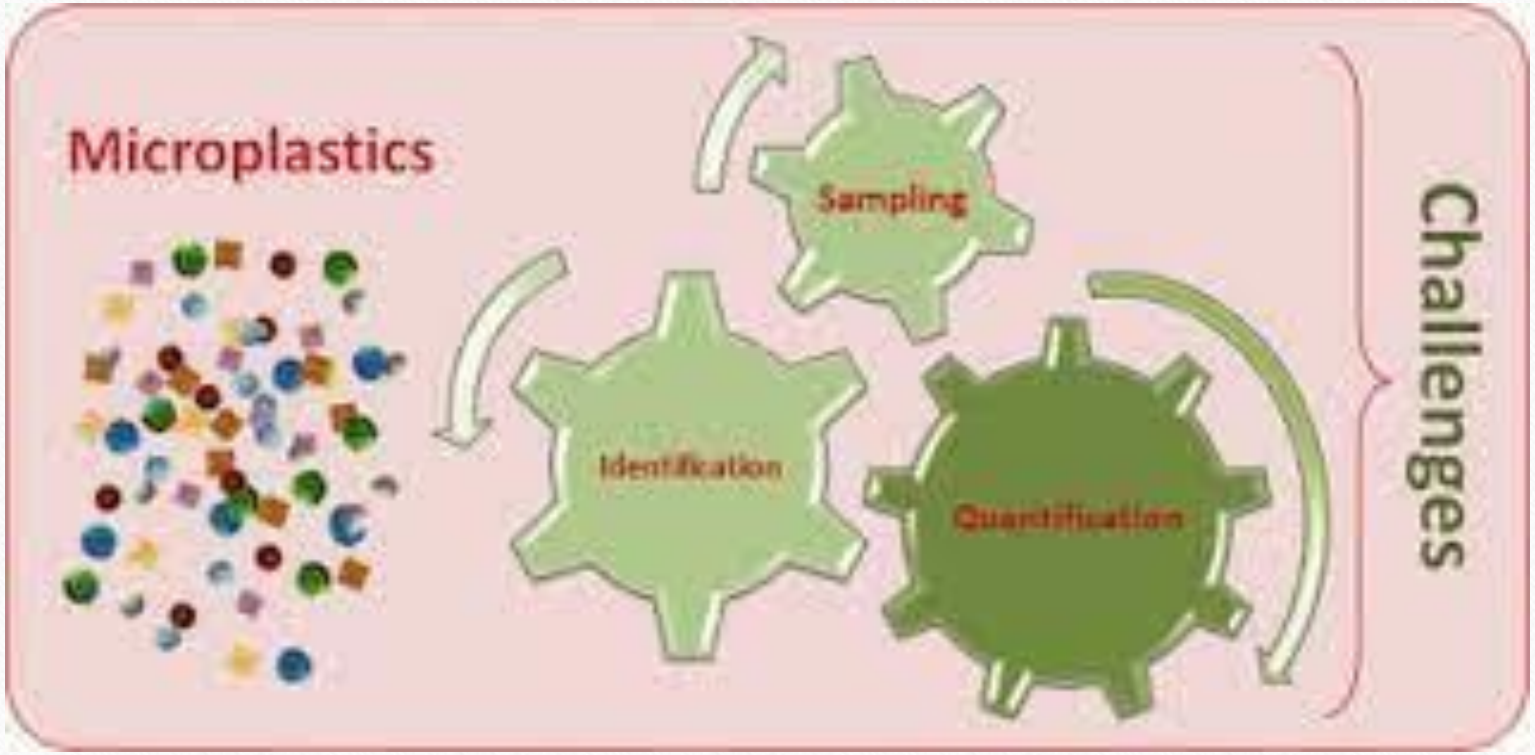
Microplastics in the environment

LECTURE 3


Microplastics
Sampling
Identification
Quantification
Challenges

Microplastics are emerging pollutants ubiquitous in marine and coastal environments.

- World production of plastic surpassed the 320 million tons mark in 2016, most of which is intended for packaging, i.e., for immediate disposal .
- Consequently, these materials greatly contribute to the generation of waste and it is estimated that between 5 and 13 million tons leaks into the World's oceans every year.
- Microplastics can be present in the environment as manufactured microplastics (known as **primary microplastics**) or resulting from the continuous weathering of plastic litter, which yields progressively smaller plastic fragments (known as **secondary microplastics**).

Primary microplastics are directly released into the environment as small plastic particles. These are intentionally engineered particles, like those found in some consumer and industrial products. Cosmetics have used microplastics as abrasives.

