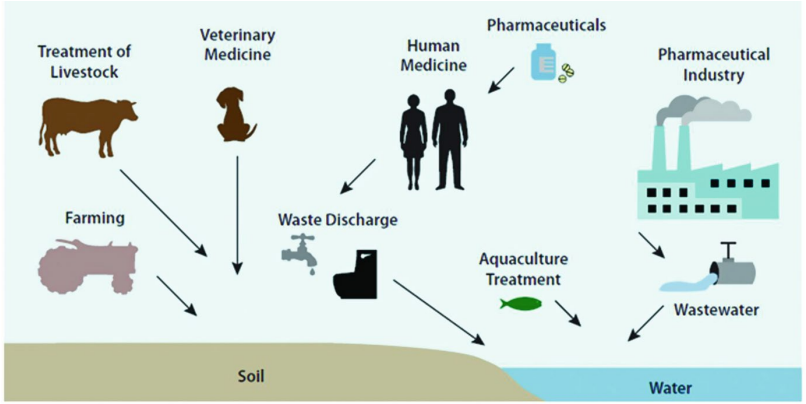

Source: https://link.springer.com/chapter/10.1007/978-3-030-96523-5_5

ENV-200
Chemistry of natural waters III: Organic micropollutants in lakes

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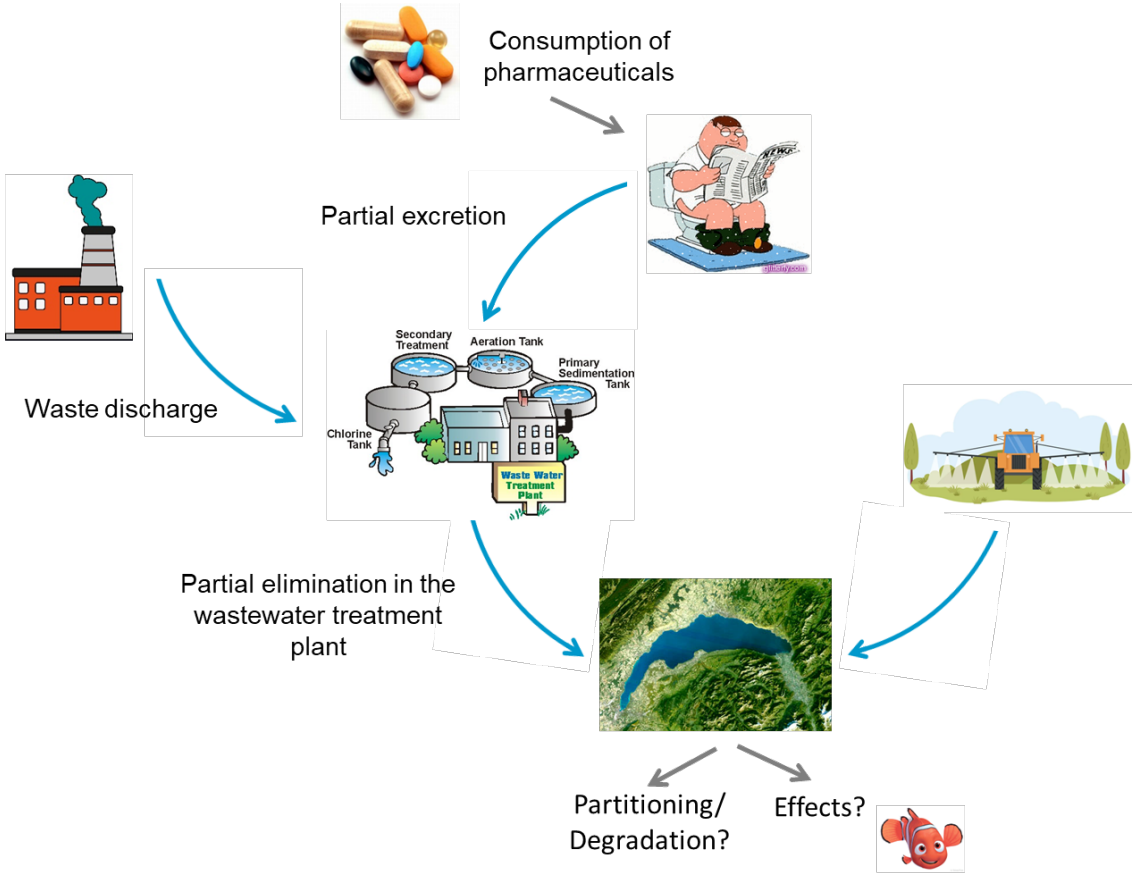
What are organic micropollutants?

