The Potential of Single Particle Inductively Coupled Plasma Mass Spectrometry for Studying Micro- and Nanoscale Particles in Water and Food

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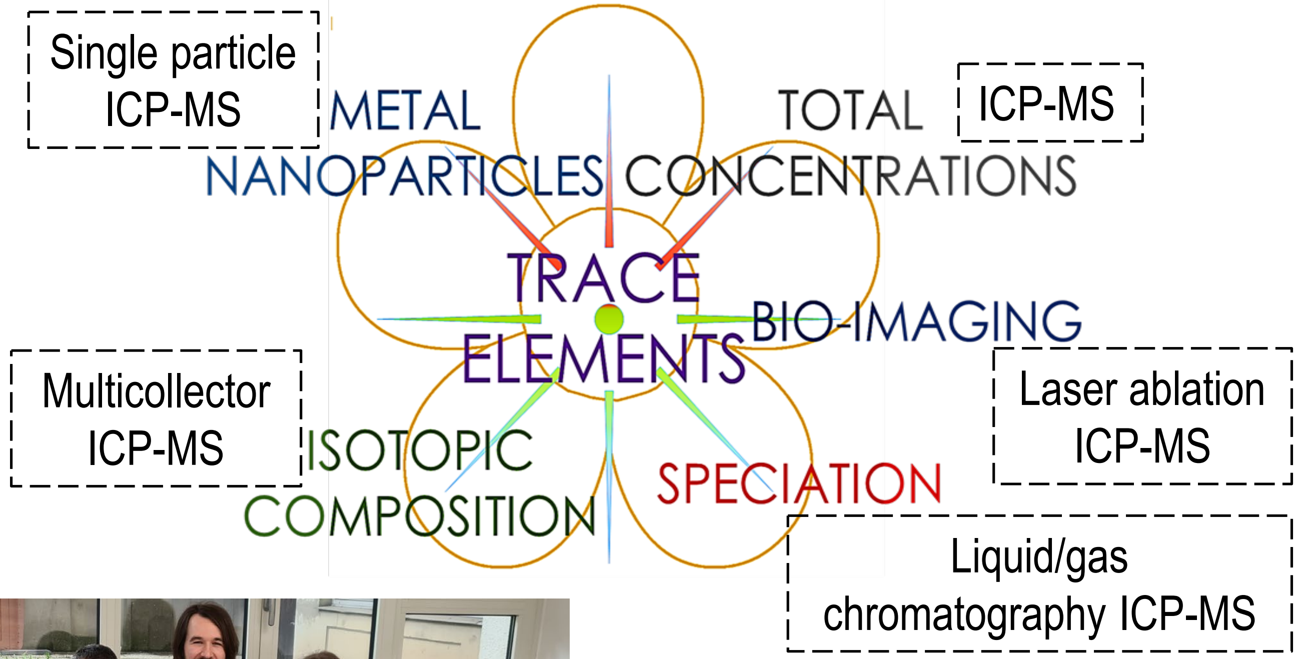
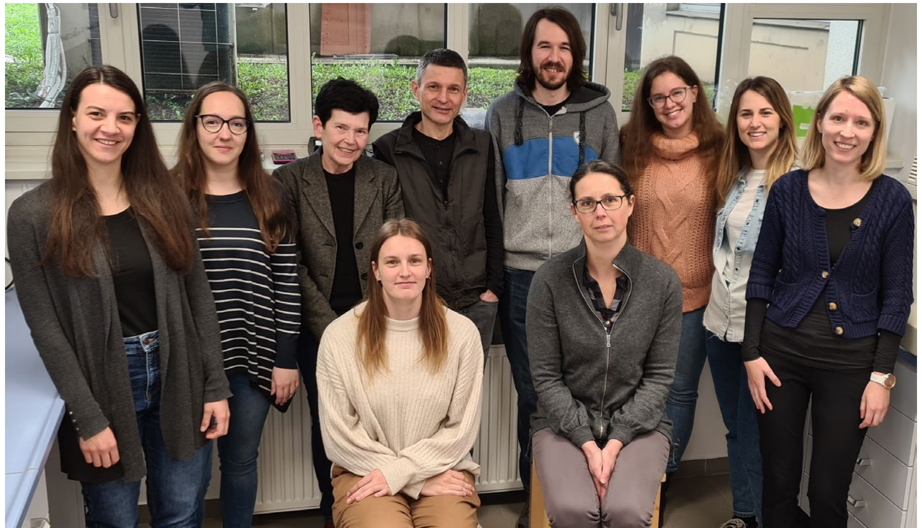
Institut
"Jožef Stefan"
Ljubljana, Slovenija

Department of
Environmental Sciences

Research Group for Trace Elements Speciation





Prof. dr. Radmila Milačič,
Head of Laboratory for analytical chemistry

Prof. dr. Janez Ščančar,
Head of Research Group for Trace element speciation

Outline

Introduction

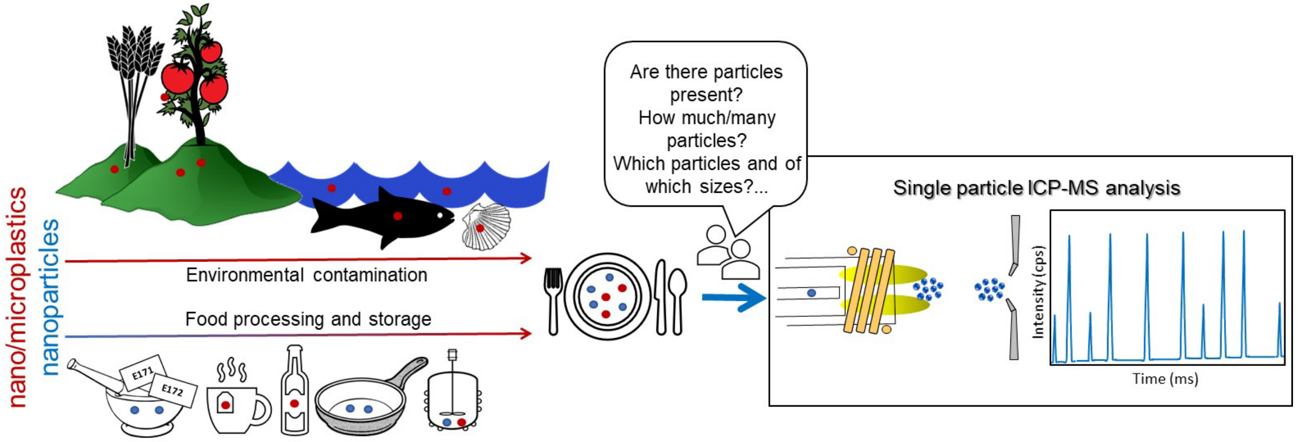
- Inorganic nanoparticles and nano/microplastics in water and food
- Why it is important to measure micro- and nanoscale particles?
- Measurements (current methods, analytical challenges)

Single particle ICP-MS method

- Main features, principles, advantages/limitations

Applicability of single particle ICP-MS method

- <u>Detection of inorganic nanoparticles:</u>
  - in river water systems
  - in food samples
- <u>Detection of nano/microplastics:</u>
  - released from teabags / in natural waters
  - in tomatoes



Nanoparticles: Definition

Nano-object: discrete piece of material with one, two or three external dimensions in the nanoscale (ISO/TR 18401:2017):

— in one dimension (nanoplates);

— in two dimensions (nanofibres);

— in all three dimensions (nanoparticles).

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European Commission recommendation on the definition of nanomaterial (2022)

- Natural, incidental or manufactured material consisting of solid particles
- 50% or more of particles in the number-based size distribution have one or more external dimensions in the size range 1 nm to 100 nm

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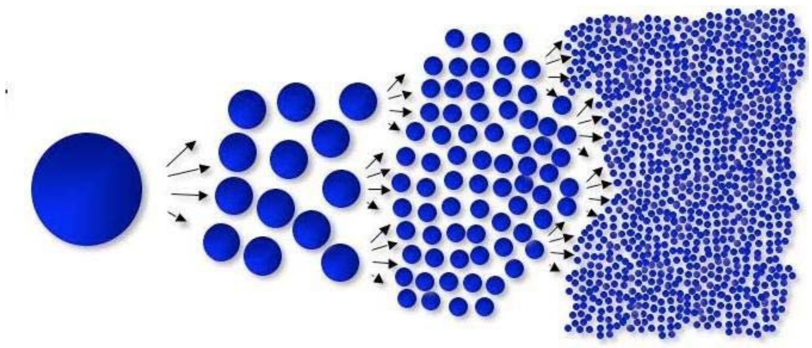

Particle size			
10 cm	1mm	1µm	1 nm
Surface			
1	100	100.000	100.000.000

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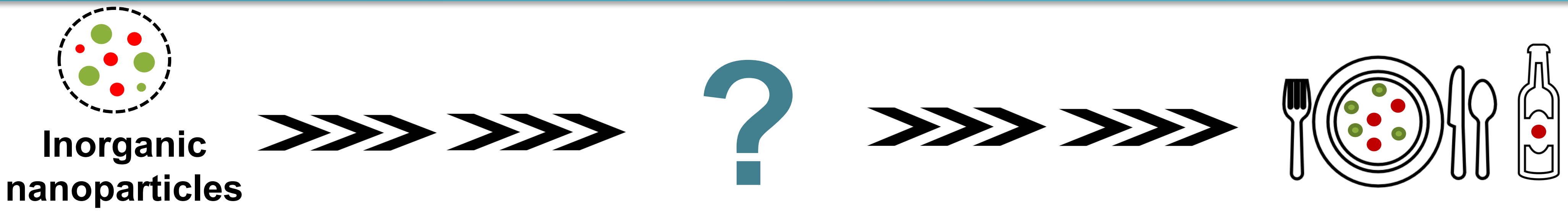
Nanoparticles: Sources and occurrence



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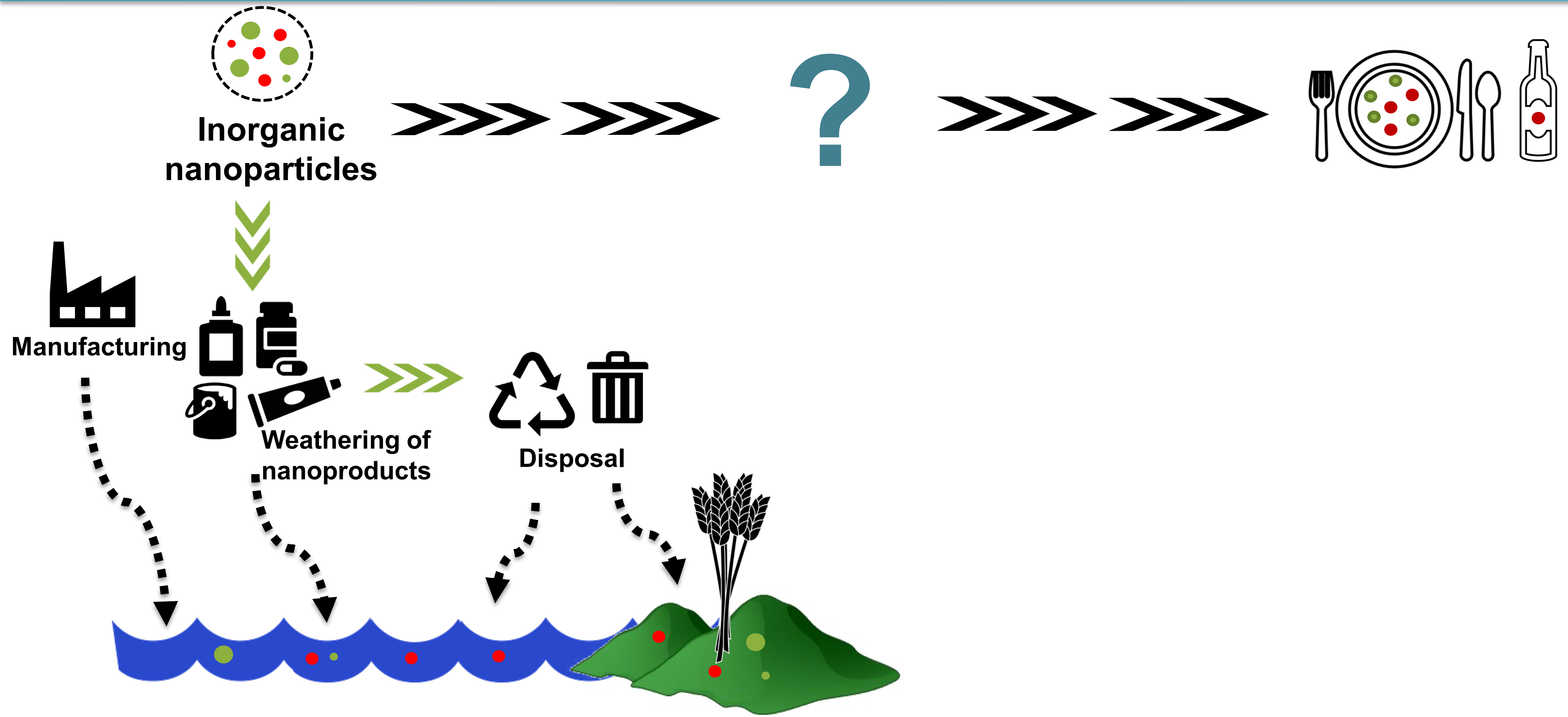

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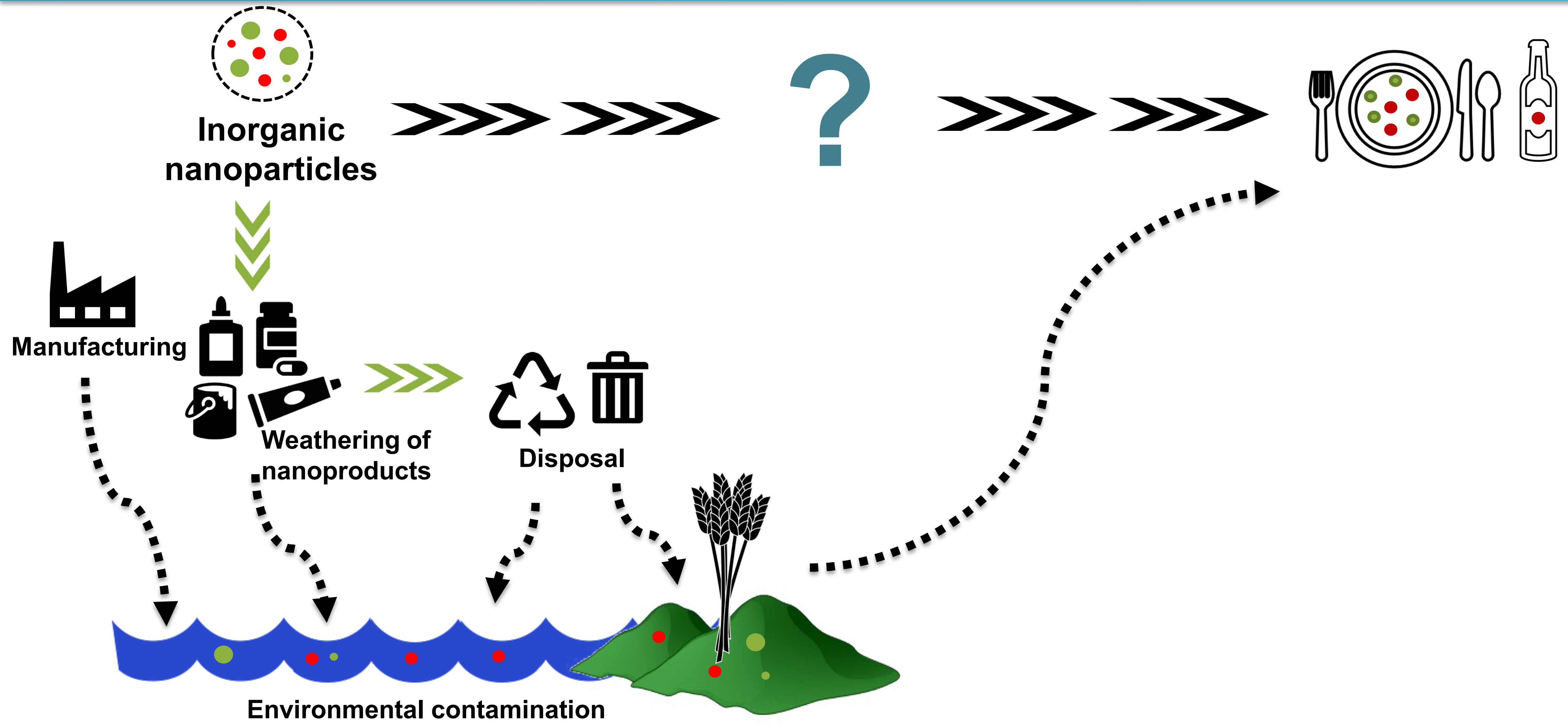

