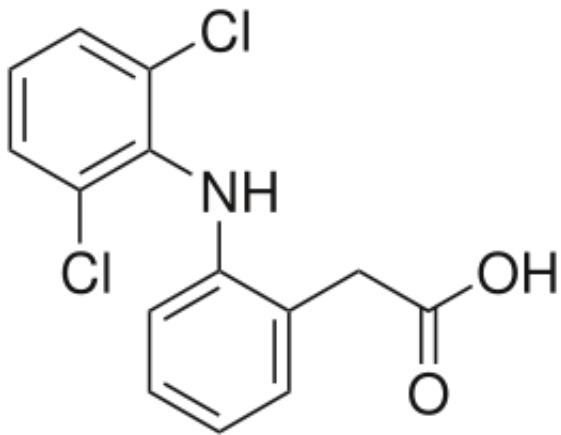


Organic micropollutant (oMP) treatment

Applied wastewater engineering

Michael Jon MATTLE



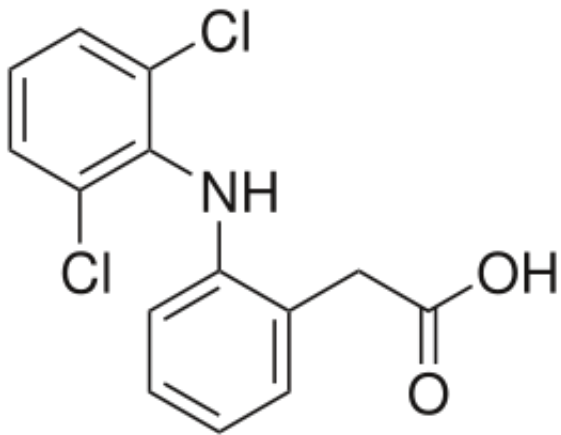
Content of organic micropollutants (oMP) treatment

- why do we treat organic micropollutants?
- Swiss legislation on micropollutants removal
- processes for organic micropollutant removal
 - biological removal of oMP
 - removal by activated carbon
 - removal by oxidation-based methods (e. g. ozone)
- wastewater treatment plants that already operate an organic micropollutant removal unit
- CO₂-Footprint of treatment of organic micropollutants
- outlook

Organic micropollutant (oMP) treatment I: why do we treat oMP?

Applied wastewater engineering

Michael Jon MATTLE



What are micropollutants?

- in previous courses on wastewater treatment you were taught how to treat “macropollutants”, like COD, BOD, TSS, NTK, P_{tot} . These macropollutants are generally found in the range of mg/L in raw wastewater and in some cases even in g/L
- high concentrations of these pollutants induce an important impact on the environment (e.g. absence of oxygen in rivers or lakes, toxicity to fish)
- ➔ hence, they are priority pollutants to be treated in wastewater treatment plants
- Nevertheless, there are many other substances present in wastewater at much lower concentrations ($\mu\text{g/L}$ or ng/L)

What are micropollutants?

- part of these substances may have or have a negative impact on the environment even though their concentrations are extremely low

→ we call these substances ‘micropollutants’

- there is no broadly accepted definition for the term ‘micropollutant’
- the definition of Wikipédia (only available in French): “*Un micropolluant est une substance (minérale, biologique, organique, radioactive..) polluante (et donc altéragène biologique, physique ou chimique) qui a des **concentrations infimes** (microgrammes ou moins) dans l'eau, l'air ou le sol, et qui peut avoir une **action toxique ou écotoxique** pour tout ou partie des organismes ou l'écosystème.*”



WIKIPÉDIA
L'encyclopédie libre

What are micropollutants?

based on the definition of Wikipédia, micropollutants can be divided into several sub-categories

- inorganic micropollutants
 - metals (e.g. nickel, cadmium, mercury, lead,...)
 - found in the $\mu\text{g/L}$ range in certain industrial wastewaters
- organic micropollutants (emerging pollutants or trace organic compounds)
 - organic molecules (e.g. pesticides)
 - generally found in the ng/L range. However, some substances are encountered in the $\mu\text{g/L}$
- biological micropollutants (not treated in this course)
 - e.g. pathogens (viruses, bacteria, protozoa,...)
- radioactive substances (not treated in this course)
 - e.g. certain hospital wastewaters



major topic of this chapter;
often simply called
micropollutants

What does the term organic mean?

- the term organic is used in many fields (medicine, physiology, agriculture, chemistry,...): e.g. food or farming methods
- in chemistry: *“an organic compound is any member of a large class of gaseous, liquid, or solid chemical compounds whose molecules contain **carbon (C)**. For historical reasons, a few types of carbon-containing compounds, such as carbides (e.g. CaC_2), carbonates (CaCO_3), simple oxides of carbon (such as CO and CO_2), and cyanides (e.g. HCN) are considered inorganic.”*

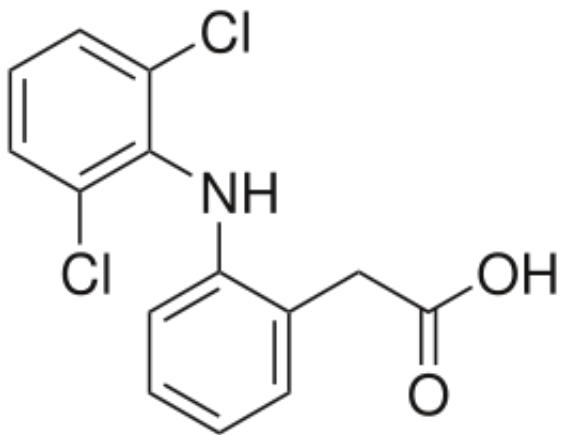
Periodic Table of the Elements

The image shows a standard periodic table of elements. The element Carbon (C) is highlighted with a red circle. The table is color-coded by groups: Alkali Metal (red), Alkaline Earth (orange), Transition Metal (yellow), Basic Metal (green), Semimetal (light blue), Nonmetal (blue), Halogen (purple), Noble Gas (pink), Lanthanide (light green), and Actinide (light purple). Carbon is located in the second row, fourth column.

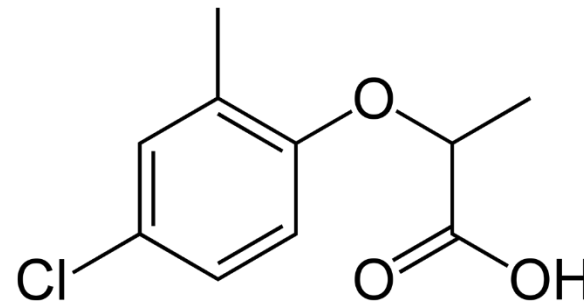
1	2											13	14	15	16	17	18		
1 H Hydrogen 1.01												6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18			
3 Li Lithium 6.94	4 Be Beryllium 9.01											11 Na Sodium 22.99	12 Mg Magnesium 24.31	13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.73	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 84.80		
37 Rb Rubidium 84.49	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29		
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [209]	85 At Astatine [209]	86 Rn Radon [222]		
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Nh Nihonium [278]	114 Fl Flerovium [289]	115 Uup Ununpentium [289]	116 Lv Livermorium [293]	117 Uus Ununseptium [293]	118 Uuo Ununoctium [294]		
57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.97	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97					
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]					
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide										

What does the term organic mean?

- organic compounds are the basis of life on earth (proteins, amino acids, lipids, carbohydrates, hormones,...)
- industrial syntheses produce thousands of different organic compounds (e.g. pharmaceutical compounds, polymers, pesticides, odorous compounds (perfumes),...)



diclofenac: anti-inflammatory drug
(e.g. sold as Voltaren)



mecoprop: herbicide (found in many household weed killers)

What are micropollutants?

How do I emit micropollutants into the environment?

- A) when I take a shower
- B) when I run the dishwasher machine
- C) when I walk
- D) when I apply volatren because I have muscle pain
- E) when I garden
- F) when I pee
- G) when I buy food

<https://web.speakup.info/room/join/30013>

What are micropollutants?

- **organic micropollutants (oMP)** include a large variety of substances

- pharmaceuticals
- hormones
- pesticides
- personal care products
- detergents
- ...

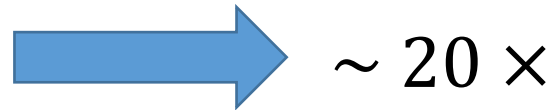
- their mode of action is also highly variable depending on the substance (e.g. hormones or pesticides)



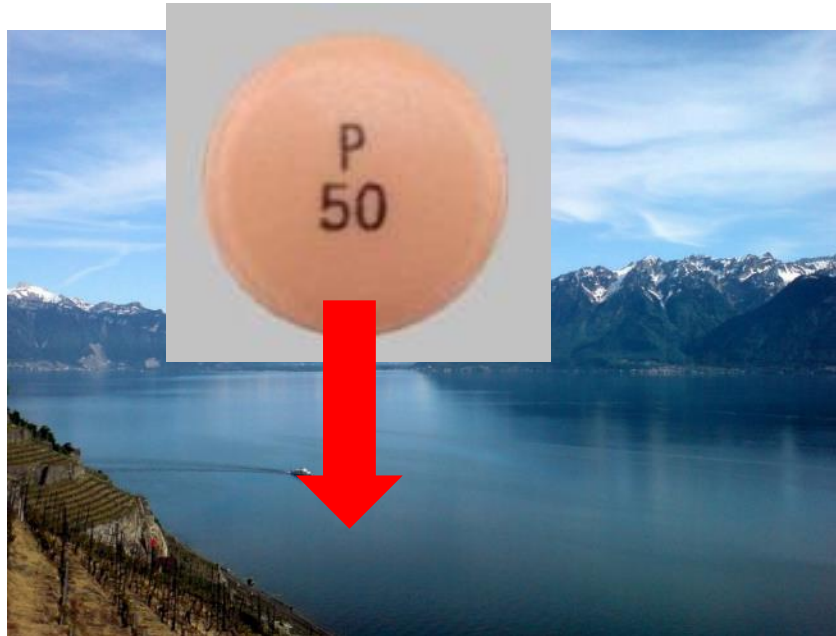
What are micropollutants?

