Enhanced municipal wastewater treatment for micropollutant abatement in Switzerland

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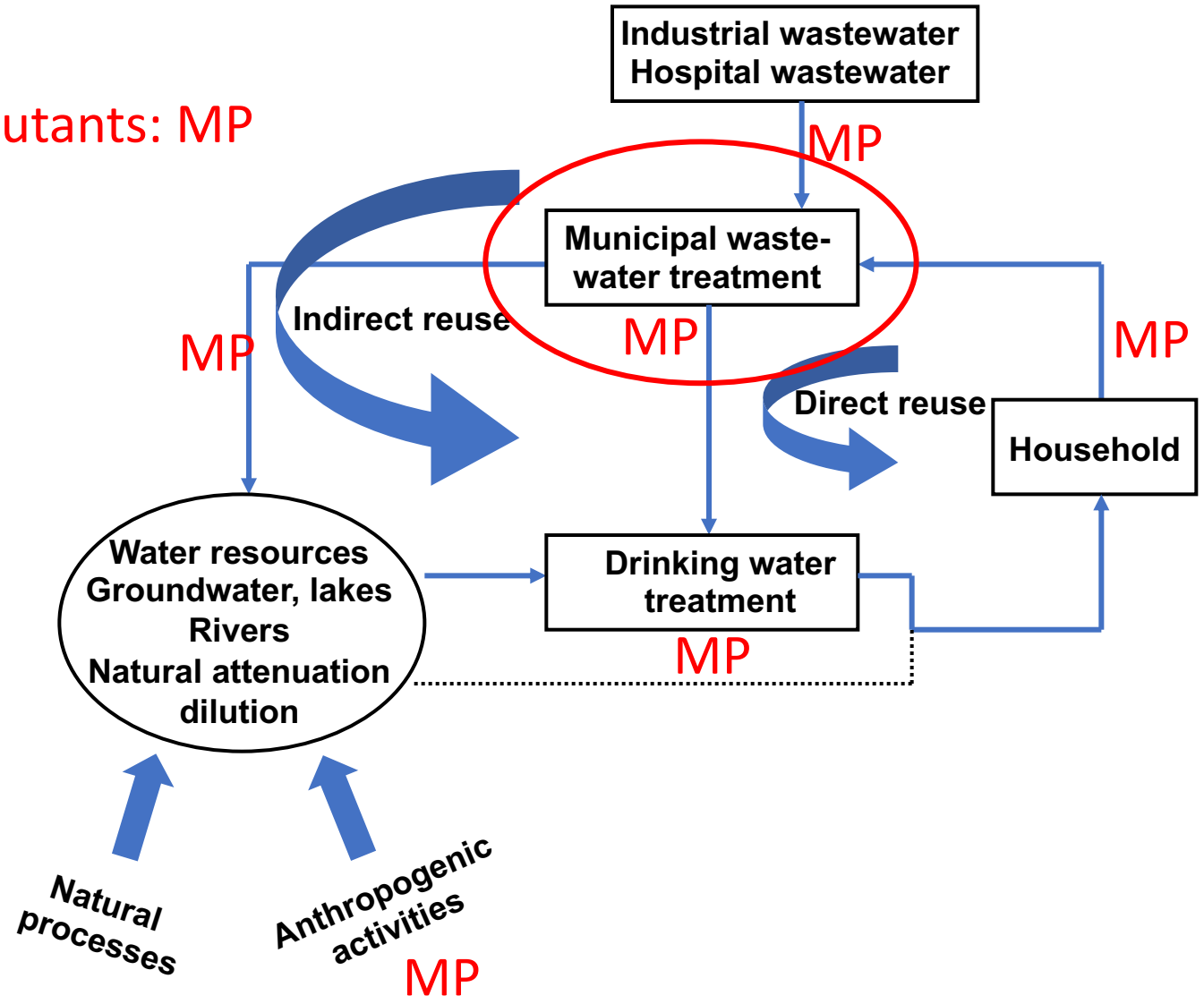
Micropollutant problem in urban water management

- Ca. 100’000 compounds are registered in the EU
- 30’000 compounds are in daily use
- > 8500 chemicals as food supplements
- > 3000 chemicals are used as human pharmaceuticals
- Progress in analytical chemistry

→ Micropollutants can be found in wastewater, water resources and drinking water

The anthropogenic/urban water cycle

Micropollutants: MP



Some “macropollutants”

Swiss national programs related to micropollutants in the aquatic environment (1998 – 2011)

- Fishnet (1998-2004) – Investigation of fish decline in Swiss rivers, triggered by the Swiss fishermen‘s association
- National research program on endocrine disruptors (2002-2007)
  - Wastewater treatment plants are the major point source
  - Problems in waters with insufficient dilution of wastewater effluents
- Swiss EPA Project „Strategy MicroPoll“ (2006-2011)

Environ. Sci. Technol. **1998**, *32*, 2498−2506

Widespread Sexual Disruption in Wild Fish

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CHARLES R. TYLER,†
GEOFF BRIGHTY,§ AND
JOHN P. SUMPTER†

The Fish Physiology Research Group, Department of Biology and Biochemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, U.K., Environment Agency, National Fisheries Laboratory, Bromholme Lane, Brampton, Cambs PE18 8NE, U.K, and Environment Agency, National Centre for Ecotoxicology and Hazardous Substances, Hawberry Park, Wallingford, Oxon OX10 8BD, U.K.

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The critical issue is
endocrine-modulatin
vironment to exert ad
and/or humans. It is
the basis of the inter

Collapse of a fish population after exposure to a synthetic estrogen

Karen A. Kidd*†, Paul J. Blanchfield*, Kenneth H. Mills*, Vince P. Palace*, Robert E. Evans*, James M. Lazorchak‡, and Robert W. Flick‡

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Men fight against boldness with the contraceptive pill

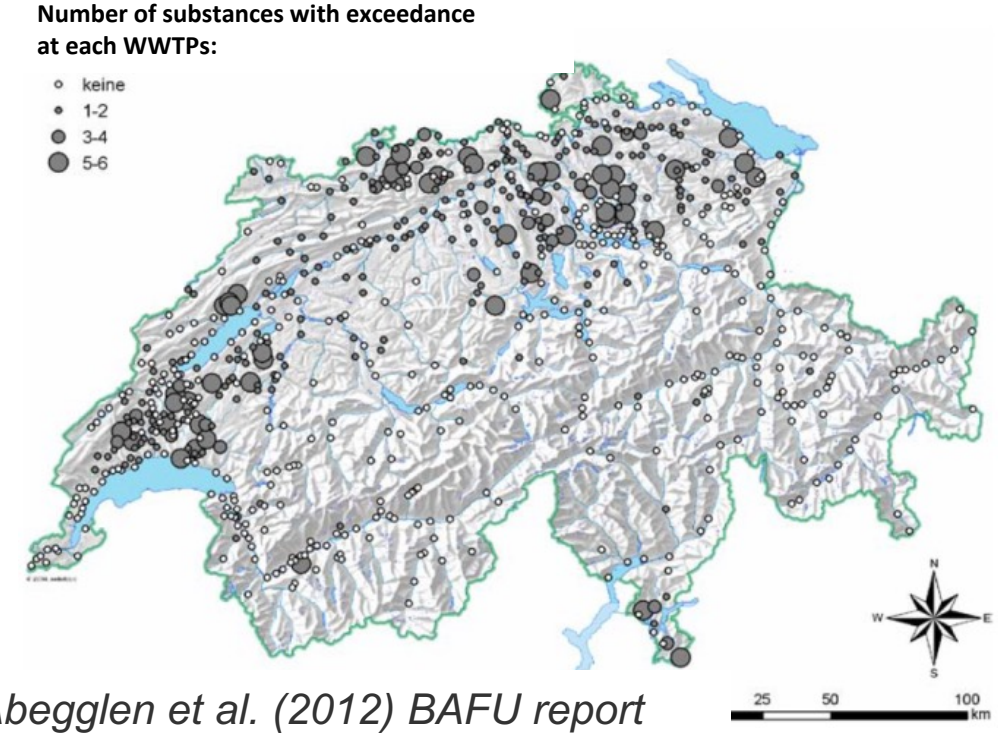
To fight hair loss, desperate men mix contraceptive pills with shampoo. This works, but may have serious side effects…

