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CENTRE FOR ENVIRONMENTAL AND MARINE STUDIES

Physicochemical Interactions of Microplastics and Pharmaceutical Residues

Teresa Rocha-Santos,
Damià Barceló

Global Detection of pharmaceutical substances in drinking/tap waters, groundwater, and surface waters.

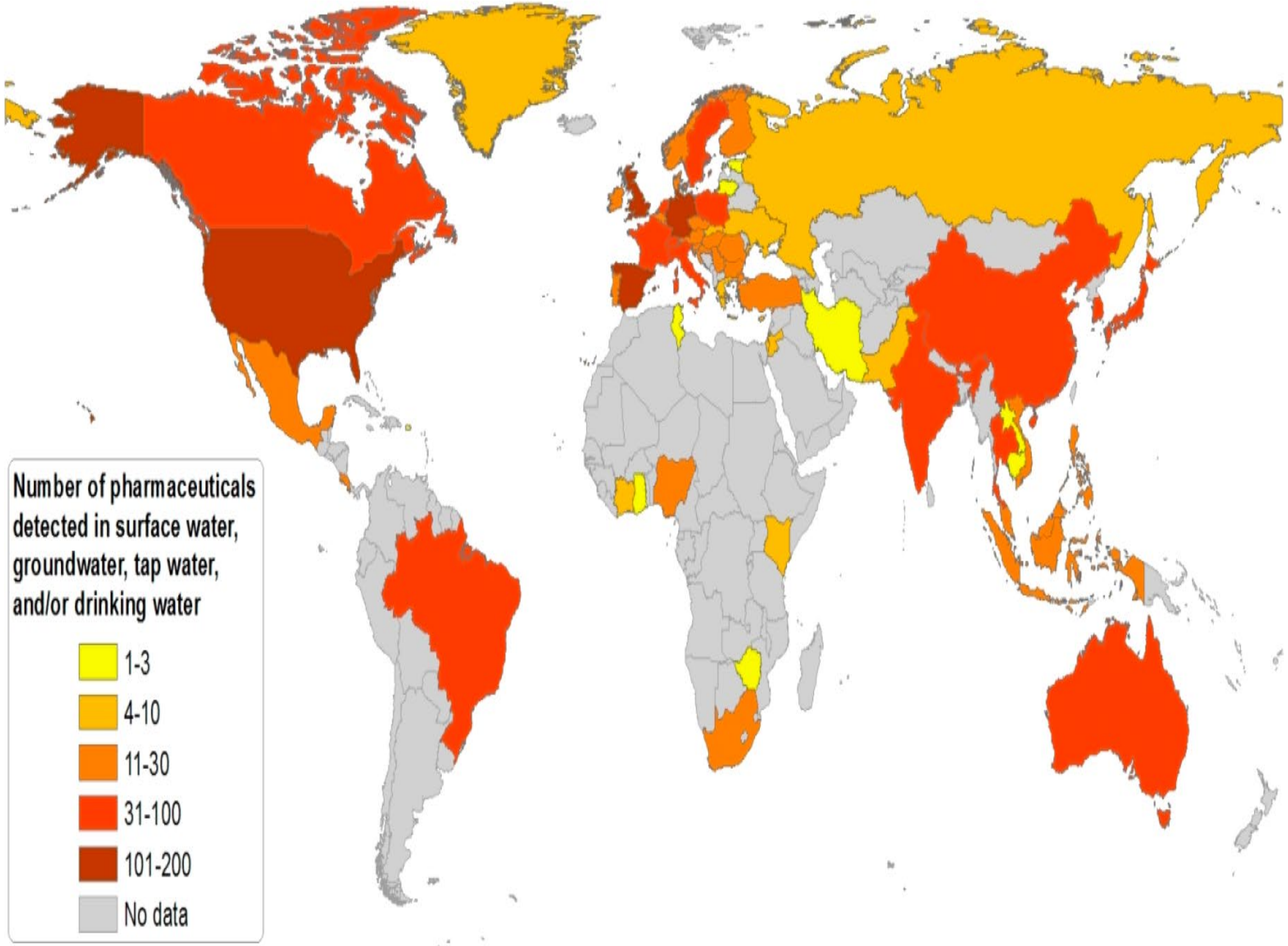

Figure from DOI: 10.1021/acs.chemrev.8b00299

- Detected 631 pharmaceuticals in 713 compounds tested
- Pharmaceuticals were found in 71 countries

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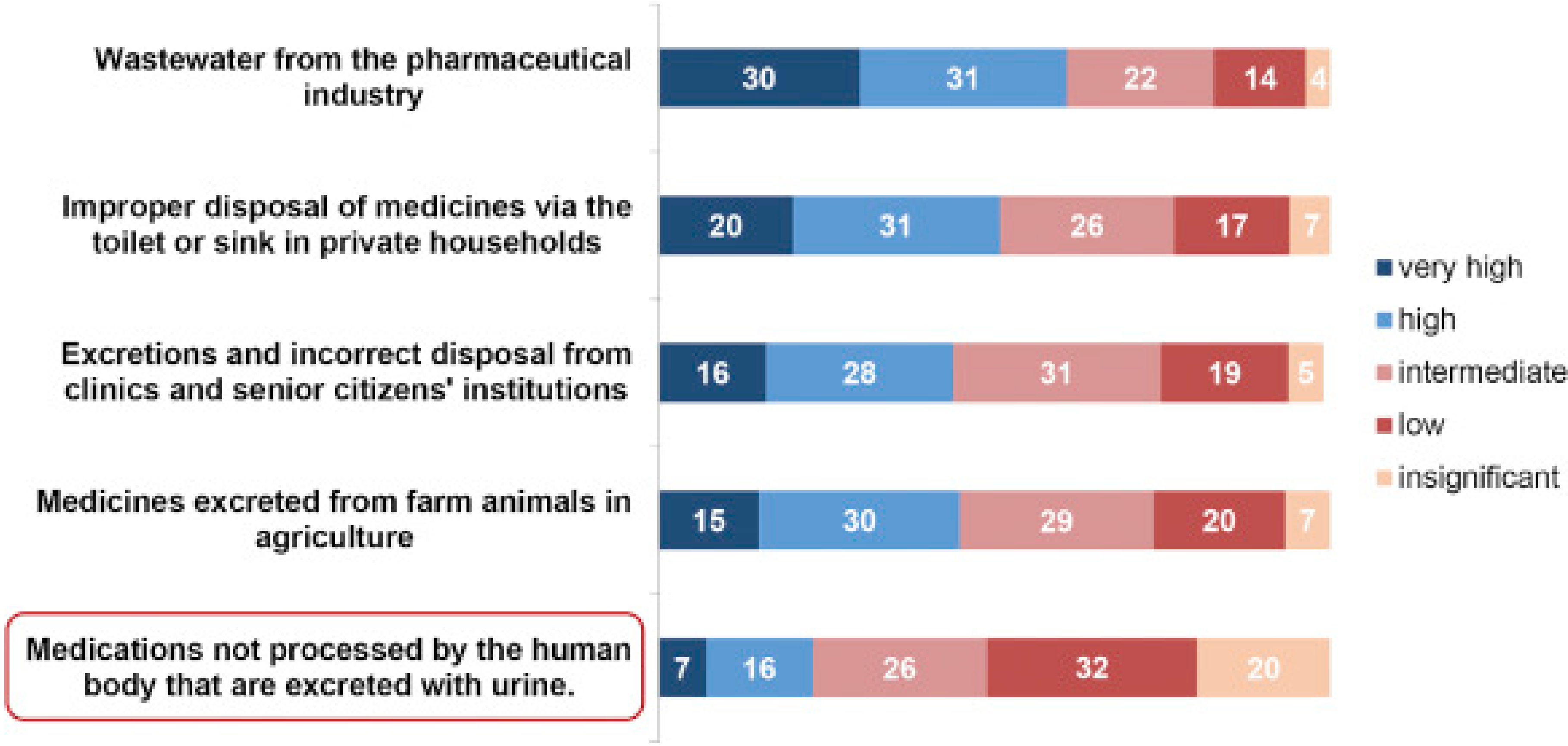
Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods

Manvendra Patel, Rahul Kumar, Kamal Kishor, Todd Mlsna, Charles U. Pittman Jr., and Dinesh Mohan*

Cite this: *Chem. Rev.* 2019, 119, 6, 3510–3673
Publication Date: March 4, 2019
https://doi.org/10.1021/acs.chemrev.8b00299

- Antibiotics, followed by analgesics, are the most frequently detected compounds
- Results vary depending on the country, region, area consumption pattern, and manufacturing industry locations
- The frequency of pharmaceutical occurrence varies from sample to sample
- Most pharmaceutical environmental detections have been in specific samples including hospital effluents, effluents, and influents of sewage treatment plants, groundwater, surface water, and drinking water.

Pharmaceutical residues in the water can have different causes. Which of the following causes do you think are responsible for the presence of pharmaceutical residues in the water?



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Management of Emerging Public Health Issues and Risks

Multidisciplinary Approaches to the Changing Environment

2019, Pages 189-224

Chapter 8 - Risk Perception of Pharmaceutical Residues in the Aquatic Environment and Precautionary Measures

Konrad Götz [1], Audrey Courtier [2], Melina Stein [1], Linda Strelau [1], Georg Sunderer [1], Rodrigo Vidaurre [3], Martina Winker [1], Benoit Roig [2]

https://doi.org/10.1016/B978-0-12-813290-6.00008-1

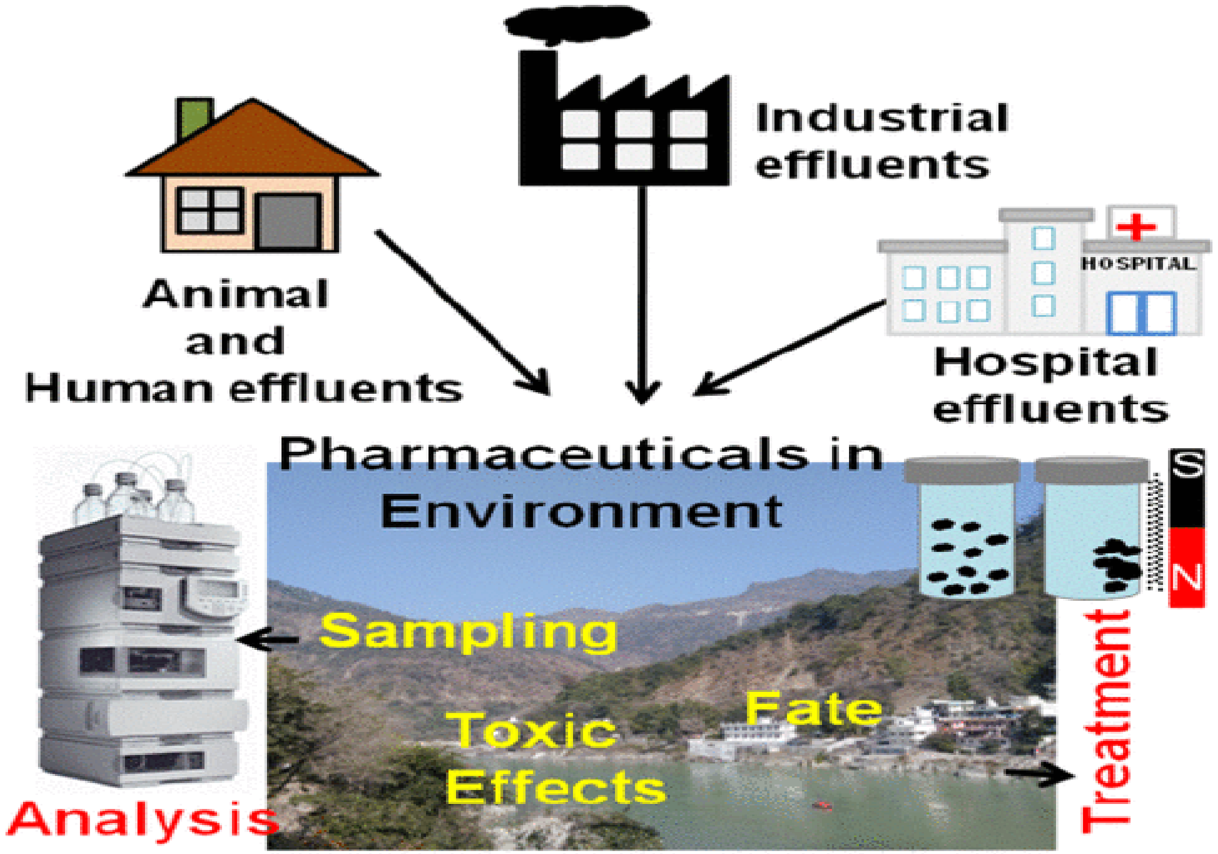


Figure from DOI: 10.1021/acs.chemrev.8b00299

Pharmaceutical concentrations follow the general order:

Industrial effluents > hospital effluents > wastewater treatment plant effluents > surface water > groundwater > drinking water.