1 ng/L corresponds to

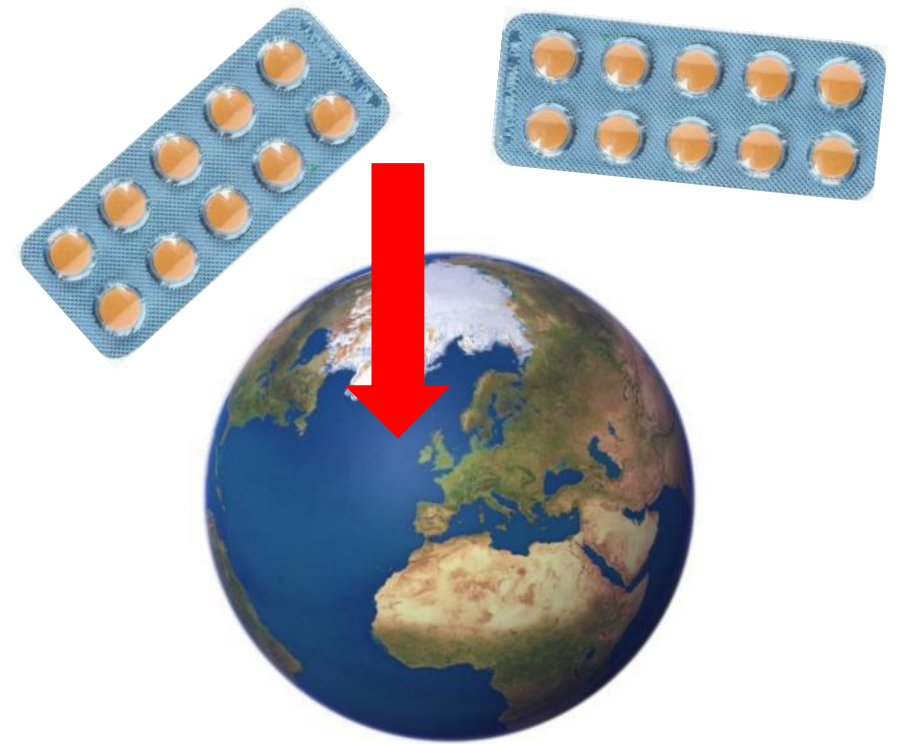
- 1 pill of Voltaren (50 mg) in ≈ 20 Olympic swimming pools



What are micropollutants?



> 1 million molecules of diclofenac in every litre of water in Lac Léman

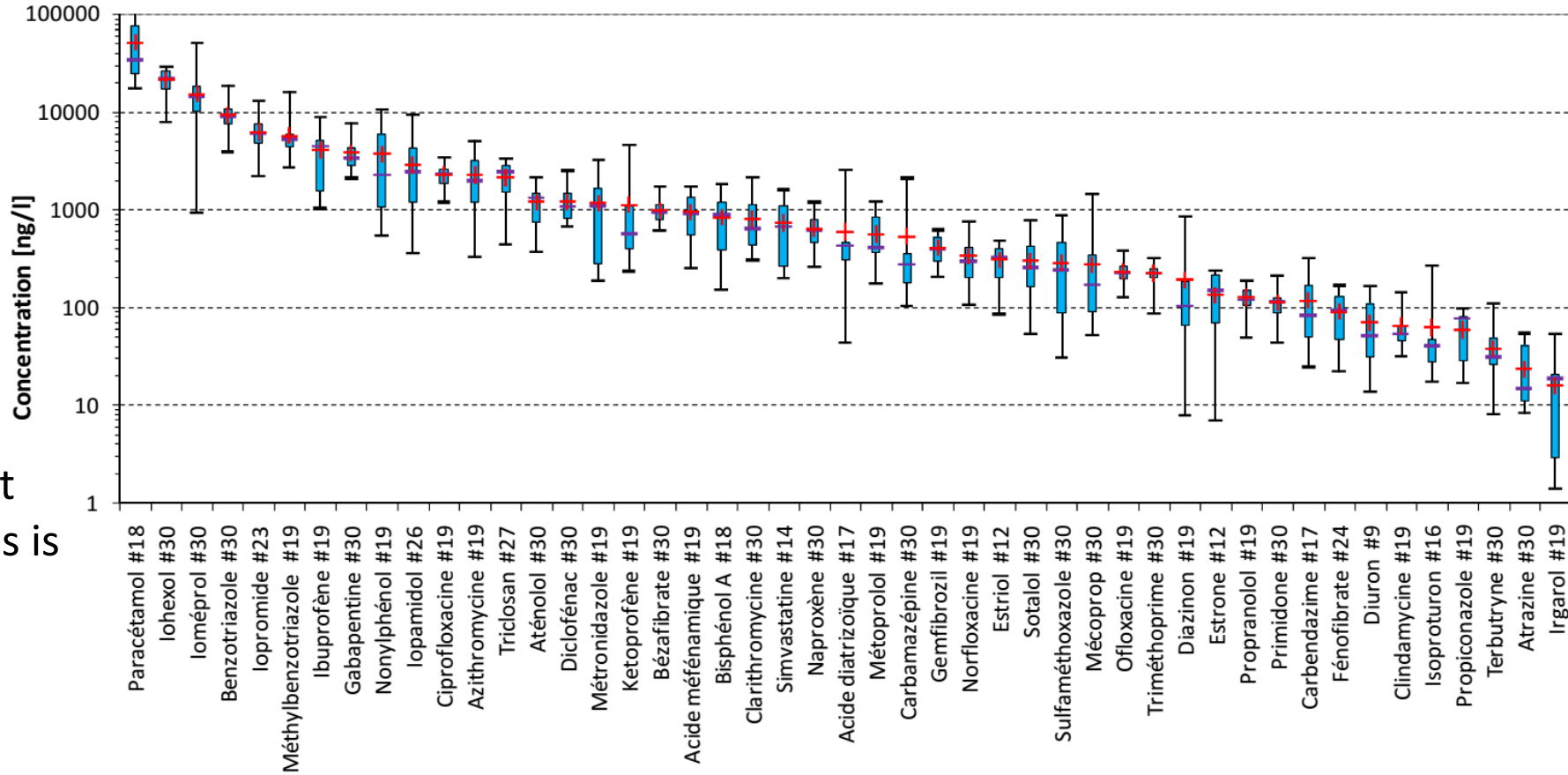


> 1 molecule of diclofenac in every litre of water in the entire world

- organic substances are nearly **everywhere** on the globe as long as they are not readily biodegradable

➔ to 'find' them is really only a question of the detection limit of the analytical method used

Concentration range of oMP in communal wastewater



- high variation in concentration among different compounds
- high variation over time (black bars)

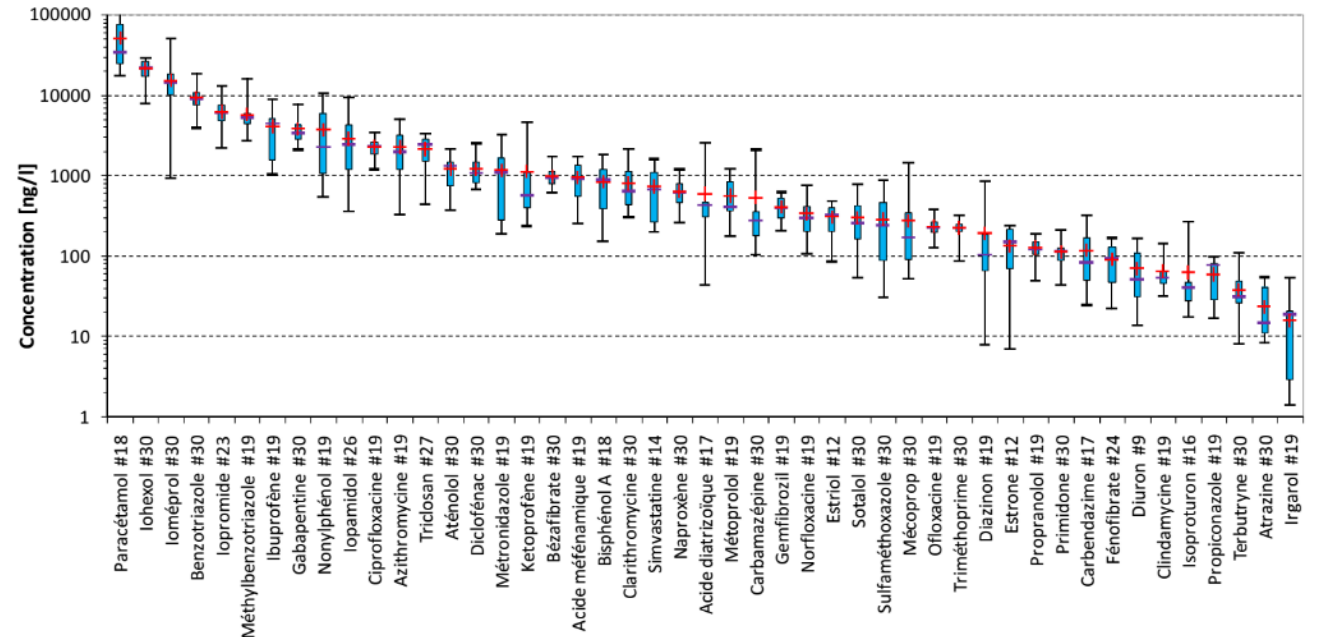
note that the y-axis is in logarithmic scale

average concentrations of oMP at the entry of the wastewater treatment plant of Vidy, Lausanne (2009 – 2010)

(#) number of analyses, quartiles 25 % - 75 % (blue bars), maximum and minimum values (in black), median (-) and average value (+)

Concentration range of oMP in communal wastewater

- concentrations from several $\mu\text{g}/\text{L}$ (e.g. paracetamol, benzotriazole and ibuprofen)
- down to the ng/L range (e.g. carbamazepine, atrazine (use forbidden in Switzerland since 2012))
- and even below the ng/L range for other substances (in graph: below detection limit for most substances analysed)



average concentrations of oMP at the entry of the wastewater treatment plant of Vidy, Lausanne (2009 – 2010)
(#) number of analyses, quartiles 25 % - 75 % (blue bars), maximum and minimum values (in black), median (-) and average value (+)

Why do we care about oMP?

