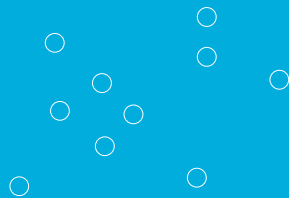


Fate and behavior of pharmaceuticals and EDCs in municipal wastewater treatment

Prof. Dr. Hansruedi Siegrist, EAWAG, Switzerland



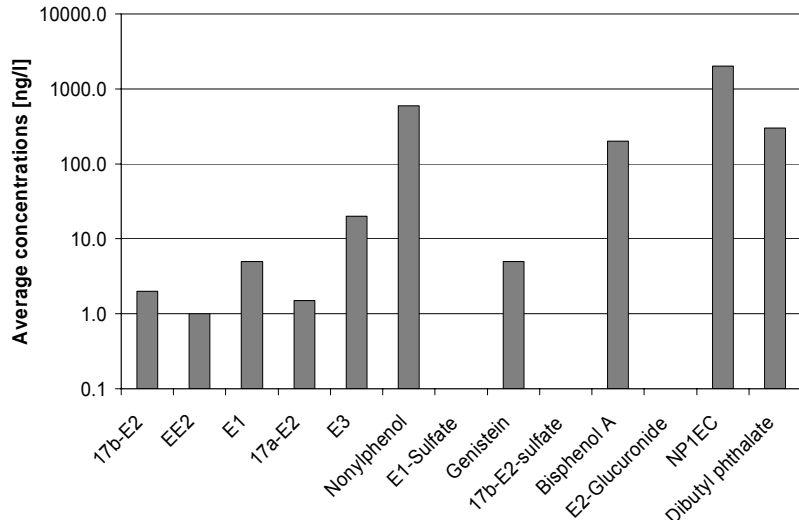
20 Years of Research in the Field of Endocrine Disruptors & Pharmaceutical Compounds Symposium, Berlin, 10 February 2010

Eawag: Das Wasserforschungs-Institut des ETH-Bereichs

Topics

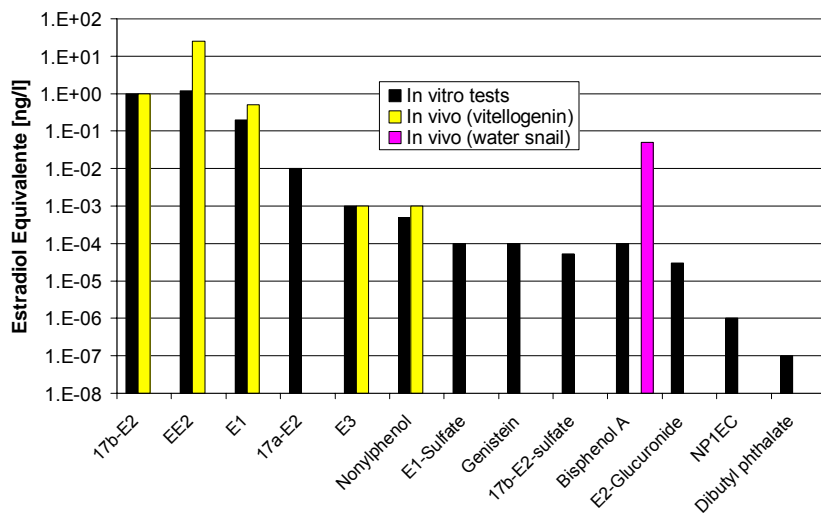
- Introduction
- Elimination processes in WWTP
- Transformation products
- Additional measures in WWTP
- Mass flux study Switzerland
- Conclusions

Average WWTP effluent concentrations of selected EDCs



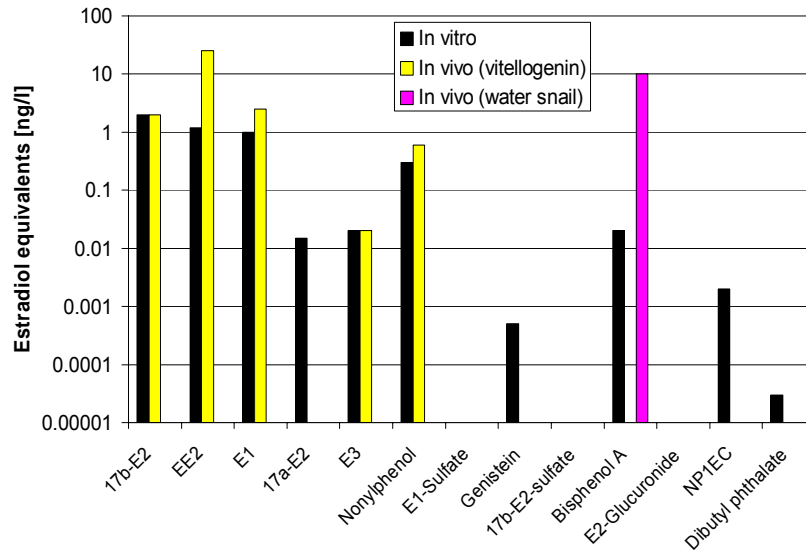
Desbrow et al. (1998) *Environ. Sci. Technol.* **32**, 1549; Routledge et al. (1998) *Environ. Sci. Tech.*, **32**, 1559; Snyder et al. (2001) *Env. Sci. & Technol.*, **35**, 3620; Johnson and Sumpter (2001) *Env. Sci. & Techn.*, **36**, 1202; Johnson et al. (2005) *Wat. Res.*, **39**, 47.