Advanced analytical techniques (such as GC-MS/MS, LC-MS/MS, UPLC/MS):

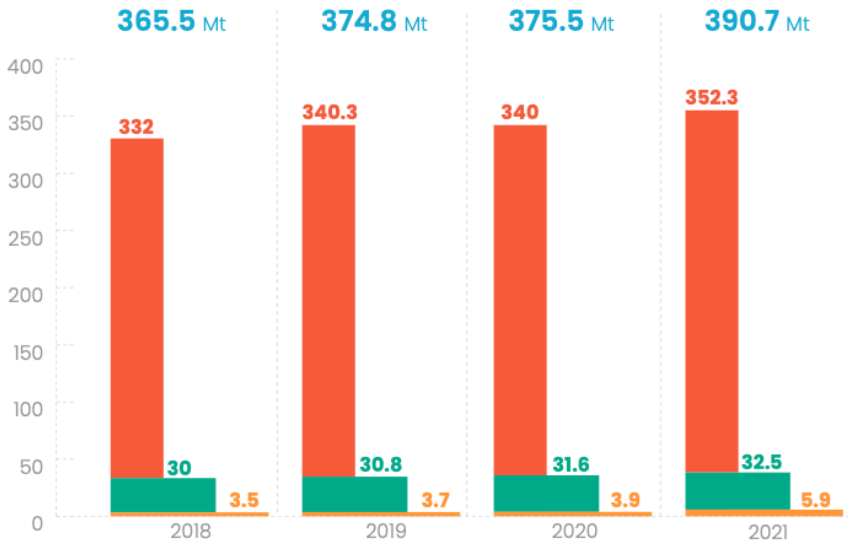
- allowed the detection of pharmaceuticals in environmental samples in the μg/L and ng/L concentration ranges
- enabled the determination and quantification of almost 3000 biologically active compounds in the environment

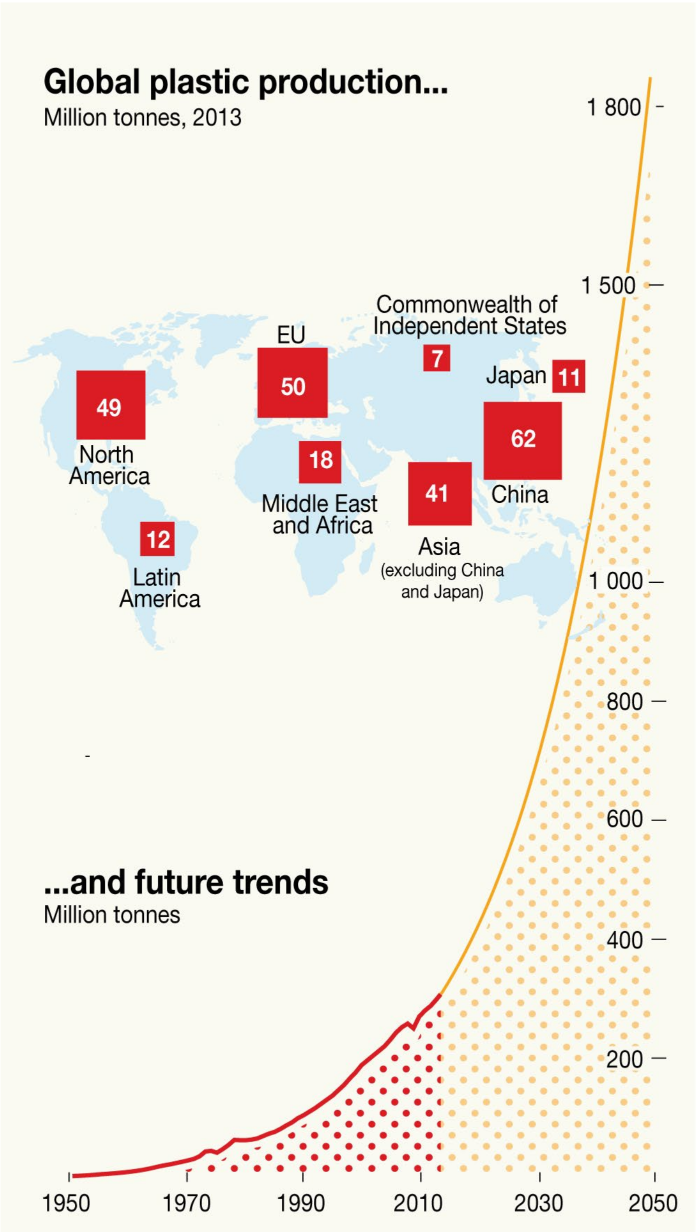
World plastics production* evolution

After a stagnation in 2020 due to the Covid-19 pandemic, the global plastics production increased to 390.7 million tonnes in 2021.