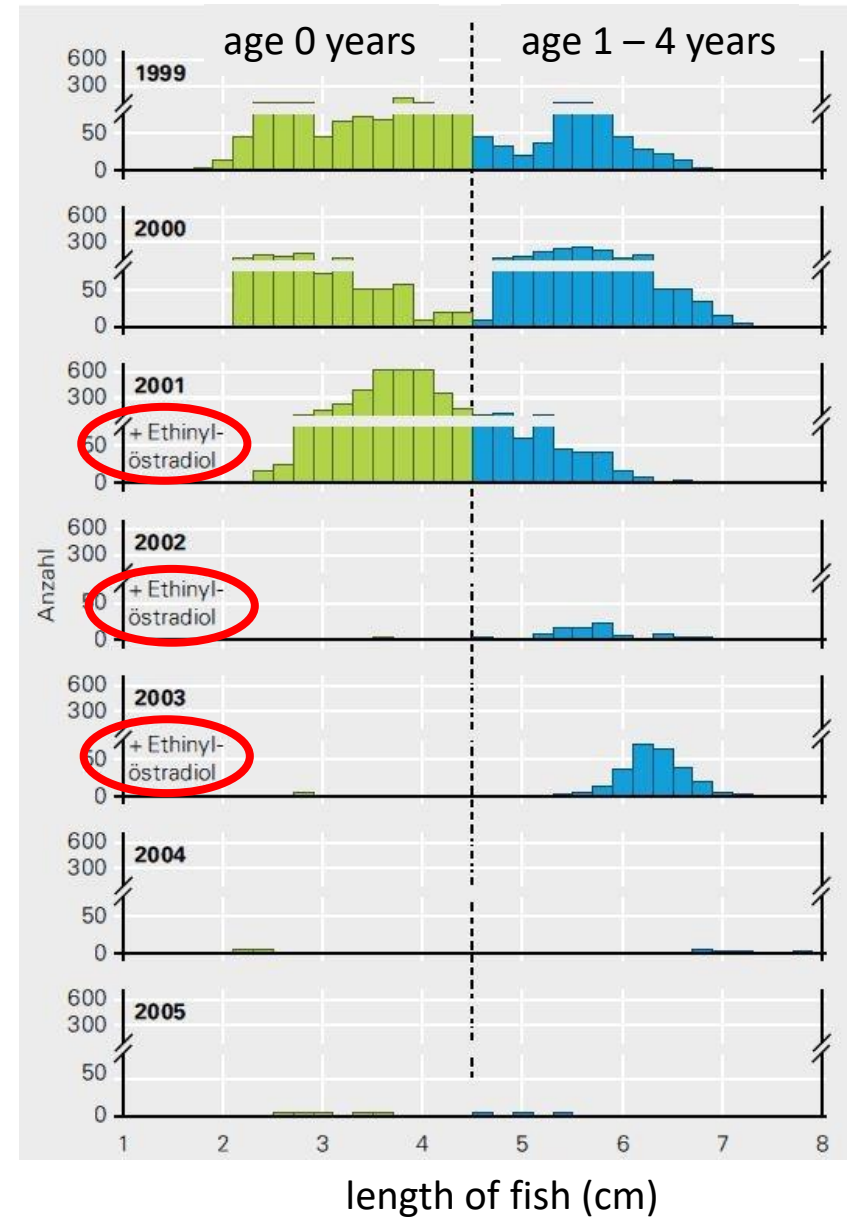
Which region in Switzerland are most impacted by organic micropollutants?

- A) Alpine region
- B) The 'plateau'

<https://web.speakup.info/room/join/30013>

Why do we care about oMP?

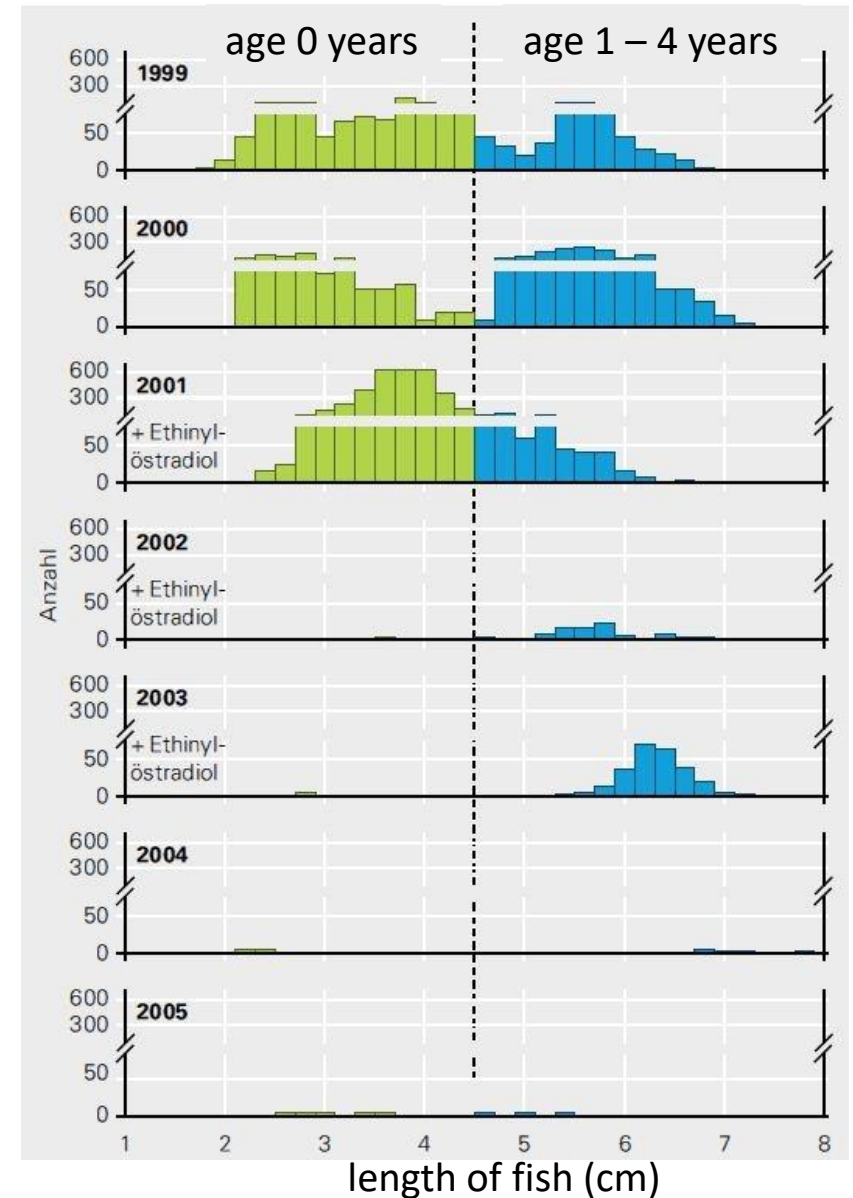
- experiment conducted in a real Canadian lake with a local fish population (fathead minnow)
 - spiking of synthetic estrogen (17 α -ethynylestradiol used in birth-control pills) to 5-6 ng/L in lake water
- within a few years the fish population was completely decimated



Kidd et al. PNAS 2007

Why do we care about oMP?

- presence of an estrogen inhibits the reproduction nearly completely
 - the presence of a single oMP at a very low concentration (5 - 6 ng/L) is able to cause the collapse of an entire fish population
- ➔ what is the effect of a mixture of thousands of oMP in our water bodies?
- we do not know (yet), the effect of such complex matrices are extremely difficult to predict



Kidd et al. PNAS 2007

Impact of oMP on biodiversity

- study investigated 26 surface water sites in Germany
- biodiversity determined with the EPT (Ephemeroptera Plecoptera and Tricoptera) taxa
- oMP content estimated based on wastewater content of surface water



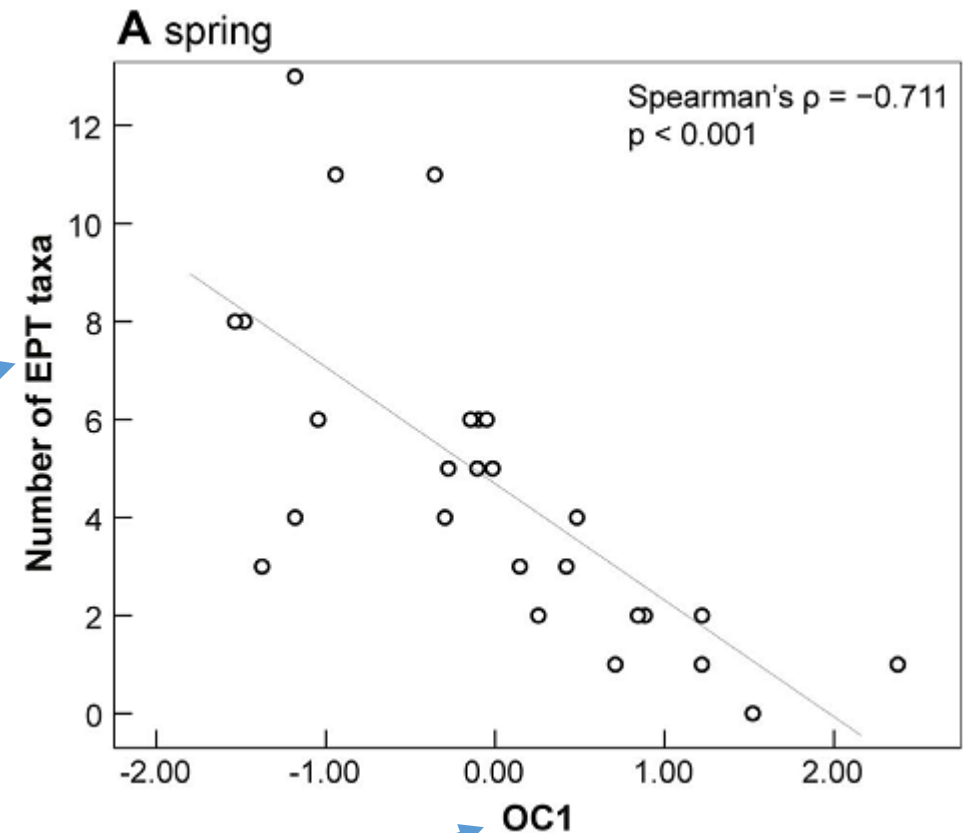
Stalter et al., PLOS ONE, 2013

Impact of oMP on biodiversity

- increased concentration of wastewater correlates with a reduction in biodiversity (EPT taxa)
- increased concentration of wastewater → higher content of oMP