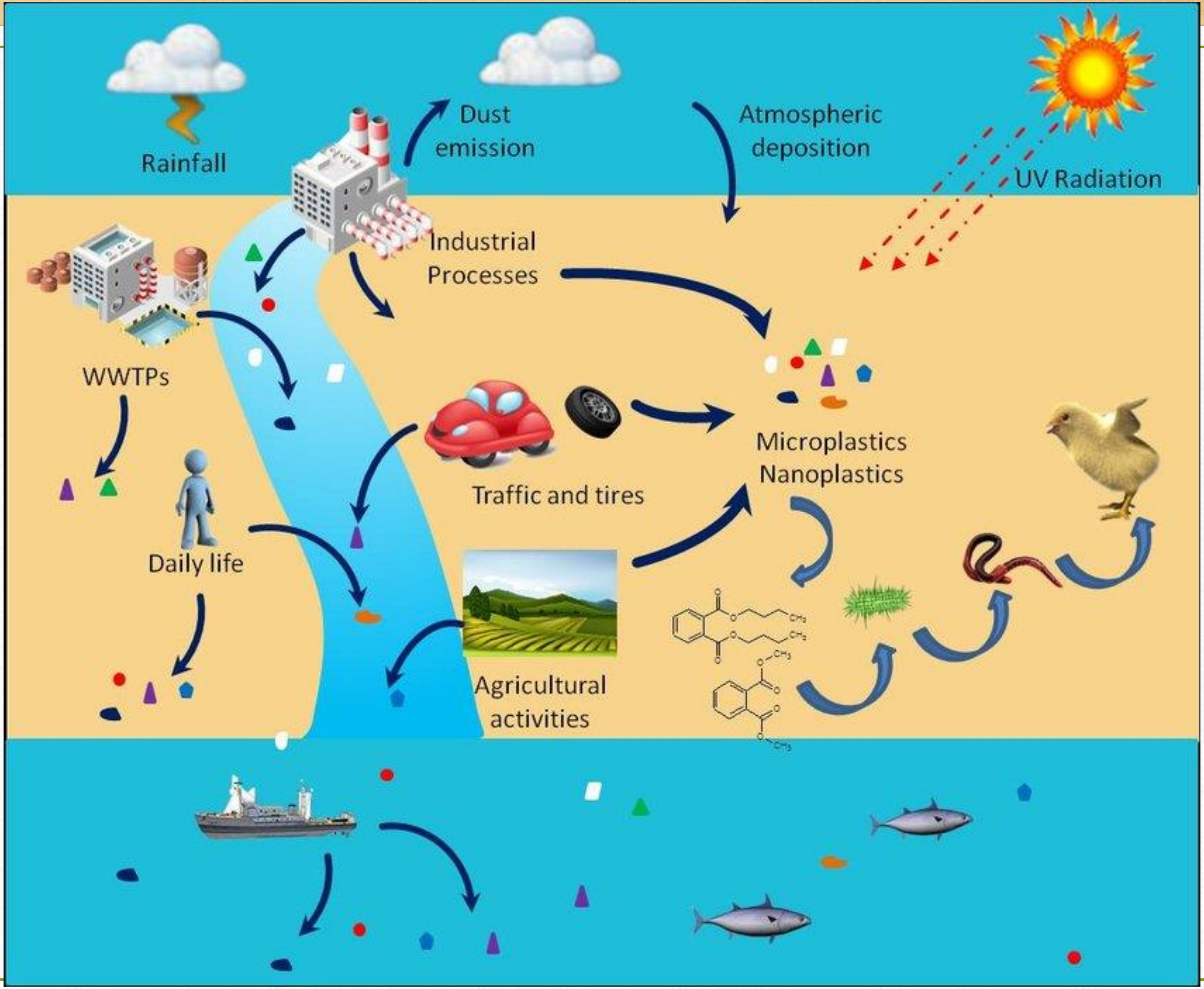
Secondary microplastics are the result of the degradation of large plastic waste, like plastic bags and bottles, into smaller plastic fragments when exposed to our environment

