From macro to nano environmental plastics

An issue of emerging concern from detection to remediation

LE STUDIUM Loire Valley Institute for Advanced Studies, Orléans, November 28th 2018

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À deriva no mar, as minúsculas partículas de
prejudicam a vida marítima. Em Aveiro, há ur
para as destruir

No edifício dos Laboratórios Tecnológicos da Universidade de Aveiro exis
maritimum, provavelmente o fungo marítimo mais falado em Portugal na
esponjoso, vive na costa e pode vir a tornar-se a primeira solução ecológi
microplásticos no oceano, já que é capaz de degradar partículas de plásti
milímetros de forma rápida e eficiente.

eliminar el plástico en el mar

'Zalerion maritimum' es la primera solución ecológica descubierta a la c
del mar

decadas en una de las grandes amenazas m

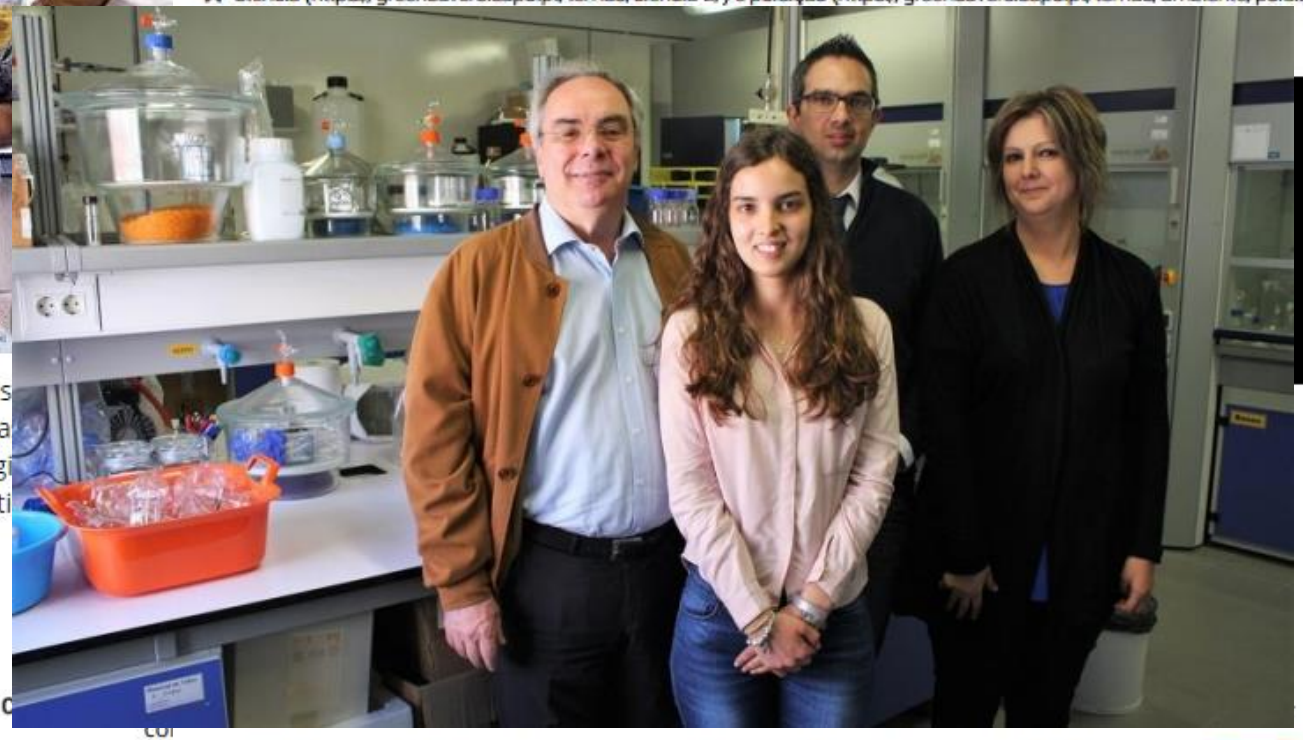
(https://greensavers.sa

GREEN SAVERS

HOME ÁGUA AMBIENTE CIDADES ENERGIA MOBILIDADE NUTRIÇÃO SOCIEDADE ECONOMIA ECONOMIA VERDE OPINIÃO

UNIVERSIDADE DE AVEIRO DESCOBRE A SOLUÇÃO PARA ERRADICAR PLÁSTICOS DO MAR

Ciência (https://greensavers.sapo.pt/temas/ciencia-2/) e poluição (https://greensavers.sapo.pt/temas/ambiente/poluicao/)



Zalerion maritimum. Se nunca ouviu o nome não se preocupe porque a maior parte da comunidade científica também não. Mas se tudo correr como Teresa Rocha Santos prevê, então vai ouvir. E muito. Porque este pequeno, na realidade, micro fungo marítimo pode bem ser a chave para o gravíssimo problema ambiental dos microplásticos nos oceanos.

acos
Em
uzir
na

ACOMPANHE AS
NOSSAS

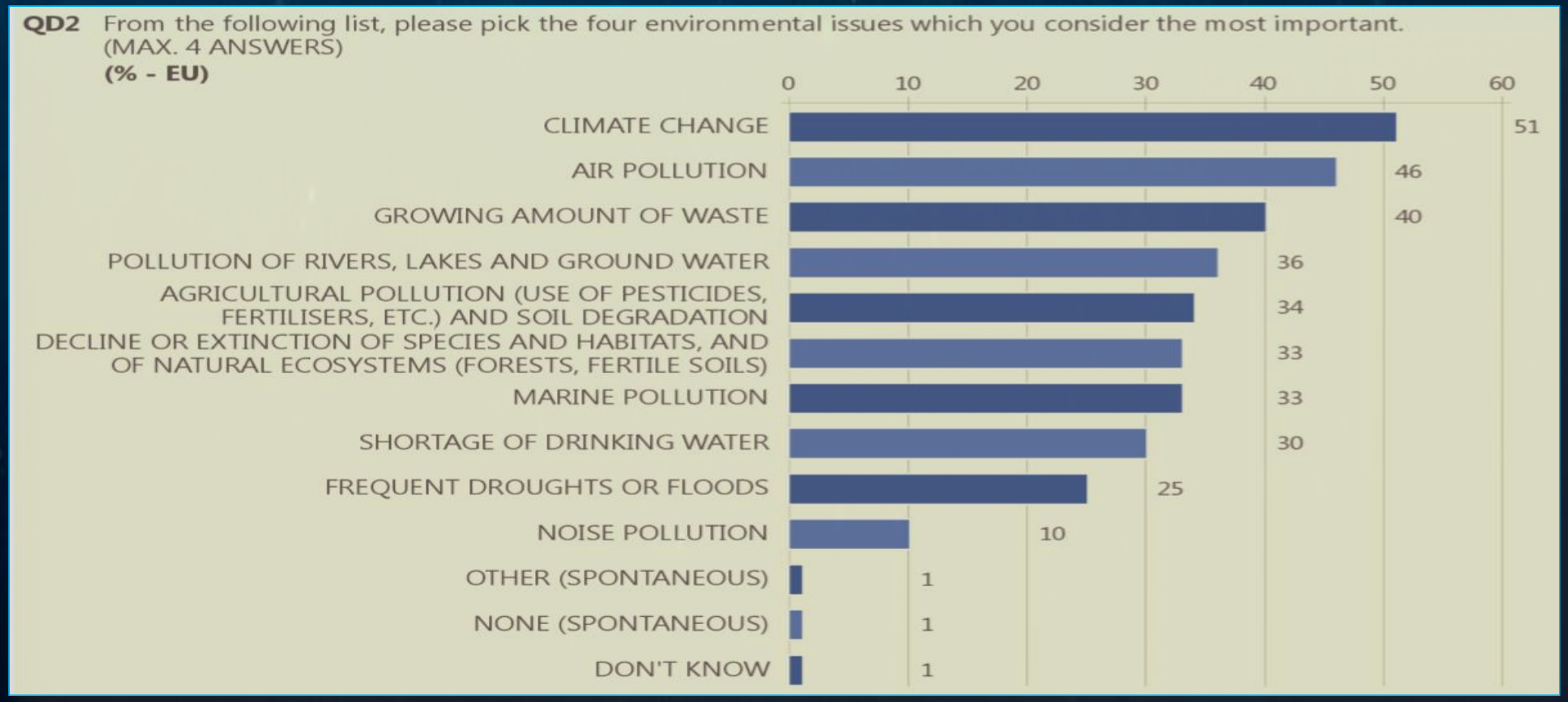
universidade de aveiro



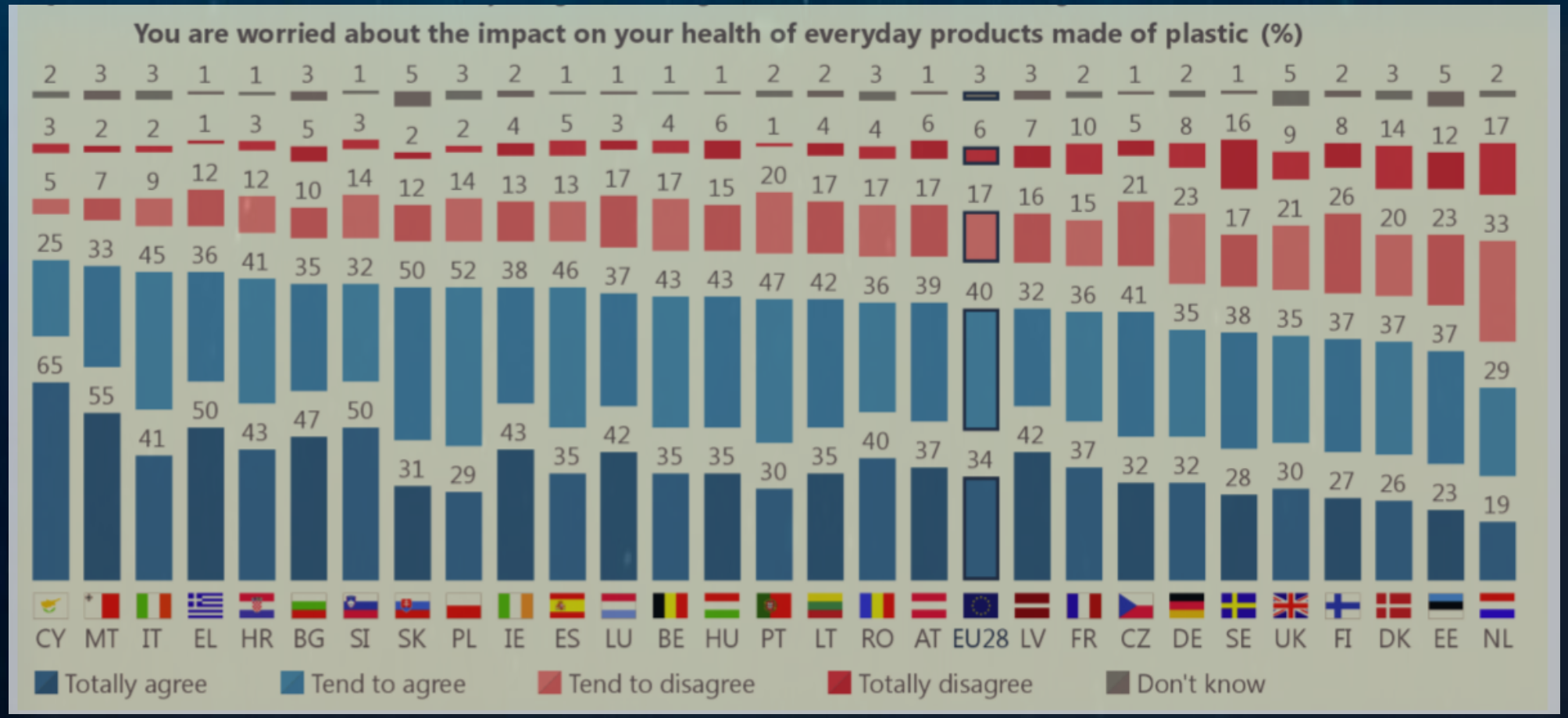
CESAM

http://www.cesam.ua.pt/

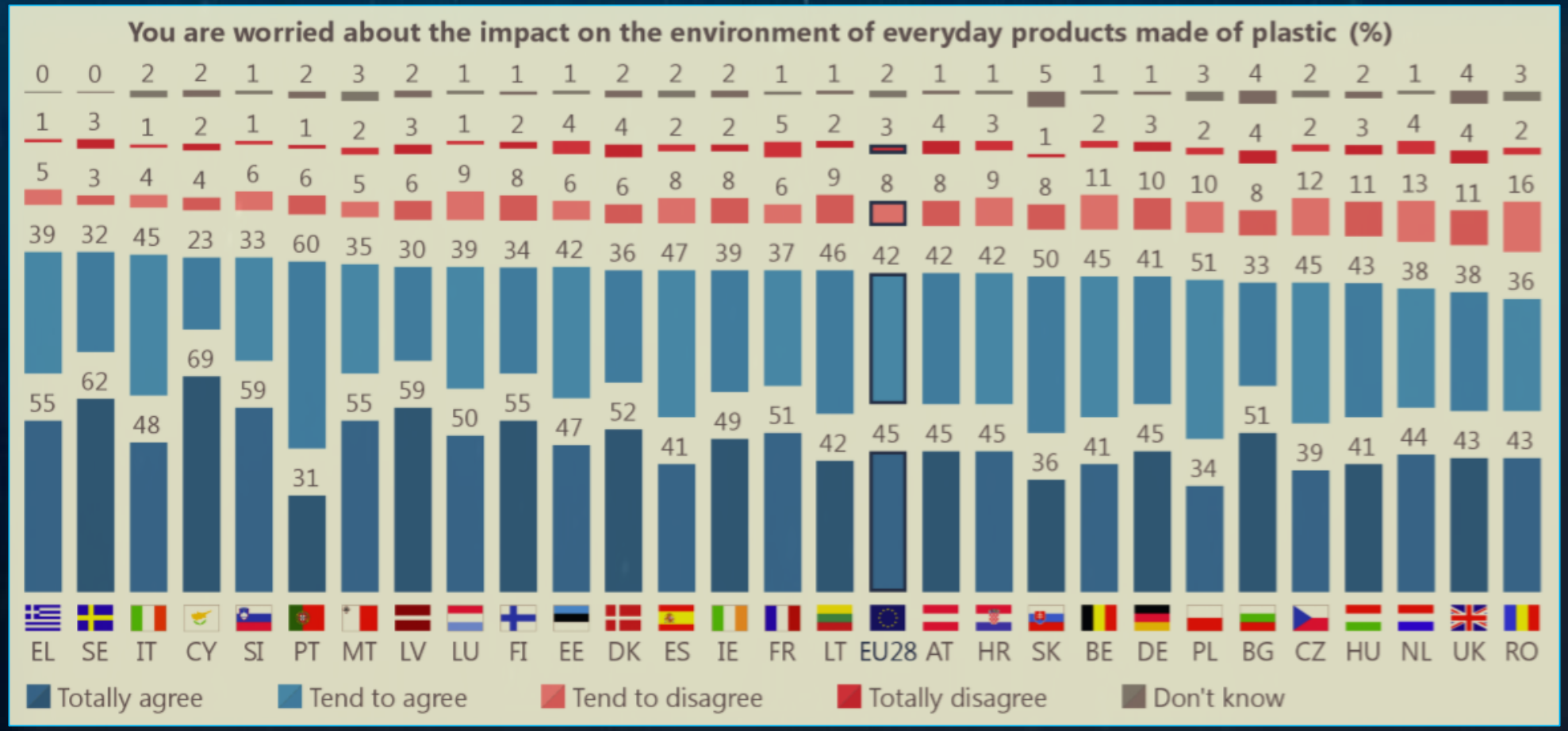
Attitudes of European citziens towards the environment



