Càtedra ATL de l'aigua potable

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ASPECTOS SANITARIOS DEL AGUA DE CONSUMO

Effects of microplastics on water disinfection and formation of disinfection by-products

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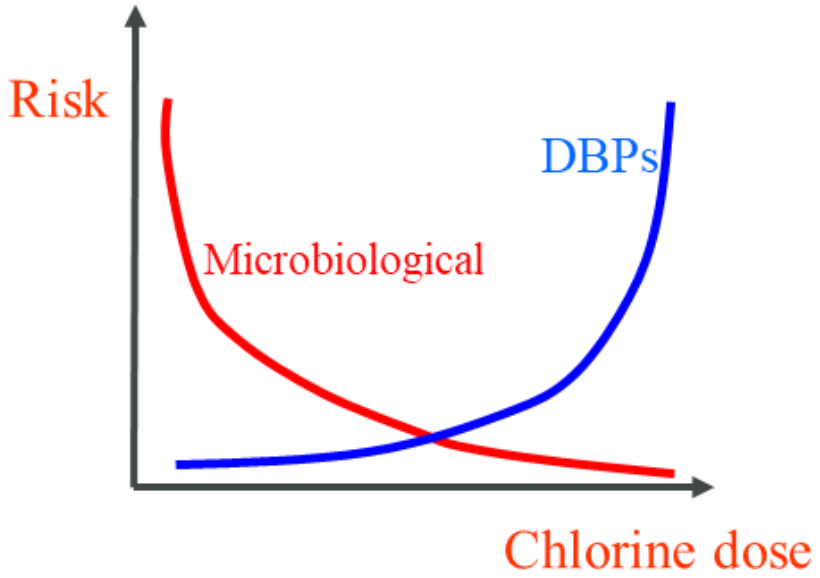
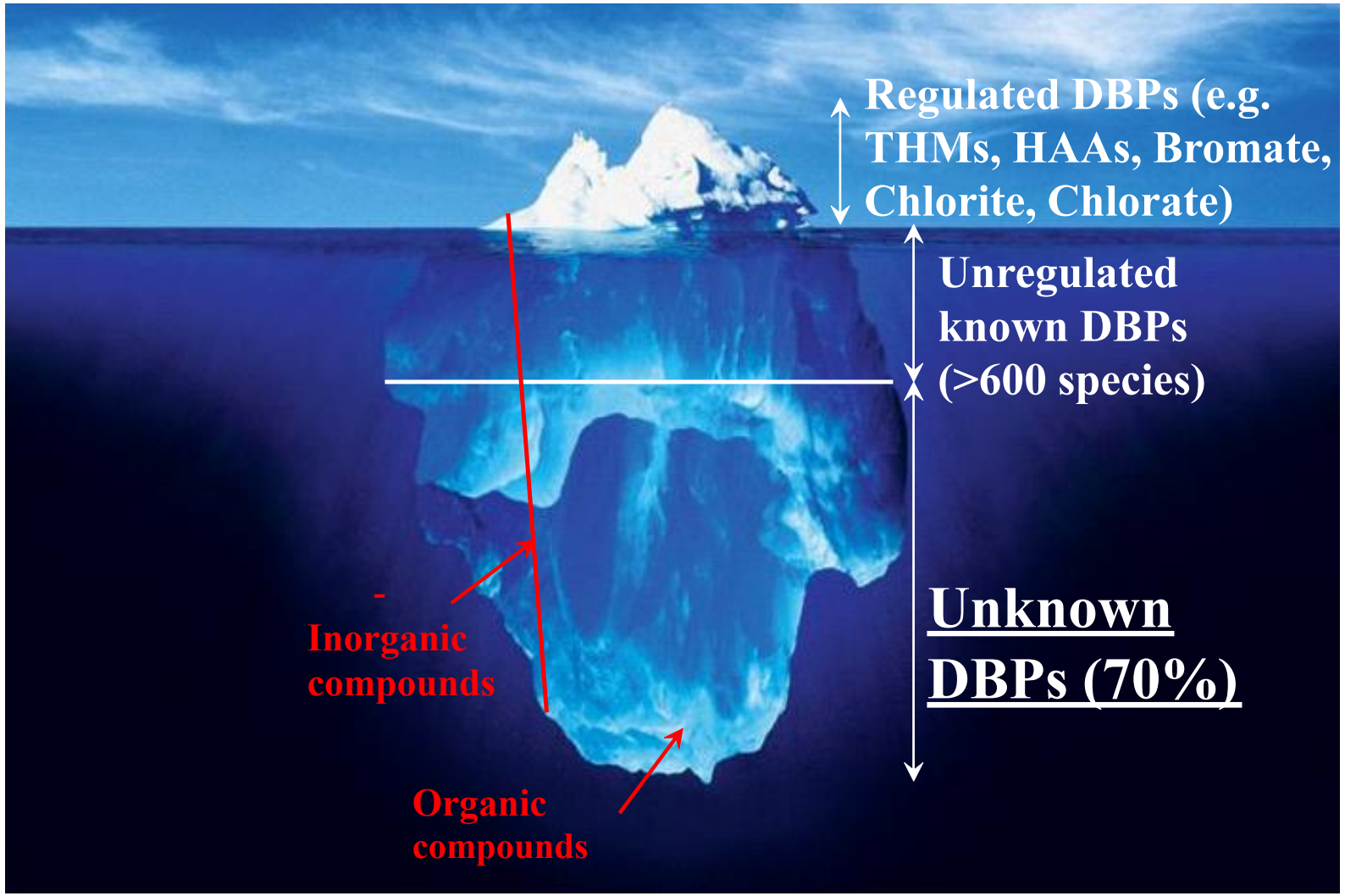
Background: Chlorination and DBPs formation

- Chlorination of drinking water has been recognized as one of the most effective public health measures ever.
- Chlorine reacts with NOM to produce chlorinated, brominated and, in much smaller levels, iodinated by-products (DBPs) (Rook, 1974; Reckhow et al., 1990; Richardson et al., 2003; Bichsel and Von Gunten, 2000).