Specific estrogenic potencies of important EDCs *in vitro* and *in vivo*

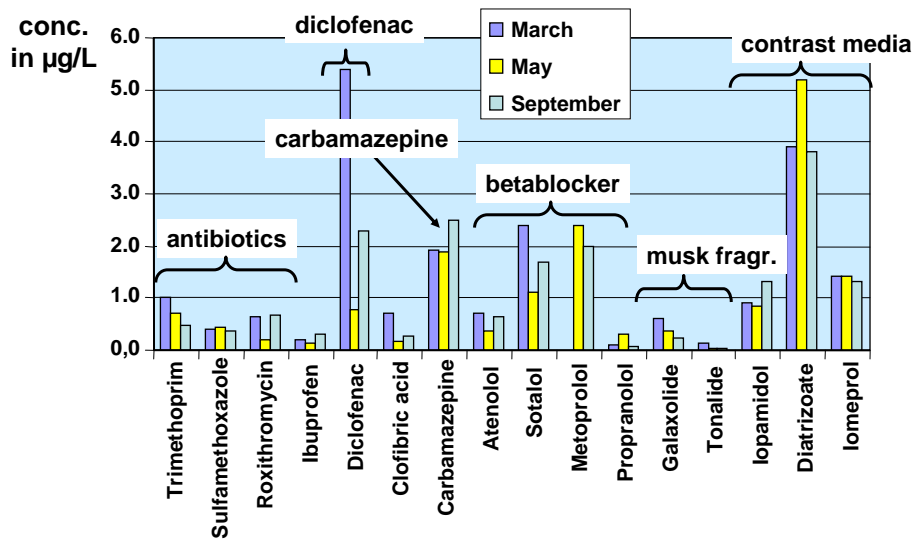


Johnson A., Sumpter J. (2001) Removal of endocrine disrupting chemicals in activated sludge treatment works. *Env. Sci. & Techn.*, **36**, 1202. Oehlmann J. et al. (2006) Bisphenol A induces superfeminization in the ramshorn snail *Marisa cornuarietis* (Gastropoda: Prosobranchia) at low concentrations. *Environ. Health Prosp.*, **114** (S-1) 127-133.

Estrogenicity of important EDCs Product of average concentration and specific estrogenic potency



Pharmaceuticals in treated wastewater



Ternes et al., Chemosphere 2007

360'000 Pop. Equiv. WWTP for Nitrification/Denitrification

Environmental quality standards (EQS) of contaminants determined according to WFD (based on ecotoxicological data)

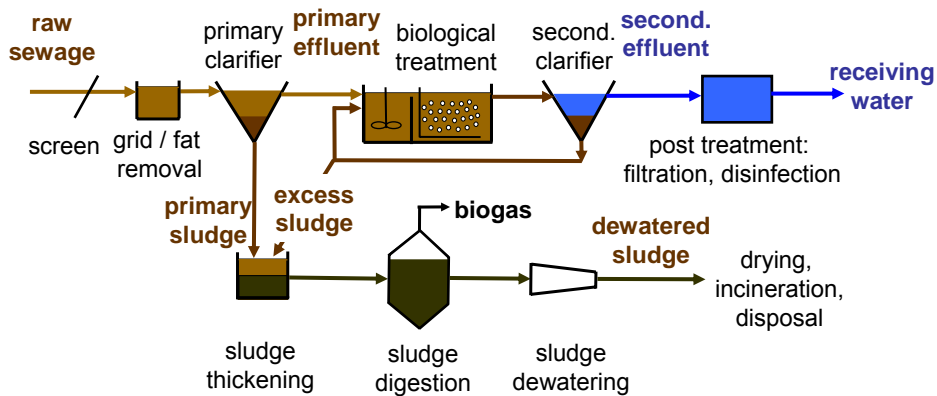
	¹ AA-EQS-S	Annual average measured concentration in German rivers
Bisphenol A	0.79 ng/L	0.5 ng/L-270 ng/L
Diclofenac	100 ng/L	50-500 ng/L
EE2	0.03 ng/L	< 1 ng/L (WWTPs)

¹: Suggested maximum annual average concentration

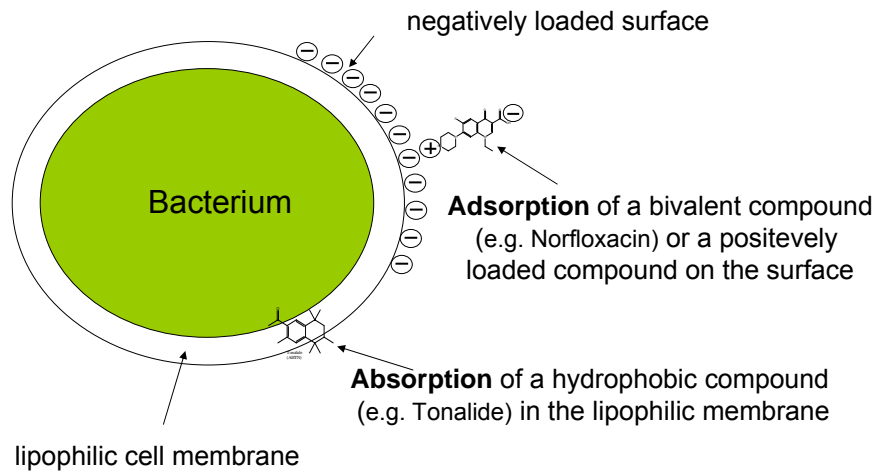
Source: Moltmann et al., 2007, German EPA report

Elimination processes in biological wastewater treatment

- Sorption on particulates (sludge)
- Stripping (negligible for PPCP's)
- Biological degrad./transformation
- potential post treatment: ozonation, PAC addition combined with filtration, (minor/no effects: UV, wetland)



Sorption of trace pollutants



Sorption of micropollutants in WWTP

Sorbed concentration:

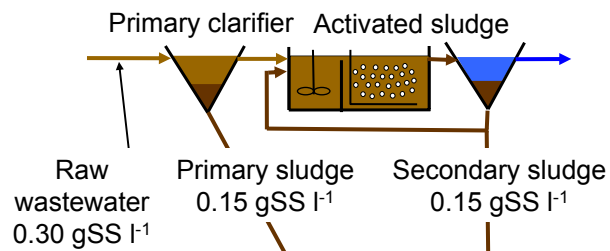
$$C_{\text{sorb}} = K_d \cdot SP \cdot C_{\text{diss}}$$

K_d = Sorption constant [$l \cdot g_{\text{TSS}}^{-1}$]