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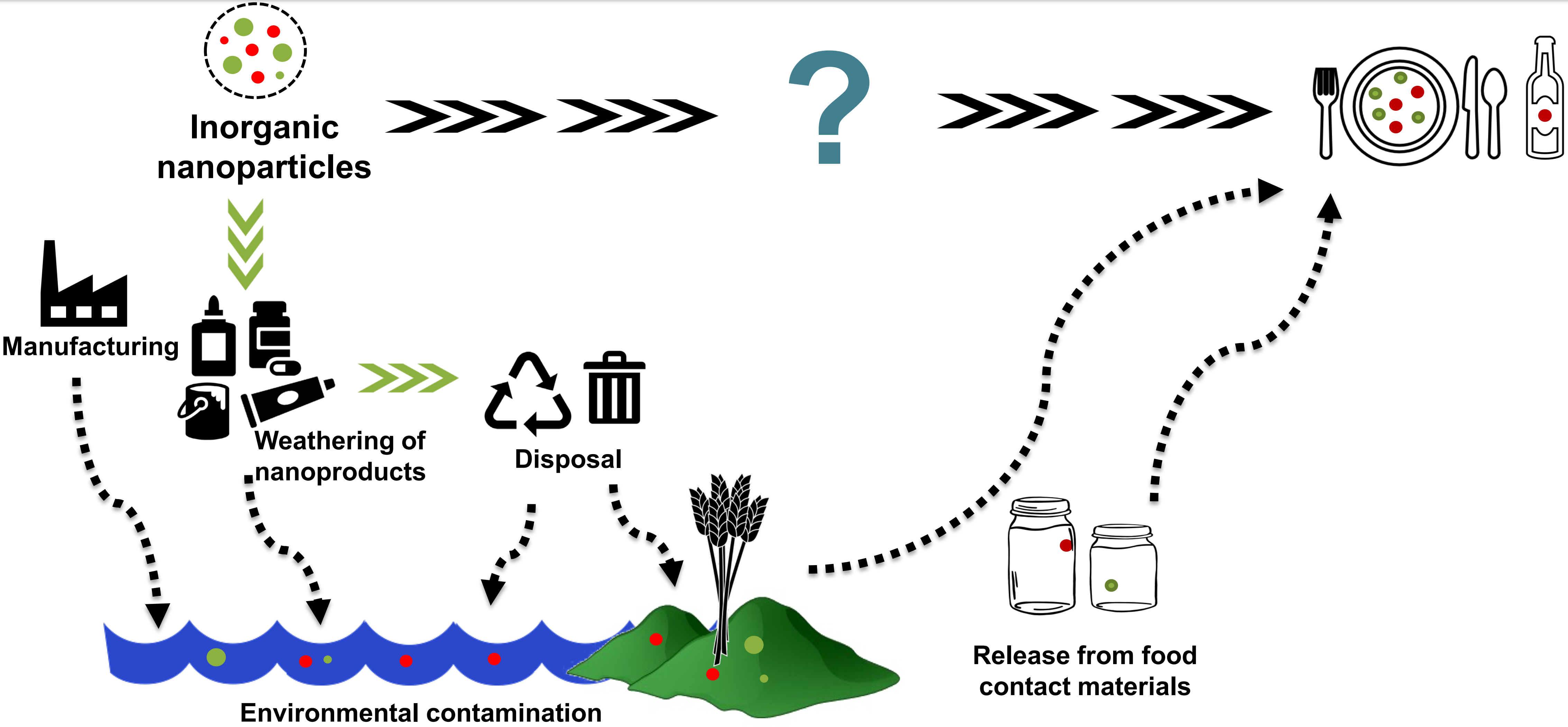

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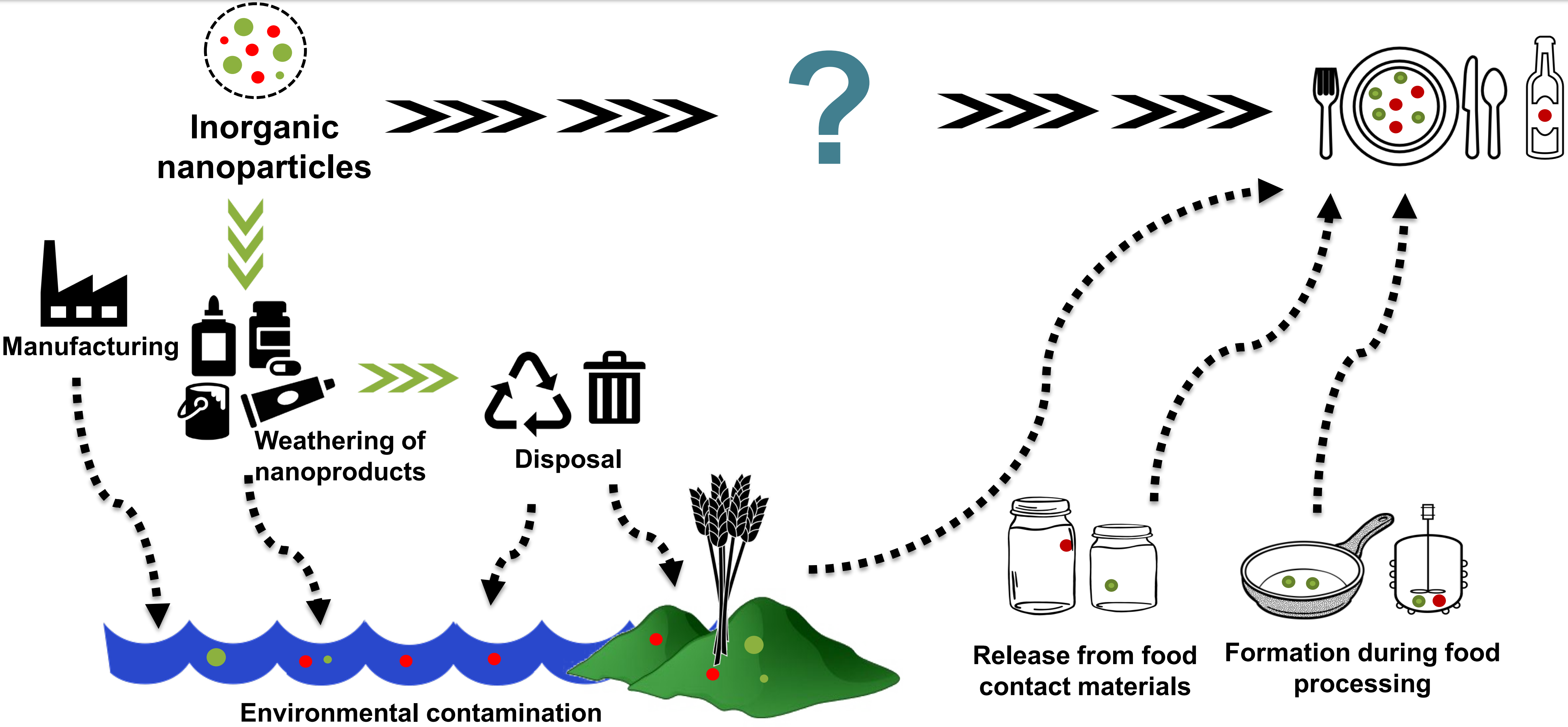
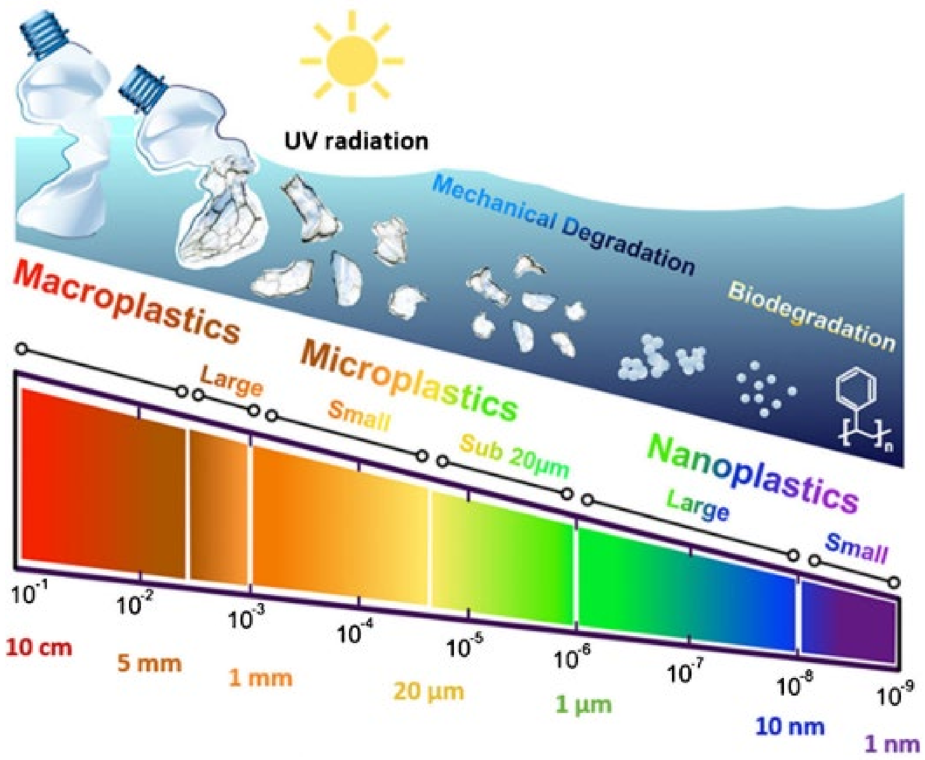


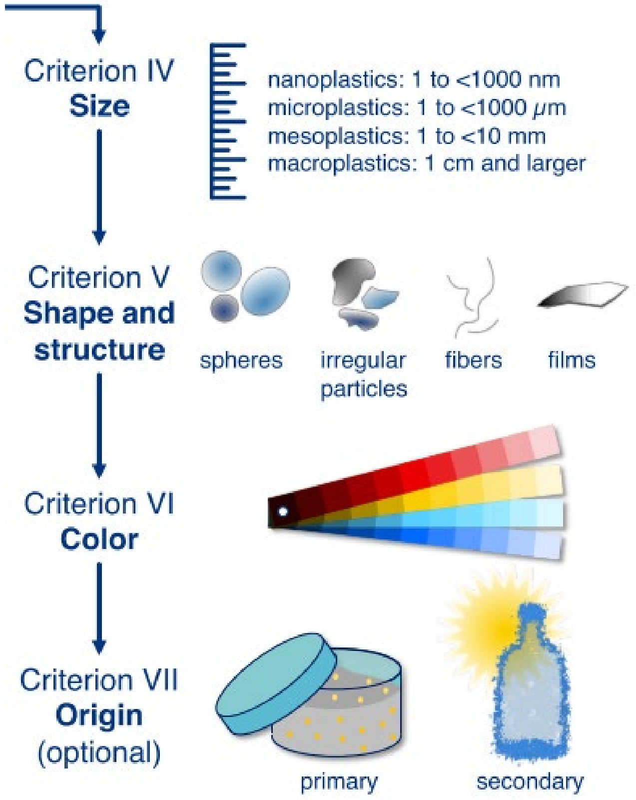
Nanoparticles: Sources and occurrence

Nanoplastics and microplastics: Definition

Microplastics: 1 µm – 5 mm (small MPs: 20 µm – 1mm; large MPs: 1 mm – 5 mm)
Nanoplastics: < 1 µm (1 – 100 nm, EFSA)



Analytical and Bioanalytical Chemistry (2021) 413:7–15



Environ. Sci. Technol. 2019, 53, 1039−1047

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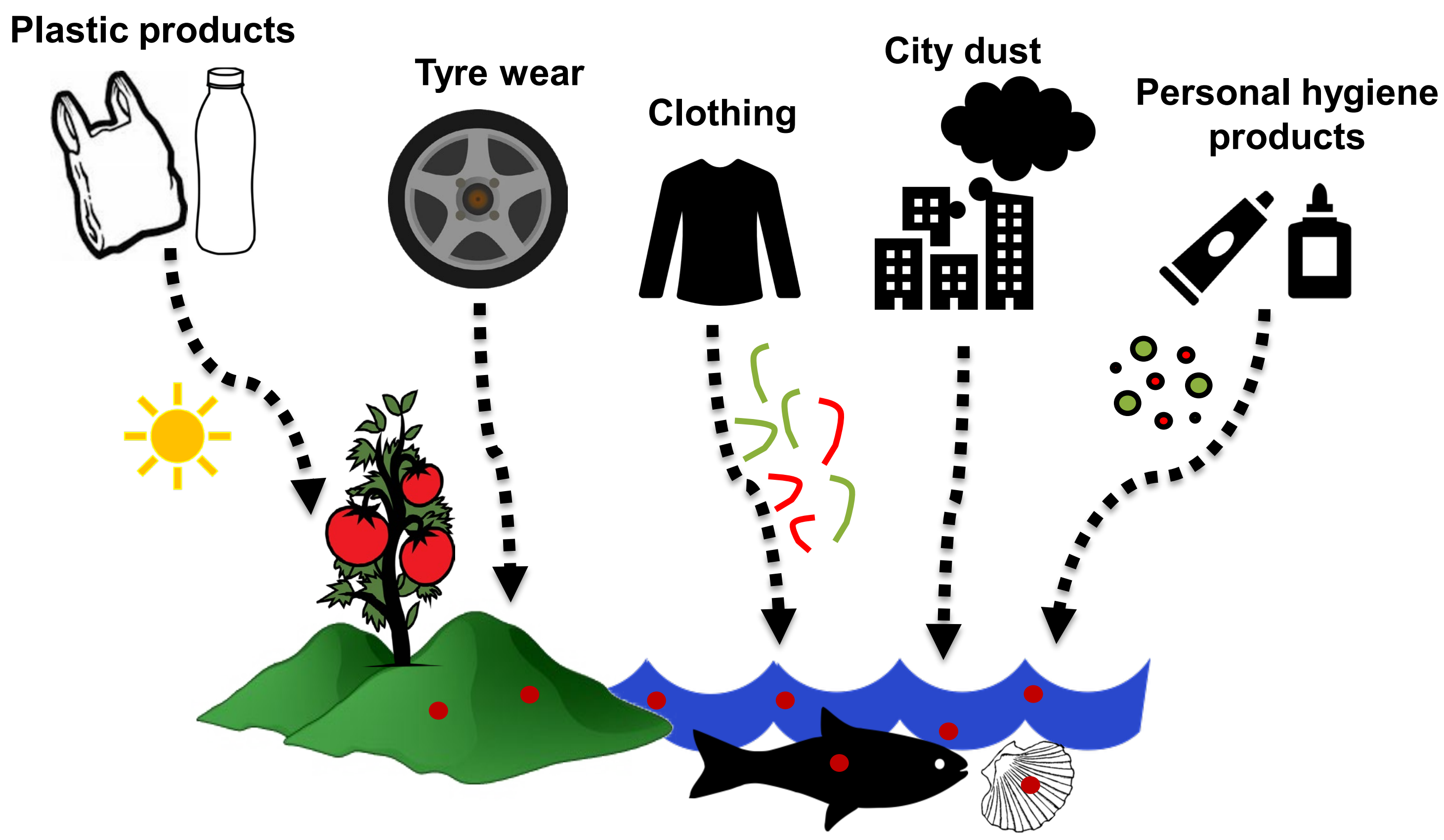

