Analysis of nano- and microplastics in the environment

Martin Hassellöv

Institutionen för Marina Vetenskaper, Göteborgs Universitet

Martin.hassellov@marine.gu.se

Acknowledgements

Prof. Martin Hassellöv

Dr. Juliana Aristéia de Lima

Dr. Karin Mattsson

Dr. Josef Brandt

MSc Tim Wilkinson

Mats Hagberg, Microtechnology and nanoscience, Chalmers

UNIVERSITAS GOTHOBURGENSIS 1891

Marine Nano Chemistry Group

NATUR VÅRDS VERKET

JPI OCEANS

Purpose?

- Selectively determine microplastic particles…
  - as abundance of individual entities (with physicochemical descriptors), or
  - as their bulk mass
- as a wide class (according to definition of what is considered microplastics), or
- as specific polymers or group of polymers
- In complex environmental matrices
- Adequate figures of merits (e.g. limit of detection, reproducibility, selectivity)
- Cost efficient for either research or monitoring
- Balanced between comprehensiveness and complexity
- Robust and objective
- QA/QC along analytical chain (e.g. validation, contamination and control samples)
- Harmonization compatible

? Why and what should we measure?
?Definition: what is a microplastics?

Sampling **Sample preparation** **Particle analysis** **Visualisation of results**

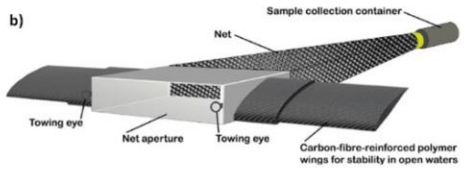
Sampling

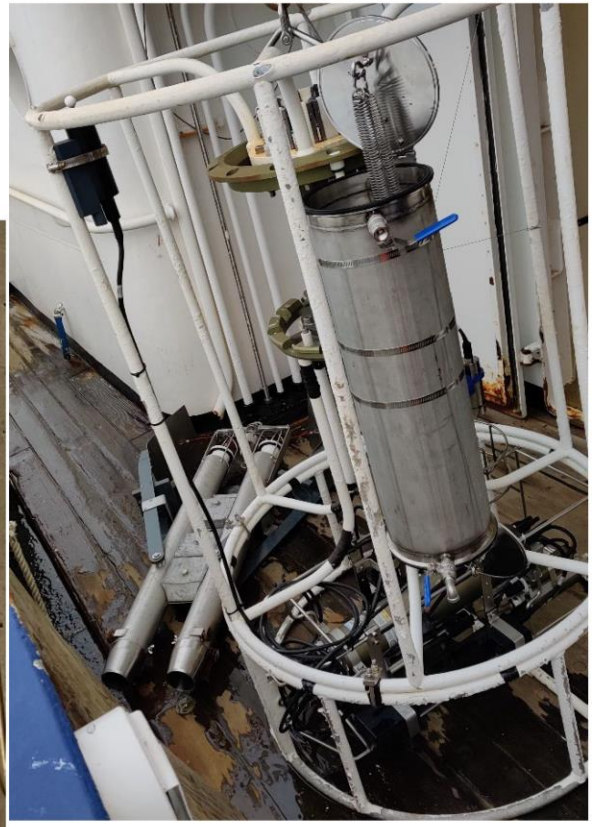
- Trawls/nets, in situ filtration pumps for large MP (often low abundance require large sample volumes)

- Small MP in pelagic, require medium volumes, plastic free samplers, on line filtration

- Drinking water: very large volumes for large sizes, medium or small volumes for small sizes. Direct coupling to tap or water works

- Sediments: in principle standard methods for sampling





Sample preparation examples

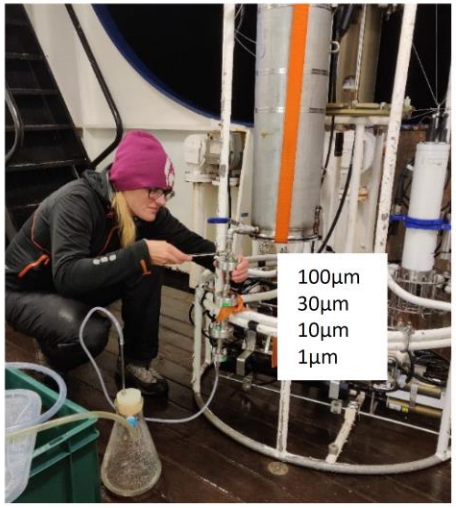
Sediments:

- Chemical pretreatment
- Suspension
- Heavy density separation
- Posttreatment

Downscaled and improved version of *MPSS* (Imhof, 2012)

