POLITECNICO
MILANO 1863

Prioritari ed emergenti nelle acque potabili: livelli e modalità di rimozione negli impianti convenzionali

Manuela Antonelli

DICA - Dipartimento di Ingegneria Civile e Ambientale, 11.06.2018

Drinking Water Treatment Plants (DWTPs) Which are the contaminants to be removed?

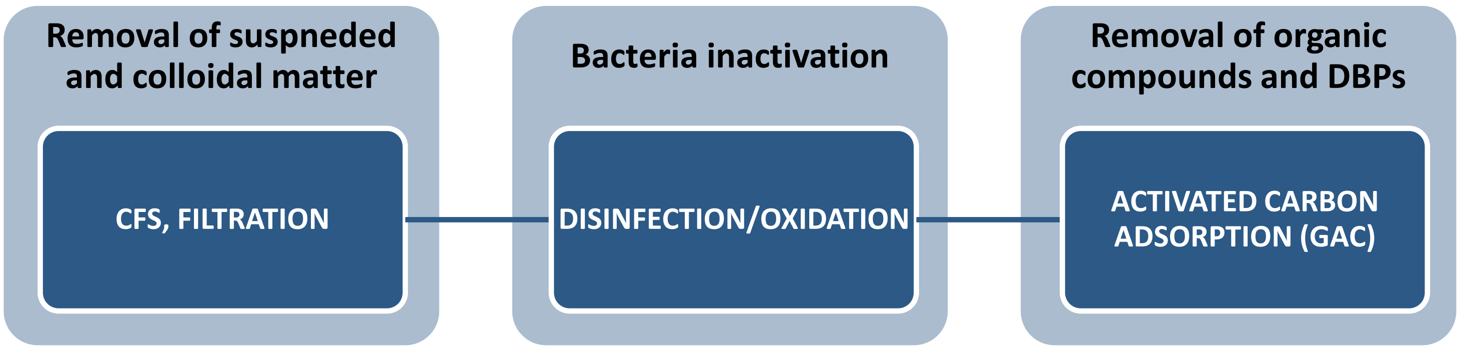
Surface water and groundwater: DWTPs designed to remove conventional contaminants and micropollutants

- suspended and colloidal matter
- natural organic matter (NOM)
- specific pollutants of natural/anthropic origin
- algae and bacteria
- disinfection by-products (DBPs)

DWTPs not specifically designed to remove emerging contaminants, present in very low concentrations in a complex and multi-component matrix

Drinking Water Treatment Plants (DWTPs)
Surface water

Conventional treatment trains: high standardization with presence of **processes potentially appropriate** to remove emerging contaminants



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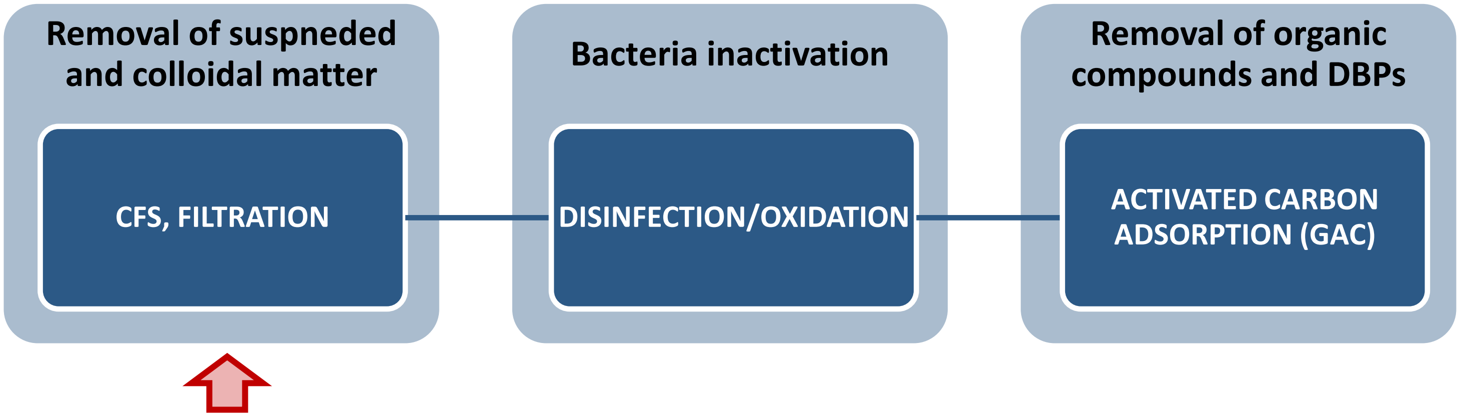


negligible removal of emerging contaminants at environmental concentrations

30-90% efficiency @ concentrations µg/L to mg/L

Potential up-grade for MF/UF coupled to PAC dosage

Drinking Water Treatment Plants (DWTPs)
Surface water

Conventional treatment trains: high standardization with presence of **processes potentially appropriate** to remove emerging contaminants

Removal of suspneded and colloidal matter
CFS, FILTRATION

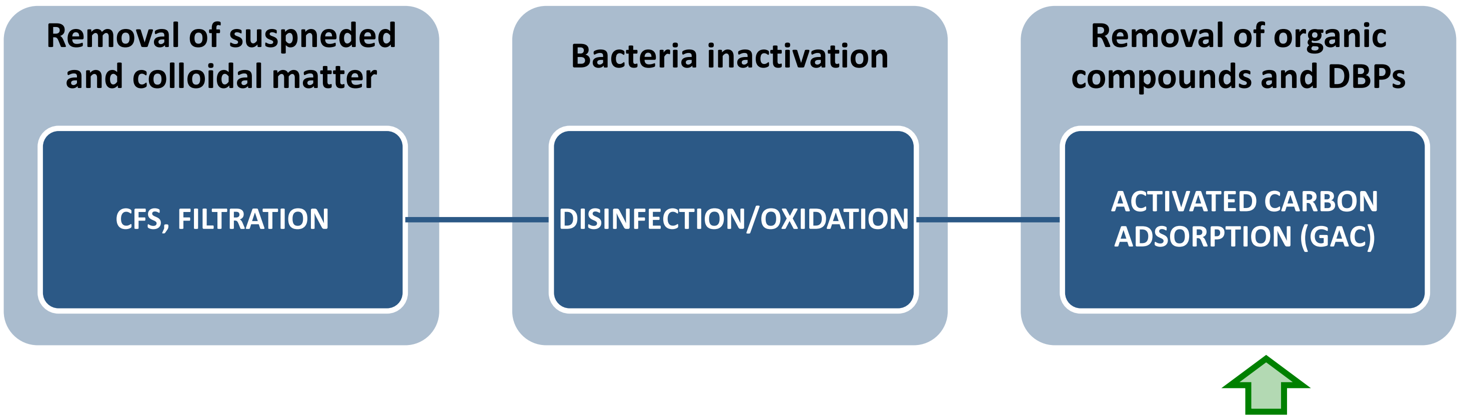
Bacteria inactivation
DISINFECTION/OXIDATION

Removal of organic compounds and DBPs
ACTIVATED CARBON ADSORPTION (GAC)

removal of emerging contaminants in case of **oxidation by ozone or advanced oxidation processes** (AOPs) such as O_3/UV or O_3/H_2O_2 or UV/H_2O_2

Drinking Water Treatment Plants (DWTPs)
Surface water

Conventional treatment trains: high standardization with presence of **processes potentially appropriate** to remove emerging contaminants



now considered the BAT (Best Available Technology), potentially improved when used as **BAC** (Biologically Activated Carbon)

Drinking Water Treatment Plants (DWTPs) Groundwater

Conventional treatment trains: low standardization due to the wide range of contaminants to be removed

➔ possible presence of **processes potentially appropriate** to remove emerging contaminants, such as:

- adsorption on activated carbon (GAC)
- pressure-driven separation processes (nanofiltration, reverse osmosis)

Drinking Water Treatment Plants (DWTPs)
When emerging contaminants can be effectively removed?

Besides their chemical characteristics and concentrations, there are various factors affecting the effective removal of emerging contaminants in a conventional DWTPs:

- presence of appropriate treatments
- process operating parameters
- process configuration

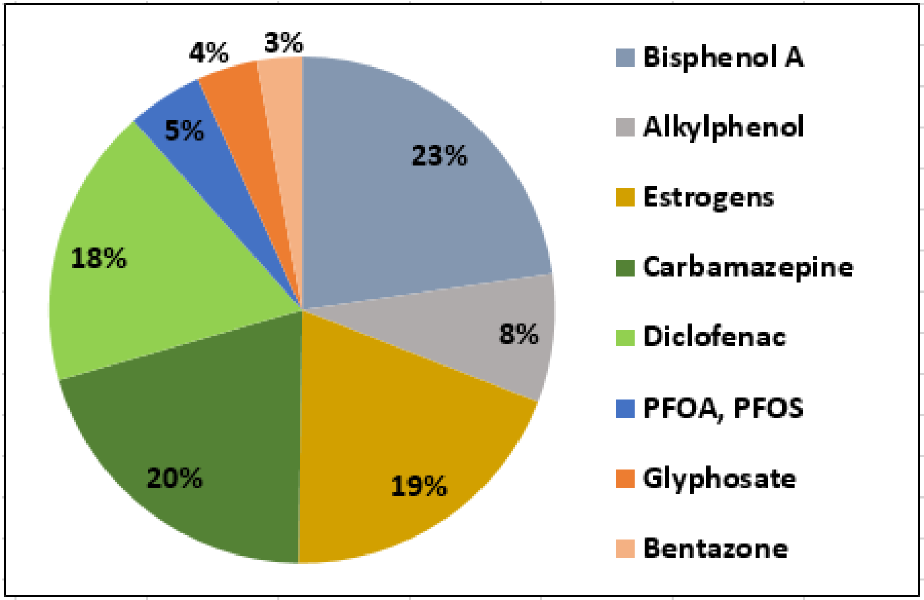
DWTPs designed according to a multi-barrier approach could be more resilient offering a higher level of protection