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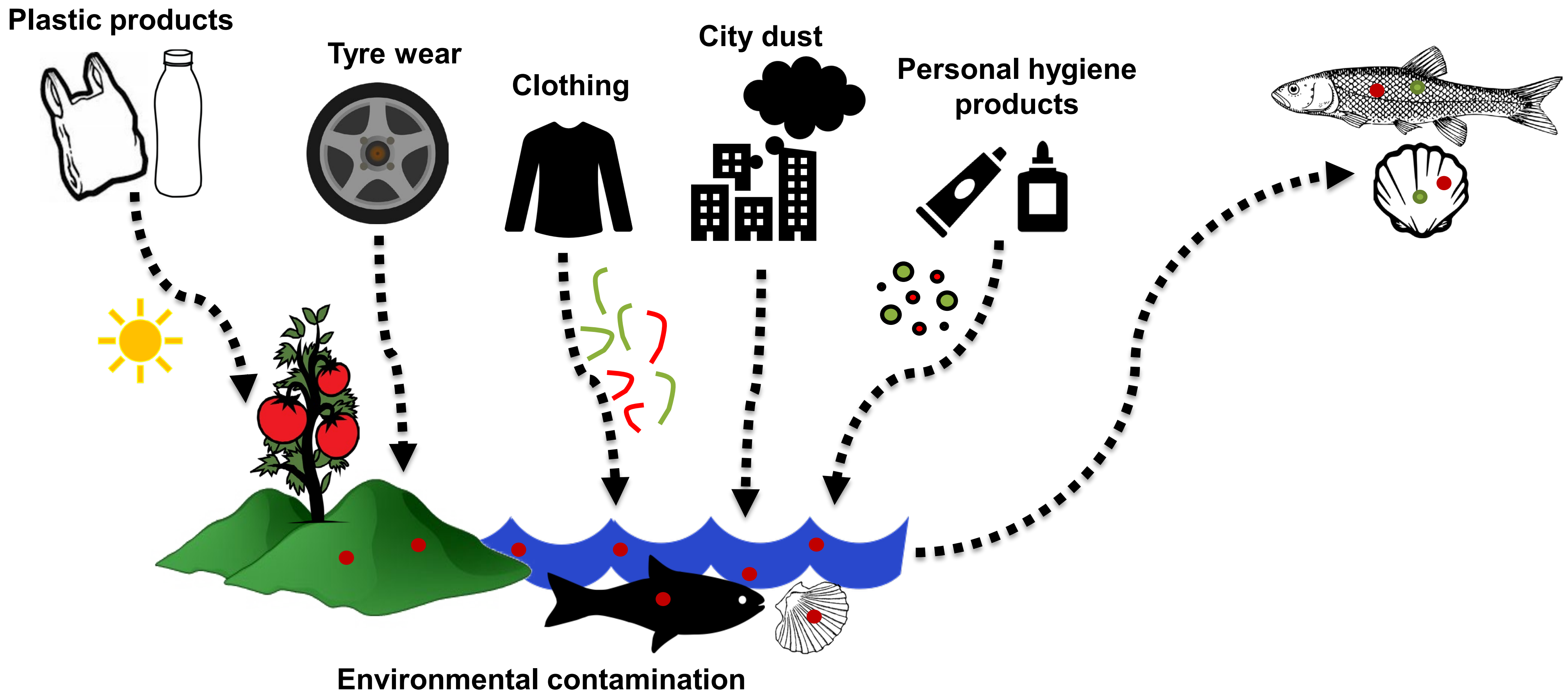

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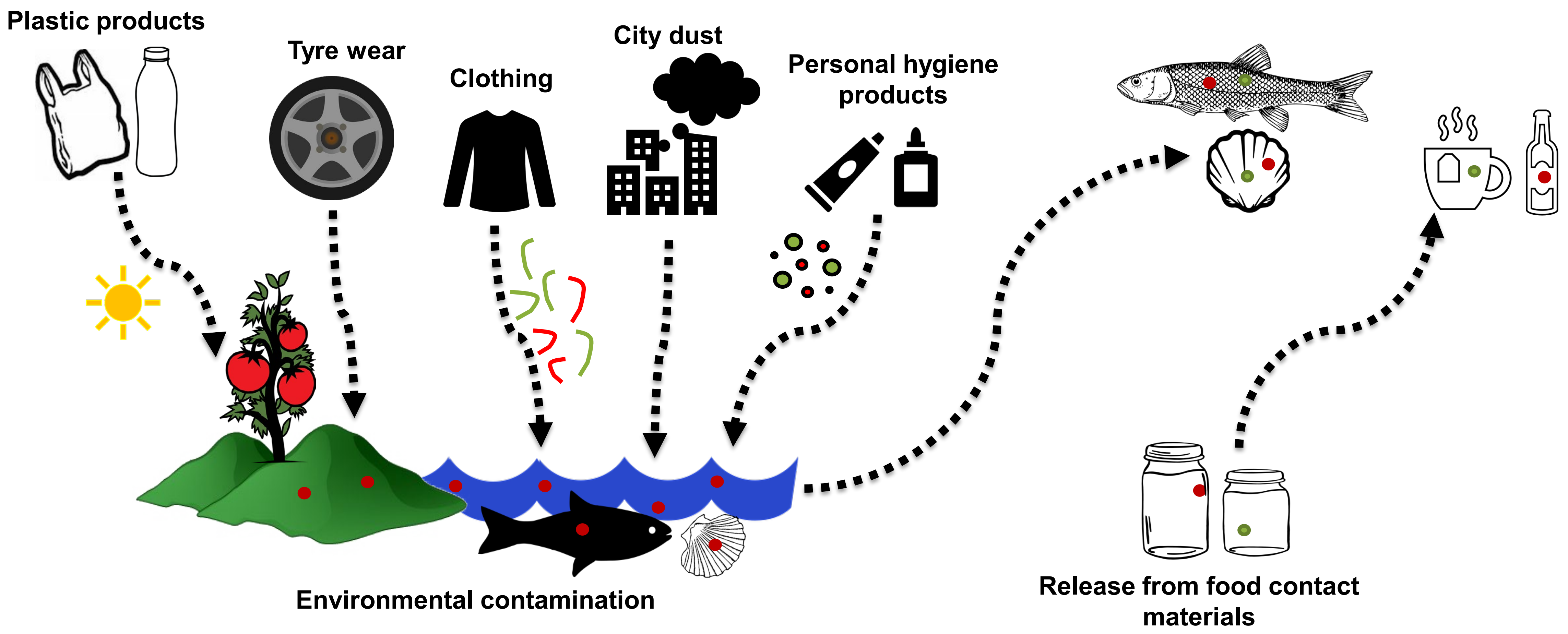

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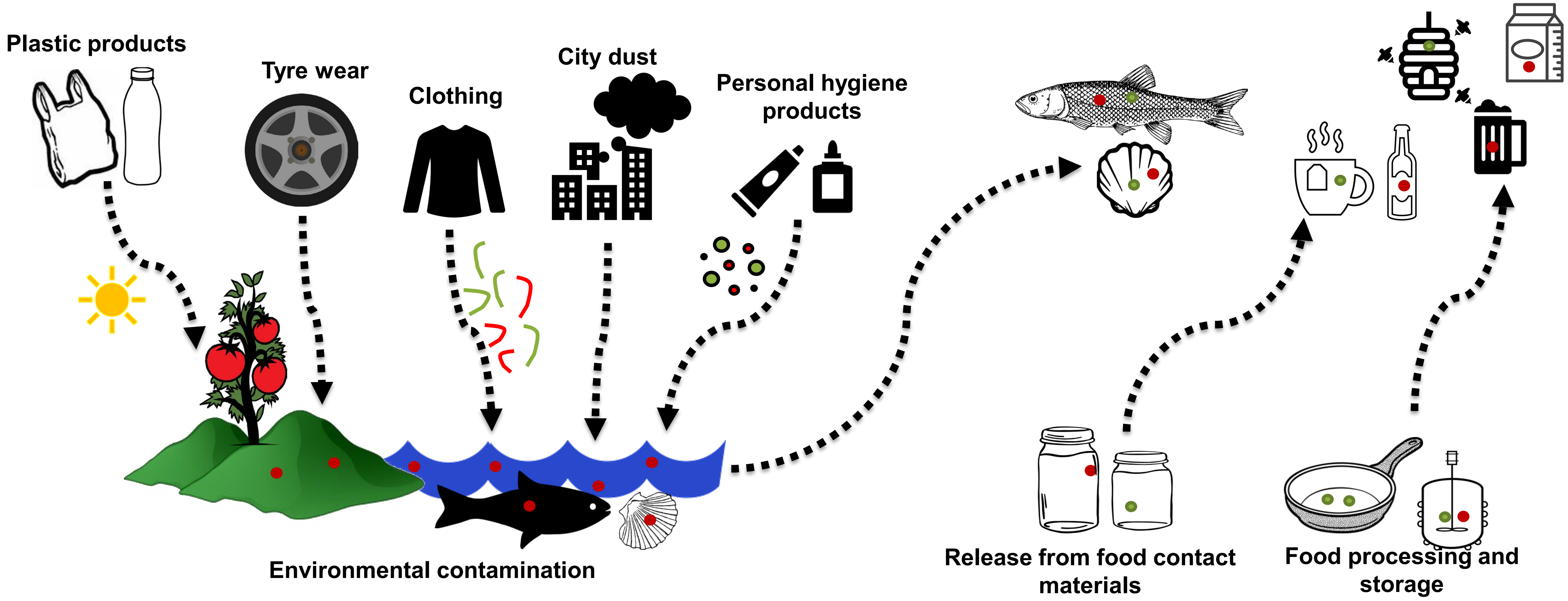
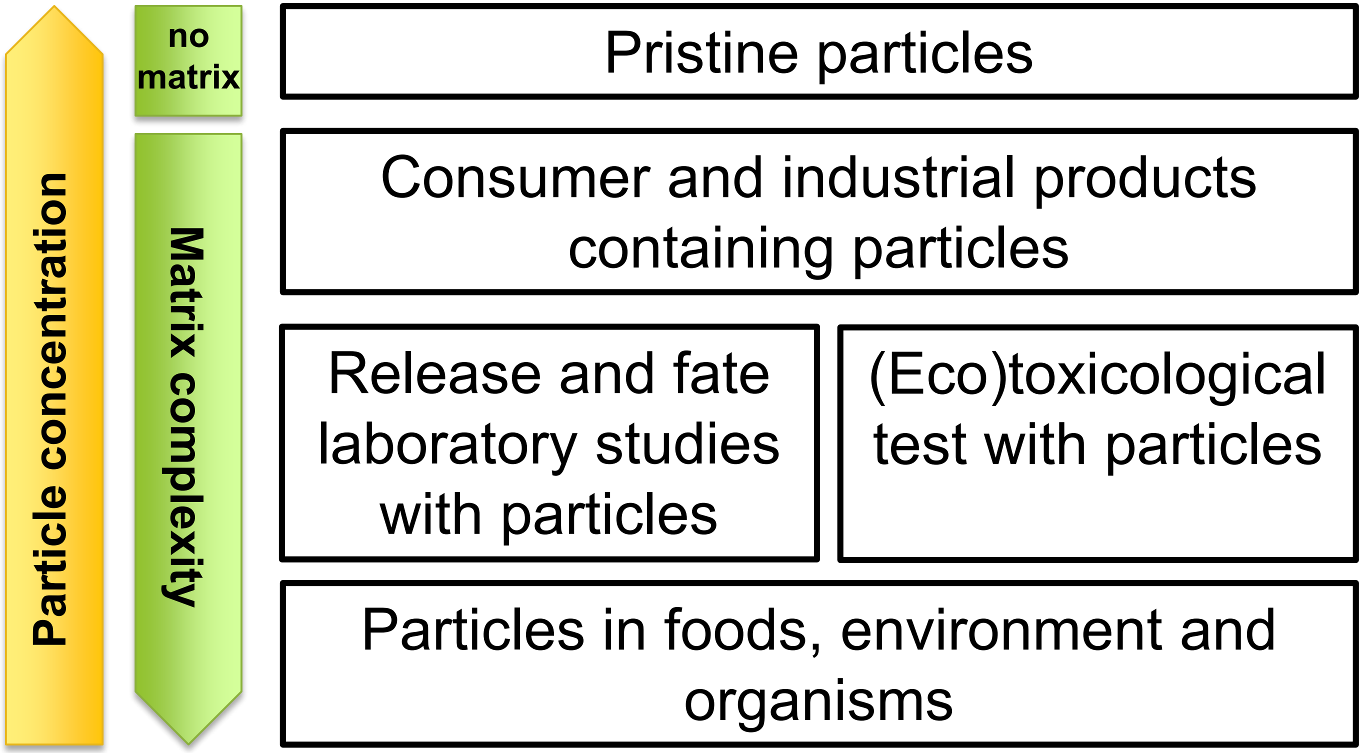


Why it is important to measure micro- and nanoscale particles?

Analytical scenarios



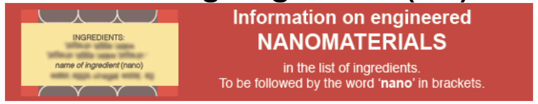
Adopted from E. Bolea, Anal. Methods, 2021,13, 2742-2795

Regulation

Nanoparticles

Guidance on technical requirements for regulated food and feed product applications to establish the presence of small particles including nanoparticles

Food labelling Regulation (EU) No 1169/2011



Novel Foods Regulation EC 2015/2283 (food with engineered nanomaterials = novel food)

Regulation EC 1935/2004 (new active and intelligent food contact materials)

E171 has been banned as a food additive!

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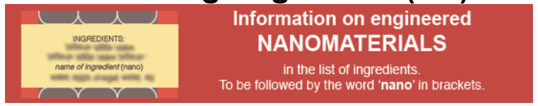

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Nano/microplastics

Drinking Water Directive (2021): microplastics on a watch list

European Commission regulation proposal amending Annex XVII to REACH Regulation No 1907/2006, as regards synthetic polymer microplastics (draft published in August 2022)

Challenges in detection of micro- and nanoscale particles

- Nanoparticles and nano/microplastics are complex with unique characteristics → many nano object parameters need to be measured (size, composition, surface charge, coatings, aggregation, etc.)

- Analysis of particles in natural systems (low concentration, complex matrices, heterogenous mixture of particles, weathered nano/microplastics)

- Lack of standard methods and reference materials

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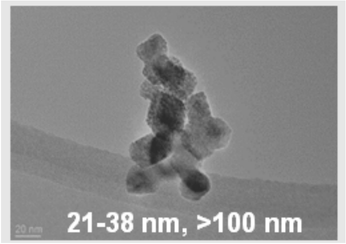
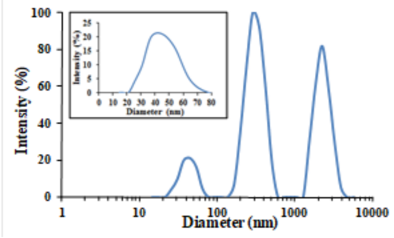
Are there particles present?
How much/many particles?
Which particles and of which sizes?...