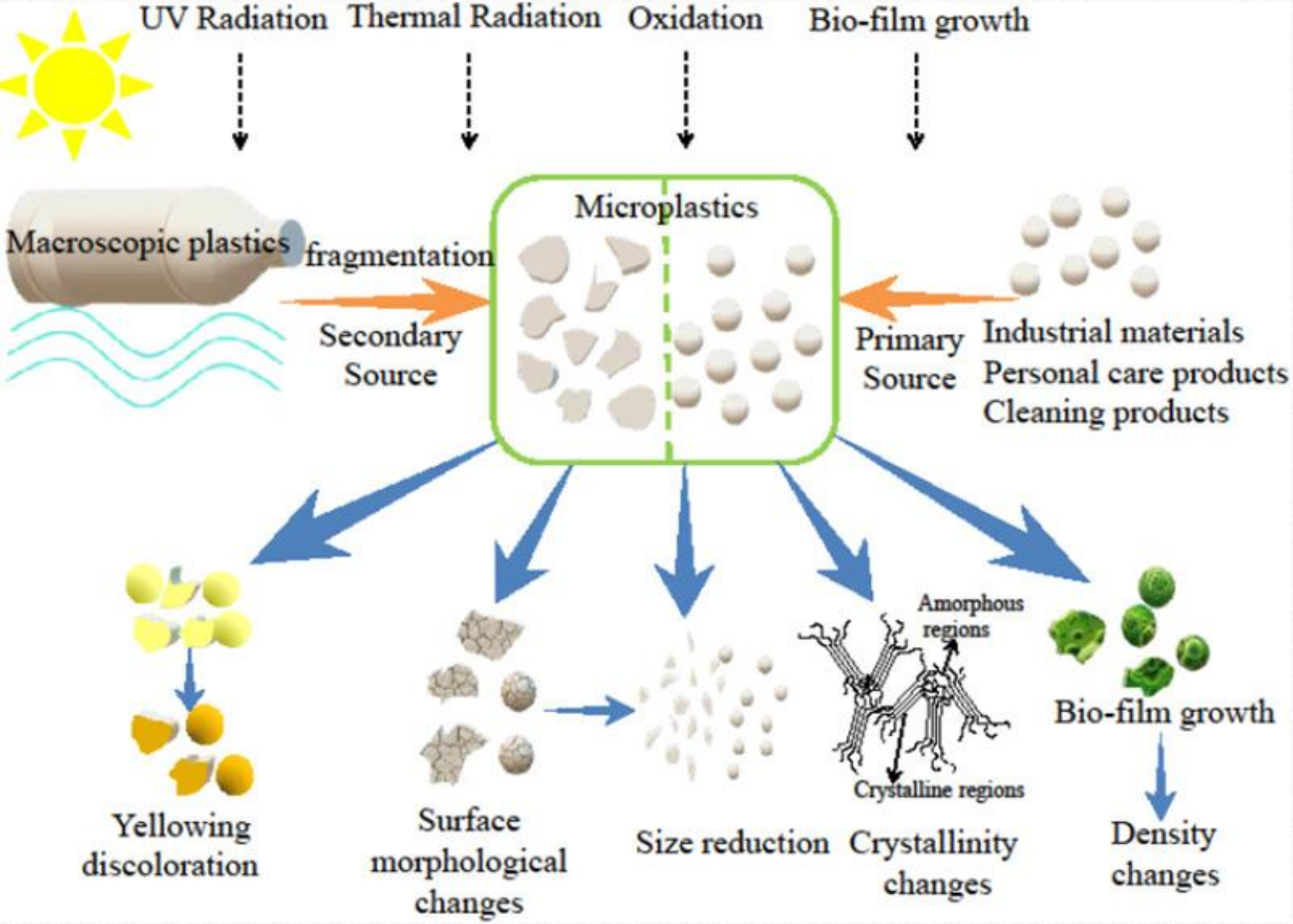
Why produce microplastics?

Manufacturers engineer primary microplastics because of the unique physical and chemical properties created by its small scale. Those properties include durability, rigidity and abrasiveness.

Density, size, shape and composition influence its properties.

Scientists use microplastics in many areas, including cosmetics, personal care, detergents, paints/coatings/inks, industrial abrasives, agriculture, pharmaceuticals, wastewater treatment and construction.


Rainfall
Dust
emission
Atmospheric
deposition
UV Radiation
Industrial
Processes
WWTPs
Traffic and tires
Microplastics
Nanoplastics
Daily life
Agricultural
activities


UV Radiation
Thermal Radiation
Oxidation
Bio-film growth
Macroscopic plastics
fragmentation
Secondary Source
Microplastics
Primary Source
Industrial materials
Personal care products
Cleaning products
Amorphous regions
Crystalline regions
Bio-film growth
Yellowing discoloration
Surface morphological changes
Size reduction
Crystallinity changes
Density changes

- When inappropriately dumped or mismanaged, plastic waste can accumulate in both terrestrial and marine environments and, once released, it may be subjected to degradation by several agents or routes,
- **such as solar radiation,**
- **mechanical forces,**
- **and microbial action**

- Degradation refers to a series of chemical reactions that breaks the structures of plastics polymers, which is often classified into **photo degradation, thermal degradation, biodegradation and thermos-oxidative degradation, according to the different weathering processes.**
- This leads to fragmentation and breakdown of those larger materials into microplastics, defined as plastic particles less than 5 mm and, eventually, nanoplastics, which range from 1 to 100 nm, though the latter has only been recently identified as potentially deleterious towards the environment and research is currently underway.

- In addition, these particles can be intentionally produced with micro- and nano-sizes and disposed directly into the environment.

Impact of microplastics to marine organisms

Microplastics in environments could be ingested by marine organisms, such as zooplankton fish turtles, and even seabirds. Microplastics pose risks to marine organism once they are ingested by these organisms.

A. Physically, microplastics lead to the mechanical damages to organisms. For example, microplastics could cause the blockage of the digestive tract, the intestinal damage (including the cracking of villi and the splitting of enterocytes), and even alter the filtering activity and phagocytosis of organisms .