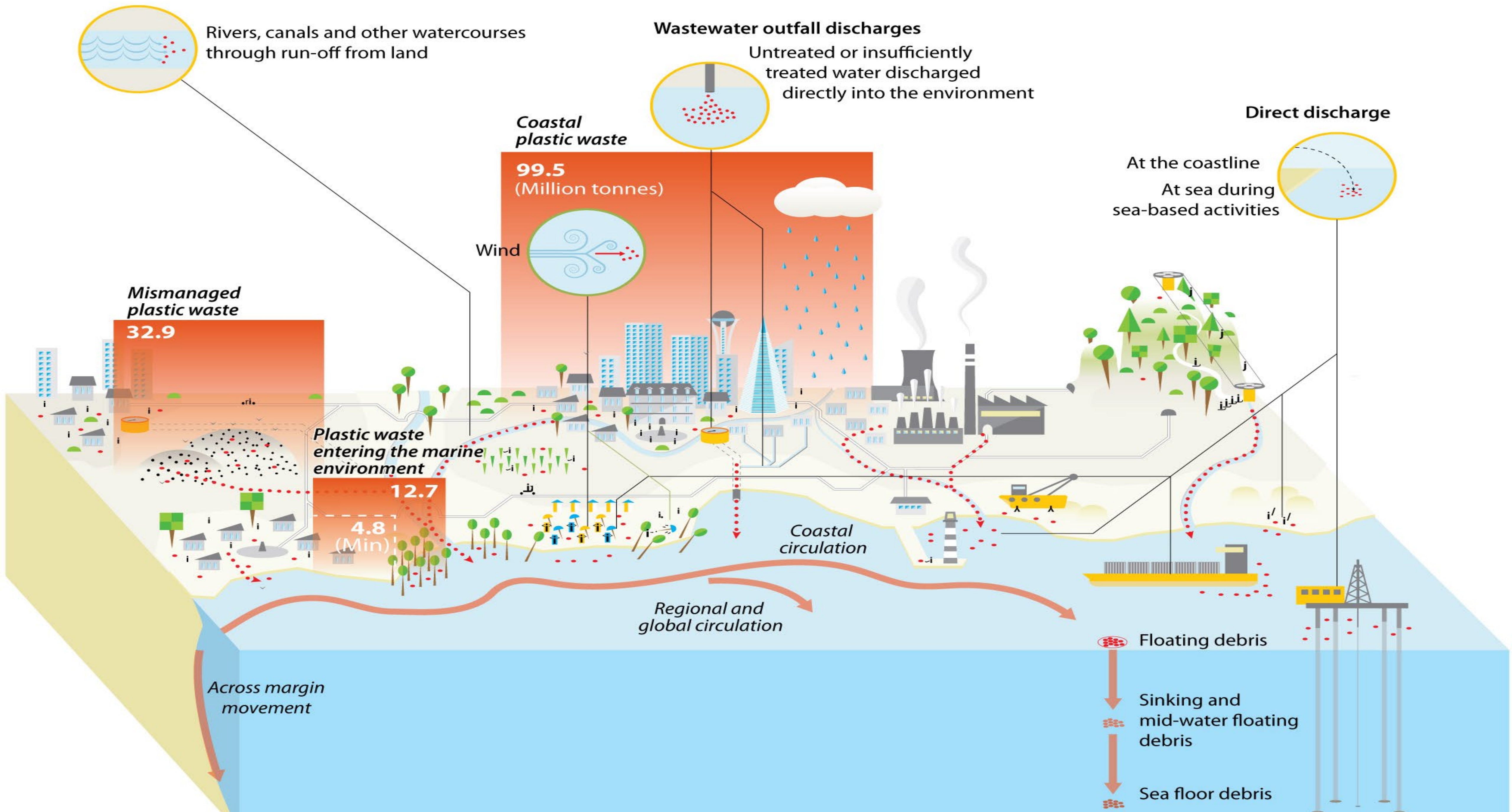
in million tonnes

- Fossil-based plastics[1]
- Post-consumer recycled plastics[2]
- Bio-based plastics (including bio-attributed plastics in 2021 data)[3]





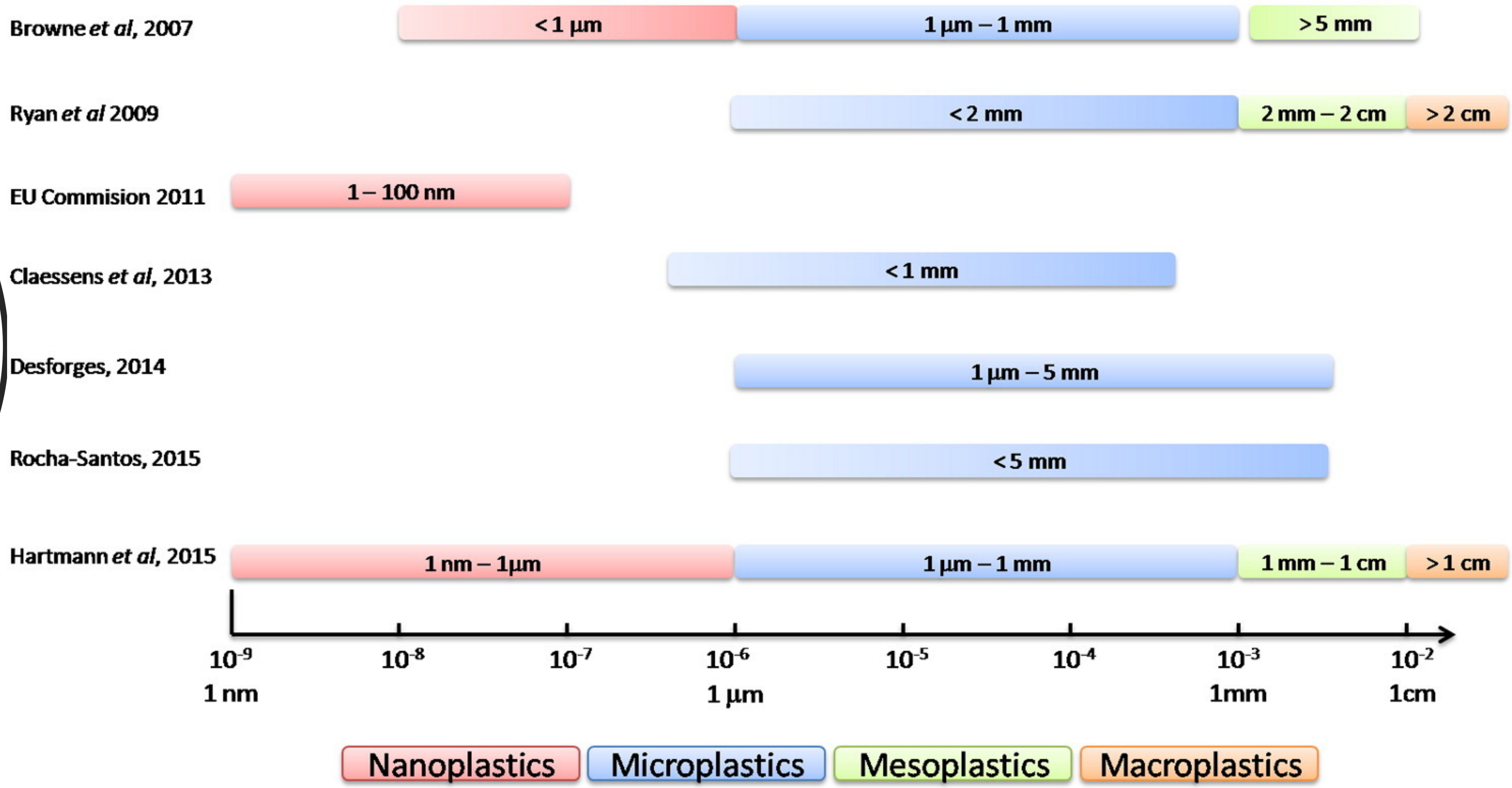
Source: Ryan, A Brief History of Marine Litter Research, in M. Bergmann, L. Gutow, M. Klages (Eds.), Marine Anthropogenic Litter, Berlin Springer, 2015; Plastics Europe