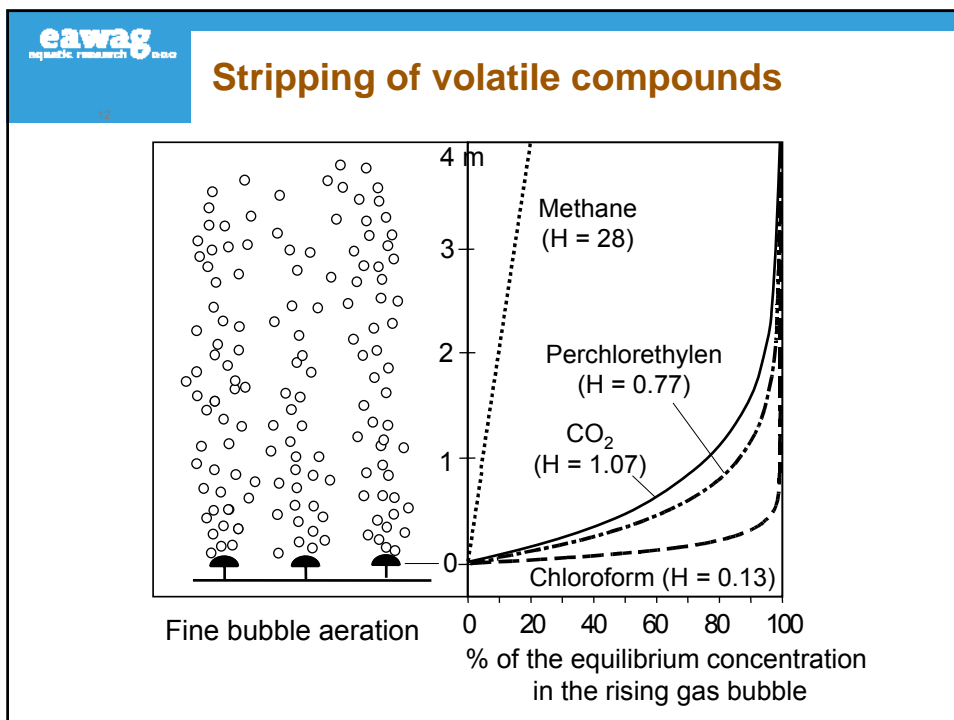
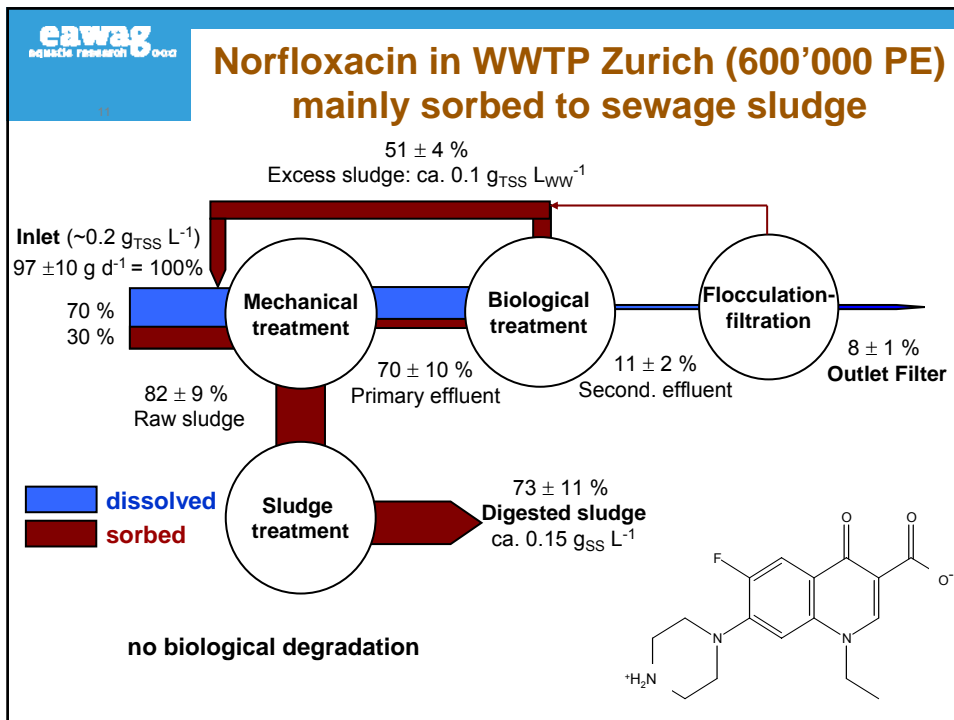
SP = sludge production [$g \cdot l^{-1}$]

Sorbed fraction:

$$\frac{C_{\text{sorb}}}{C_{\text{diss}} + C_{\text{sorb}}} = \frac{K_d \cdot SP}{1 + K_d \cdot SP}$$

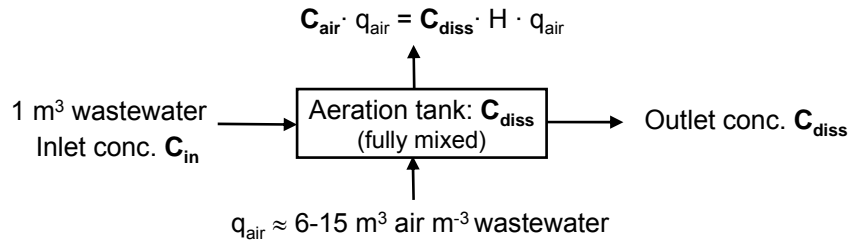


Compound	K_d ($l \cdot g_{\text{SS}}^{-1}$)	sorbed fraction (%)		
		Primary clarifier	Activated sludge	Secondary clarifier
Diclofenac	0.1	3	1.5	1.5
Ethinylestradiol	0.4	11	6	6
Tonalide	2 / 5	47	23	43
Norfloxacin	2 / 25	38	23	79



Stripping of volatile compounds

Due to small Henry coefficient air bubble in equilibrium: $C_{air} = H \cdot C_{diss}$

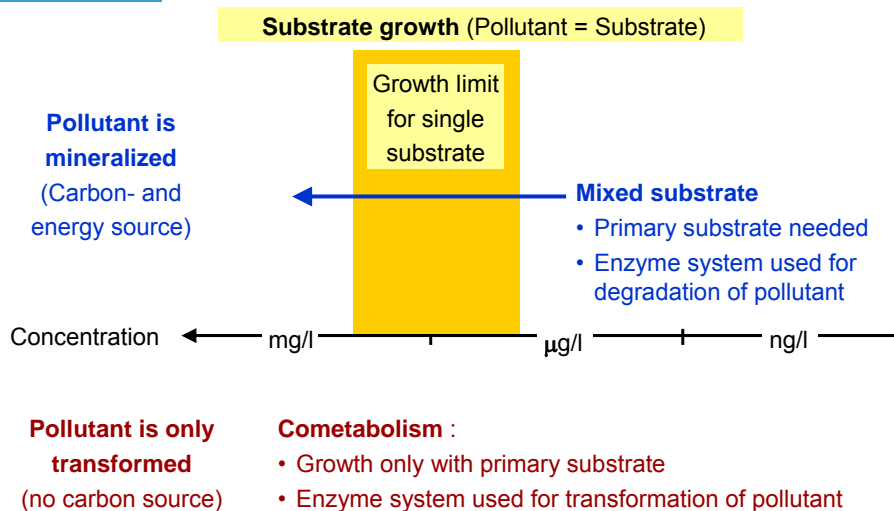


Mass balance: $C_{in} = C_{diss} + C_{diss} \cdot H \cdot q_{air} = C_{diss} \cdot (1 + H \cdot q_{air})$