- Anthropogenic organic compounds that are present in the environment at very low concentrations (ng - µg/L; 1 Dafalgan tablet in 10 olympic sized pools)
- Includes pharmaceuticals, pesticides, solvents, personal care products, caffeine…

How do micropollutants get into the water?



Important micropollutant categories

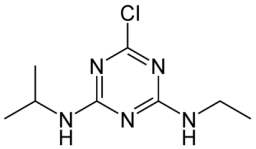
Source: Adeola et al., STOTEN 2024

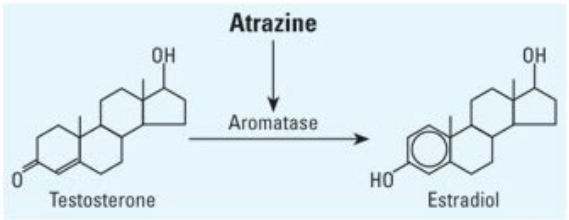
Do they matter?

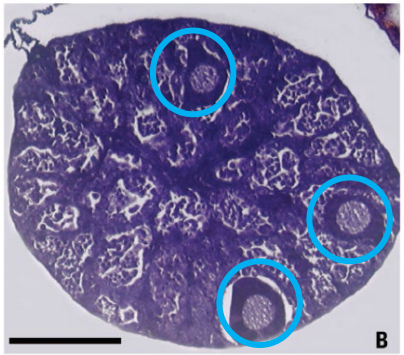
We are mainly concerned about effects on the ecosystem, not humans!

Example atrazine

- one of the most widely used herbicide in the world, mainly used for corn
- the most common contaminant of ground and surface water
- endocrine disrupting activity at low concentrations (0.1 ppb = 100 ng/L)
- chronic exposure can lead to malformations and feminize frogs and fish







Gonad of a « male » frog.
Hayes et al. Env. Health Perspectives, 2003

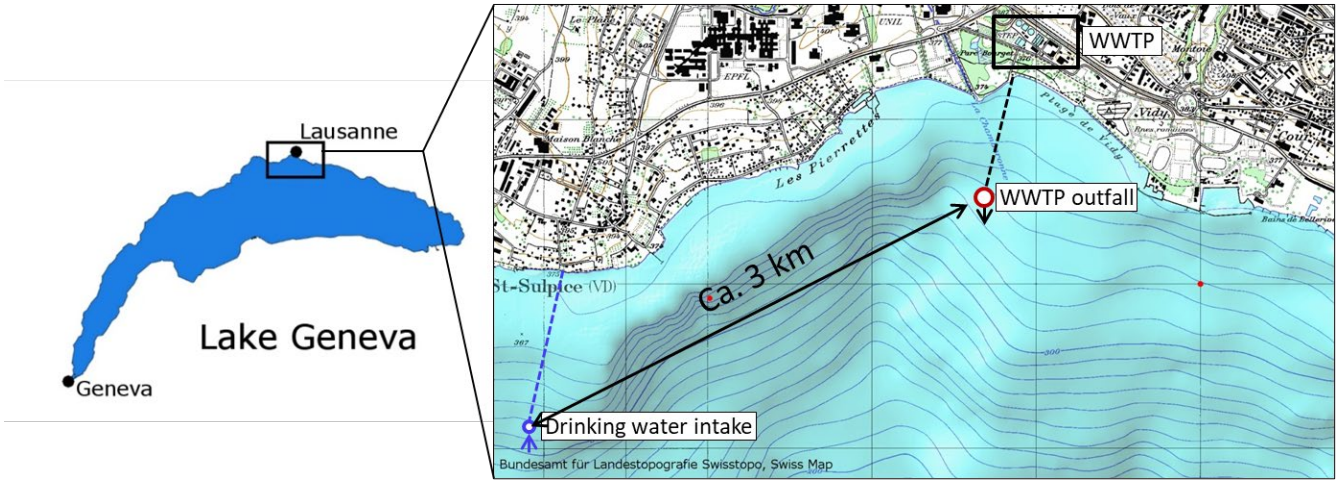
Today's focus: pharmaceuticals

- Frequently **detected in surface waters**
- Increasing production and consumption : 100'000 tons/year
- Are designed to have an effect on organisms (humans)
- A variable fraction is excreted **unmetabolized**