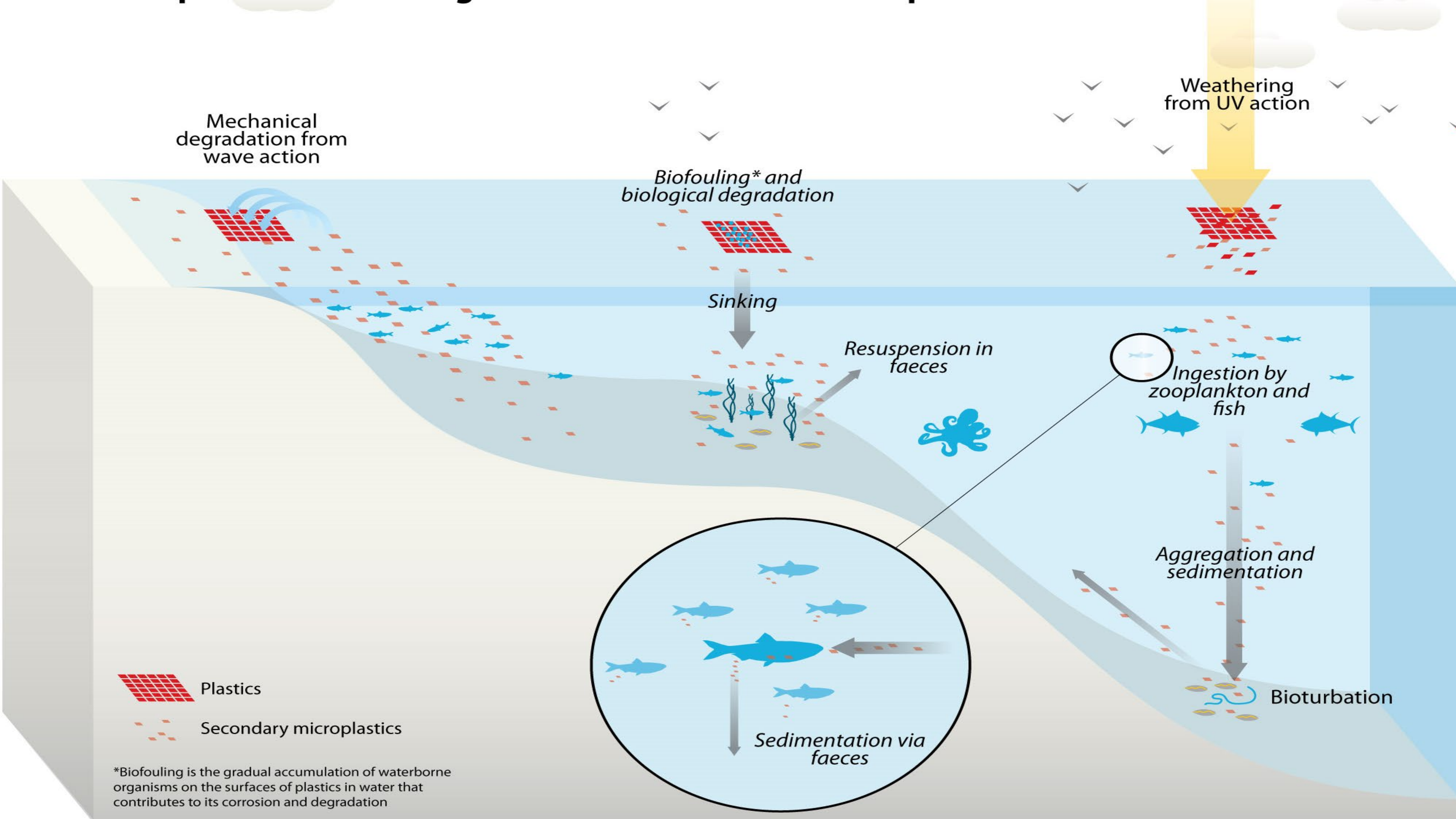


Source: Jambeck, J., R., et al., Plastic waste inputs from land into the ocean, Science, 2015; GRID-Arendal

GRID-Arendal and Maphoto/Riccardo Pravettoni

Plastics classification: size




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

Microplastics in freshwater samples

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Science of The Total Environment
Volume 897, 1 November 2023, 165414

Review

Interaction between antibiotics and microplastics: Recent advances and perspective

Shuting Zhuang [a], Jianlong Wang [b c]

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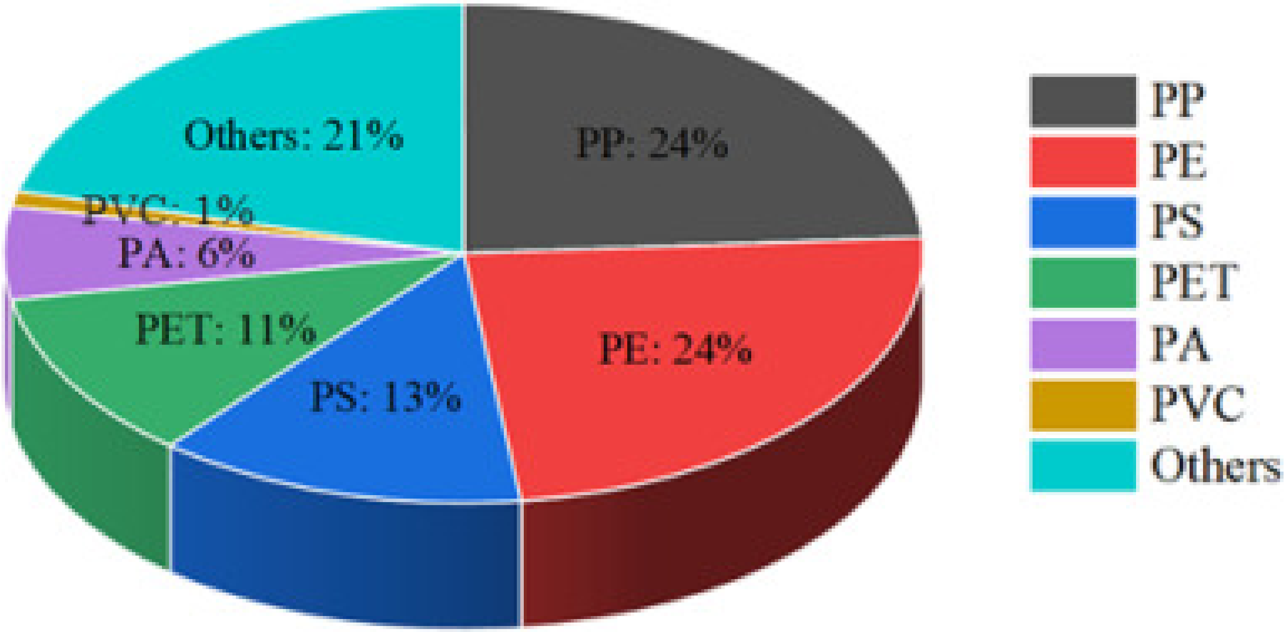

Fate and transport of Pharmaceuticals (PhAC) and Microplastics (MPs) in the marine environment