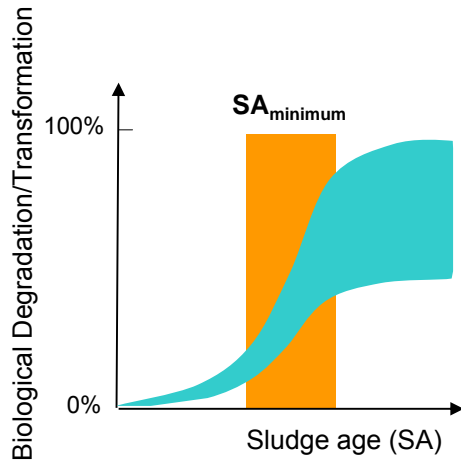
Stripping efficiency: $\eta_{Stripping} = H \cdot q_{air} / (1 + H \cdot q_{air}) \approx H \cdot q_{air}$

Musk fragrance Tonalide ($H_{Ton} = 0.005$) $\Rightarrow \eta_{Stripp, Ton} = 10 \cdot 0.005 = 0.05$ (-)
 \Rightarrow Stripping efficiency low, except for surface aeration and MBR

Biological degradation or transformation



Biological Degradation / Transformation



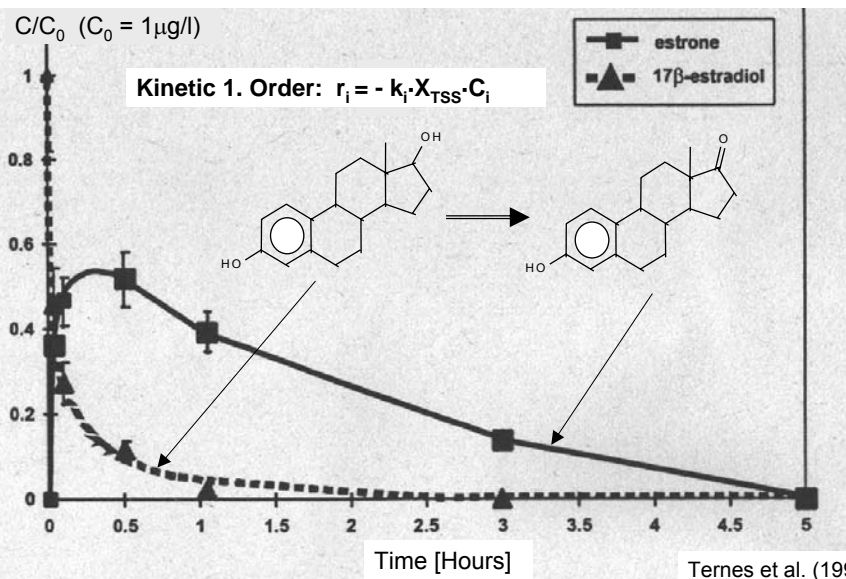
degradable at 15°C and SA_{min}

- | | |
|----------|---|
| 2 - 5 d | Bezafibrate
Sulfamethoxazole
Ibuprofen |
| 5 - 15 d | Ethinylestradiol
Iopromide
Roxithromycin
Bisphenol A |

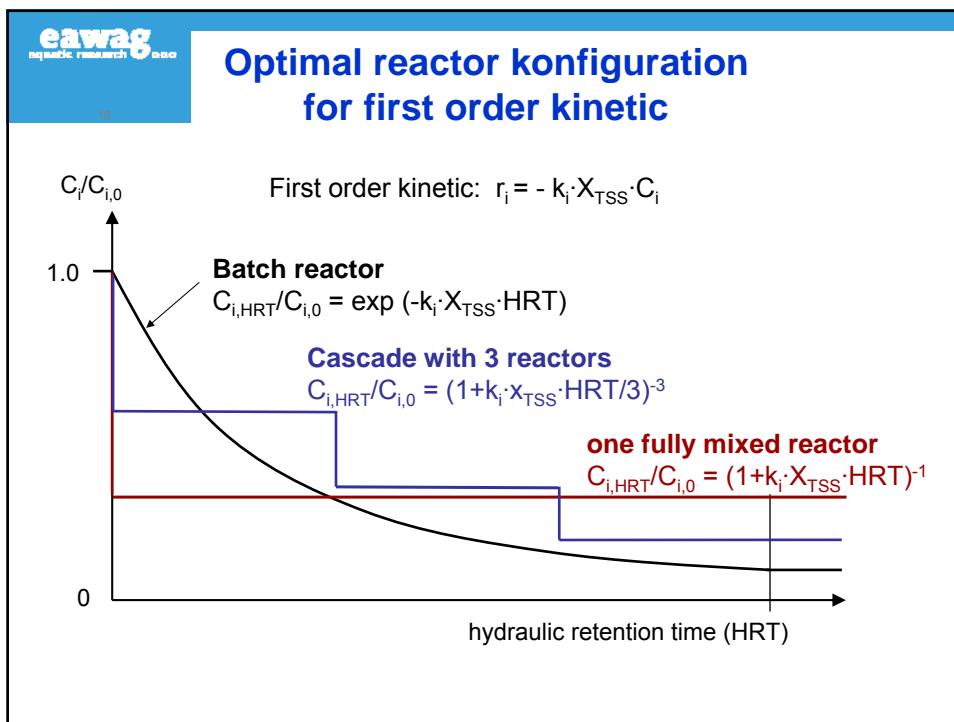
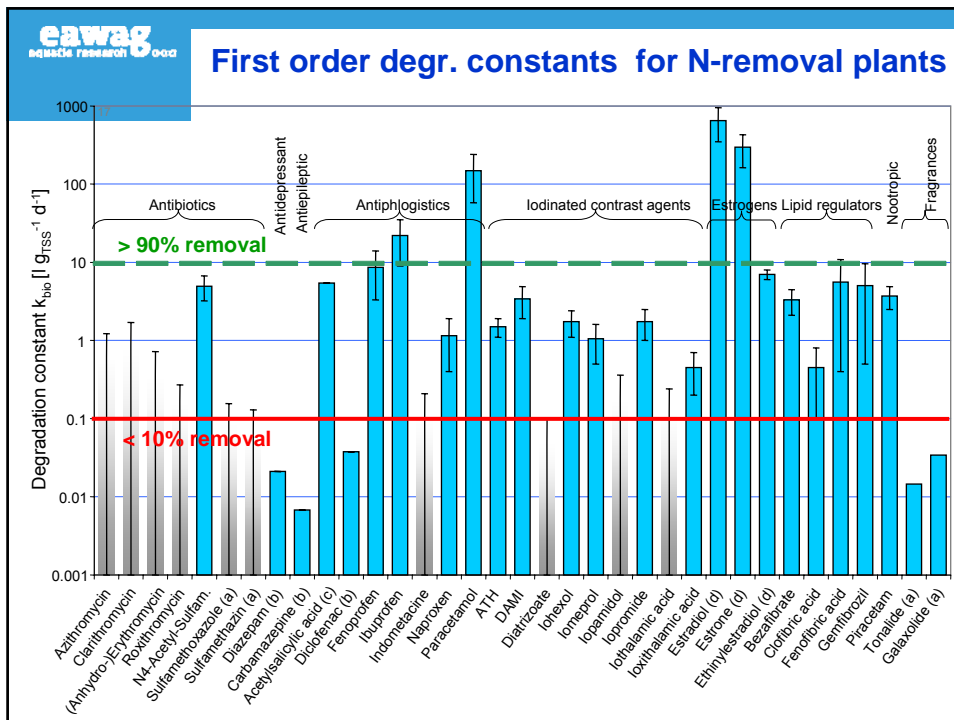
not degradable

