

# PRIORITY AND EMERGENT CONTAMINANTS IN MUNICIPAL WASTEWATERS: LEVELS AND REMOVAL IN CONVENTIONAL WWTPs

Valeria Mezzanotte, Francesca Malpei



# OUTLINE

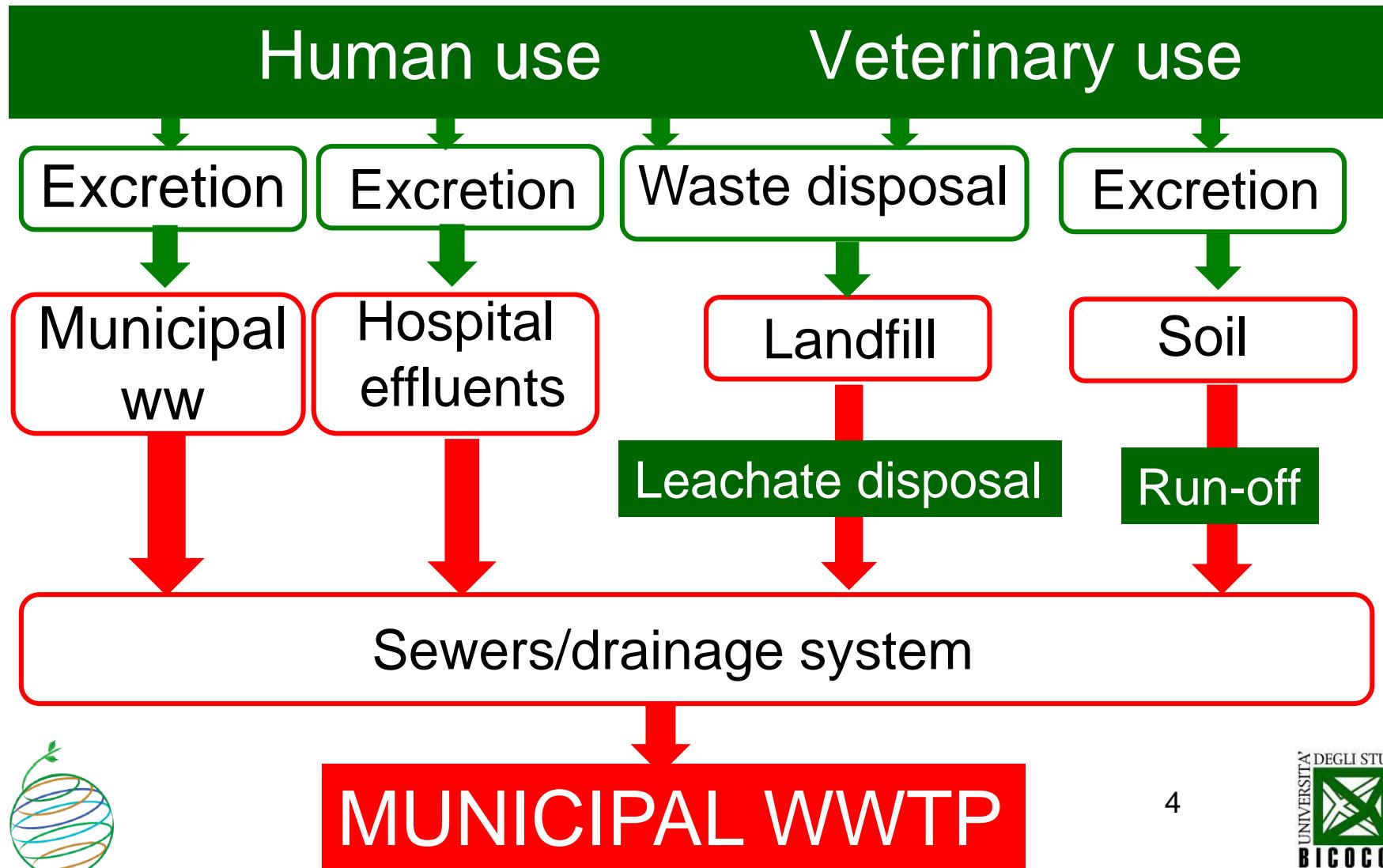
- Sources and concentrations in the influents
- Removal mechanisms
- Removal efficiencies
- Concentrations in the effluents



