A scenic view of a river with rapids and a rainbow. The river flows through a lush green landscape with trees and buildings in the background. A vibrant rainbow is visible in the sky above the rapids. The water is turbulent and white with foam. In the foreground, there are some dark green plants.

Emerging substances in water

A new challenge for water management

Thomas A. Ternes

Content of the presentation

- Which chemicals are relevant?
- Do we have a problem with “emerging” micropollutants?
- How can we remove micropollutants?
- Conclusions

Which chemicals are relevant?

Chemicals used in the EU

- **100000 "old chemicals" until 1981**
 - **4000 "new chemicals" since 1981**
-
- **30000 chemicals > 1 t yr⁻¹**
 - **2900 chemicals > 100 t yr⁻¹**
 - **2600 chemicals > 1000 t yr⁻¹**

Predicted application and production quantities

Application quantities in Germany

- ↪ Human-use pharmaceuticals (ca. 2800): about 6500 t yr⁻¹
corresponds to 78 g cap⁻¹ yr⁻¹
- ↪ Veterinary pharmaceuticals: about 1000 t yr⁻¹
- ↪ Pesticides (ca. 200): about 30000 t yr⁻¹
- ↪ Surfactants: 188629 t yr⁻¹ (2.3 kg cap⁻¹ yr⁻¹)

Production quantities in Germany

- ↪ Personal care products: > 500000 t yr⁻¹ (> 6.1 kg cap⁻¹ yr⁻¹)
- ↪ EDTA: 29560 t yr⁻¹