→ advanced removal of oMP should increase the biodiversity of our surface waters

three water insect orders commonly used to assess surface water quality



organic pollutants concentration associated with wastewater

Stalter et al., PLOS ONE, 2013

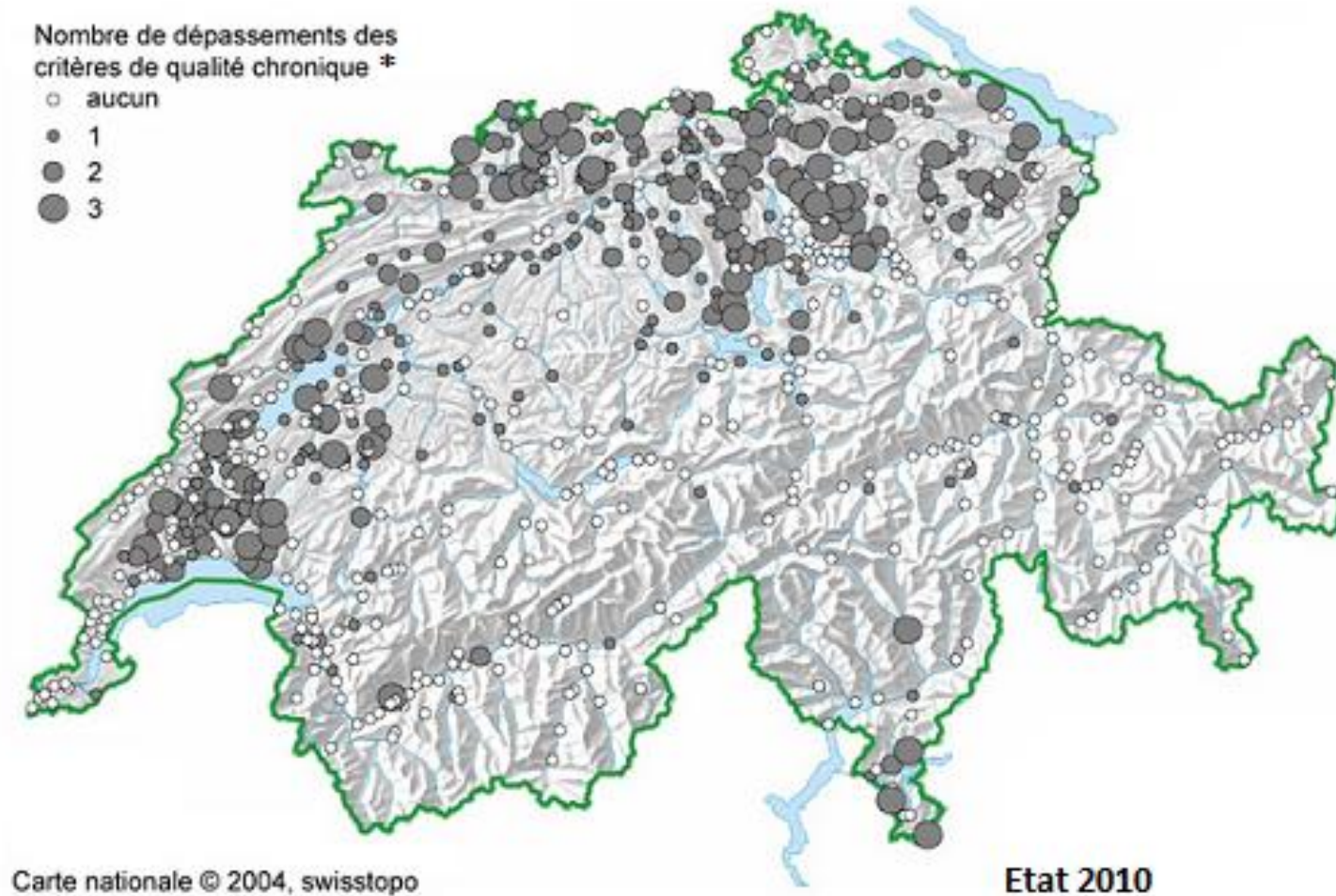
Presence of oMP in Swiss surface waters

- map showing the percentage of wastewater in Swiss water bodies (Q347: at minimum residual flow)
 - most water bodies contain between 0 and 10 % of wastewater
 - many water bodies in densely populated zones (plateau) contain 20 % or more wastewater
- as classical wastewater treatment only removes a small fraction of oMP, therefore this map also shows water bodies which contain high levels of oMP



Presence of oMP in Swiss surface waters

- map showing the number of exceeded 'chronical quality standards' (critères de qualité exposition chronique) based on six modelled oMP concentrations
- chronical quality standards are proposed for several substances by the ecotox centre (Eawag-EPFL)

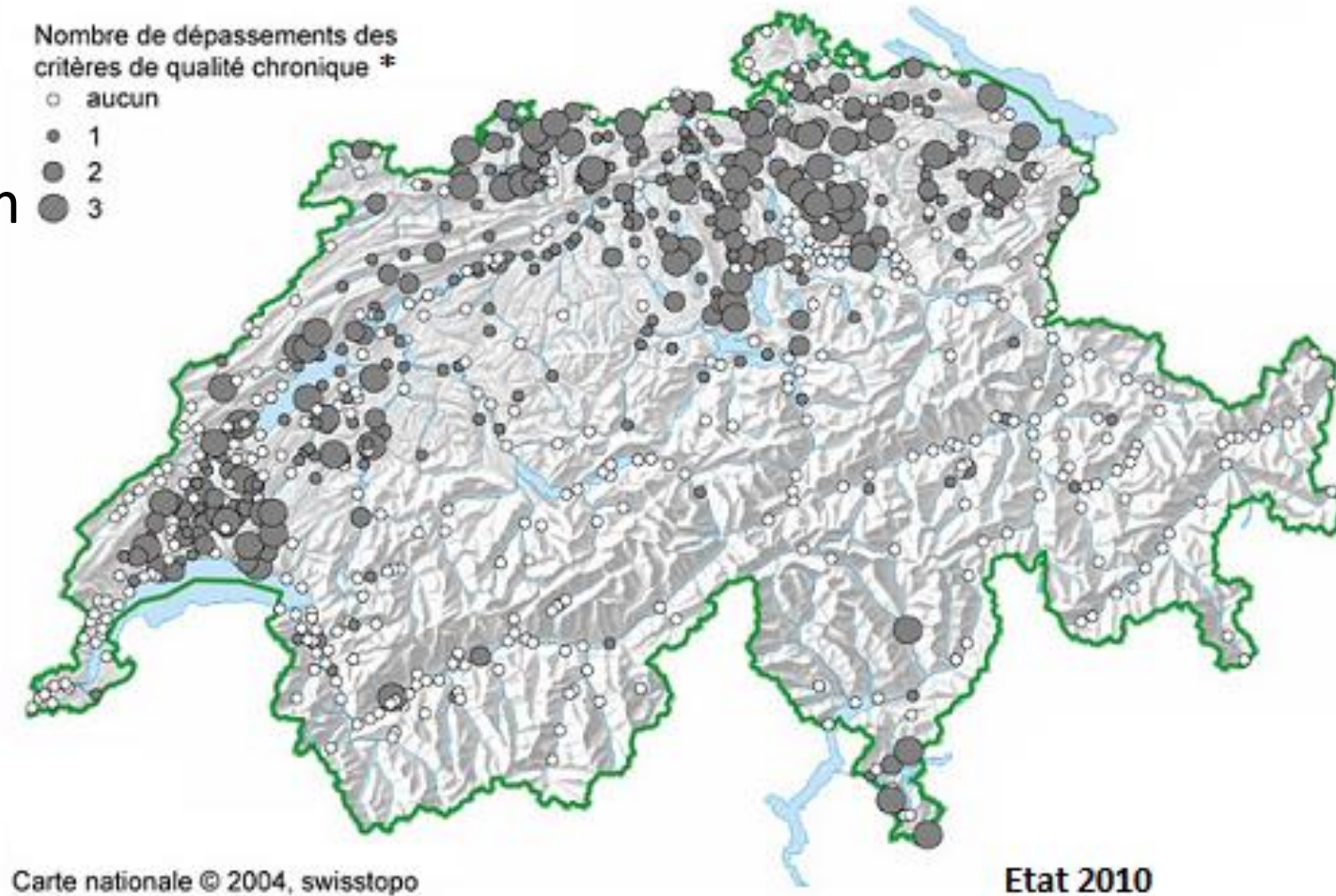


Presence of oMP in Swiss surface waters

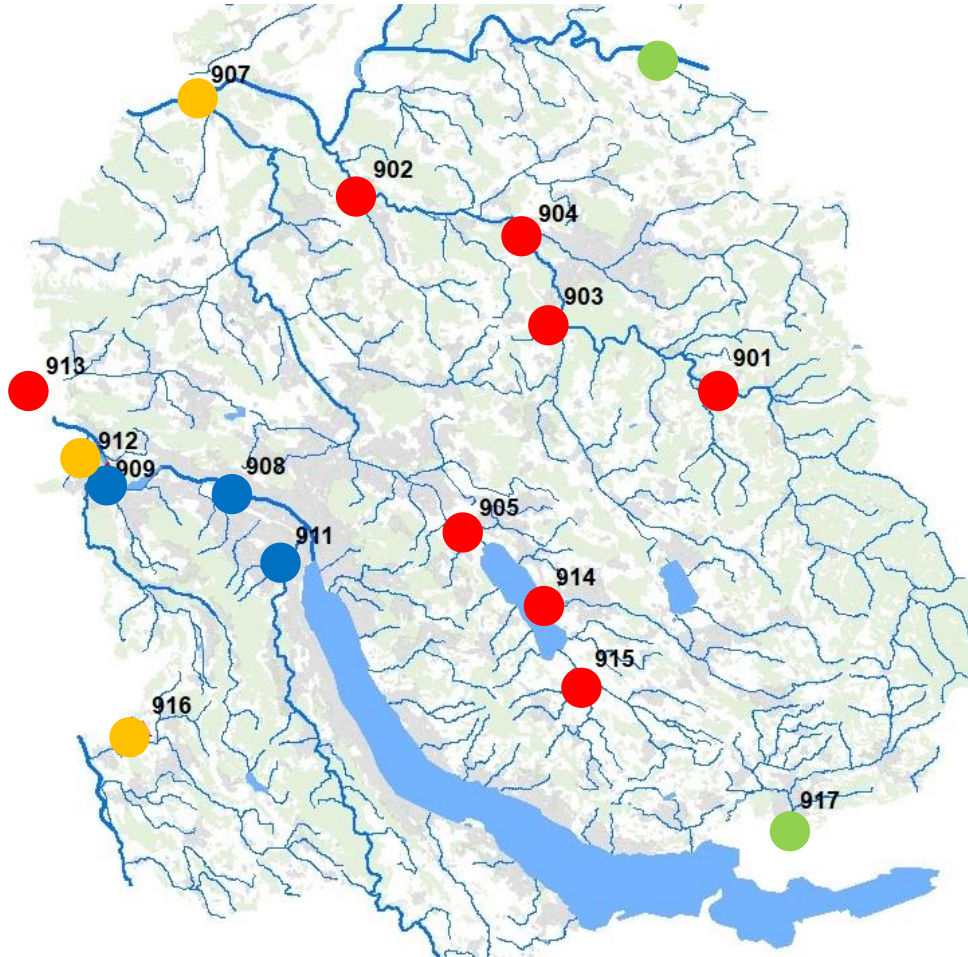
- coloured points indicate water bodies which present potential risks to animals inhabiting them

➔ concentrations of oMP are in many water bodies all over Switzerland at levels that may have a negative effect on the environment

➔ furthermore, oMP also enter our drinking water (e.g. infiltration in groundwater or use of lake water for drinking water supply (e.g. Lausanne))