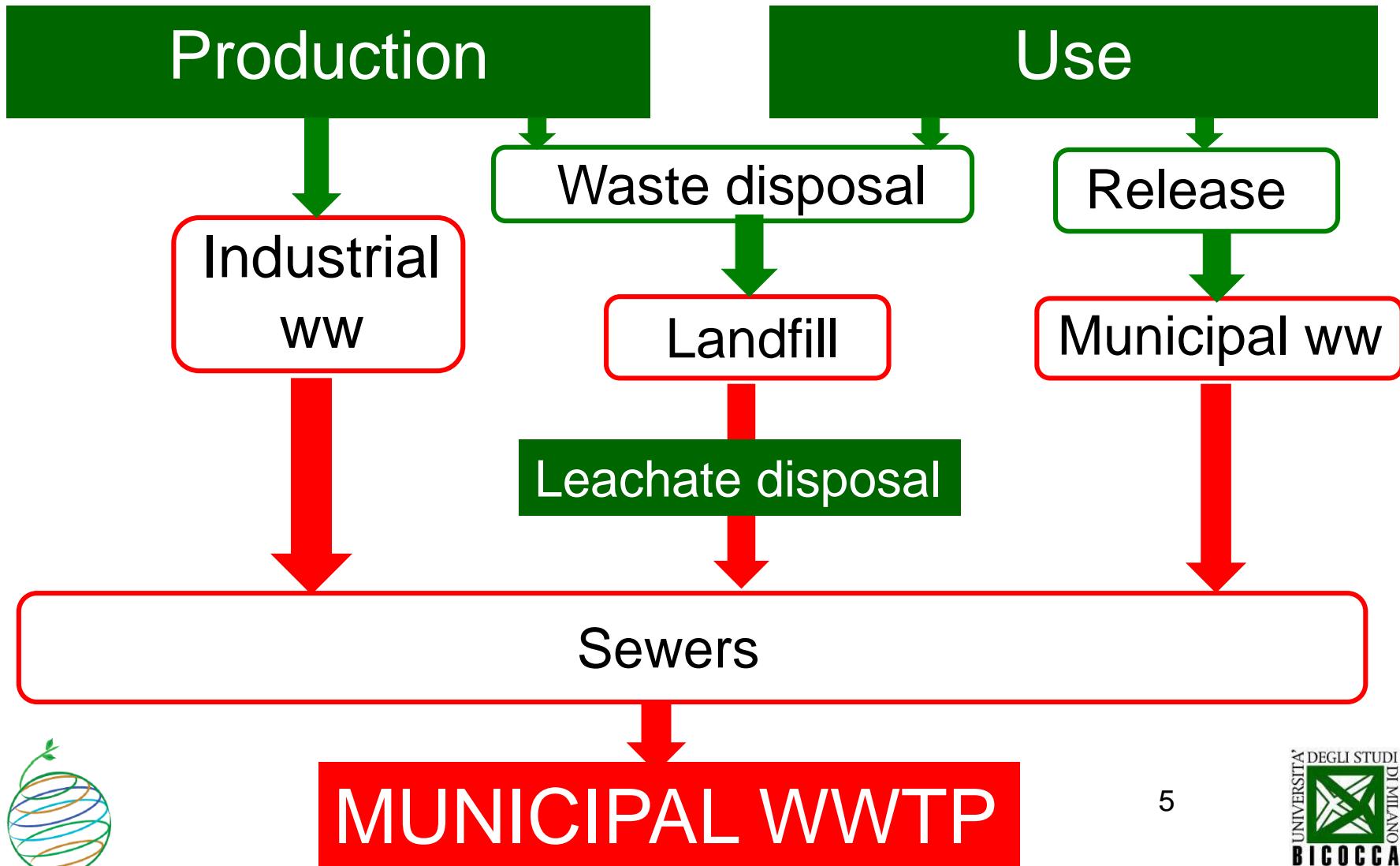
# SOURCES



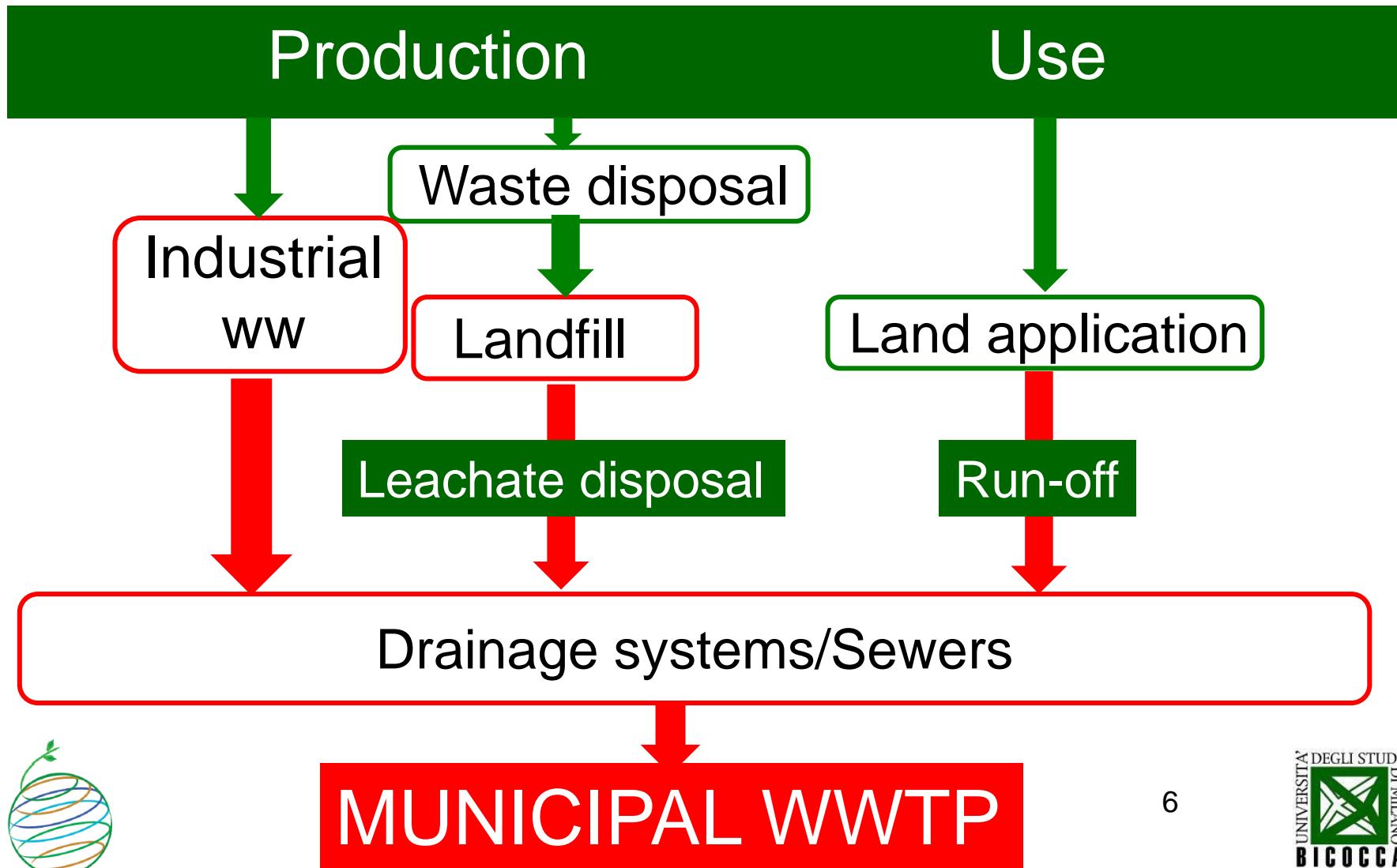
# PREVAILING SOURCES FOR SPECIFIC MICROPOLLUTANT CLASSES: PHARMACEUTICAL COMPOUNDS



# PREVAILING SOURCES FOR SPECIFIC MICROPOLLUTANT CLASSES: PFOA/PFAS, FLAME RETARDANTS, PCPs



# PREVAILING SOURCES FOR SPECIFIC MICROPOLLUTANT CLASSES: PESTICIDES



# PREVAILING SOURCES FOR SPECIFIC MICROPOLLUTANT CLASSES: PAH

Production and use

Combustion

Waste disposal

Industrial  
ww

Landfill

Land deposition

Leachate disposal

Run-off

Drainage systems/Sewers



MUNICIPAL WWTP

# CONCENTRATIONS

## Significant time and space variations depending on:

- Local production and use/consumption (accessibility)
- Excretion rates (pharmaceuticals)
- Disposal ways (solid wastes, animal farming wastewaters)



# CONCENTRATIONS: SOME EXAMPLES FROM INTERNATIONAL LITERATURE (Luo et al., 2014)

PHARMACEUTICALS	
<i>Category</i>	<i>Range (µg/L)</i>
Analgesic and antinflammatory	<0.001-603
Anticonvulsant	<0.04-3.78
Lipid regulator	0.05-1.39
Antibiotic	<0.003-17.1
B-blocker	0.002-33.1
Nervous stimulant	0.22-209



# CONCENTRATIONS: SOME EXAMPLES FROM INTERNATIONAL LITERATURE (Luo et al., 2014)

## PERSONAL CARE PRODUCTS (PCPs)

<i>Category</i>	<i>Range (<math>\mu\text{g/L}</math>)</i>
Musk fragrance	<0.05-25
Disinfectant	0.03-23.9
Insect repellent	2.56-3.19
UV-filter	<0.079-0.90



