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ANALYSIS OF SMALL MP AND NP IN SIMPLE AND COMPLEX MATRICES

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The 'new' projects

ANDROMEDA

To develop a toolbox of coherent, complementary, analytical instrumental methods and workflows to consistently and reliably detect, identify, quantify (mass/number) and characterize sMP and NP in environmental samples.

WP3

REVEAL

Develop a toolbox of complementary analytical methods to reliably detect, identify, and quantify sMP and NP in aquatic environmental samples and to understand their behaviour in different aquatic matrices.

WP1

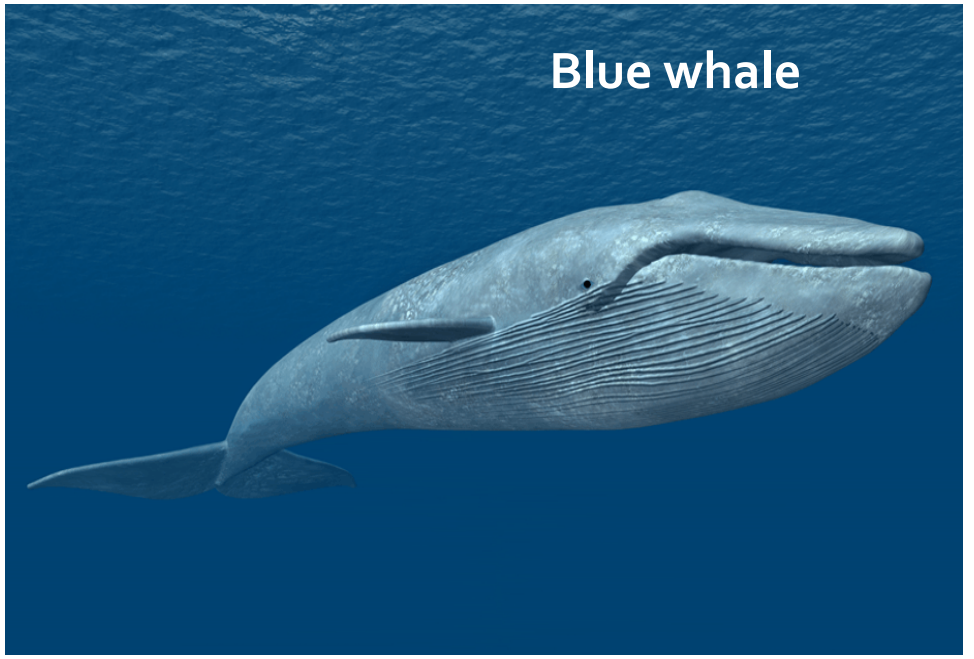
JPI OCEANS

The Research Council of Norway

Handelens Miljøfond

Microplastic ≠ Nanoparticles

A **200 µm** particle is **10,000x** larger than a **20 nm particle**



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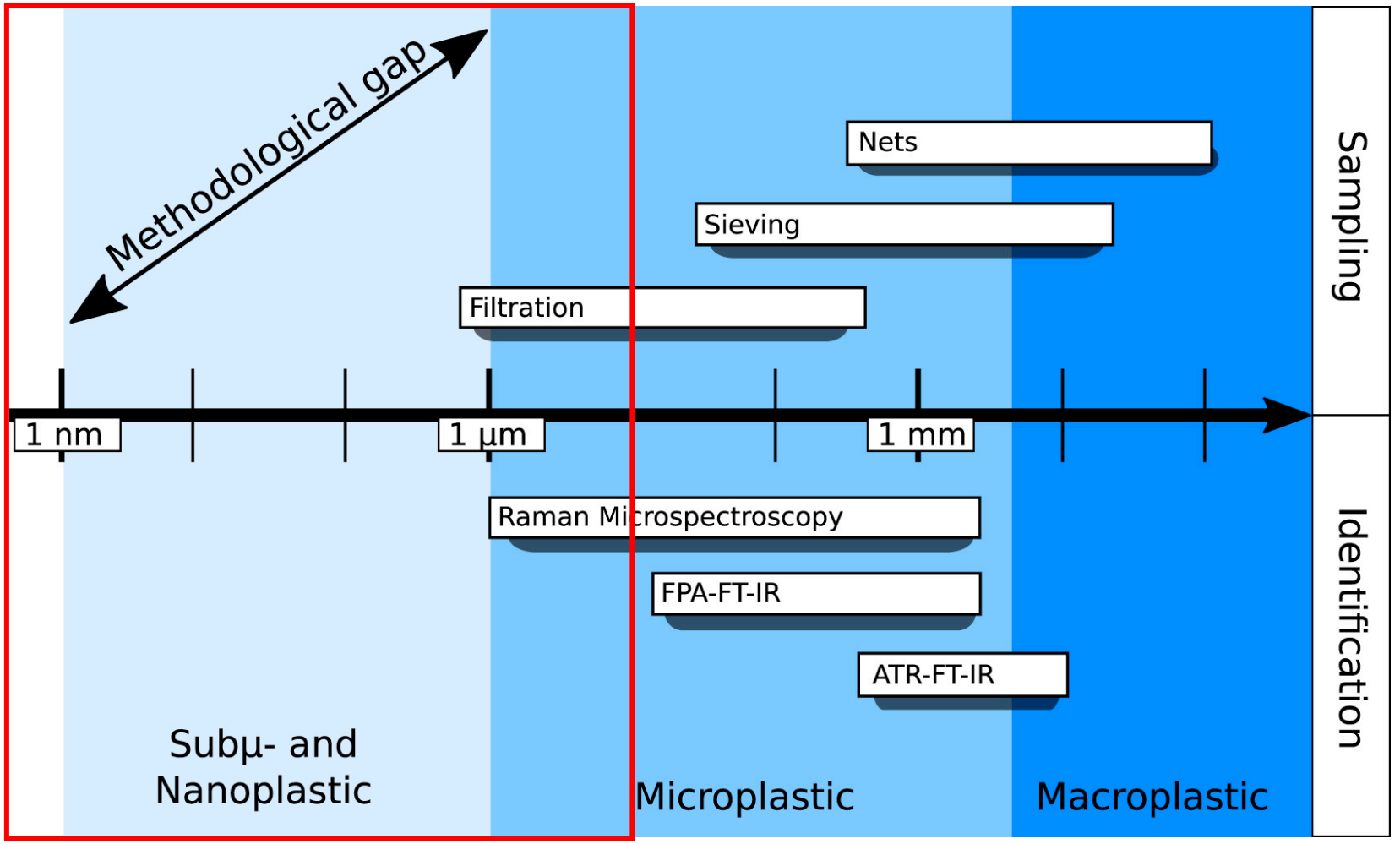
Current status



Sampling, extraction and analysis approaches for microplastic (>10 µm) are not suitable for particles <10 µm