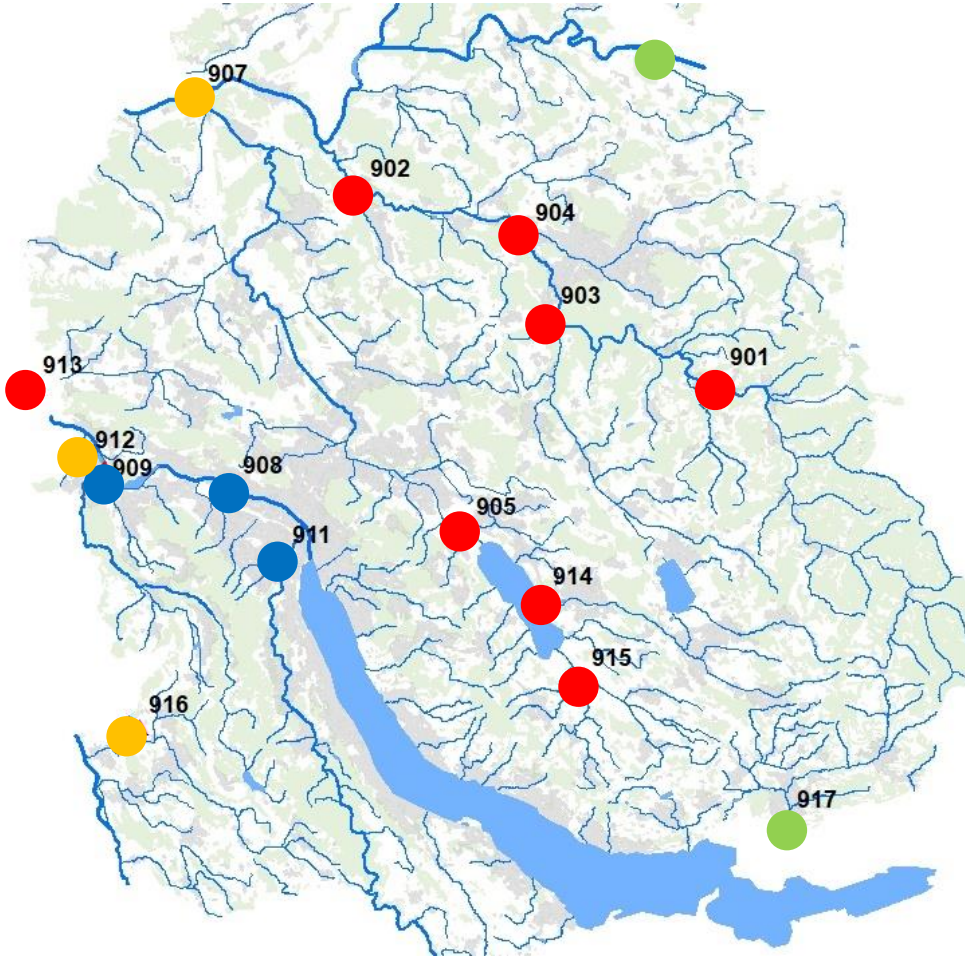
Quality of surface water in Canton of Zurich



- risk coefficient (RC) =
$$\frac{\text{measured concentration}}{\text{chronic quality standard (CQS)}}$$
- about 120 substances analysed of which about 20 were insecticides
- quality of surface water (four samples taken over two weeks)
 - very good quality ($RC < 0.1$)
 - good ($0.1 \leq RC < 1$)
 - intermediate ($1 \leq RC < 2$)
 - unsatisfactory ($2 \leq RC < 10$)
 - bad ($10 \leq RC$)

C. Götz, AWEL 2019

Quality of surface water in Canton of Zurich



C. Götz, AWEL 2019

- identified problematic substances:
 - Cypermethrin (CQS: 0.03 ng/L)
 - lambda-Cyhalothrin (CQS: 0.02 ng/L)
 - Chlorpyrifos (CQS: 0.04 ng/L)
- highly toxic substances at even extremely low concentrations
- these three substances are problematic in most river systems of the Canton of Zurich


How quickly does a river get polluted?



River system	Chamberonne	Venoge	Rhône
flowrate	0.76 m ³ /s	4.2 m ³ /s	250 m ³ /s
glyphosate	7.8 kg/d	44 kg/d	2'600 kg/d
lambda-Cyhalothrin (CQS)	1.3 mg/d	7 mg/d	430 mg/d
Kendo-Gold (0.75 g/L of lambda-Cyhalothrin)	1.75 mL	10 mL	600 mL

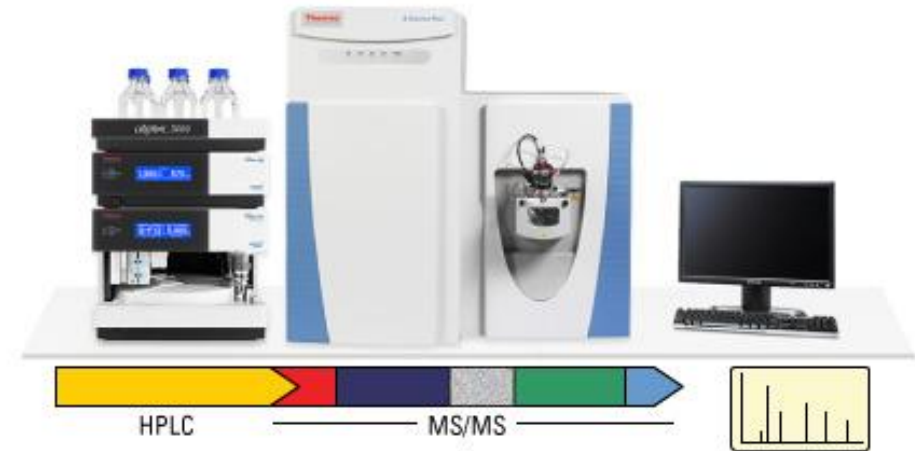


Why do we care about oMP?

- many studies have shown the **negative affect oMP** may have **on the environment**
- oMP are **widely used** (> 30'000 synthetic substances) and are present in water bodies all over Switzerland
 - what is the ecological impact currently and in the future?
- oMP may **bio-accumulate** in certain animals and climb the food chain
- we consume these substances **via our drinking water and via our food, what is the impact on us humans?**
 - what is the effect on the long term?
-  the Swiss government decided to reduce the spreading of oMP via a new legislation obliging around 100 wastewater treatment plants to install advanced oMP treatment units

Why did the topic of oMP only emerge relatively recently?

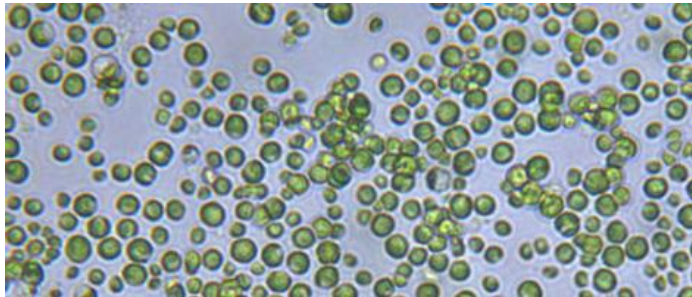
- before the development of highly advanced analytical instruments (HPLC-MS/MS) it was extremely difficult to measure such low concentrations ($\mu\text{g/L}$ or ng/L)



- the ecotoxicological effect of oMP is only “visible” if natural waters contain low concentrations of macropollutants (low levels of COD, BOD, ammonia, P_{tot})
 - otherwise other pollutants induce a high toxicity on the environment (e.g. ammonia on fish)
 - effective wastewater treatment covering a large fraction of households is required

Why did the topic of oMP only emerge relatively recently?

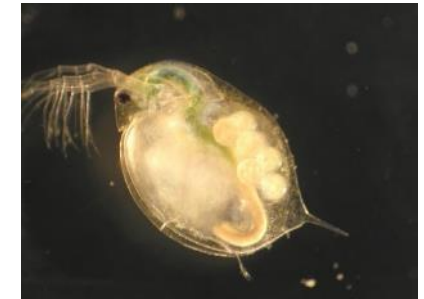
- the ecotoxicological effect on the environment is complicated to estimate for oMP and especially for mixtures of oMP
 - each organism reacts differently (different tests required to cover 'the environment')



algae



fish (fish egg)



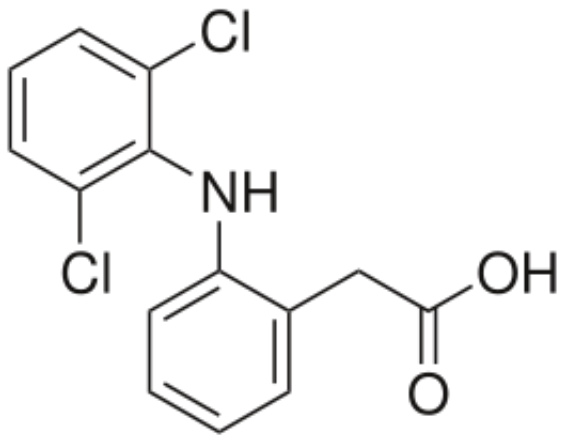
daphnia

- ecotoxicological tests are generally complicated to conduct (specialised lab) and require time → expensive
- in the last decade(s) important progress has been made concerning ecotoxicological tests
- cause-effect is difficult to determine for mixtures of oMP

Organic micropollutant (oMP) treatment II: Swiss legislation

Applied wastewater engineering

Michael Jon MATTLE



Swiss legislation



- the ‘Ordonnance sur la protection des eaux’ (OEaux) – ‘Waters Protection Ordinances’ (WPO) defines the parameters and their required treatment levels for communal and industrial wastewater before it can be **discharged** into the environment or into the communal sewer system (industrial wastewater)
- it also defines maximum tolerated **concentrations** of pollutants in surface and ground waters

814.201

English is not an official language of the Swiss Confederation. This translation is provided for information purposes only and has no legal force.

**Ordonnance
sur la protection des eaux
(OEaux)**

814.201

**Waters Protection Ordinance
(WPO)**

du 28 octobre 1998 (Etat le 1^{er} mai 2017)

of 28 October 1998 (Status as of 1 May 2017)

Swiss legislation

Which pollutants have to be treated according to 'Waters Protection Ordinances' (WPO) at all WWTP in Switzerland?

- A) COD
- B) Ammonia
- C) Organic micropollutants
- D) Total Nitrogen
- E) DOC

<https://web.speakup.info/room/join/30013>

‘Ordonnance sur la protection des eaux’ (OEaux) – ‘Waters Protection Ordinances’ (WPO)

- Chapter 1 General Provisions
- Chapter 2 Disposal of Waste Water
- Chapter 3 Disposal of Sludge
- Chapter 4 Requirements for Animal Husbandry Farms
- Chapter 5 Protection for Waters in terms of Area Planning
- Chapter 6 Maintaining Appropriate Rates of Residual Water Flow
- Chapter 7 Prevention and Remediation of Other Harmful Effects on Waters
- Chapter 8 Enforcement
- **Chapter 8a Federal Waste Water Charge**
- Chapter 9 Granting of Federal Subsidies
- **Chapter 10 Commencement**



‘Ordonnance sur la protection des eaux’ (OEaux) – ‘Waters Protection Ordinances’ (WPO)

- Annex 1 Ecological Objectives for Waters
- **Annex 2 Requirements on Water Quality**
- **Annex 3 Requirements for the Discharge of Polluted Waste Water**
 - **Annex 3.1 Discharge of communal waste water into waters**
 - **Annex 3.2 Discharge of industrial waste water into waters or into public sewer systems**
 - Annex 3.3 Discharge of Other Polluted Waste Water into Waters or into Public Sewers
- Annex 4 Planning the Protection of Waters
- Annex 4a Planning Remediation Measures for Hydropeaking and Bed load Budget
- Annex 5 Repeal and Amendment of Previous Law



Swiss legislation on inorganic micropollutants (iMP)