Die Antibabypille mit Shampoo mischen und die Haare damit waschen. Diese Methode hilft zwar gegen Haarausfall, wirkt aber wie ein Kastrationsmittel.

Why advanced municipal wastewater treatment in Switzerland?

Municipal wastewater treatment plants are important point sources for micropollutants

- **Feminization of fish** due to estrogens
- Locations with **exceedance of chronic quality standard** in Swiss rivers



Abegglen et al. (2012) BAFU report
Ort et al. (2009) ES&T 43, 3214

- Based on the strategy “Micropoll”, Swiss Federal Office for the Environment suggests micropollutant abatement from treated municipal wastewater
- Ozonation and activated carbon are selected treatment options. They were developed at Eawag from the laboratory to full-scale
- Currently Swiss full-scale wastewater treatment plants are upgraded

Swiss Strategy Micropollutants

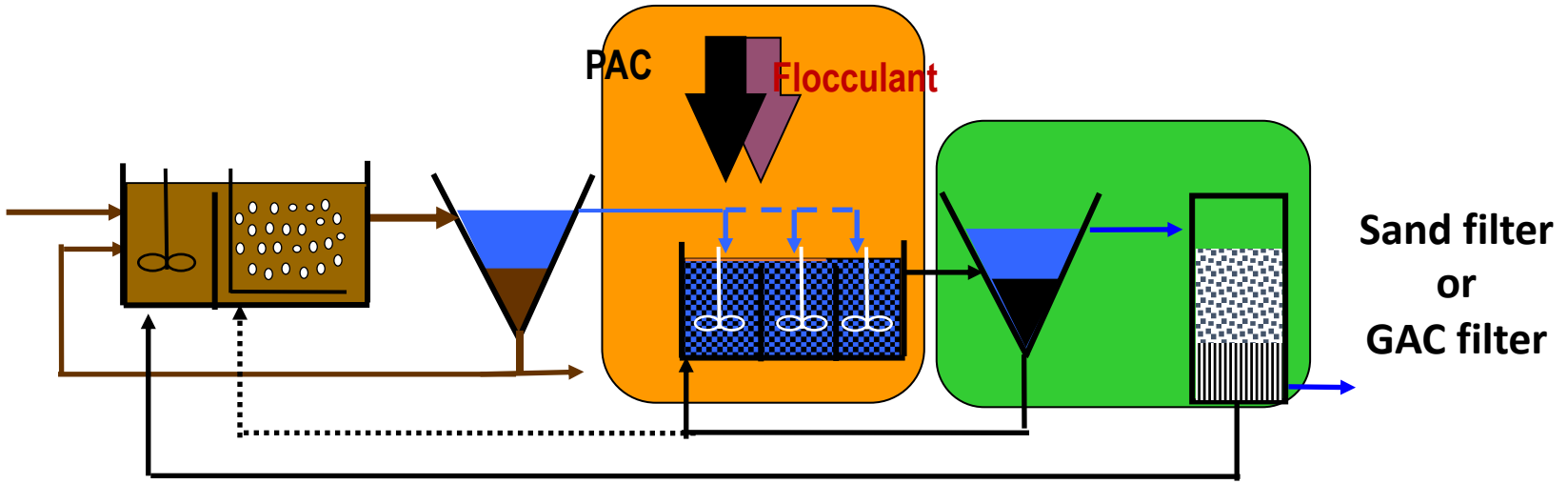
- Swiss EPA recommends upgrading of wastewater treatment plants to **remove micropollutants** (reduction of 50% of the total load) for **ecological reasons**
- Swiss parliament decided to go forward with it (March, 2014), new water protection law is in force since 2016
- Upgrade of ca. **120 WWTPs** (out of 700) until 2040:
  - Large WWTPs (>100‘000 inhabitants) to reduce the load (economic and international responsability (Rhine river))
  - WWTPs discharging into rivers with high percentage of wastewater (ecosystems protection)
  - WWTPs discharging into rivers with important bankfiltration (protection of drinking water resources)




Swiss Strategy Micropoll: Treatment

- Treatment options:
  - Ozonation/biological treatment
  - (Powdered/granular) activated carbon (PAC/GAC)
- Investment costs: 1.2 billion USD, additional yearly costs 120 Mio USD
- Ca. 10 USD/person/year
- Increase of costs at WWTPs: 2-25%
- Overall increase in electricity consumption (0.1%), mostly compensated by additional biogas production and photovoltaics

Powdered or granular activated carbon (PAC, GAC)



- Contact and mixing zone: addition and mixing of PAC into or after biological treatment
- Recirculation and removal by sand filtration
- Alternative: GAC filtration
- Removal: Various processes possible, e.g. sedimentation + filtration; sandfiltration; membrane separation, …