„Older organic chemicals“ detected in rivers

Giger, 2006

Hydrophilic

POLARITY

Lipophilic

Herbicides/Fungicides
Phenoxy herbicides
Phenyl urea herbicides

Atrazine

NTA
EDTA

Surfactants

Insecticides
DDT

Hydrocarbons

PCB

PAH

PCDD, PCDF

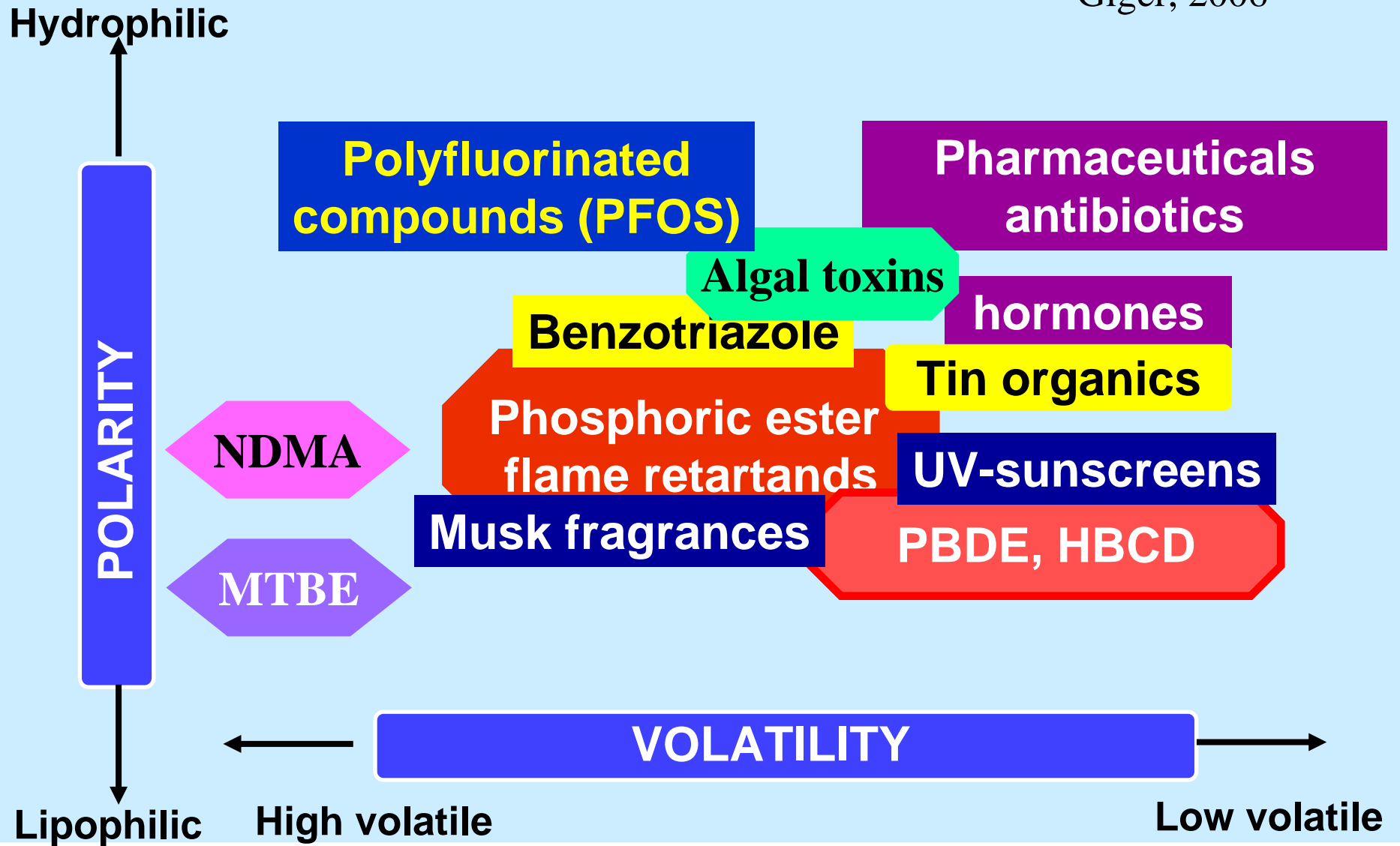
VOLATILITY

volatile

nonvolatile

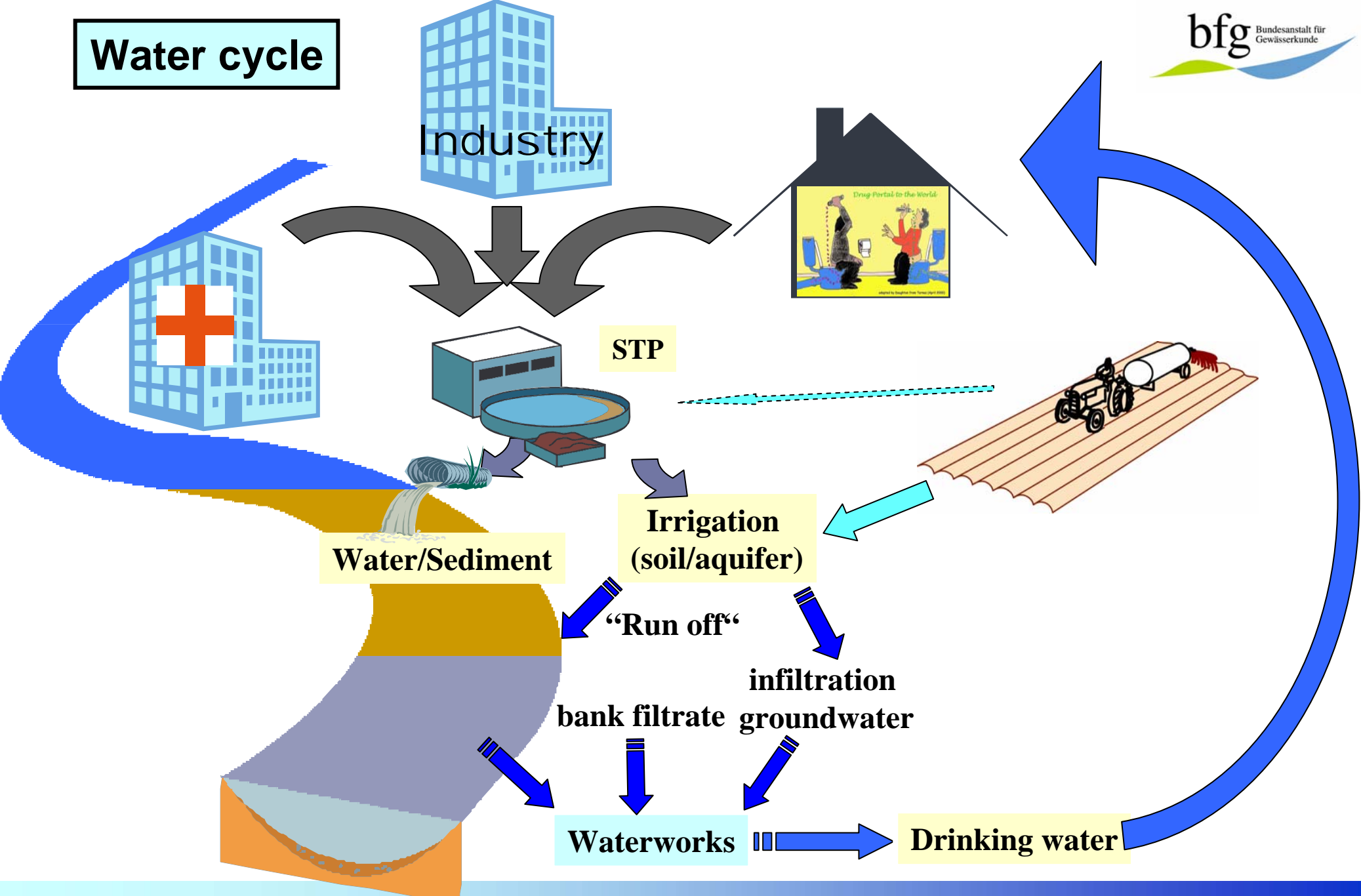
„Emerging” Contaminants in rivers

Giger, 2006



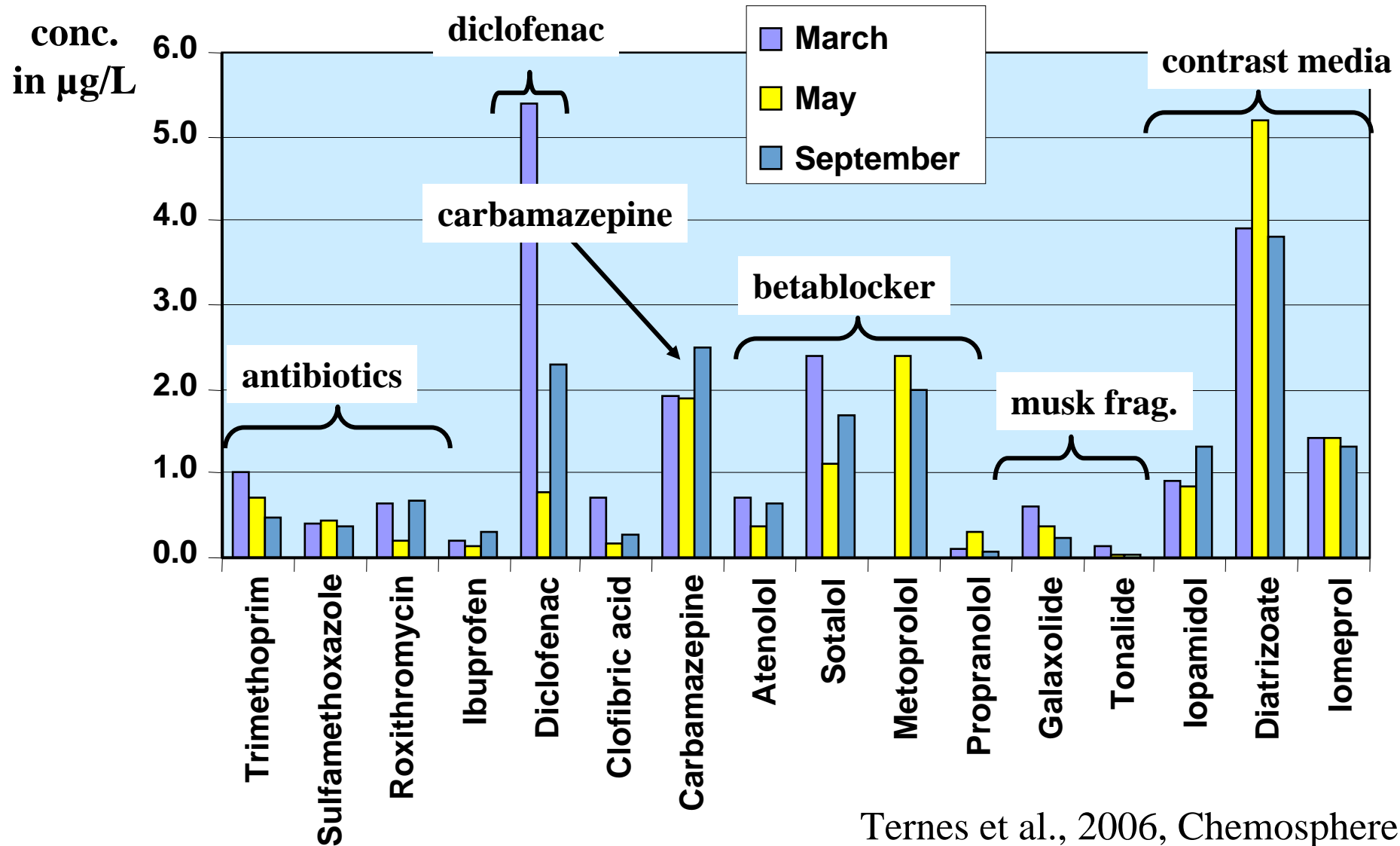
Routes into the environment and drinking water

Water cycle



Do we have problems with emerging substances?