Emerging Contaminants (ECs) removal
Available references

Many studies sometimes not directly comparable for a multiplicity of working and boundary conditions

- published studies mainly carried out under controlled or not-fully representative conditions of the DWTP operating conditions
- published studies related to monitoring campaign rarely considering DWTP operating conditions to design the sampling campaign

Antonelli et al. (2018), review on progress



→ **Alkylphenol**: octylphenol, ter-octylphenol, nonylphenol

→ **Estrogens**: estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), estriol (E3)

207 references from 2000 to 2018

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Available references

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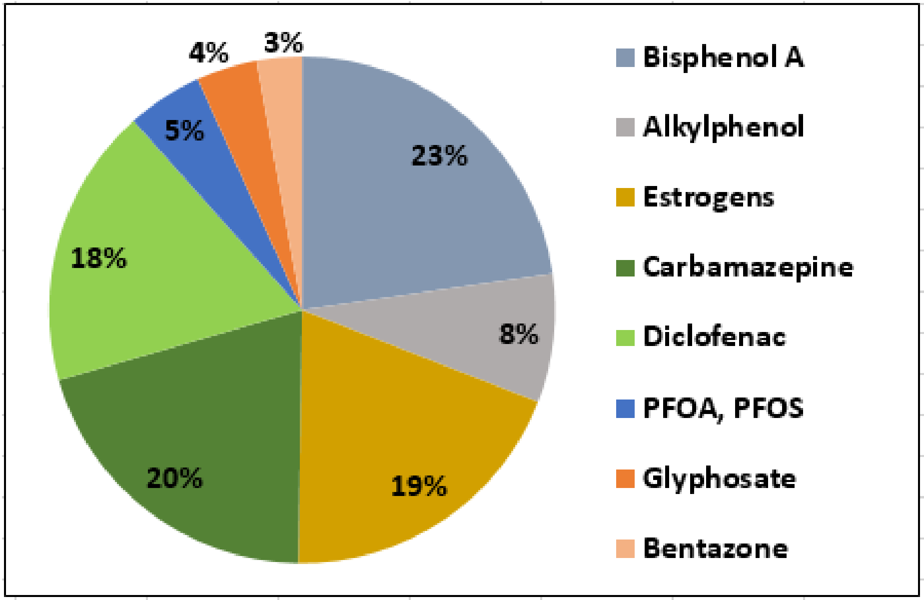

Number of studies:
- pharmaceuticals (38%)
- alkylphenols including BPA (31%)
- estrogens (19%)
- PFAS (5%)
- pesticides (7%)

Evolution over time: studies on estrogens strongly reduced in the last couple of years

Emerging Contaminants (ECs) removal
Available references

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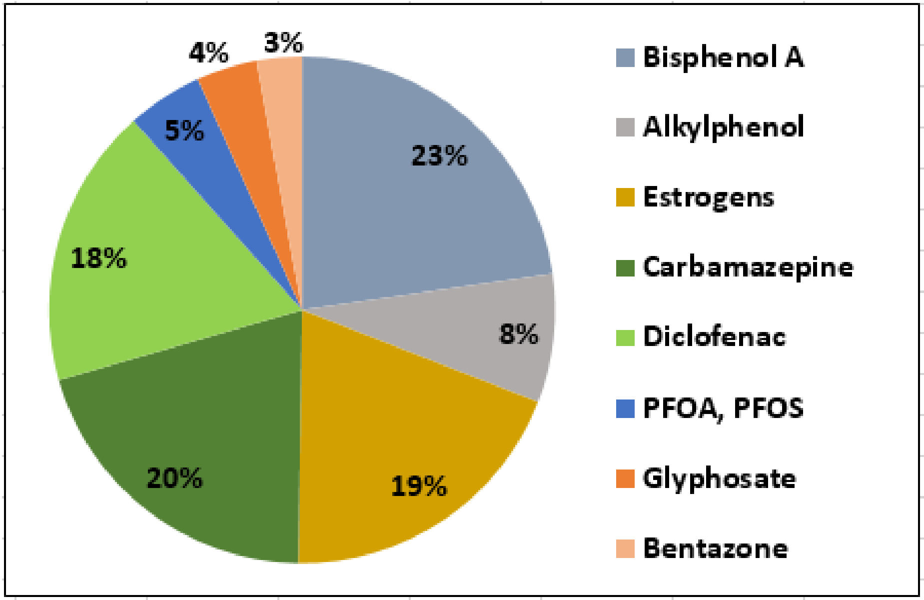
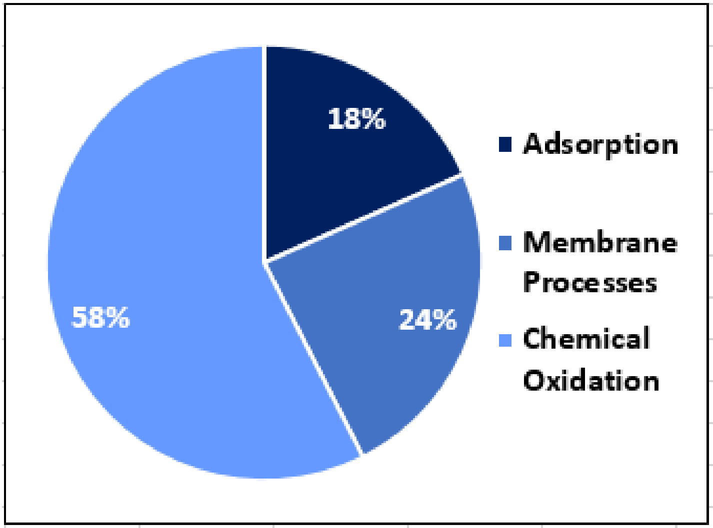
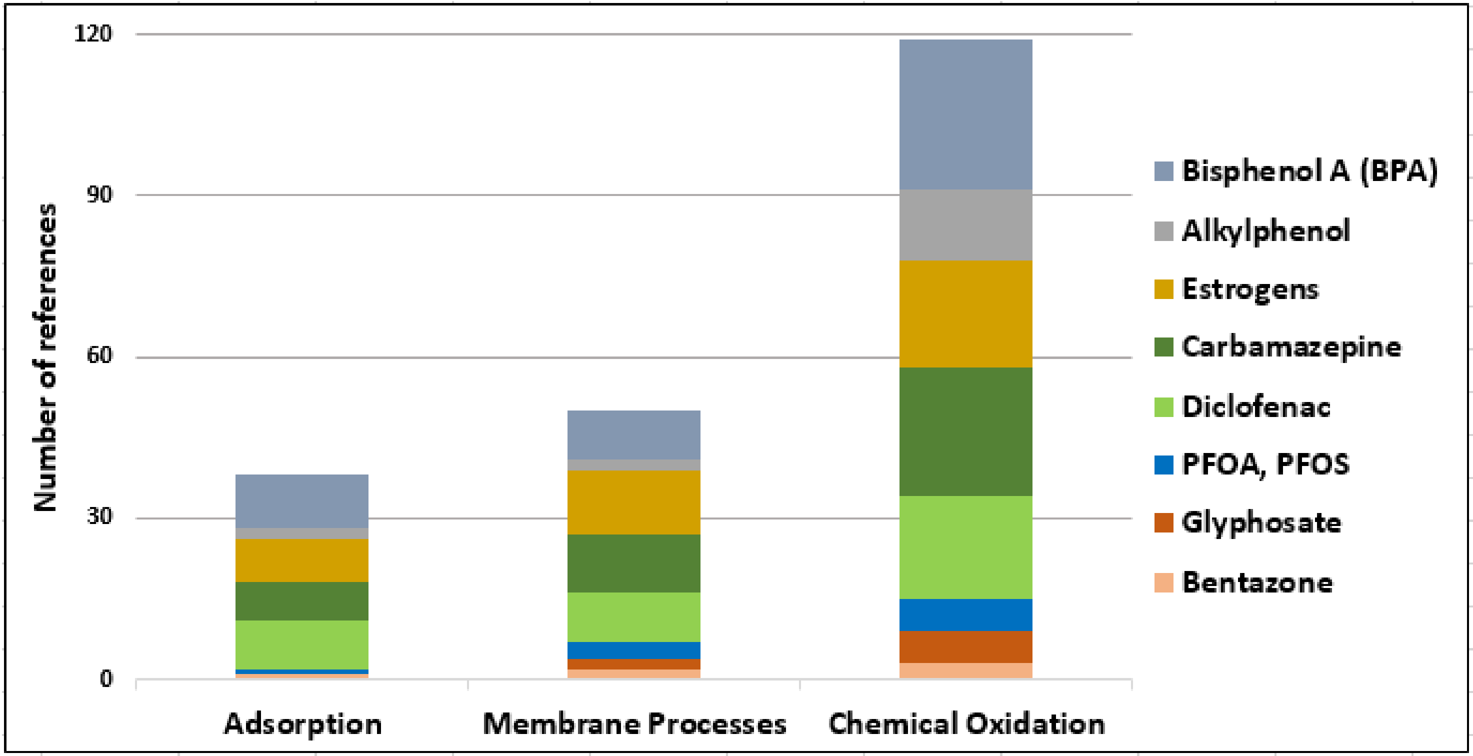