Background: DBP ICEBERG
What we know of unknown DBP (Richardson et al., 2002)



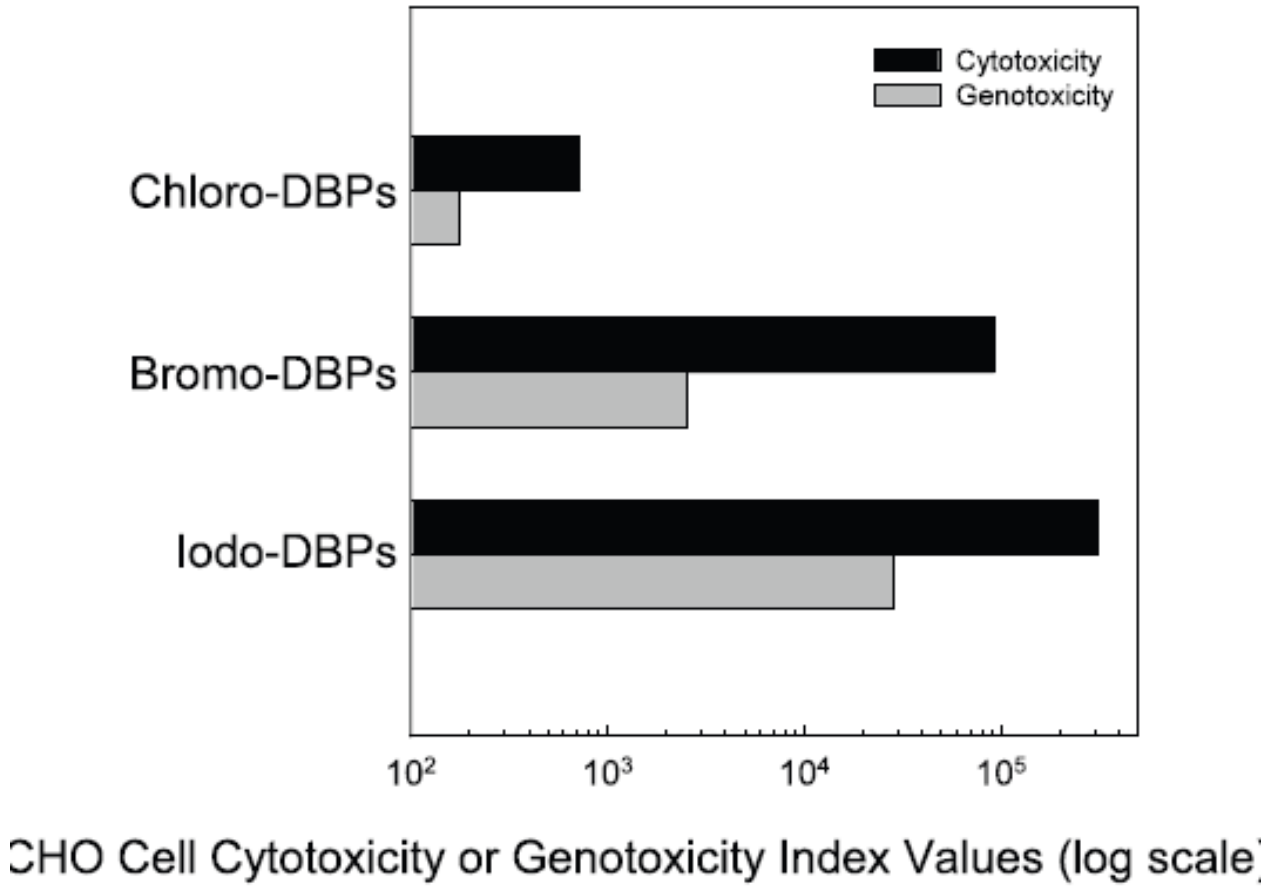
Background: DBPs occurrence

Unlike other contaminants that may or may not be present in drinking water…

DBPs are ubiquitous

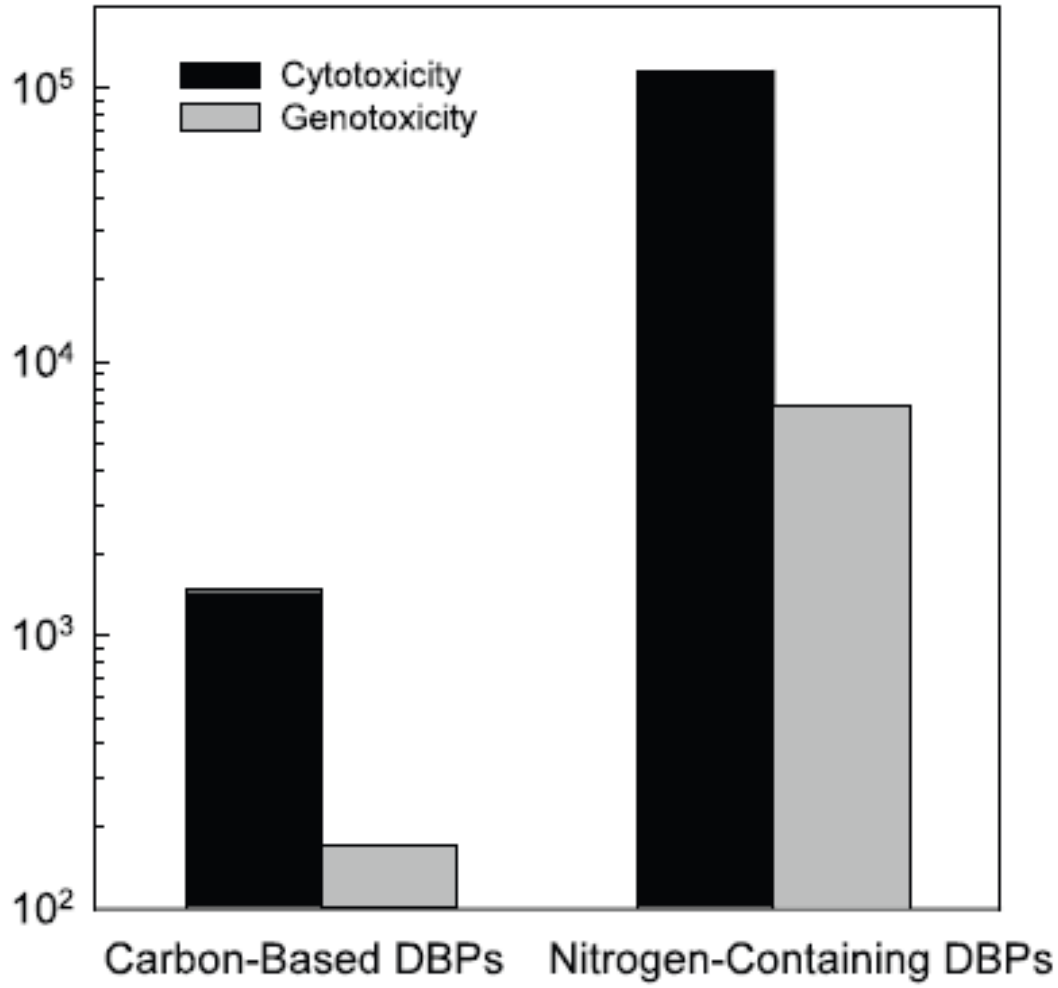
Background: DBPs toxicity

The nature of halogen atoms incorporated in DBPs also affects their toxicity which follows an **I > Br >> Cl** order (Richardson et al., 2007)



Background: DBPs toxicity

Nitrogenous DBPs (e.g. HANs and HNMs) are much more toxic than carbonaceous DBPs (Richardson et al., 2007)



Chlorination (HOCl)

- **Advantages:**
  - **Effective and economic;**
  - **Residual in the distribution system;**
- **Disadvantages:**
  - **Chlorine resistant pathogens (e.g. Giardia e Criptosporidium)**
  - **Formation of DBP (e.g. THM, HAA, HAN, HNM);**
  - **Effluent ecotoxicity;**

Chloramination (NH_2Cl)

- **Advantages:**
  - **Effective, economic, biofilm control;**
  - **No THM, less HAA;**
- **Disadvantages:**
  - **Less effective than chlorine;**
  - **Formation of other DBP (e.g. HAA, HAN, HNM, NDMA);**
  - **Nitrification.**

Chlorine dioxide (ClO_2)

- **Advantages:**
  - **Effective against viruses;**
  - **No THM, No HAA;**
- **Disadvantages:**
  - **Not stable –in situ production;**
  - **Higher cost than chlorine;**
  - **Formation of other DBP (e.g. chlorite ClO_2^- e chlorate ClO_3^-);**