Attitudes of European citizens towards the environment

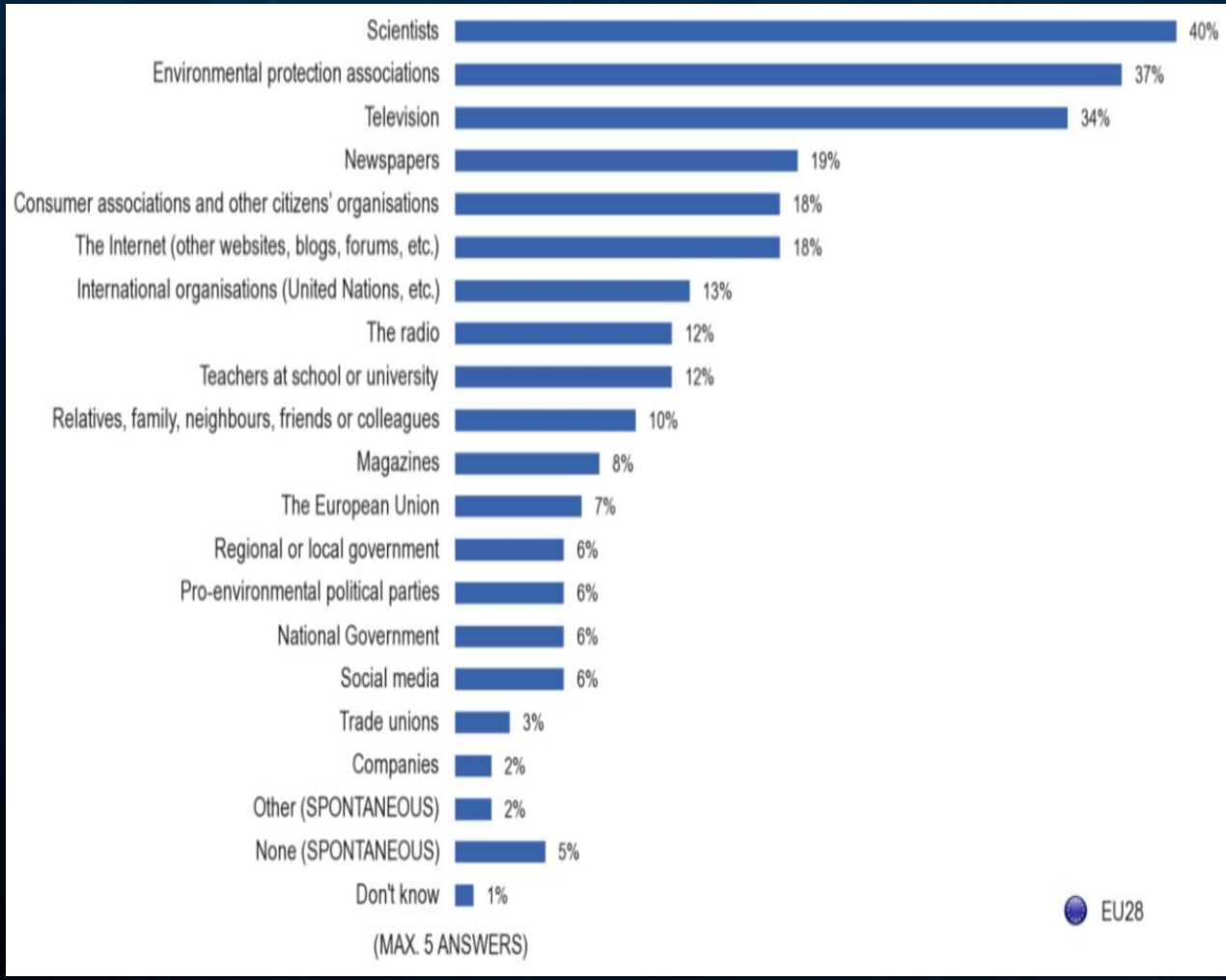


Attitudes of European citizens towards the environment

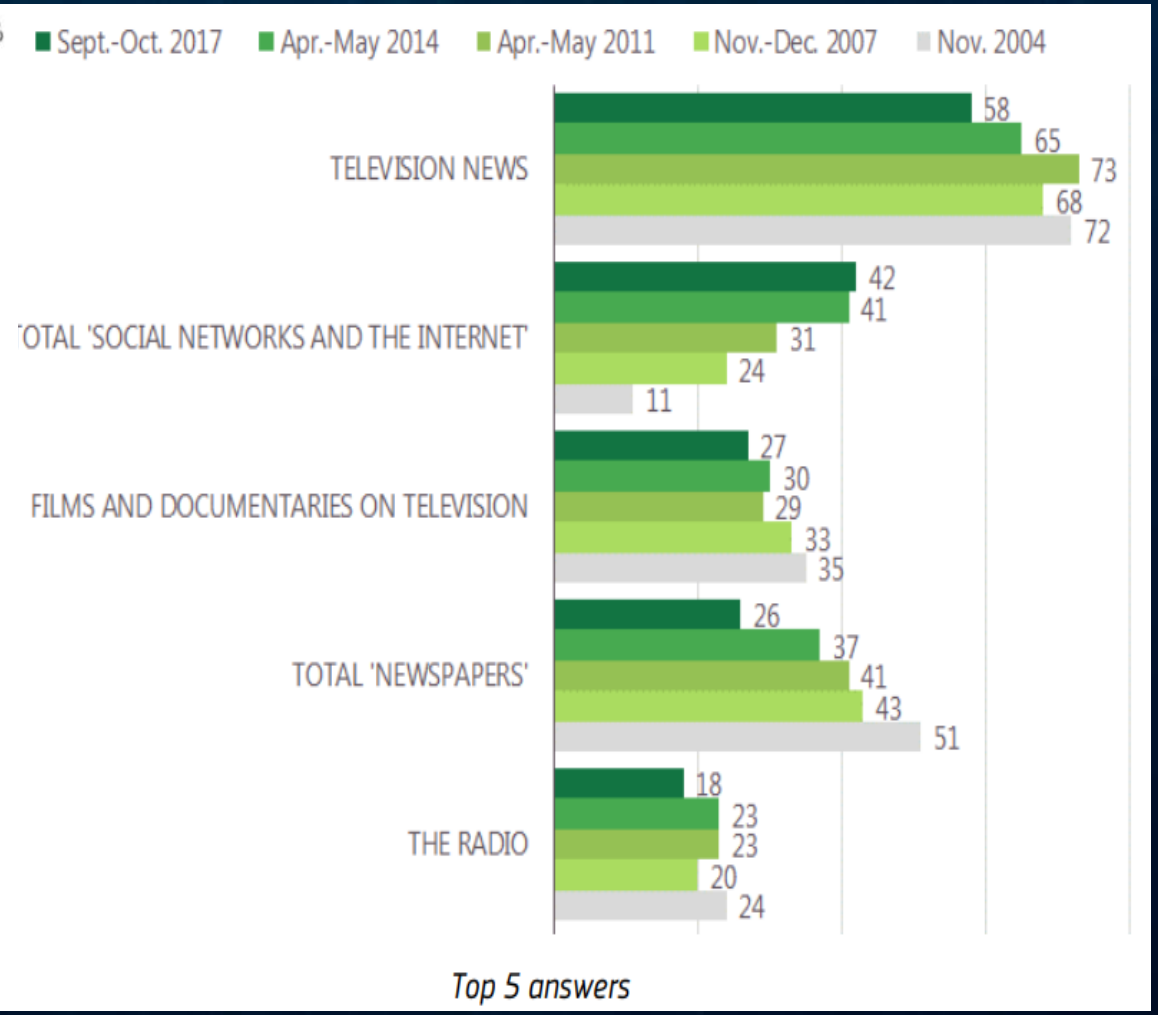


Sources of information

2014



2017



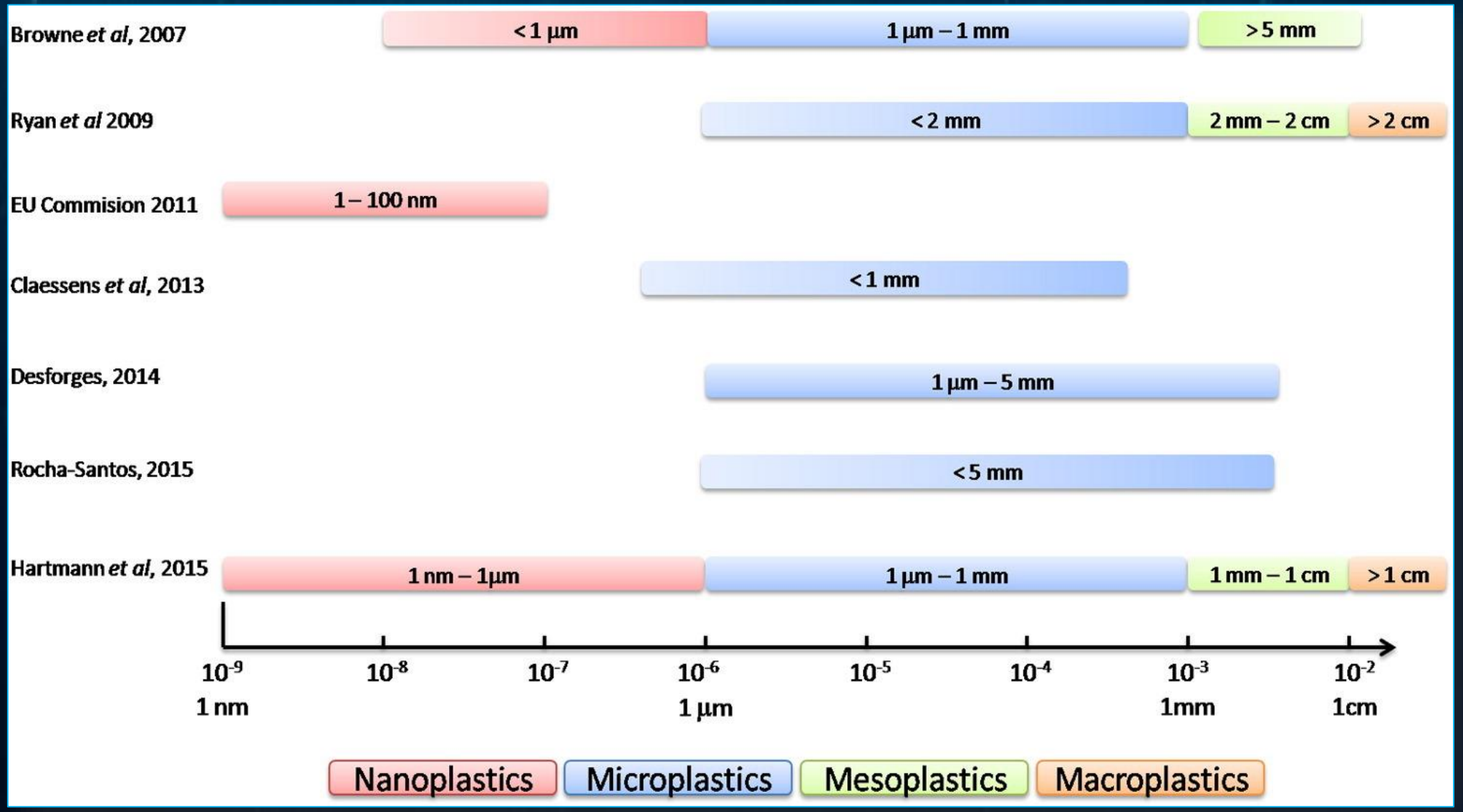
Macro-, Meso-, Micro-, and Nanoplastics

- Where do they come from?

- Where do they go to?

- Issues, trends, and proposals

Size?