207 references from 2000 to 2018

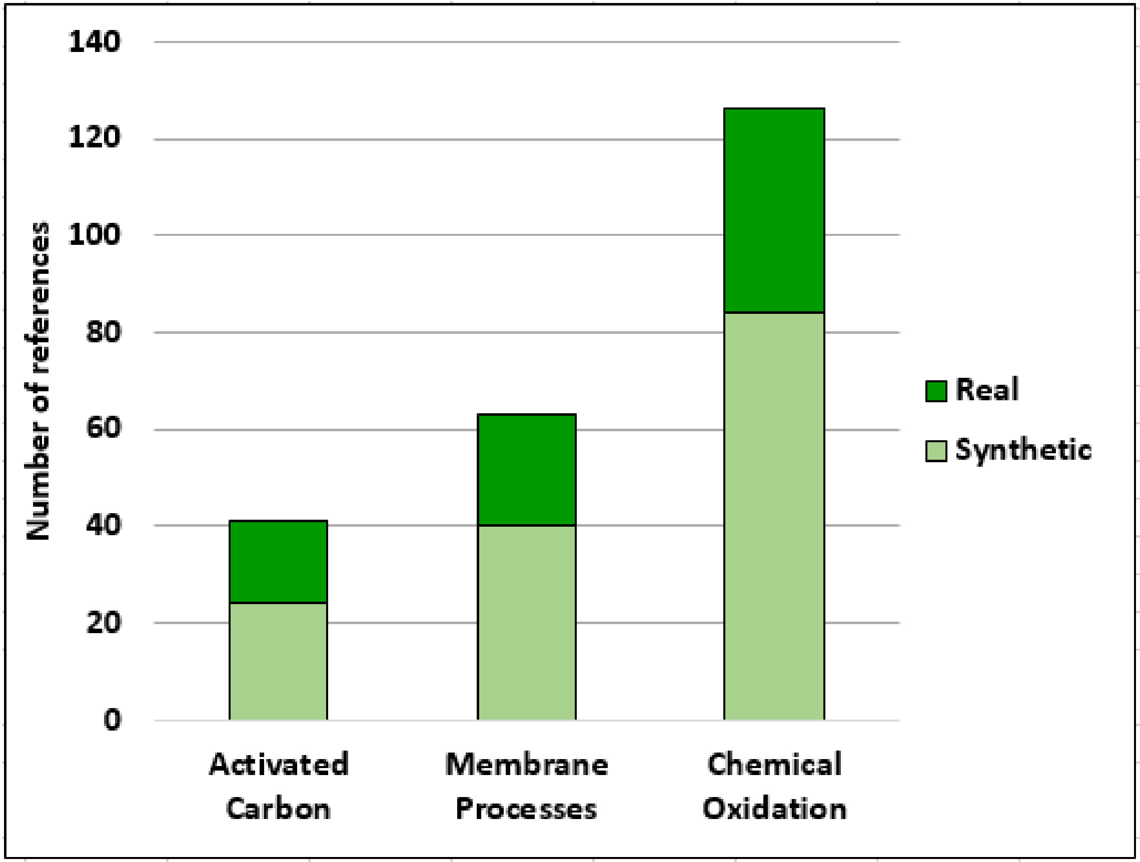
Emerging Contaminants (ECs) removal
Available references

Comparable distribution of the various contaminants among the selected removal processes, except for PFAS about which studies are focused mainly on adsorption



Emerging Contaminants (ECs) removal
Available references: synthetic vs. real water

Most of the studies refer to **synthetic water matrices**, especially for chemical oxidation

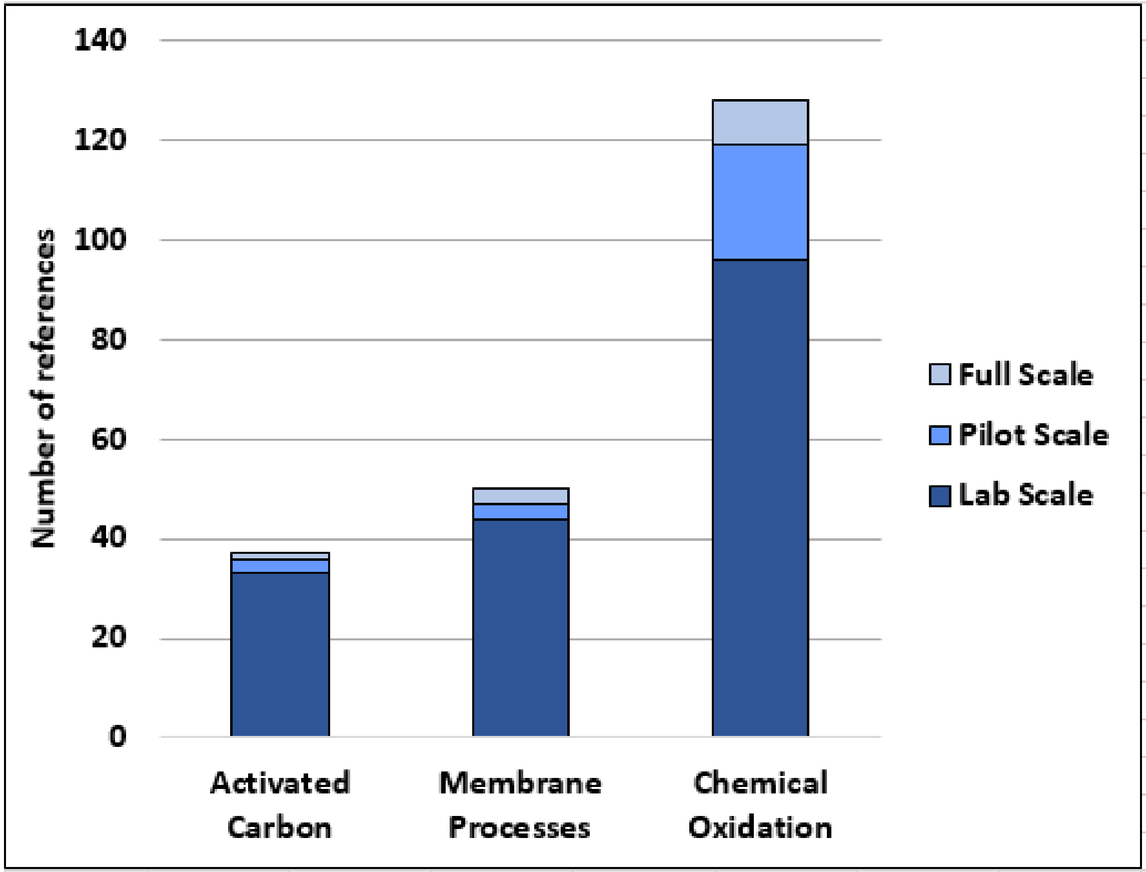


Main concern:

transferability of the results obtained with synthetic water to real water

Emerging Contaminants (ECs) removal
Available references: experimentation scale

Most of the studies refer to **lab-scale experiments**



Main concern:

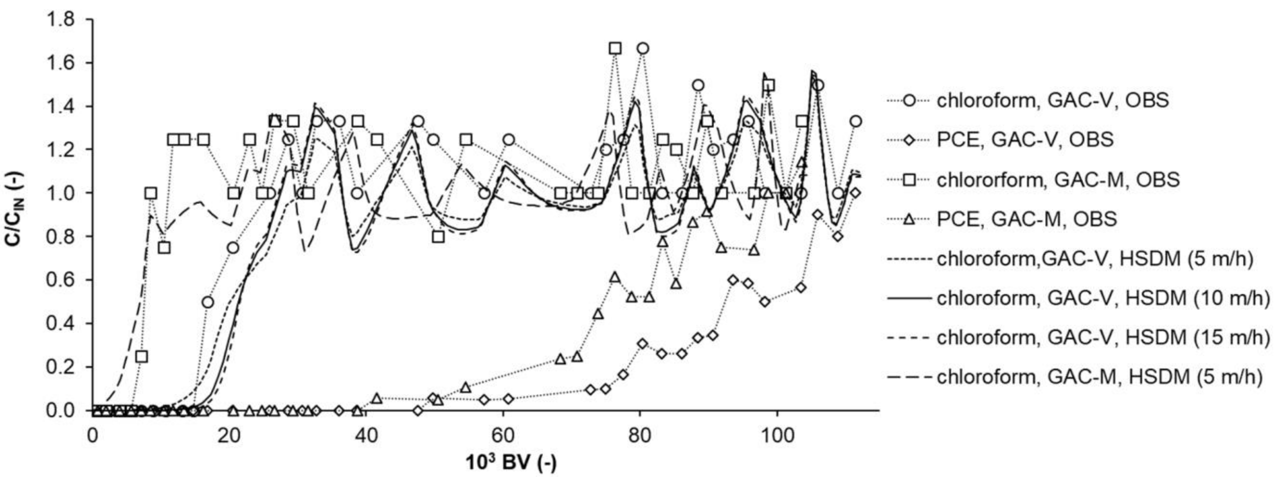
transferability of the results obtained at full scale with feasible engineering parameters

Emerging Contaminants (ECs) removal
Activated carbon adsorption (1/6)

Adsorption of ECs behaves similarly to compounds at higher concentration, being affected by the same properties of solutes and adsorbents

Key-elements in determining the extent of adsorption:

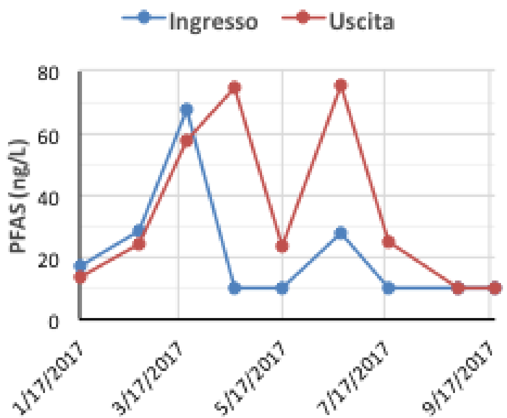
- presence of compounds at concentrations differing by orders of magnitude (NOM, order of mg/L, and micropollutants, order of μg/L)
- competition phenomena among water constituents in a multi-component systems, including ECs
- potential leakage of adsorbed compounds, especially those having lower affinity towards the adsorbent, due to fluctuations in the input concentrations

