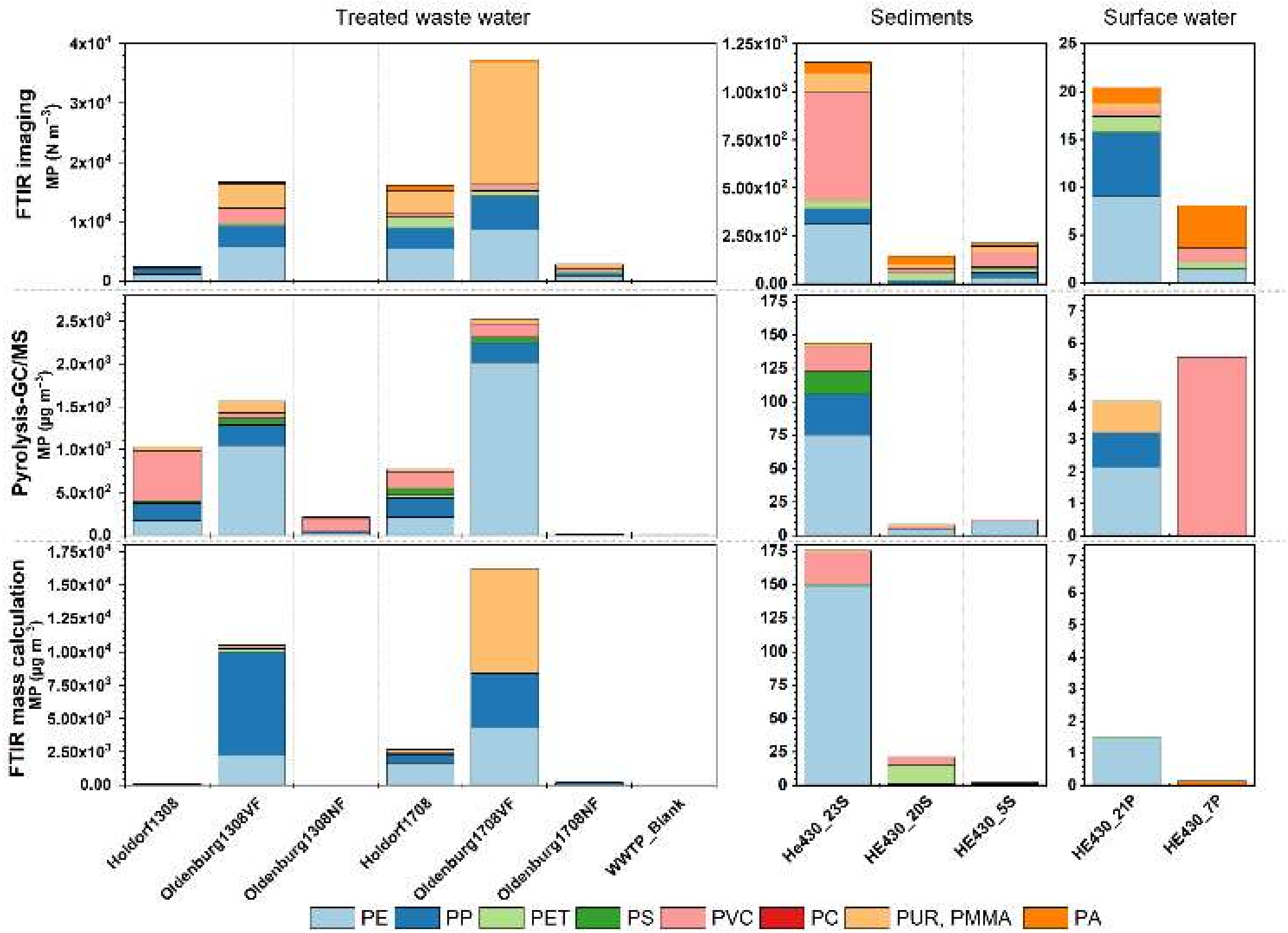
1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