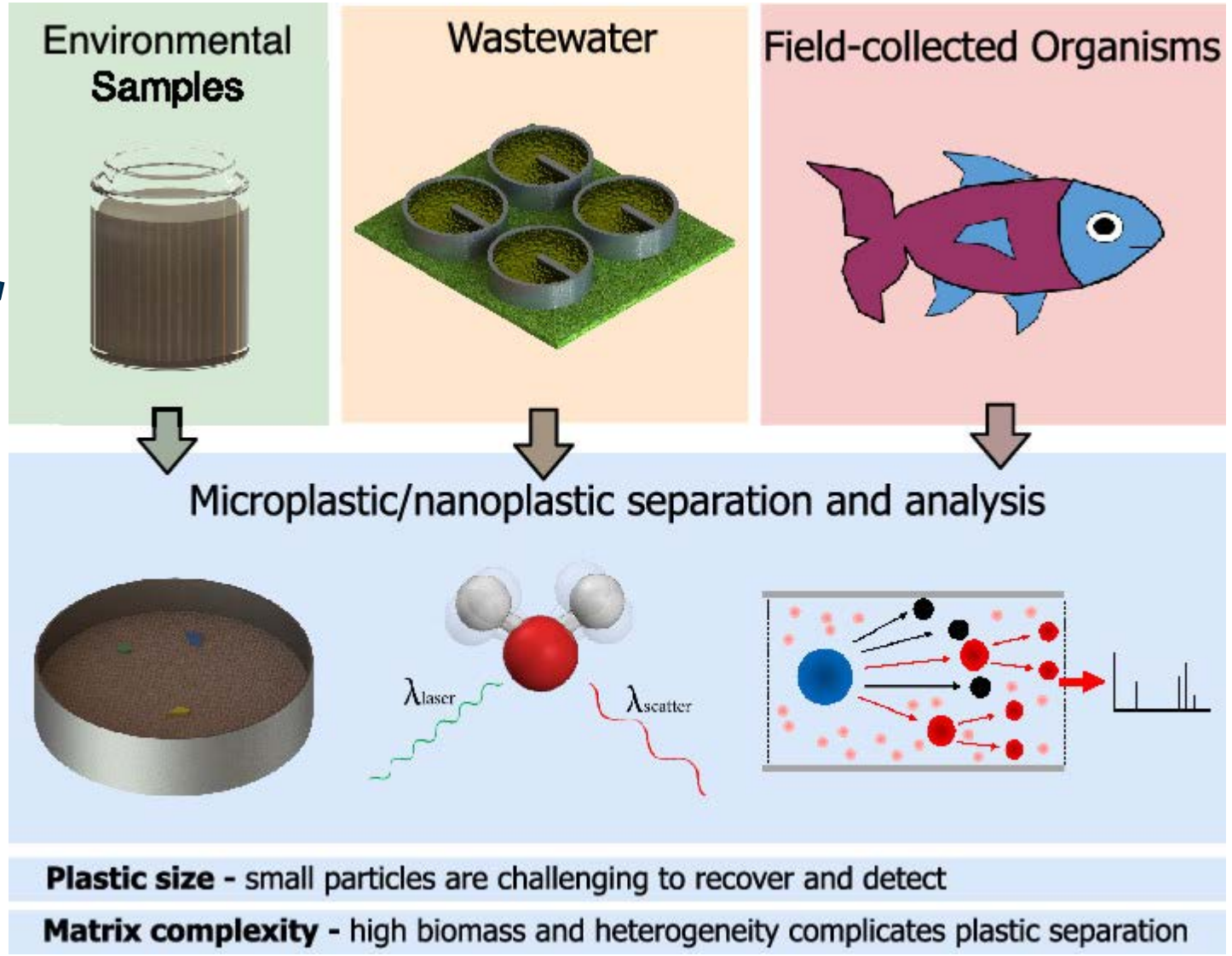
*Schwaferts, C.; Niessner, R.; Elsner, M.; Ivleva, N. P., Methods for the analysis of submicrometer- and nanoplastic particles in the environment. TrAC Trends in Analytical Chemistry **2019,** 112, 52-65.*

Challenge #1

How do we go from this?

To this?

Start with simple matrices first!!!



Nguyen et al., *Accounts of Chemical Research* **2019** *52* (4), 858-866

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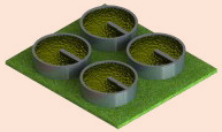
BIOLOGICAL SAMPLES

Fish Mussels Plankton

Lack of terrestrial organisms

WASTEWATER SAMPLES



Influent
Effluent
Sludge

Lack of proper organic matter content characterization

WATER SAMPLES

Drinking water
Sea water
Fresh water

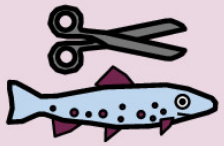
SEDIMENT SAMPLES

Beach sediments
Deep sea sediments

PRE-SEPARATION

DISSECTION

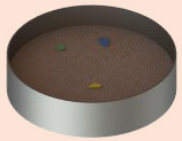
Gastro-intestinal tract or whole body



Recovers >500 µm

IN SITU SIEVING

Plankton net
Stack filters device
Mesh size
10 - 300 µm



Clogging issues
Loss of smallest fraction

CLEAN-UP & SEPARATION

DENSITY SEPARATION

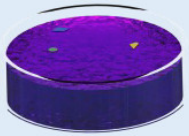
Flotation
Not suitable for small particles
Organic matter? Bubbles?

Centrifugation
Lack of method development

Ultrasonic Separation

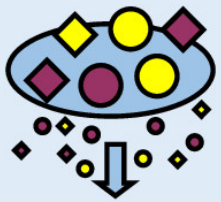
DIGESTION

Plastic degradation?
pH, temperature?
Standard protocol?
Organic matter content?
Enzymes, H_2O_2, HNO_3, KOH, NaOH, HCl?



FILTRATION

Filter size
0.5 - 10 µm



Underestimation of smallest fraction because of retention on filter

ANALYSIS METHODS

VISUAL

Couple with staining?