# CONCENTRATIONS: SOME EXAMPLES FROM INTERNATIONAL LITERATURE (Luo et al., 2014)

<i>Category</i>	<i>Range (<math>\mu\text{g/L}</math>)</i>
Steroid hormone	0.001-0.8
Surfactants	<0.03-101.6

## INDUSTRIAL CHEMICALS

<i>Category</i>	<i>Range (<math>\mu\text{g/L}</math>)</i>
Plasticizers	ND-70.0
Fire retardant	0.06-4.0



# CONCENTRATIONS: SOME EXAMPLES FROM INTERNATIONAL LITERATURE (Luo et al., 2014)

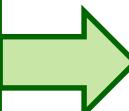
PESTICIDES	
Category	Range ( $\mu\text{g/L}$ )
Herbicide	0.02-28.0
Insecticide	<0.684
Fungicide	ND-1.89



# FACTORS AFFECTING THE TREATMENT APPLICABILITY AND EFFICIENCY

**Molecular and physical-chemical properties:**

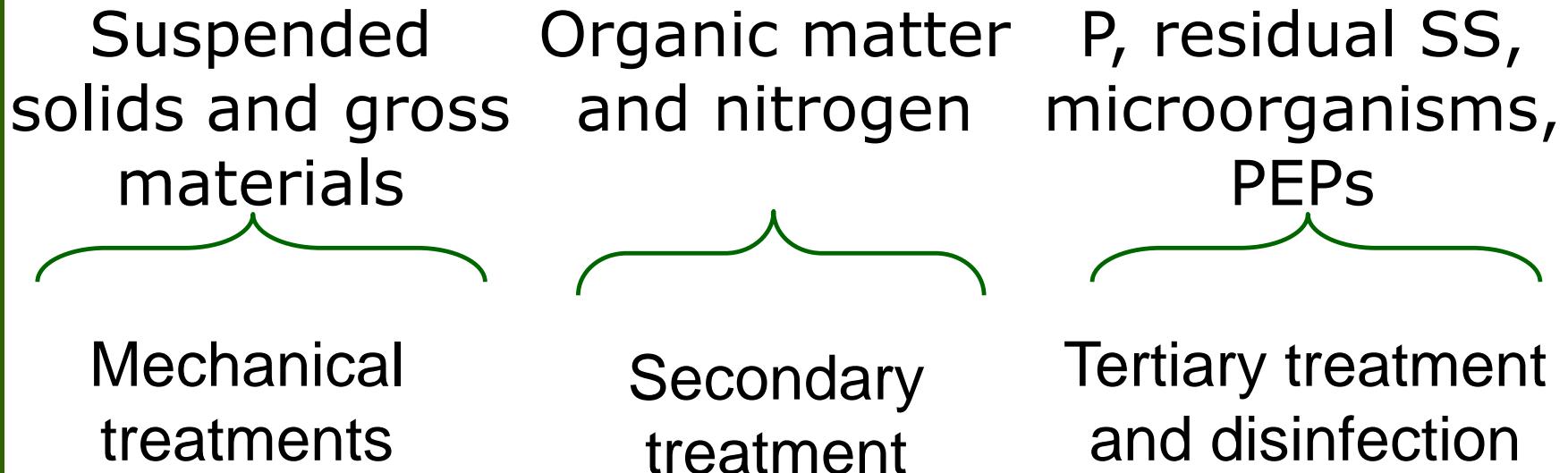
- ✖ molecular weight
- ✖ solubility
- ✖ volatility
- ✖ polarity
- ✖ adsorbability
- ✖ biodegradability



**Treatment processes:**

- ✖ **PHYSICAL:** by membranes, gravity, electric potential (electrodialysis), physical adsorption
- ✖ **CHEMICAL:** oxidation, chemiadsorption, ion exchange
- ✖ **BIOLOGICAL:** Biodegradation

# CONVENTIONAL WWTPs



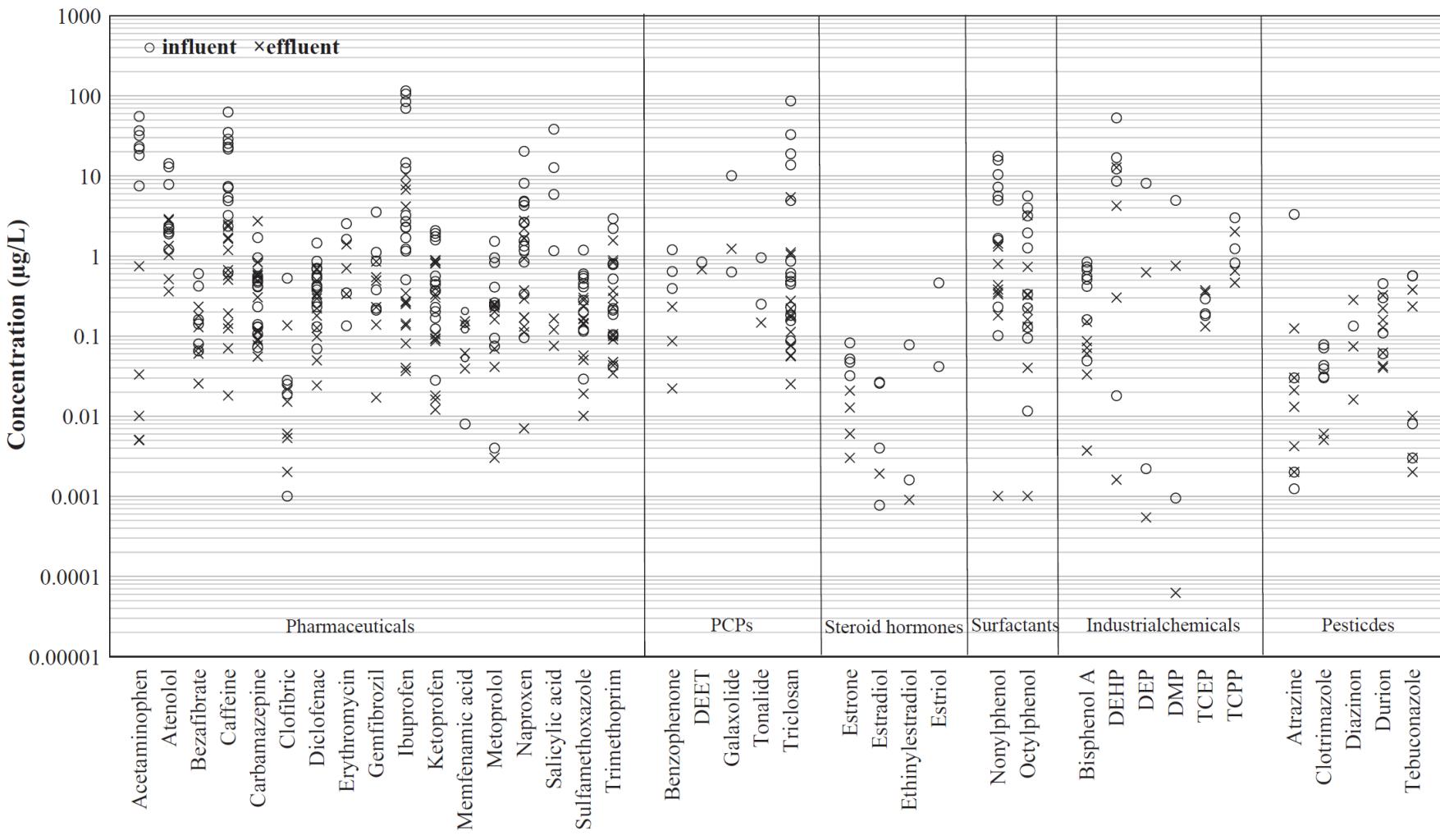
Removal may occur by:

- biodegradation;
- Sludge adsorption;
- (stripping)

Secondary sludge

Removal may occur by:

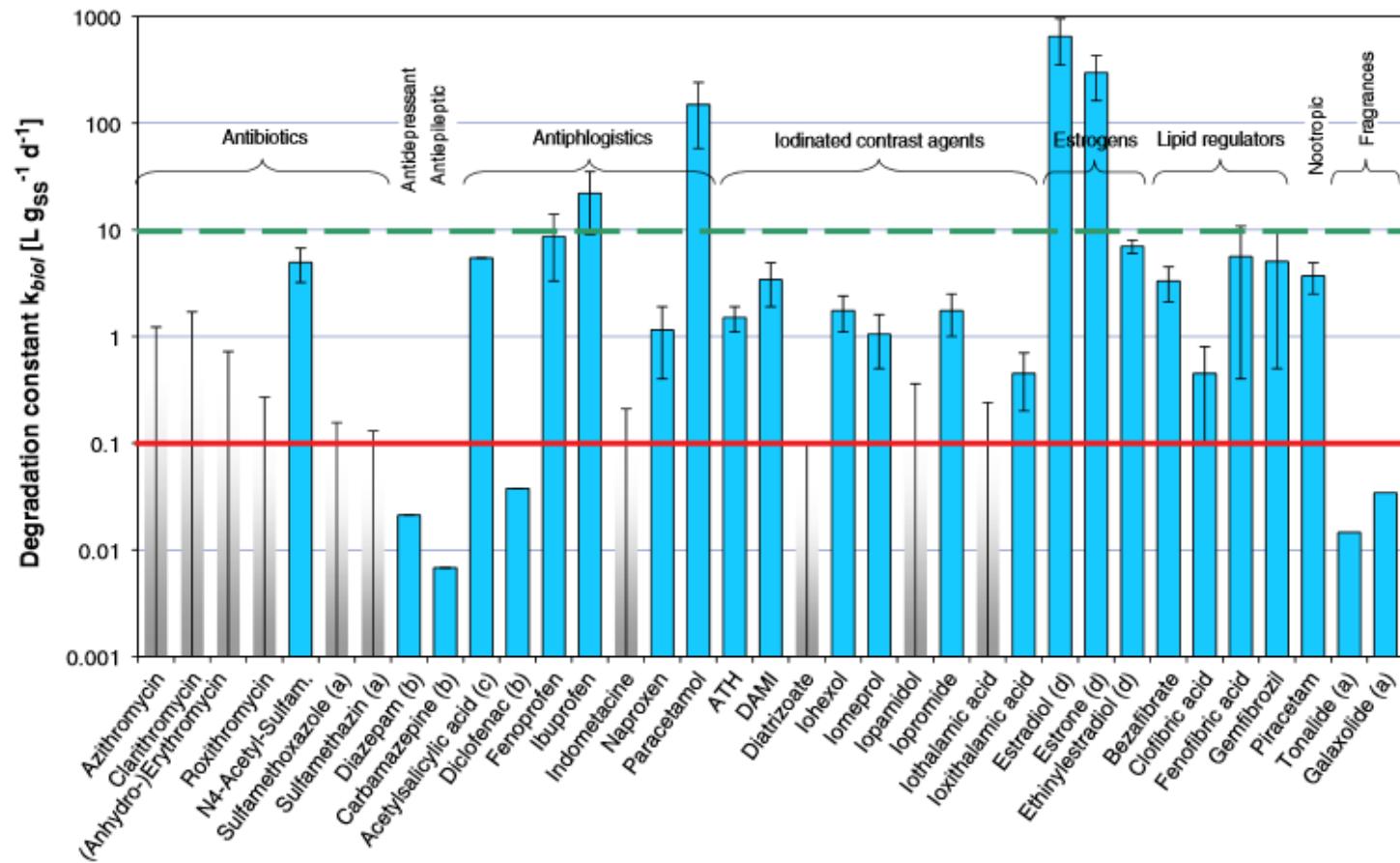
- Flocculation/ precipitation
- Chemical oxidation
- Adsorption
- Membrane filtration
- (Stripping)



# Average concentrations (on logarithmic Y axis) reported for the selected micropollutants in WWPT influents and effluents