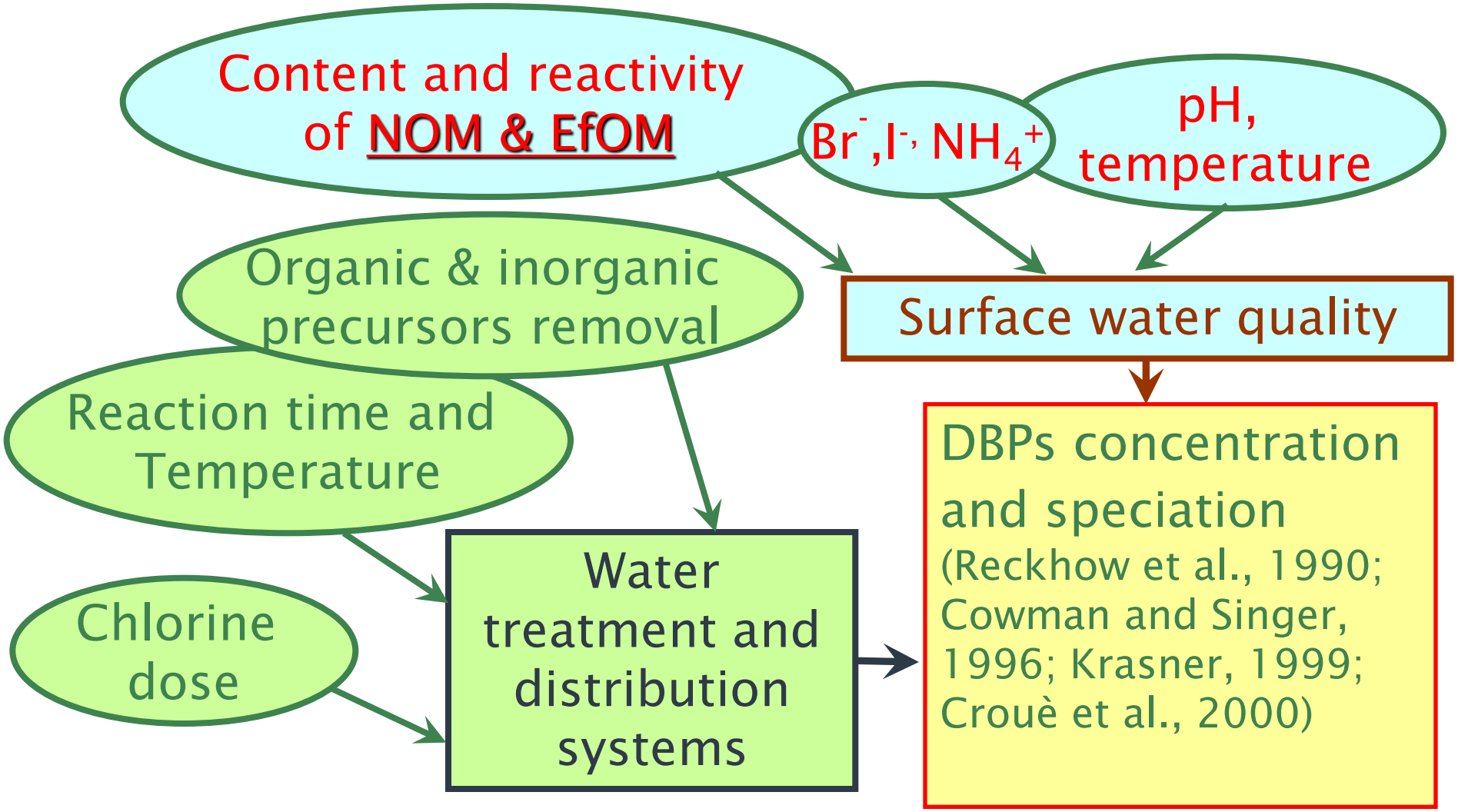
Ozonation

- **Advantages:**
  - **Effective against viruses and bacteria;**
  - **Short reaction time (5-10 min.);**
  - **Removes trace micropollutants;**
- **Disadvantages:**
  - **Not stable –in situ production;**
  - **High CAPEX and OPEX;**
  - **May form of other DBP - very toxic (e.g. BrO_3^-, NDMA)**