Shape, size, color
N/A below 200 nm
Cannot identify chemical composition

Microscope
SEM, TEM

Plastic spatial structure in tissues by microsection

VIBRATION SPECTROSCOPY

Raman microscopy
<20 µm

FTIR
>20 µm or films

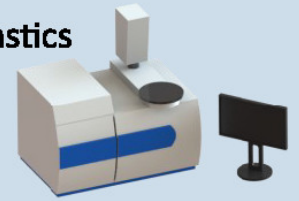
↑ Spatial resolution

MASS SPECTROSCOPY

Suitable for nanoplastics

TDS-GC-MS
qualitative analysis

py-GC-MS
greater sensitivity



↑ Sensitivity

SPIKE CONTROLS — accurate recovery? effect of plastic size, shape, composition on recovery?

BLANK CONTROLS — background level and contamination? False positives from natural organic particles or dyes?

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Where to start?

To develop and optimise the sample preparation, extraction and concentration steps, we first need to establish need robust analysis methods

BUT…….

…..we need suitable reference materials to develop the analysis methods.

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Challenge #2

How do we produce a mixture of irregular shaped plastic particles with a size distribution covering 1 nm to 1 µm?

Cryomilling

- Final product can be dry sieved to produce <100 µm fraction
- Needs further fractionation using alternative methods

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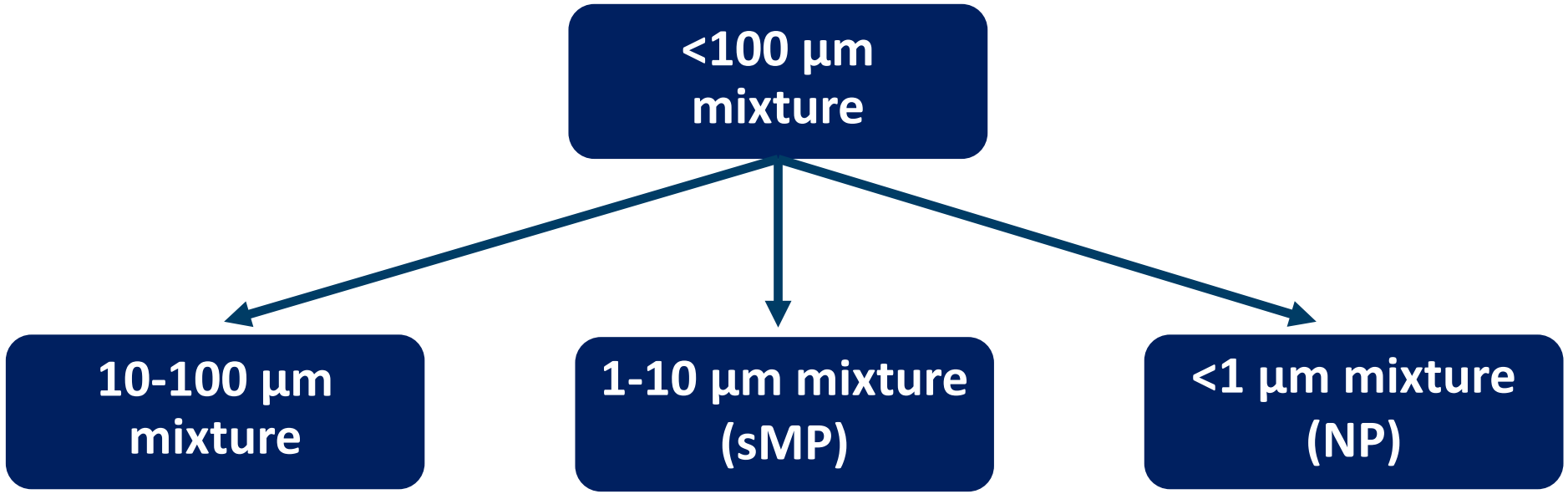
Reference material goal



Sample preparation – Filtration

'Standard' filtration approaches do not work for sub-micron particles

Stirred Cell

Cross flow ultrafiltration

Challenges

- Filters/membranes that can withstand high pressures.
- Recovery of NMP from filter media.
- Custom-made system?

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Challenge #3

Which analysis method (s) to use?