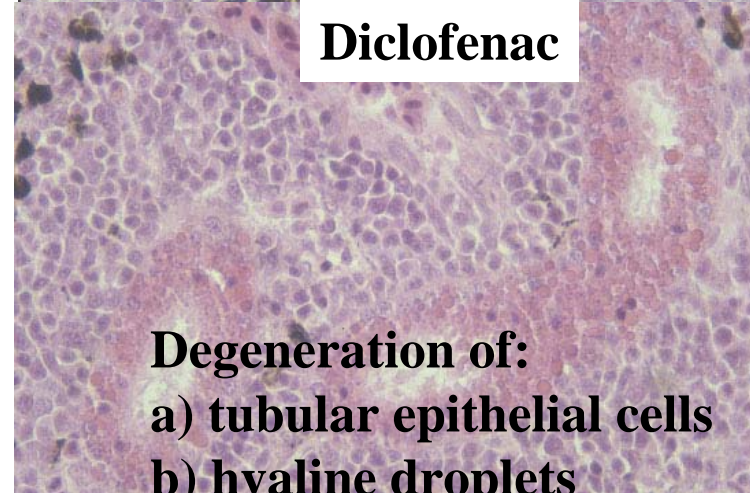
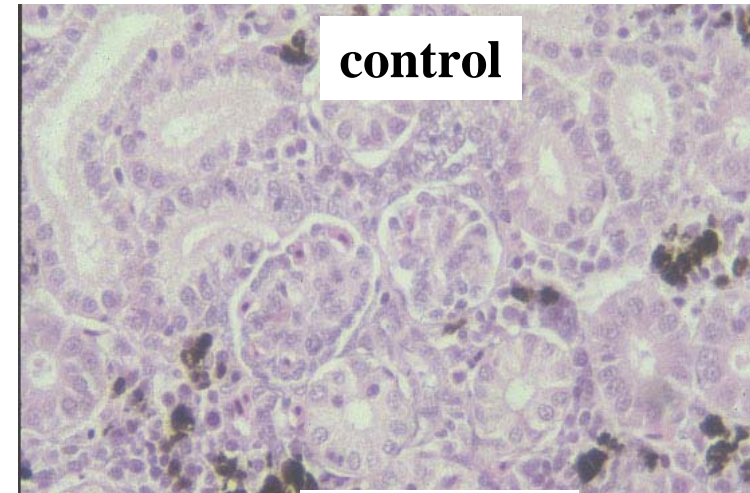
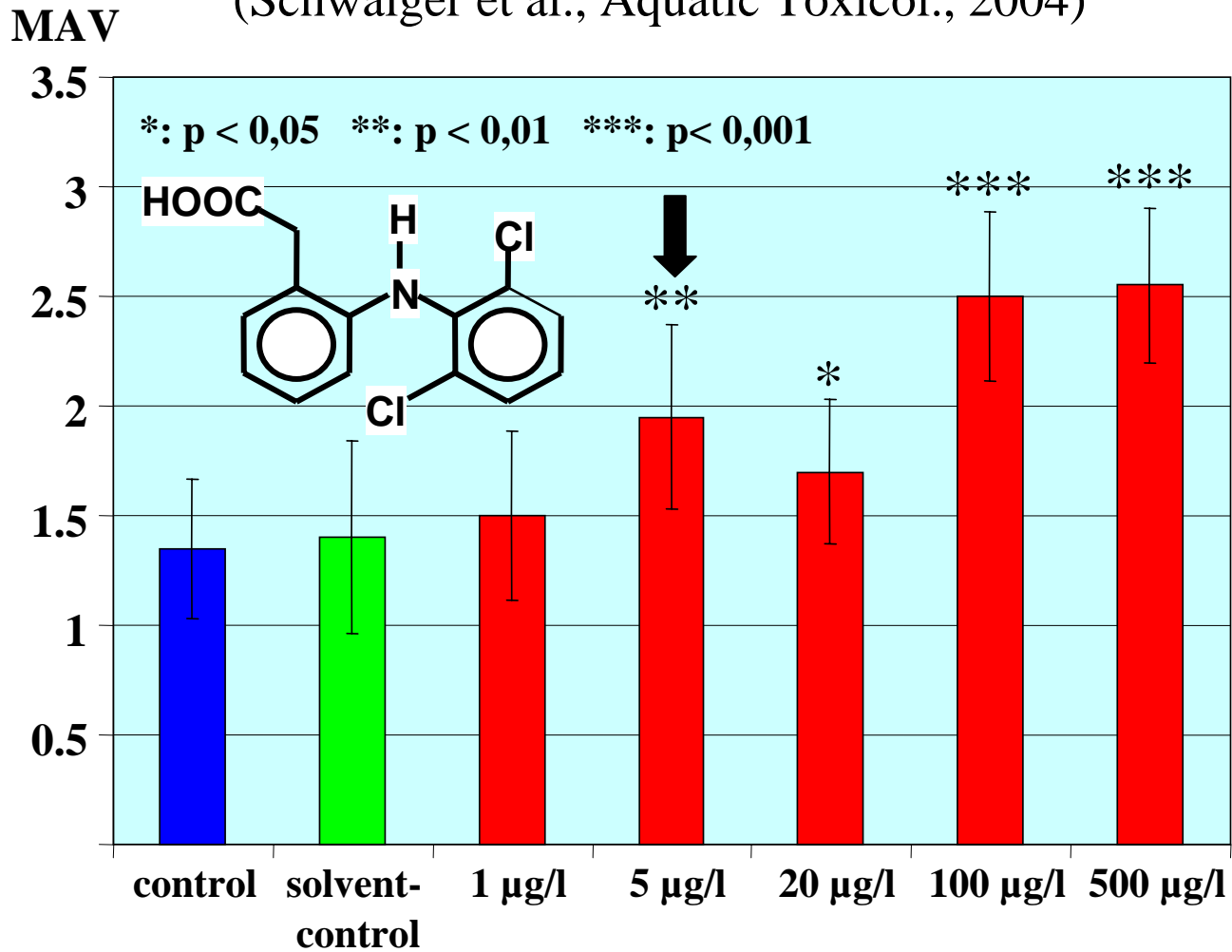
Micropollutants in municipal STP effluents



Ternes et al., 2006, Chemosphere, in press

Rainbow trout exposure with diclofenac *histopathological alterations of kidneys*