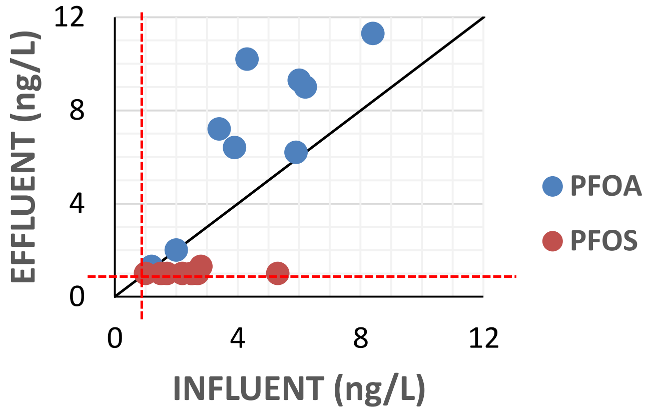


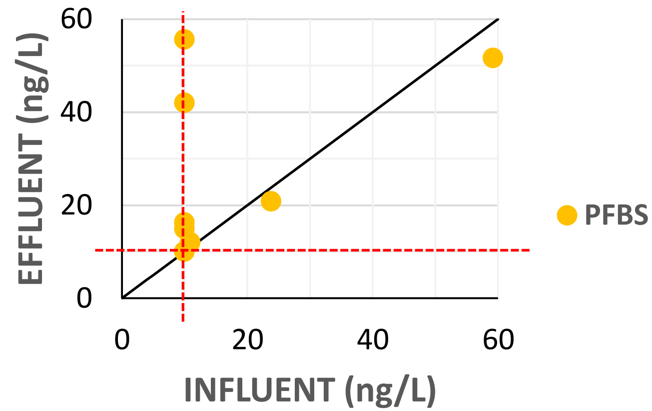
Piazzoli & Antonelli (2018), PSEP

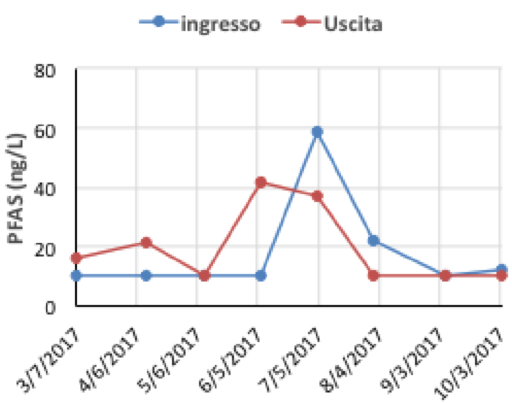
Emerging Contaminants (ECs) removal
Activated carbon adsorption (2/6)

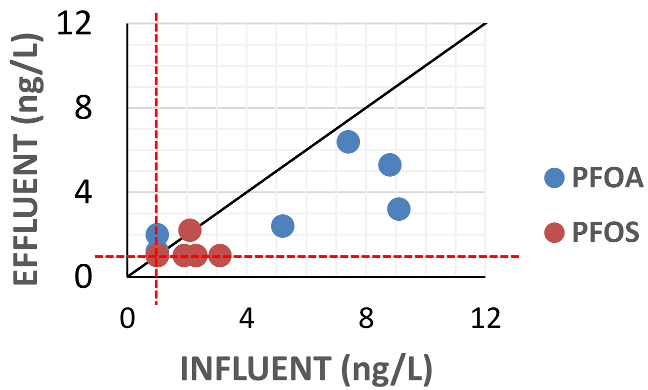
Two DWTPs as case-study for PFAS removal (10 months monitoring campaign)

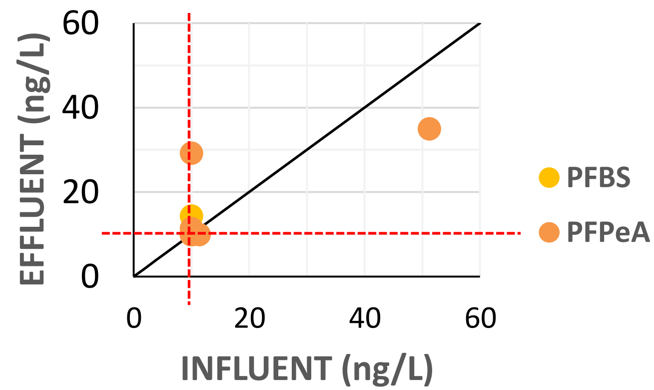








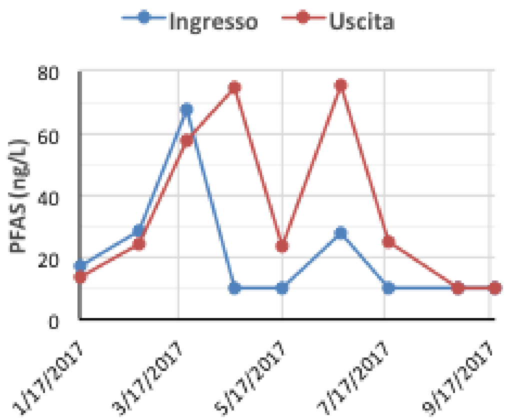


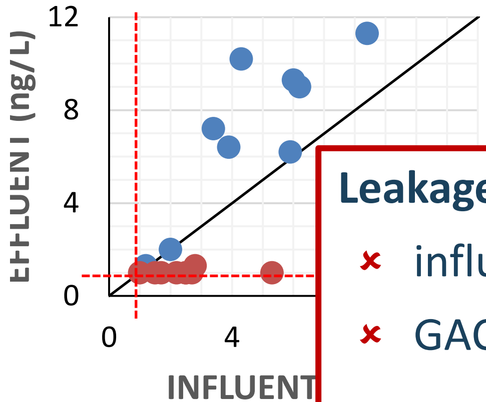


Courtesy of Romagna Acqua

Emerging Contaminants (ECs) removal
Activated carbon adsorption (3/6)

Two DWTPs as case-study for PFAS removal (10 months monitoring campaign)





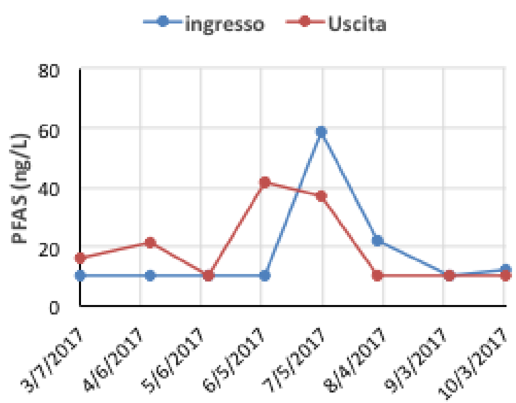
Leakage due to:

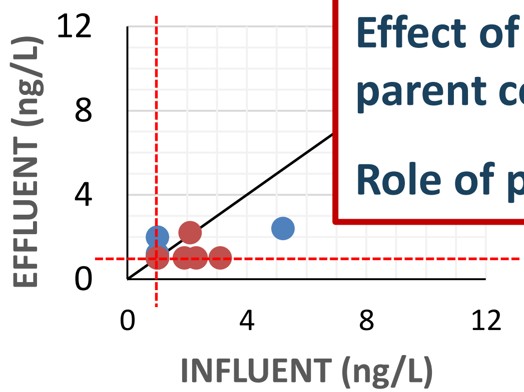
- influent fluctuations
- GAC exhaustion