These damages may finally lead to the death of organisms. Moreover, microplastics could accumulate in food web by predation. For example, Setälä et al. (2014) found that microplastics were fed through pelagic food web (from zooplankton to mysid shrimps).

Cedervall et al. (2012) found that microplastics transferred from algae to zooplankton to goldfish. Thus, microplastics may accumulate in organisms in several alternate routes. Microplastics in seafood as protein sources may also cause potential health risks to human.

B. Chemically, microplastics in aqueous environments would sorb and accumulate pollutants.

The ingestion of contaminated microplastics may therefore introduce toxic pollutants to marine organisms, and even to food. In this sense, microplastics act as vectors for toxic pollutants. But there are still no clear evidence for the effect of trophic transfer of microplastics and contaminants from food web to human health.

Concentrations of pollutants on microplastics in global marine and coastal environments
Microplastics could accumulate pollutants, such as **metals ions, and organic pollutants** from surrounding water because of their small size, huge specific area, and hydrophobic nature.

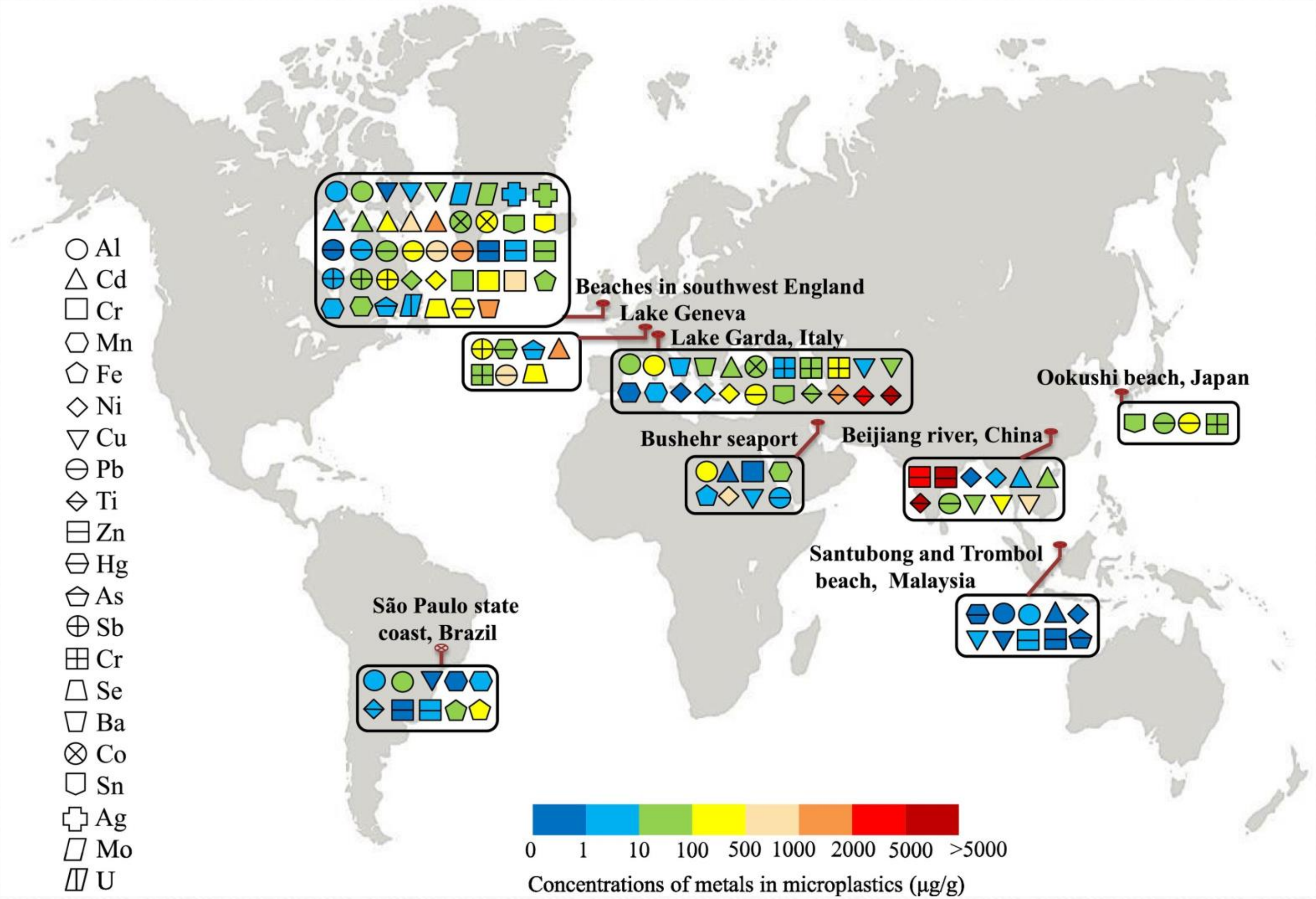
Types of pollutants

1. Heavy metals

At low initial concentrations (<20 μg/L), the uptakes of Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn by microplastics are ranging from 0.0004 to 2.78 μg/g