Browne et al, 2007
< 1 µm
1 µm – 1 mm
> 5 mm
Ryan et al 2009
< 2 mm
2 mm – 2 cm
> 2 cm
EU Commision 2011
1 – 100 nm
Claessens et al, 2013
< 1 mm
Desforges, 2014
1 µm – 5 mm
Rocha-Santos, 2015
< 5 mm
Hartmann et al, 2015
1 nm – 1µm
1 µm – 1 mm
1 mm – 1 cm
> 1 cm
10-9
1 nm
10-8
10-7
10-6
1 µm
10-5
10-4
10-3
1mm
10-2
1cm
Nanoplastics
Microplastics
Mesoplastics
Macroplastics

Macro-, Meso-, Micro-, and Nanoplastics

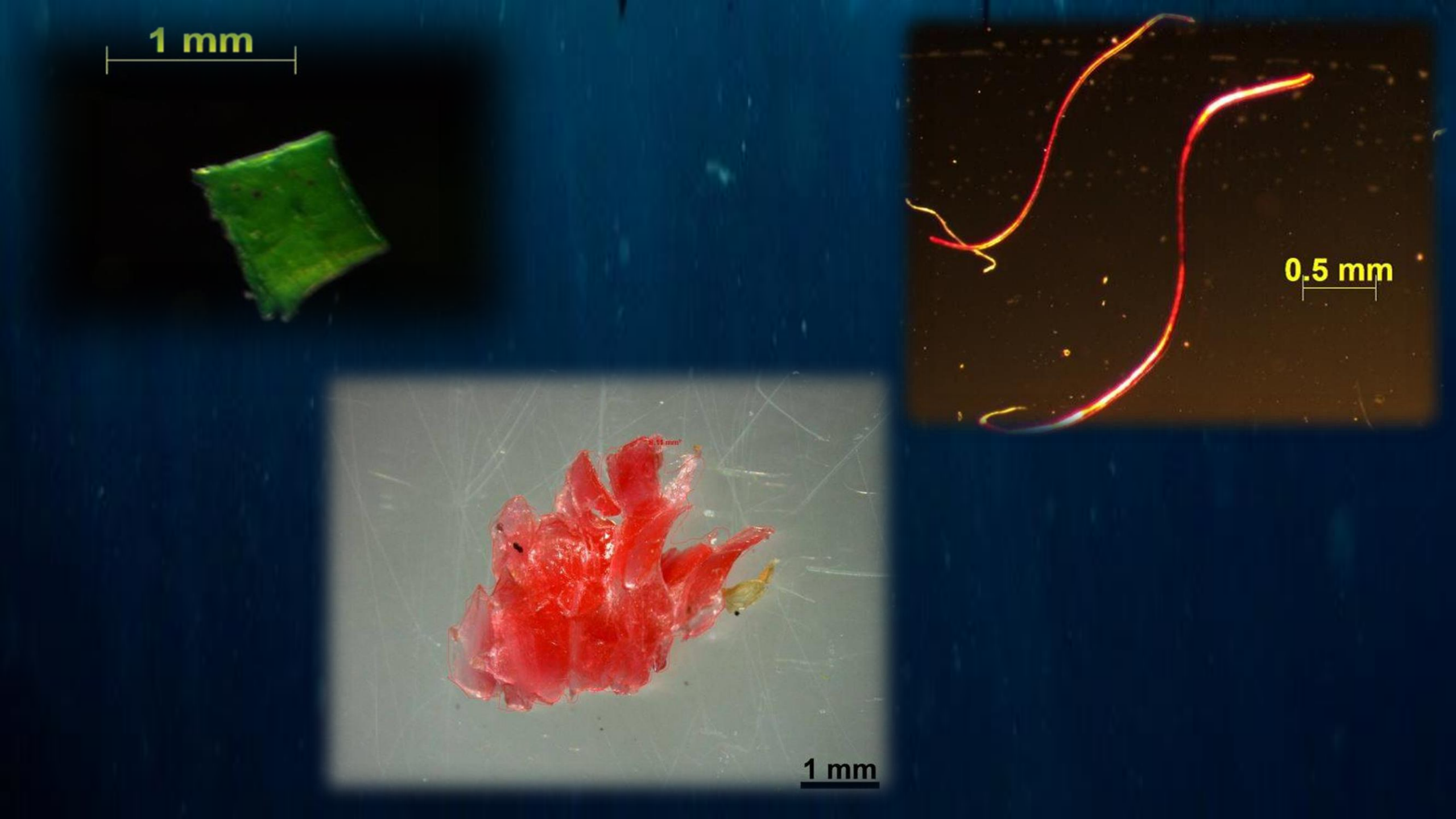
Plastic particles according to their size:

Nanoplastics	**(<0.1 µm)**
Microplastics	**(0.1 µm - 5 mm)**
Mesoplastics	**(5-25 mm)**
Macroplastics	**(>25 mm)**

Primary microplastics

< 5 mm => microplastics produced for certain functions (abrasives in cosmetics (skin cleansing creams), dental hygiene products (toothpaste), industrial applications (sandblasting polishing), vector for medications)

~ 5 mm => pellets or granulates, which is the form under which plastics are normally produced to be transported to industries that will convert them into a plethora of different products (bags, bottles, toys, fishing nets,...)


1 mm
0.5 mm
1 mm

Critical elements of assessment, and any proposed restriction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Note on substance identification and the potential scope of a restriction on uses of 'microplastics'

Version 1.1 – 16/10/2018 Page 1 of 13

Note on substance identification and the potential scope of a restriction on uses of 'microplastics'

a) **how and to what extent the polymer-based materials contribute to concern**

b) **how these should be appropriately identified (*the ' microplastic' definition*)**

Main sources of microplastics

Litter of plastic

Synthetic fibers

Microspheres

Main sources of microplastics

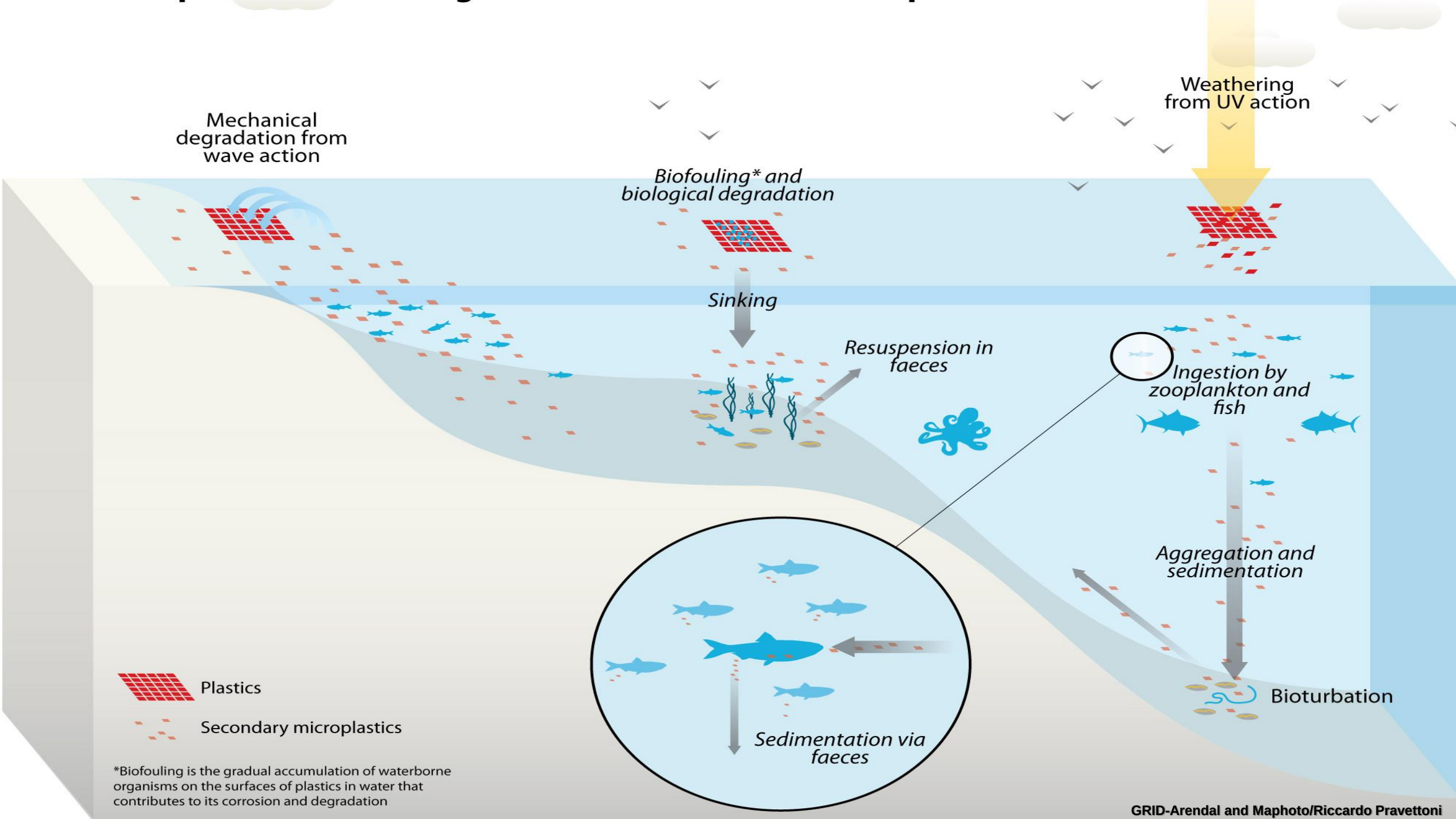
Litter of plastic

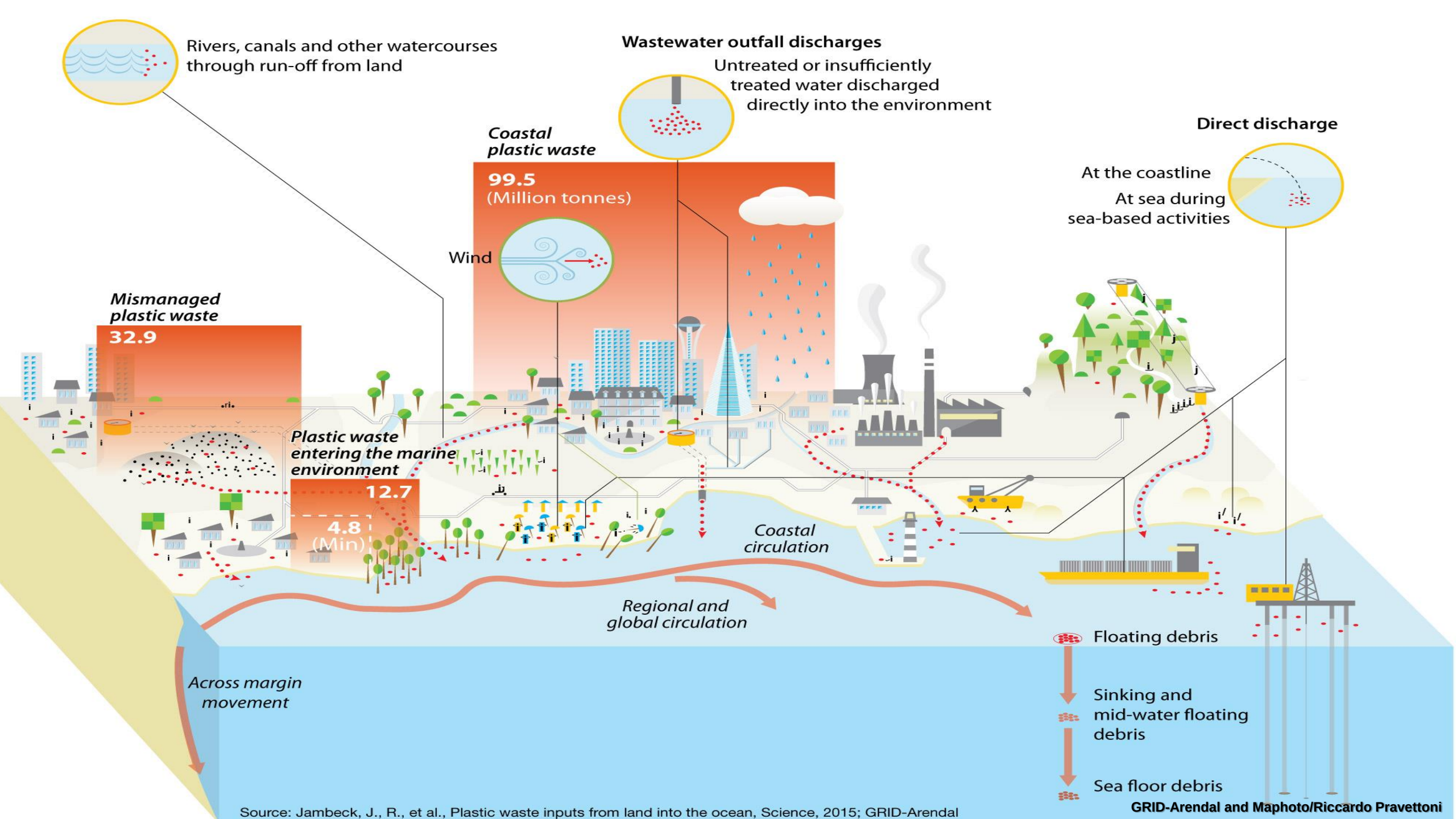
Synthetic fibers

Microspheres

Secondary

Primary


Mechanical degradation from wave action
Biofouling* and biological degradation
Weathering from UV action
Sinking
Resuspension in faeces
Ingestion by zooplankton and fish
Aggregation and sedimentation
Bioturbation
Sedimentation via faeces
Plastics
Secondary microplastics
*Biofouling is the gradual accumulation of waterborne organisms on the surfaces of plastics in water that contributes to its corrosion and degradation
GRID-Arendal and Maphoto/Riccardo Pravettoni


Rivers, canals and other watercourses through run-off from land
Wastewater outfall discharges
Untreated or insufficiently treated water discharged directly into the environment
Direct discharge
At the coastline
At sea during sea-based activities
Coastal plastic waste
99.5
(Million tonnes)
Wind
Mismanaged plastic waste
32.9
Plastic waste entering the marine environment
12.7
4.8
(Min)
Coastal circulation
Regional and global circulation
Across margin movement
Floating debris
Sinking and mid-water floating debris
Sea floor debris
Source: Jambeck, J., R., et al., Plastic waste inputs from land into the ocean, Science, 2015; GRID-Arendal
GRID-Arendal and Maphoto/Riccardo Pravettoni

UK: about 86 tons of exfoliating microspheres are discharged annually in the marine environment.

US is responsible for the discharge of 263 tons per year of polyethylene microplastics.