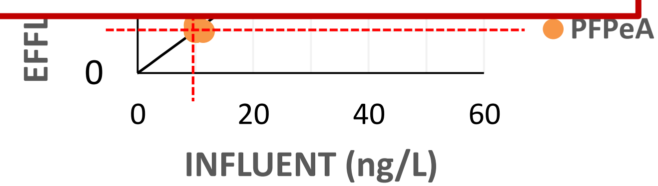
Effect of AC reactivation

Effect of different chemical characteristics of parent compounds on adsorption

Role of pre-treatments for removing NOM



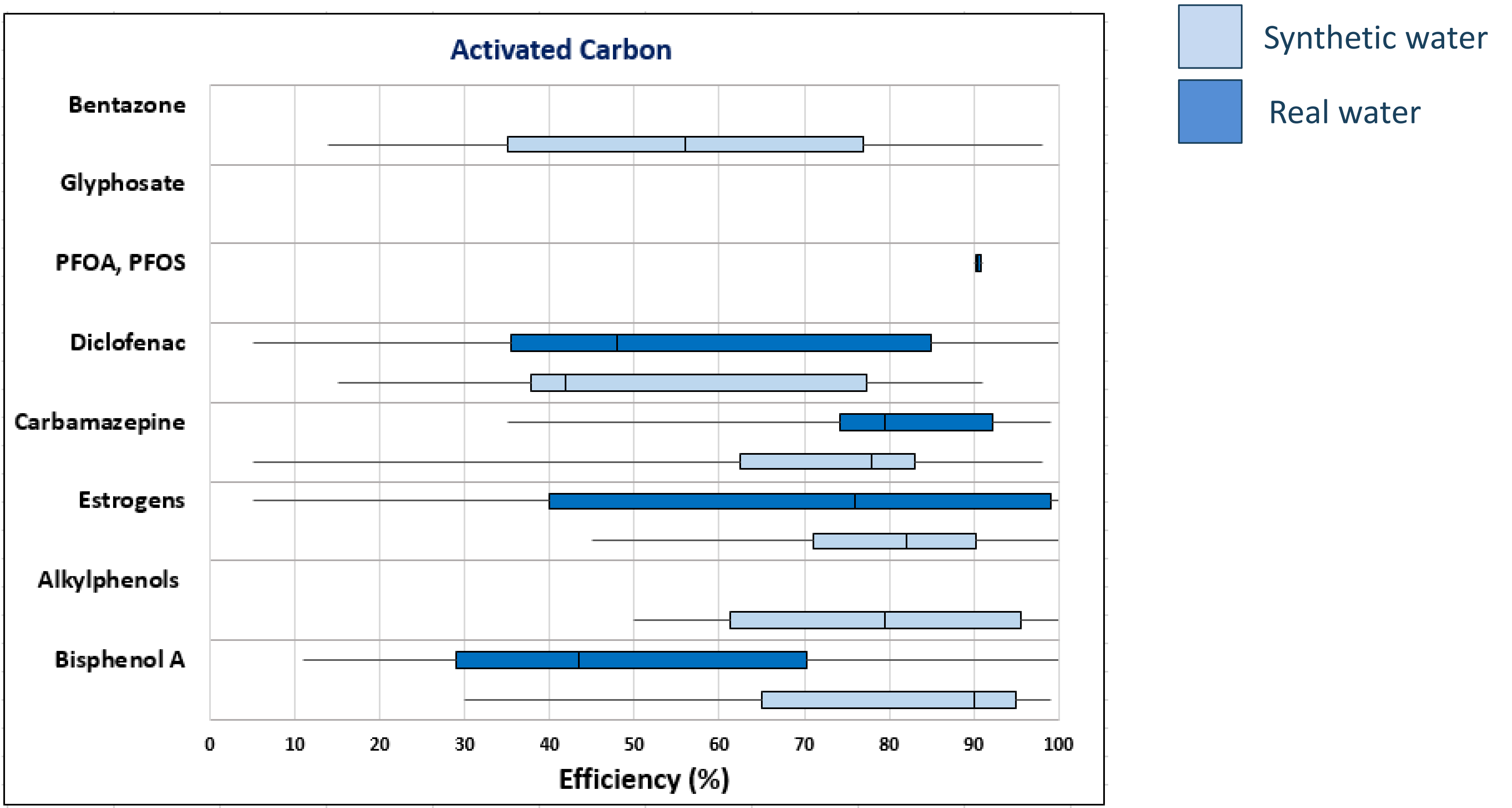




Courtesy of Romagna Acqua

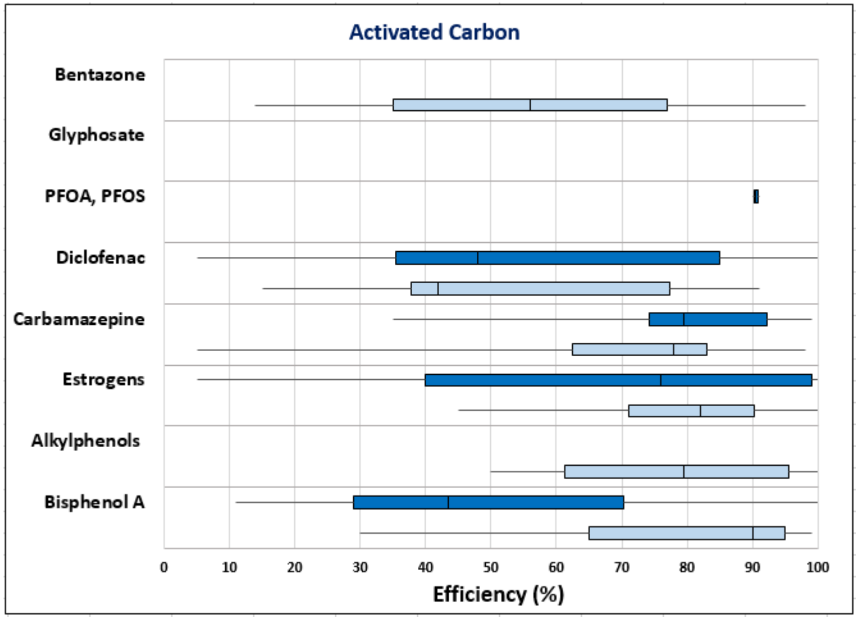
Emerging Contaminants (ECs) removal
Activated carbon adsorption (4/6)

Range of ECs removal efficiency



Emerging Contaminants (ECs) removal
Activated carbon adsorption (5/6)

Range of ECs removal efficiency



Synthetic water

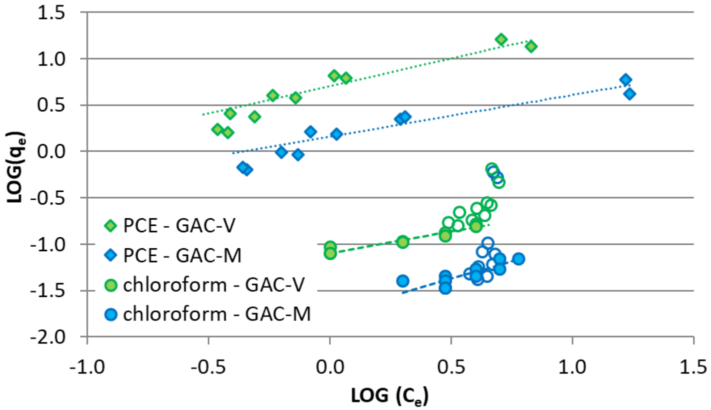
Real water

C_{AC} [g/L]	
Synthetic	Real
0.01 - 45	0.005 - 1

	C_{in} [μg/L]	
	Synthetic	**Real**
Bisphenol A	20 – 350,000	1 - 60
Alkylphenol	1 – 1,600	~ 0.1
Estrogens	1 – 3,000	0.1 - 200
Carbamazepine	1 – 100,000	0.005 - 200
Diclofenac	100 – 100,000	0.04 - 200
PFOA, PFOS	5 – 250,000	0.02 - 300
Glyphosate	5,000 – 100,000	~ 1,000
Bentazone	5,000 – 250,000	-

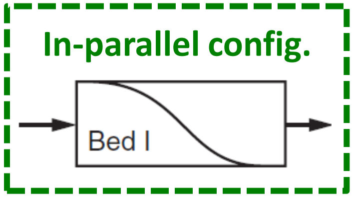
Adsorption isotherms are an effective tool to define the actual affinity of a target contaminant towards a given activated carbon, anyway:

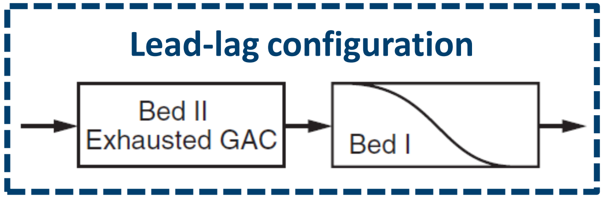
- **extrapolation** of values for low concentration **not admissible** since the parameters of adsorption isotherm depend on the concentration range
- **no** information about the **dynamic nature** of the adsorption process over time
- **overestimation** of the **activated carbon lifetime**, especially if referred to conventional in-parallel GAC configurations



Piazzoli & Antonelli (2018), PSEP

Lead-lag configurations help to improve the performance of GAC absorbers and to minimize the risk of leakage, minimizing the overall risk associated to water quality



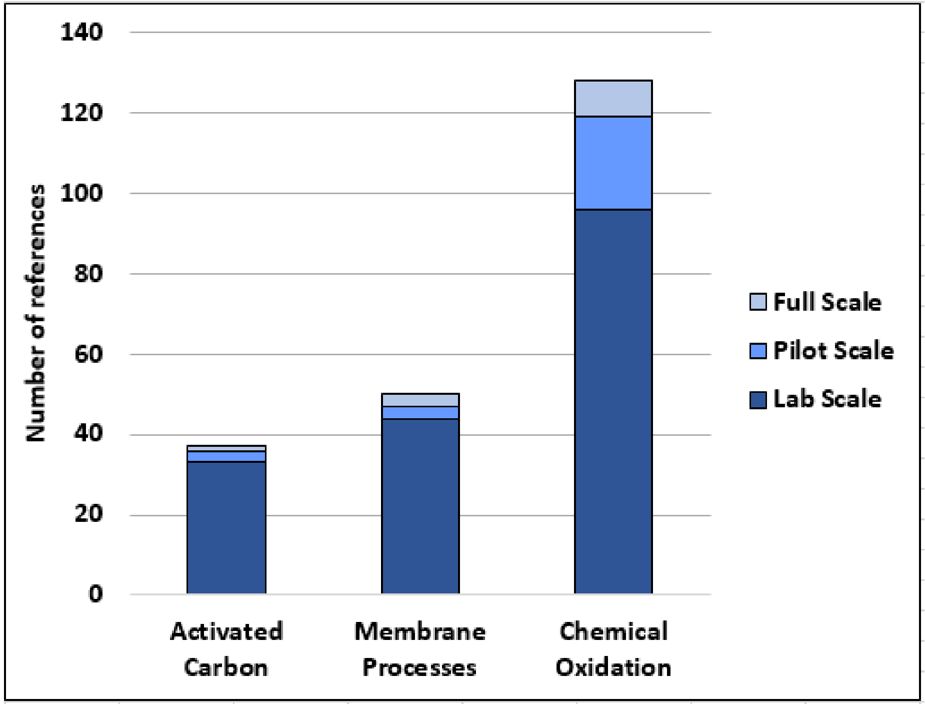


Emerging Contaminants (ECs) removal
Pressure-driven membrane (1/4)

Only **nanofiltration** (NF) and **reverse osmosis** (RO) membranes can be considered as self-standing treatment units for ECs removal