Therapeutic group	Unchanged in urine
Antibiotics	53%
Analgesics	28%
X-Ray contrast media	94%

- **Often incomplete elimination in wastewater treatment plants (WWTP)**
- Continual release into the environment -> largely **unknown consequences**

Case study: micropollutants in Lake Geneva



Bonvin et al, Environmental Science & Technology 2011:

Monitored 39 micropollutants over 10 months at the WWTP outfall, as a function of depth. Also monitored electrical conductivity (EC) and temperature (T).

Sampling Lake Geneva: the normal way

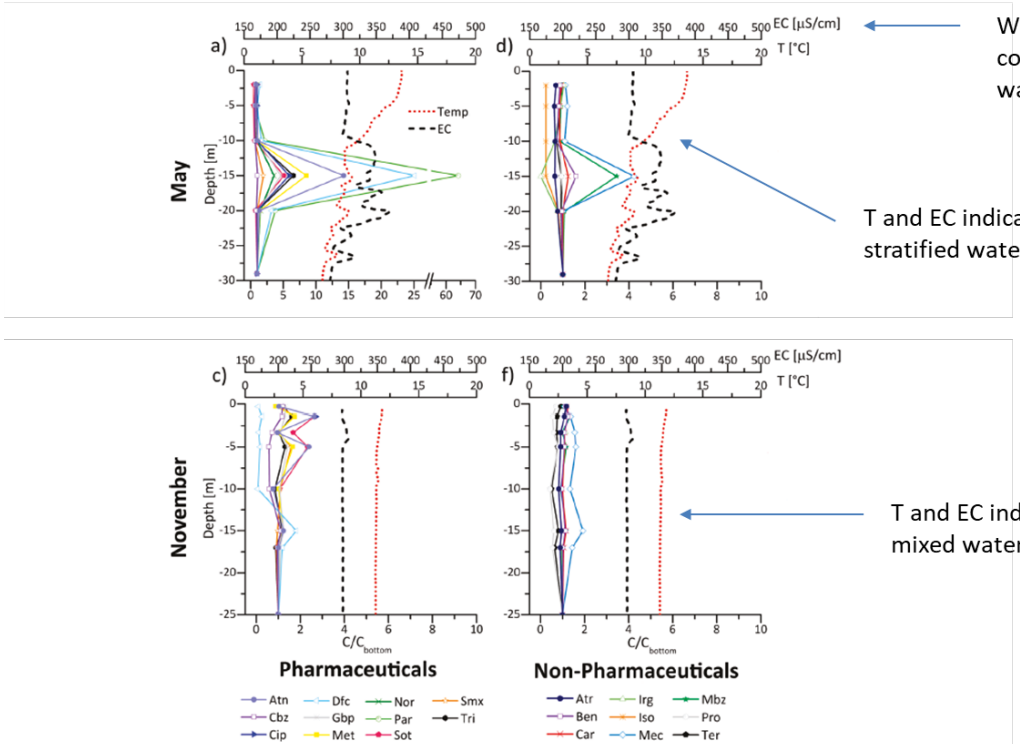
Sampling Lake Geneva: the crazy way

Same MIR submarine!

In a scene from the movie "Titanic," written and directed by James Cameron, the bow of the Titanic wreckage, left, and the lights of the deep-sea research vessel Mir 1 can be seen.