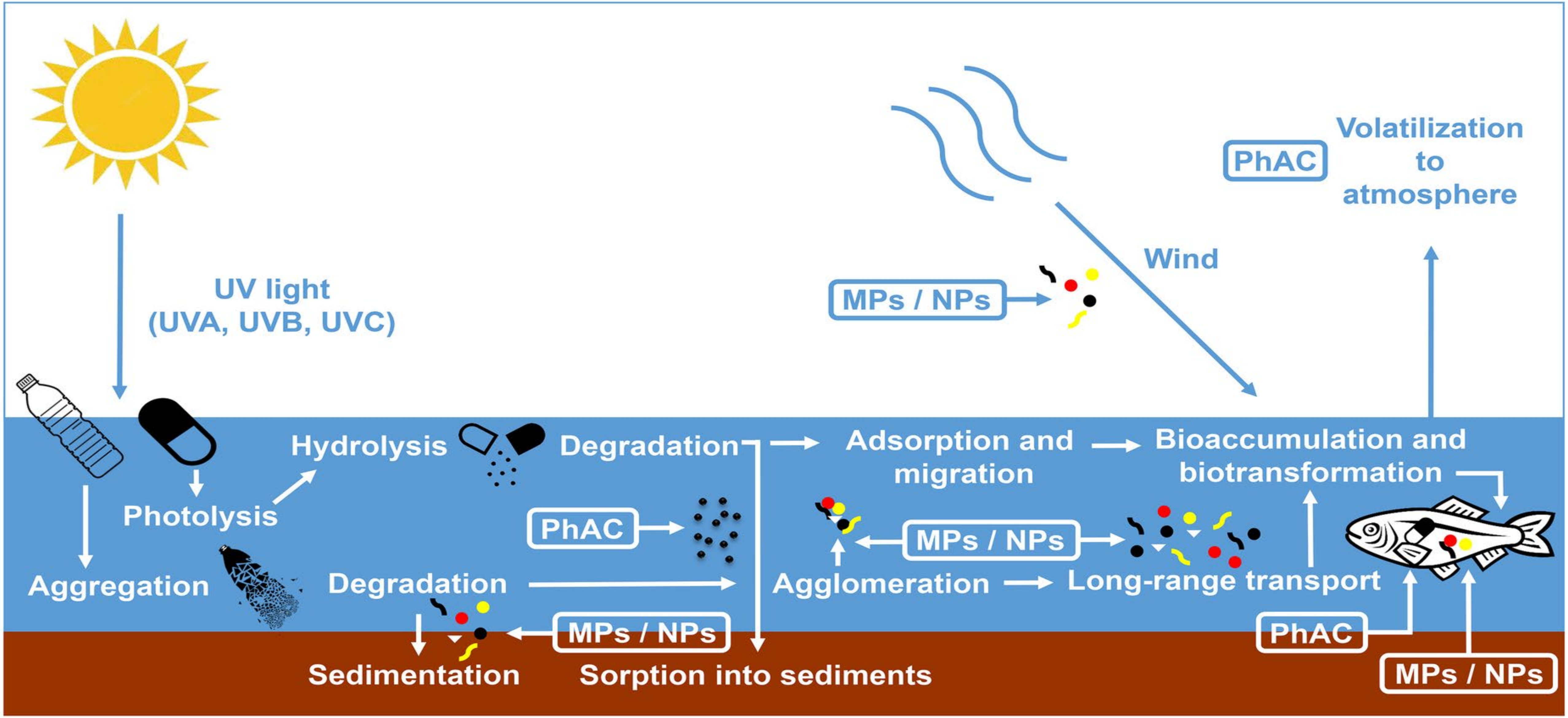

Figure 2 from https://doi.org/10.1007/s10661-022-09751-w

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Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods

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Publication Date: March 4, 2019
https://doi.org/10.1021/acs.chemrev.8b00299

Published: 19 September 2022

Sorption of pharmaceuticals over microplastics' surfaces: interaction mechanisms and governing factors

Rajshekher Upadhyay, Surya Singh & Gurjot Kaur

Environmental Monitoring and Assessment **194**, Article number: 803 (2022) | Cite this article

ELSEVIER
Science of The Total Environment
Volume 753, 20 January 2021, 141981

Review

Microplastics physicochemical properties, specific adsorption modeling and their interaction with pharmaceuticals and other emerging contaminants

Yasmin Vieira [a], Eder C. Lima [b], Edson Luiz Foletto [c], Guilherme Luiz Dotto [a, c]

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ELSEVIER
Environment International
Volume 149, April 2021, 106367

Review article

Interactions between microplastics, pharmaceuticals and personal care products: Implications for vector transport

Thilakshani Atugoda [a], Meththika Vithanage [a], Hasintha Wijesekara [b], Nanthi Bolan [c], Ajit K. Sarmah [d], Michael S. Bank [e], Siming You [f], Yong Sik Ok [g]

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ELSEVIER
Case Studies in Chemical and Environmental Engineering
Volume 3, June 2021, 100079

Microplastics as vectors of pharmaceuticals in aquatic organisms – An overview of their environmental implications

Lúcia H.M.L.M. Santos [a, b], Sara Rodríguez-Mozaz [a, b], Damià Barceló [a, b, c]

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ELSEVIER
Science of The Total Environment
Volume 897, 1 November 2023, 165414

Review

Interaction between antibiotics and microplastics: Recent advances and perspective

Shuting Zhuang [a], Jianlong Wang [b c]

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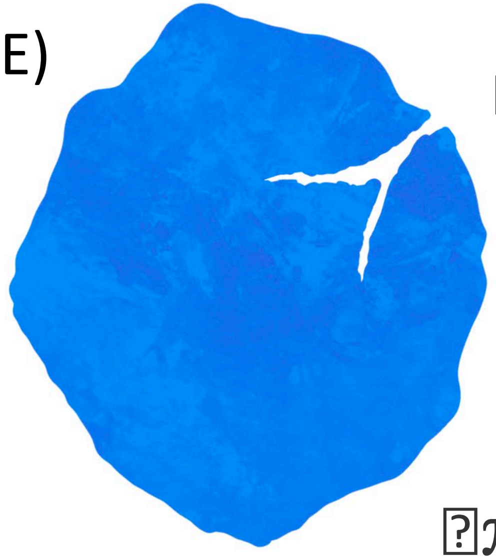
Interactions driving the sorption of pharmaceuticals onto the microplastics' surfaces

Partition
(ex: 17β-Estradiol /PP)

Electrostatic
(ex: Ciprofloxacin/PE)



Pore-filling mechanism

Hydrogen bonding
(ex: Diclofenac /PS, PP)

Van der Waals forces
(ex: Sulfamethoxazole /PE)

π-π interaction
(ex: levofloxacin / PS-COOH-NP)

Hydrophobic interaction
(ex: Tetracycline / PE, PP, PS)

Cation competition
(ex: Tylosin /PP)

Adapted from a https://doi.org/10.1007/s10661-022-10475-0 and https://doi.org/10.3390/molecules25081827

Environmental Factors

- pH
- Ionic strength
- Dissolved organic matter
- Mechanical weathering
- Photodegradation

Microplastics

- Type of polymer
- Surface charge
- Surface area
- Crystallinity
- Degree of weathering

Pharmaceuticals

- Log Kow
- pKa

Adapted from https://doi.org/10.1016/j.cscee.2021.100079 and https://doi.org/10.1016/j.envint.2020.106367

In-situ microplastic sorption experiments conducted in NYC waterways

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Science of The Total Environment

Volume 729, 10 August 2020, 138766

Assessing the sorption of pharmaceuticals to microplastics through in-situ experiments in New York City waterways

Debra L. Magadini [a], Joaquim I. Goes [b], Sarah Ortiz [c], John Lipscomb [d], Masha Pitiranggon [b], Beizhan Yan [b]

https://doi.org/10.1016/j.scitotenv.2020.138766

Virgin pre-production plastic pellets, ranging in diameter from 2.3 mm to 5 mm, of PET, HDPE, PVC, LDPE, PP were used.

Plastic shopping bags (LDPE) and plastic straws (PP) were cut into pieces ≤35 mm in size.

Pharmaceuticals were extracted from the filtered surface water using solid phase extraction.

The extract was analyzed for atenolol, sulfamethoxazole and ibuprofen by LC/MS/MS

Microplastics were removed from the surface water and then transferred into separate vials containing 1:1 methanol acetonitrile solution

The extracts were injected for analyzing atenolol, sulfamethoxazole and ibuprofen using LC/MS/MS.