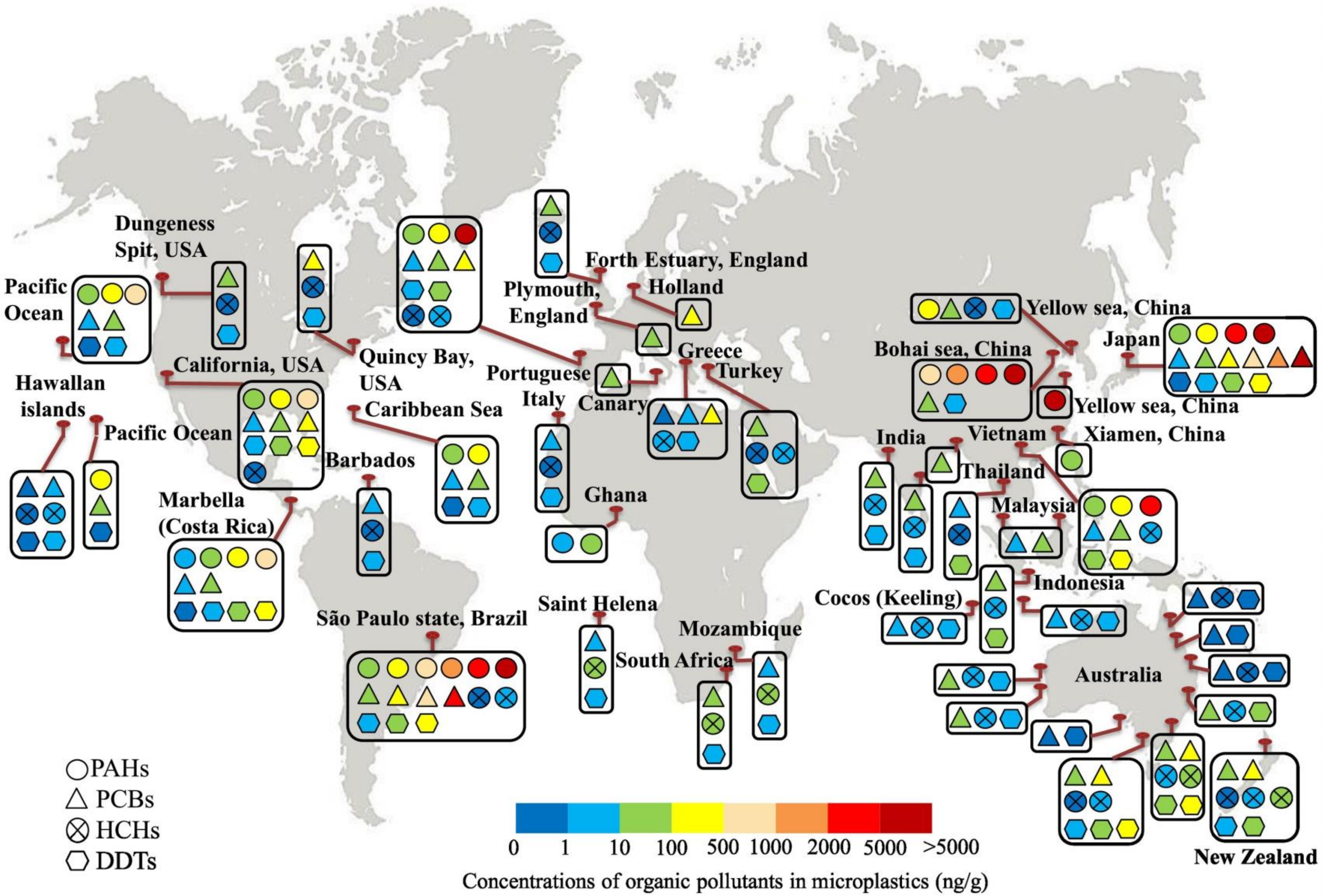
The average concentrations of metals on microplastics are distinct in different sampling locations. The concentrations of metals on microplastics from beaches of inland rivers/lakes in big cities (such as Beijiang River, China, Lake Garda, Italy, and Lake Geneva) are higher than coastal areas and remote areas (such as Santubong and Trombol in Kuching, Malaysia).

The local factors, such as industrialization of the sampling locations and the presence of anthropogenic activities may affect the concentrations of metals on microplastics.