There is a concern this can be harmful to marine life

Kara L. Law & Richard C. Thompson, Microplastics in the Seas, Science, 345,144-145 (2014) **DOI: 10.1126/science.1254065**

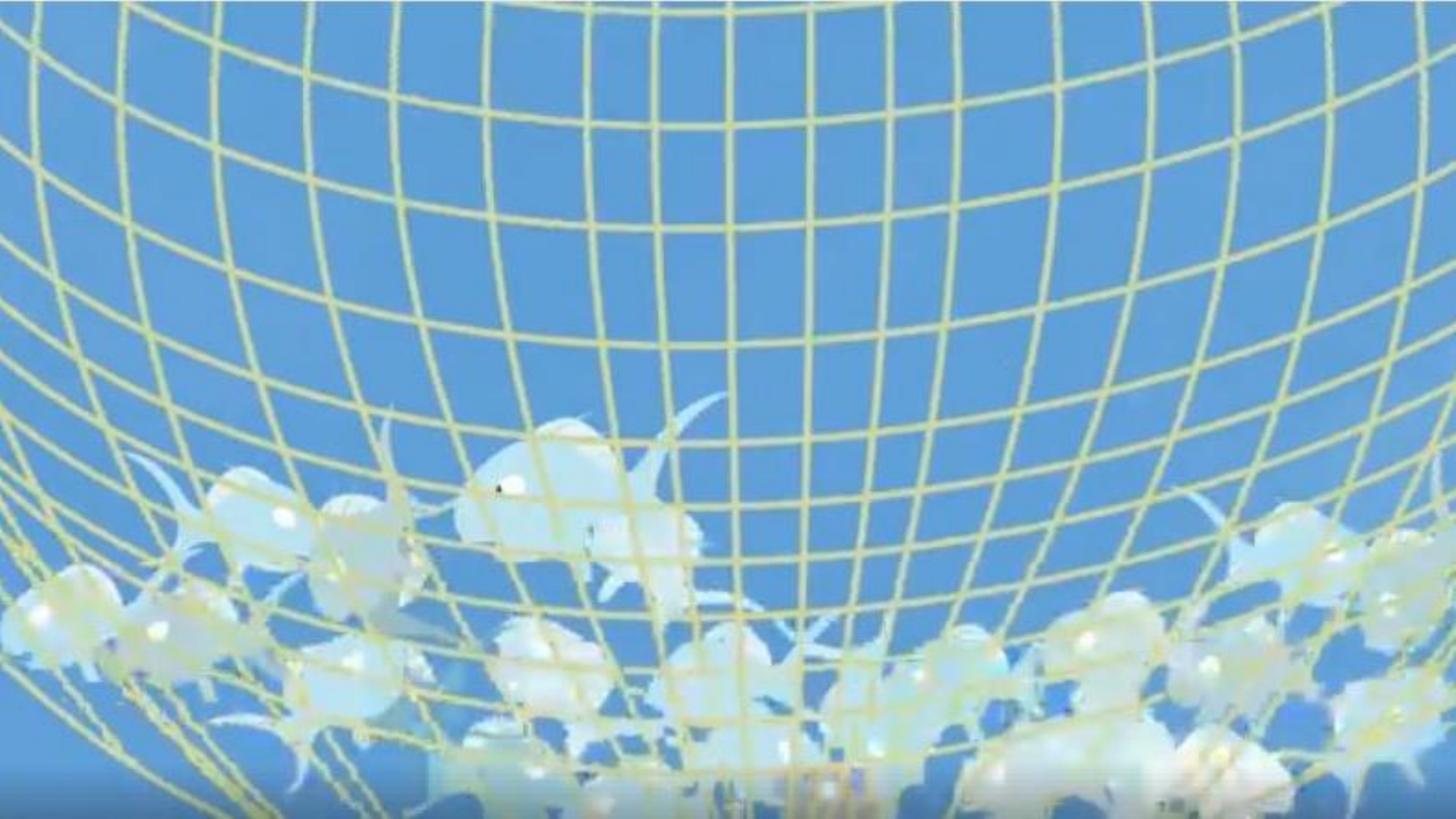
Impacts are particularly relevant in the marine environment:

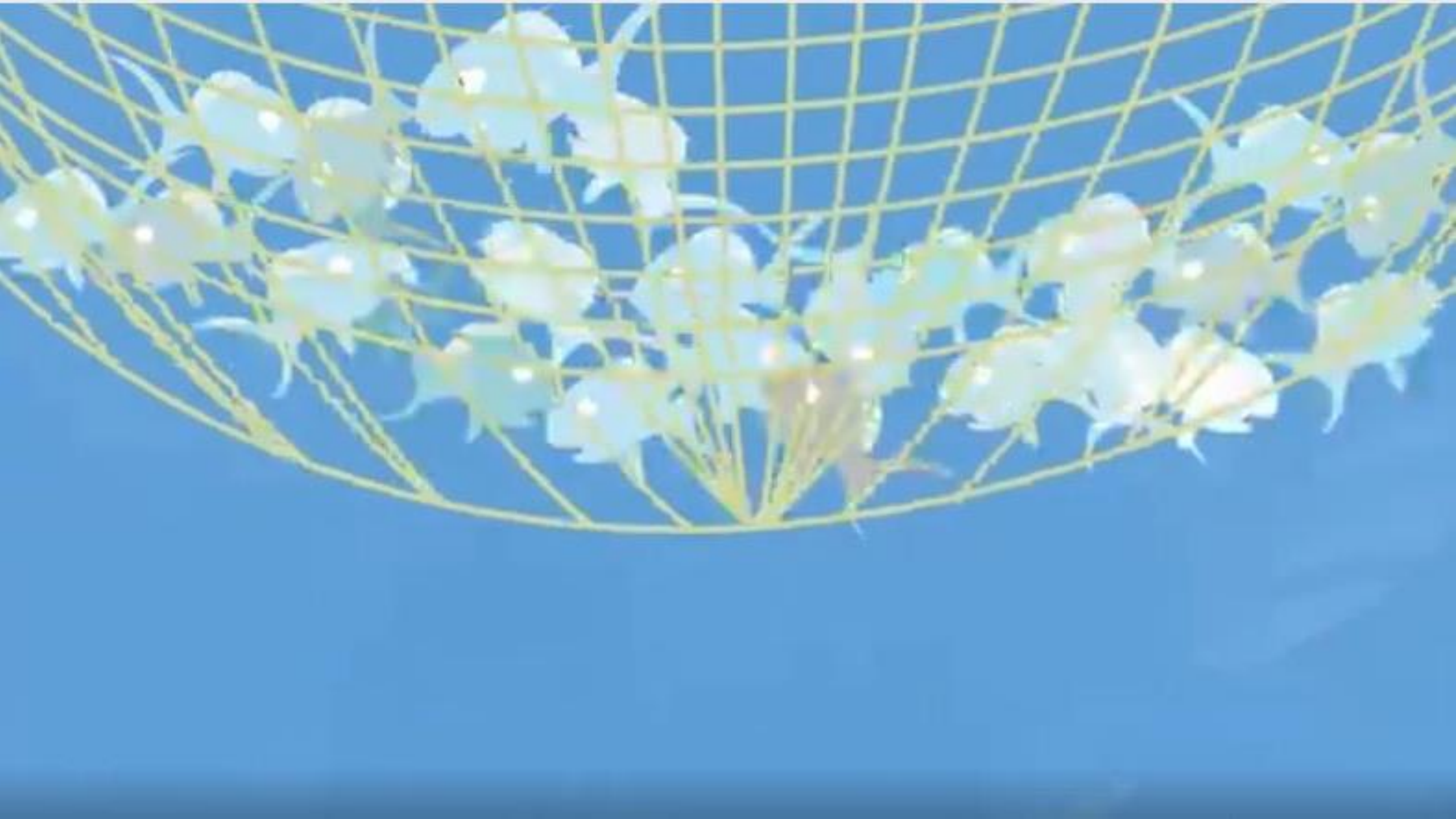
i) fragmentation and photochemical degradation induce its **introduction into the food chain** by ingestion by marine organisms

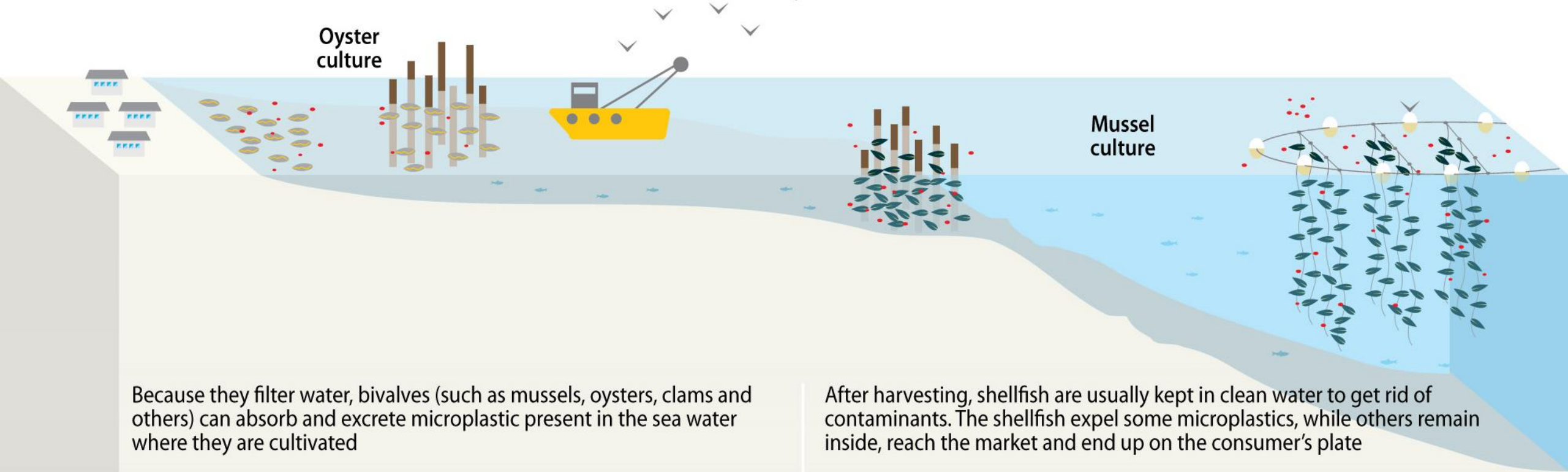
ii) low density and high fluctuation capacity => **emerging at locations far from its source**

iii) high **adsorption capacity of persistent organic pollutants**

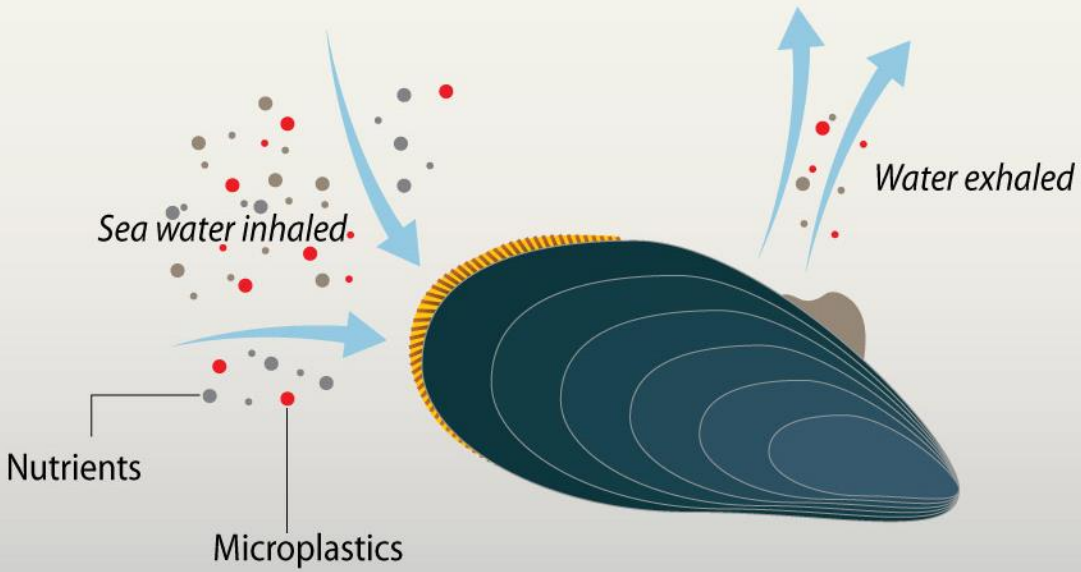
iv) high dispersion capacity => **substrate and vector of invasive species**



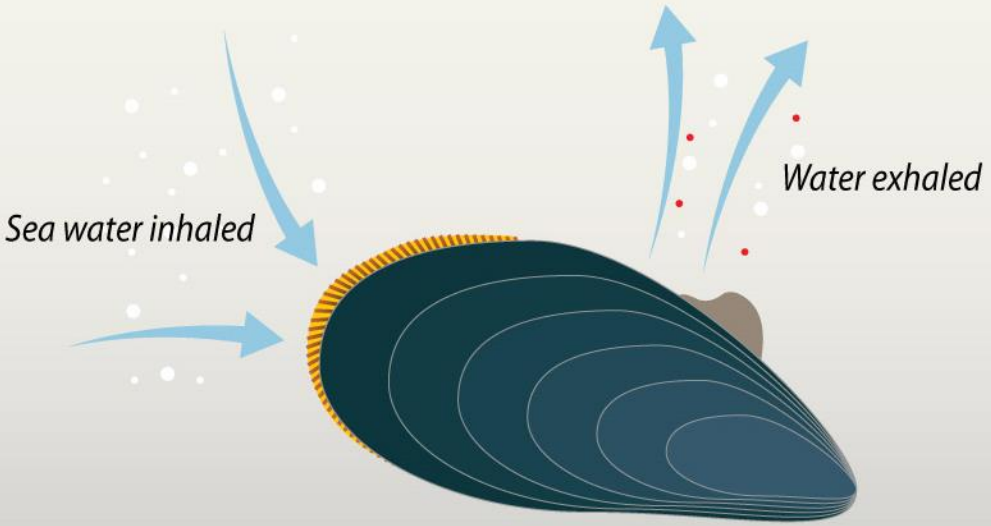




Because they filter water, bivalves (such as mussels, oysters, clams and others) can absorb and excrete microplastic present in the sea water where they are cultivated