Ozonation

Liquid oxygen

Evaporator

Ozone generator

Off-gas treatment

Secondary clarifier

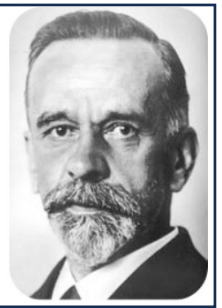
Ozonation reactor

Sandfiltration

or other biol. treatment

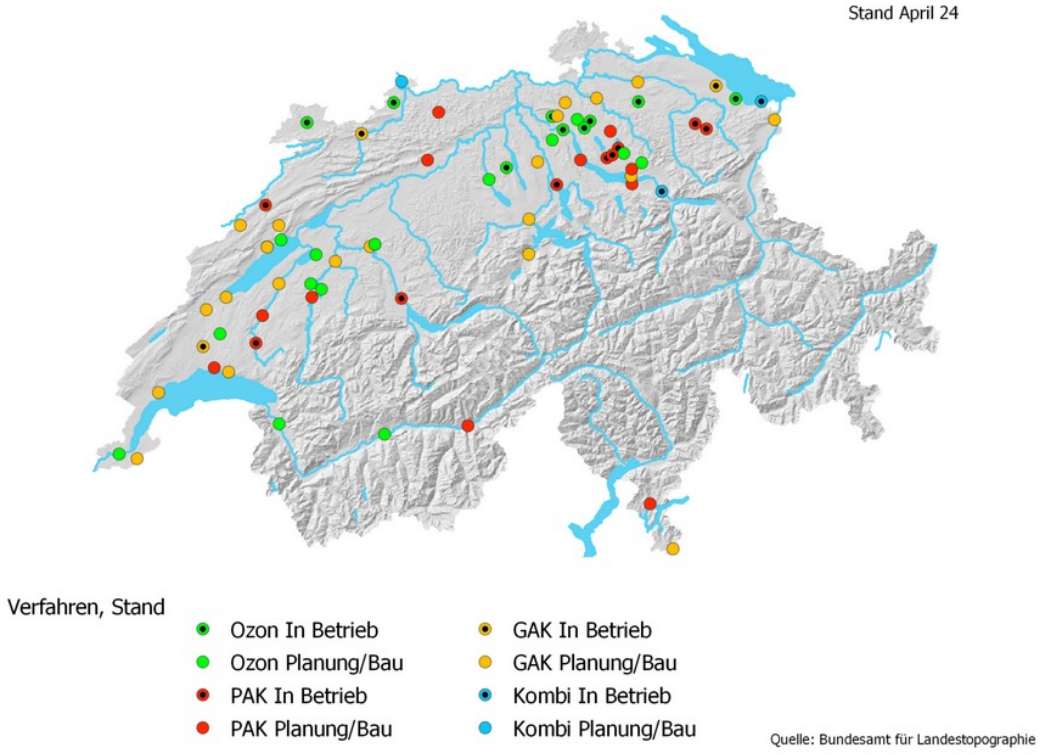
Backflush: to biological step

Sandmeyer Award 2024

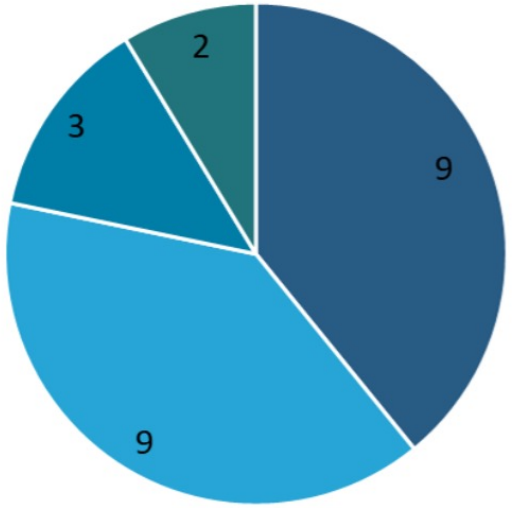


SCS Swiss Chemical Society

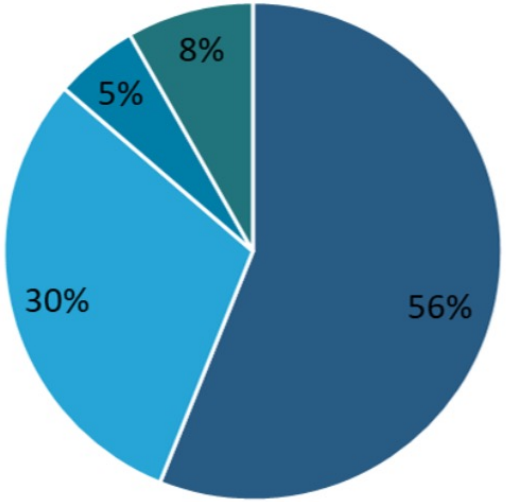
Current state of implementation of enhanced wastewater treatment in Switzerland: Number of plants and processes



Distribution of processes

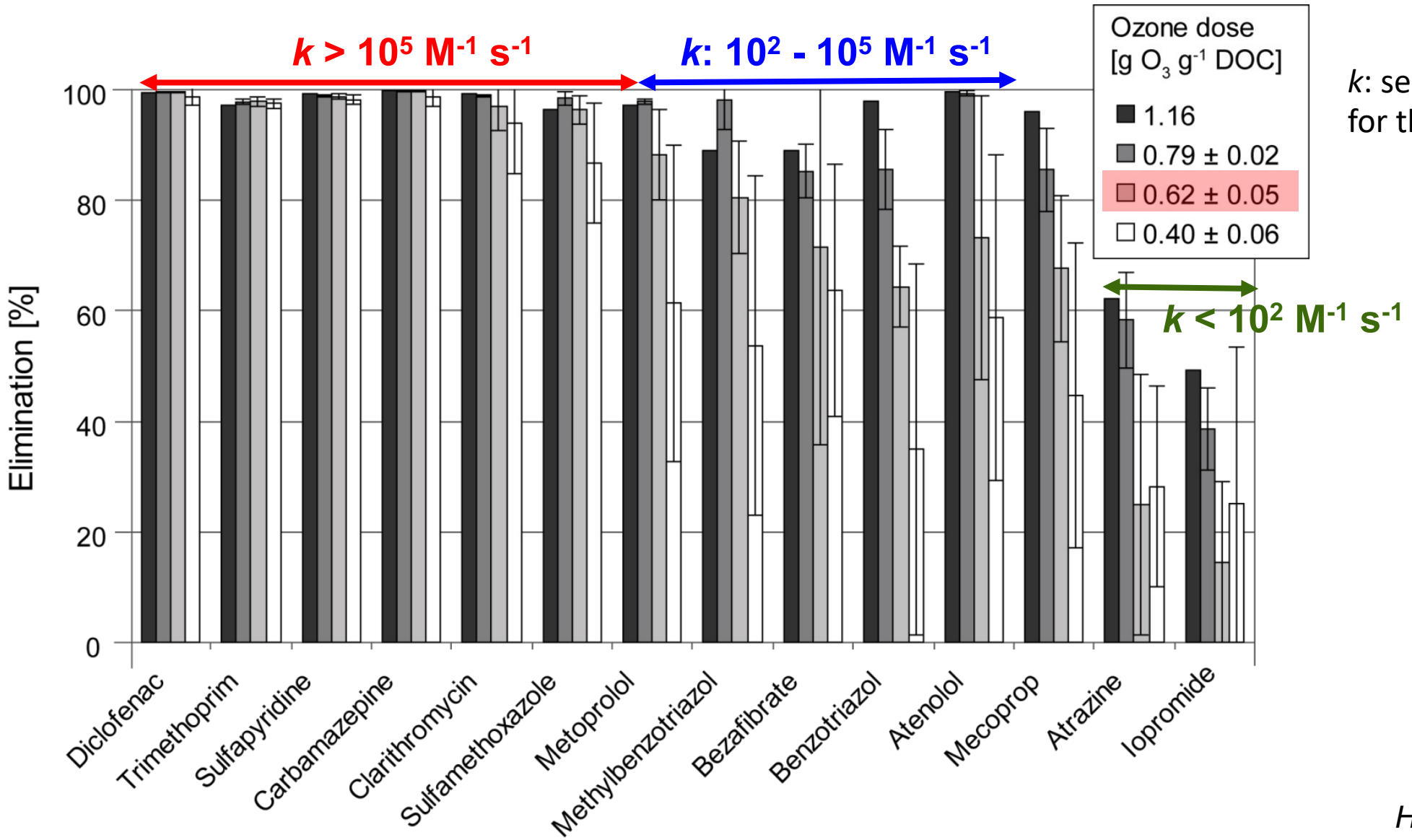


% connected persons



- Ozon / Ozone / Ozono
- PAK / CAP / PAC
- GAK / CAG / GAC
- Kombi / Combinaison/ Combination / Combinazione