Measurements: Multi-method approach

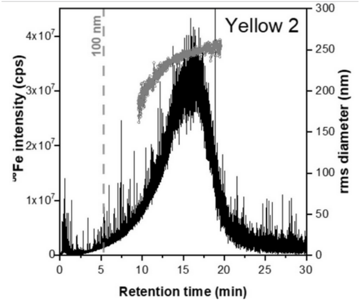
Nanoparticles



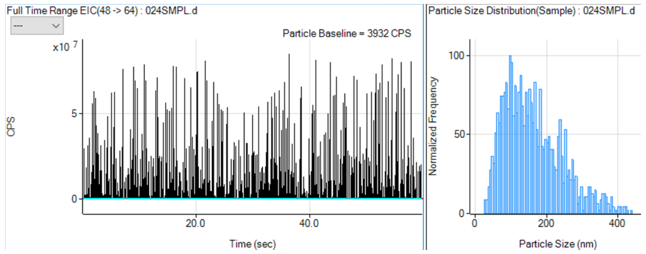
Transmission electron microscopy



Dynamic light scattering



Asymmetric flow field-flow fractionation coupled to ICP-MS



Single particle ICP-MS

Measurements: Multi-method approach

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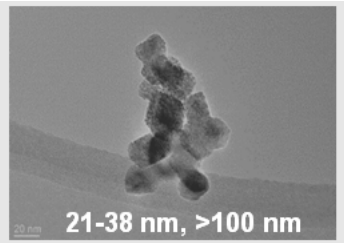

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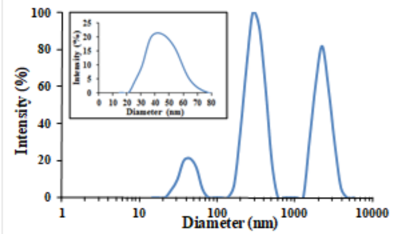

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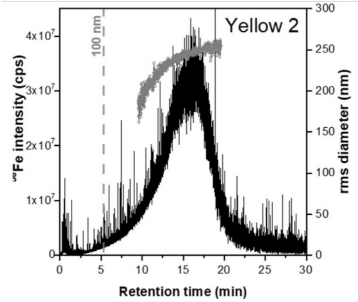

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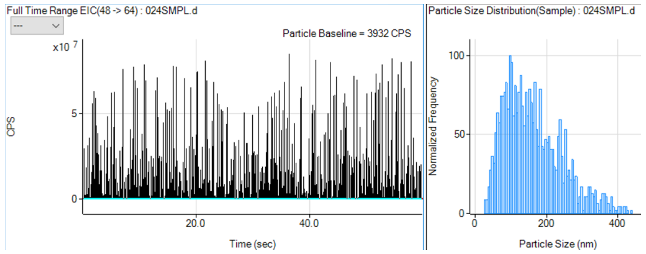
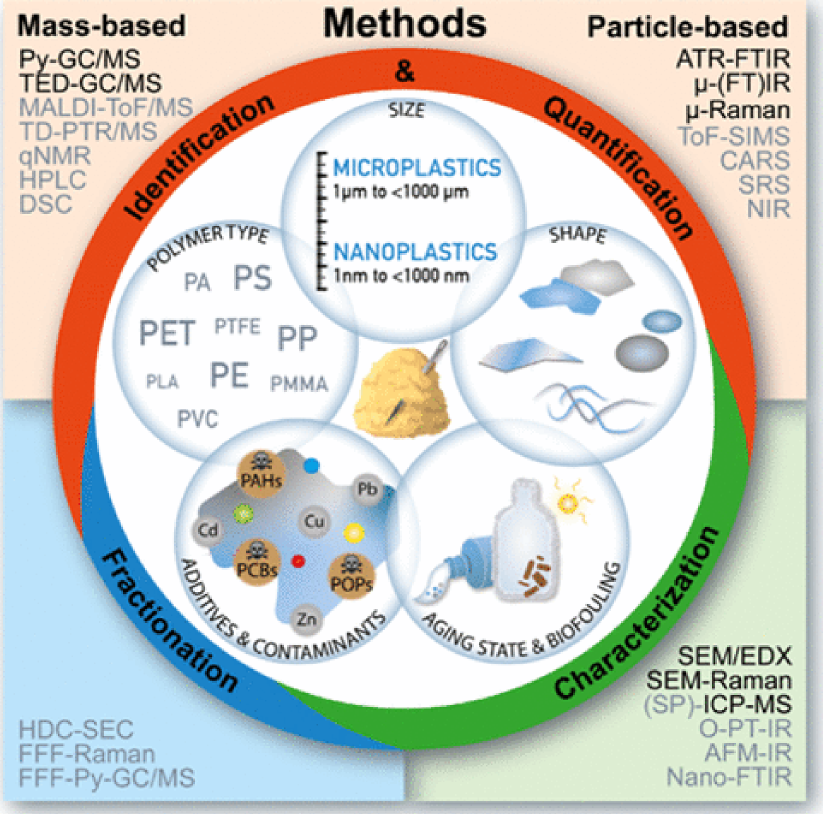


Single particle ICP-MS

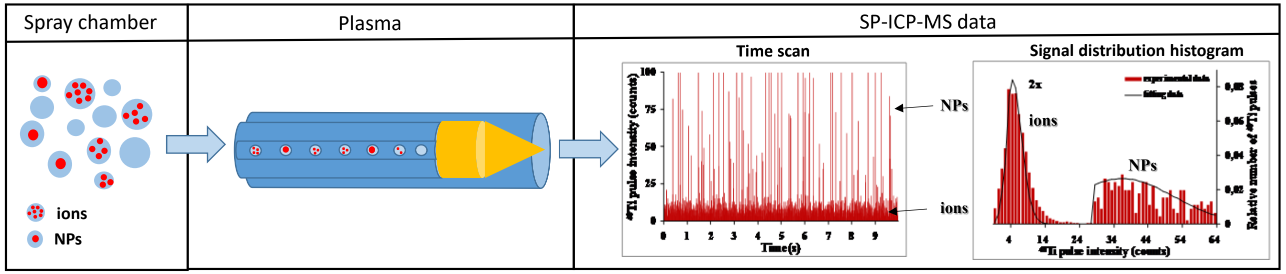
Nano/microplastics



Chem. Rev. 2021, 121, 19, 11886–11936

spICP-MS method: Main features

- Measurement of individual particle



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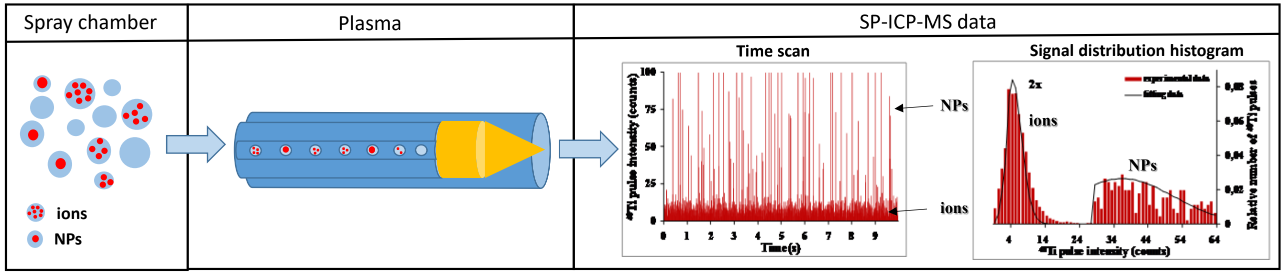

- Measurement of individual particle

- spICP-MS provides information on:
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  - Mass concentration of particles and ions (without prior separation)
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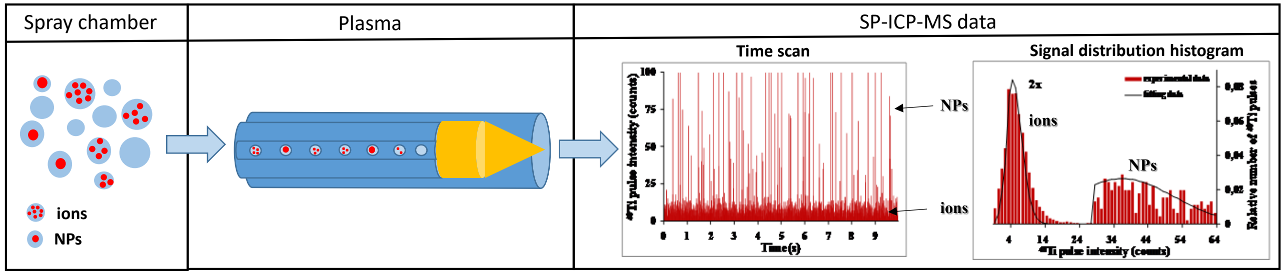

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- Element specific
- Sensitive

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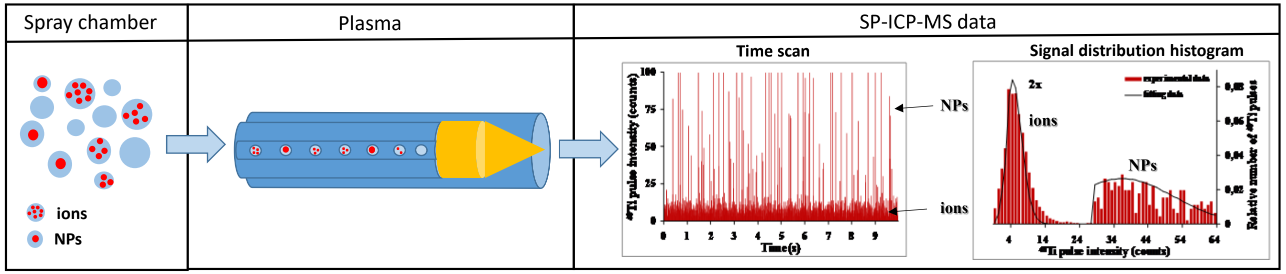

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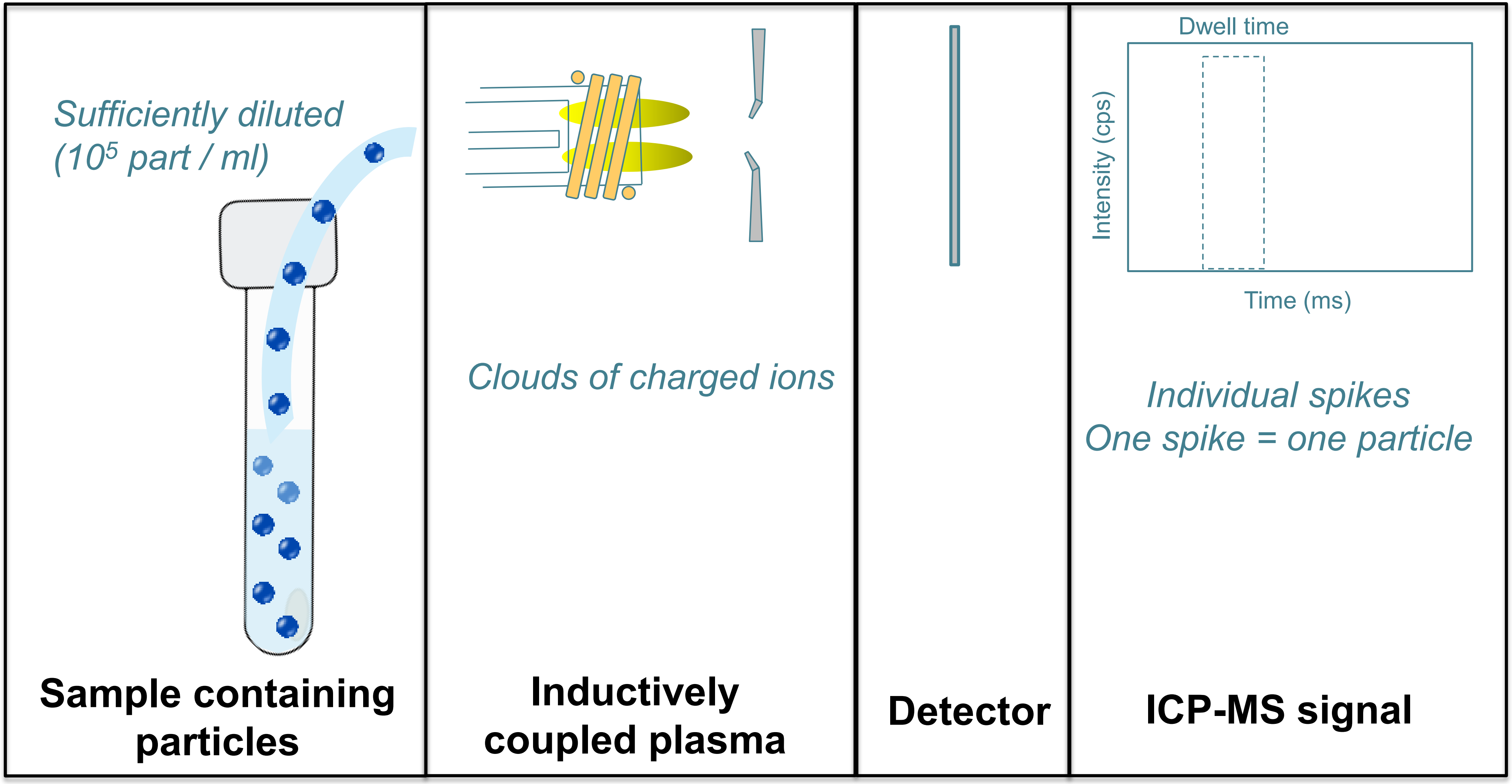
- Allows following particle transformations (dissolution, agglomeration, microplastic aging, etc.)

… in suspensions but also more complex matrices, like food and biological tissues → sample preparation required

spICP-MS method: Principles



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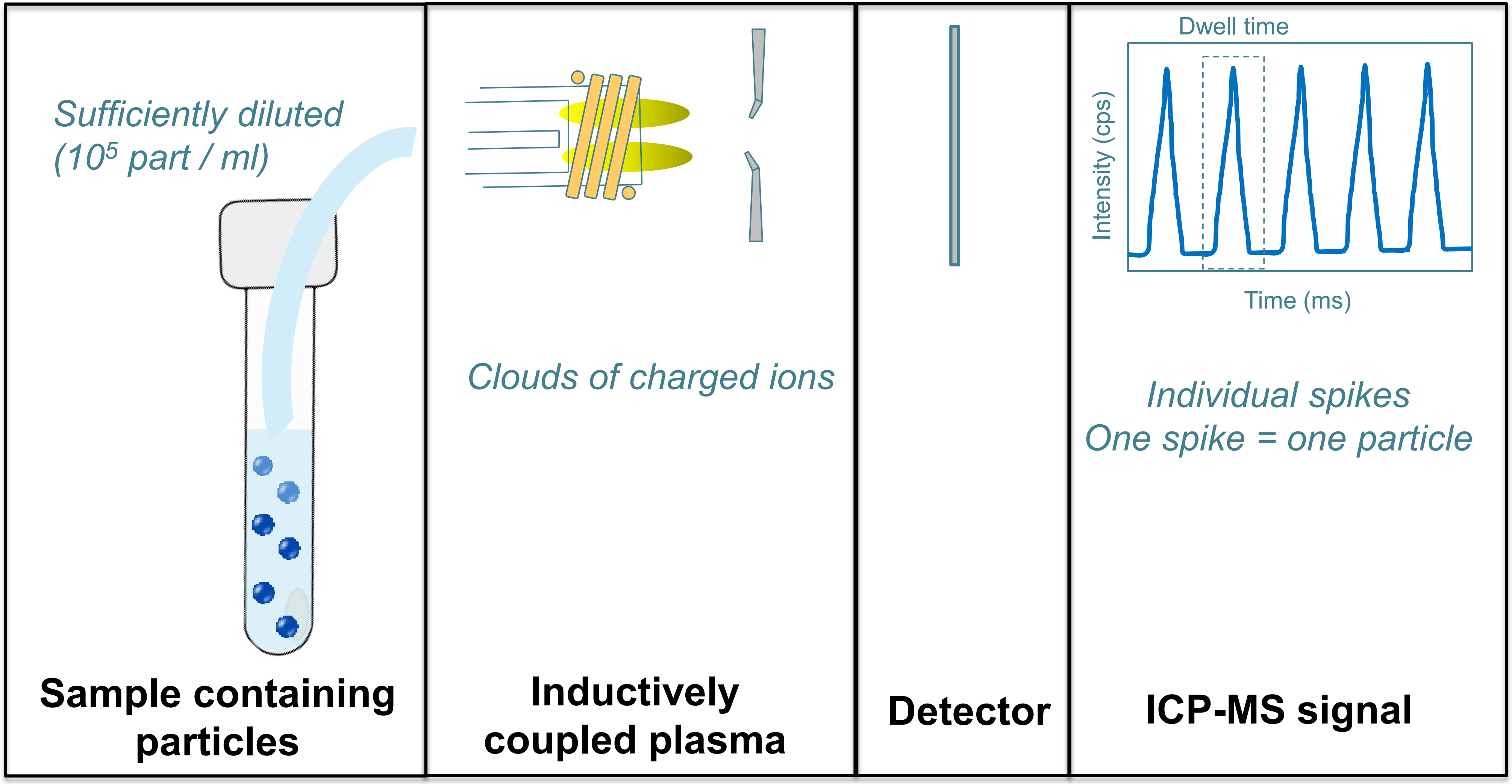