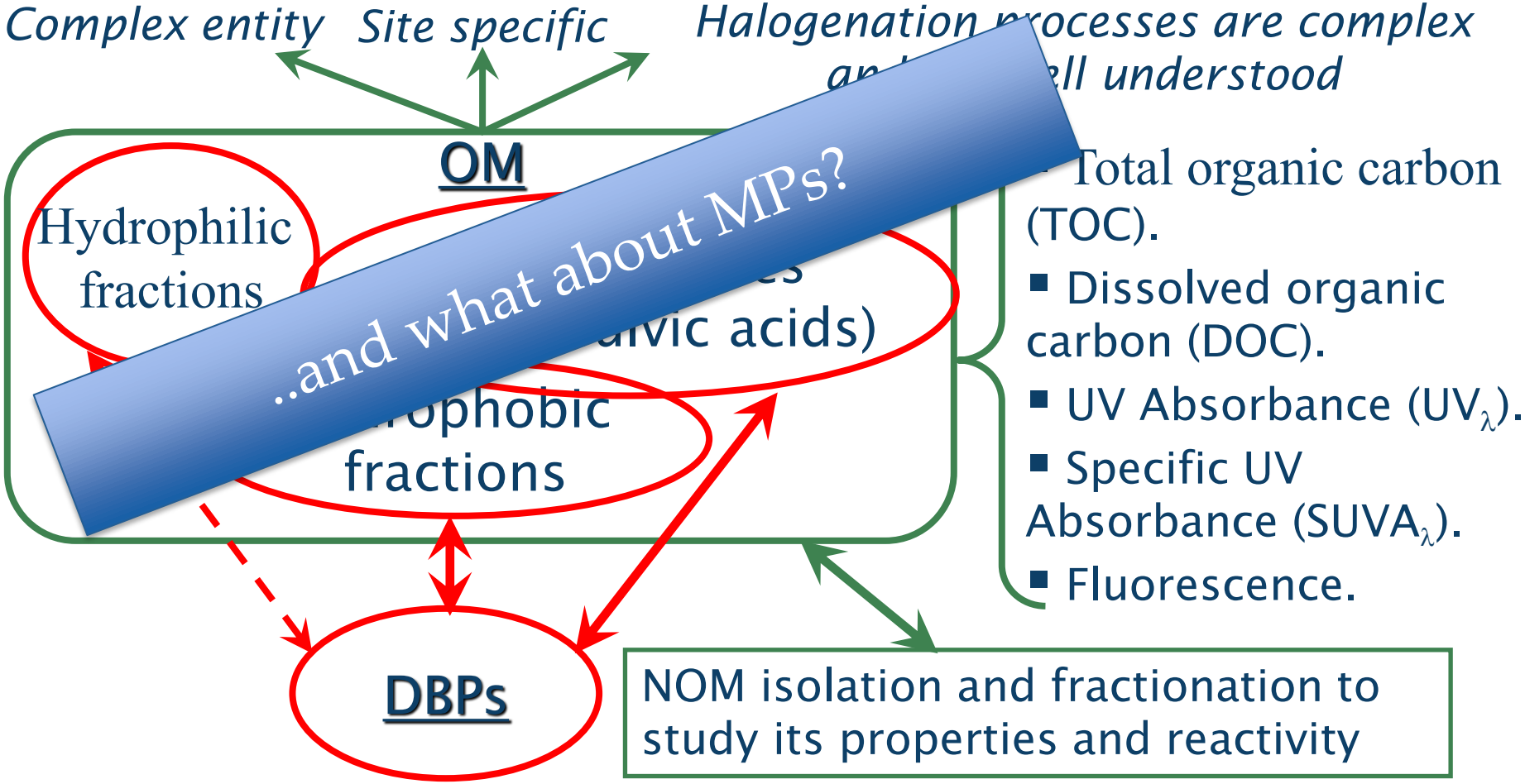
UV irradiation

- **Advantages:**
  - **No chemical added;**
  - **Short reaction time (6-10 sec.);**
  - **No DBP formation????????**
- **Disadvantages:**
  - **Relevant effects of SST;**
  - **Difficulty in dose measurements;**
  - **High energy;**
  - **No residual effect;**
  - **Affects NOM and inorganic compounds (e.g. NO_3^-) resulting in higher DBPs formation during subsequent chlorination**