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Higher level of pharmaceutics on locations close to WWTP discharge sites

Similar sorption coefficients of pharmaceutics among different plastics

Rapid biofouling appeared to be the predominant factor controlling the sorption

Sorption studies of pharmaceuticals such as antibiotics are generally performed:

- Non-environmentally relevant concentrations

  Environmental concentrations of antibiotics generally range from ng L^{-1} to µg L^{-1}
  Higher concentrations were used to assess the maximum adsorption capacity of microplastics.

- Non-environmentally relevant conditions

  Ex: 1 Pharmaceutical and 1 MP tested

- Experimental design not based on statistics

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Science of The Total Environment

Volume 701, 20 January 2020, 135021

Pharmaceuticals, pesticides, personal care products and microplastics contamination assessment of Al-Hassa irrigation network (Saudi Arabia) and its shallow lakes

Yolanda Picó [a], Rodrigo Alvarez-Ruiz [a], Ahmed H. Alfarhan [b], Mohamed A. El-Sheikh [b], Hamad O. Alshahrani [b], Damià Barceló [b, c]

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Pharmaceuticals

Extraction:

- Water samples were subjected to solid-phase extraction

Analysis:

- High-Performance Liquid Chromatograph (UHPLC) combined with a Triple Quadrupole Mass Spectrometer (MS/MS)

Microplastics

- Water samples were filtered through stainless steel sieve (0.3 mm of diameter)

- The organic matter was removed using Fenton reagent followed by visual inspection of the suspected particles

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Science of The Total Environment

Volume 701, 20 January 2020, 135021

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https://doi.org/10.1016/j.scitotenv.2019.135021

Highest concentrations of pharmaceuticals in water:

- diazinon (up to 1016 ng L^{-1})
- caffeine (up to 20663 ng L^{-1})
- diclofenac (up to 1390 ng L^{-1})
- paracetamol (up to 3069 ng L^{-1})

Concentration of microplastics in water ranged from:

- 0.7 to 7.8 items/L in the Al-Asfar lake
- 1.1 to 9.0 items/L in the Al-Hubail lake

ELSEVIER

Chemosphere
Volume 266, March 2021, 129007

An assessment of the concentration of pharmaceuticals adsorbed on microplastics

Sergio Santana-Viera, Sarah Montesdeoca-Esponda, María Esther Torres-Padrón, Zoraida Sosa-Ferrera, José Juan Santana-Rodríguez

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https://doi.org/10.1016/j.chemosphere.2020.129007 Get rights and content

TEN PHARMACEUTICALS STUDIED

Antineoplastic compounds:
- cyclophosphamide and tamoxifen

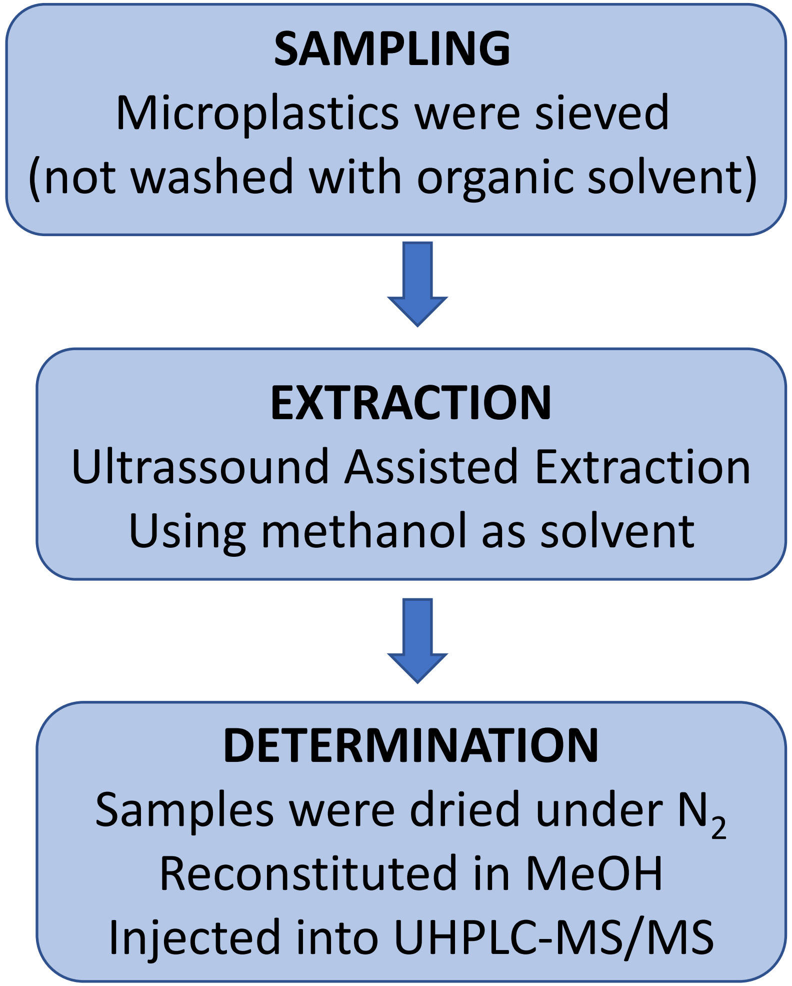
Stimulants:
- nicotine, caffeine, paraxanthine