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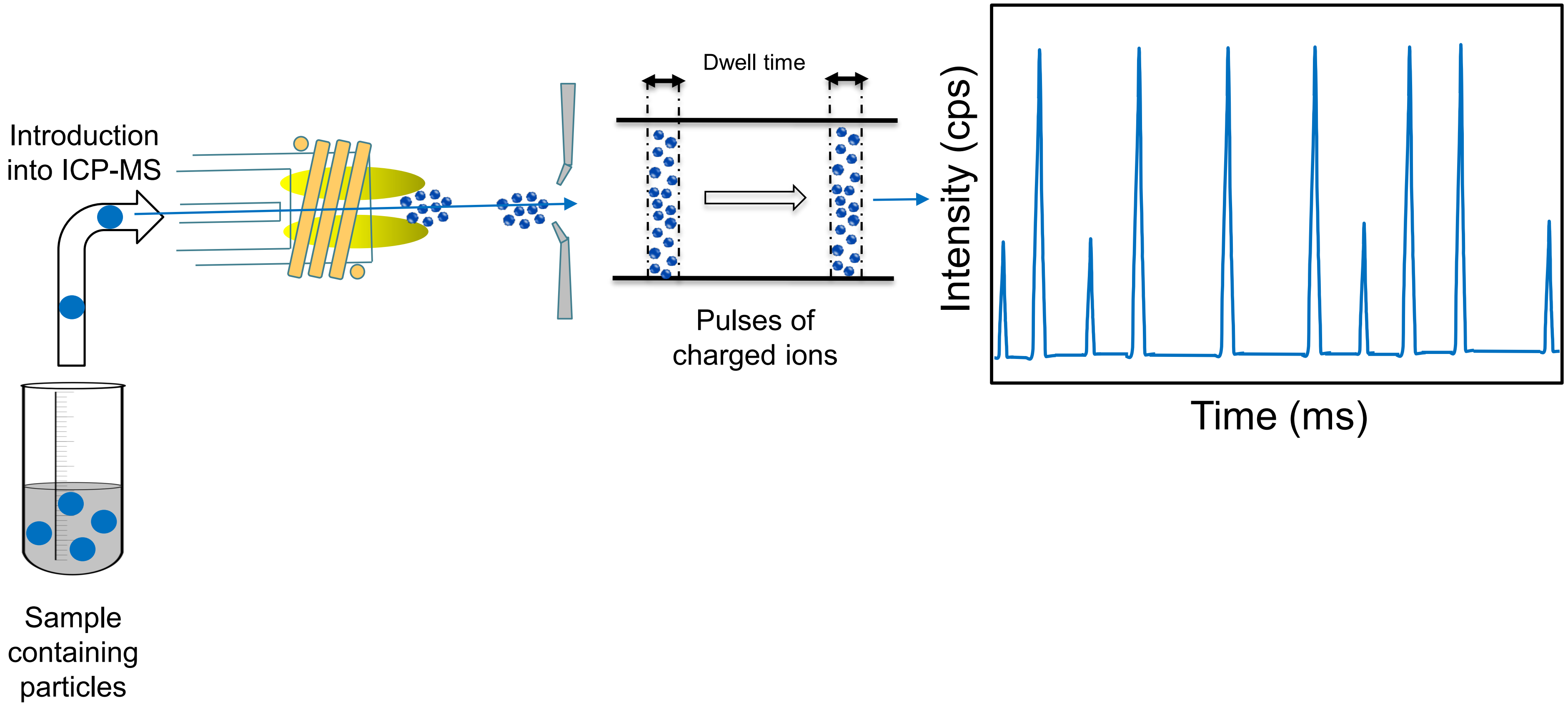

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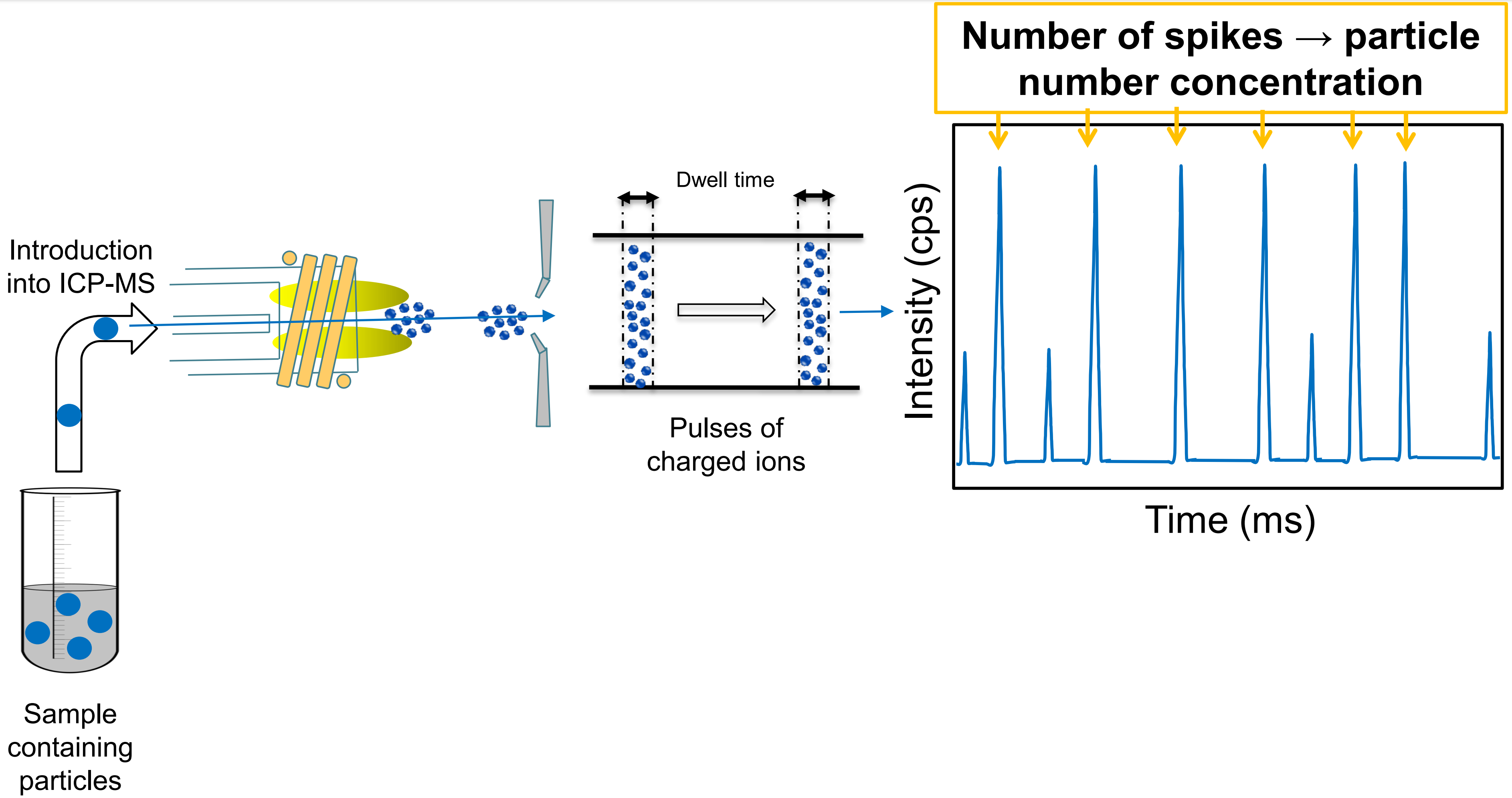

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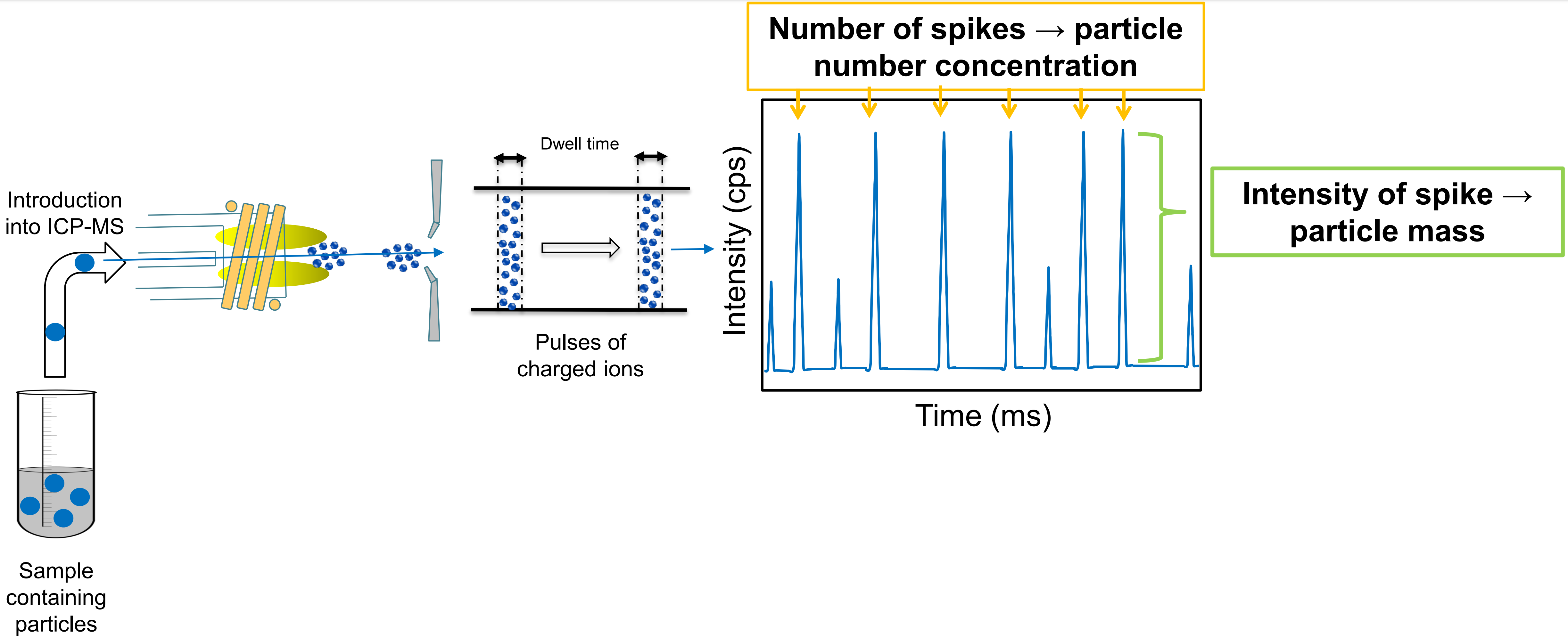

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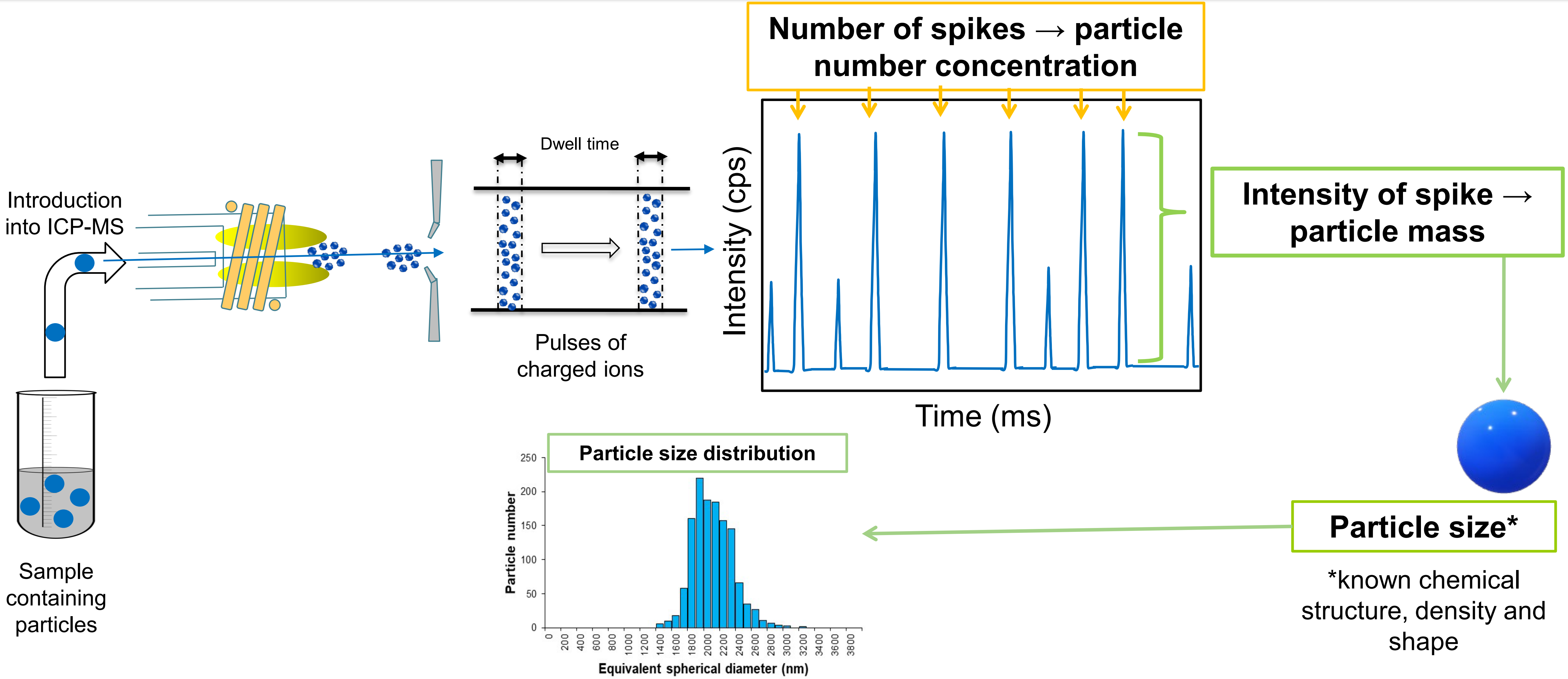