Results



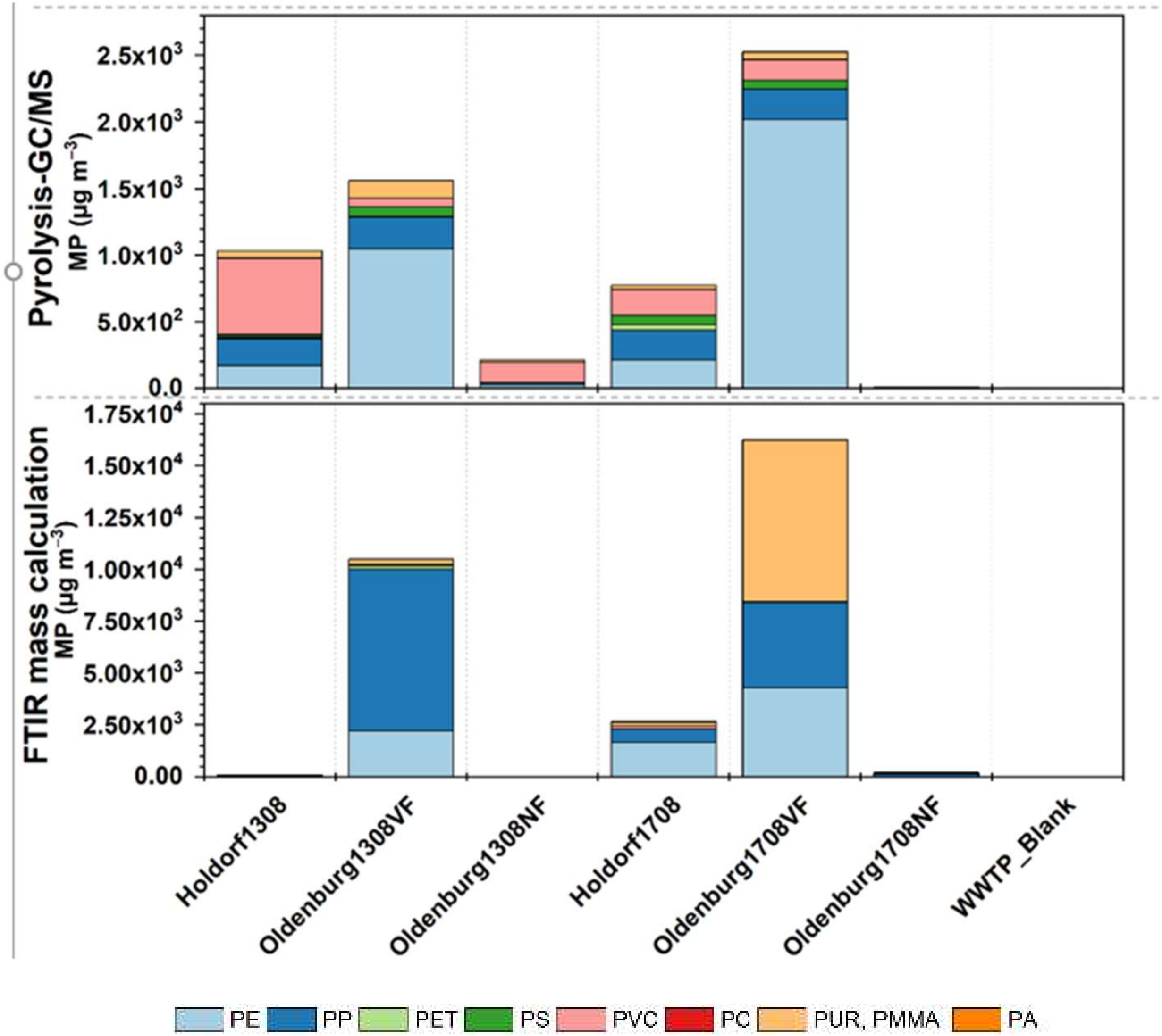
1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