Lipid regulator:
- gemfibrozil

Anti-hypertensive
- atenolol

Anti-convulsant
- carbamazepine

Antibiotics
-trimethoprim, erythromycin



Adapted from Figure 3

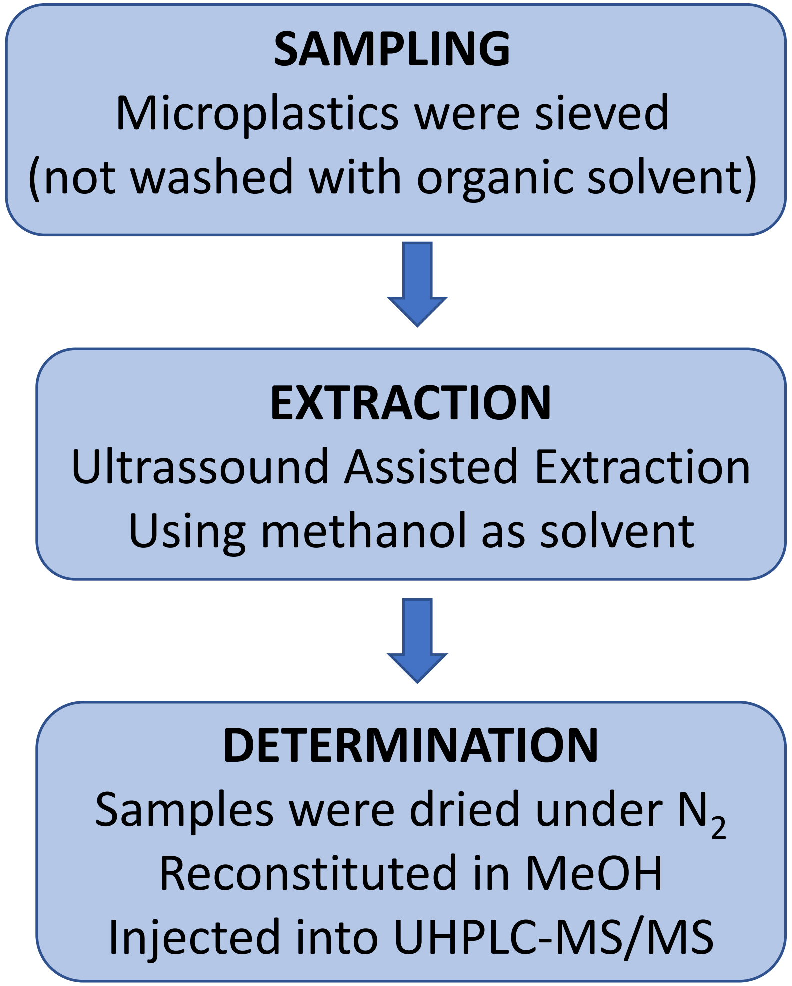
Require 300 mg of microplastics

For extraction uses 7.5 mL of methanol (MeOH) within 10 min.

Spiked samples

- 30 pellets (approximately 900 mg of MPs)
- contact with 10 mL of the analytes at a concentration of 500 ng mL^{-1} in methanol for 24 h (until the methanol dried completely at room temperature)

https://doi.org/10.1016/j.chemosphere.2020.129007

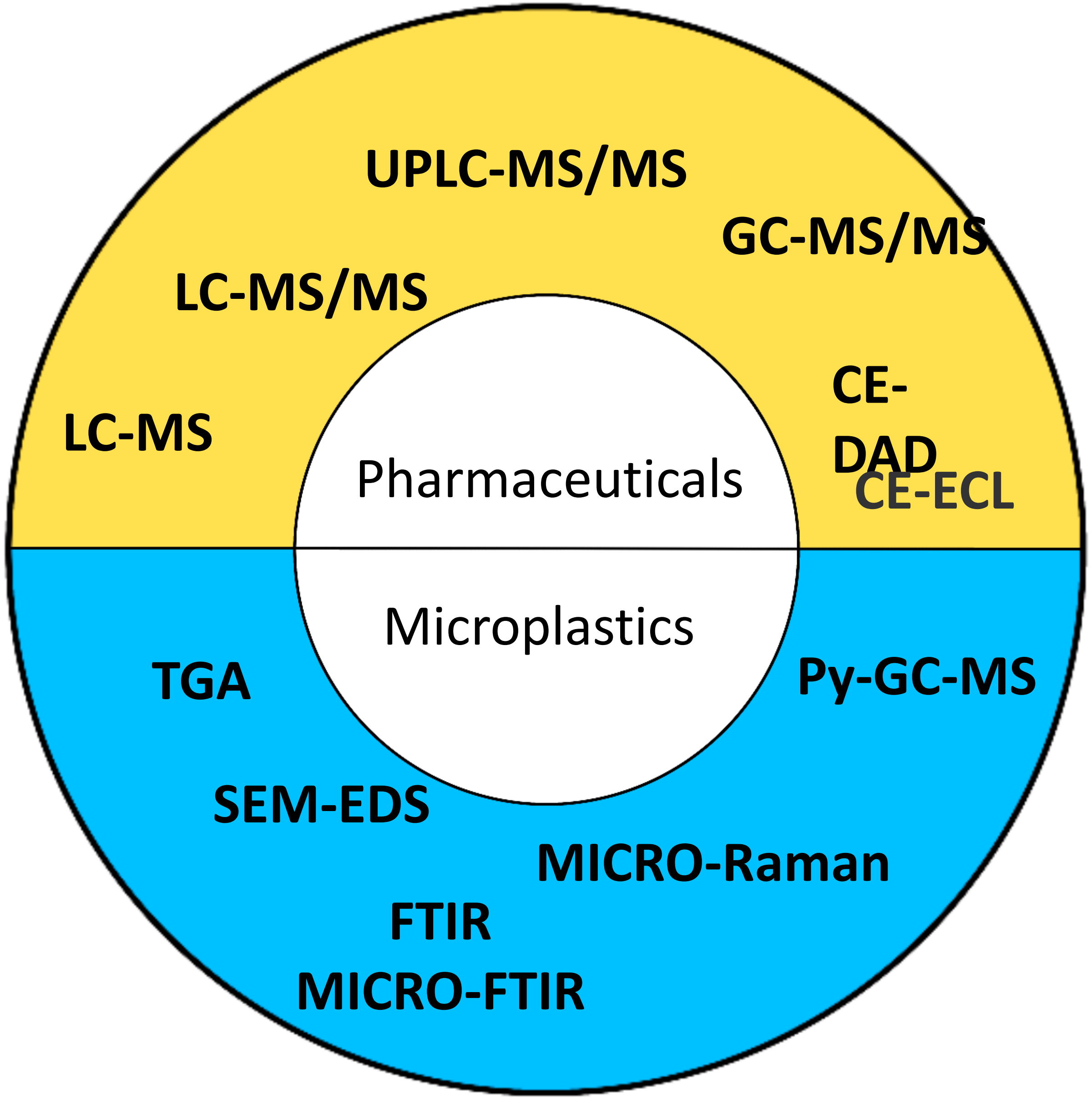


Adapted from Figure 3

LODs ranging from 0.25 ng g^{-1} to 15.8 ng g^{-1}.

Pharmaceuticals were detected in the samples of microplastics from 3 beaches (the Gran Canaria, Lanzarote and La Graciosa islands) in concentrations between 34 and 111 ng g^{-1}.

https://doi.org/10.1016/j.chemosphere.2020.129007



Adapted from:
https://doi.org/10.1007/s10661-022-09751-w
https://doi.org/10.1080/00032719.2021.1942031
https://doi.org/10.3390/app12199789

GC-MS/MS
Gas chromatography-tandem mass spectrometry

LC-MS
Liquid chromatography– mass spectrometry

LC-MS/MS
Liquid chromatography tandem–mass spectrometry

UHPLC-MS/MS
Ultra-high-performance liquid chromatography-tandem mass spectrometry

UPLC-MS/MS
Ultra-performance liquid chromatography–tandem mass spectrometry

TGA Thermogravimetric analysis

Pyr-GC-MS
Pyrolysis gas chromatography-mass

CE-ECL
Capillary Electrophoresis - Electrochemiluminescence detection

Conclusions:

- Sorption studies taking into consideration environmentally relevant concentrations and conditions
- Optimisation of conditions using statistical methods
- Studies on the monitoring of microplastics and pharmaceuticals in the same environmental samples
- Methodologies for the extraction of pharmaceuticals on microplastics
- Studies on the quantification of pharmaceuticals on microplastics