Full-scale ozonation for enhanced wastewater treatment: Role of reaction kinetics for micropollutant abatement



k: second-order rate constant for the reaction with ozone

Hollender et al., ES&T, 2009

New standards in natural waters for three pharmaceuticals and twelve pesticides

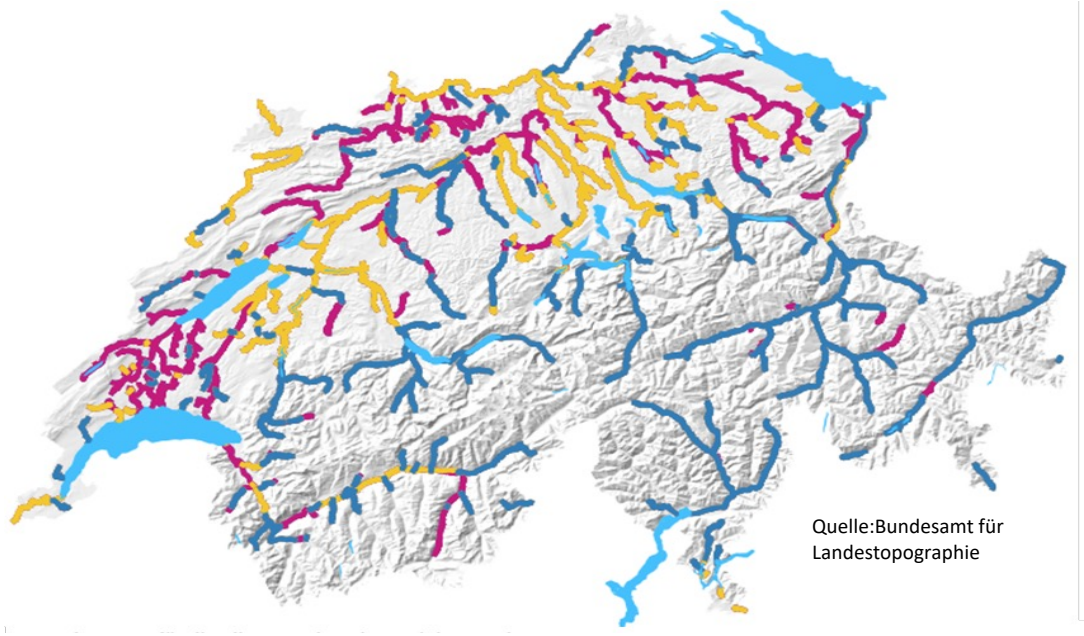
- Since 2020 there are ecotoxicological standards for micropollutants in natural waters (pharmaceuticals and pesticides)
- Standards for pharmaceuticals are relevant for WWTPs
- 3 pharmaceuticals from communal wastewater
  - Azithromycin 0.019 µg/L
  - Clarithromycin 0.12 µg/L
  - Diclofenac 0.05 µg/L

What is the situation in water bodies? How is this affected by an upgrade of WWTPs?

How many kilometers of river flow are affected?

Micropollutants with wastewater contribution at Q347

- 5’000 km with treated wastewater discharge
- **3’000 km with >2% WW contribution** → without enhanced WW treatment violation
  - 1’300 km okay with planned WWTP upgrade from 2016
  - **1’700 km remain with expected violations**



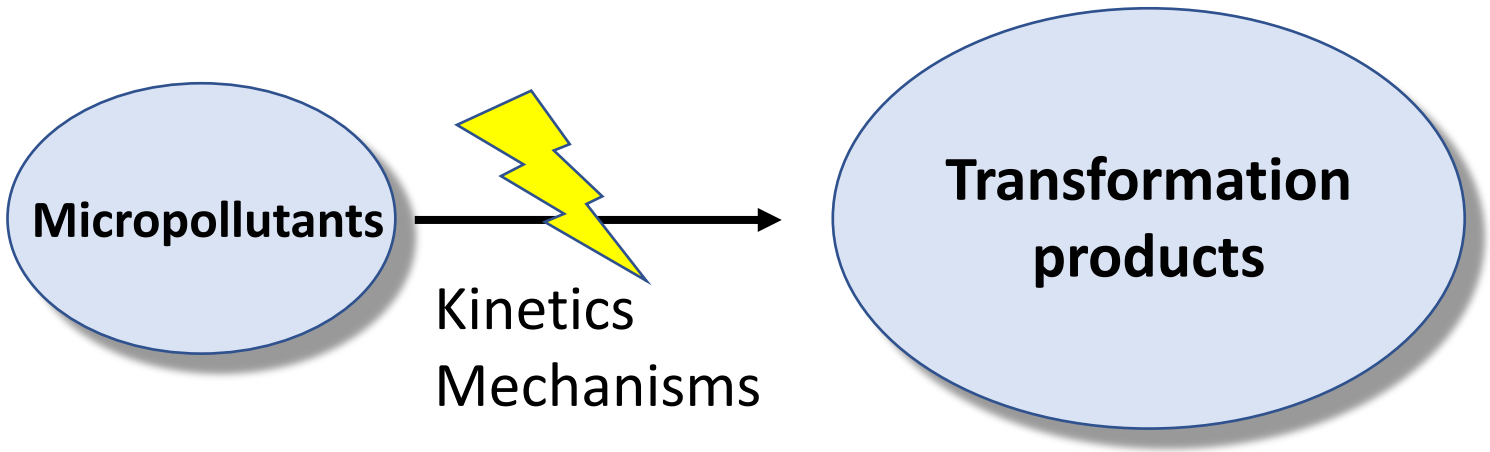
Current planned upgrade (2016) reduces the flow distance with violations to 50%

Relative abatement efficiency of azithromycin (AZM), clarithromycin (CLM) and dicolfenac (DIC) from a hospital wastewater: Powdered activated carbon, ozone, UV

Compound	Influent µg/L	PAC dose (mg/L)			Specific ozone dose ($gO_3/gDOC$)		UV fluence (J/m^2)		
		8	23	43	0.64	0.89 ($k_{O3,pH7}$ $M^{-1}s^{-1}$)	800	2400	7200
AZM	0.11	20%	100%	100%	>91%	>91% ($1.1x10^5$)	5%	14%	23%
CLM	1.28	100%	100%	100%	100%	100% ($4x10^4$)	6%	5%	14%
DIC	2.5	96%	98%	99%	100%	100% (10^6)	10%	72%	96%