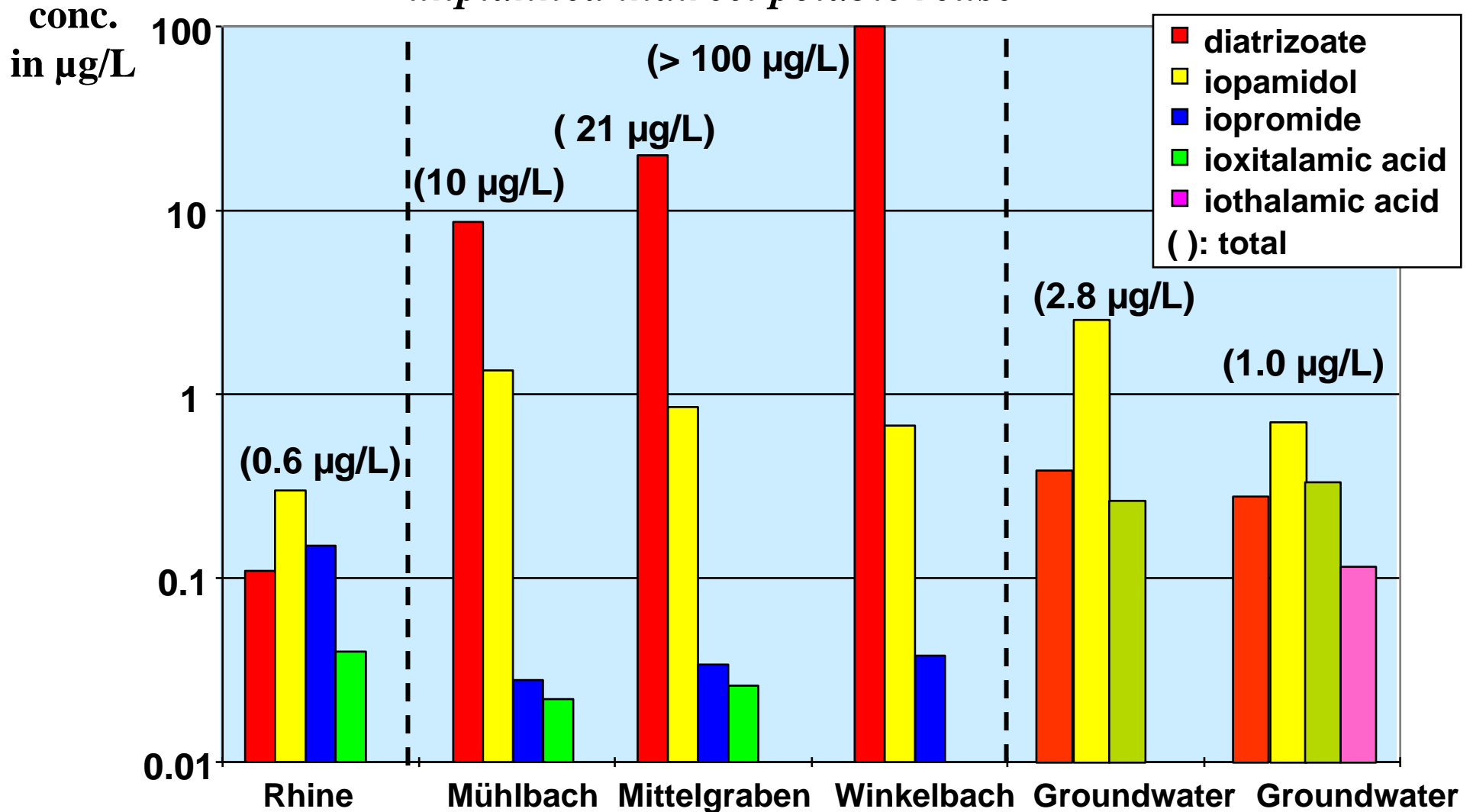
(Schwaiger et al., Aquatic Toxicol., 2004)



Degeneration of:
a) tubular epithelial cells
b) hyaline droplets
Interstitial nephritis

Iodinated contrast media: surface water and groundwater

unplanned indirect potable reuse



Ternes & Hirsch, Environ. Sci. Techn. (2000) 34, 2741-2748

Relevant micropollutants: surface water, drinking water

Contaminants of water resources

- Iodinated contrast media (e.g. Diatrizoate, Iopamidol)
- Antiepileptics (e.g. Carbamazepine, Primidone)
- Lipid regulators and anti-inflammatories (e.g. Clofibric acid, Ibuprofen)
- Complexing agents (e.g. EDTA, DTPA)
- Aromatic naphthalene sulfonates
- Polar pesticides (e.g. atrazine, diuron, glufosinate, glyphosate)
- MTBE, triclosan, phthalates, tris(2-chloroethyl)phosphate, benzotriazole
-

Compounds leaching from materials (e.g. waterworks/distr. networks)

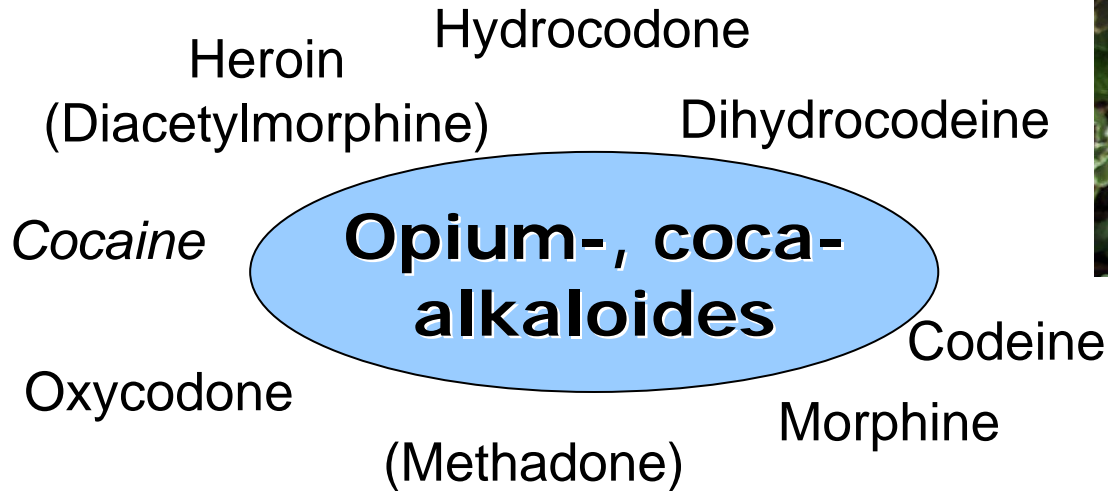
- Tubes with DBT contains 1 % TBT
- Phytosteroides leaching out from biological GAC filters

Disinfection by-products (THM, NDMA, halo acids, Br/NO₂-meth., ...)