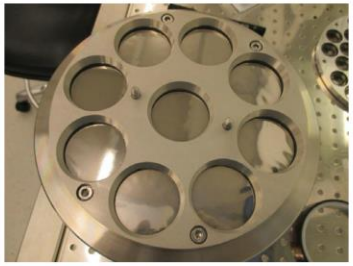
Water:

- On-line cascade filtration
- Chemical pretreatment

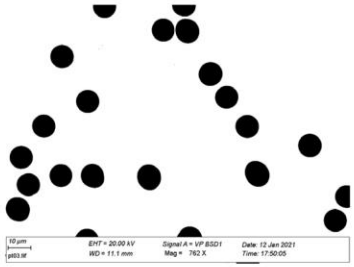


Development of Pt coated polycarbonate membranes

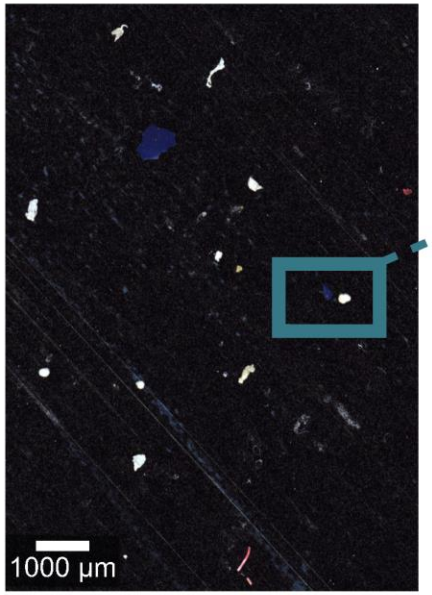
Filter holders



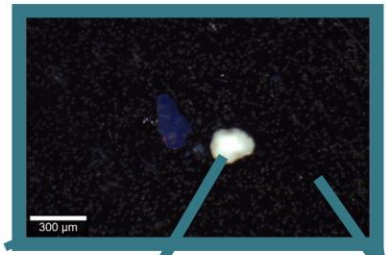
Coated membranes



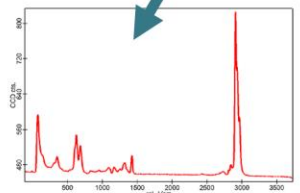
SEM image of membrane



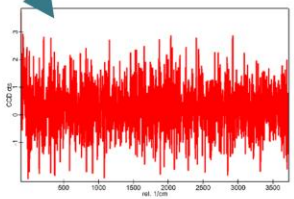
Confocal image of anthropogenic particles



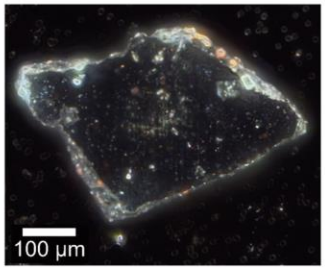
Confocal image of paint and plastic particle on Pt coated membrane