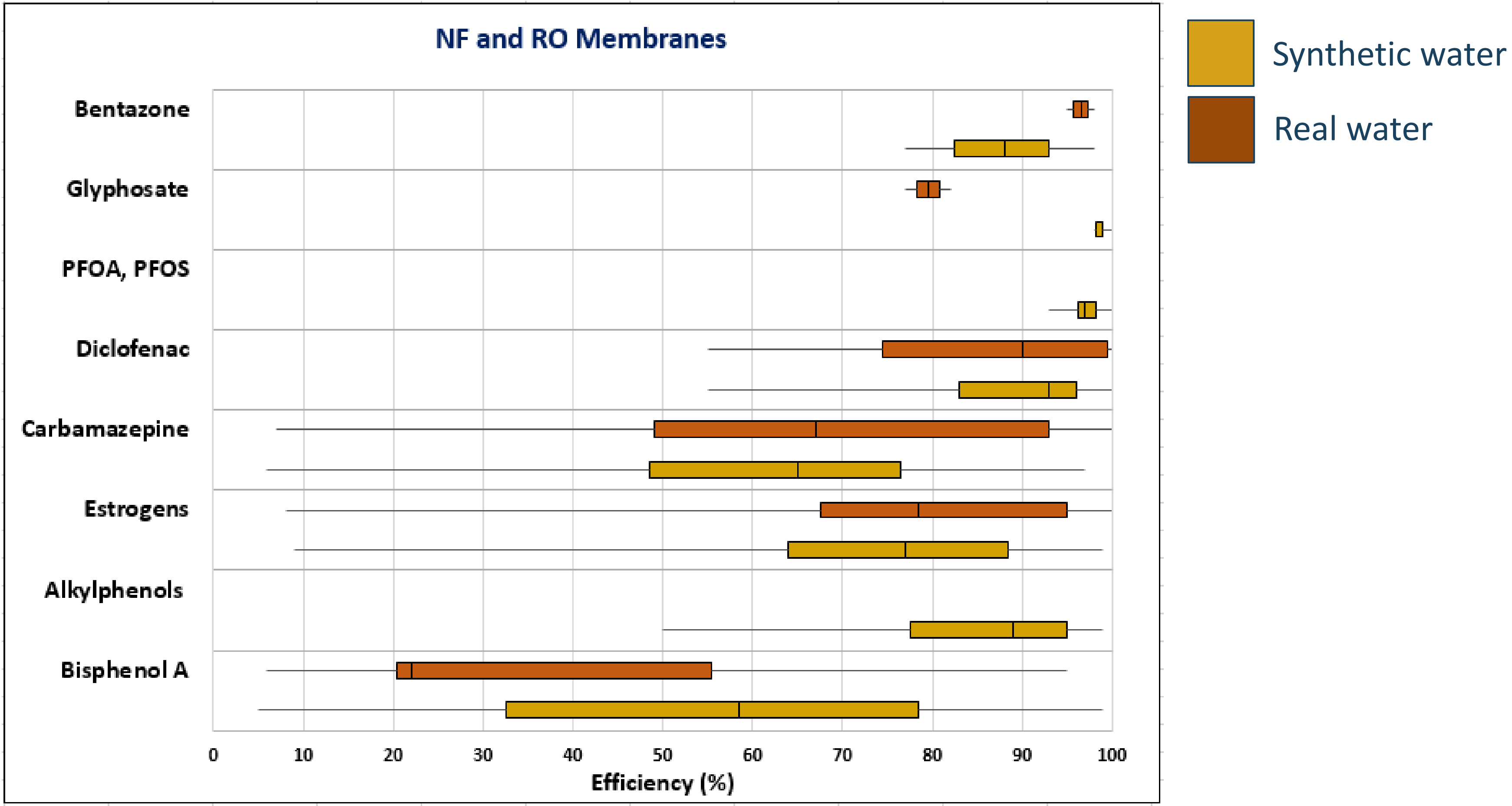
Scarce availability of data from full-scale DWTPs:

- usual positioning of membranes along the treatment train downstream of other processes, hiding their effect on ECs
- when present, system configuration or operating parameters are not fully representative of systems specifically addressed to the rejection of ECs as primary process objective



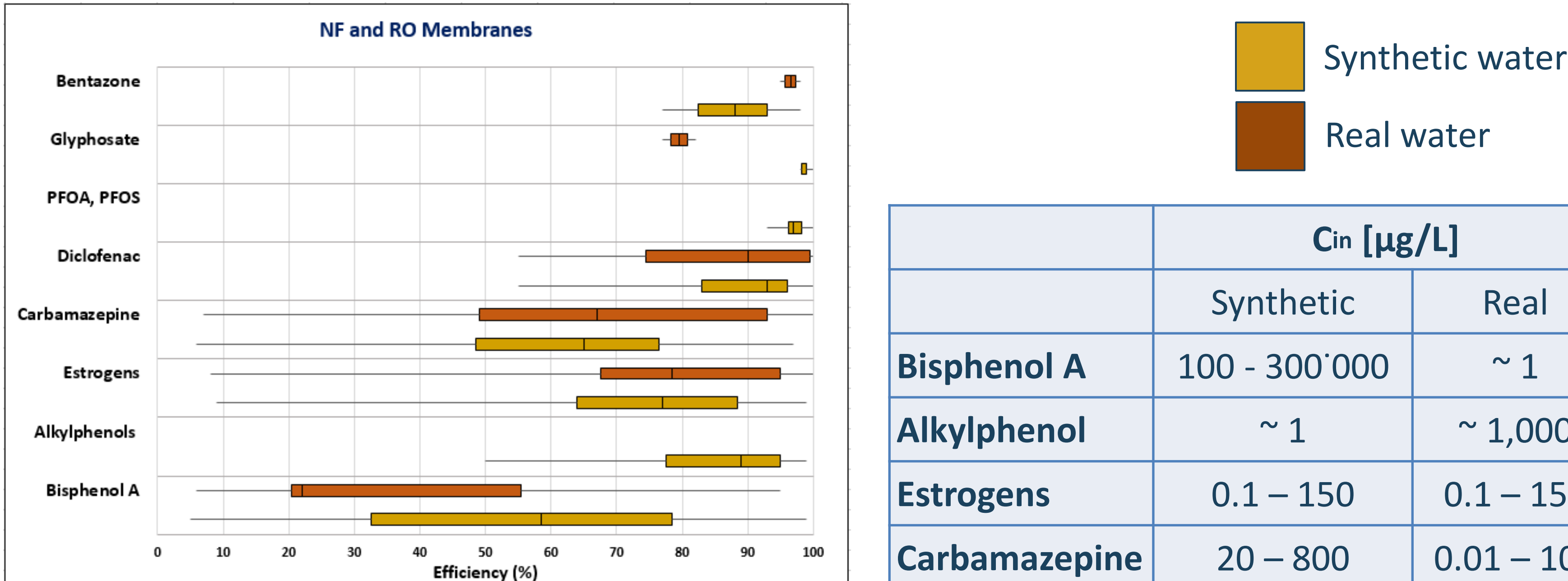
Emerging Contaminants (ECs) removal
Pressure-driven membrane (2/4)

Range of ECs removal efficiency



Emerging Contaminants (ECs) removal
Pressure-driven membrane (3/4)

Range of ECs removal efficiency



Independence of process performance from the initial concentration of target contaminants, differently from other processes, whose practical sustainability is strongly affected by this factor

	C_{in} [µg/L]	
	Synthetic	Real
Bisphenol A	100 - 300˙000	~ 1
Alkylphenol	~ 1	~ 1,000
Estrogens	0.1 – 150	0.1 – 150
Carbamazepine	20 – 800	0.01 – 100
Diclofenac	0.03 – 10,000	0.01 – 0.3
PFOA, PFOS	1 – 120,000	–
Glyphosate	40 – 200,000	~ 48,000
Bentazone	~ 10	~ 1,000

Emerging Contaminants (ECs) removal
Pressure-driven membrane (4/4)

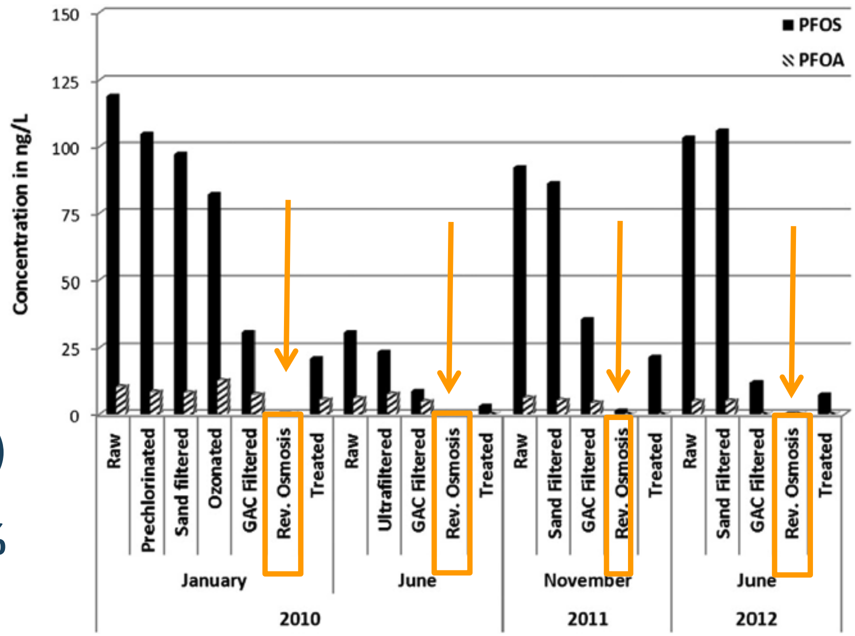
Factor affecting removal efficiency:

- operating parameters play a secondary role
- main role of the **characteristics of both water matrix** (pH, concentration of other solutes, including both inorganics and organics) **and membrane** (➡ rejection mechanism: diffusion, electrostatic interaction, adsorption, not only size exclusion)

NF membranes appear to be more promising

DWTP in Barcellona (Spain)