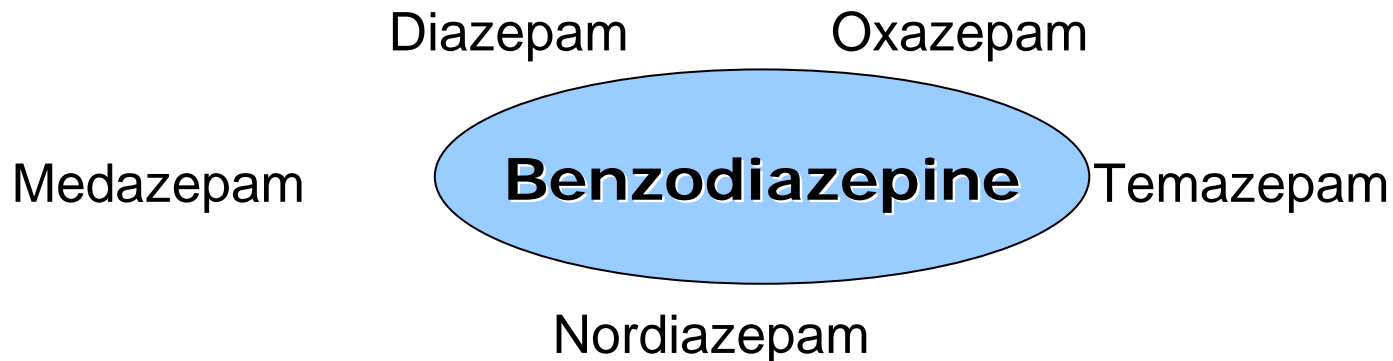
Opium alkaloids, Benzodiazepines



Coca leaves

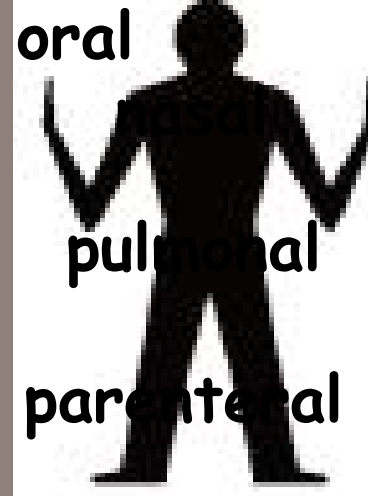
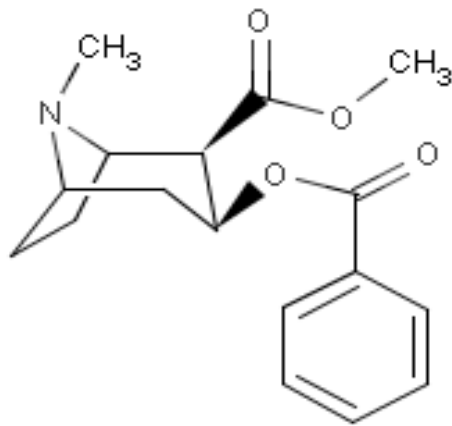


Papaver
somniferum
(opium poppy)