PARAMOUNT PICTURES VIA GETTY

Some of the micropollutants at the WWTP outfall



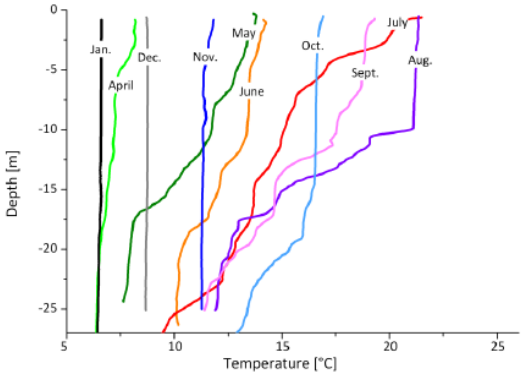
Wastewater has a higher conductivity than lake water

T and EC indicate a stratified water column

T and EC indicate a mixed water column

Figure 2. Conductivity, temperature, and concentration profiles of a selection of pharmaceuticals (a,b,c) and nonpharmaceuticals (d,e,f) relative to the concentration detected at the bottom. Shown profiles were taken above the WWTP outfall in May (a,d), August (b,e), and November (c,f) 2010. EC, electrical conductivity; T, temperature; Atn, atenolol; Cbz, carbamazepin; Cip, ciprofloxacin; Dfc, diclofenac; Gbp, gabapentin; Met, metoprolol; Nor, norfloxacin; Par, paracetamol; Sot, sotalol; Smx, sulfamethoxazol; Tri, trimetoprim; Atr, atrazin; Ben, benzotriazol; Car, carbendazim; Irg, irgarol; Iso, isoproturon; Mec, mecoprop; Mbz, methylbenzotriazol; Pro, propiconazol; Ter, terbutryn.

Temperature, conductivity and plume throughout the year



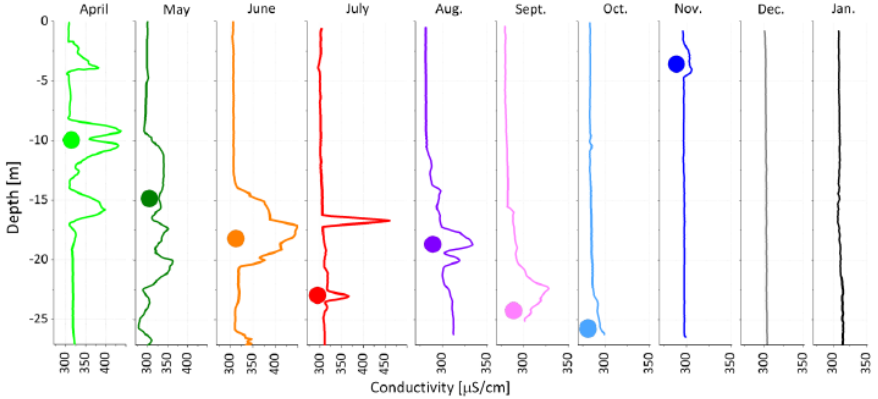
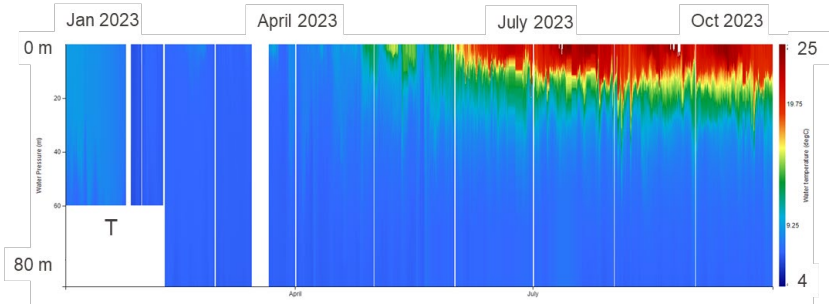


FIGURE S2. Chronology of temperature and electrical conductivity profiles above the WWTP outfall. Peaks in conductivity indicate the location and depth of the wastewater plume. Round symbols indicate depth at which highest concentrations (plume) of micropollutants were detected in the water sample profile. Conductivity profiles coincide with the sampling cast, whereas temperature profiles were taken in the surrounding water column.



For comparison: T-profile in lake Geneva in 2023 (from datalakes, see last case study)

Where do the different micropollutants go?