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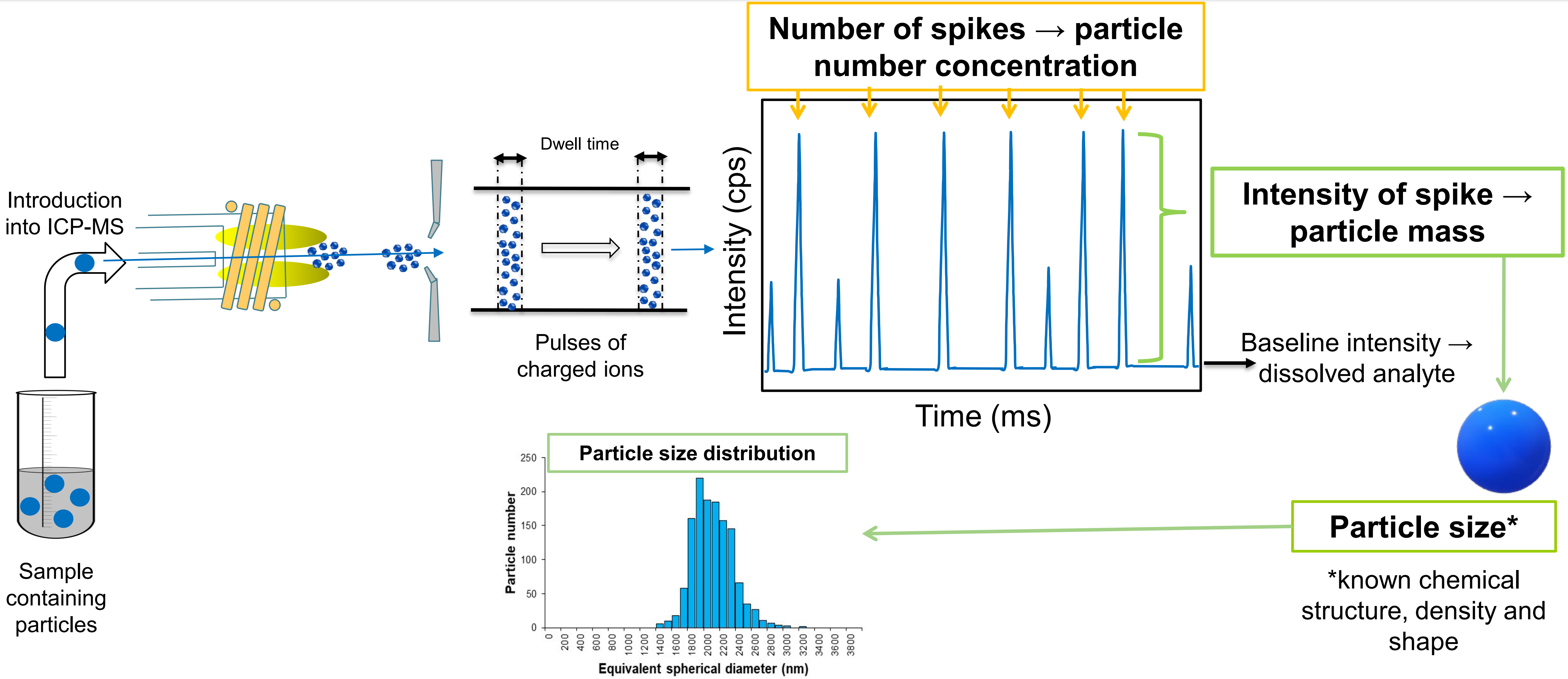

Applicability of spICP-MS

- Easily implementable in state-of-the art ICP-MS instruments
- Fast analysis (screening)
- Non invasive sample preparation (no acid digestion, sufficient sample dilution)
- Fit for monitoring if EU recommended nanodefinition is complied with

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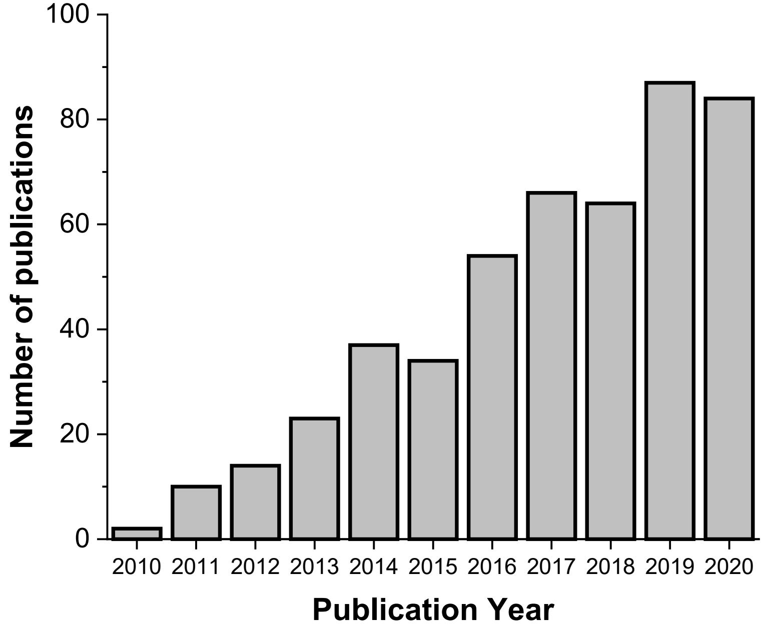
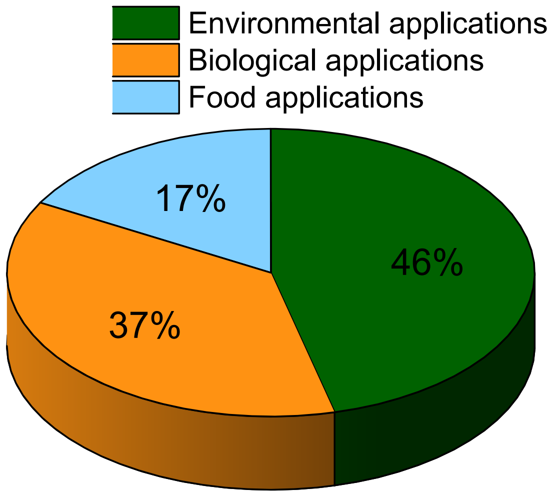


Number of publications on spICP-MS analysis over the last 10 years (2010-2020)



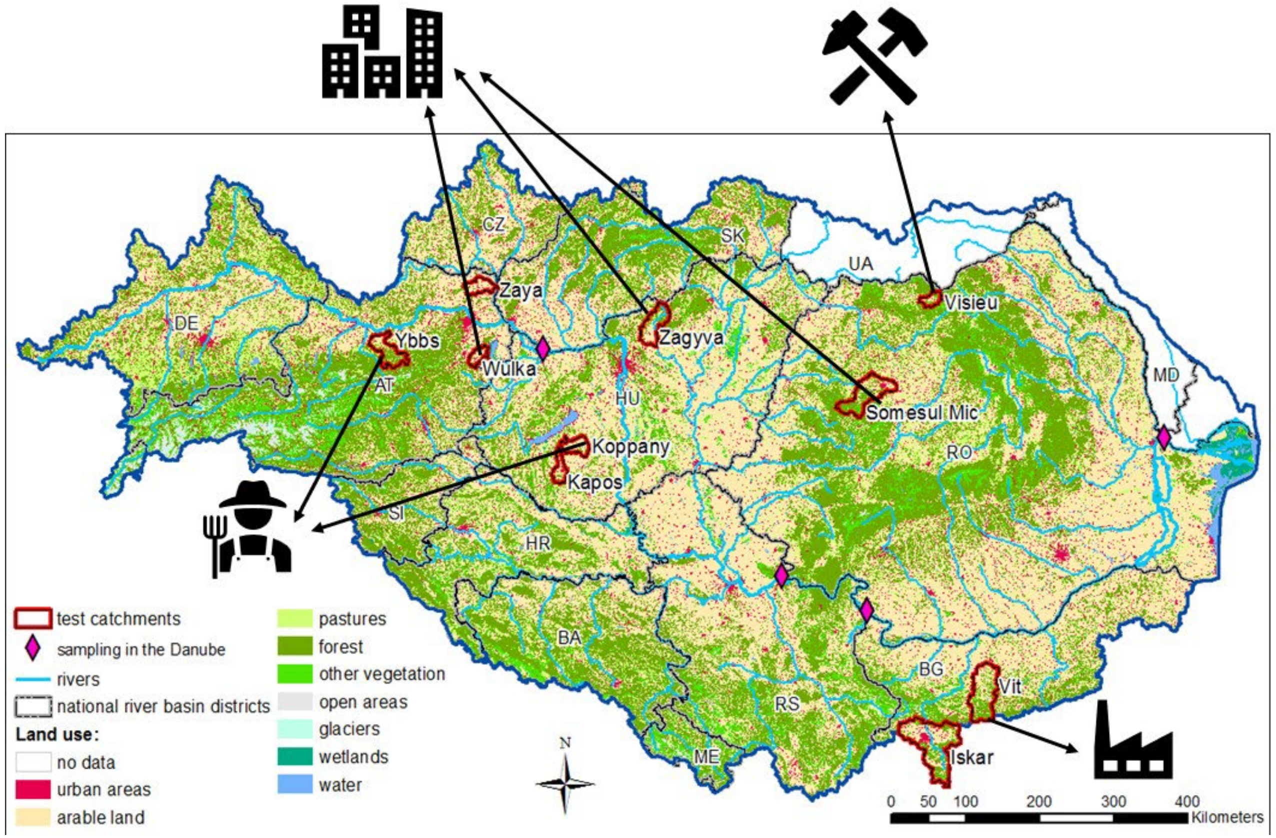
Percentage of spICP-MS publications by the type of application

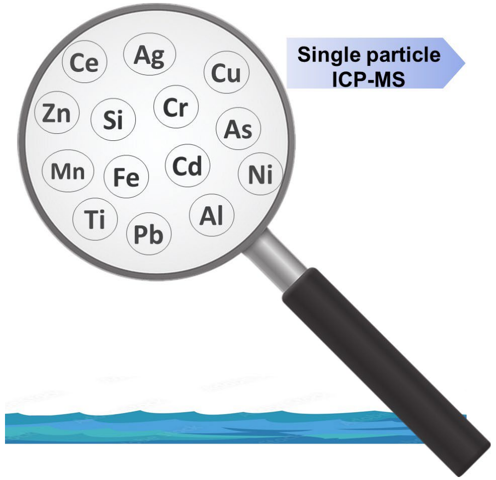
Comprehensive Analytical Chemistry, Analysis and Characterisation of Metal-Based Nanomaterials, Volume 93, 2021, Pages 345-380

Detection of inorganic nanoparticles in river water systems

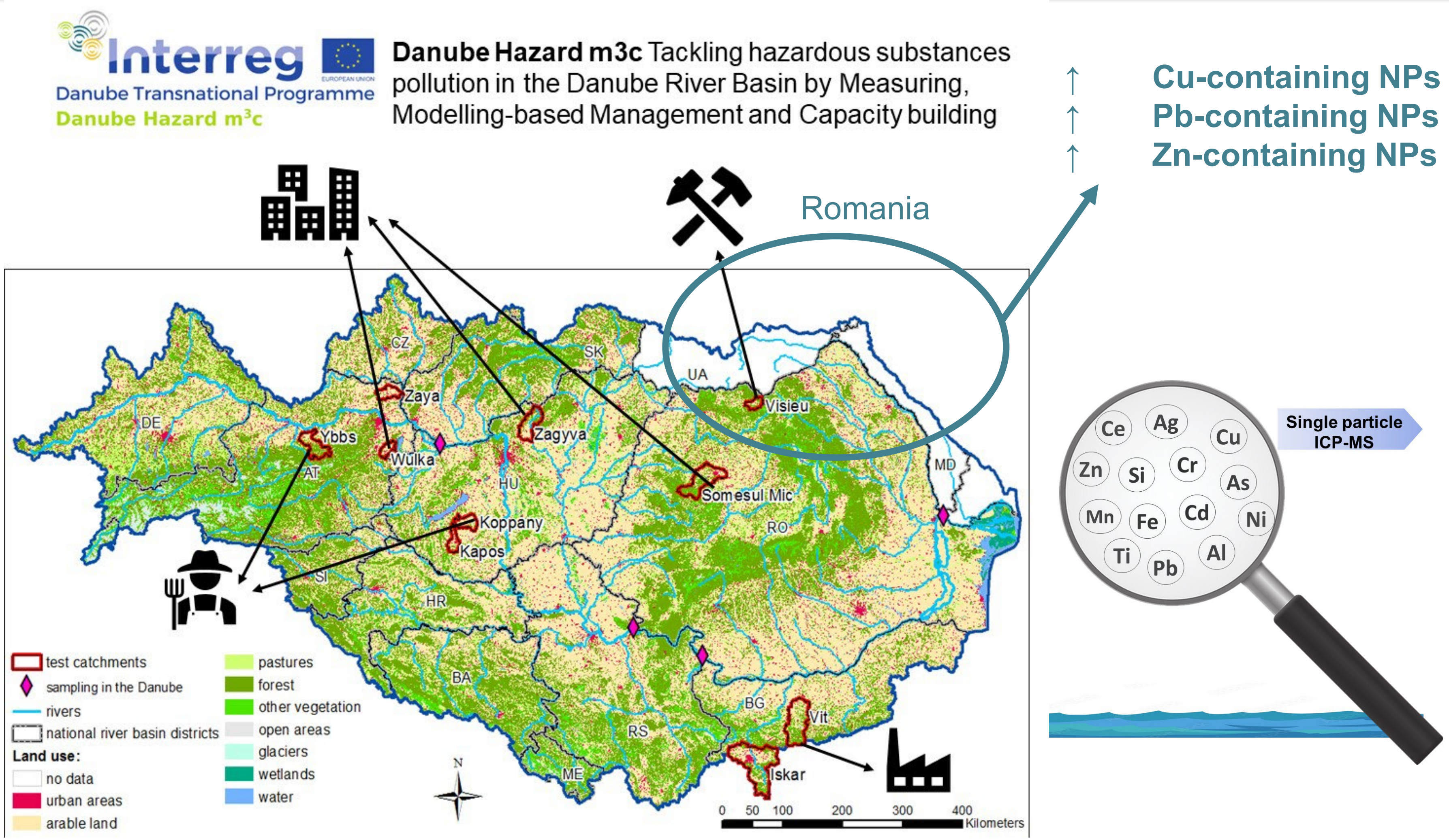
Interreg
EUROPEAN UNION
Danube Transnational Programme
Danube Hazard m³c

Danube Hazard m3c Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building





Detection of inorganic nanoparticles in river water systems



Detection of inorganic nanoparticles in river water systems

water MDPI

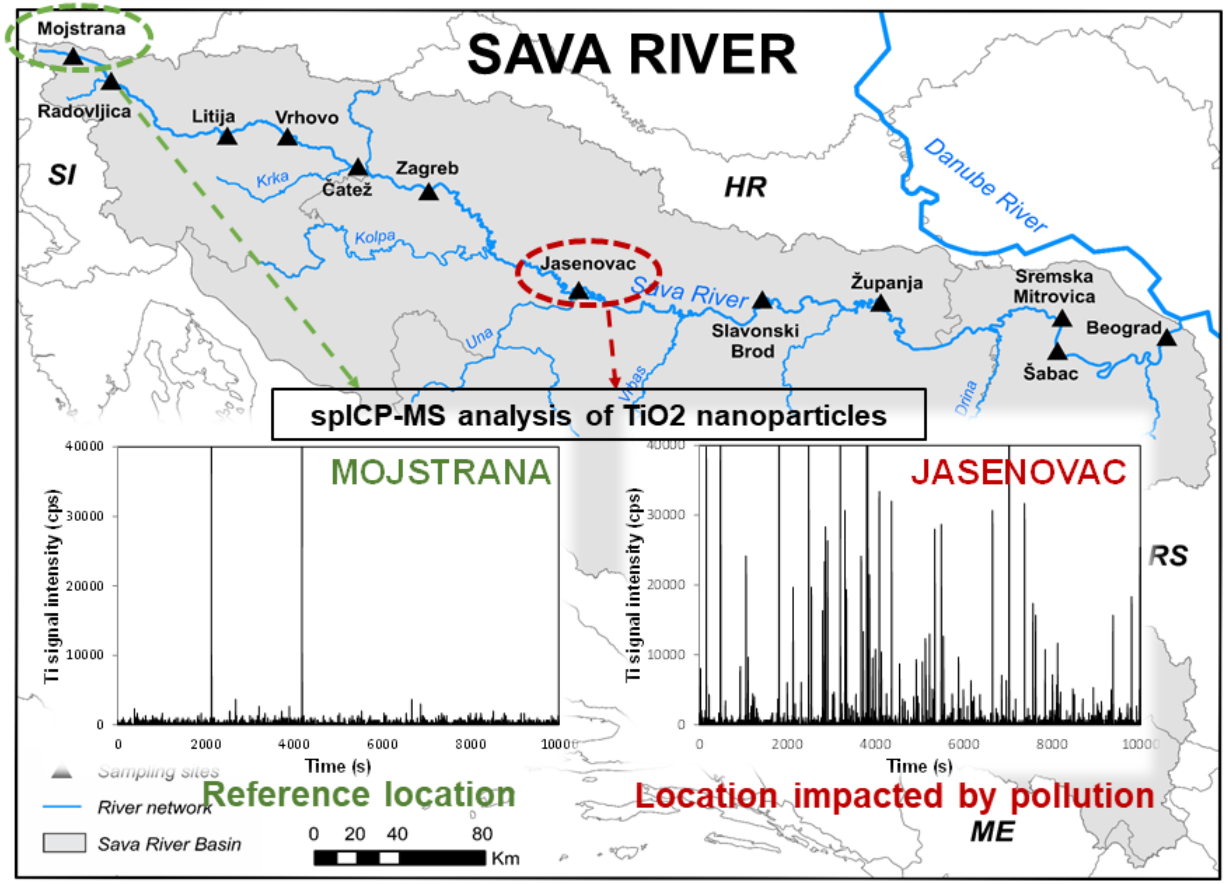
Article

Following the Occurrence and Origin of Titanium Dioxide Nanoparticles in the Sava River by Single Particle ICP-MS