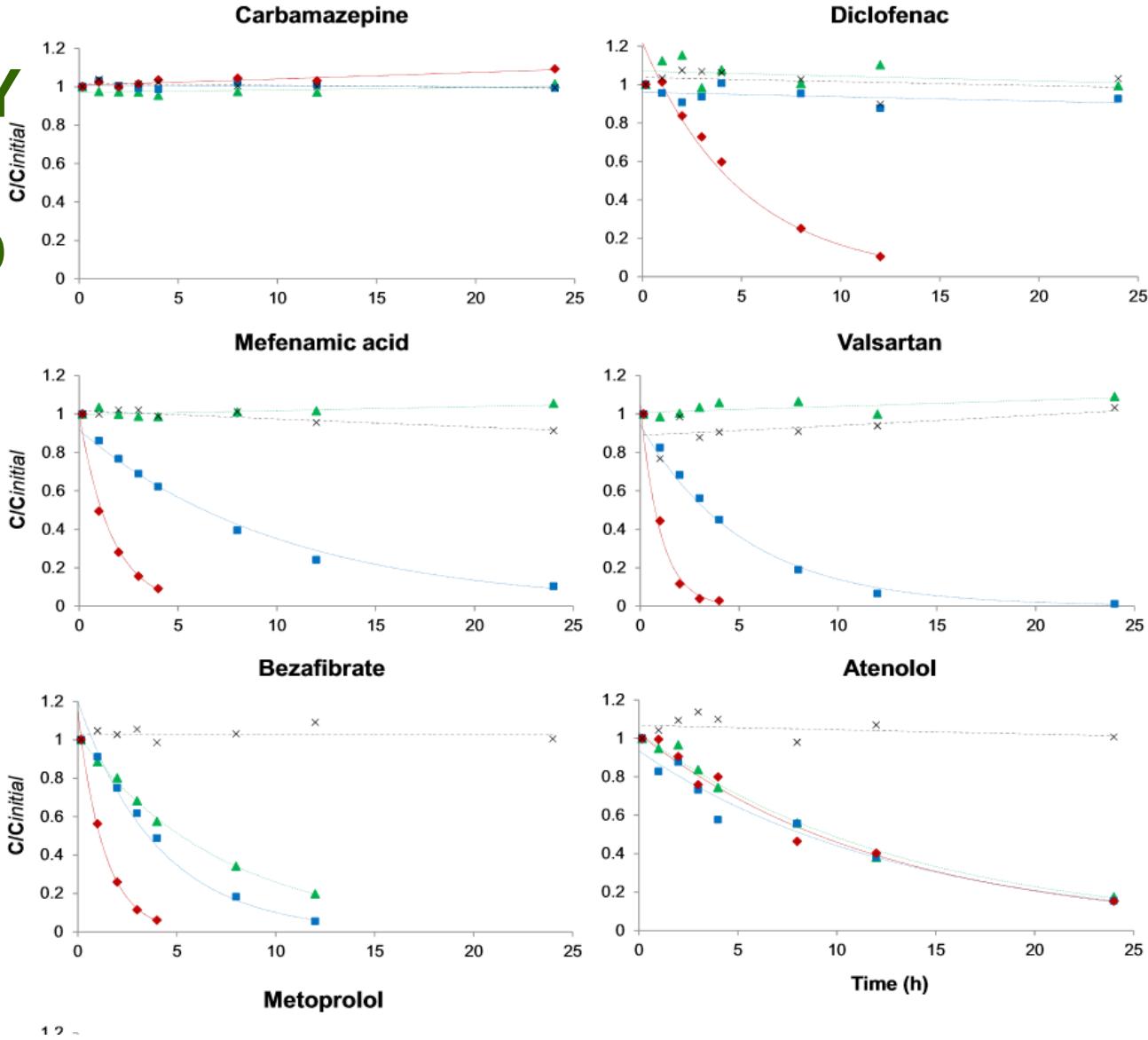
# CLASSIFICATION OF BIODEGRADABILITY OF PHARMACEUTICALS (JOSS ET AL., 2008)



- $K_{biol} < 0.1$  L/g SS/d: no removal
- $0.1 < K_{biol} < 10$  L/g SS/d: partial removal
- $K_{biol} > 10$  L/g SS/d: removal  $\geq 90\%$



# REMOVAL BY FIXED AND SUSPENDED BIOMASS



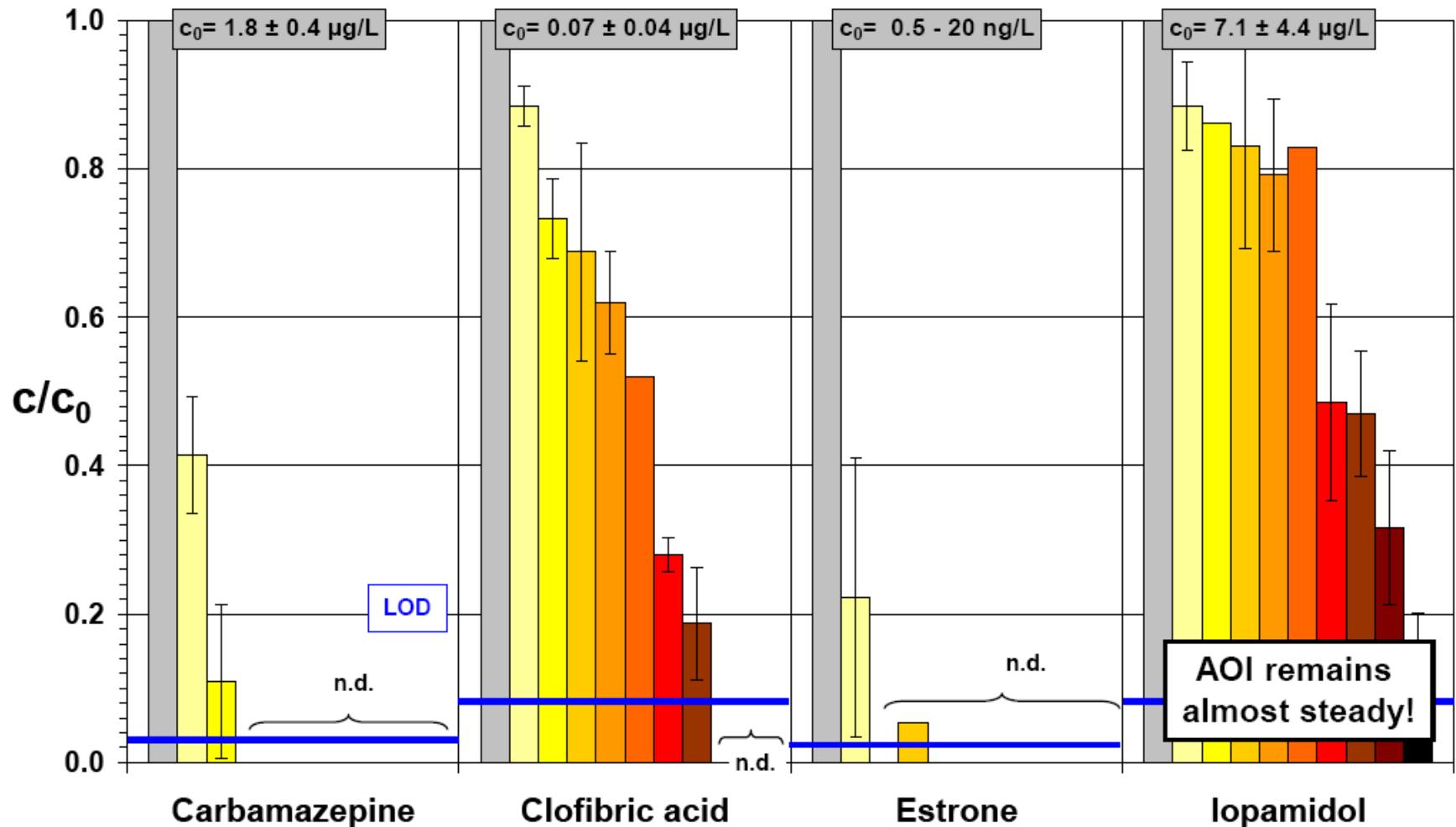
Falas et al, Wat.Res. (2013)