Assume the micropollutants can be present in the following 4 compartments:

Water (w), air (a), particles (p), sediment (s)

Recall: the fraction of i in a given phase x: $f_{i,phase\ x} = \frac{mass\ of\ i\ in\ phase\ x}{total\ mass\ of\ i}$

Example: fraction in water (x = water)

$$f_{i,w} = \frac{C_{i,w}V_w}{C_{i,w}V_w + C_{i,a}V_a + C_{i,p}M_p + C_{i,s}M_s} = \frac{1}{1 + \frac{C_{i,a}}{C_{i,w}}\frac{V_a}{V_w} + \frac{C_{i,p}}{C_{i,w}}\frac{M_p}{V_w} + \frac{C_{i,s}}{C_{i,w}}\frac{M_s}{V_w}} = \frac{1}{1 + K_{aw}\frac{V_a}{V_w} + K_{pw}\frac{M_p}{V_w} + K_{sw}\frac{M_s}{V_w}}$$

K_{aw}: can be estimated from solubility and vapor pressure.

K_{pw} and K_{sw}: these are solid-water distribution coefficients (K_d in the notes. $K_d = K_{oc} * f_{oc}$, and K_{oc} can be estimated from K_{ow})

To determine distribution, need the following:

Phys-chem properties of the micropollutant: solubility, vapor pressure, K_{ow}

Properties of the environmental system: V_w, V_a, M_p, M_s, f_{oc}

Use CHEMFATE excel sheet for a quick fate estimate

Example: fate of carbon tetrachloride

SUMMARY OF INPUTS

Compound **Carbon Tetrachloride** input values from Appendix C, Schwarzenback et al., 2003,

Physical Properties	Value	Units
Molecular weight	1.5380E+02	g/mol
Aqueous solubility	8.2600E+02	g/m^3
Vapor pressure	1.4400E+04	Pa
log K_{ow}	2.7700E+00	--
Temperature	2.5000E+01	°C

Compartment Properties

	Volume [m^3]	Density [kg/m^3]	Organic Fraction [--]
Air	6.00E+10	1.21E+00	N/A
Water	8.90E+07	1.00E+03	N/A
Soil	0.00E+00	1.50E+03	2.00E-02
Sediment	2.10E+05	1.50E+03	4.00E-02
Susp. aq matr	4.75E+01	1.50E+03	4.00E-02

You need to find these physical-chemical properties (at 25 C) for your compound of interest. Places to look:

- Pubchem: *https://pubchem.ncbi.nlm.nih.gov/*
- Appendix C of Env. Org. Chem. Book (on moodle)
- Episuite: can be downloaded from: *https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface*
- Any other reliable database
- If you can't find anything, use the estimation methods discussed in class

These are given in the excel sheet for Lake Geneva. They apply to all compounds studied.
Set volume of soil to 0 as we are considering the lake only.

Use CHEMFATE excel sheet for a quick fate estimate

Calculated as $K_H \approx \frac{p^*_{i,L}}{C^{sat}_{i,w}}$

Calculated as $K_{aw} = K_H/RT$

SUMMARY OF OUTPUTS

Henry's Constant	K_H [(Pa)(m³)/mol)]	K_{aw} [--]
	1.0157E-03	4.0977E-07

Partition Coefficients	K_p [--]
soil	6.12E+02
sediment	1.22E+03
susp. solids	1.22E+03
biota	

K_p is a dimensionless solid-water partitioning coefficient K_d, where $K_p = K_d$ *density of the solid, and $K_d = K_{oc}*f_{oc}$.

K_{oc} is here determined from K_{ow} via Karickhoff's relationship:

$K_{oc} = 0.63*10^{-6} * K_{ow}$; ($m^3/g$)