Removal > 99%

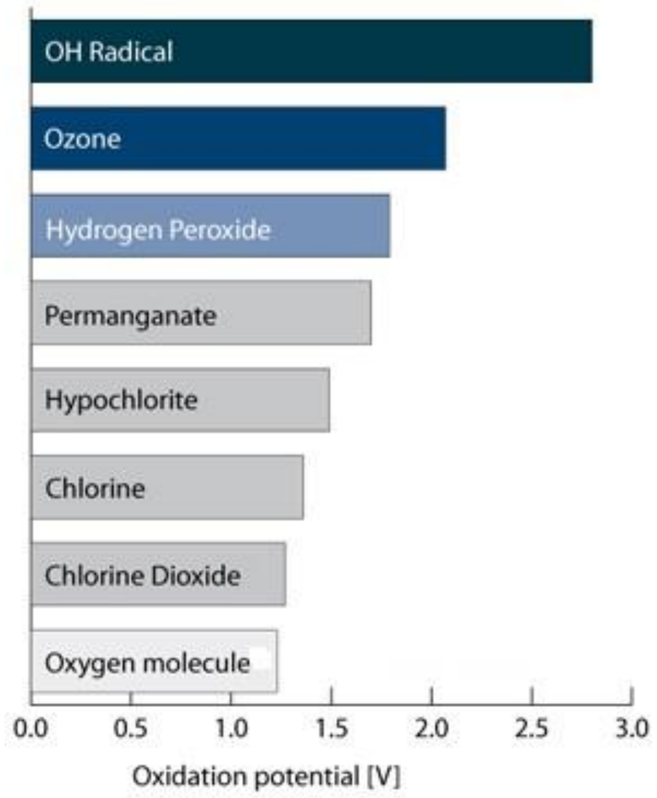


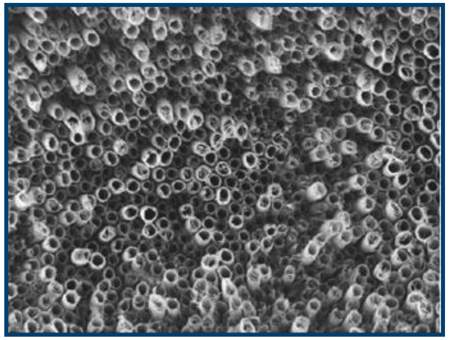
Flores et al. (2013), Sci. Total Environ.

Emerging Contaminants (ECs) removal
Oxidation processes (1/6)

Two groups of studies:

- established technologies
  - oxidation by **ozone**
  - advanced oxidation processes (**AOPs**) obtained combining ozone with hydrogen peroxide and UV radiation, and the photolysis of hydrogen peroxide by UV radiation
- under-developing solutions aimed at improving reactive oxygen species production

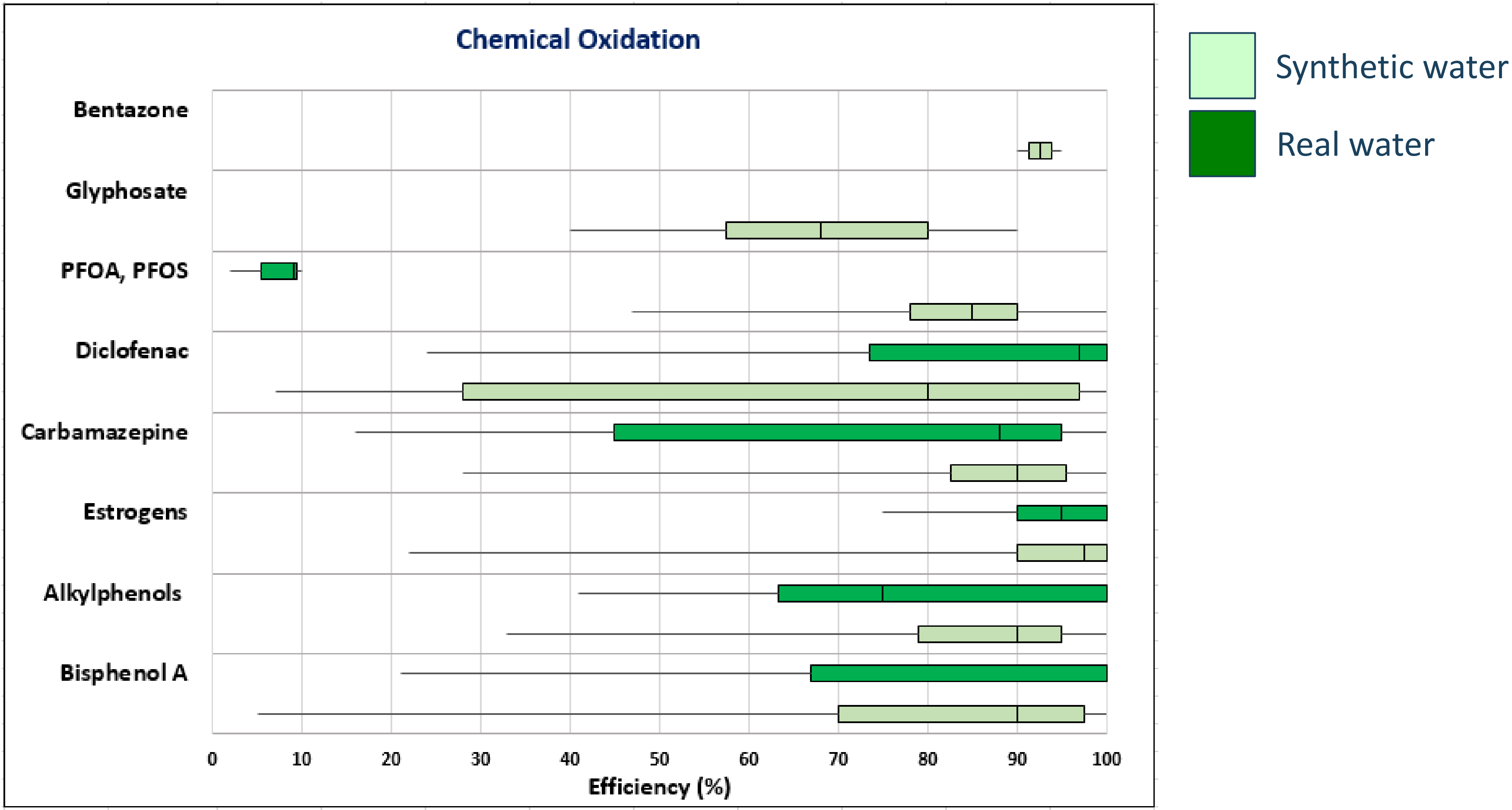




Turolla et al. (2011), Desalination

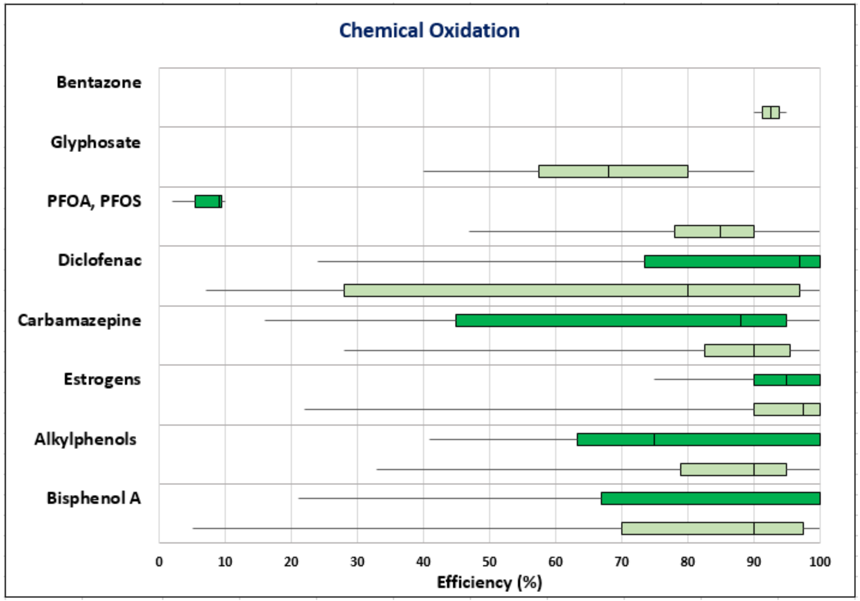
Emerging Contaminants (ECs) removal
Oxidation processes (2/6)

Range of ECs removal efficiency



Emerging Contaminants (ECs) removal
Oxidation processes (3/6)

Range of ECs removal efficiency



Synthetic water

Real water

	Oxidant	
	Synthetic	Real
O_3 [mg/l]	1.4 – 120	0.2 – 5
H_2O_2 [mg/l]	5 – 1,360	0.2 – 100

	C in [µg/L]	
	Synthetic	Real
Bisphenol A	400 – 300,000	0.01 – 50,000
Alkylphenol	1,000 – 100,000	0.04 – 1,000
Estrogens	50 – 30,000	0.03 – 15,000
Carbamazepine	1˙000 – 20,000	0.001 - 150
Diclofenac	4,000 – 80,000	0.002 - 500
PFOA, PFOS	50 – 5,000	0.001 - 0.3
Glyphosate	100 - 500	-
Bentazone	500 – 35,000	-

Factor affecting removal efficiency:

- **competing phenomena** among water constituents
  - surface water: NOM

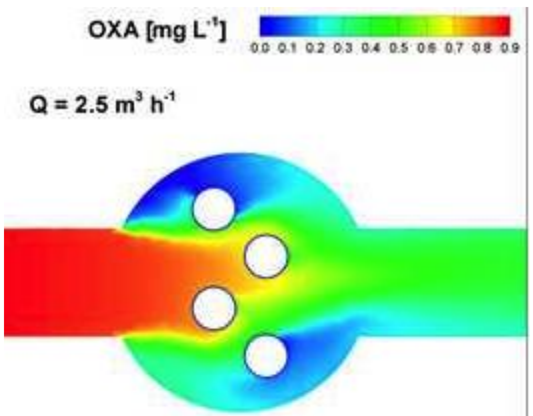
TOC over 1-2 mg/L can lead to O_3 dosage increase over 30%

- **scavenging action** of background constituents
  - groundwater: alkalinity and ionic inorganic species
  - AOPs: hydrogen peroxide concentration

5 to 20 times increase in energy consumption

- **Reactor engineering** being the reaction rate linearly depending on the concentration of the target pollutant

the extent of degradation is proportional to the number of collision events between reactive species and target pollutant: **oxidation of ECs is disadvantaged**



Santoro et al. (2017), Water Res.