# ADVANCED TREATMENTS: OZONATION

## (Jekel, 2010)

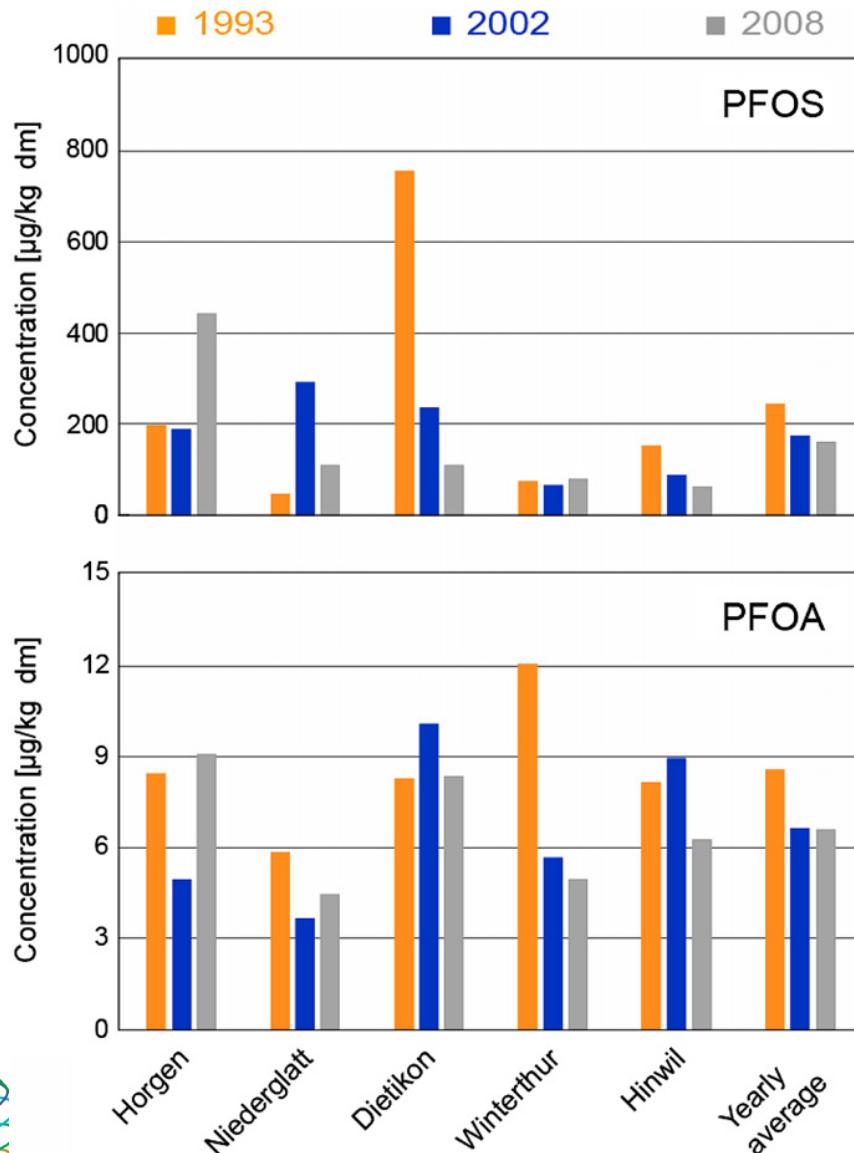
### Removal of pharmaceuticals by ozonation

$DOC_0 = 10-12 \text{ mg/L}$



spec.  $\text{O}_3$  - Consumption: 0.0 0.2 0.3 0.4 0.5 0.6 0.8 1.0 1.2 1.4 mg $\text{O}_3$ /mg $DOC_0$

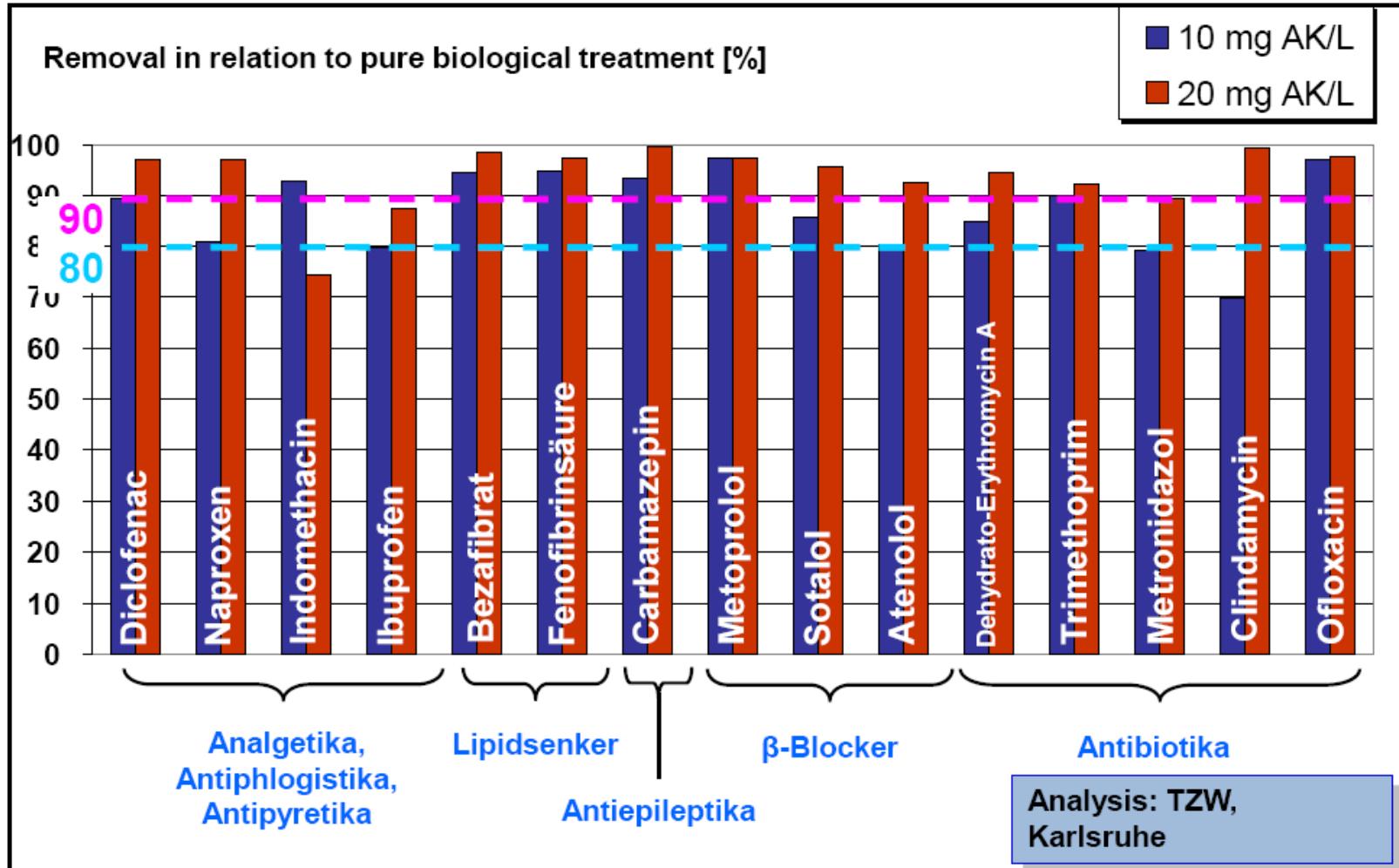
# PFOS E PFOA: CAN BE ADSORBED BUT NOT BIODEGRADED