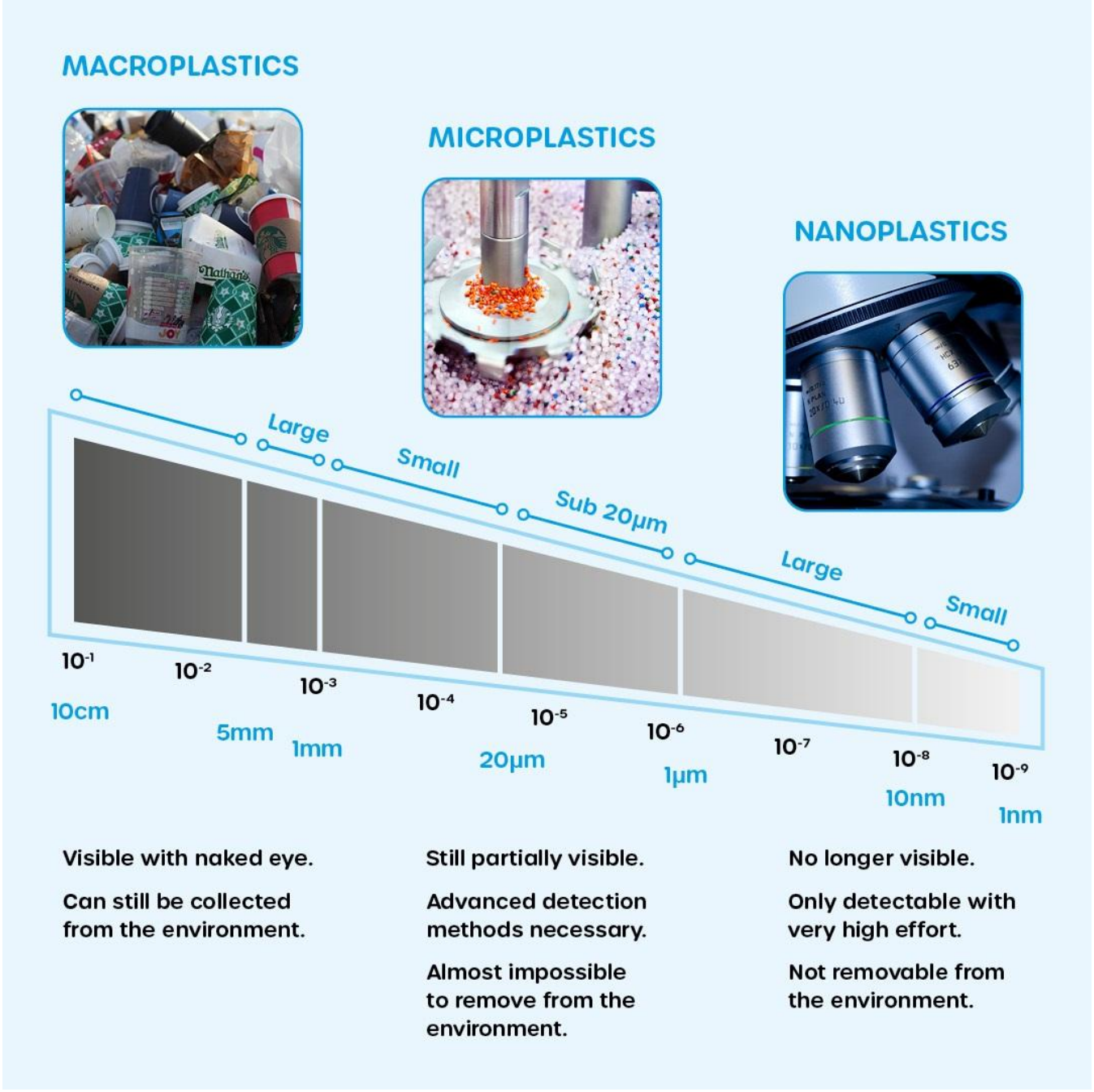
Disinfection and DBPs formation



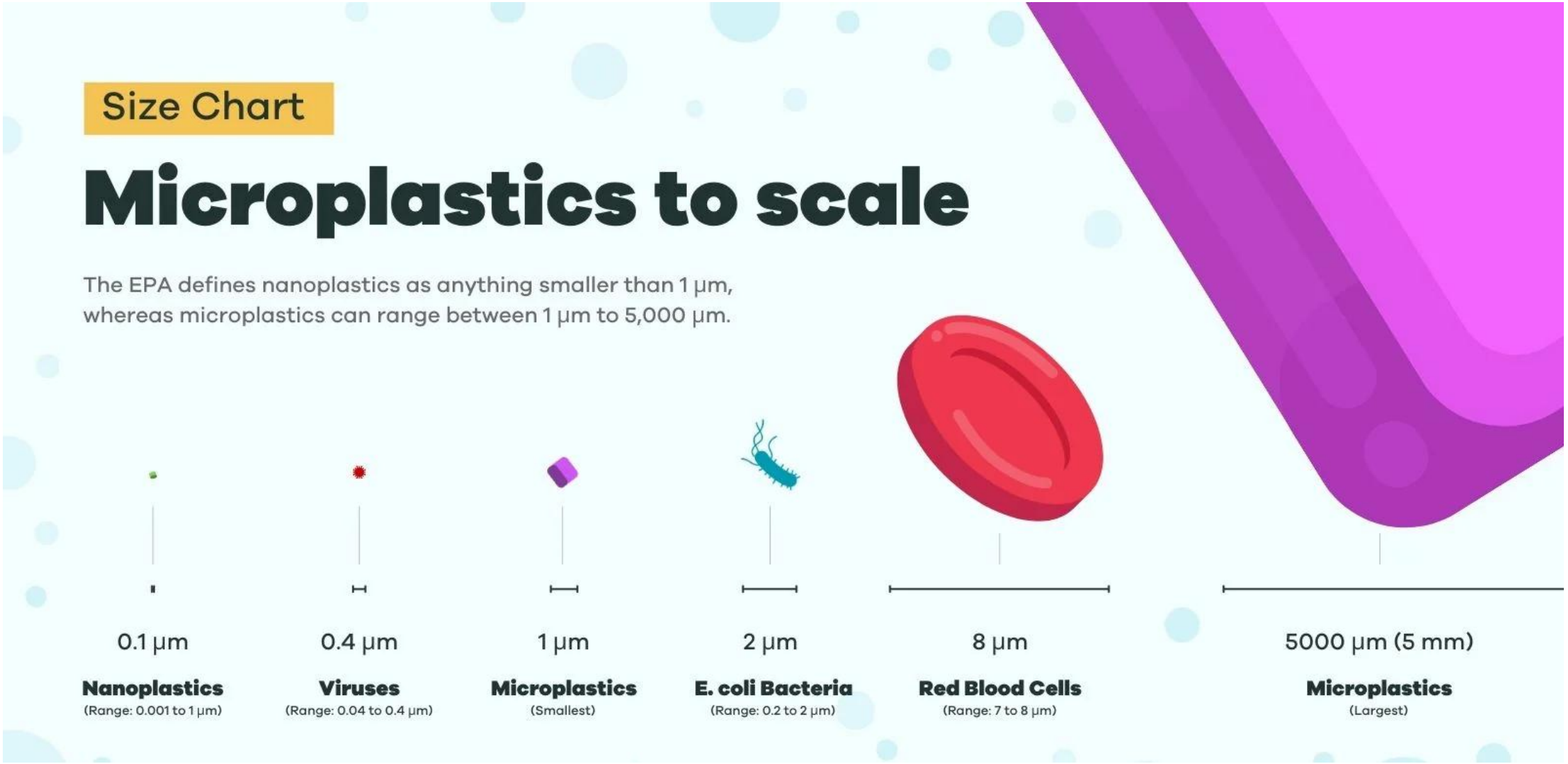
Organic Matter (OM)



MPs: definition



MPs: definition



MPs analysis: one of the major issues

Giannattasio et al. Environment International 190(2024) 108839

Table 1
Main techniques for qualitative, morphological, microstructural and quantitative analysis of marine synthetic polymer debris.

	Identification			Morphological		Structural	Quantification					Ref.
	Particle count									By weight		
	Per type		Total				Per type		Total	Per type	Total	
	MPs	NPs		MPs	NPs		MPs	NPs				
OM	🟡	🔴	🔴	🟢	🔴	🔴	●	🔴	🔴	🔴	🔴	(Wang et al., 2017; Song, 2015; Ding, 2019)
FM	🟡	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🟡	🔴	🔴	(El Hayany, 2020)
SEM-EDX	🟡	🟡	🟡	🟢	🟢	🔴	🟢	🟡	🟡	🔴	🔴	(Wagner, 2017; Girão et al., 2020; Fries, 2013; Shi, 2022)
STEM-EDX	🟢	🟢	🟡	🟢	🟢	🔴	🟢	🟢	🟡	🔴	🔴	(Watteau et al., 2018; Gniadek and Dąbrowska, 2019)
FTIR	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	(Käppler, 2016)
Raman	🔴	🔴	🟢	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	(Araujo et al., 2018; Sobhani, 2020; Schymanski et al., 2018)
μ-FTIR	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Hufnagl, 2022)
μ-Raman	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Araujo et al., 2018; Schymanski et al., 2018)
LDIR	🟢	🟡	🟡	🟡	🔴	🟡	🟢	🟡	🟡	🔴	🔴	(Ourgaud, 2022)
LS	🔴	🔴	🔴	🟡	🟡	🔴	🟢	🟢	🟢	🔴	🔴	(Liu, 2021; Choobbari, 2022)
pyr-GC/MS	🔴	🔴	🟢	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢	(Fries, 2013; Santos, 2023)
TED-GC/MS	🔴	🔴	🟢	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢	(Zhou et al., 2019; Sorolla-Rosario et al., 2023)
NMR	🔴	🔴	🟢	🔴	🔴	🟢	🔴	🔴	🔴	🟢	🟢	(Corti, 2020; Peez and Imhof, 2020; Peez et al., 2019; Peez, 2019)

🟢: particularly effective; 🟡: effective; 🔴: not suitable.