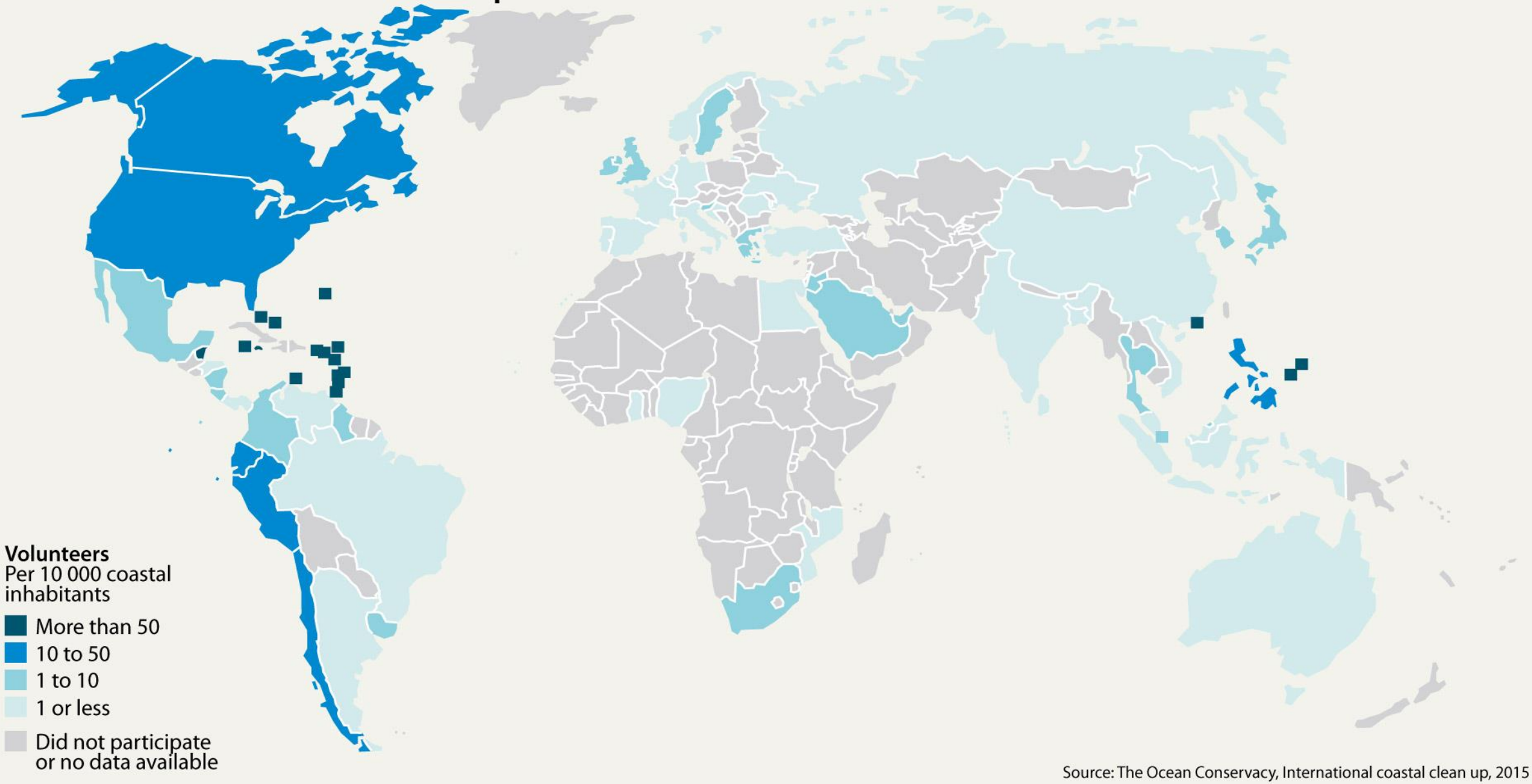
After harvesting, shellfish are usually kept in clean water to get rid of contaminants. The shellfish expel some microplastics, while others remain inside, reach the market and end up on the consumer's plate



Sources: Tjärnö Marine Biological Laboratory, Strömstad, Sweden; personal communication with Dr. Sarah Dudas

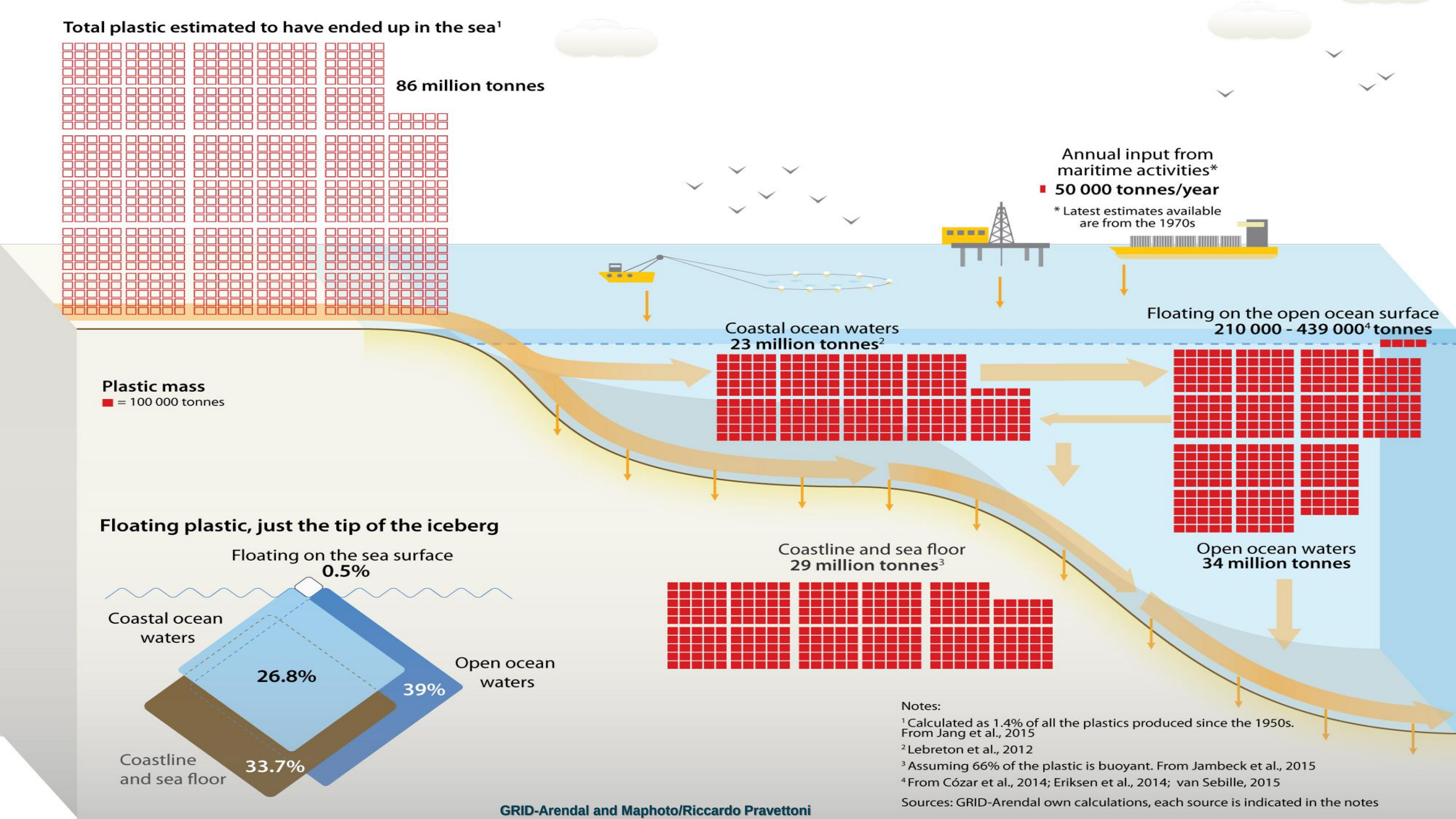
Marine plastic garbage clean up efforts

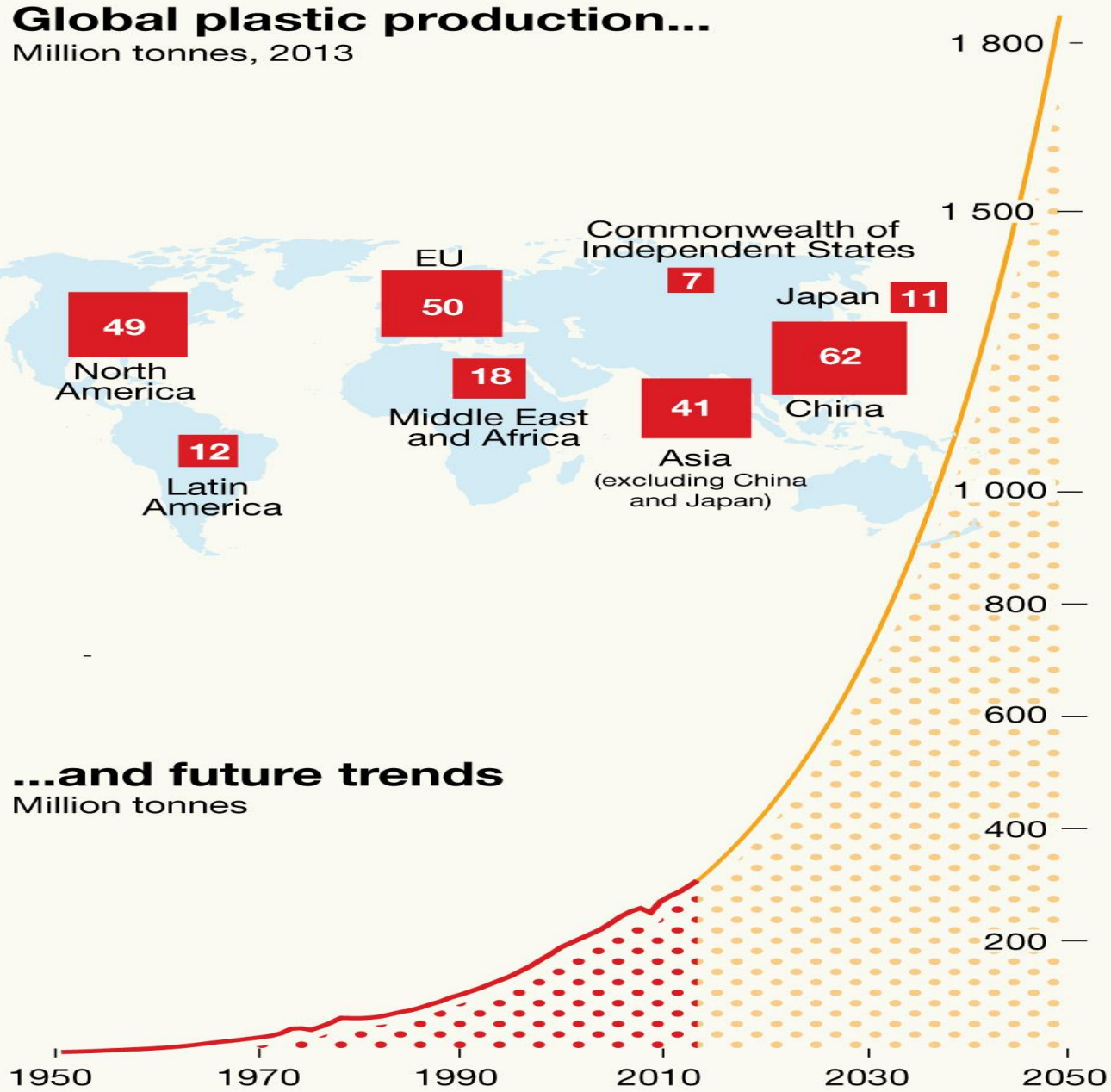
2014 International coastal clean up



Source: The Ocean Conservacy, International coastal clean up, 2015

GRID-Arendal and Maphoto/Riccardo Pravettoni


Total plastic estimated to have ended up in the sea[1]
86 million tonnes
Annual input from maritime activities*
50 000 tonnes/year
* Latest estimates available are from the 1970s
Plastic mass
= 100 000 tonnes
Coastal ocean waters
23 million tonnes[2]
Floating on the open ocean surface
210 000 - 439 000[4] tonnes
Coastline and sea floor
29 million tonnes[3]
Open ocean waters
34 million tonnes
Floating plastic, just the tip of the iceberg
Floating on the sea surface
0.5%
Coastal ocean waters
26.8%
Open ocean waters
39%
Coastline and sea floor
33.7%
Notes:
[1] Calculated as 1.4% of all the plastics produced since the 1950s. From Jang et al., 2015
[2] Lebreton et al., 2012
[3] Assuming 66% of the plastic is buoyant. From Jambeck et al., 2015
[4] From Cózar et al., 2014; Eriksen et al., 2014; van Sebille, 2015
Sources: GRID-Arendal own calculations, each source is indicated in the notes
GRID-Arendal and Maphoto/Riccardo Pravettoni



Source: Ryan, A Brief History of Marine Litter Research, in M. Bergmann, L. Gutow, M. Klages (Eds.), Marine Anthropogenic Litter, Berlin Springer, 2015; Plastics Europe