- important loads of **inorganic** (micro)pollutants (iMP) come from industries
 - effluents discharged from industries need to comply with the legislation (OEaux-WPO, Annex 3.2 Discharge of industrial waste water into waters or into public sewer systems)
 - there are general and specific requirements for certain industrial sectors (OEaux-WPO, Annex 3.2)
 - if certain metal concentrations are above the limits fixed by the legislation, the wastewater has to be pre-treated before being discharged into the sewer system
 - concentrations are not in the micropollutant range (mg/L)

2 General requirements

No.	Parameter	Column 1: requirements for discharge into waters	Column 2: requirements for discharge into public sewers
1	pH	6.5 to 9.0	6.5 to 9.0; divergences are admissible if there is sufficient mixing with other waste waters in the sewers.
2	Temperature	At most 30°C. The authorities may allow minor short-term excesses in summertime.	At most 60°C. The temperature in the sewer system must not exceed 40°C after mixing.
3	Transparency (<i>Snellen method</i>)	30 cm	–
4	Total suspended solids	20 mg/l	–
5	Arsenic (<i>As</i>)	0.1 mg/l As (total)	0.1 mg/l As (total)
6	Lead (<i>Pb</i>)	0.5 mg/l Pb (total)	0.5 mg/l Pb (total)
7	Cadmium (<i>Cd</i>)	0.1 mg/l Cd (total)	0.1 mg/l Cd (total)
8	Chromium (<i>Cr</i>)	2 mg/l Cr (total); 0.1 mg/l Cr-VI	2 mg/l Cr (total)
9	Cobalt (<i>Co</i>)	0.5 mg/l Co (total)	0.5 mg/l Co (total)
10	Copper (<i>Cu</i>)	0.5 mg/l Cu (total)	1 mg/l Cu (total)
11	Molybdenum (<i>Mo</i>)	–	1 mg/l Mo (total)
12	Nickel (<i>Ni</i>)	2 mg/l Ni (total)	2 mg/l Ni (total)
13	Zinc (<i>Zn</i>)	2 mg/l Zn (total)	2 mg/l Zn (total)
14	Cyanide (<i>CN⁻</i>)	0.1 mg/l CN ⁻ (free and easily releasable cyanide)	0.5 mg/l CN ⁻ (free and easily releasable cyanide)
15	Total hydrocarbons	10 mg/l	20 mg/l
16	Volatile chlorinated hydrocarbons (<i>VOCl</i>) or volatile organic halogens (<i>VOX</i>)	0.1 mg/l Cl or 0.1 mg/l X	0.1 mg/l Cl or 0.1 mg/l X

OEaux-WPO, Annex 3.2 Discharge of industrial waste water into waters or into public sewer systems, 2 General requirements

Swiss legislation on iMP

- concentrations of **inorganic micropollutants (iMP)** in river systems need to be below certain levels fixed by the legislation (WPO, Annex 2 Requirements on Water Quality, 11 General requirements)
- concentrations are in the micropollutant range
- ➔ discharge of iMP is controlled
- ➔ special treatment systems are installed at point sources (e.g. galvanising industry)

No	Parameter	Requirements
1	Nitrate ($NO_3^- - N$)	For waters which serve as a source of drinking water: 5.6 mg/l N (corresponds to 25 mg/l Nitrate)
2	Lead (Pb)	0.01 mg/l Pb (total) ¹ 0.001 mg/l Pb (dissolved)
3	Cadmium (Cd)	0.2 µg/l Cd (total) ¹ 0.05 µg/l Cd (dissolved)
4	Chromium (Cr)	0.005 mg/l Cr (total) ¹ 0.002 mg/l Cr (III and VI)
5	Copper (Cu)	0.005 mg/l Cu (total) ¹ 0.002 mg/l Cu (dissolved)
6	Nickel (Ni)	0.01 mg/l Ni (total) ¹ 0.005 mg/l Ni (dissolved)
7	Mercury (Hg)	0.03 µg/l Hg (total) ¹ 0.01 µg/l Hg (dissolved)
8	Zinc (Zn)	0.02 mg/l Zn (total) ¹ 0.005 mg/l Zn (dissolved)
9	Organic pesticides (biocidal and plant protection products)	0.1 µg/l per individual substance unless regulated otherwise below.

¹ The dissolved concentration is determinant. If the value specified for the total concentration is respected, it may be assumed that the value for the dissolved concentration is also respected.

WPO, Annex 2 Requirements on Water Quality, 11 General requirements

Swiss legislation on oMP

- until the end of 2015, only very few parameters concerning **organic micropollutants** were included in the Swiss law (WPO):
 - communal wastewater treatment (WPO, Annex 3 Requirements for the Discharge of Polluted Waste Water)
 - adsorbable organic halogen (AOX) < 0.08 mg/L
 - industrial wastewater treatment (table on the right)
 - total hydrocarbons, volatile chlorinated hydrocarbons (VOCl) or volatile organic halogens (VOX)

2 General requirements

No.	Parameter	Column 1: requirements for discharge into waters	Column 2: requirements for discharge into public sewers
1	pH	6.5 to 9.0	6.5 to 9.0; divergences are admissible if there is sufficient mixing with other waste waters in the sewers.
2	Temperature	At most 30°C. The authorities may allow minor short-term excesses in summertime.	At most 60°C. The temperature in the sewer system must not exceed 40°C after mixing.
3	Transparency (<i>Snellen method</i>)	30 cm	–
4	Total suspended solids	20 mg/l	–
5	Arsenic (<i>As</i>)	0.1 mg/l As (total)	0.1 mg/l As (total)
6	Lead (<i>Pb</i>)	0.5 mg/l Pb (total)	0.5 mg/l Pb (total)
7	Cadmium (<i>Cd</i>)	0.1 mg/l Cd (total)	0.1 mg/l Cd (total)
8	Chromium (<i>Cr</i>)	2 mg/l Cr (total); 0.1 mg/l Cr-VI	2 mg/l Cr (total)
9	Cobalt (<i>Co</i>)	0.5 mg/l Co (total)	0.5 mg/l Co (total)
10	Copper (<i>Cu</i>)	0.5 mg/l Cu (total)	1 mg/l Cu (total)
11	Molybdenum (<i>Mo</i>)	–	1 mg/l Mo (total)
12	Nickel (<i>Ni</i>)	2 mg/l Ni (total)	2 mg/l Ni (total)
13	Zinc (<i>Zn</i>)	2 mg/l Zn (total)	2 mg/l Zn (total)
14	Cyanide (<i>CN⁻</i>)	0.1 mg/l CN ⁻ (free and easily releasable cyanide)	0.5 mg/l CN ⁻ (free and easily releasable cyanide)
15	Total hydrocarbons	10 mg/l	20 mg/l
16	Volatile chlorinated hydrocarbons(<i>VOCl</i>) or volatile organic halogens (<i>VOX</i>)	0.1 mg/l Cl or 0.1 mg/l X	0.1 mg/l Cl or 0.1 mg/l X

OEaux-WPO, Annex 3.2 Discharge of industrial waste water into waters or into public sewer systems, 2 General requirements

Swiss legislation on oMP

- until the end of 2015, only very few parameters concerning **organic micropollutants** were included in the Swiss legislation (WPO) (continued):
 - river systems (WPO, Annex 2 Requirements on Water Quality, 11 General requirements):
 - pesticides < 0.1 µg/L (for each substance)
 - Underground waters which is used for drinking water or intended as such (table on the right)
 - pesticides, halogenated compounds, aliphatic and aromatic hydrocarbons

No.	Parameter	Requirement
1	Dissolved organic carbon (<i>DOC</i>)	2 mg/l C
2	Ammonium (sum of NH_4^+ - N and NH_3 - N)	In oxic conditions: 0.08 mg/l N (corresponds to 0.1 mg/l ammonium) In anoxic conditions: 0.4 mg/l N (corresponds to 0.5 mg/l ammonium)
3	Nitrate (NO_3^- - N)	5.6 mg/l N (corresponds to 25 mg/l nitrate)
4	Sulphate (SO_4^{2-})	40 mg/l SO_4^{2-}
5	Chloride (Cl^-)	40 mg/l Cl^-
6	Aliphatic hydrocarbons	0.001 mg/l per single substance
7	Monocyclic aromatic hydrocarbons	0.001 mg/l per single substance
8	Polycyclic aromatic hydrocarbons (<i>PAH</i>)	0.1 µg/l per single substance
9	Volatile organic halogens (<i>VOX</i>)	0.001 mg/l per single substance
10	Adsorbable organic halogens (<i>AOX</i>)	0.01 mg/l X
11	Organic pesticides (biocidal products and plant protection products)	0.1 µg/l per single substance.

WPO, Annex 2 Underground waters, 22 Additional requirements for groundwater which is used for drinking water or is intended as such

Swiss legislation on other micropollutants

- treatment of biological micropollutants (pathogens like bacteria or viruses) are not included in the OEaux with the exception of industries working with pathogens
- disinfection of pathogens can be necessary for certain wastewater treatment plants if their effluent enters a bathing zone (chapter on disinfection)
- treatment of radioactive micropollutants in wastewater is extremely rare (not treated in this course)
 - legislation on the protection against radiation and on nuclear energy applies

Swiss legislation (before 2016)

- before 2016, only few micropollutants (certain metals and some organic substances) were regulated
 - no specific treatment for micropollutants were installed at communal wastewater treatment plants
 - industrial effluents have to respect general and industry-specific pollutant concentrations before they can be released to the communal sewer system
 - many industries have to install wastewater pre-treatment systems in order to comply with the legislation



wastewater pre-treatment at atelier
CFF, Yverdon-les-Bains

Swiss legislation (before 2016)

- if elevated concentrations for regulated micropollutants are observed at a communal wastewater treatment plant, the point source (generally an industry) is identified and local treatment can be required
- if a micropollutant without legislation induces problems to the good-functioning of a wastewater treatment plant, the point source is identified and special treatment can be required (rare case)

 the legislation (before 2016) described here continues to be valid today



wastewater pre-treatment at atelier
CFF, Yverdon-les-Bains

Modified Swiss legislation (OEaux 2016)

- the OEaux-WPO has been modified in 2016 and the parameter oMP has been added in order to
 - protect the flora and fauna
 - protect drinking water sources
 - assume responsibility for countries lying downstream of Swiss rivers and streams
- ➔ the new legislation is based on many years of applied research conducted on oMP removal in laboratories and at WWTP (e.g. trials at WWTP of Vidy, Lausanne)
 - the research was principally financed by the Federal Office for the Environment (FOEN) but also by Cantons and cities/towns

Modified Swiss legislation (OEaux-WPO 2016)

No.	Parameter	Requirements
8	Organic substances that can pollute waters even in low concentrations <i>(organic trace substances)</i>	The removal efficiency with respect to raw waste water and measured using selected substances must amount to 80 % for waste water from: WPO, Annex 3 Requirements for the Discharge of Polluted Waste Water, Discharge of communal waste water into waters, 2 General requirements

- 80 % removal of oMP is required as compared to raw wastewater
- the efficiency of the oMP treatment is measured with wastewater collected over 48 h (normal parameters are measured over 24 h)