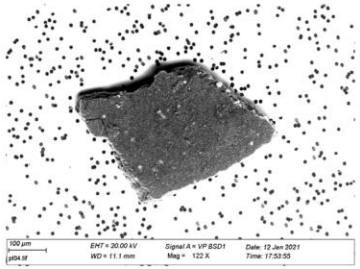
Spectra from plastic particle



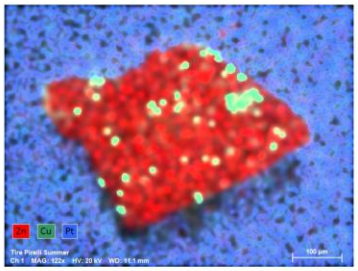
Spectra from background



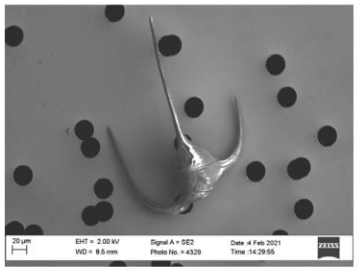
Confocal Raman image



SEM image



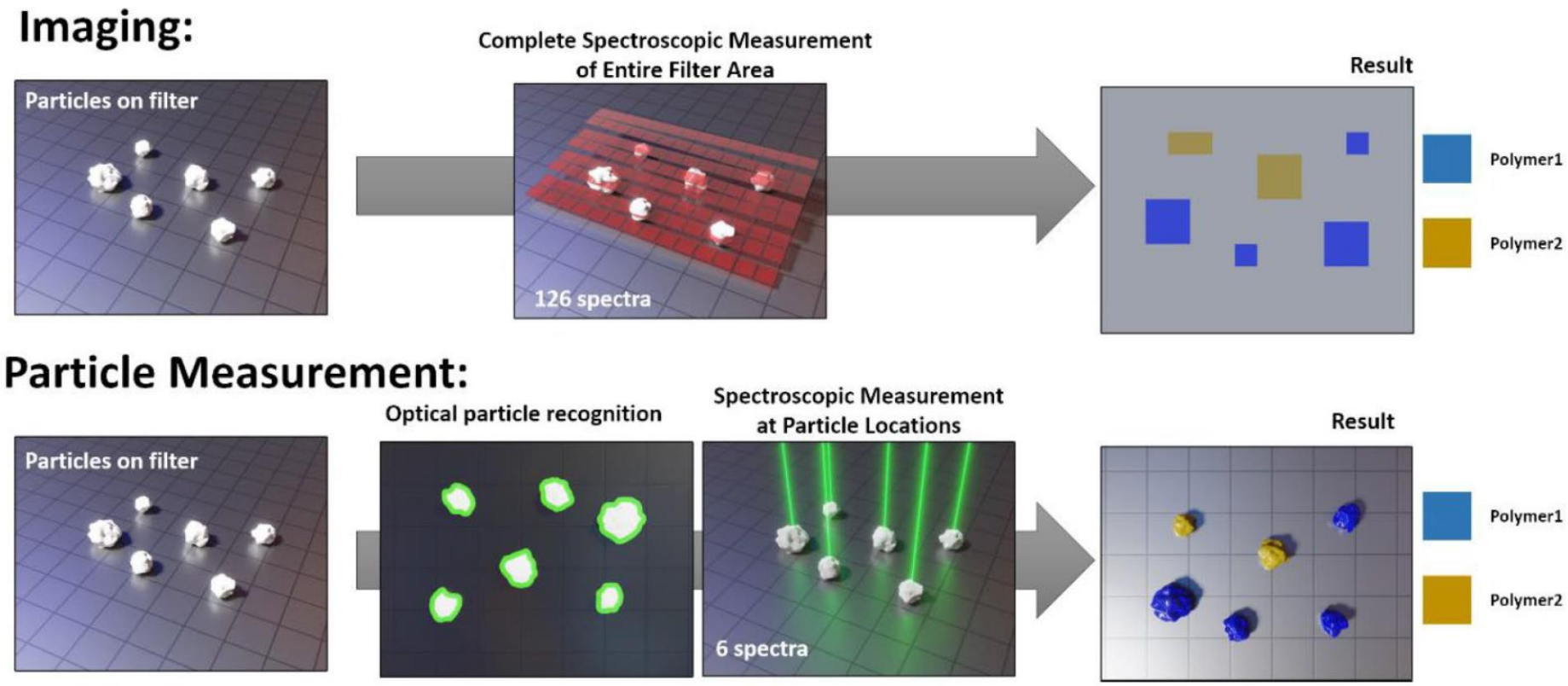
SEM-EDX



SEM image of dinoflagellate

Manuscript in prep. Collaboration with Chalmers µFab

Two approaches to microspectroscopic analysis of microplastics with FTIR and/or Raman

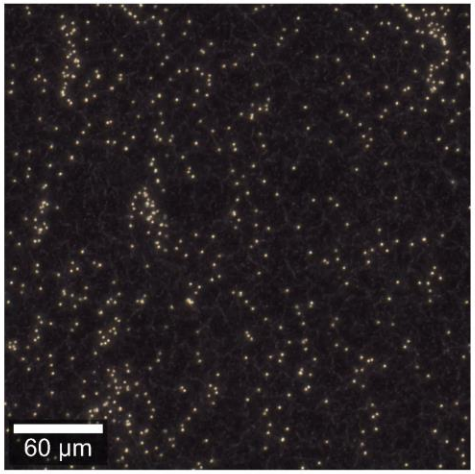


Brandt J, Bittrich L, Fischer F, et al. High-Throughput Analyses of Microplastic Samples Using Fourier Transform Infrared and Raman Spectrometry. *Applied Spectroscopy*. 2020;74(9):1185-1197. doi:10.1177/0003702820932926

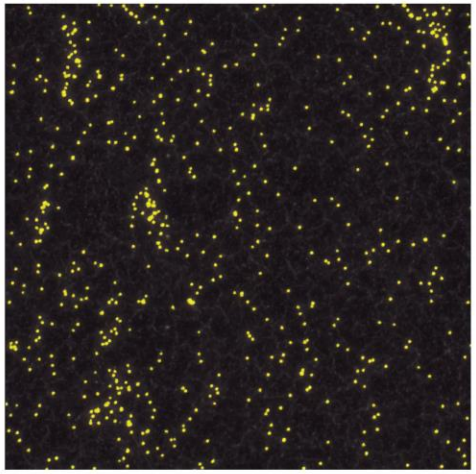
Automated LM-Raman using commercial software ParticleScout