Al
Cd
Cr
Mn
Fe
Ni
Cu
Pb
Ti
Zn
Hg
As
Sb
Cr
Se
Ba
Co
Sn
Ag
Mo
U
Beaches in southwest England
Lake Geneva
Lake Garda, Italy
Ookushi beach, Japan
Bushehr seaport
Beijiang river, China
Santubong and Trombol beach, Malaysia
São Paulo state coast, Brazil
0 1 10 100 500 1000 2000 5000 >5000
Concentrations of metals in microplastics (μg/g)

2.Organic pollutants

Organic pollutants with different polarity and hydrophobicity show different affinities to microplastics. Organic pollutants (PAHs, PCBs, HCHs, and DDTs) on microplastics. PCBs, PAHs and HCHs on microplastics from big cities, small cities, and remote areas, suggested that the pollutants concentrations on microplastics from big cities were almost an order of magnitude higher than those from small cities and remote areas. In the case of HCHs and DDTs, the concentrations on microplastics are lower than PAHs and PCBs, especially in remote areas. For most studied areas, the concentrations of HCHs are <10 ng/g. Therefore, Microplastics have different affinities for different kinds of pollutants.


Dungeness Spit, USA
Pacific Ocean
California, USA
Hawallan islands
Pacific Ocean
Quincy Bay, USA
Caribbean Sea
Barbados
Marbella (Costa Rica)
São Paulo state, Brazil
Forth Estuary, England
Plymouth, England
Holland
Portuguese
Italy
Canary
Greece
Turkey
Ghana
Saint Helena
South Africa
Mozambique
Yellow sea, China
Bohai sea, China
Japan
Yellow sea, China
Xiamen, China
India
Vietnam
Thailand
Malaysia
Indonesia
Cocos (Keeling)
Australia
New Zealand
PAHs
PCBs
HCHs
DDTs
0 1 10 100 500 1000 2000 5000 >5000
Concentrations of organic pollutants in microplastics (ng/g)

C.**Biologically,** microplastics are inclined to be colonized by microorganisms. Microplastics could influence the evolution of microbial communities and the exchange of genes (such as antibiotic resistance genes and metal resistance genes) between different bacterial taxa (Yang et al., 2019). Yang et al. (2019) suggested that the microbial community composition was the determining factor of the antibiotic resistance genes profile.

The World Health Organization reported in 2019 that the current level of microplastics in drinking water doesn't pose a health risk—yet.

But the group said we need to know more.
Researchers from **Johns Hopkins** looked at the impact of eating seafood contaminated with microplastics. Their conclusion? The accumulated plastic we take in could damage the immune system and upset a gut's balance.
Still, the research on health effects are slim.
Recent research, through particle analysis and Raman spectroscopy has begun to identify various microplastic types. Scientist are developing sampling, extraction and analysis methods so we can trace these particles back to its sources. That way, we can create public policy to address this potential threat.

ANALYSIS OF MICROPLASTICS,

1. Sampling and sample handling

Microplastics can be found throughout the water column, in numerous types of sediments and across various tissues and cells of multiple organisms from aquatic environment. Various types of equipments are used for sampling of microplastics in seawater.

The net mesh sizes vary widely, ranging from 53 mm to 3 mm, thus influencing the volume and nature of the microplastics obtained from samples .
Specifically, for the marine environment (sea surface, water column, sediment, and biota), sampling methods may be categorized according to the classification proposed by Hidalgo-Ruz et al.

1) selective sampling, where the samples (usually sediment) are collected by direct extraction, as they are identifiable to the naked eye (particles between 1 and 5 mm Ø);
2) bulk sampling, where the volume of the sample (water or sediment) is entirely collected without reduction of the sample; and,
3) volume-reduced sampling, which reduces the volume of bulk sample (water or sediment), only preserving the portion of interest.

2. Identification and quantification of micro- and nanoplastics

2.1. Optical techniques The first examination of the sample is frequently performed by visual observation, which can be achieved through simple naked eye observation or assisted by optical microscopy.

Characteristics like colour, shape, surface texture, and any other characteristic that may contribute for distinguishing microplastics from other particles, are used for their separation from the other components.

2.2. Electron microscopy

The use of SEM for identification of microplastics provides extremely clear and high-magnification images of plastic particles, facilitating the discrimination of microplastics from organic particles but it could also have some limitations.

When coupled to EDS (SEM-EDS), the elemental composition of plastic particles is obtained, thus discerning carbon-dominant plastics from inorganic particles.