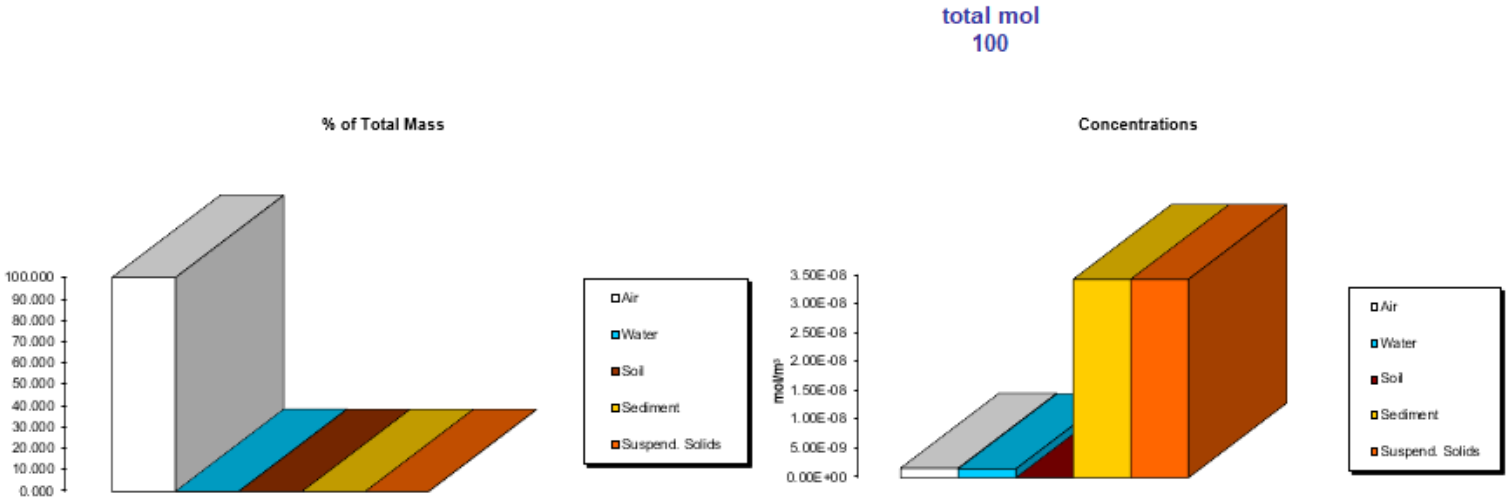
Compartment	Volume [m³]	Density [kg/m³]	Fraction of Mass [--]	Amount [mol]	% of Total Mass	Concentrations [mol/m³]	Concentrations [ppm]
Air	6.00E+10	1.21E+00	7.11E-05	7.11E-03	0.007	1.18E-13	2.90E-08
Water	8.90E+07	1.00E+03	2.57E-01	2.57E+01	25.726	2.89E-07	8.56E-05
Soil	0.00E+00	1.50E+03	#DIV/0!				
Sediment	2.10E+05	1.50E+03	7.42E-01	7.42E+01	74.250	3.54E-04	6.98E-02
Suspend. Solids	4.75E+01	1.50E+03	1.68E-04	1.68E-02	0.017	3.54E-04	6.98E-02

Taken from input

Calculated assuming a total input of 100 mol

Calculated according to principle explained on slide "Where do the different micropollutants go?"

Use CHEMFATE excel sheet for a quick fate estimate



The largest **mass** of carbon tetrachloride is in the air – BUT the highest **concentration** is in particles and sediment !

Exercise

Pick **one** of the following compounds that Bonvin et al. found in Lake Geneva:

- Diclofencac (a pain killer)
- Gabapentin (an antiepileptic)
- Sulfamethoxazole (an antibiotic)

Find the physical-chemical properties (attention to units!!), and estimate the distribution in Lake Geneva.

Note: depending on the source, you may find slightly different values for some properties.