Results



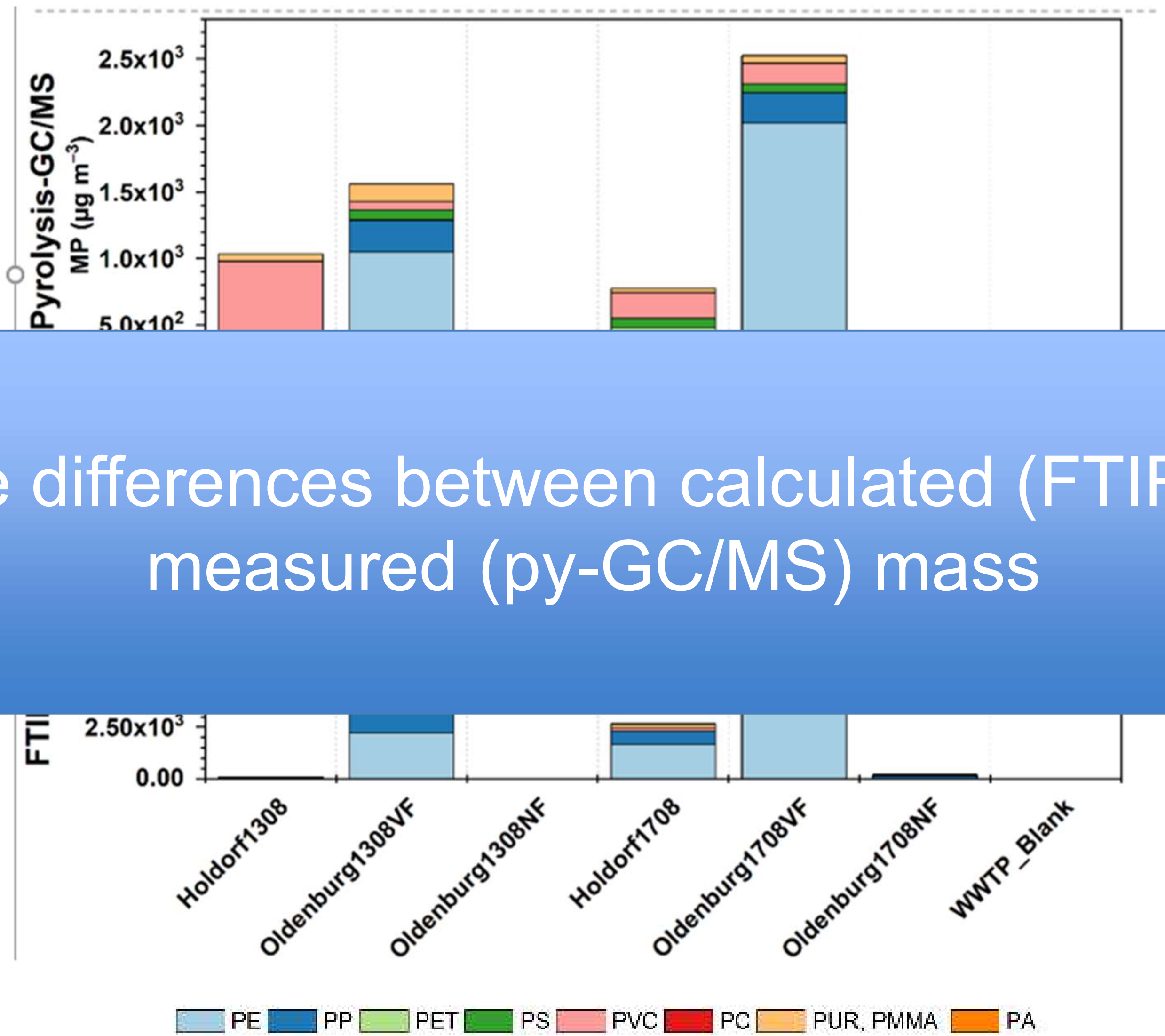
1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