Workflow ParticleScout

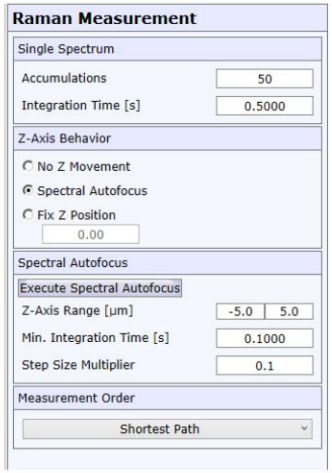
1. Mosaik image



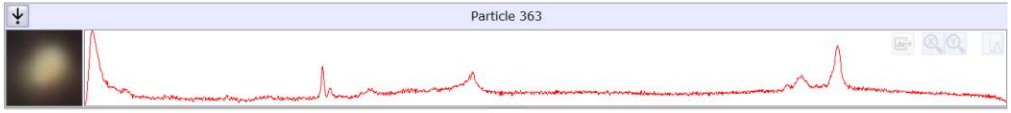
2.Treshold (particles to identify)

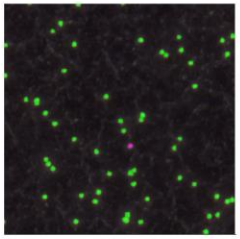


3. Raman settings



4. Results

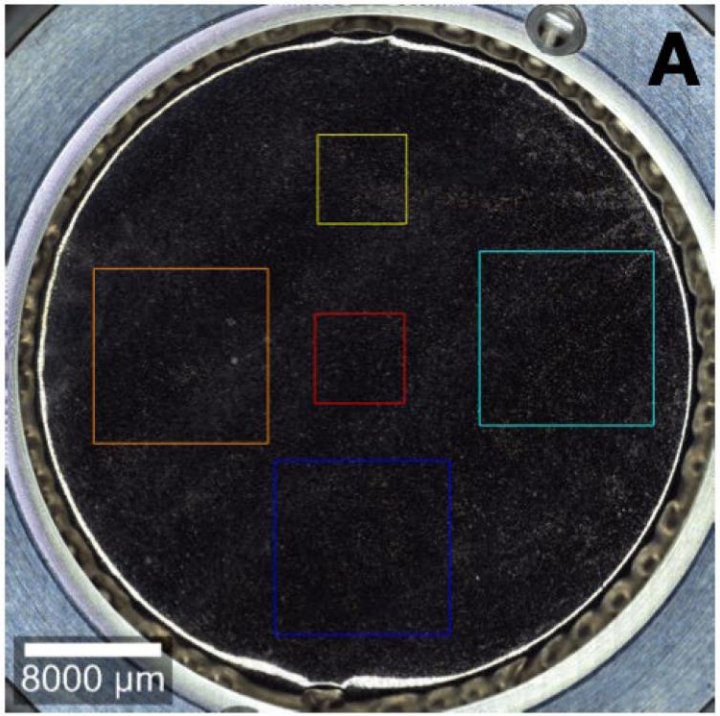


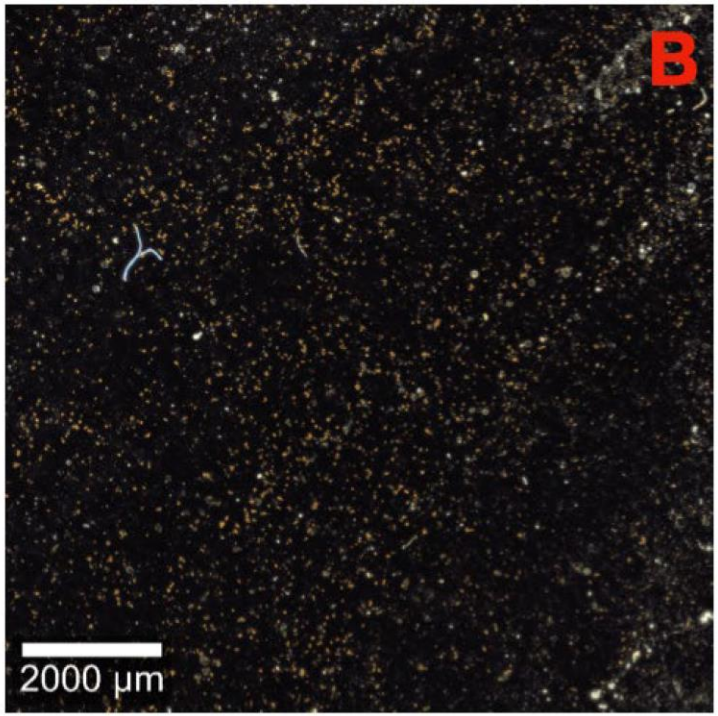


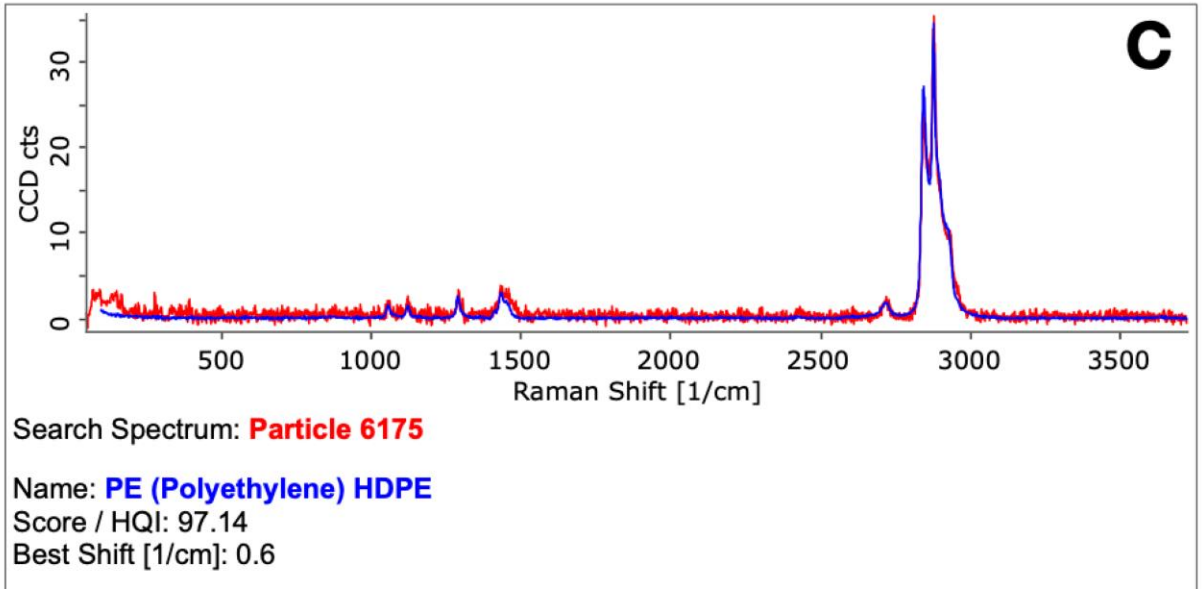
Select on particle (purple) and you can see the spectra and parameters of interest.

Material	**PS Polystyrene** HQI: 84.22
Length [µm]	2.1
Width [µm]	1.6
Aspect Ratio	0.750
Num Pixels	44.500
Area [µm²]	2.7
Convex Area [µm²]	2.8
Perimeter [µm]	6.3
Convex Perimeter [µm]	6.2
Feret Max [µm]	2.1
Feret Min [µm]	1.6
CE Diameter [µm]	1.9
Circularity	0.925
Convexity	0.979
Solidity	0.967
SE Volume [µm³]	3.3
Visual Center Point	X: 14323.2 Y: 518.4

Commercial particle analysis software*