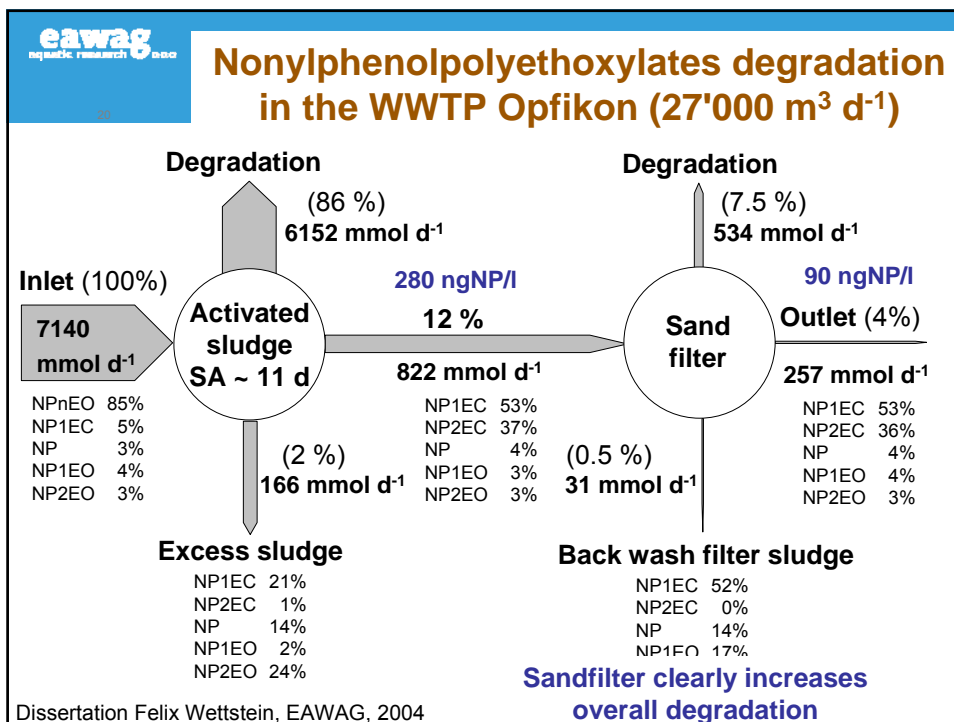
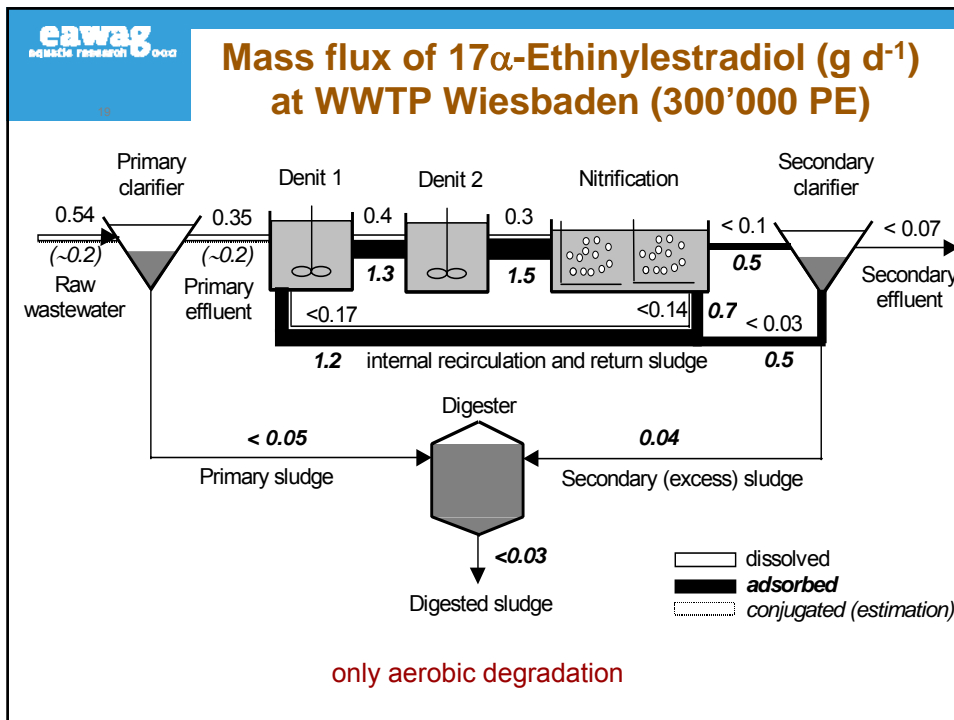
- | | |
|----------|---------------------------|
| SA < 20d | Carbamazepine
Diazepam |
|----------|---------------------------|

Degradation of 17β-Estradiol and Estrone in batch reactor with activated sludge (0.26 g l⁻¹)