Janja Vidmar [1,2,*], Tea Zuliani [1,2], Radmila Milačič [1,2] and Janez Ščančar [1,2]

GLOBAQUA

TiO_2 NPs in river water and sediments



Detection of inorganic nanoparticles in food samples

JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

pubs.acs.org/JAFC Article

Single-Particle ICP–MS as a Screening Technique for the Presence of Potential Inorganic Nanoparticles in Food

Janja Vidmar, Luisa Hässmann, and Katrin Loeschner*

Cite This: J. Agric. Food Chem. 2021, 69, 9979–9990

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National Food
Institute

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Detection of inorganic nanoparticles in food samples

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

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DTU Food National Food Institute

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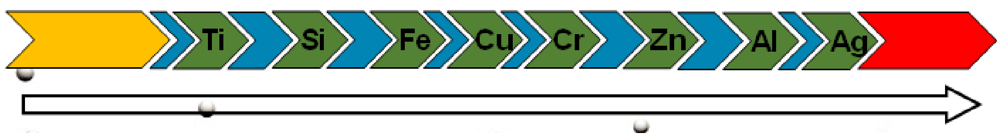
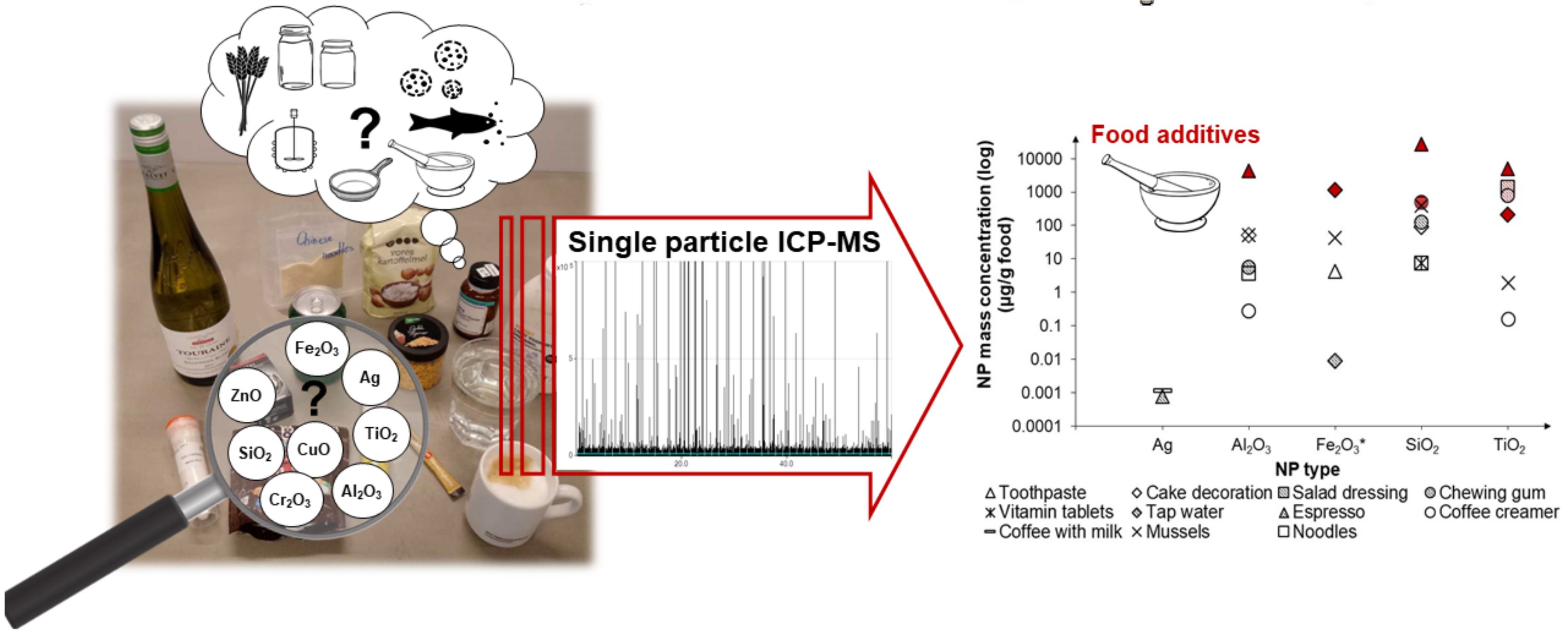
Multi-element spICP-MS method





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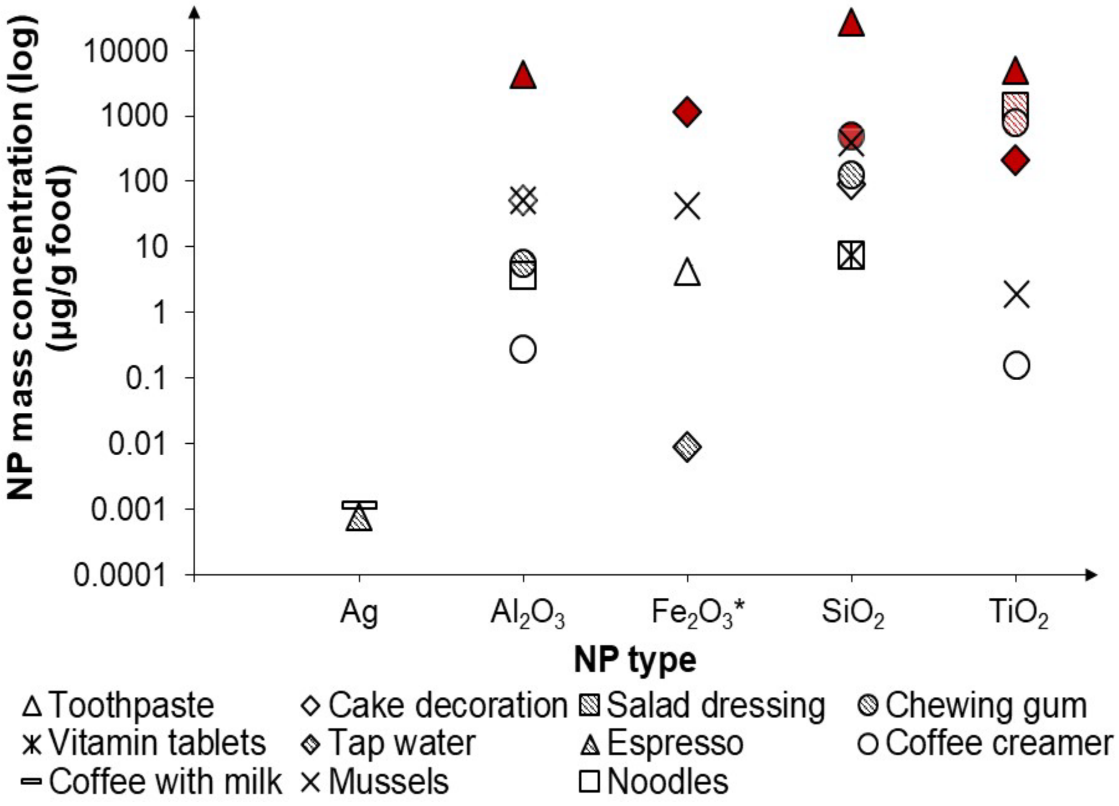

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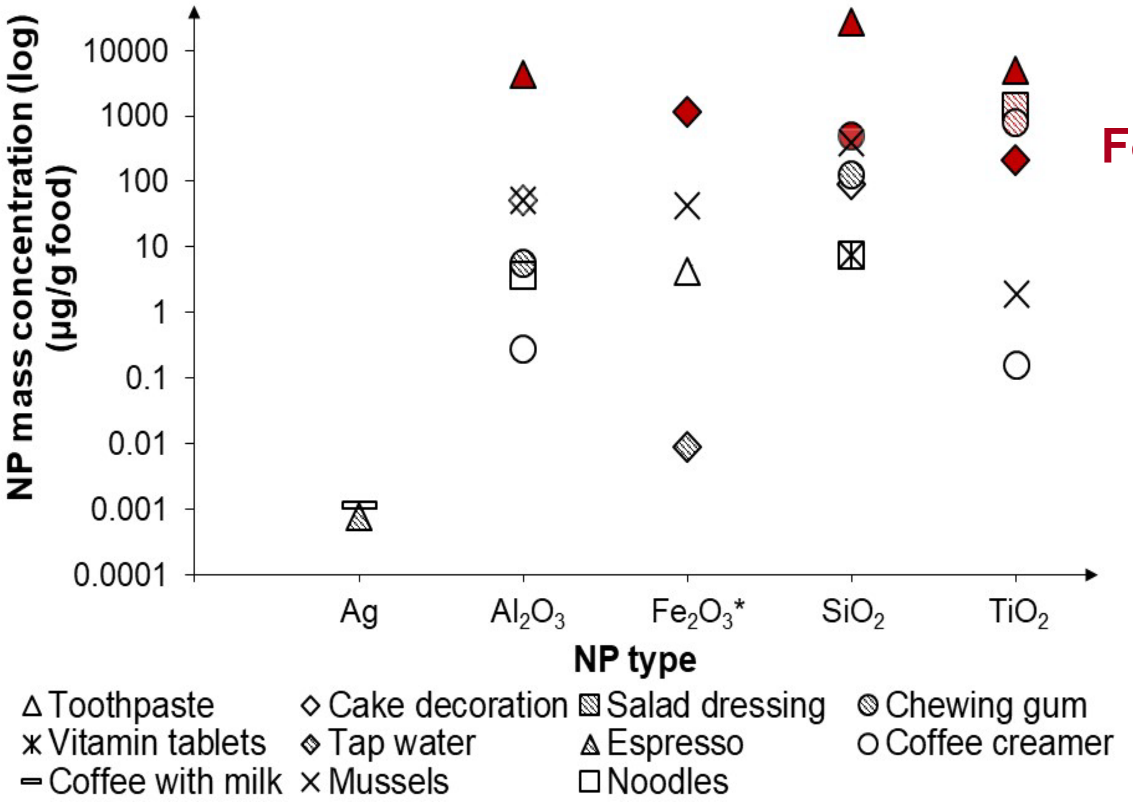
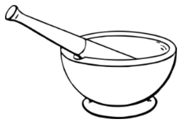
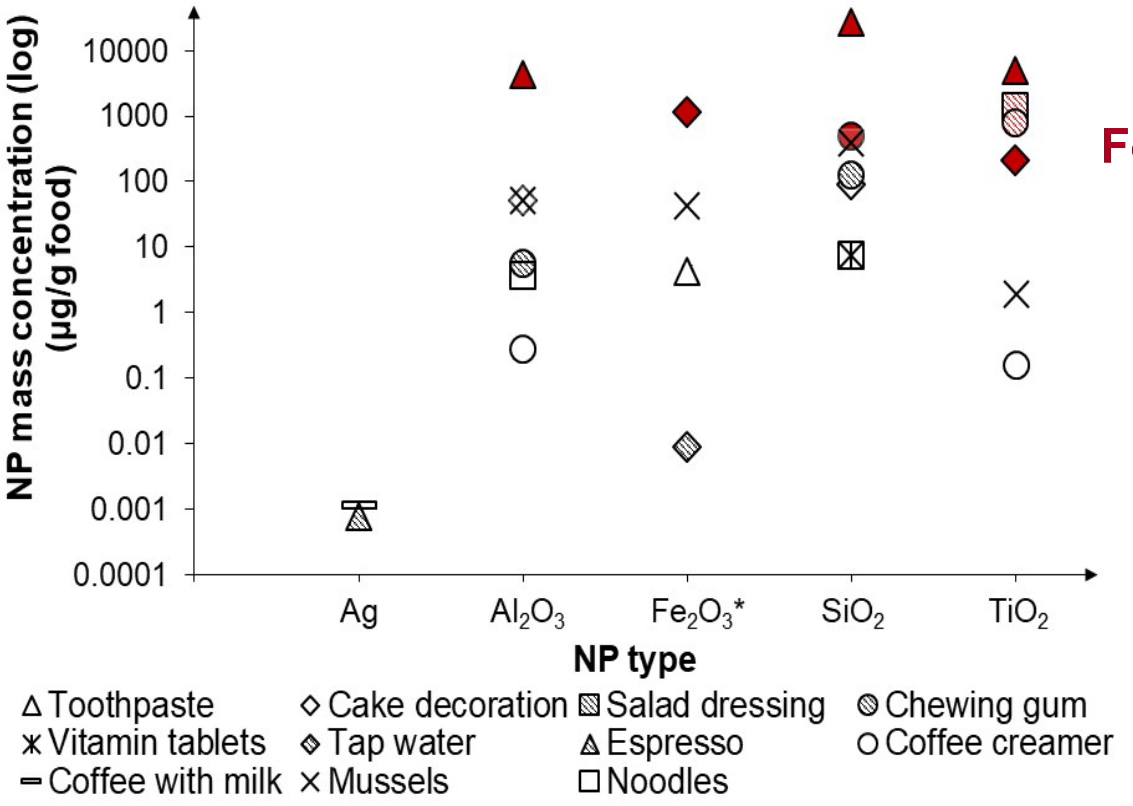