Results



1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

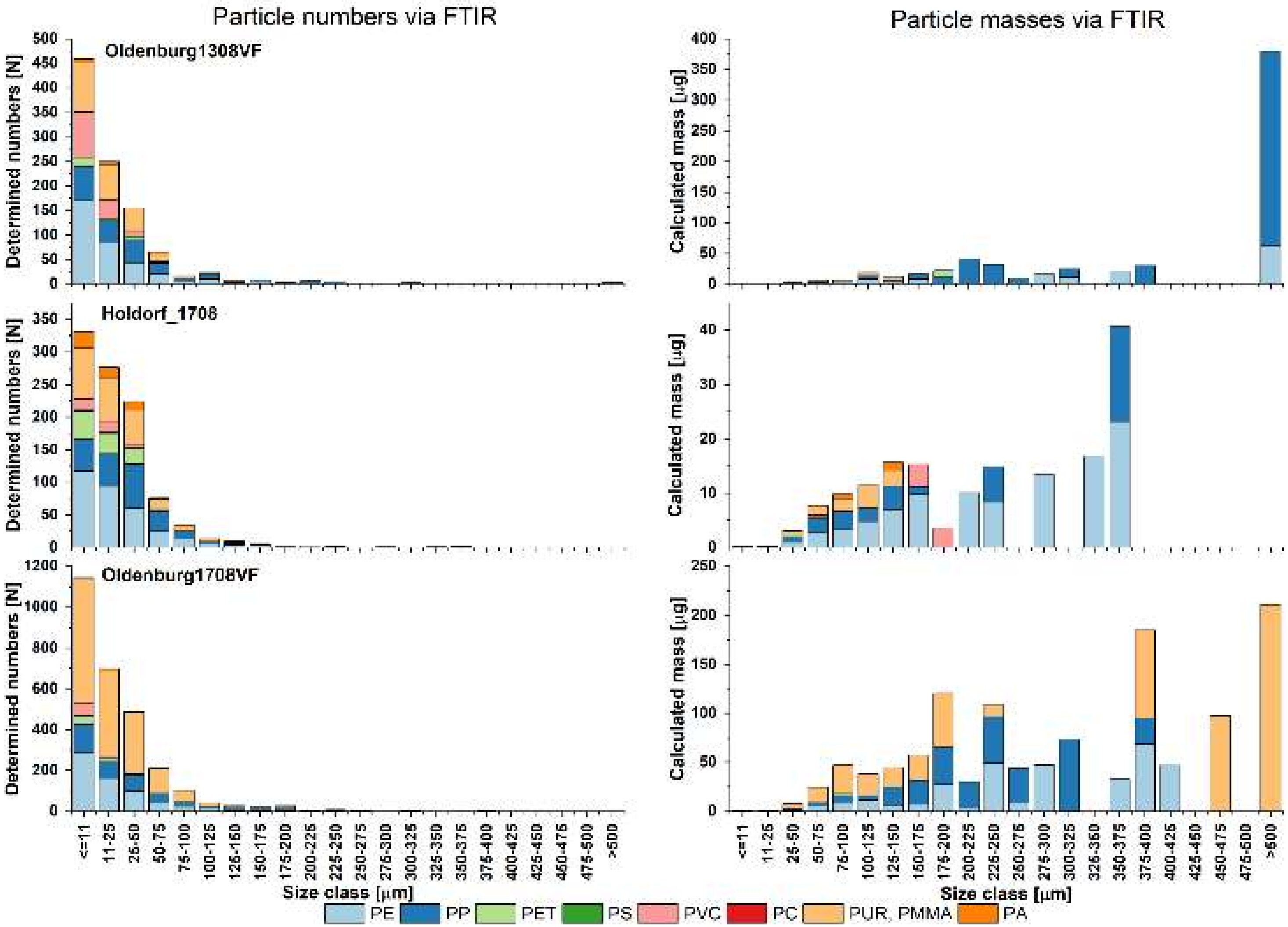
Results



Large differences between calculated (FTIR) and measured (py-GC/MS) mass

1. S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.*, 2020, *412*, 8283-8298

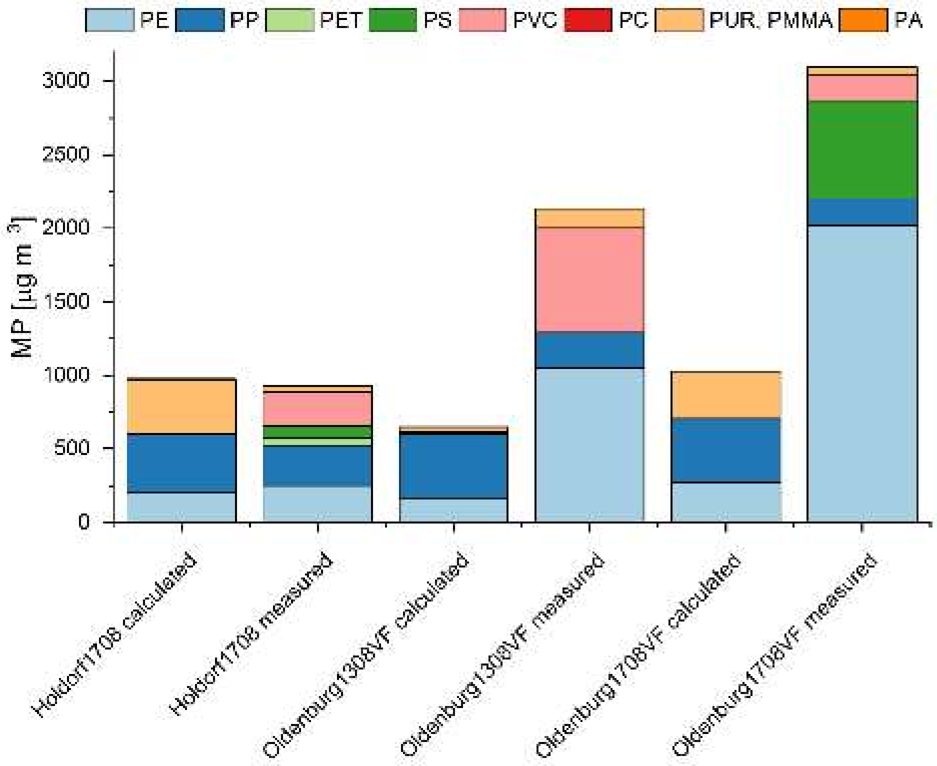
Particle versus mass data



1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.,* 2020, *412,* 8283-8298

Alternative approach

- Based on average particle sizes as reference particles
- Calculation of reference particles represented per particle by the measured area
- Yields closer results if many large particles are present.