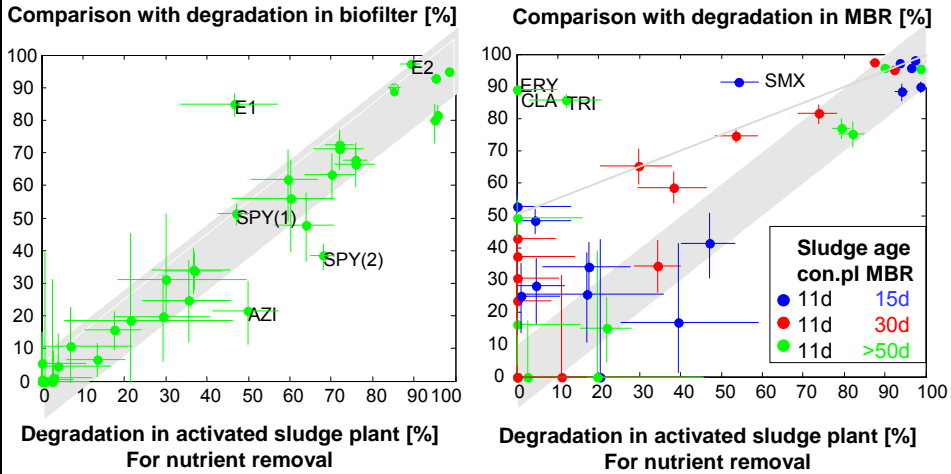


Ternes et al. (1999)





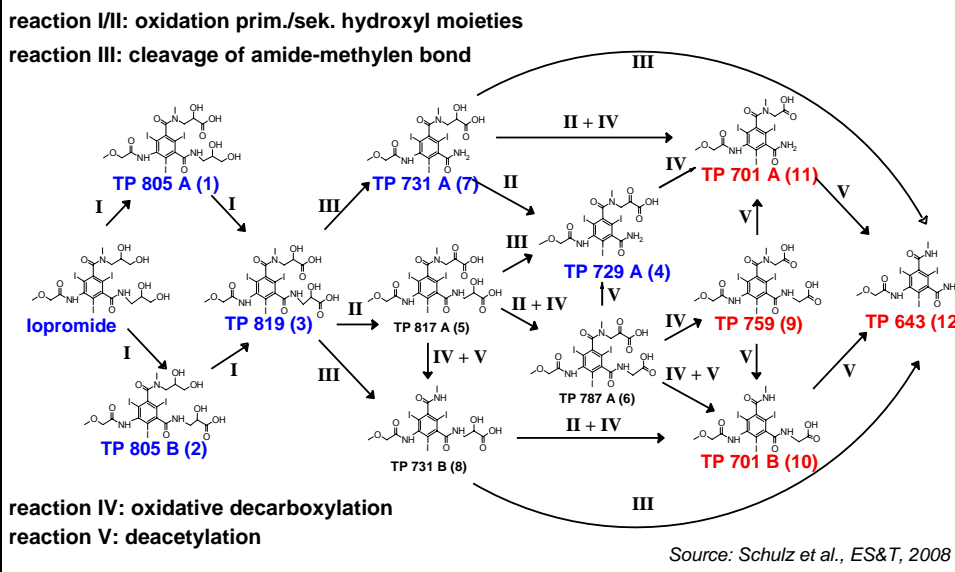
Comparison of biological degradation of biofilter and MBR with activated sludge



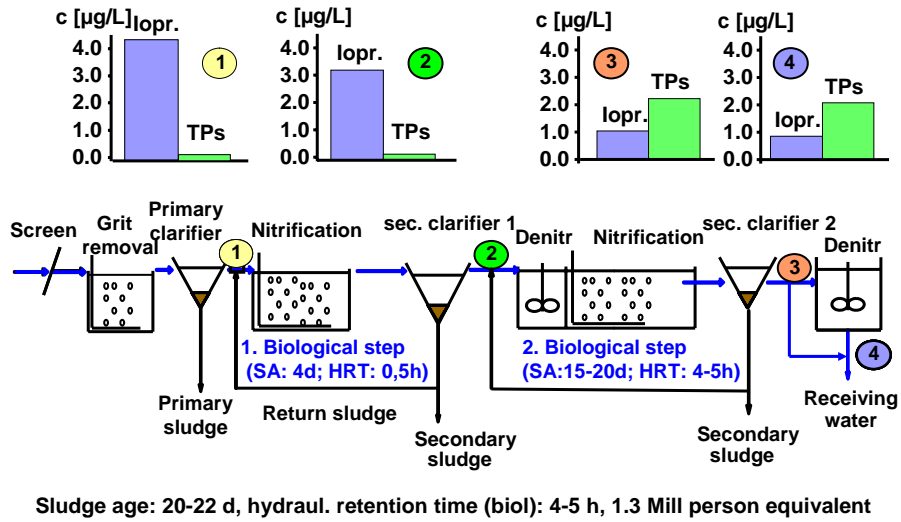
Degradation efficiency similar for plants with similar nutrient removal

Source: Joss und Siegrist, 2005, Eawag News

Potential aerobic degradation pathway of lopromide (contrast media)