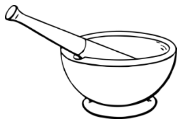


Food additives

- Toothpaste
- Cake decoration
- Chewing gum
- Coffee creamer
- Salad dressing

Detection of inorganic nanoparticles in food samples





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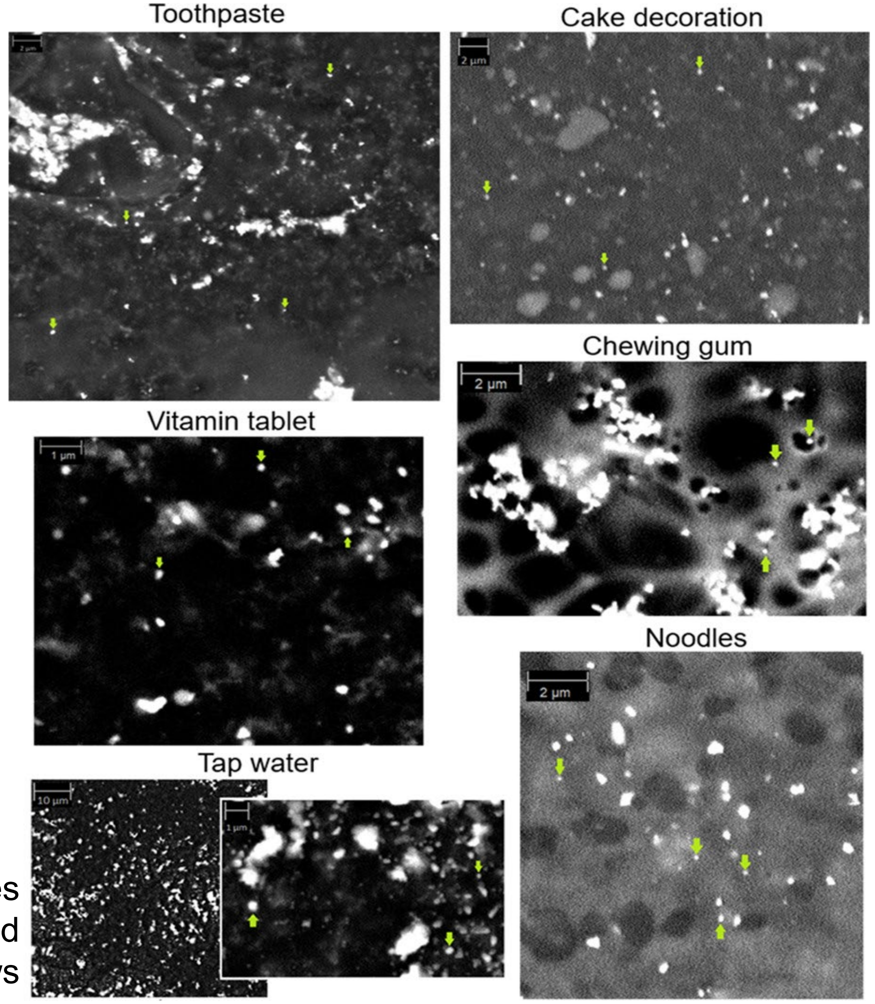
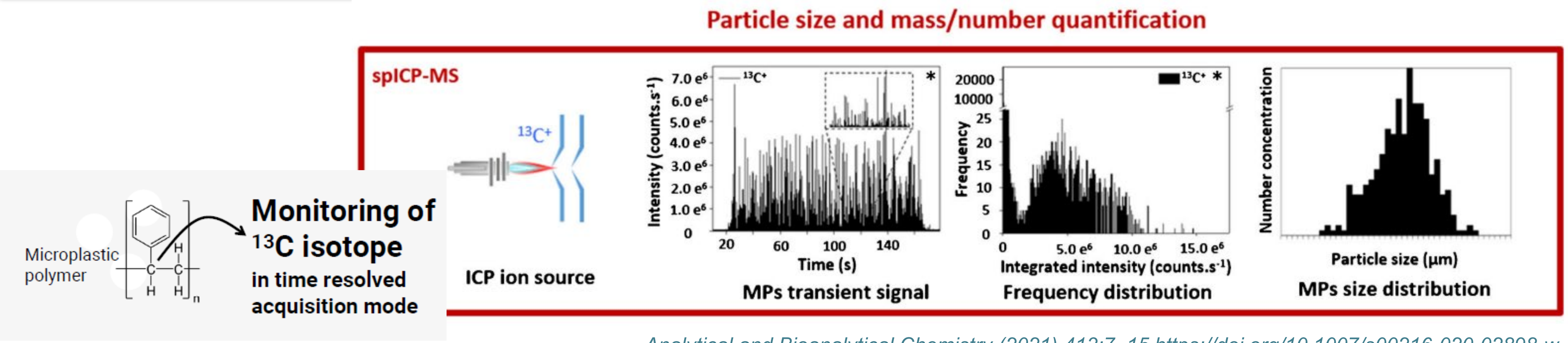


SEM images (i.e., particles smaller than 100 nm) are marked with green arrows

Analysis of microplastics by detection of carbon



Analytical and Bioanalytical Chemistry (2021) 413:7–15 https://doi.org/10.1007/s00216-020-02898-w

Detection range: **620 nm - up to 10 µm**;
LOD_{conc} down to **100 particles/mL**

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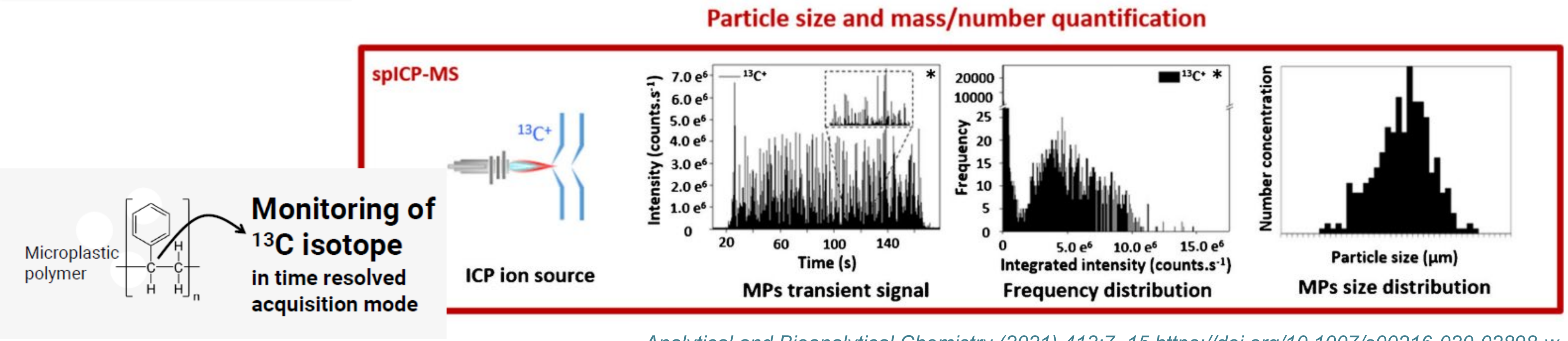

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Carbon analysis by ICP-MS is challenging:

- High ionization potential: 11.26 eV
- Low ionization efficiency: 5%
- High carbon background: CO_2 in water and air

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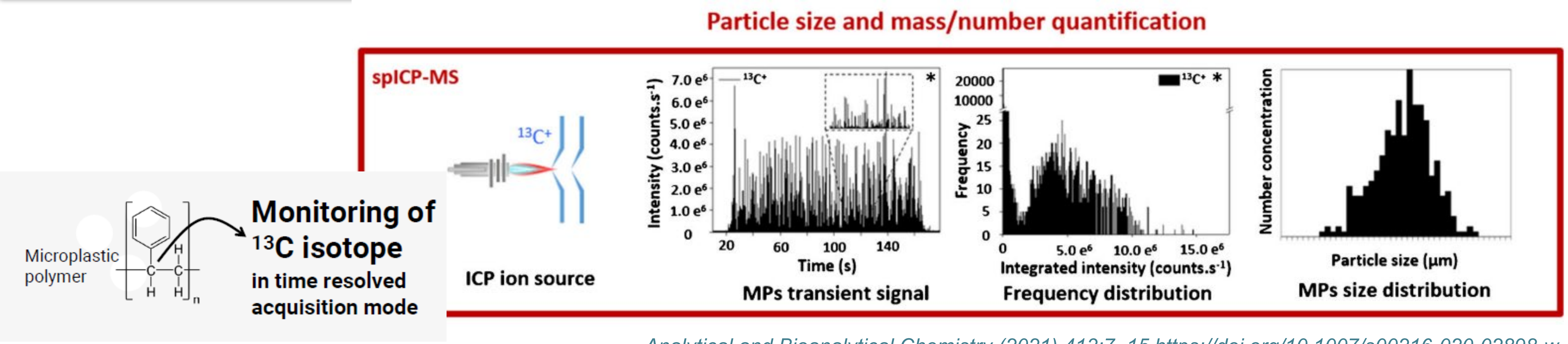

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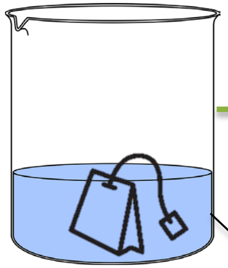
Carbon-containing compounds present in natural water samples (dissolved organic matter, carbonates, algae cells, etc.) that could interfere with analysis of MPs require **additional sample pre-treatment**
For polymer identification, other techniques are required

Analysis of microplastics by detection of carbon_applications

Release of microplastics from teabags

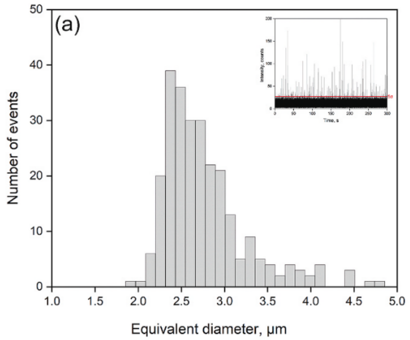
F. Laborda et al., Talanta, 221, 2021, 121486



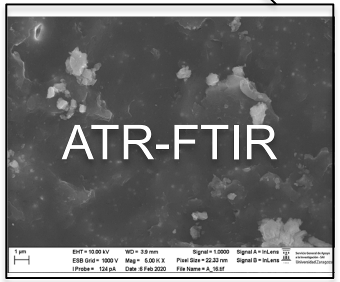
spICP-MS

particles released per teabag: 1.9–5.5 x 10^4

plastic teabags brewed at 100℃



Size distributions corresponding to microplastics released from plastic teabags



Polylactic acid, polyethylene terephthalate

Analysis of microplastics by detection of carbon_applications

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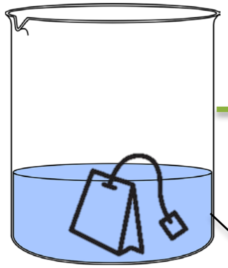
F. Laborda et al., Talanta, 221, 2021, 121486



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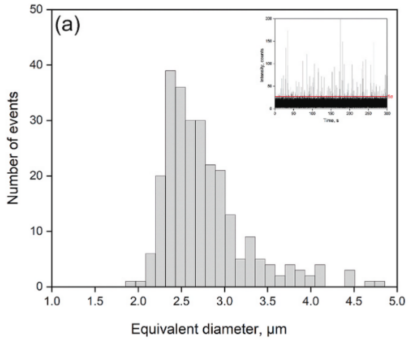

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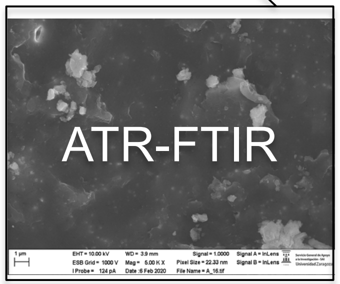
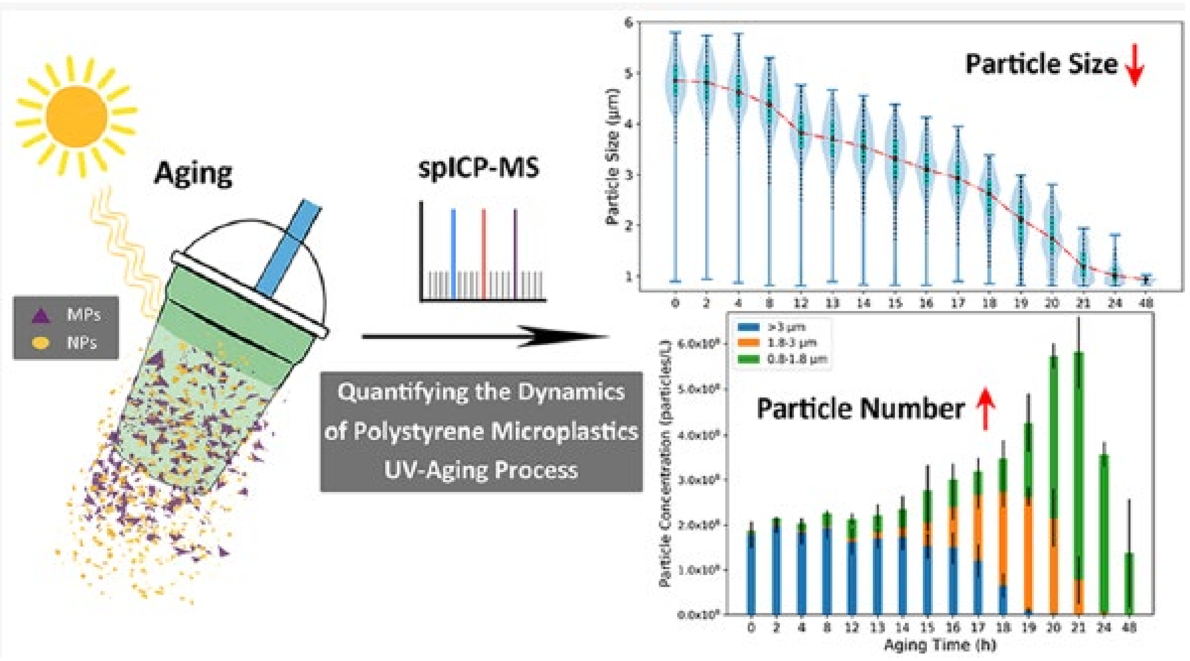


ATR-FTIR

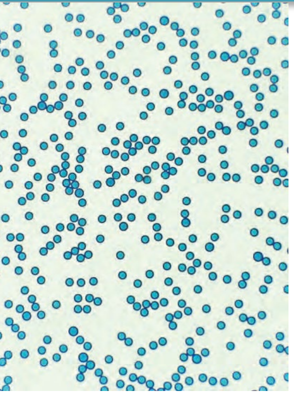
Polylactic acid, polyethylene terephthalate

UV-aging of PS microplastics

Liu et al., Environ. Sci. Technol. Lett. 2022, 9, 50−56



Utility of metal-doped plastics for nano- and microplastic research


Dyed polystyrene microspheres

- Fate and transport, at laboratory and pilot scale
- Biological uptake, passing barriers, trophic transfer
- Assessment of sampling and extraction protocols

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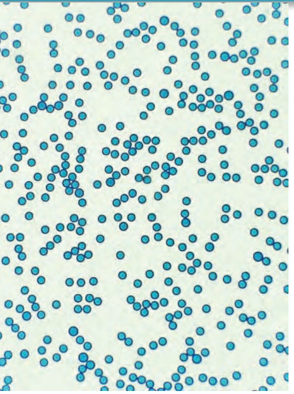

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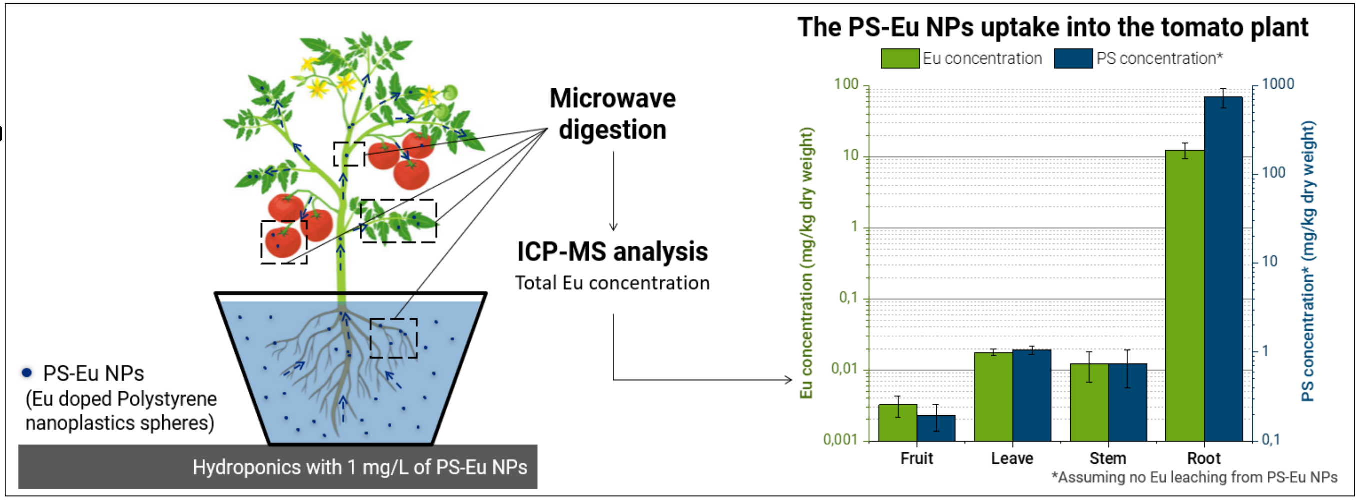
POSTER
Session 4:
NANOMATERIALS &
NANOTECHNOLOGIES

Studying the uptake and distribution of metal-doped nanoplastics in hydroponically grown tomato plants (Pia Leban)



ARRS project “UPTAKE” (L7-4422)

Conclusions

- Single particle ICP-MS is a powerful (screening) method for inorganic nanoparticles and nano/microplastics in water and food samples
- Additional techniques are required for particle detection (determination of particle composition, shape and density, polymer identification, etc.)
- Many types of inorganic nanoparticles can be found in food and river water systems
- Single particle ICP-MS method for the analysis of microplastics and nanoplastics and its application in the environment and food has room for improvement

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Luisa Hässmann

National Food Institute, Technical University of Denmark

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Thank you for your attention!

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Research Group for Trace Elements Speciation