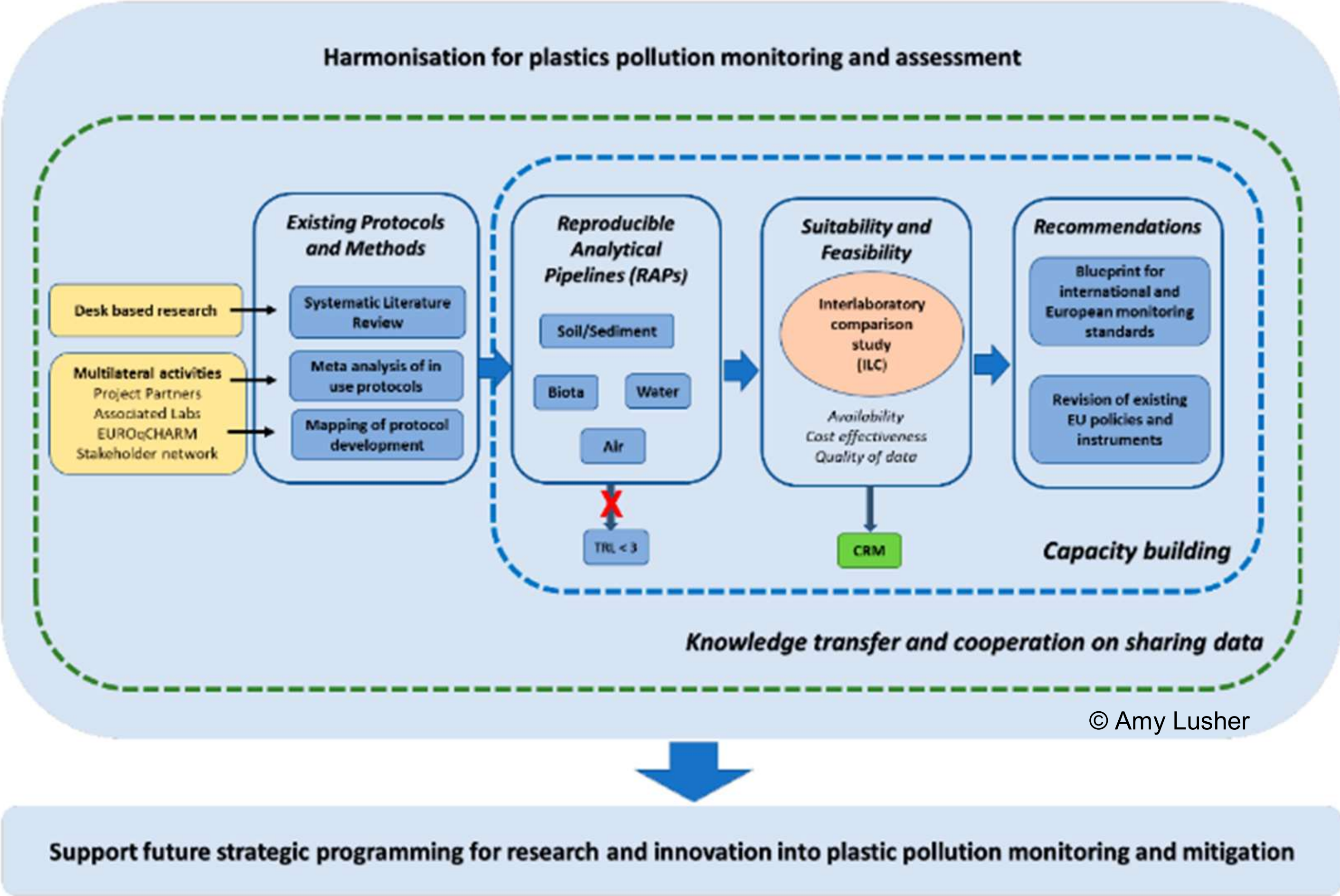
1. Graph: CC 4.0-BY S. Primpke, M. Fischer, et al., *Anal. Bioanal. Chem.*, 2020, *412*, 8283-8298

Summary

Lessons learned by the harmonization

- Fast and reliable analyses are available (< 1 hour)
- Mass conversion from spectroscopic data is currently limited for larger particles
- (FT)-IR, Raman and thermoanalytical methods are complementary and can be applied in a step-by-step approach on the same samples

Outlook: EURO CHARM



https://www.euroqcharm.eu/en

Acknowledgements

AWI, Germany: Gunnar Gerdts (Leader WG)
Antje Wichels (Co-leader WG),
Michaela Meyns (former PostDoc), Hannah Jebens (TA), Serena Abel, Lisa Roscher, Nick Mackay-Roberts (PhD students), Annika Fehres, Minh Trang Nguyen, Lorenz Reiser, Laura Stutzinger (Master students), Marcus Bach (former TA)

AWI Bremerhaven: Ilka Peeken, Melanie Bergmann

Utrecht University, Netherlands: Svenja Mintenig

Centre for Ecology and Hydrology/Wallingford, UK: Richard K. Cross

Marquette University, USA: Philipe Ambrozio Dias

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

University Oldenburg and ICBM: Barbara Scholz-Böttcher and Martin Fischer

Matthias Godejohann

www.mgopticalsolutions.com

DRS Daylight Solutions (Spero QT as a loan)

AWI and the German Federal Ministry of Education and Research (BMBF) for financial support (BASEMAN, grant 03F0734A)

BASEMAN MICROPLASTICS ANALYSES IN EUROPEAN WATERS
JPI OCEANS
Bundesministerium für Bildung und Forschung

EUROqCHARM has received funding from the European Union’s Horizon 2020 coordination and support action under grant agreement No. 101000805

HELMHOLTZ

Question ?