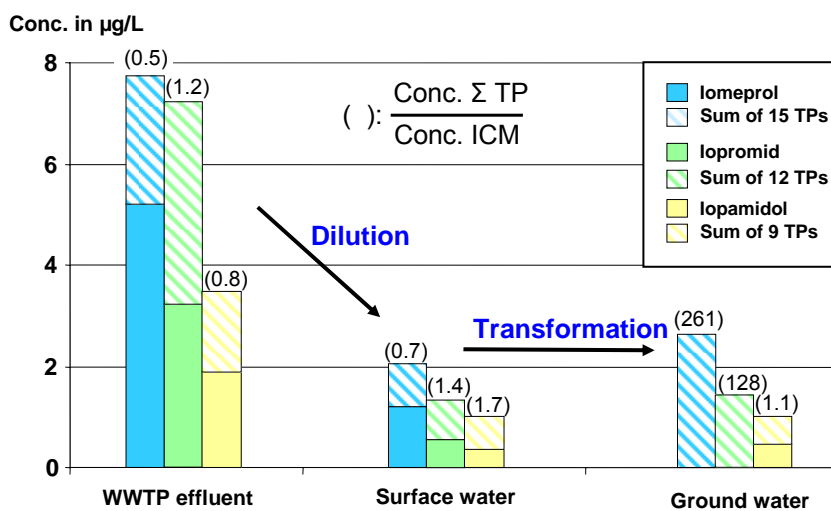


Transformation products of lopromide in WWTP Frankfurt



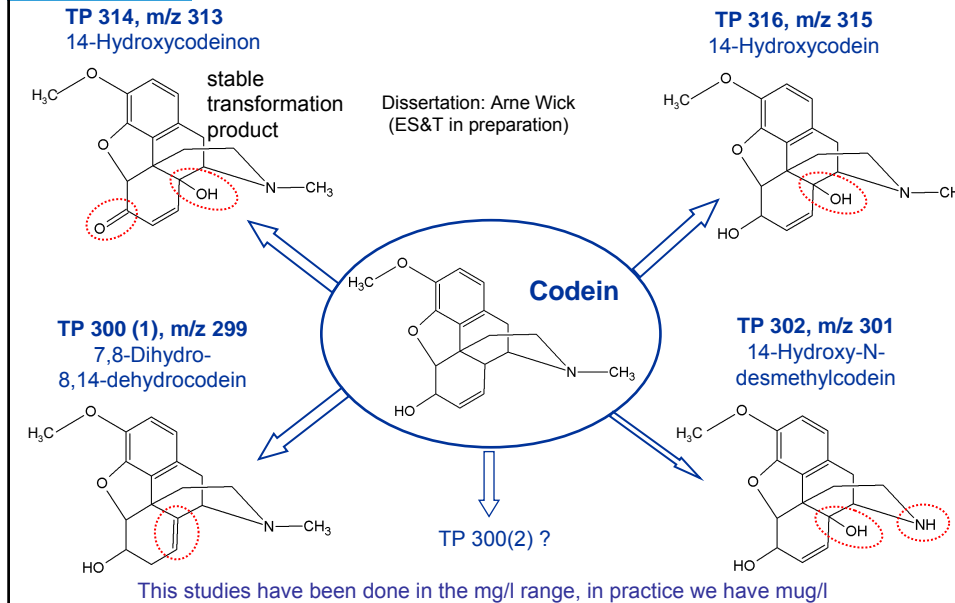
Source: Schulz et al., ES&T, 2008

Transformation products of iodated contrast media in surface and ground water



Source: Kormos et al., ES&T, in preparation

Transformation of Codein

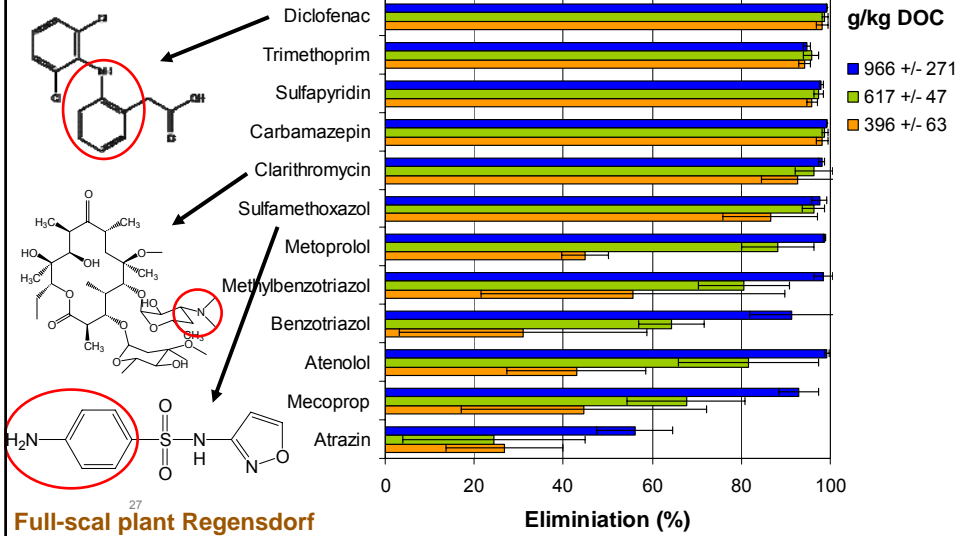


Measures at the WWTP

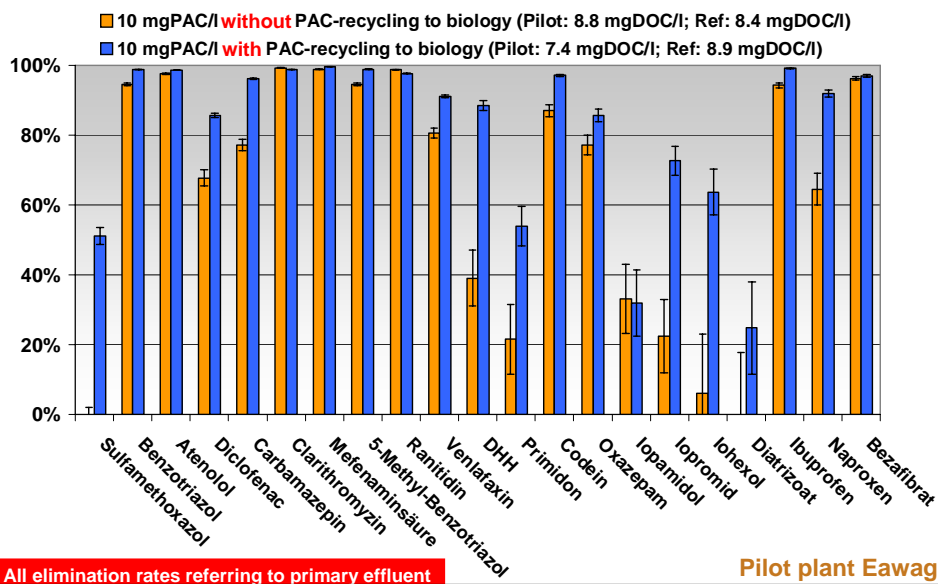
- Increasing the sludge age to 10 -15 days, which means Nitrification and Denitrification
- Cascade of reactors or SBR
- For critical cases (low dilution in receiving water, ground water infiltration, water reuse,...) additional treatment with chemical and physical processes, e.g.:
 - partial ozonation,
 - powder activated carbon addition