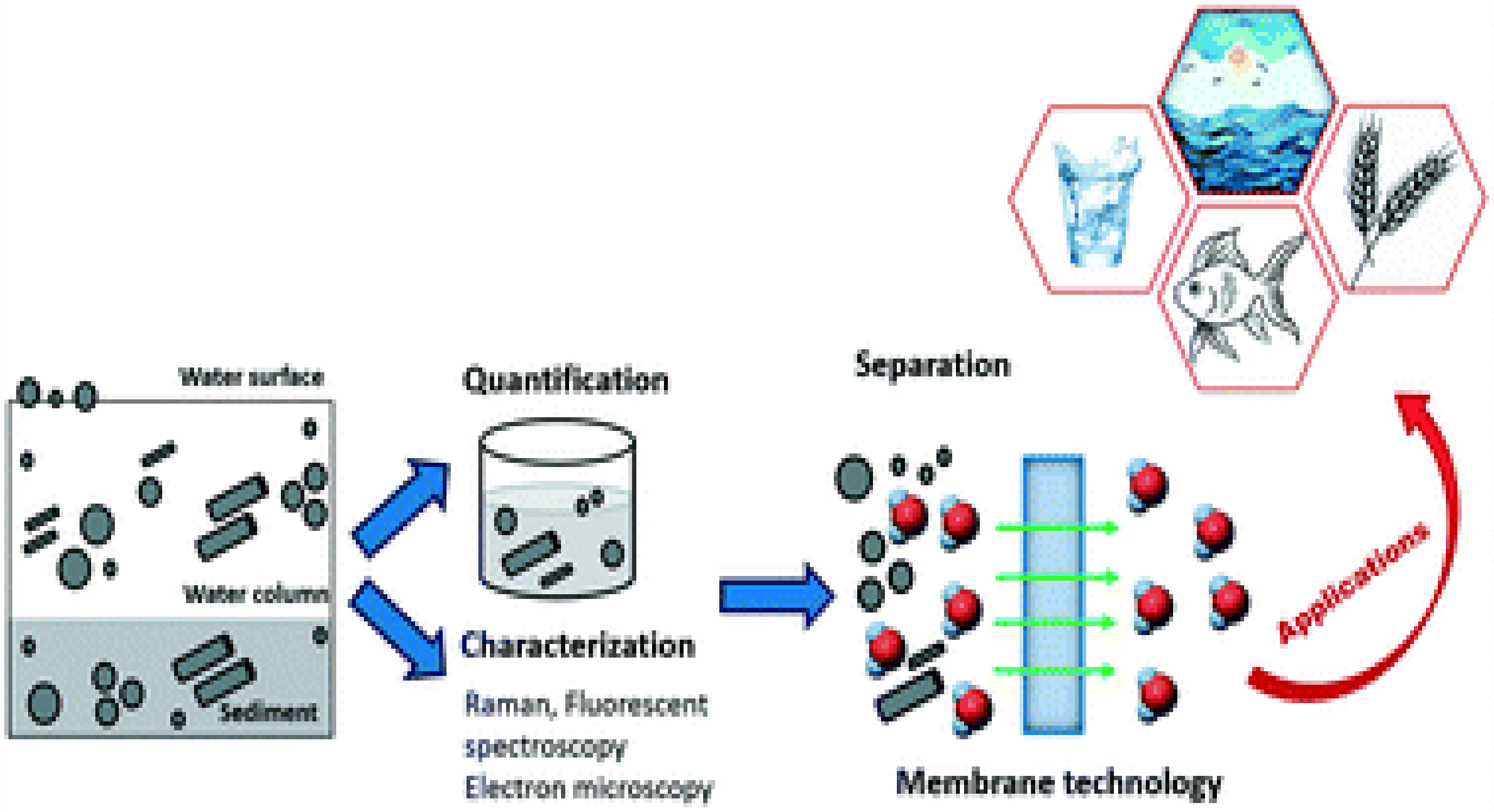
2.3. Infrared and Raman spectroscopies

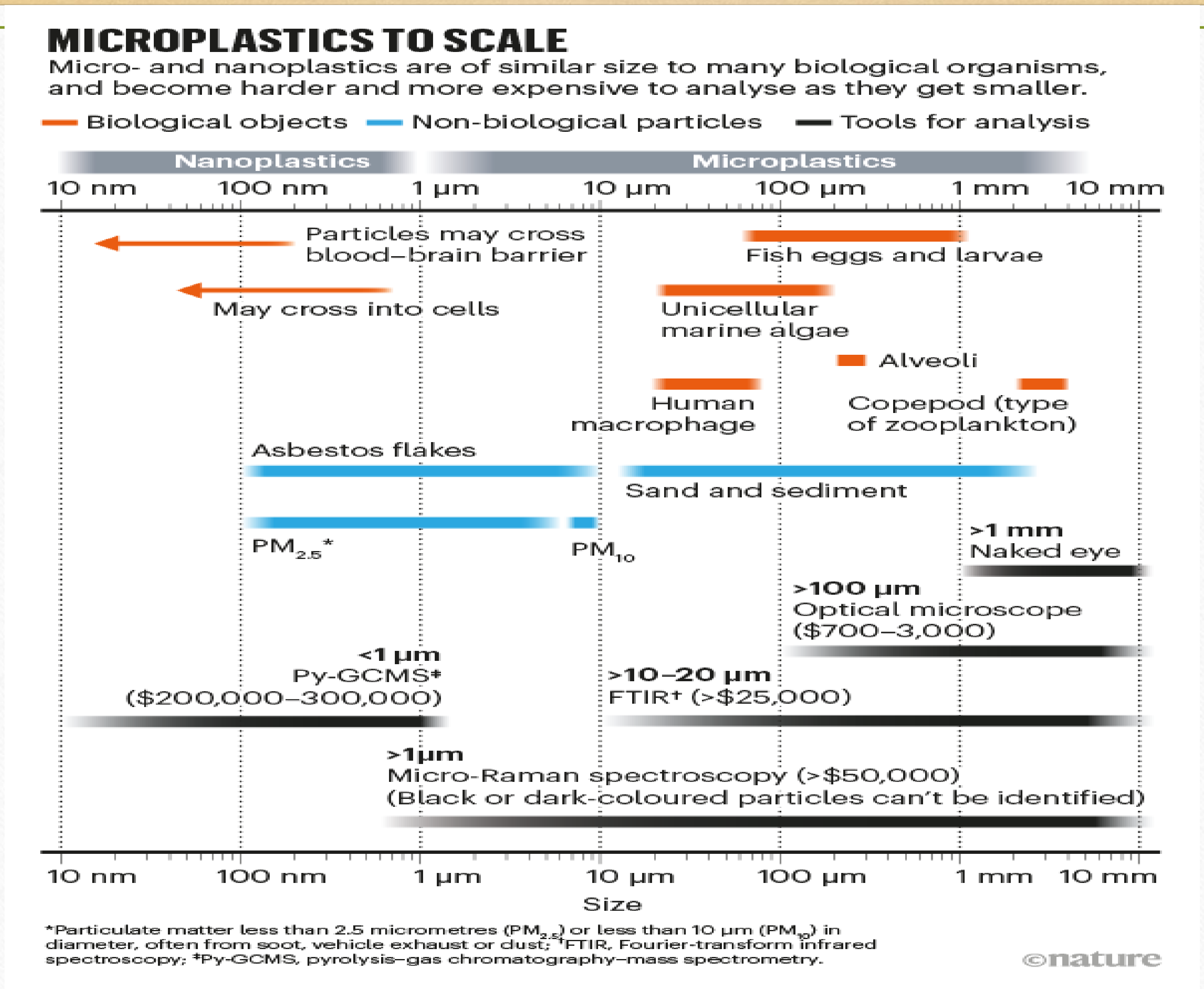
Infrared and Raman spectroscopies are the two most commonly used techniques for the characterization of microplastics and are, in fact, recommended by the Marine Strategy Framework Directive Technical Subgroup. These spectroscopic techniques required low sample amounts with minimal sample preparation.

Raman spectroscopy is able to assess microplastic samples higher than 1 mm while infrared spectroscopy only could identify microparticles higher than 10-20 microm. **FTIR spectroscopy** is frequently used for the qualitative analysis of microplastics (>10 microm), as the polymer type can be quickly and directly identified when their spectra is compared with those of known plastics. With FTIR spectroscopy, the functional groups present in microplastics polymers can be identified.

2.4. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) is a destructive technique that has also been described for the characterization of microplastics in terms of identification of polymer type, by analysing their thermal degradation products. This technique eliminates the need of pre-treatment of sample since it directly examines the solid polymer sample; in addition, only a small quantity of sample is analysed in one measurement.


Water surface
Water column
Sediment
Quantification
Characterization
Raman, Fluorescent
spectroscopy
Electron microscopy
Separation
Membrane technology
Applications


MICROPLASTICS TO SCALE
Micro- and nanoplastics are of similar size to many biological organisms, and become harder and more expensive to analyse as they get smaller.
Biological objects
Non-biological particles
Tools for analysis
Nanoplastics
Microplastics