Risk is influenced by initial concentration, degradation and ecotoxicity

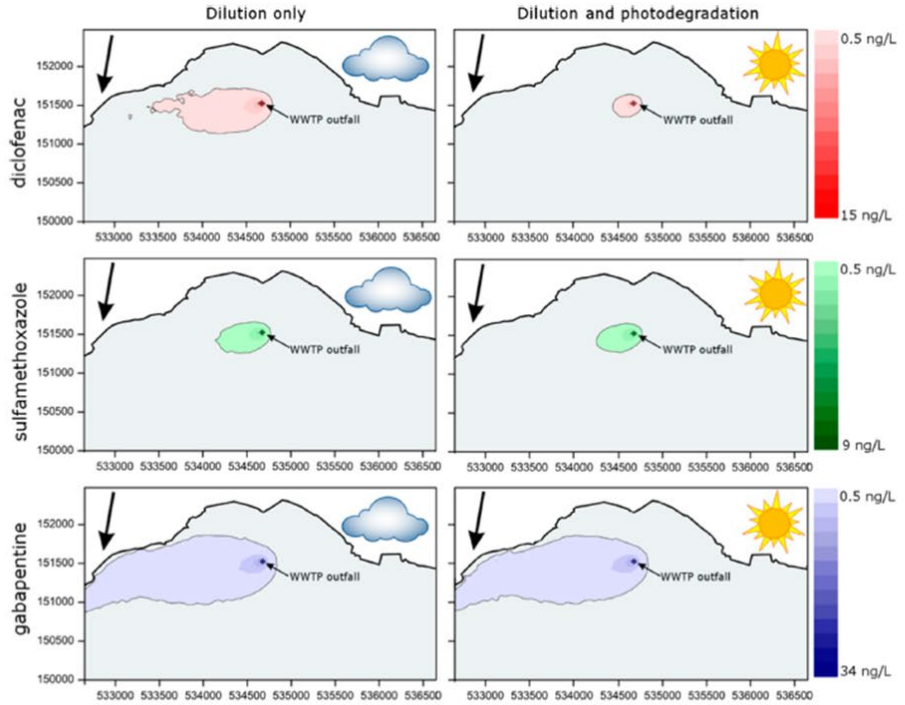


Figure 1. Predicted concentrations of diclofenac (top), sulfamethoxazole (middle), and gabapentine (bottom) in the surface layer (0 to 2 m depth) around the wastewater outfall, assuming a small surface plume under unstratified conditions, under the influence of the Bise (arrow shows wind direction). The concentrations are shown down to 0.5 ng/L, under cloudy (only dilution, left panel) and sunny weather conditions (dilution and photolysis, right panel). Axes show the latitudinal and longitudinal coordinates (Swiss Grid system with datum CH1903).

Medium initial concentration
Rapid degradation by sunlight
Predicted no-effect concentration (PNEC): 100 ng/L

Low initial concentration
Intermediate degradation by sunlight
PNEC: 26.8 ng/L

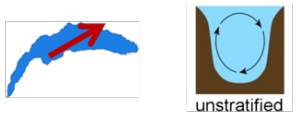
High initial concentration
Very slow degradation by sunlight
PNEC: 1000000 ng/L

Bonvin et al., Environ. Sci. Technol. 2013

Resulting ecotoxicological risks: sulfamethoxazole > diclofenac >> gabapentin

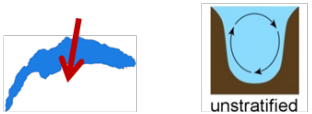
Stratification and wind conditions also affect ecotox risk

4 Scenarios

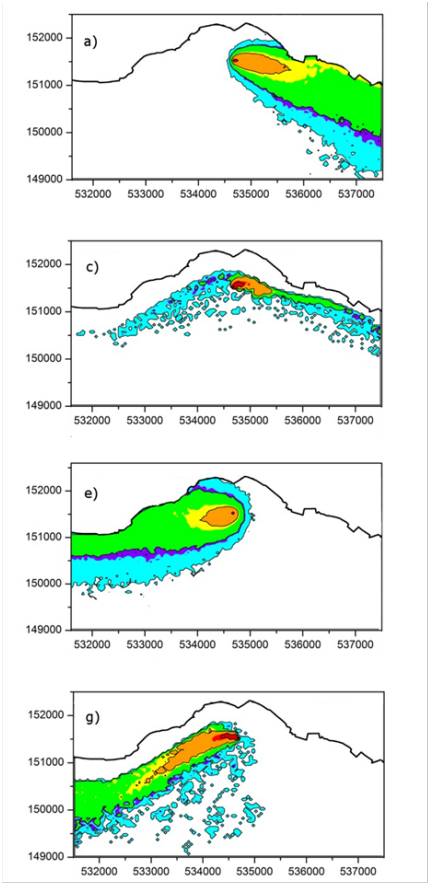


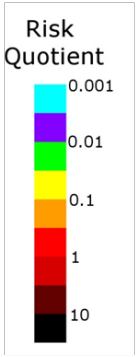
Stratified (summer) + *«Vent»*

Unstratified (winter) + *«Bise»*



Stratified (summer) + *«Bise»*





Potential ecotox risk if quotient > 1

Bonvin et al., Environ. Sci. Technol. 2013

Summary

- Many relevant micropollutants accumulate in the aqueous phase
- Plume extent and location is largely influenced by wind conditions and solar irradiation
- The micropollutant plume causes a potential ecotoxicological risk
- Area of risk is greatest under stratified conditions (>1 km)
- The total ecotoxicological risk can mainly be attributed to a few compounds (mainly antibiotics) → priority compounds for WWTP optimization and monitoring campaigns