**Concentration in  
sewage sludge**  
(Sun et al., 2011  
Env.Poll.)



# POWDERED ACTIVATED CARBON (JEKEL, 2010)

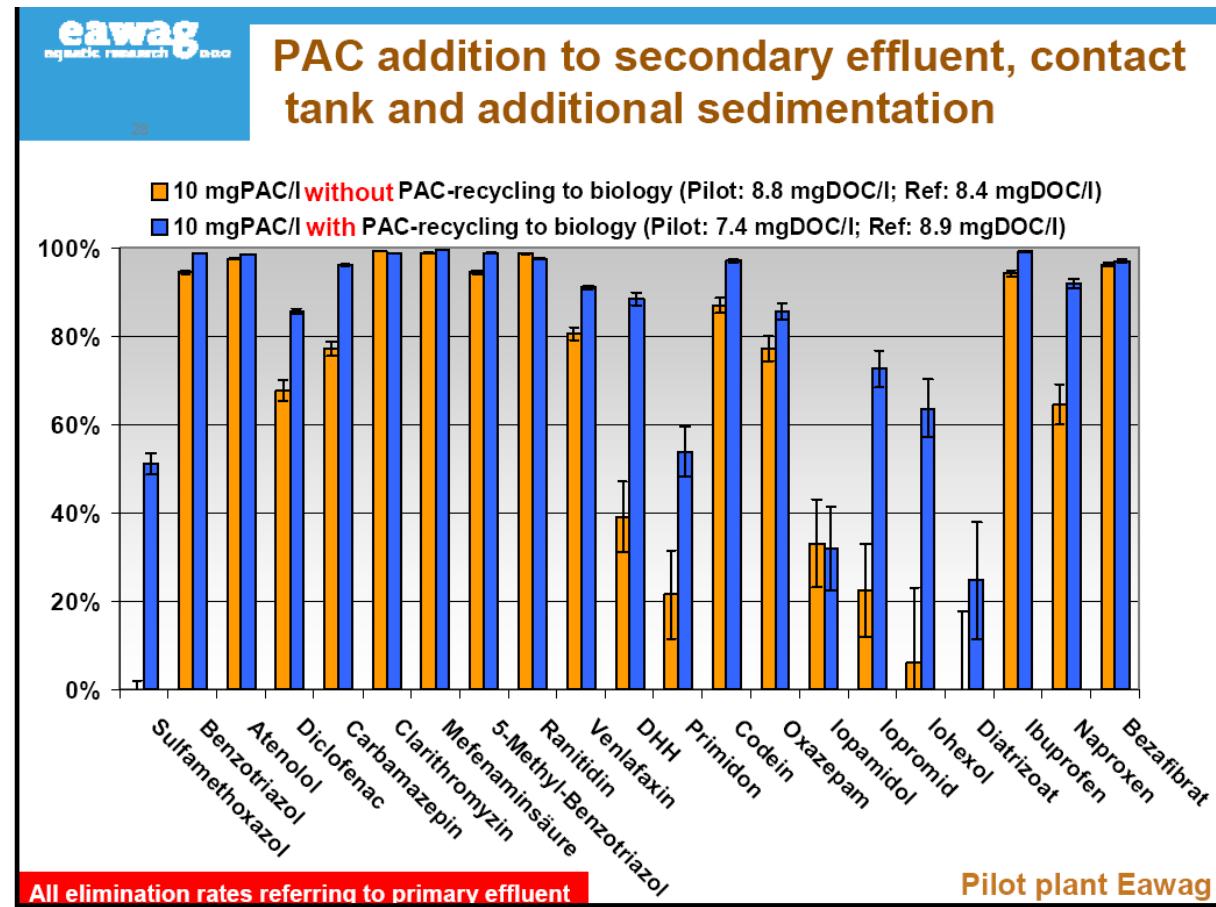


PAC added directly upflow final filtration.

Adsorption efficiency also related to dissolved organic carbon concentration



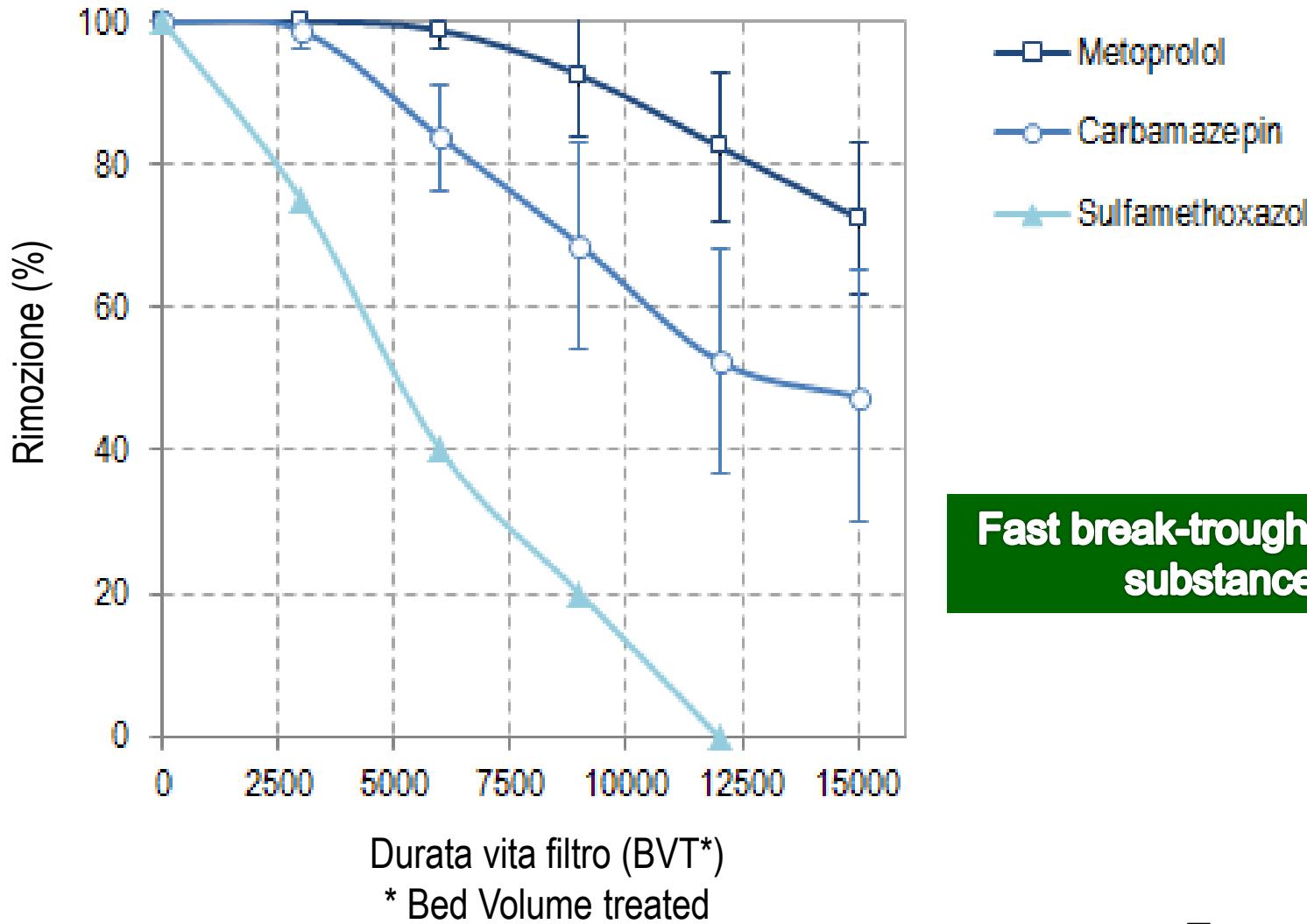
# POWDERED ACTIVATED CARBON (SIEGRIST, 2010)