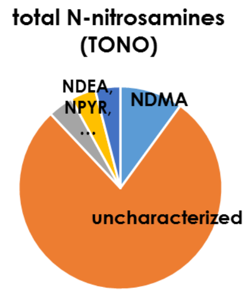
Emerging Contaminants (ECs) removal
Oxidation processes (5/6)

Main drawbacks and key elements:

- wide range of compounds that can be generated, whose accurate detection is often difficult
- scarcity of toxicological data in literature referred to ECs-related by-products ➡ estrogenicity, acute or chronic ecotoxicity, …

ECs, even at very low concentration, can be precursors of carcinogenic DBPs

ES.: N-nitrosamine formation from PPCPs
NDMA about 5% of total N-nitrosamine
(Dai and Mitch, 2013)



Von Gunten (2018), Environ. Sci. Technol.

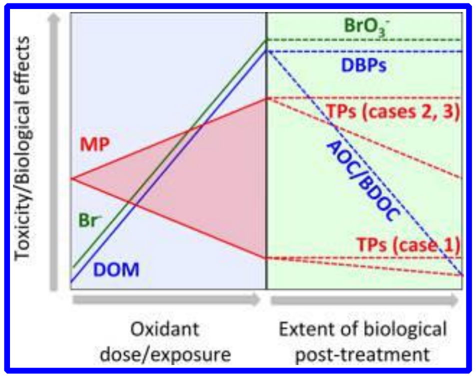


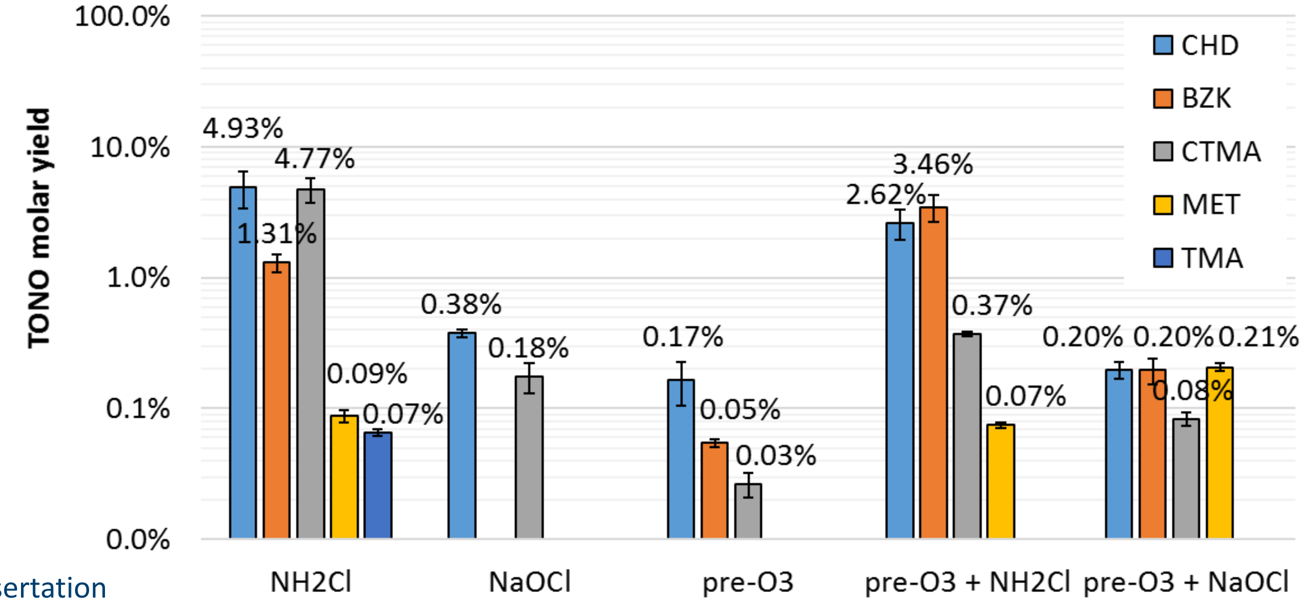
Figure 2. Relative evolution of toxicity (human health) and/or biological effects during oxidative treatment of micropollutant-containing waters as a function of the oxidant dose/exposure and the extent of biological post-treatment. MP: micropollutant; DOM: dissolved organic matter; TPs: Transformation products; DBPs: Disinfection byproducts; AOC: Assimilable organic carbon; BDOC: Biodegradable organic carbon.

Emerging Contaminants (ECs) removal
Oxidation processes (6/6)

Specific and total N-nitrosamine formation potential of PPCPs during oxidation treatments (NH_2Cl, NaOCl, O_3)

Precursors selected (containing tertiary amines and quaternary-ammonium compounds):

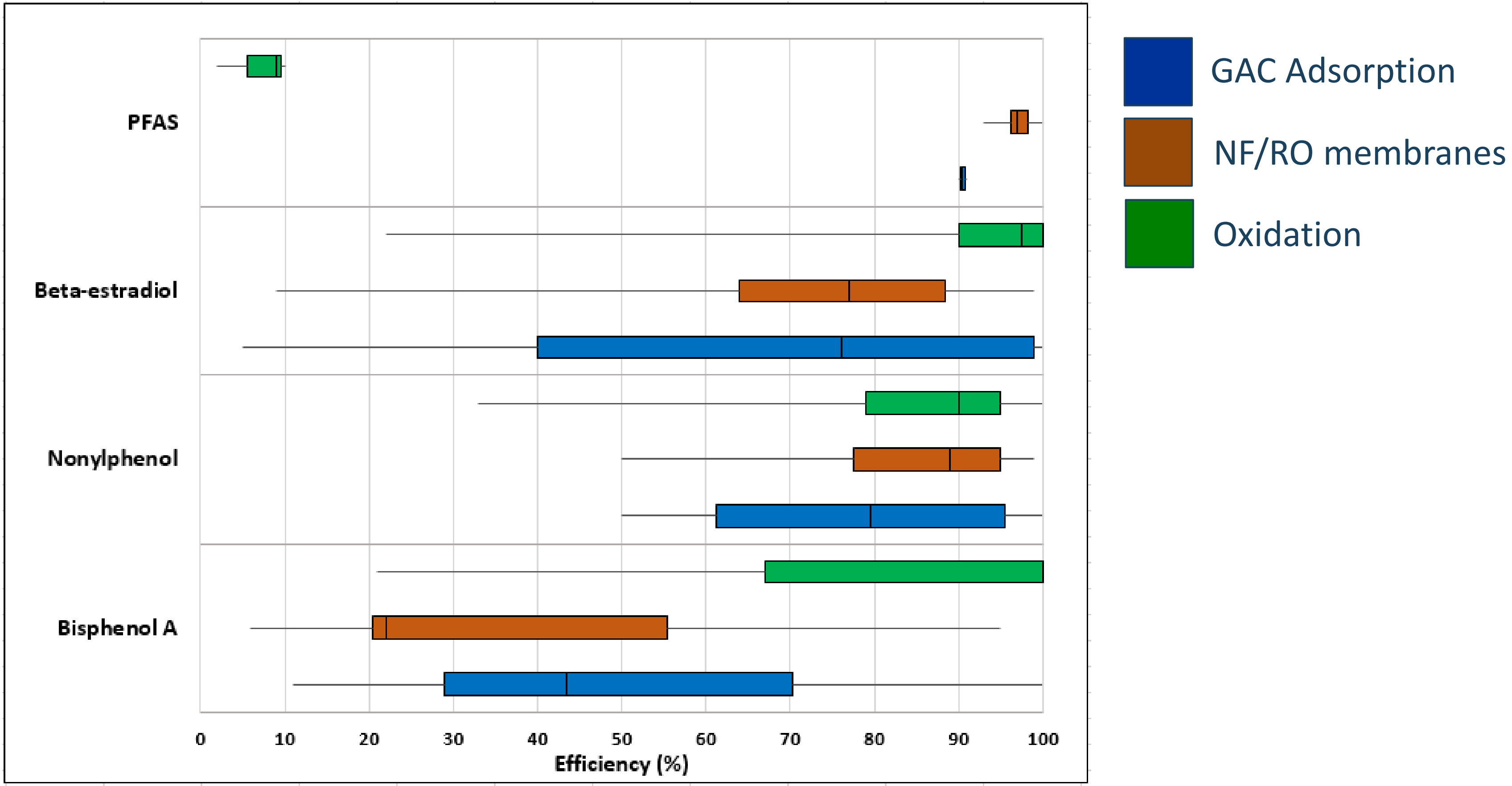
- Chlorhexidine (CHD)
- Benzalkonium chloride (BZK)
- Cetyltrimethyl ammonium (CTMA)
- Metformin (MET)



Piazzoli A. (2018). PhD Dissertation
Piazzoli et al. (2018), Water Res.

Emerging Contaminants (ECs) removal
Removal of ECs in the DW directive under revision

Range of ECs removal efficiency



Emerging Contaminants (ECs) removal
Conclusions

When communicating the outcomes of a research work:

- reliable indications on the presence of compounds in water other than the target pollutant
- reliable indications about the operating conditions of the DWTP

Fundamental the upstream improvement of water characteristics aimed at enhancing the performance of the process

Fundamental the control of degradation by-products by downstream treatment processes, as adsorption on activated carbon

from the engineers' point of view, work in progress

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Thank you

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manuela.antonelli@polimi.it