*Particle Scout, WITEC

GEPARD 2: Open source acquisition and analysis software

- Written in Python
- Available at: https://gitlab.ipfdd.de/GEPARD/gepard
- Compatible to Raman (WITec, Renishaw) and FTIR (Perkin Elmer, Thermo)
- Import images from Zeiss microscope
- Developed By Josef Brandt, et al at IPF, Germany and GU, Sweden

GEPARD Analysis Pipeline

Features:

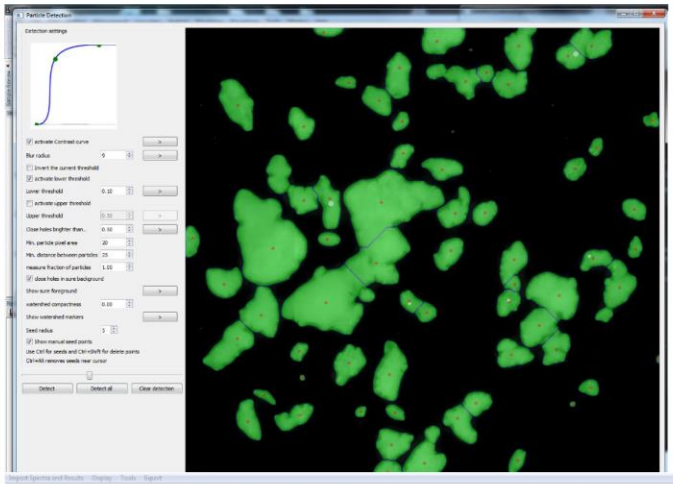
- image with height information (z-stack)
- full optical resolution (< 1 µm/px) -> large images (> 17k x 17k px)
- optional: Import optical image from Zeiss microscope
- controllable image segmentation (watershed)
- potentially high particle count (5,000 – 130,000 particles per sample)
- steer microscope for measurement or export coordinate set for Raman or FTIR
- rich reviewing options
- export to xls or SQL database