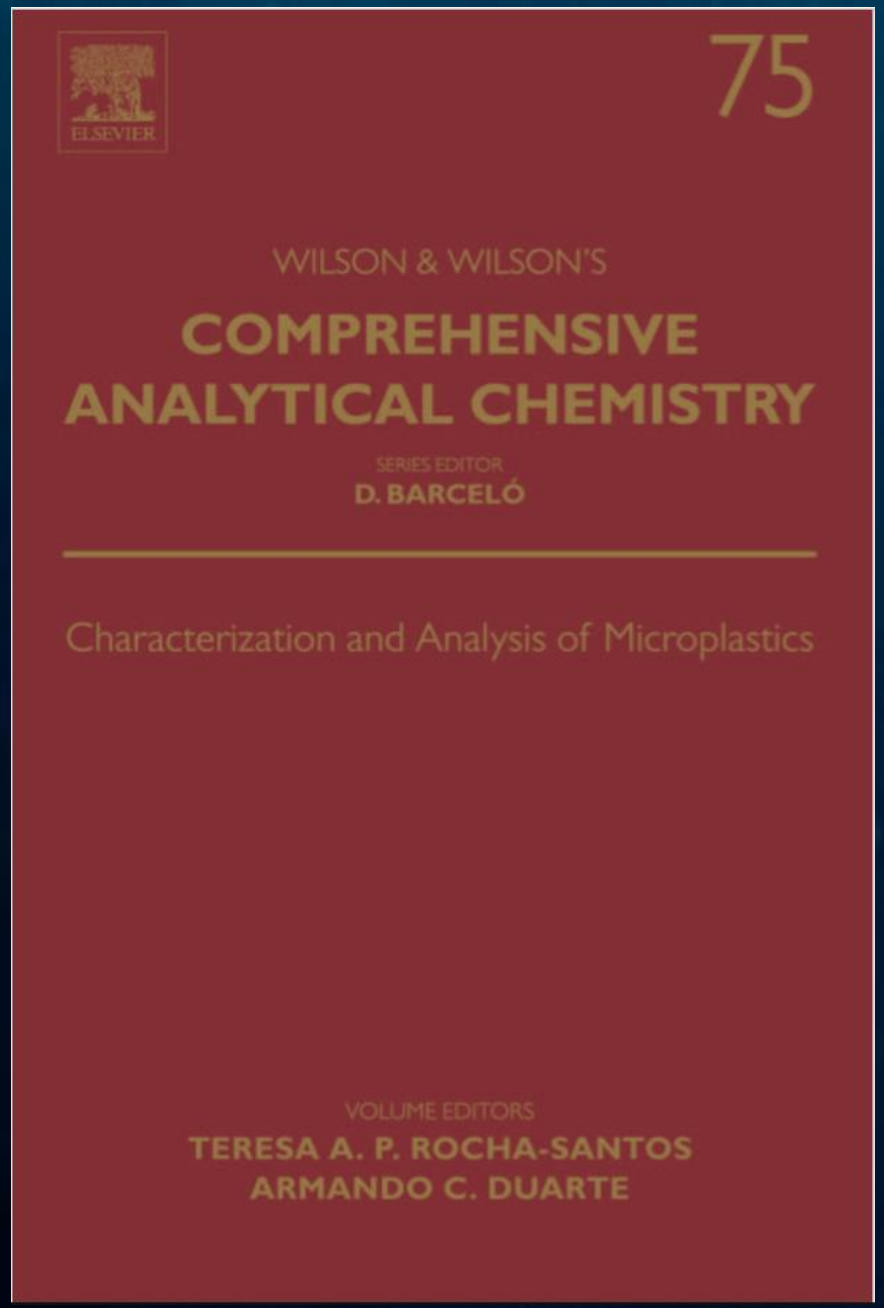
GRID-Arendal and Maphoto/Riccardo Pravettoni

Issues, trends, and proposals

Fragmentation of **macroplastics** and wasted **nurdles**
have been producing
microplastics (0.1 µm - 5 mm)
and
nanoplastics (<0.1 µm)

at an accelerated pace,

and
they are becoming an **ever-increasing problem**

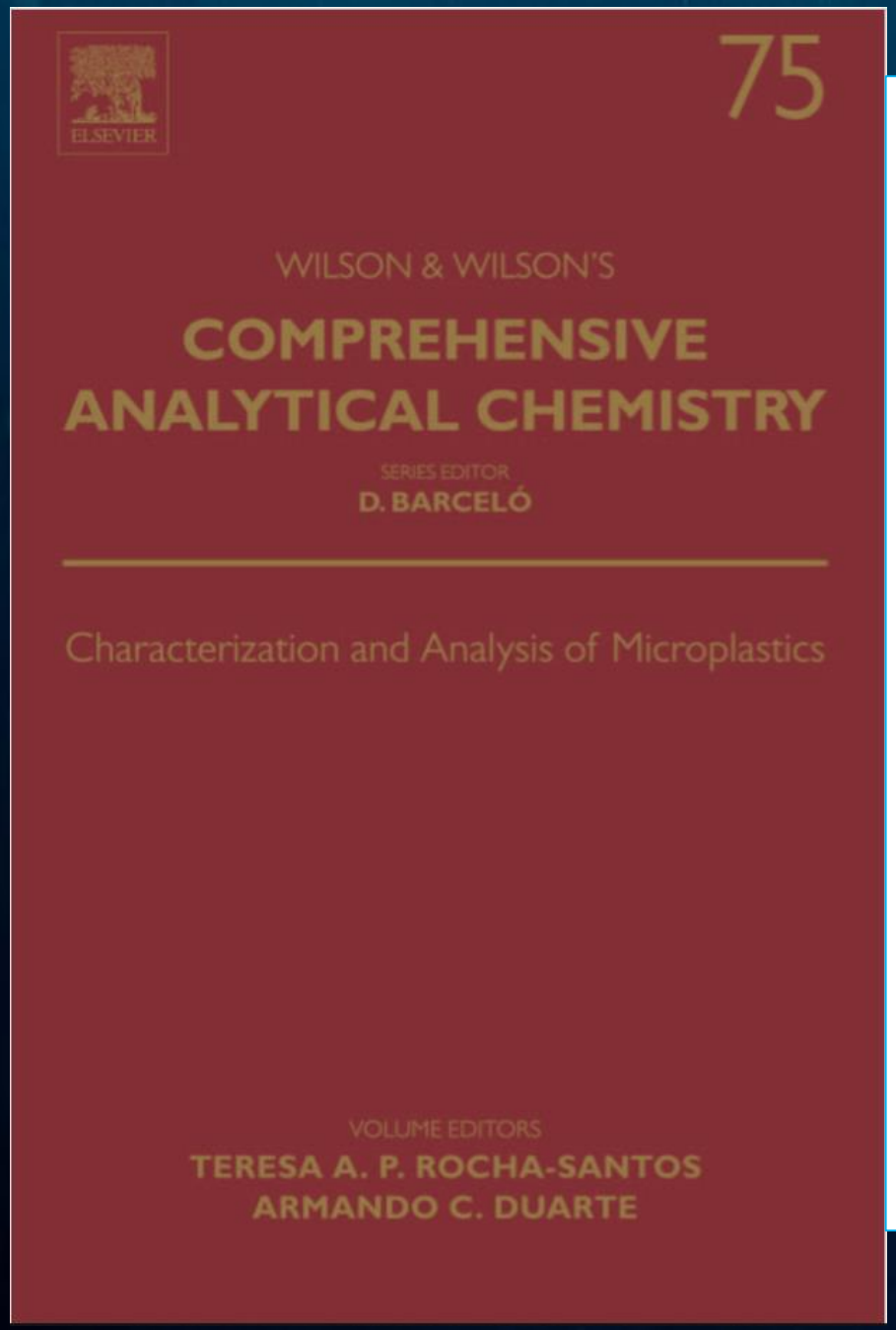


Description

Characterization and Analysis of Microplastics, Volume 75 presents the latest information on new and published analytical methodologies for the identification and quantification of microplastics. This series focuses on a variety of interesting topics surrounding the field of microplastics, with this new release in the series covering sampling and sample handing, the characterization of microplastics by raman spectroscopy, and techniques for assessing the chemical compounds related to microplastics. Users will find a variety of useful information that includes morphological, physical and chemical characterizations, along with analytical techniques and future perspectives of analytical methodologies in this rapidly advancing field.

Key Features

- Concise, comprehensive coverage of analytical techniques and applications
- Clear diagrams adequately support important topics
- Includes real examples that illustrate applications of the analytical techniques on the sampling, characterization, and analysis of microplastics



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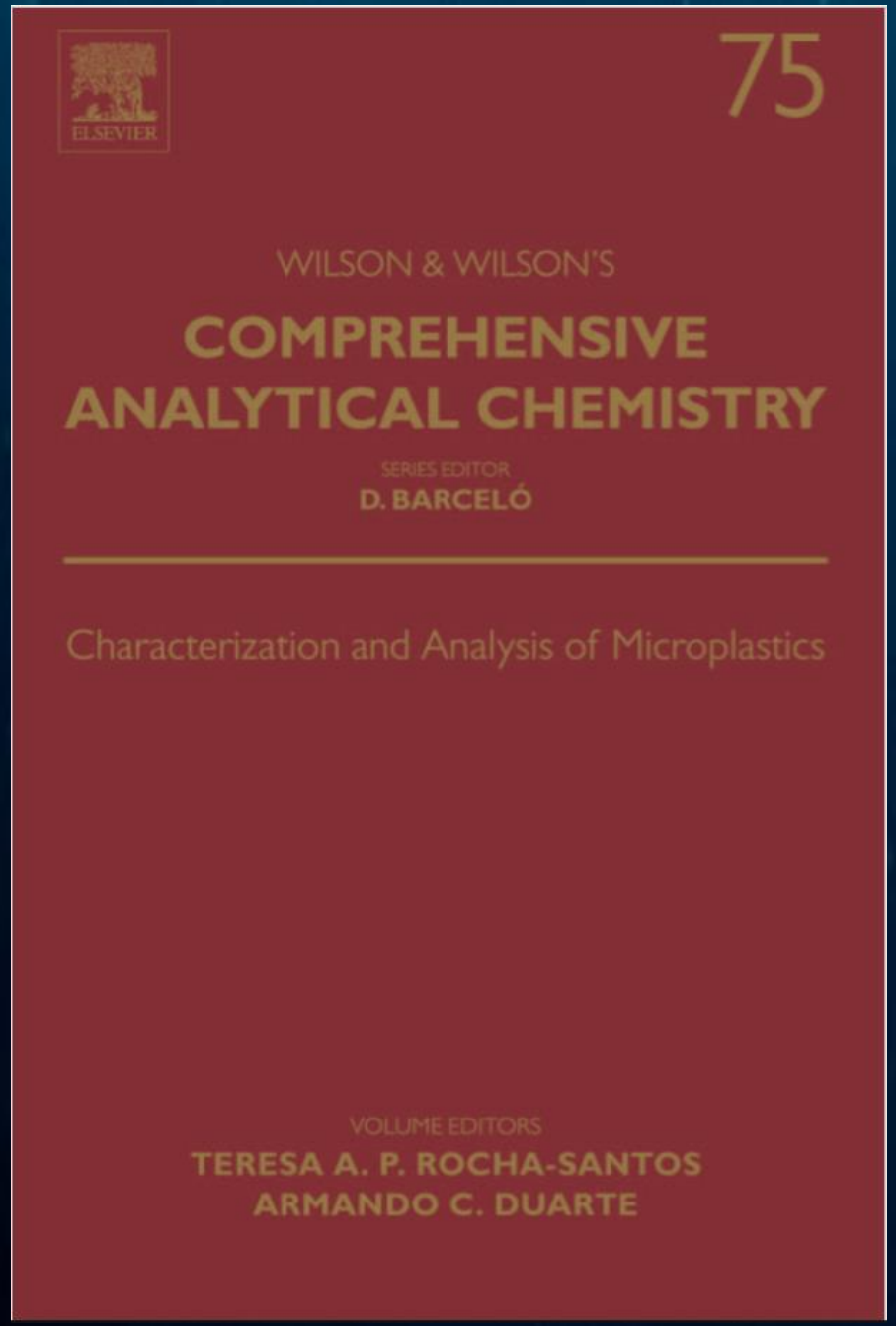
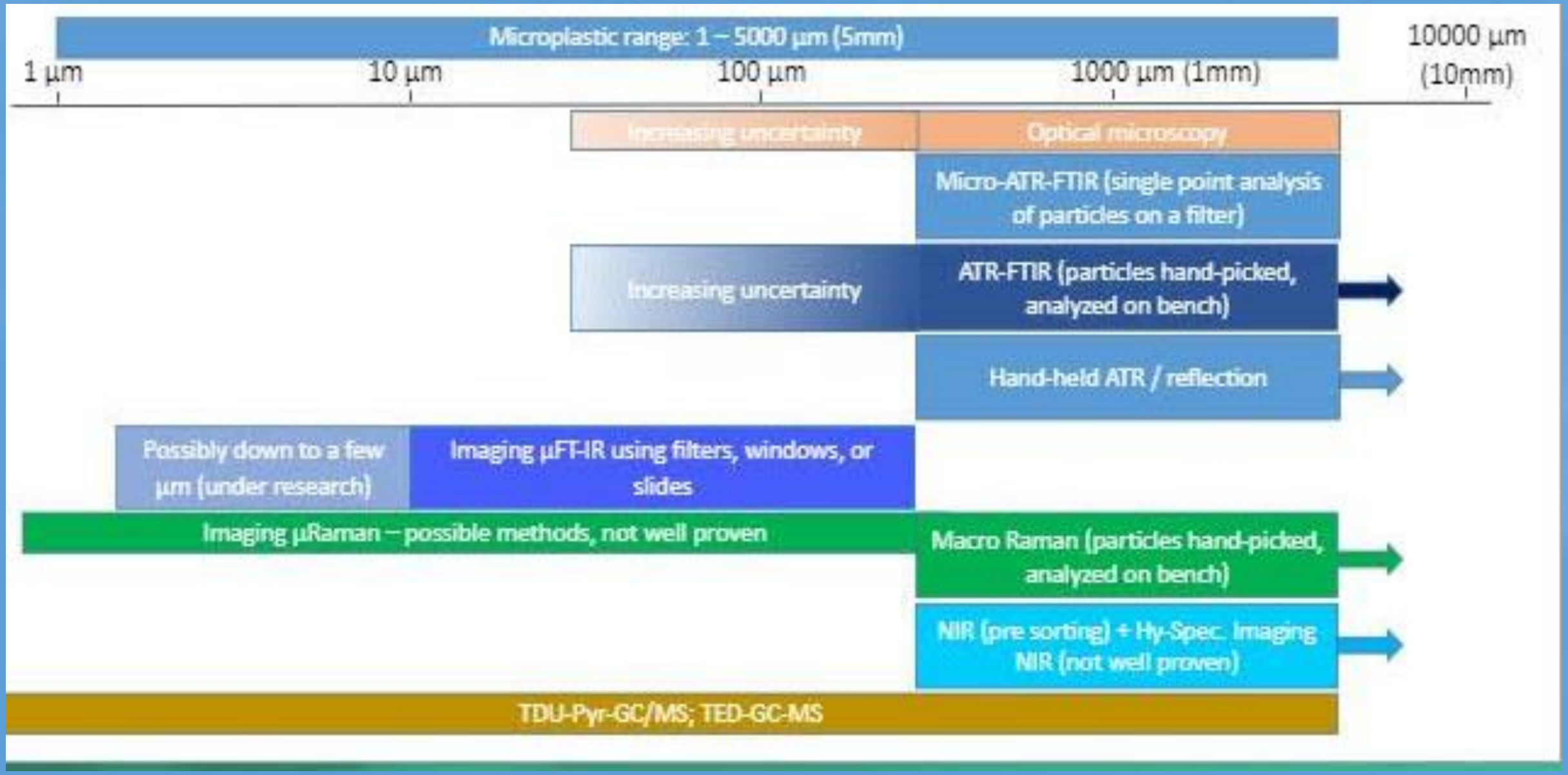