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Quantification – Microplastic (>10 µm)

Measurements

Polymer identification (individual particles)

Particle counting

Particle size

Quantification

Total number of particles

Particles of particular polymer type

Particles of particular size (range)

FPA-µFTIR

µRaman

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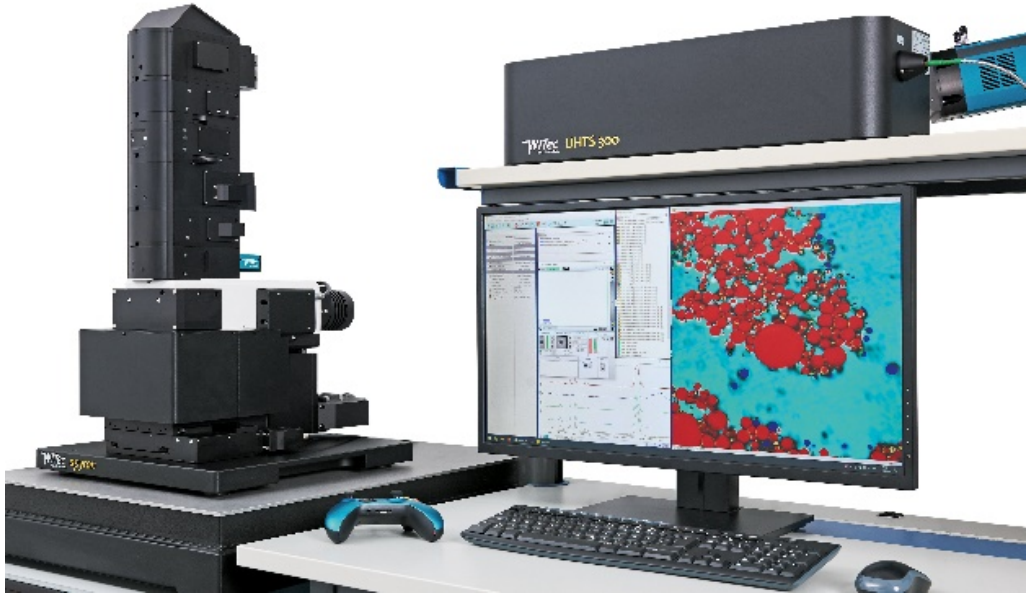
Robust techniques for sMP 1-10 µm

- Implementation of automated particle finder in the Raman workflow
- Define instrumental LoDs (size) for µFTIR and µRaman as 'start point' for other techniques:
  - Laser confocal Raman - apply autofocus procedures, optimize the laser power and automate workflow.
  - Time-of-Flight secondary ion mass spectrometry (TOF-SIMS) - ion imaging of particles 10-1 µm.
- Investigate combining light or hyperspectral microscopy with Raman spectroscopy and nano-TOF-SIMS.



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Quantification – Nanoplastic (<1 µm)

Measurements

Polymer identification (individual particles)

Particle counting

Particle size

No single instrument currently capable of achieving this for MP <1 µm and nanoplastic

Quantification

Total number of plastic particles

Total mass of particular polymer type (defined size range)

Possible to achieve

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Techniques for particles <1 µm

Direct Approach

- Optimize cascade filtration down to 0.45 µm/0.2 µm for metal-coated polycarbonate membranes.
- HR SEM as particle finding step.
- Correlative SEM-Raman and SEM-TOF/SIMS to identify polymer particles.

High-Res SEM

Techniques for particles <1 µm

Py-GC-MS

Indirect Approach

Isolate particle fractions <0.45 µm using cross flow ultrafiltration

Field flow fractionation techniques (Centrifugal or Flow) will be studied

Establish py-GC-MS for plastic quantification in each fraction

Complex samples – Challenge #4

SEPARATION METHODS

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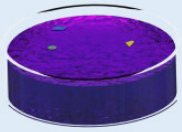
DIGESTION



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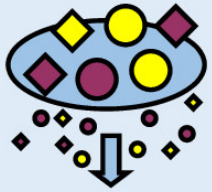

Filter size
0.5 - 10 µm

Underestimation of smallest fraction because of retention on filter

If the filtration and analysis of sMP and NP is successful for simple matrices, digestion methods for MP can be assessed for sMP and NP.