Modified Swiss legislation (OEaux-WPO 2016)

- about 100 WWTP will be equipped for oMP removal based on the following criteria:
- large treatment plants ($\geq 80'000$ inhabitants connected)
- medium-size treatment plants ($\geq 24'000$ inhabitants connected) upstream of a lake (protection of the environment and drinking water sources)

No.	Parameter	Requirements
8	Organic substances that can pollute waters even in low concentrations (<i>organic trace substances</i>)	The removal efficiency with respect to raw waste water and measured using selected substances must amount to 80 % for waste water from: <ul style="list-style-type: none">– plants with 80 000 or more connected residents;– plants with 24 000 or more connected residents in the catchment area of lakes; the canton may authorise exceptions if the benefit of removal for the environment and for the drinking water supply is negligible;

WPO, Annex 3 Requirements for the Discharge of Polluted Waste Water, Discharge of communal waste water into waters, 2 General requirements

Modified Swiss legislation (OEaux-WPO 2016)

- WWTP with $\geq 8'000$ inhabitants on a river system containing $\geq 10\%$ of wastewater without treatment of oMP
 - plants with 8000 or more connected residents that discharge into a watercourse containing more than 10 % waste water untreated for organic trace substances; the canton shall identify the plants that must take measures as part of a plan for the catchment area;
 - other plants with 8000 or more connected residents if removal is required due to special hydrogeological conditions;
 - ...¹¹⁵
- other WWTP with $\geq 8'000$ inhabitants if treatment is required due to special hydrogeological conditions
- an additional criteria will be added in 2028 for small WWTP with $\geq 1'000$ inhabitants and $\geq 20\%$ of wastewater without treatment of oMP

WPO, Annex 3 Requirements for the Discharge of Polluted Waste Water, Discharge of communal waste water into waters, 2 General requirements

Modified Swiss legislation (OEaux-WPO 2016)

- based on these criteria each Canton decides which WWTP have to be equipped with an oMP treatment
- the Cantons also fix a date for each WWTP when they have to start their construction (based on the ‘urgency of the situation’)
- all constructions have to be started at the latest before the end of 2035

Transitional Provision to the Amendment of 4 November 2015¹⁰³

¹ The cantons shall ensure that the implementation of all the measures required to comply with the requirements of Annex 3.1 clause 2 no 8 begin by 31 December 2035 at the latest. They shall fix the last possible date for implement the measures according to their urgency and in doing so take account of the following:

- a. the remediation and renewal cycles of the waste water treatment plants;
- b. the size of the waste water treatment plants;
- c. the volume of waste water in the receiving waters;
- d. the length of the flow section in waters that are affected by the discharge of waste water.

WPO, Chapter 10 Commencement

Modified Swiss legislation (OEaux-WPO 2021)

- since 2021 new maximal concentrations for medicines and pesticides were defined in Annex 2 for surface waters based on ecotoxicological criteria
- concentrations can be higher than the originally defined value of 0.1 µg/L
- what is the dilution required to respect the criteria of diclofenac without elimination at a WWTP (based on data from WWTP Vidy)?

No	Parameter	Requirements
3	Medicinal products	
	Azithromycin (CAS No 83905-01-5)	0.18 µg/l 0.019 µg/l (continuous) ²
	Clarithromycin (CAS No 81103-11-9)	0.19 µg/l 0.12 µg/l (continuous) ²
	Diclofenac (CAS No 15307-86-5)	0.05 µg/l (continuous) ²

How will the installations for oMP removal be financed?

- Starting in 2016, each Swiss WWTP has to pay 9 Swiss francs per year for all inhabitants connected to it unless the WWTP has an oMP removal treatment in operation
 - this tax is indirectly payed as each WWTP without oMP treatment receives a bill in function of the number of inhabitants connected to it
 - the taxes for wastewater treatment were/will have to be increased in the coming years to cover this additional tax

Art. 51a Charge rate

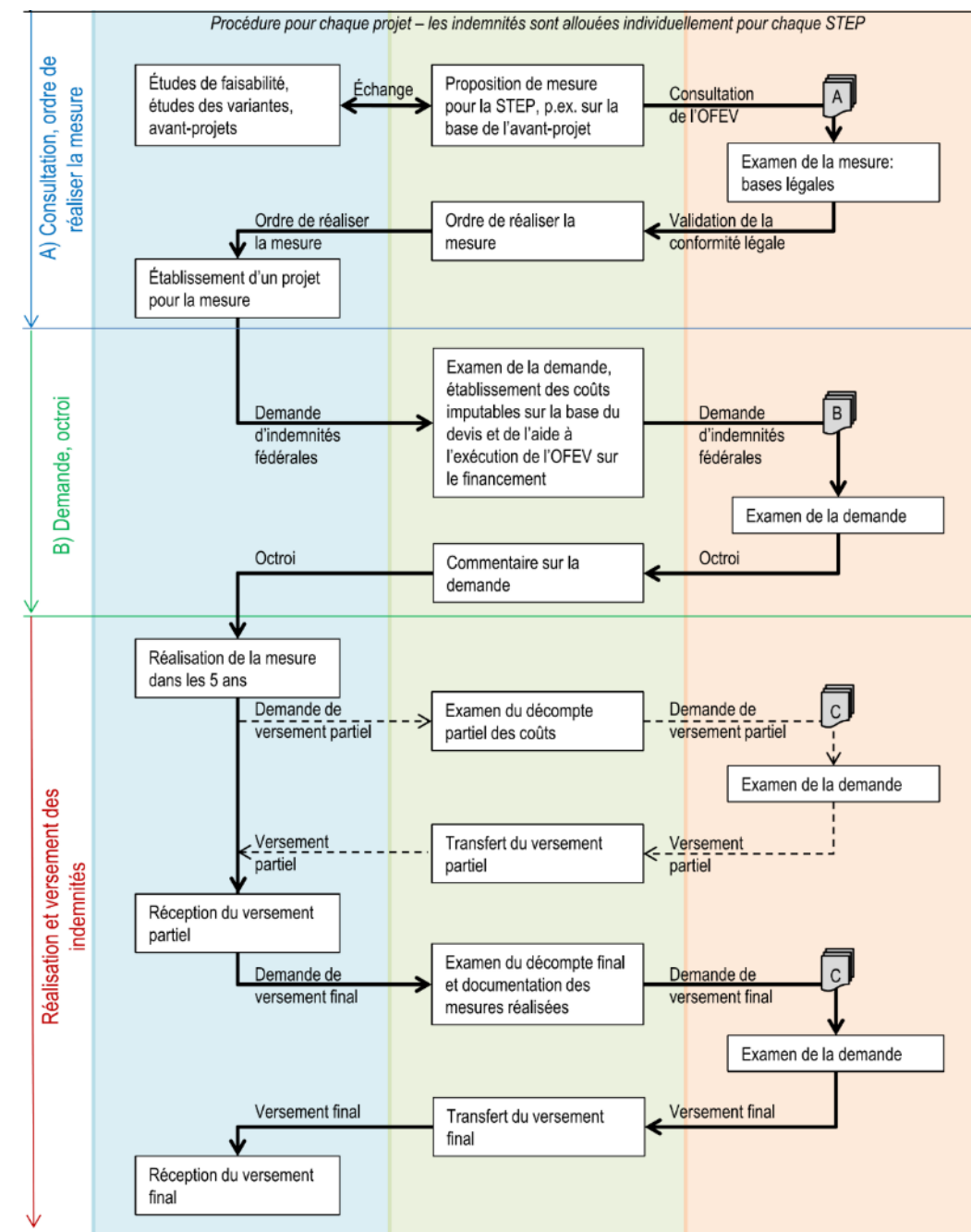
The level of the charge in accordance with Article 60b WPA amounts to 9 francs per resident per annum. The charge is based on the number of residents that are connected to the waste water treatment plant on 1 January of the calendar year in which the charge is collected.

WPO. Chapter 8a Federal Waste Water Charge



How will the installations for oMP removal be financed?

- each oMP project has to be submitted via the Canton to the Federal Office for the Environment (FOEN) at different stages of the project/construction (see table)
- once the construction of the oMP treatment is completed, the FOEN pays 75 % of the total costs if sufficient funds are available
 - construction costs, engineering costs, preliminary laboratory testing



document to submit

How will the installations for oMP removal be financed?

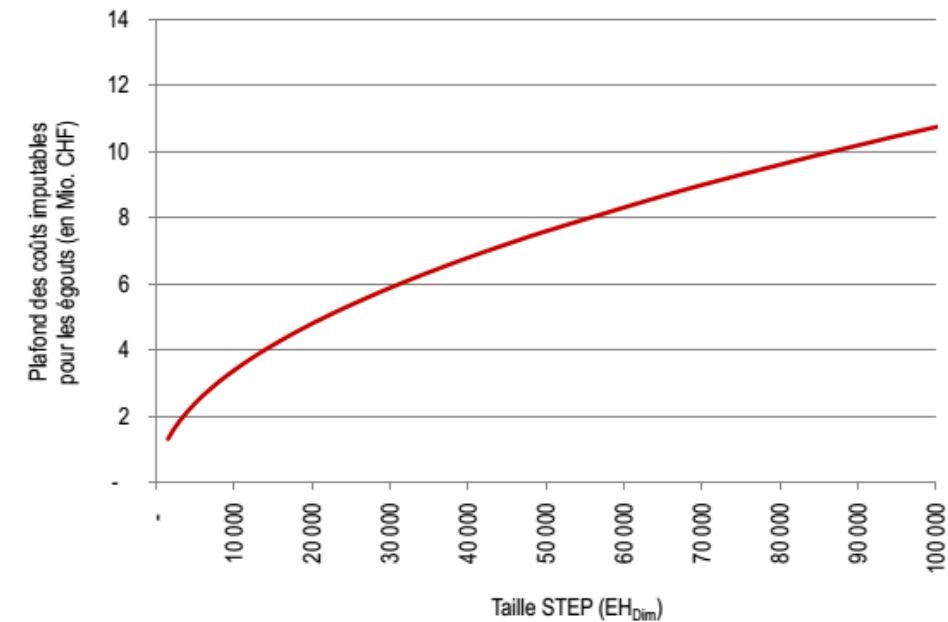
- furthermore, the OFEN also finances the construction of new sewer systems if a WWTP (required to treat oMP) is connected to a WWTP with an oMP treatment
- maximum creditable costs for a sewer system are:
$$= 34'000 \sqrt{\text{size of WWTP}(PE)}$$
- the FOEN pays 75 % of the creditable costs if sufficient funds are available



Fig. 3 > Plafond des coûts imputables des égouts en fonction de la taille de la STEP

coûts arrondis mathématiquement en milliers de francs.

$$\text{Plafond des coûts imputables des égouts} \\ = 34\,000 \cdot \sqrt{\text{taille STEP (EH}_{DIM})}$$