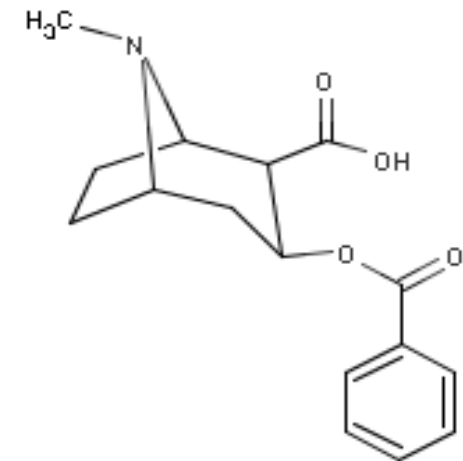


Cocain

Benzoylcocaine methyl ester

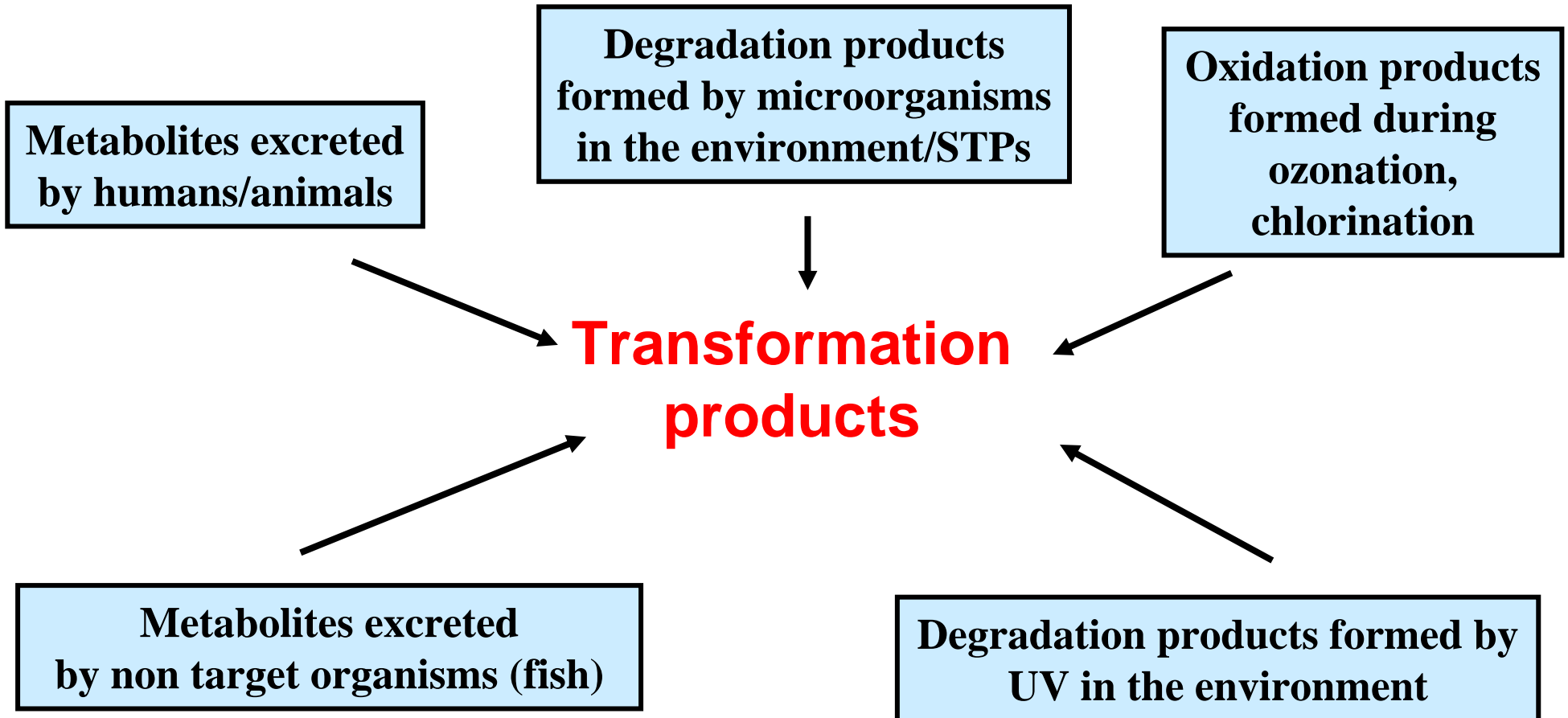


Benzoylcocaine

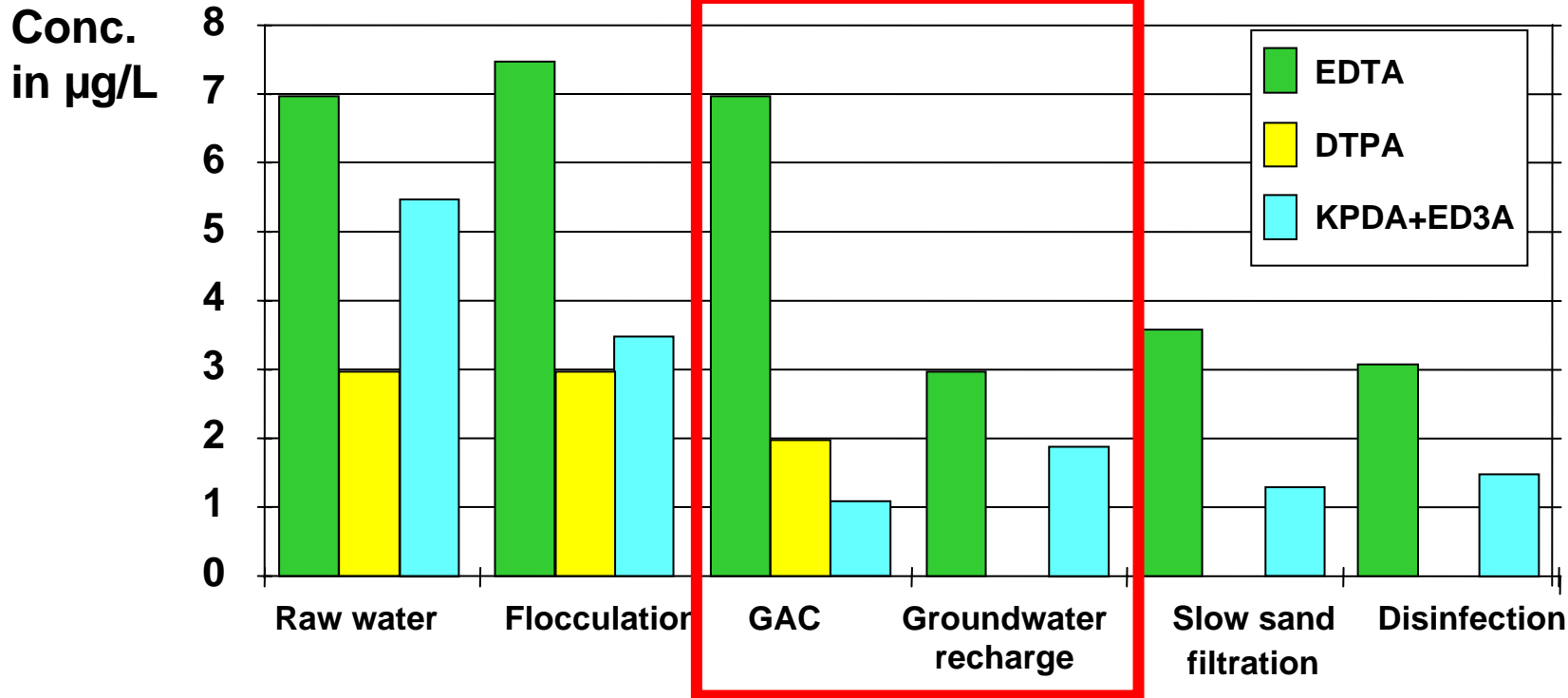
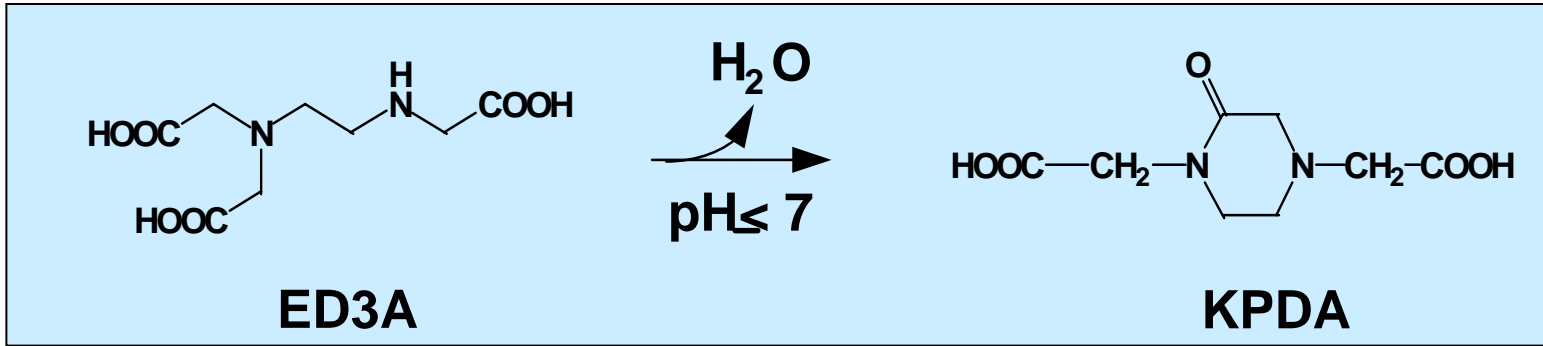


excretion: 25-40%

Transformation products: mostly unknown and polar



Transformation products formed in the environment



Ternes et al.,
Vom Wasser,
1997

How we can remove emerging micropollutants?

Perspectives for „up-graded“ wastewater discharged into rivers

Removal of pathogens and hazardous chemicals

Wastewater design

- ⇒ Source separation (e.g. urine, feces separation)
- ⇒ Source control
 - i) separate treatment of hospital wastewater
 - ii) eco-labeling of medicines and other products (PBT concept)
 - iii) controlling of the rainwater dilution in the sewers prevents the discharge of raw wastewater to rivers and streams



Advanced (polishing) treatment processes

- ⇒ Chemical oxidation (ozone, UV/O₃, UV/H₂O₂); O₃ : < 0,05 €/m³
- ⇒ Adsorption on activated carbon (PAC, GAC)
- ⇒ Nanofiltration