Microplastics that escape treatment reach disinfection, the stage where by-products form

Preliminary treatment → Primary treatment → Secondary treatment → **Disinfection: chlorine, ozone, UV**

Residual microplastics (MPs) reach the disinfection unit, where disinfection by-products (DBPs) form

160 million

MPs per day, estimated in the final effluent of a wastewater treatment plant in Northern Italy

~95%

of the MPs left after drinking-water treatment are 1–10 µm in size

>700

halogenated DBPs identified from chlorine and organic matter

Why it matters

Many DBPs are considered potential human carcinogens and mutagens

Drinking-water plants need upgrades for the DBP standards of Directive (EU) 2020/2184

MPs at the disinfection stage can create a new set of challenges

Open question

What do MPs do at the disinfection stage?

Shukla et al. Current Opinion in Environmental Science & Health 46 (2025) 100632

Three questions, answered by critically examining the conditions of prior studies

The gap: a recent review covered the impact of MPs on chlorination and ozonation efficacy, but did not focus on MPs as potential DBP precursors

Four questions

Q1 Are MPs precursors of DBPs?

Q2 Do MPs interfere with disinfection and carry antibiotic- and disinfectant-resistance genes (ARGs, DRGs)?

Q3 Do laboratory results apply to real treatment plants?

Q4 Can MPs be removed at Water and wastewater treatment plants?

Approach: a critical examination of prior research

Prior studies of MPs with chlorine, ozone and UV → Their conditions: MP concentration, disinfectant dose and time, water, set-up → Compared with water and wastewater treatment plants → Answers to Q1–Q3; DBP data compiled in Table 1

Shukla et al. Current Opinion in Environmental Science & Health 46 (2025) 100632

Yes, in lab tests: MPs release organic matter that forms THMs and HAAs under chlorination

Study	MPs	Chlorine dose	Time	THMs, µg/L	HAAs, µg/L
Zhou et al. 2022	PVC / PP / PE / PS	3 × DOC	72 h	62 / 241 / 99 / 68	811 / 780 / 1235 / 421
Wang et al. 2024	PS	3 × DOC	58 h	413	330
Parveen et al. 2024	PVC / PE / PP / PET	10 mg/L	120 h	142 / 125 / 100 / 140	74 / 30 / 39 / 30
Lee et al. 2022	EPS / PVC	5 mg/L	72 h	104 / 112	118 / 122
Lin & Su 2022	PE / PS	2 mg/L	96 h	80 / 125	4 / 7
Hao et al. 2022	PP	10 mg/L	72 h	22	3
Miao et al. 2022	PE / PP / PS / TPU	10 mg/L	72 h	38 / 19 / 37 / 80	10 / 3 / 6 / 25
Zhang et al. 2024	PE / PP / PVC	5 mg/L	0.5 h	TOX 320 µg/L for each polymer	
Liu et al. 2023	PA6 / PBAT / PLA / PET	1.5–36.5 mg/L	24 h	48 / 12 / 14 / 06	292 / 8 / 9 / 6
Ye et al. 2022	PVC	15 mg/L	72 h	42	5
Du et al. 2023	PET	1.5 mg/L	24 h	62	41

Caveat of the studies: MP concentrations in these tests are often artificially higher than in plants, and may exaggerate the effect of chlorination on DBP formation

Shukla et al. Current Opinion in Environmental Science & Health 46 (2025) 100632

Yes, in lab tests: MPs can lower disinfection efficacy and shelter resistance genes