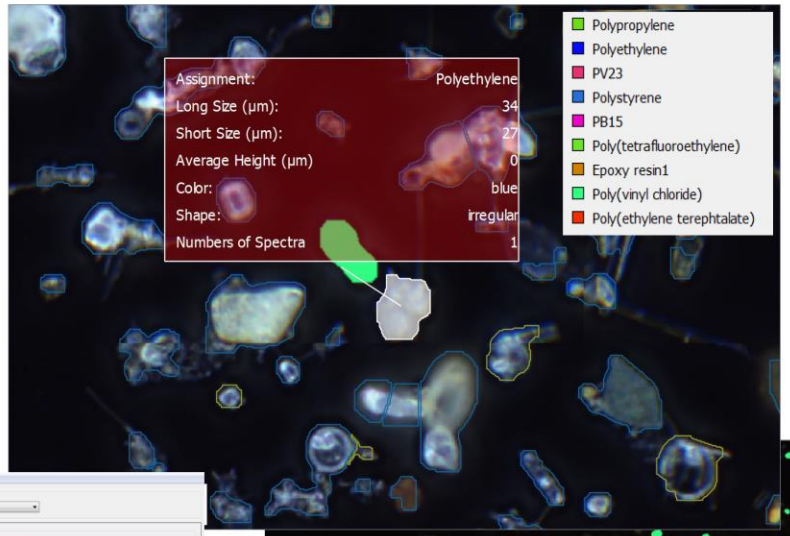
Automated Microspectroscopy using GEPARD software

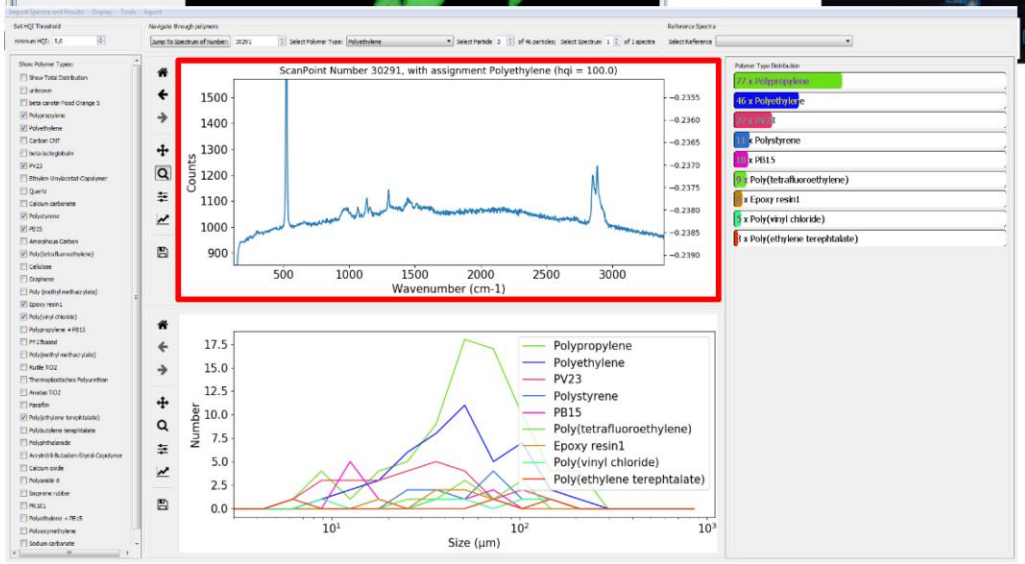
Versatile image segmentation

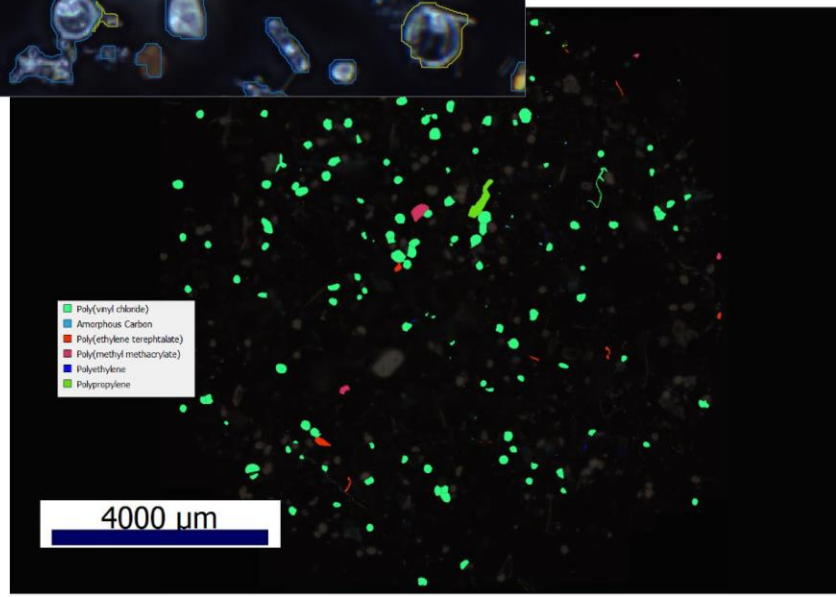
(either watershed or neural net algorithms with manual adjustments)