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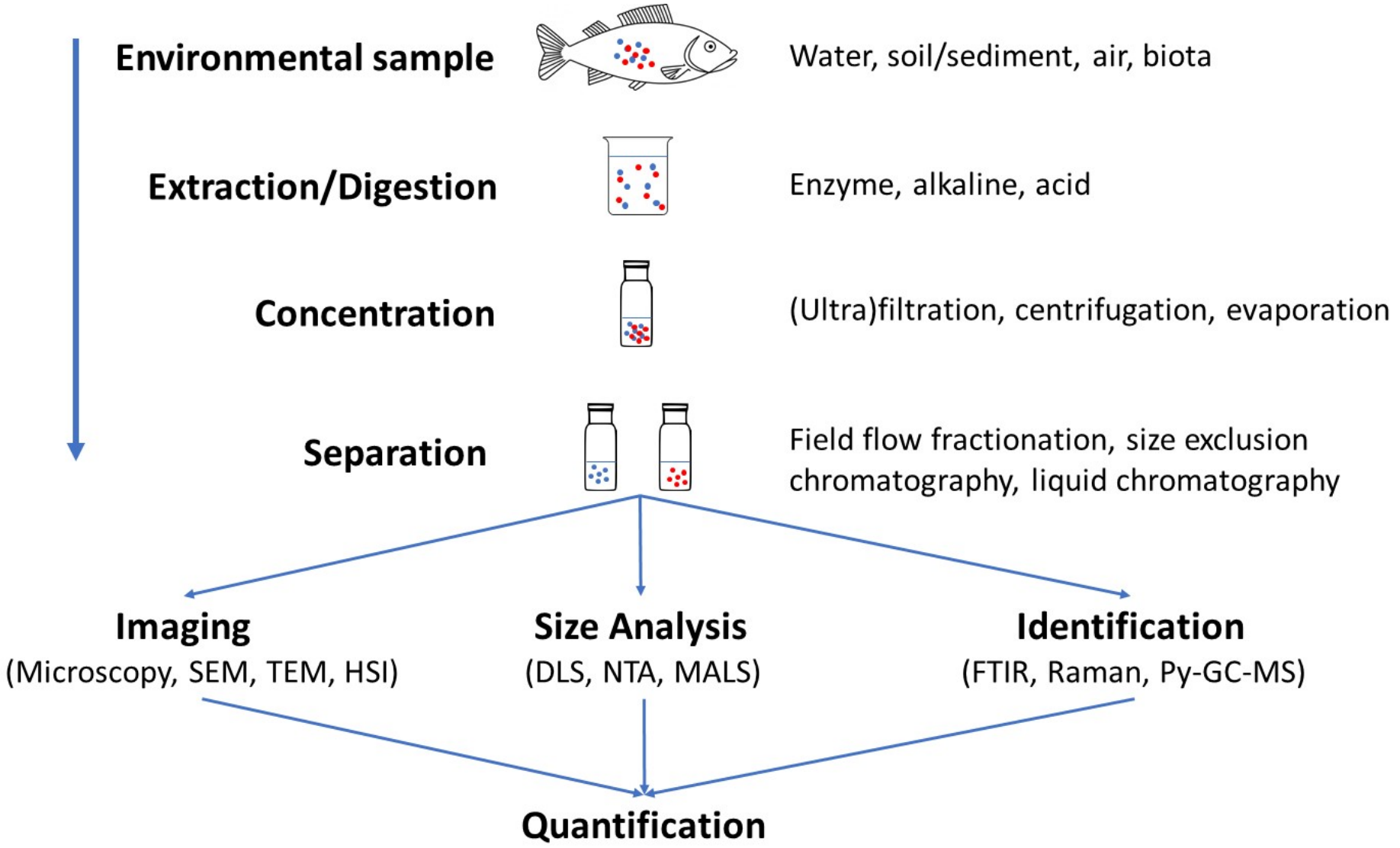
Approach we're aiming for



Nanoplastic in Microred

GC-MS

LC-MS

List of non-leachable target analytes

HDPE pipe

1. Solvent extraction

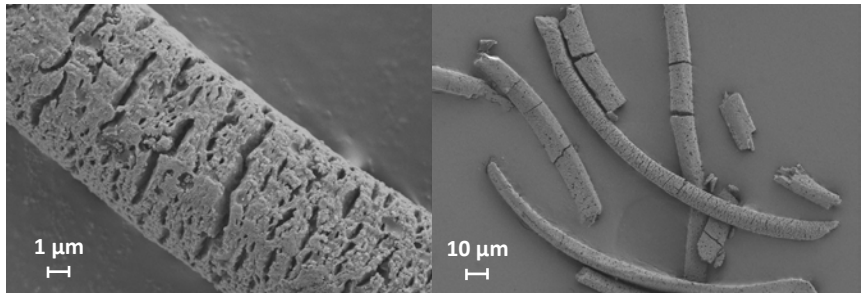
2. Aqueous leaching

4. Target analysis of non-leachable chemicals

5. Nanoplastic quantification

Eroded sample, clean up (T2.1)

3. SEM Imaging



Thanks for your attention!

REVEAL

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