Kovalova et al., ES&T, 2013

Oxidation of micropollutants



Laboratory experiments
QSAR
Quantum chemical computations

LC-UV/FL
LC-HRMS/MS
GC-MS/MS
IC-MS
NMR
Pathway prediction tools

Toxicity
Bioactivity

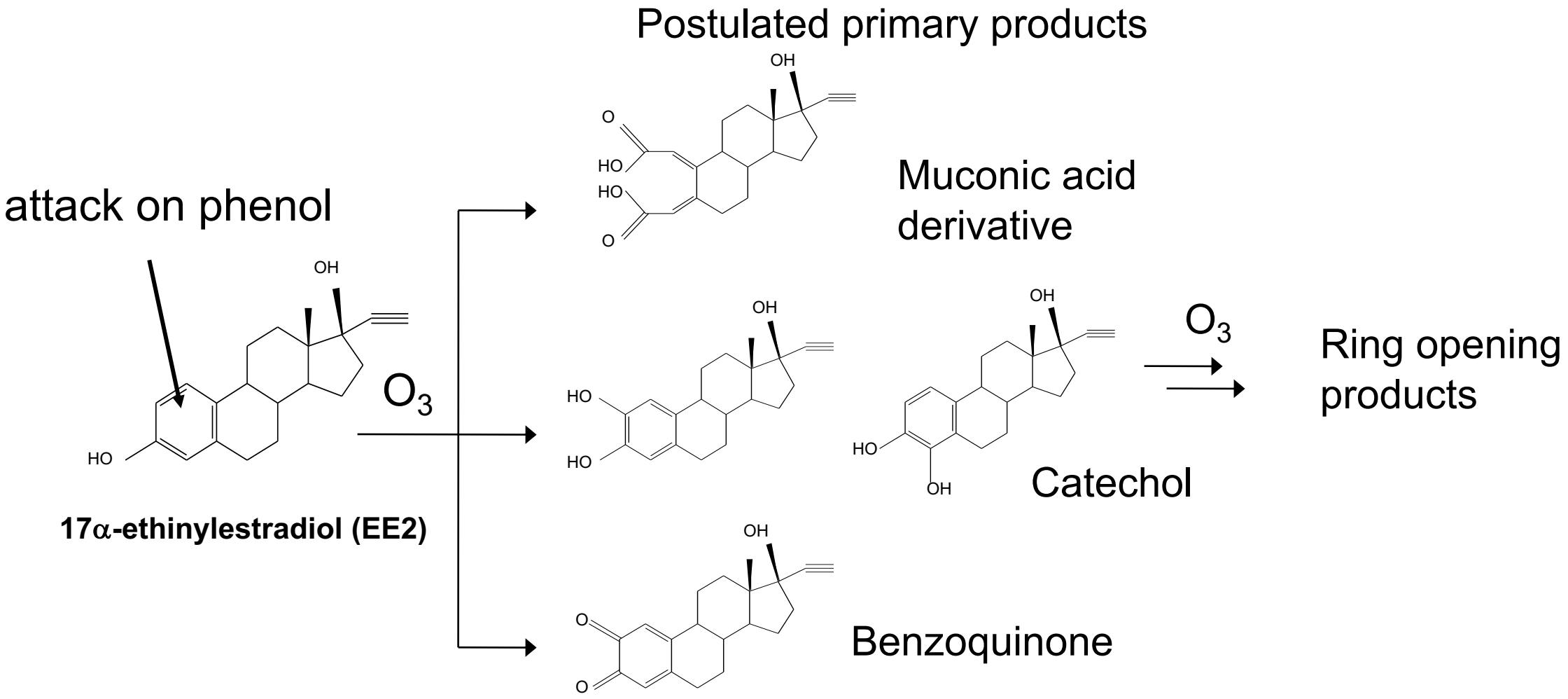
Bioassays
In silico toxicity evaluation

Biodegradability

Culture experiments
Biofiltration (pilot-, full-scale)
Biodegradability models

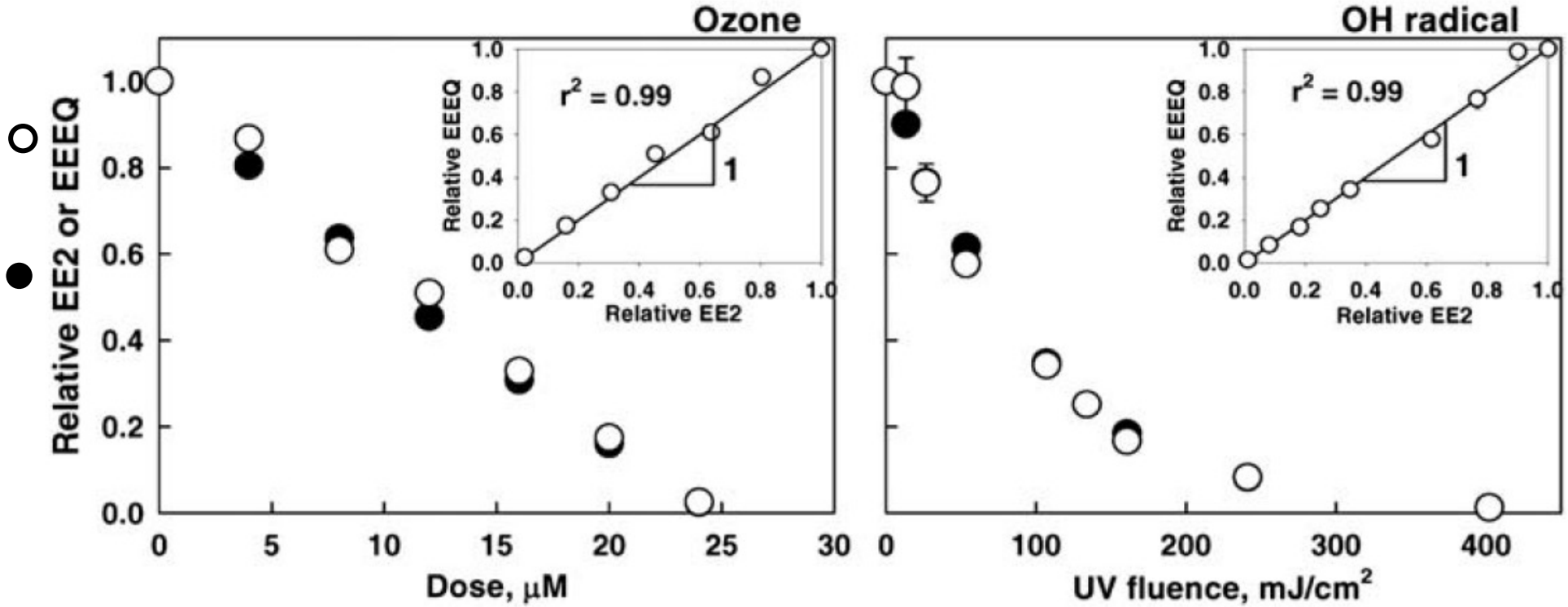
von Gunten, Water Research, 2024

Beyond transformation products:
Effects of 17α-ethinylestradiol (EE2) and its transformation products



Huber et al., ES&T, 2004

Biological effects: abatement of 17α-ethinylestradiol (EE2) and of the estrogenic activity (EEEQ-YES) by oxidation



- ❑ Loss of estrogenicity is proportional to loss of EE2
- ❑ Residual estrogenicity of products is <<10% of EE2