Rich reviewing and editing options



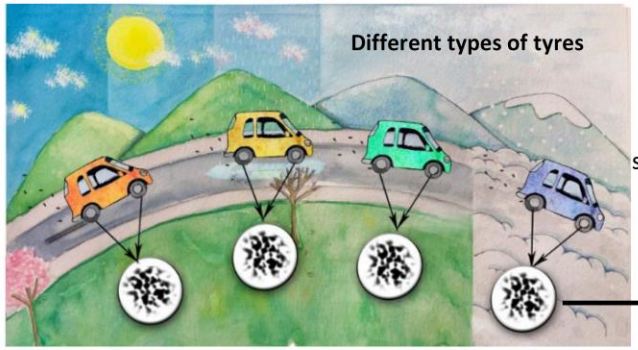




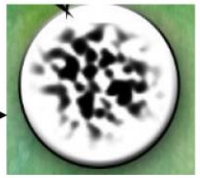


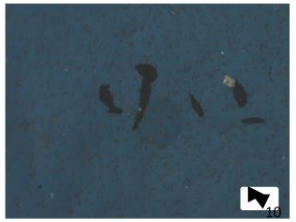
Tire and road wear particles: going from a visual-tactile probing to chemical identification…

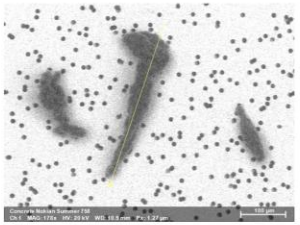
Tire road wear particles (TRWP)
in complex environmental samples



sampling

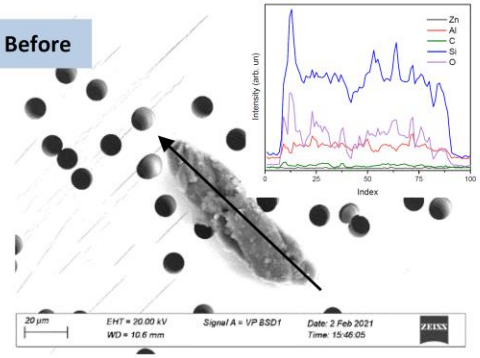




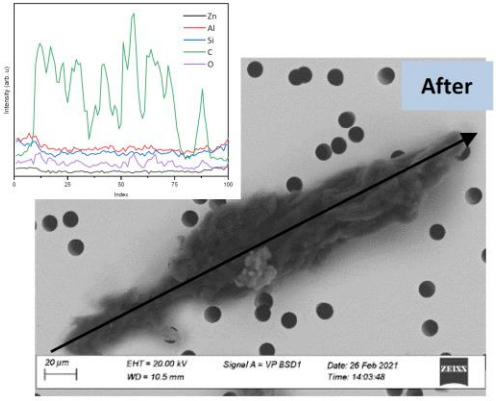


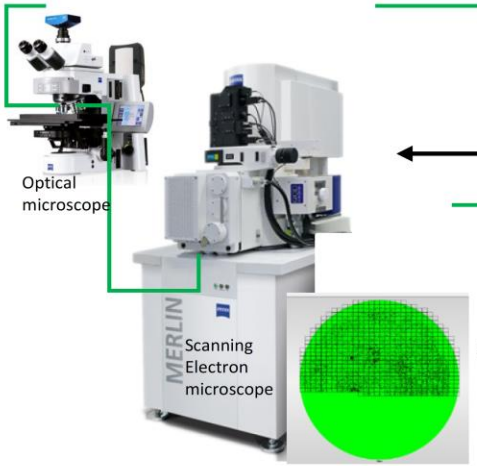
sample preparation developments

Before

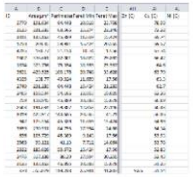


After





automated correlative methods

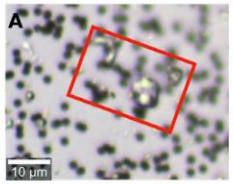


- **Generates statistical report for thousands of particles per filter**
- <u>decrease the lack in the validated knowledge in the TRWP</u>

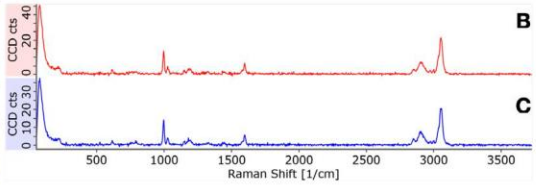
Can environmental nanoplastics be measured in microscopy?