PAC added in tertiary treatment, with or without returning tertiary sludge to biological process



# ADSORPTION ON GAC



From: VSA

# MBR: RESULTS WITH DIFFERENT SRT: 15 vs. 35 vs. 50 DAYS

Similar removal for most substances.  
However:

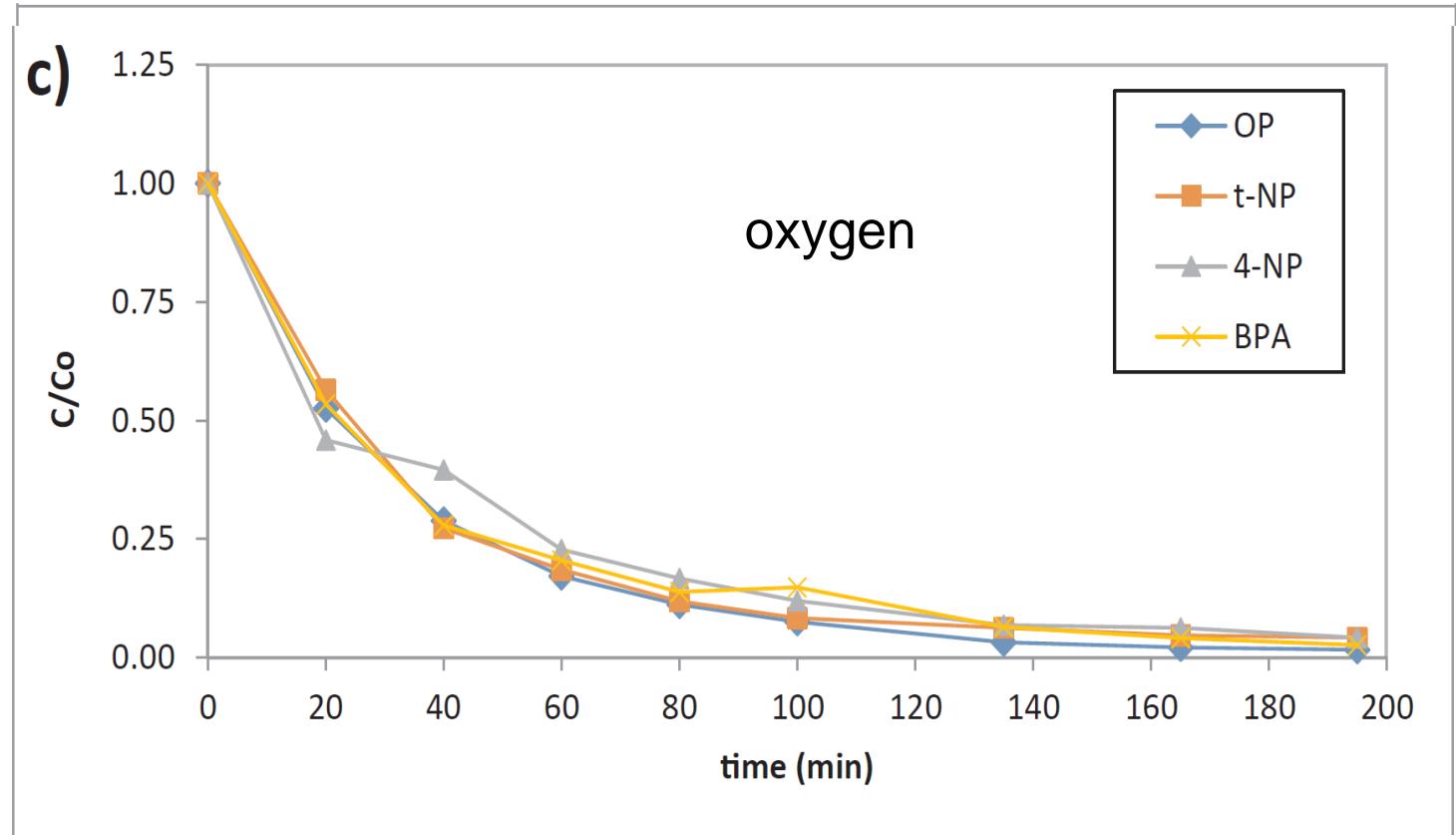
- **Diclofenac** and **Furosemide**: removal  
 $15d < 35d < 50d$
- **Atorvastatin**: removal  $15d < 35d$
- **Ketoprofen** and **Ciprofloxacin**: removal  
 $15d > 35d > 50d$
- **Salbutamol, Ofloxacin** and **Demethyldiazepam**:  
removal  $15d > 35 d$

# MICROALGAE

Removal by:

- chemical oxidation,
- photooxidation
- Biodegradation
- Sorption

**In algal culturing the conditions promote all such processes**



OP = 4-tert-octylphenol, t-NP = technical-nonylphenol, 4-NP = 4-nonylphenol, BPA = bisphenol-A

# FINAL REMARKS

- Emerging pollutants reach sewers and WWTPs from a wide variety of sources and processes
- CSOs also contribute significantly to EP load to surface waters
- Different compounds behave differently behaviours towards treatments
- Removal efficiencies are case specific, with great variability depending on the properties of the compound, its starting concentration and the operative conditions of the WWTP.
- In general, conventional WWTPs without tertiary treatments are not able to ensure a sharp and, especially, a reliable and constant removal of emerging pollutants

# OPEN QUESTIONS...

- Due to the differences among micropollutants and process efficiencies, reliable performances can just be obtained by combining different tertiary treatments
- With respect to treatment, micropollutants should be considered not only for the category they belong but, especially, for their physical-chemical properties
- Considering the costs involved, interventions on the drainage systems and sewer overflows should also be considered
- The true need for advanced treatments should be evaluated with respect to the flow and conditions of the receiving waters
- ...

**THANK YOU FOR YOUR  
ATTENTION**