Lee et al. 2008

Degradability of transformation products: Pilot plant water supply Zürich

Ozonation

Sand filtration

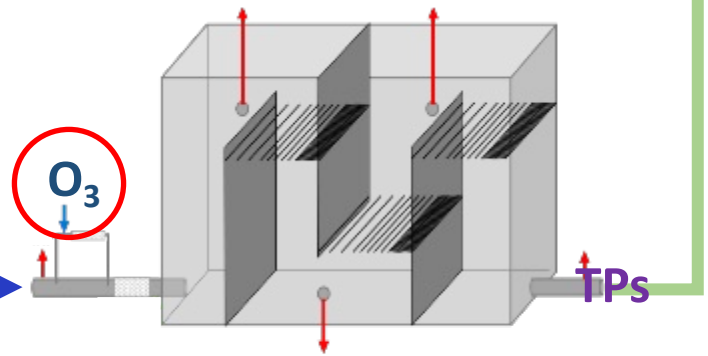
Ultrafiltration

4.2 m^3/h

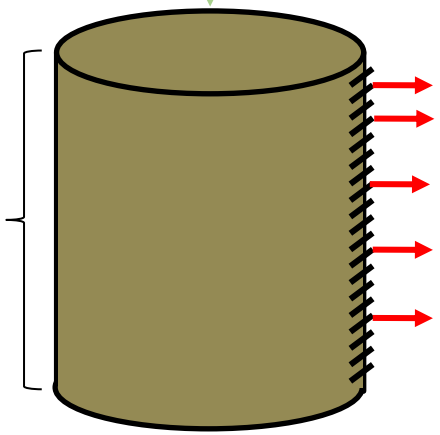
51 micropollutants

Lake water

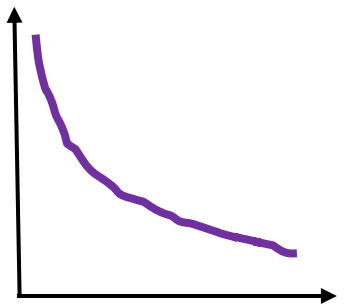
With/without ozone
$0.8gO_3/gDOC$



2m Sand



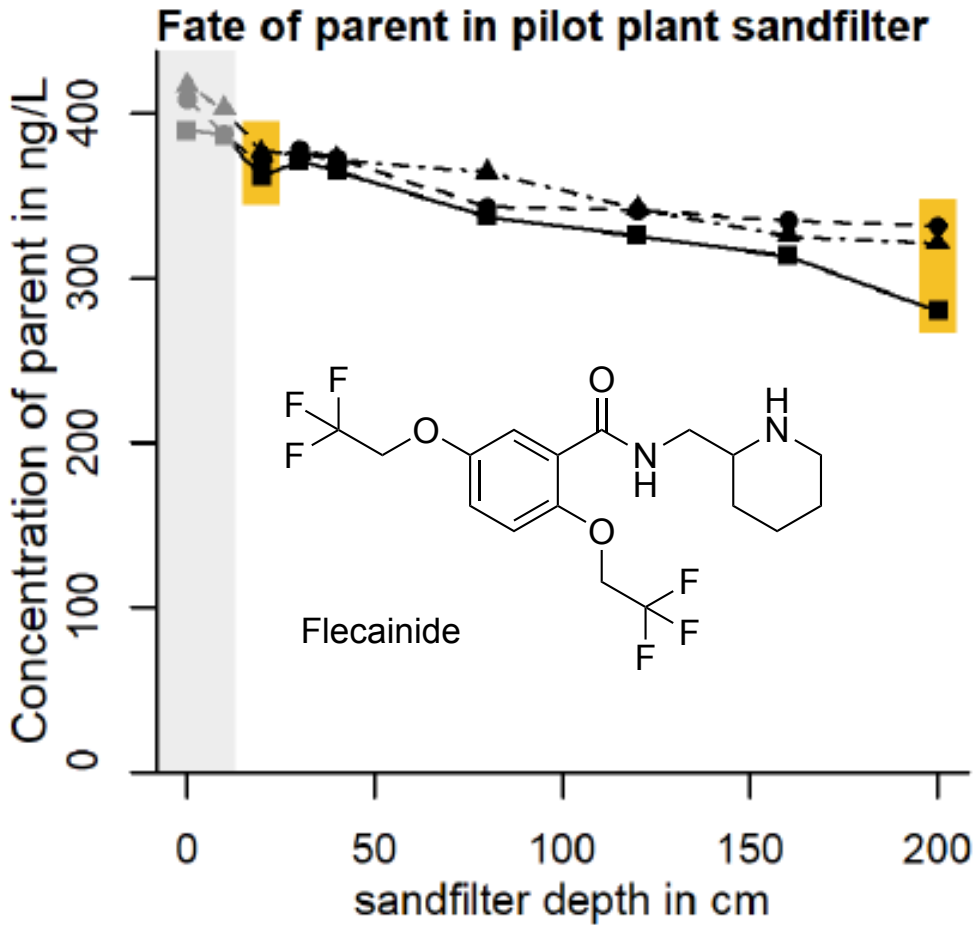
Fate of TPs in the biological sand filtration