Automated Microspectroscopy using correlative microscopy workflows:

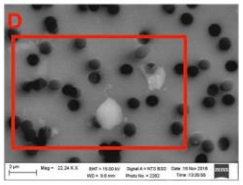
→ SEM-Raman for NPs works in principle but further development of workflow, automatisation, feasability of principle and pushing size limitations is needed.



Confocal Raman image



Raman spectra from b) reference spectra and c) from sample



SEM image

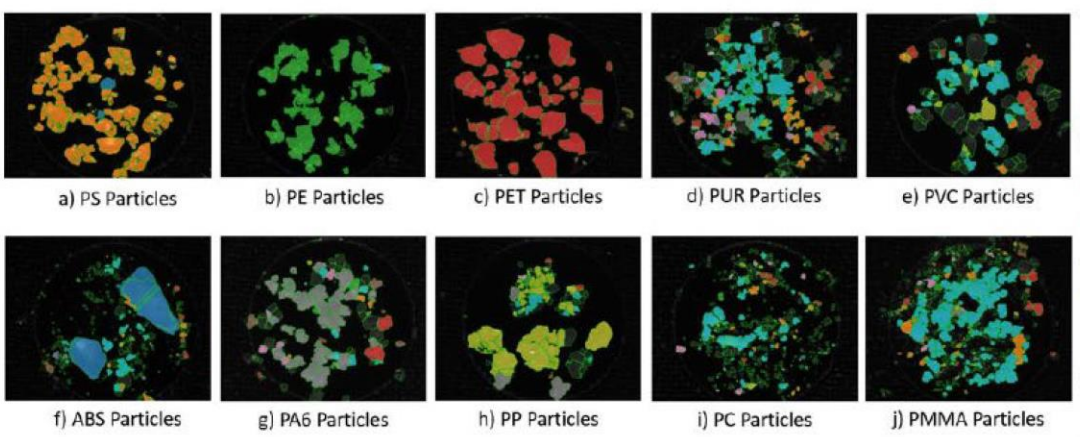

Light microscope

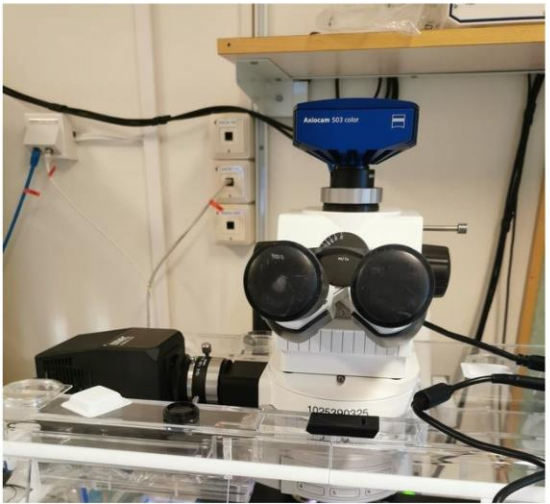

Stand alone confocal Raman

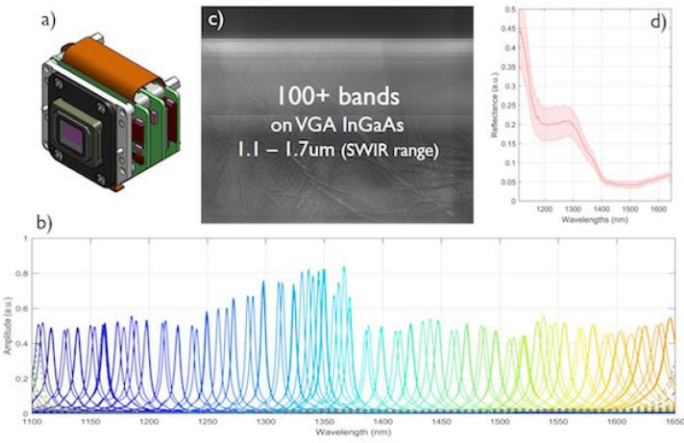
SEM Gemini with in situ Raman

Development of cost effective methods: hyperspectral SWIR, in progress…

Classification of acquired snapshots with particle from polyethylene and sediment.







Schwarte et al.,2022 in prep

Mass based thermal determinations

Py-GC-MS

TED-GC-MS

- Rapid, cost effective
- Require varying degree of sample prep
- Total mass content on specific polymer proxies
- Limit of detection not always sufficient
- No info on particles