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
10 mm
Particles may cross blood–brain barrier
Fish eggs and larvae
May cross into cells
Unicellular marine algae
Alveoli
Human macrophage
Copepod (type of zooplankton)
Asbestos flakes
Sand and sediment
$PM_{2.5}$*
PM_{10}
>1 mm
Naked eye
>100 µm
Optical microscope ($700–3,000)
<1 µm
Py-GCMS‡
($200,000–300,000)
>10–20 µm
FTIR† (>$25,000)
>1µm
Micro-Raman spectroscopy (>$50,000)
(Black or dark-coloured particles can't be identified)
Size
*Particulate matter less than 2.5 micrometres ($PM_{2.5}$) or less than 10 µm (PM_{10}) in diameter, often from soot, vehicle exhaust or dust; †FTIR, Fourier-transform infrared spectroscopy; ‡Py-GCMS, pyrolysis–gas chromatography–mass spectrometry.
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The future works are recommended as follows:

1. To establish the standard methods for sampling and analyzing of microplastics in marine and coastal environments. The abundance, distribution and properties of microplastics in global environments need statistical monitoring and assessment based on the standard methods or criterion.
2. To relevant the laboratory studies and environmental application. Long term field sorption experiments are recommended in the future work.
3. To study the mechanisms of pollutants sorption on microplastics, and to evaluate the risk and fate of microplastics in environments.
4. To further study the interactions of microplastics and wider ranges pollutants, (e.g. radioactive heavy metals and antibiotics).
5. To evaluate the risk of microplastics to marine organisms and human. Studies to evaluate the microplastics as vectors to transport pollutants, especially toxic pollutants through food webs are needed in this sense.

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