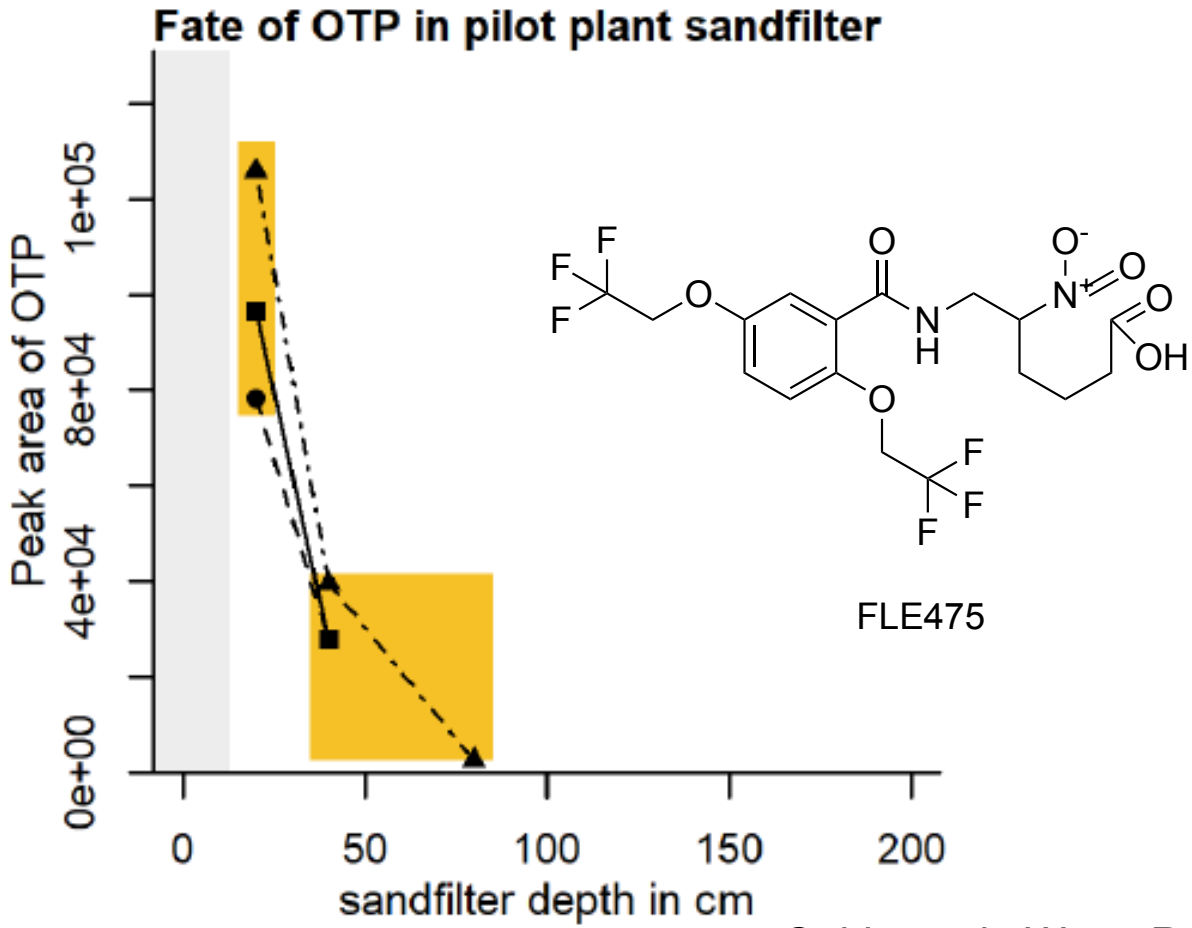


Gulde et al., Water Res., 2021

Fate of Flecainide and OTPs in biological sand filtration

- Flecainide slightly biodegradable
- Most OTPs similar or worse
- FLE475 better biodegradability





Gulde et al., Water Res., 2021

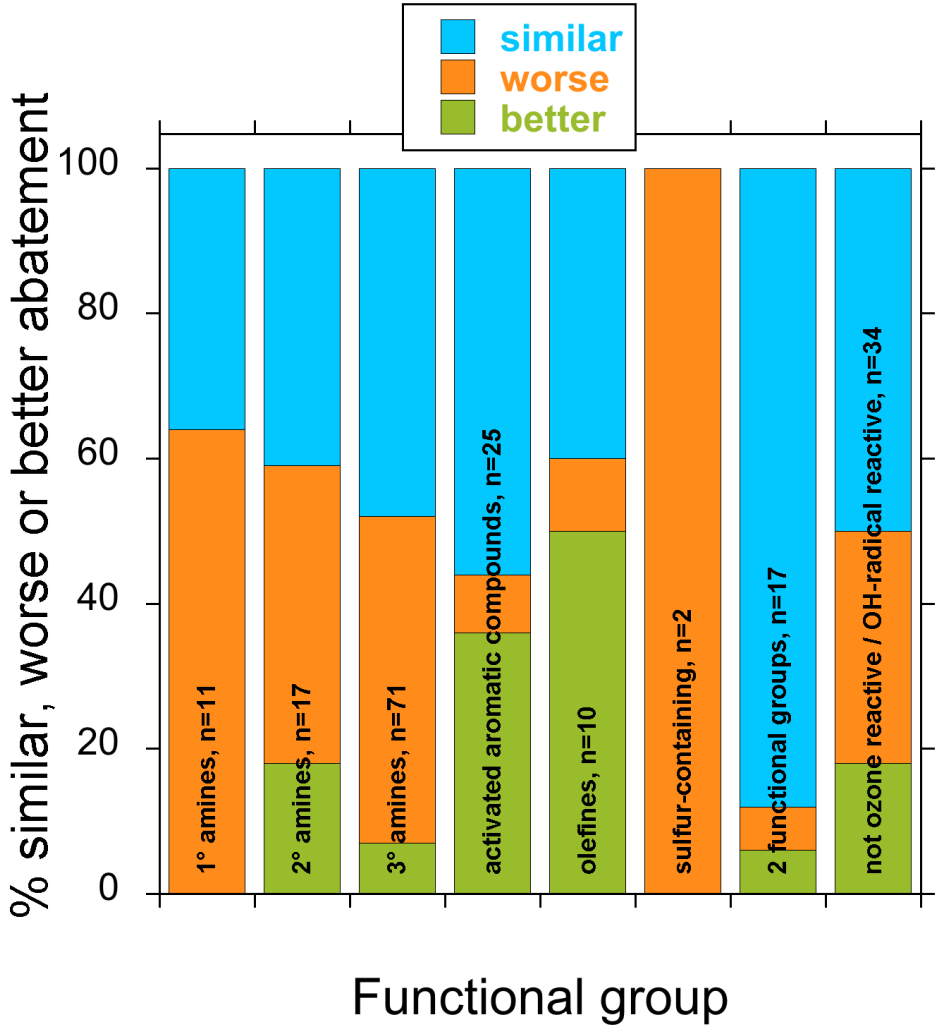
Pilot-scale ozonation-sand filtration of lake water: Biodegradability of transformation products relative to their parent compounds

Ozonation:

- TP measurement with LC-HRMS/MS (pos./neg. mode)
- 51 compounds spiked, TPs from 39
- 187 TP: 143 (76%) stable, 35 (19%) abatement, 9 (5%) formation

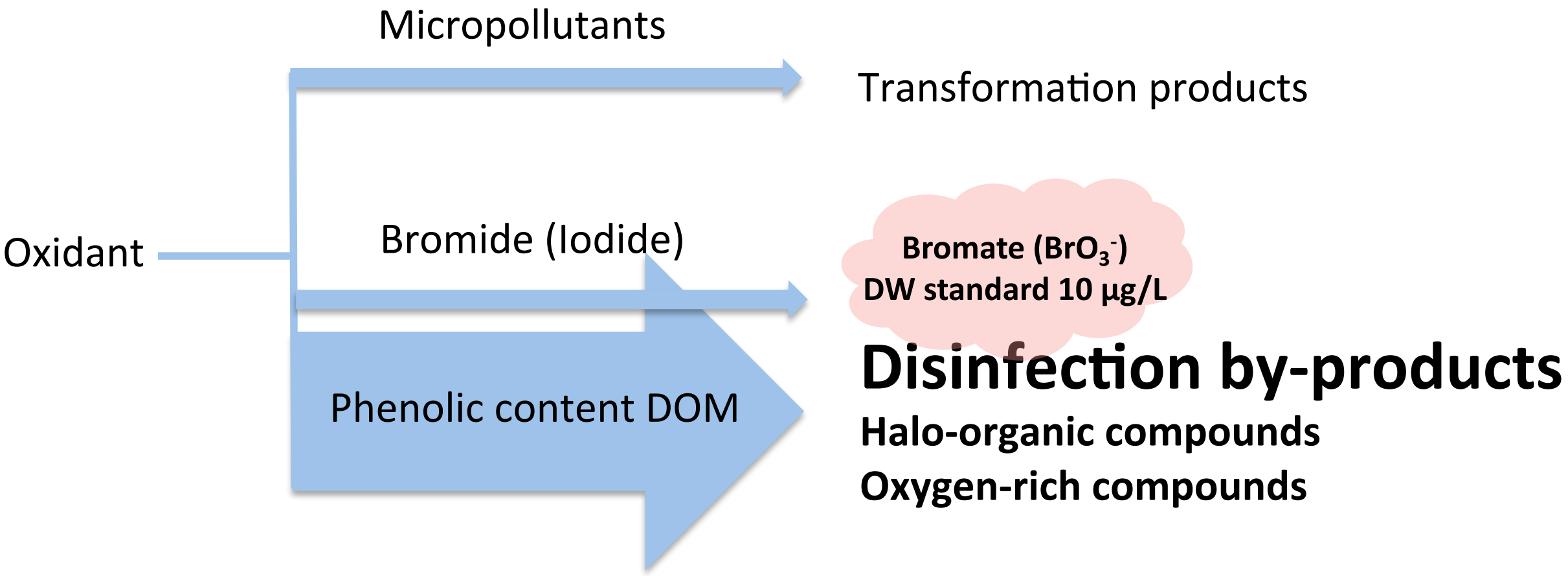
Sand filtration:

- Abated structures contain: Aldehydes, carbonyls, carboxylic acids, alcohols, amides
- Formed from **aromatic**, **olefinic**, aliphatic functional groups
- 24 (13%) of TPs were better biodegradable than the parent compounds

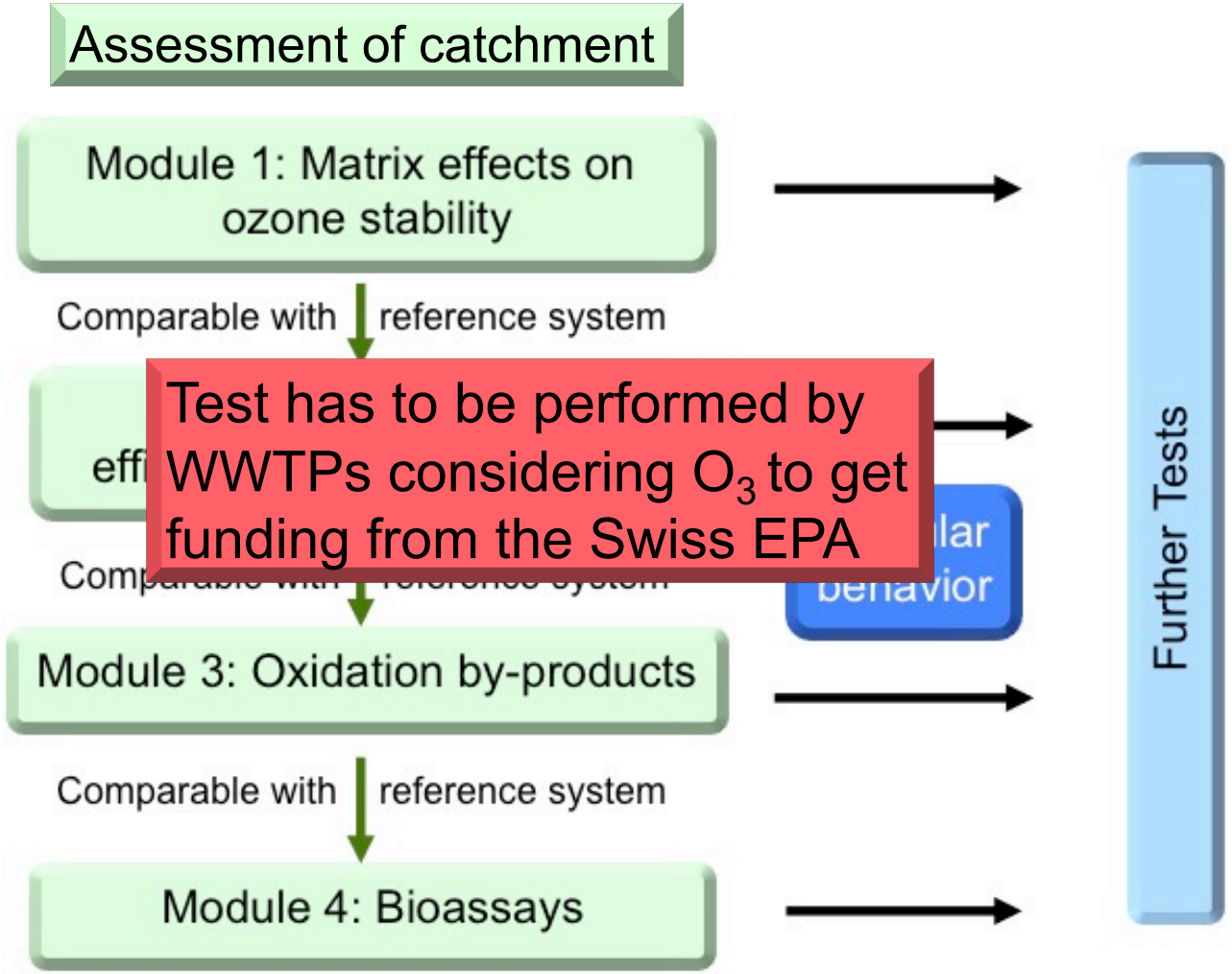


Gulde et al., Water Res., 2021

Impact of matrix components on oxidation processes: Dissolved organic matter (DOM) and bromide (iodide)



Swiss assessment of feasibility of ozonation for enhanced wastewater treatment: Ozone test procedure



- Ames test
- Algae test (*Pseudokichneriella subcapitata,* photosynthesis, growth inhibition)
- Daphnia (*Ceriodaphnia Dubia*)

Schindler Wildhaber et al., Water Res., 2015

• EU proposal urban wastewater treatment directive (UWWTD

- **October 2022**: revision of UWWTD (Council Directive 91/271/EEC) proposed
  - reduce pollution, energy use and greenhouse gas emissions
  - improve water quality by addressing urban wastewater pollution
  - **quaternary treatment** to remove micropollutants: similar to the Swiss approach
    - all WWTPs > 150 000 p.e. (Switzerland > 80 000)
    - all WWTPs > 35 000 p.e. in sensitive areas (Switzerland > 8 000)
    - 80% removal of 12 indicator substances on dry weather flow
    - More substances of high risk to be removed are proposed (Category 3: Telmisartan, Bisphenol, Beta-estradiol, PFOS)
- **10 April 2024: The European Parliament adopts provisional agreement** (reached by Council and Parliament on 29 January 2024)
  - Extended Producer Responsibility (EPR) scheme: ≥80% of **costs should be covered by producers** of human pharmaceuticals and cosmetic products (responsible for 92% of toxic load in wastewaters)
- Before becoming EU law: the deal needs to go through European Parliament again after election (6-9 June 2024, corrigendum procedure) and be approved by Member States in the Council
- Upgrade >150’000 p.e. five years, >35’000 p.e. fifteen years after the entry into force

https://environment.ec.europa.eu/topics/water/urban-wastewater_en

Conclusions

- Several programs were initiated by the Swiss EPA to investigate the contribution of municipal wastewaters to the release of chemicals to the environment
- Basic research combined with engineering approaches established solid processes
- Switzerland is currently successfully implementing enhanced WW treatment for MP removal
- New considerations regarding micropollutants of concern
- Based on these experiences similar programs have started in the EU
- Knowledge transfer to the field of water reuse