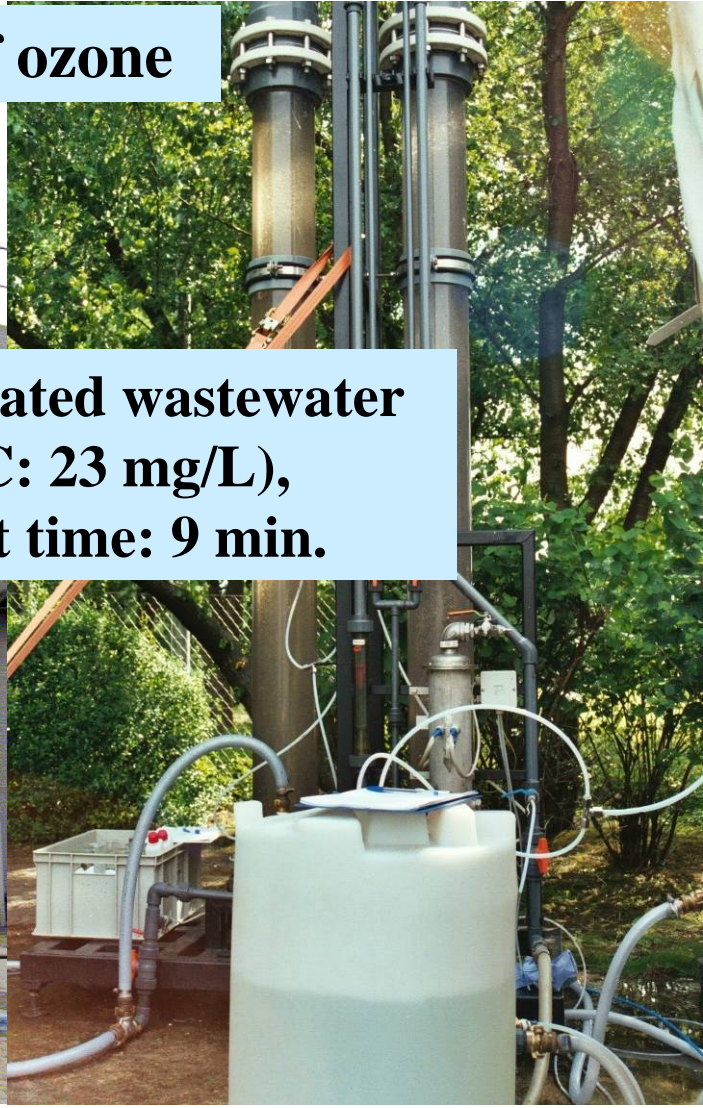
Siegrist et al., 2006

Ozonation of STP effluents



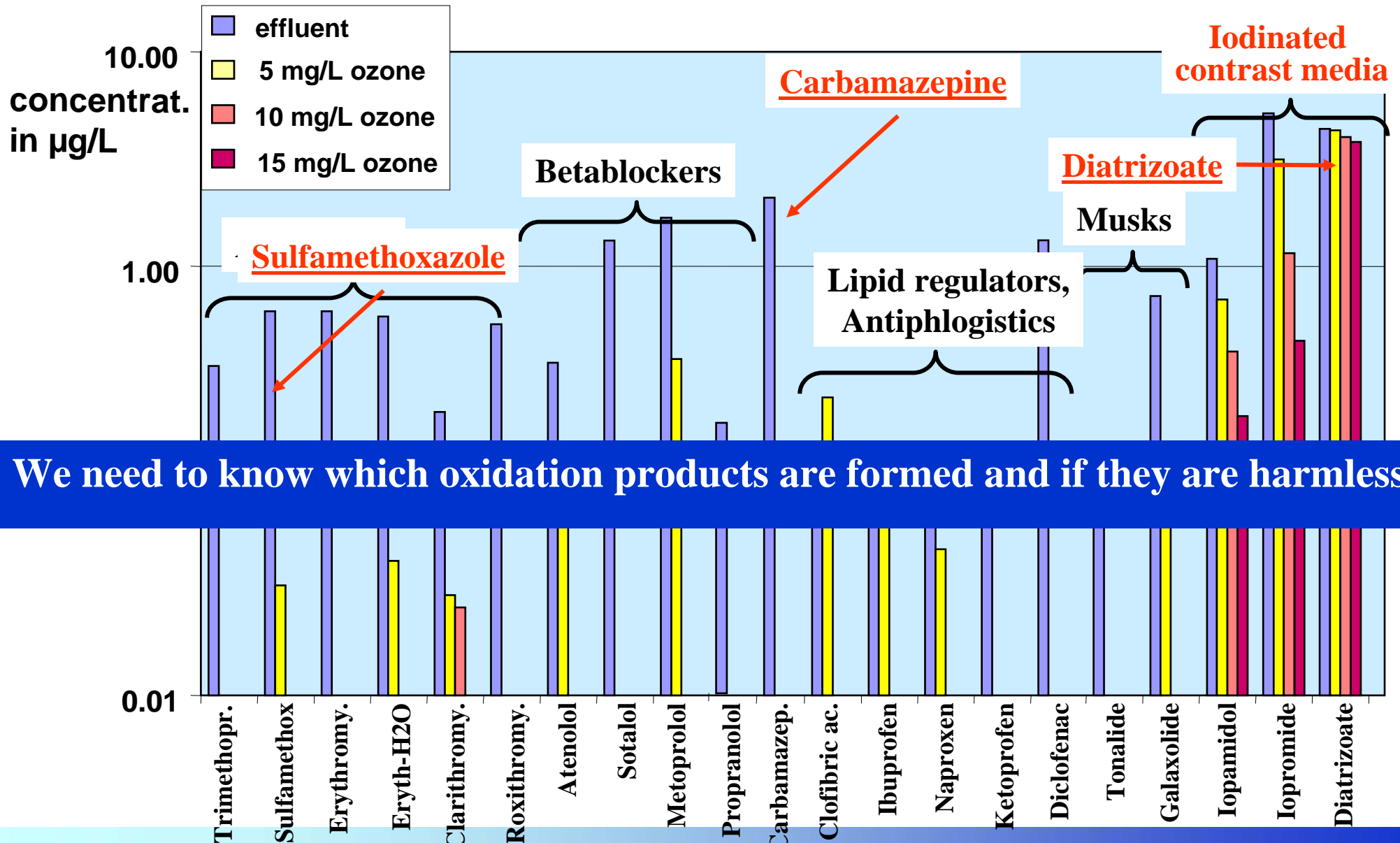
Addition of ozone

**2 m³/h treated wastewater
(DOC: 23 mg/L),
contact time: 9 min.**



WEDECO

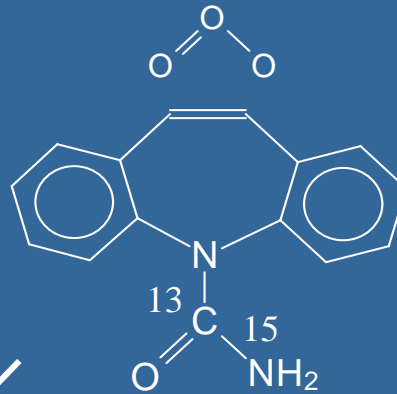
Ozonation of the municipal STP effluent (DOC: 23 mg/L)



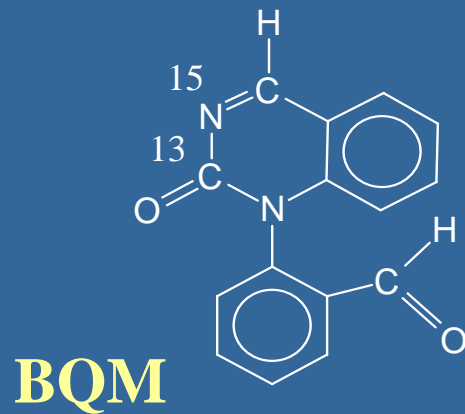
We need to know which oxidation products are formed and if they are harmless!