Microplastic range: 1 – 5000 µm (5mm)
1 µm
10 µm
100 µm
1000 µm (1mm)
10000 µm (10mm)
Increasing uncertainty
Optical microscopy
Micro-ATR-FTIR (single point analysis of particles on a filter)
Increasing uncertainty
ATR-FTIR (particles hand-picked, analyzed on bench)
Hand-held ATR / reflection
Possibly down to a few µm (under research)
Imaging µFT-IR using filters, windows, or slides
Imaging µRaman – possible methods, not well proven
Macro Raman (particles hand-picked, analyzed on bench)
NIR (pre sorting) + Hy-Spec. Imaging NIR (not well proven)
TDU-Pyr-GC/MS; TED-GC-MS

This first studies looked into a microscopic and said “This is plastic”

There are no standardized methods yet

Much of the published data is dubious if not useless

Many say “we can measure it”

– but few feel the need to prove that they measure it correctly

Microplastic analysis has become the “Wild West” of Analytical Chemistry

Volvo Ocean Race 2017-18

Microplastics Data / Turn the Tide on Plastic preliminary results

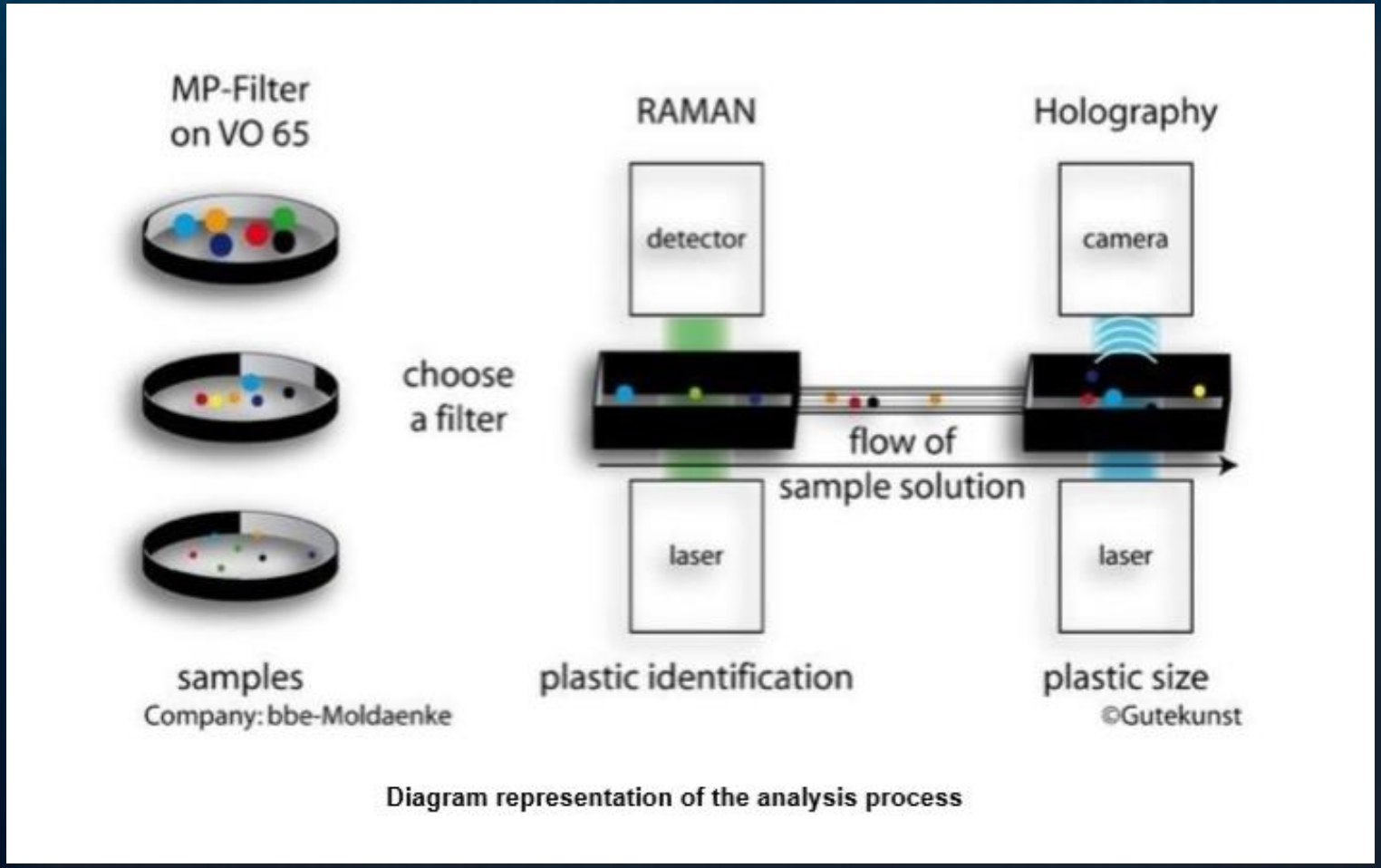


Diagram representation of the analysis process

Volvo Ocean Race
2017-2018

A holographic camera measured the size of particles and a RAMAN spectrometer identified which particles were plastic. The process, although still quite time-consuming (6 hours per filter), is considerably more efficient and less subjective than manual analyses using a microscope.

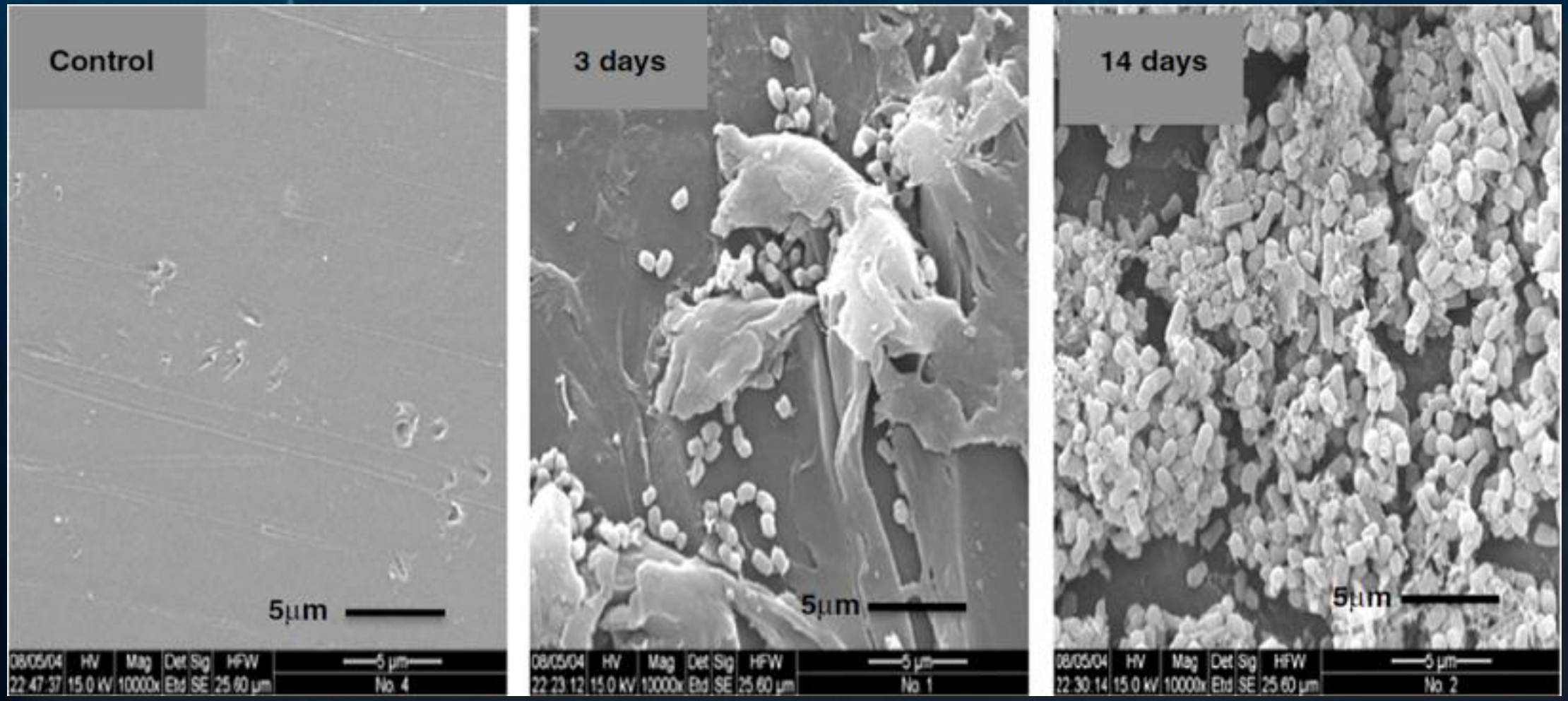
Microplastics have become an established issue in marine ecosystem health
and
It has been subject to scientific and regulatory interest

By comparison,

monitoring efforts on microplastics in freshwater environments were given less attention

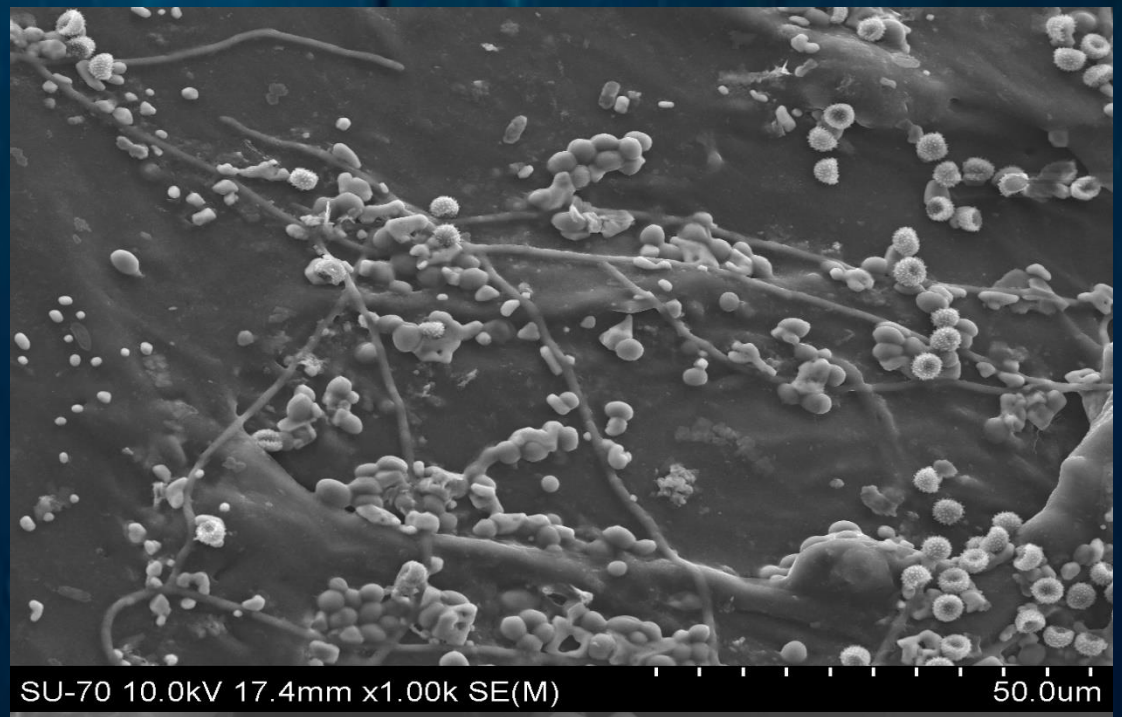
WHY?