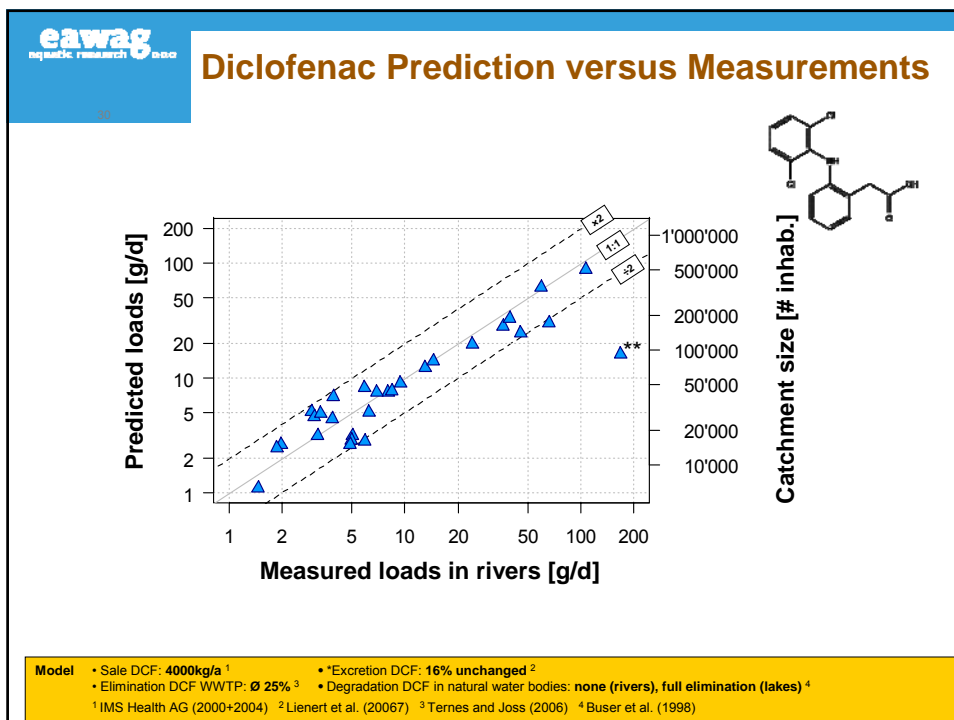
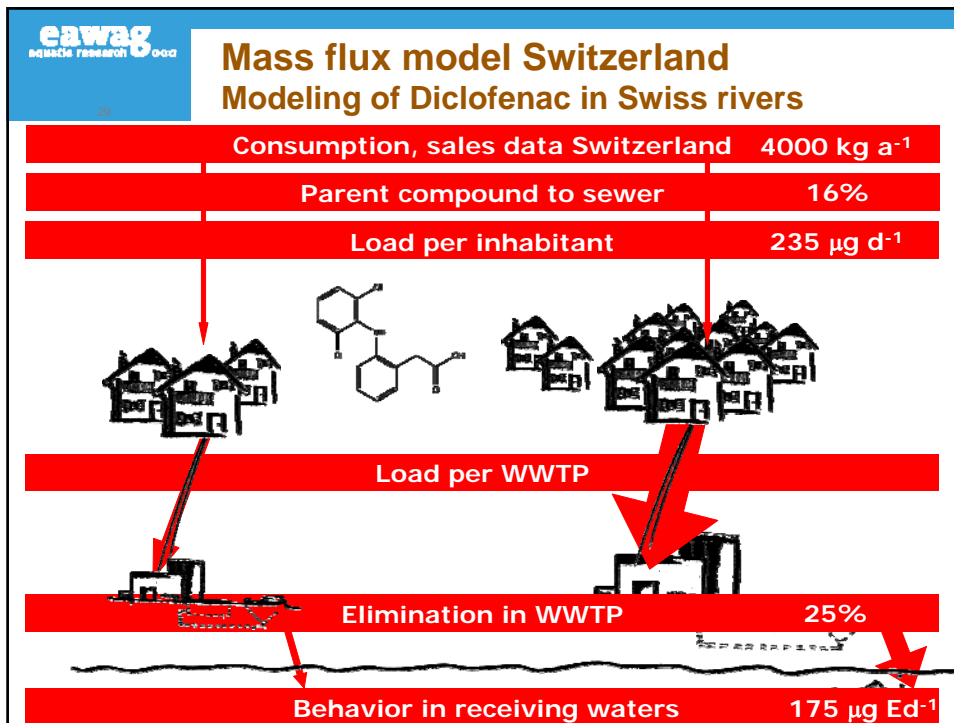
Effect of ozone concentr. on elimination efficiency (0.4-1.0 g_{O3}/g_{DOC} = 2-5 g_{O3}/m³)

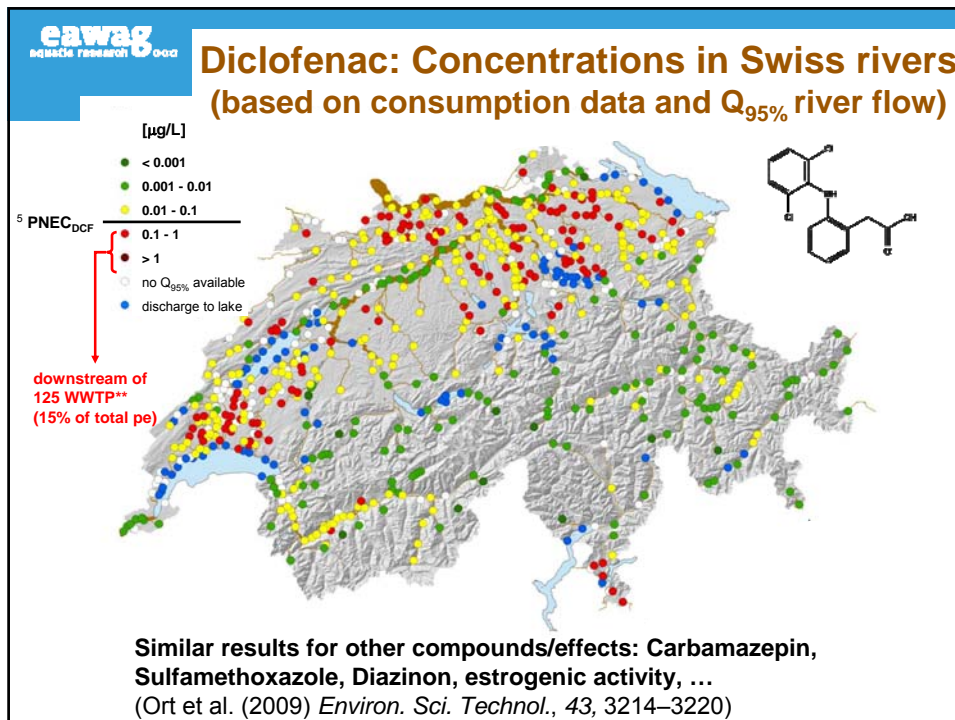
Calculation: $100 - 100 \cdot C_{\text{after ozonation}} / C_{\text{secondary effluent}}$



PAC addition to secondary effluent, contact tank and additional sedimentation







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aquatic research

Conclusions

- Micropollutants are eliminated in WWTP mainly by sorption and biological degradation or transformation
- Elimination of a lot of trace pollutants is insufficient even at high solid retention times (sludge ages)
- Losses to surface water by combined sewer overflows (1-2%) and exfiltration from sewer (3-8%) to groundwater
- Additional measures are required for critical cases (low dilution of wastewater in receiving waters, substantial infiltration to groundwater and reuse of treated wastewater)
- Advanced processes (e.g. ozone and PAC addition) have been successfully tested in pilot and full-scale and are available for an acceptable price in comparison to overall treatment cost.

Thank you for your attention

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