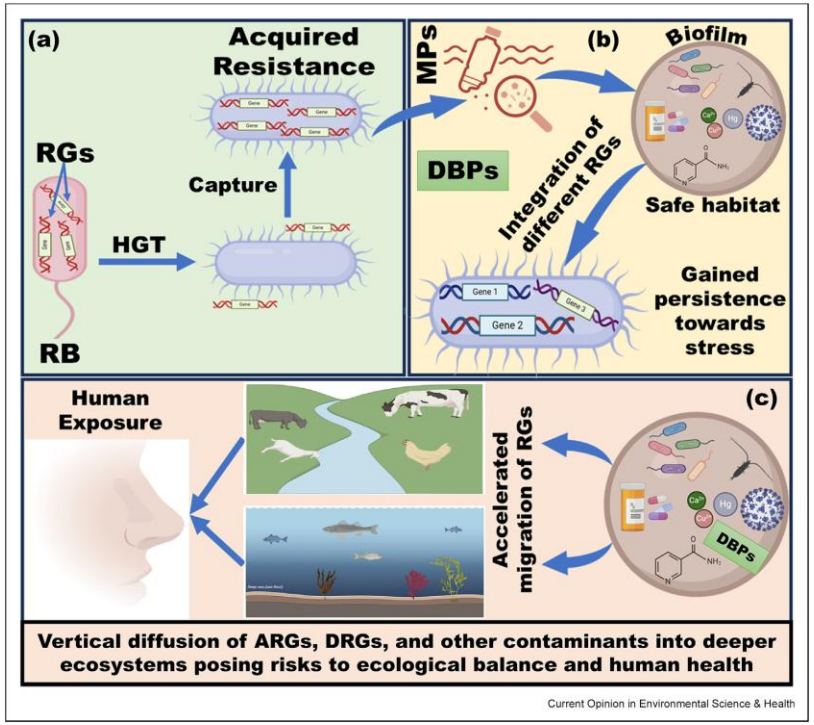


Figure 1 of the review

0.99–1.88 log
antibiotic-resistant *E. coli*

0.80–1.69 log
antibiotic-resistant *E. faecalis*

Chlorine disinfection obstructed by polyethylene MPs (Huang et al. 2024)

Also: disinfection efficacy inversely related to MP concentration (Shen et al. 2021); slower UV inactivation of MP-associated bacteria (Manoli et al. 2022)

How it works, in Figure 1

a Bacteria acquire resistance genes by horizontal gene transfer; MPs tend to act as media for it

b MPs offer a safe habitat where biofilms form, lower the disinfectant around the bacteria and may retain DBPs

c MPs speed up the migration of resistance genes and contaminants, which reach people through water, seafood and crops

Shukla et al. Current Opinion in Environmental Science & Health 46 (2025) 100632;
Huang et al., J. Water Process Eng. 61 (2024) 105233, and refs 21, 23, p. 3

Not necessarily: most studies used more MPs and more disinfectant than real plants

Study	MPs tested	Disinfection	Limitation noted in the review
Kelkar et al. 2019 *Water Research*	Virgin PP, HDPE, PS; weathered HDPE, PP	Chlorine 2.5 and 5 mg/L for 30 min, simulating plants	Reagent-grade water: no pollutants, microorganisms or biofilms
Ziembowicz & Kida 2024 *Sci. Total Environ.*	PE, PP, PS, PVC at 10 g/L and 200 particles/L	Ozone 3000–3500 mg/h with H_2O_2, for 5, 15 and 30 min	Deionized water; open system with ozone losses; batch mode
Hao et al. 2023 *Chemosphere*	PE, TPU at 500 mg/L, then 100 mg/L	Ozone 5 mg/L for 1 h, then chlorine 7.5 mg/L	MP concentration amplified
Shen et al. 2021 *J. Cleaner Prod.*	Above 50 mg/L	UV or chlorine at increasing doses	Very high MP concentration
Miao et al. 2022 *Chemosphere*	PE, PP, PS, TPU at 50 mg/L	Chlorine 10 mg/L for 3 days	Same trend of unrealistic conditions
Ateia et al. 2020 *Chemosphere*	Leachates of MPs	Chlorine 100 mg/L for 5 days	Same trend of unrealistic conditions

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Yes, but: advanced separation processes are effective, still MPs in the effluent

Study	Treatment train and size	Plant type	Limitation noted in the review
Lares et al., 2018	WWTP: G-Ds-SI-AS-SII-Di WWTP: Ana-Aer-MBR (pilot)	η_{tot}: 98% η_{tot}: 99%	Fibers in the effluent ands in the sludge
Ziajarhomi et al., 2017	WWTP: G-Ds-SI WWTP: G-Ds-SI-AS-C/F-Di-UF	η_{tot}: 66% η_{tot}: 87%	PET fibers in the effluent
Talvitie et al., 2017	WWTP: SI -AS-BAF-DF (pilot) WWTP: SI -AS-RSF WWTP: SI -AS-C/F-DAF WWTP: MBR-UF (pilot)	η_{tot}: 40-98% η_{tot}: 97% η_{tot}: 95% η_{tot}: 99%	-
Yang et al., 2019	WWTP: G- SI *-A2O-SII*-UF-O3-UV*	η_{I}:58,8 (±8,05)% η_{II}:54,47 (±14,73)% η_{III}:71,67 (±11,58)% η_{tot}:95,16 (±1,57)%	-
Wang et al., 2020	WTP: C/F- SI*-RSF*-O3*-GAC*	η_{SI}:40,5-54,5% η_{RSF}:29-44,4% η_{GAC}:56,8-60,9% $\eta_{ozone-BAC}$:17,2-22,2% η_{tot}:82,1-88,6%	High removal of MPs fibers > 10um Good removal of 1um≤MPs≤10um Effluent rich in PET fibers in the range 1-5um

Conclusions and perspectives

Q1	In laboratory tests, organic matter released by MPs forms THMs and HAAs under chlorination
Q2	MPs can lower disinfection efficacy and carry ARGs; they may worsen the situation with DRGs
Q3	Most studies used MP concentrations and disinfectant doses above those of real plants; the roles of MPs in real-world conditions remain underexplored
Q4	Water treatment processes remove a large part of MPs, but still many are in the effluent and in the sludge

More studies are needed

- Actual wastewater and drinking-water matrices
- Alternative separation processes at pilot and full-scale plants
- Temporal and spatial variation of MP loads
- In situ monitoring, with pilot or full-scale studies

Enhancing tertiary/quaternary treatment processes will result in efficient MPs removal

Acknowledgments

EFFECTS OF MICROPLASTICS ON WATER DISINFECTION AND FORMATION OF DISINFECTION BY-PRODUCTS



Thank you!

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