Stable ozonation products of Carbamazepine

Ozone dosis
6 μM
react. time: 20 min



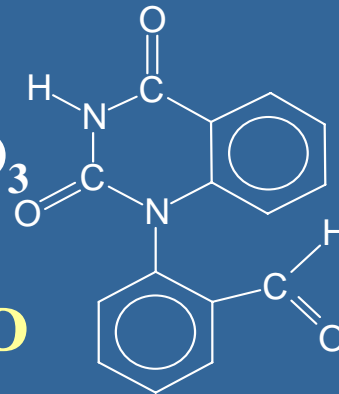
Carbamazepine (1 μM)
M.W. = 236.3



O_3

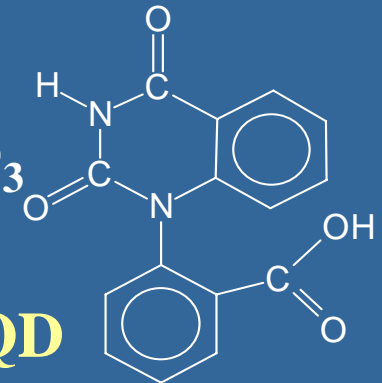
OH/O_3

BQD



OH/O_3

BaQD



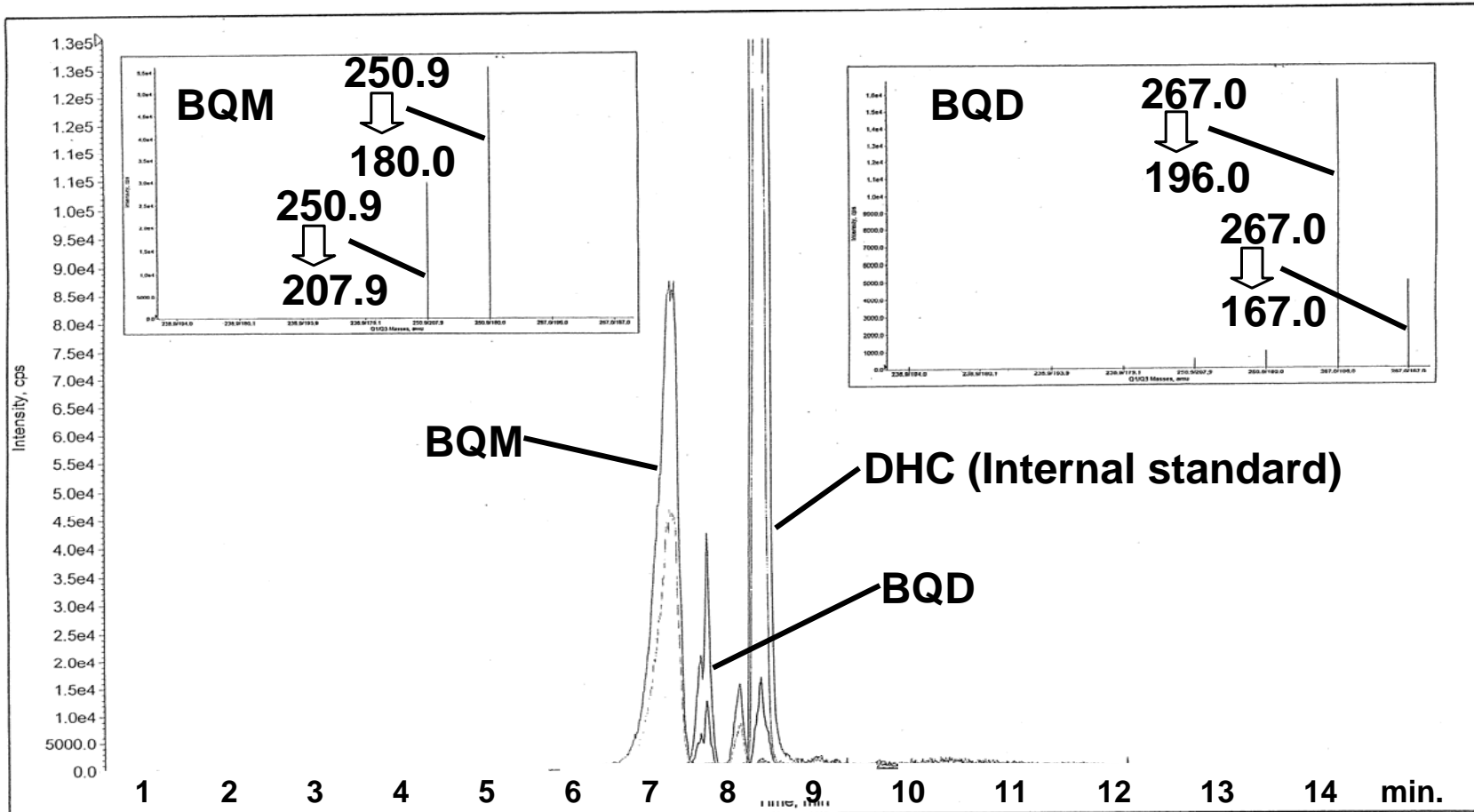
?

$$k_{\text{ozone}} = \sim 6.9 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{\text{OH}} = \sim 6.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{\text{ozone}} = \sim 1.0 \text{ M}^{-1}\text{s}^{-1}$$

Detection of BQM and BQD in a waterworks after ozonation



McDowell et al., ES&T, 2005

Occurrence of micropollutants

Pharmaceuticals (human use) and other polar emerging contaminants are present up to the $\mu\text{g/L}$ range in rivers, lakes and groundwater. *Present in drinking water of waterworks using groundwater resources with an unexpected proportion of wastewater*

Occurrence of transformation products (TPs) from micropollutants

- Metabolites of pharmaceuticals (human use) such as clofibric acid
- TPs formed in the environment such as ketopiperazines
- Oxidation-by-products such as BQD
- Disinfection by products (e.g. THMs, haloacids, NDMA)

Only those “micro(nano, pico)pollutants” are found which have been included into the monitoring programs



Toxicological risks

For drinking water consumers the detected residues are unlikely to cause effects, even though long term studies (a „whole life“ intake) are missing.

However, their presence indicate that a significant proportion stems from wastewater or landfill site water



Ecotoxicological risks

It is very likely that for more micropollutants or for mixtures severe environmental effects will be found.

Additionally, most of the transformation products have never been identified and their toxicity is totally unknown.

Human Pharmaceuticals, Hormones and Fragrances



Challenge for Urban Water Management

Editors
Thomas Ternes
Adriano Joss