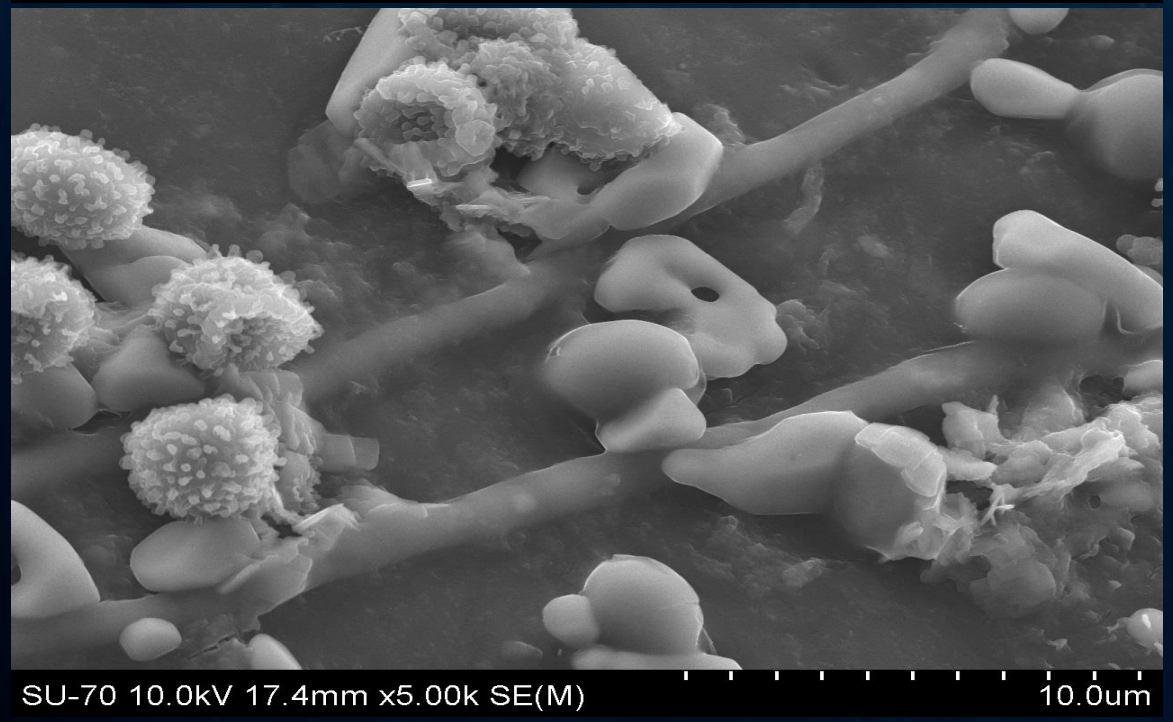
BIOADHESION: DANGEROUS LIASIONS

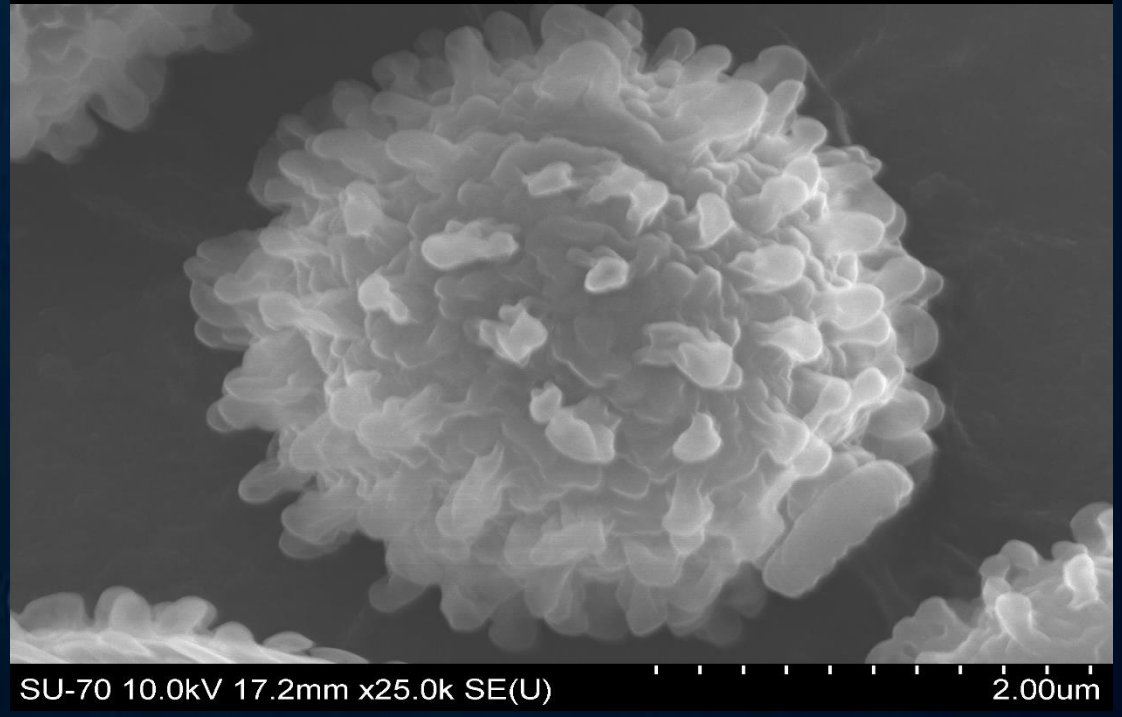


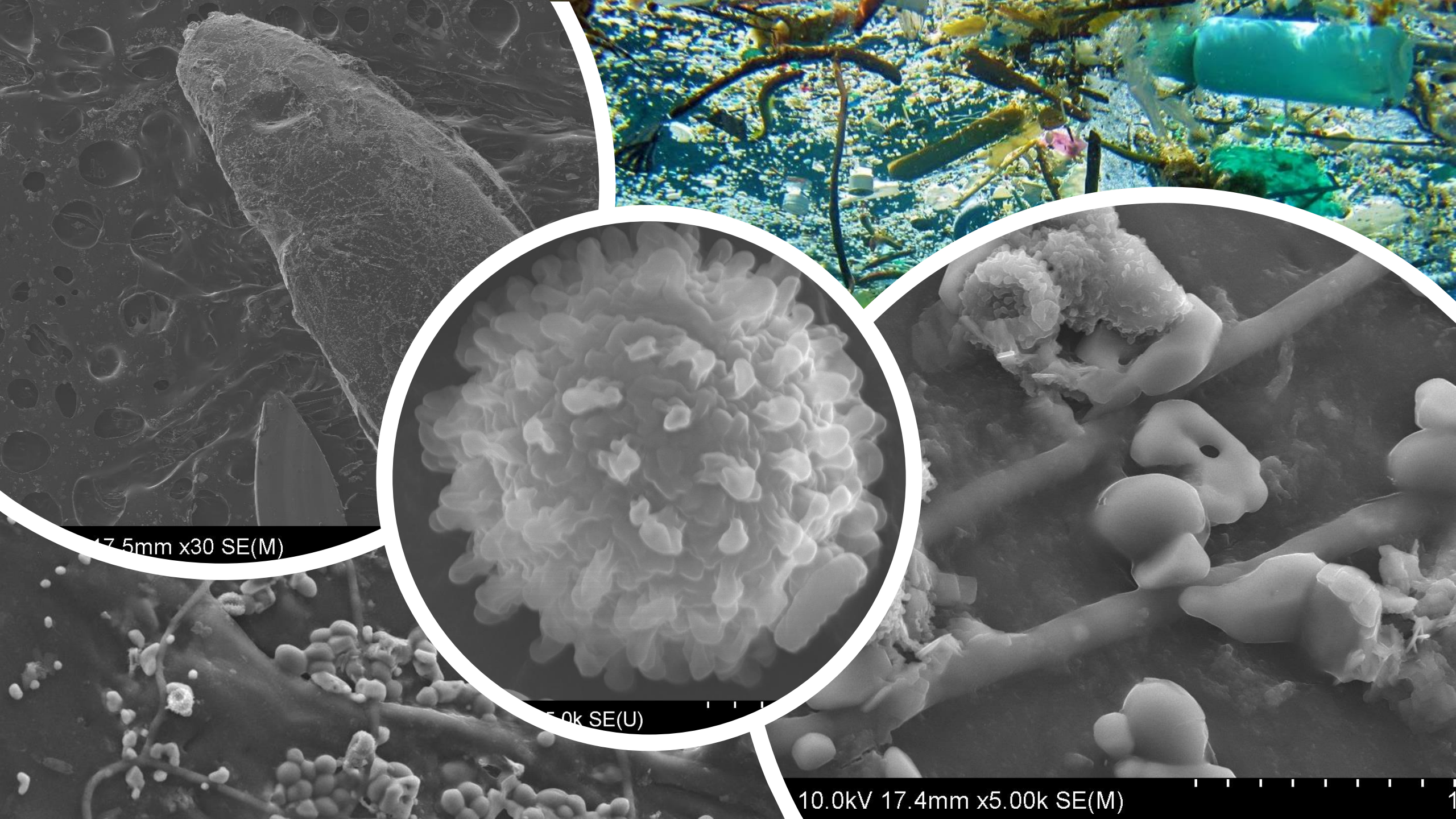
Biofilm formation on the surface of UV photo-oxidised polyethylene under scanning electron microscopy. Initiation of biodegradation was detected after 3 days. UV irradiated but not inoculated served as control.
(DOI:10.1016/j.copbio.2011.01.013)


SU-70 10.0kV 17.5mm x30 SE(M)
1.00mm


SU-70 10.0kV 17.4mm x1.00k SE(M)
50.0um


SU-70 10.0kV 17.4mm x5.00k SE(M)
10.0um


SU-70 10.0kV 17.2mm x25.0k SE(U)
2.00um


17.5mm x30 SE(M)
5.0k SE(U)
10.0kV 17.4mm x5.00k SE(M)

REACHING OUT FOR NANOPLASTICS

In what concerns nanoplastics the situation is rather more complex.

There is an increasing awareness of our limited understanding of nanoplastics pollution and its potential effects on human health.

In fact the impacts in human health are unknown.

REACHING OUT FOR NANOPLASTICS

Studies using nanosized chemical polymers have little significance since they do not into account the surface 'bio-transformation' of nanomaterials.

On one hand, studies on of effects of pristine surfaces will not likely describe what happens in nature, and on the other hand the characterization of a corona on aged plastics is not a straightforward task.

Very challenging and most welcome for research sake.

REACHING OUT FOR NANOPLASTICS

Nanoplastics are poorly defined:

- **size x shape x chemical nature**
- **isolation**
- **characterisation**

Definition of nanoplastics

- **What size range**
- **What are the size limits for analysis? 800nm? 80nm?**

Nanoplastics difficult to isolate

- **Isolation techniques?**
- **How can they be isolated from environment**

REACHING OUT FOR NANOPLASTICS

Hypothesis relating to human health

- particles < 40nm → too small to accumulate, they will be excreted quickly

- particles 50-200nm → where the bigger threat resides due to bioaccumulation in secondary organs after crossing into the bloodstream (likely to cause endocrine and immune response)

Sources and routes of nanoplastics need to be identified

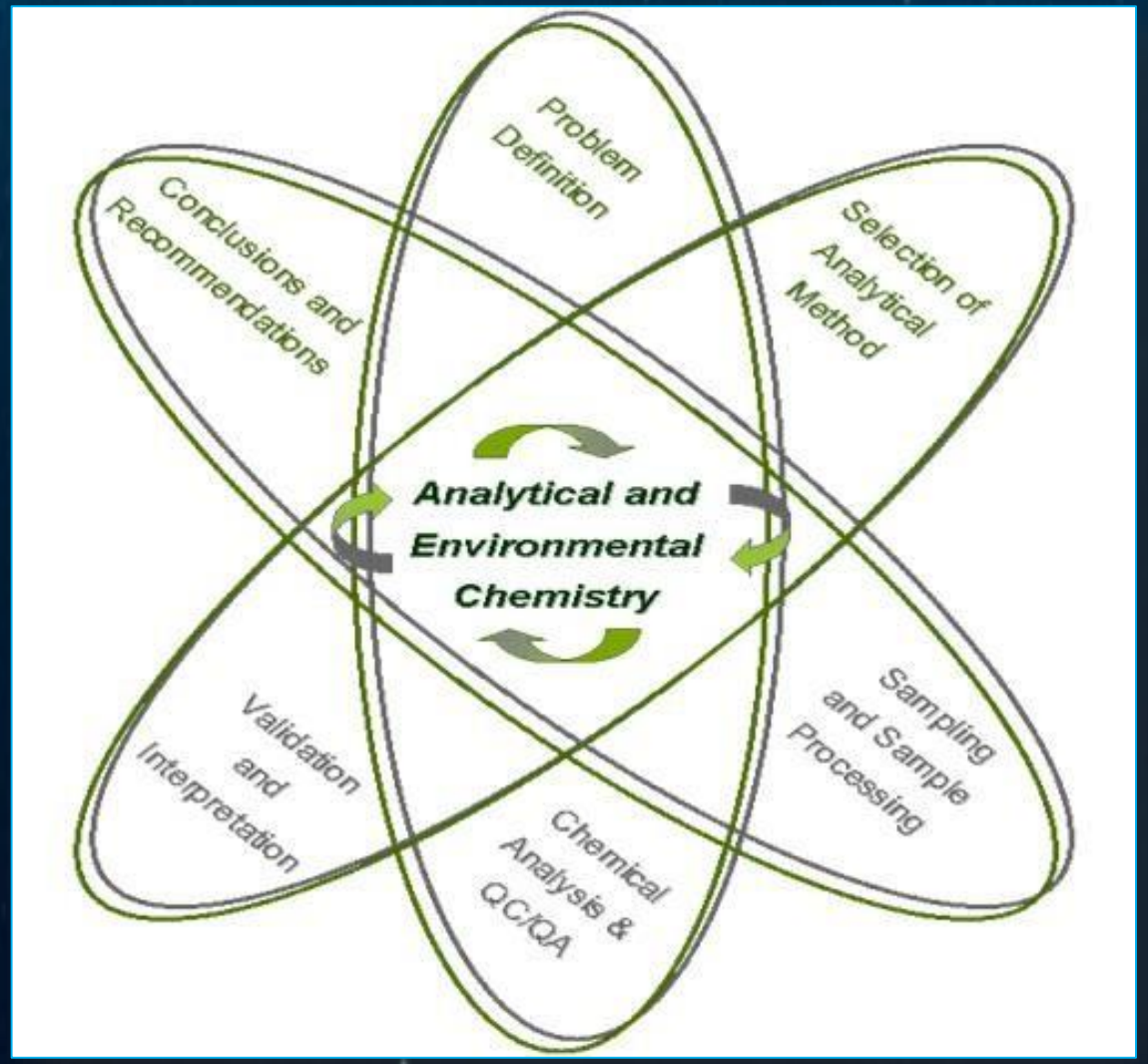
rendering from microplastics / cosmetics / clothing?

rate of transfer into body is unknown

HOW DO WE GO FROM HERE? A ROADMAP FOR COLLABORATIVE RESEARCH FROM MACRO TO NANO

For microplastics, besides the migration of inventories into monitoring programs, there is a need for inception of risk analysis methodologies incorporating the concept of aged (environmental) plastic materials, and analytical chemistry concepts fit for purpose.

For nanoplastics, there is a need for fundamental research as it happens in the field of nanomaterials. Environmental nanoplastics most likely will experience surface ‘bio-transformation’ and will develop a biomolecular corona with changes in functionality in a rather unpredictable manner.


Problem Definition
Selection of Analytical Method
Sampling and Sample Processing
Chemical Analysis & QC/QA
Validation and Interpretation
Conclusions and Recommendations
Analytical and Environmental Chemistry