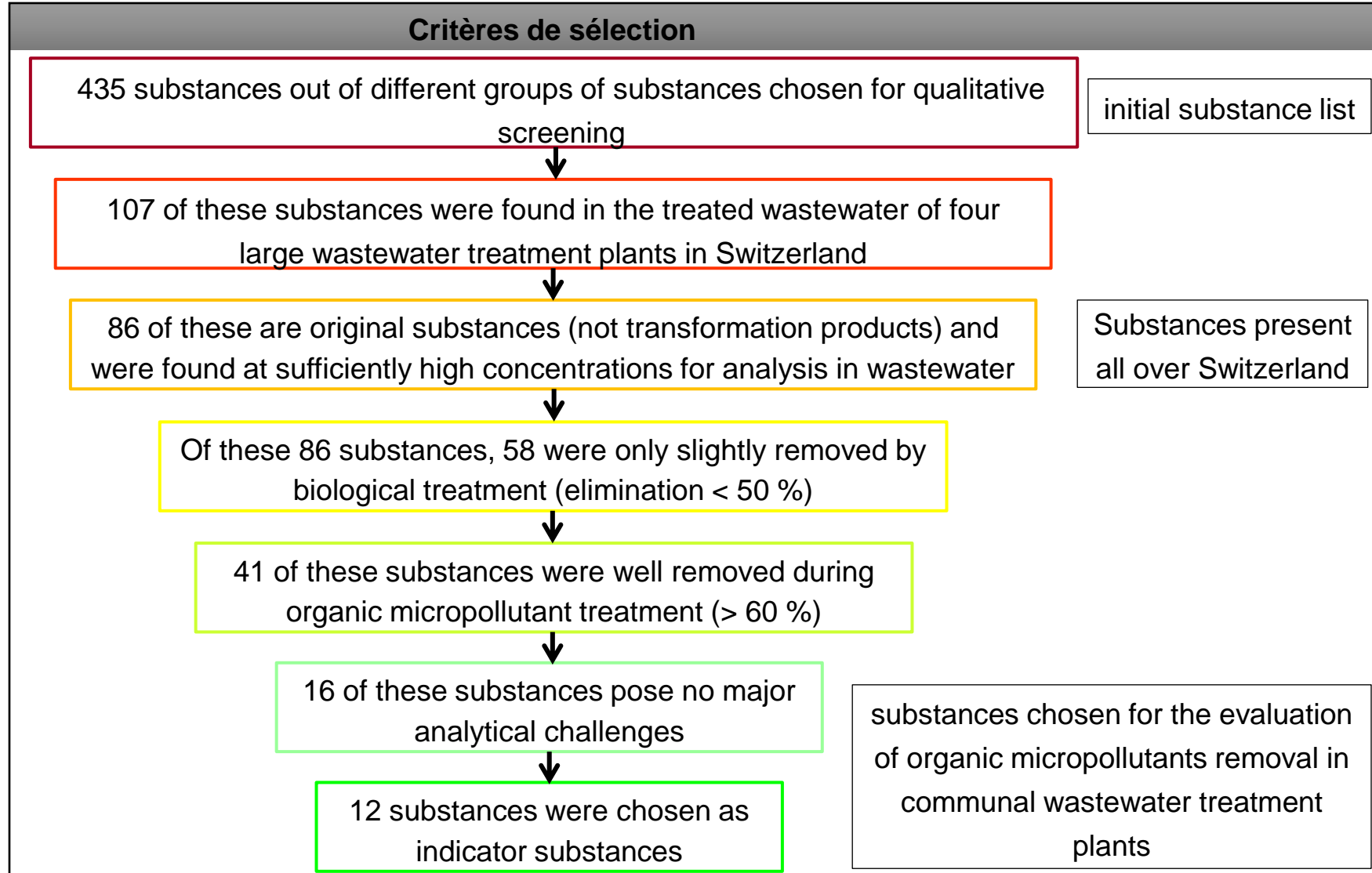
FOEN: Elimination des composés traces organiques dans les stations d'épuration : Financement des mesures

Choice of substances to monitor the 80 % removal of oMP

- the Federal Department of the Environment, Transport, Energy and Communications (DETEC) defines these substances in a modifiable decree (ordonnance)
- the substances are selected based on the following criteria
 - no chemical or biological transformation products
 - measurable with standard analytical methods
 - presence in all large Swiss WWTP (> 10'000 PE)
 - removal in biological treatment below 50 %
 - similar removal efficiencies by ozone and activated carbon
 - present frequently in raw wastewater

 choice currently not based on ecotoxicological impact of substances

Current choice of substances to monitor the 80 % removal of oMP: procedure



Current choice of substances to monitor the 80 % removal of oMP

elimination: > 80 % ; between 50 et 80 % ; < 50%

	Substance	type of substance	removal in biology	removal with ozonation	removal with activated carbon
group 1: very easy to remove with advanced oMP treatment	amisulpride	pharmaceutical psychiatric	Yellow	Blue	Blue
	carbamazepine	pharmaceutical anticonvulsant	Yellow	Blue	Blue
	citalopram	pharmaceutical antidepressant	Yellow	Blue	Blue
	clarithromycin	pharmaceutical antibiotic	Yellow	Blue	Blue
	diclofenac	pharmaceutical analgesic	Yellow	Blue	Blue
	hydrochlorothiazide	pharmaceutical diuretic	Yellow	Blue	Blue
	metoprolol	pharmaceutical beta blockers	Yellow	Blue	Blue
	venlafaxine	pharmaceutical psychiatric	Yellow	Blue	Blue
group 2: easy to remove with advanced oMP treatment	benzotriazole	anti-corrosive agent	Yellow	Light Green	Light Green
	candesartan	pharmaceutical antihypertensive	Yellow	Light Green	Light Green
	irbesartan	pharmaceutical antihypertensive	Yellow	Light Green	Blue
	4-methylbenzotriazole/ 5-methylbenzotriazole	anti-corrosive agent	Yellow	Diagonal Stripes	Blue

Current choice of substances to monitor the 80 % removal of oMP

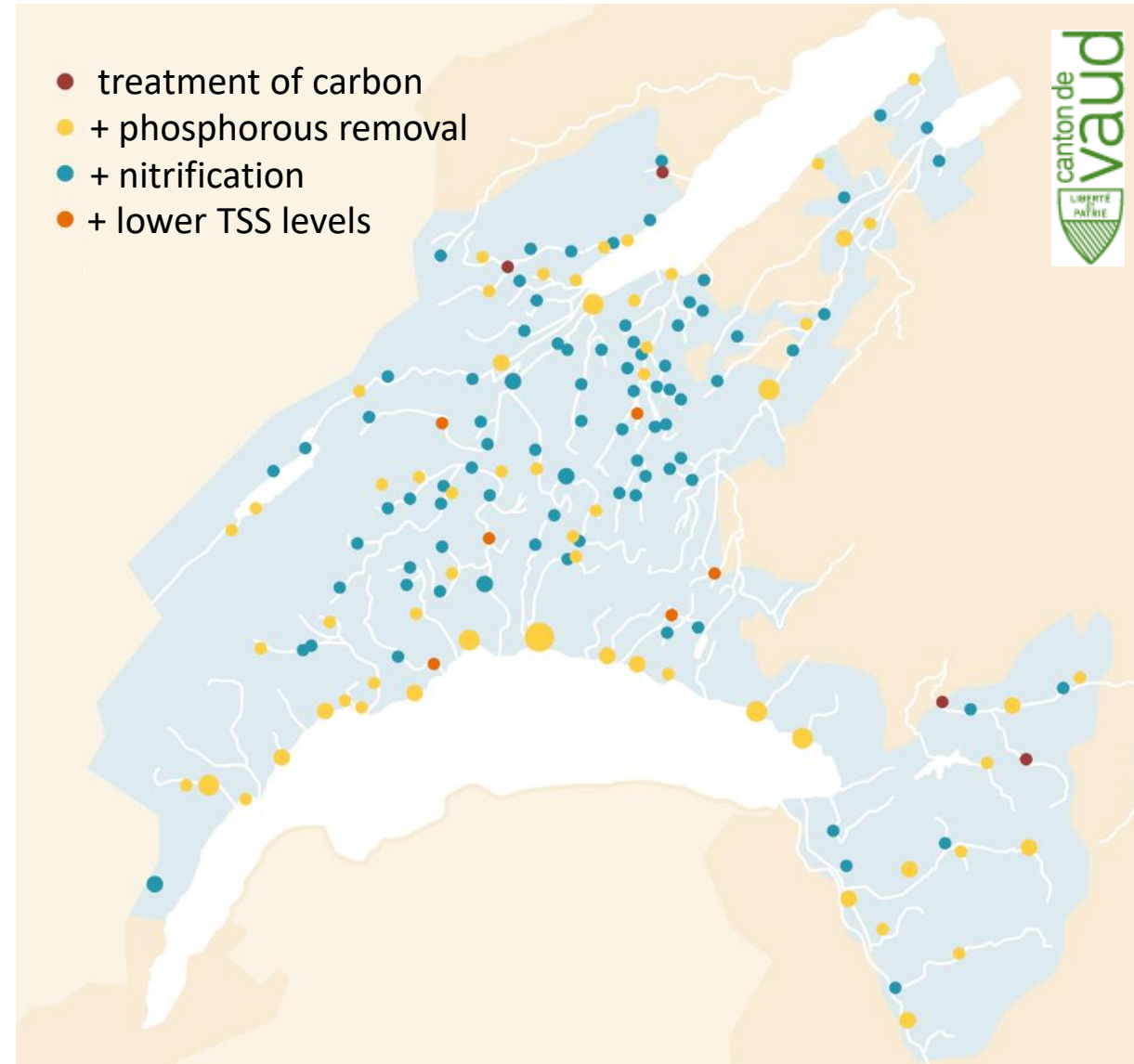
- removal efficiency is computed based on at least six substances
- proportion of substances of group 1 and group 2 has to be 2:1
- total removal efficiency (RE) corresponds to the average of the removal efficiency of each selected substance expressed in percent

	Substance	type of substance
group 1: very easy to remove with advanced oMP treatment	amisulpride	pharmaceutical psychiatric
	carbamazepine	pharmaceutical anticonvulsant
	citalopram	pharmaceutical antidepressant
	clarithromycin	pharmaceutical antibiotic
	diclofenac	pharmaceutical analgesic
	hydrochlorothiazide	pharmaceutical diuretic
	metoprolol	pharmaceutical beta blockers
	venlafaxine	pharmaceutical psychiatric
group 2: easy to remove with advanced oMP treatment	benzotriazole	anti-corrosive agent
	candesartan	pharmaceutical antihypertensive
	irbesartan	pharmaceutical antihypertensive
	4-methylbenzotriazole/ 5-methylbenzotriazole	anti-corrosive agent

- $$RE(\%) = \frac{RE_{substances_1}(\%) + RE_{substances_2}(\%) + \dots + RE_{substances_n}(\%)}{n}$$

Cantonal Plan (Vaud)

- the Canton Vaud has developed a plan including 16 WWTP that will have to install an oMP treatment
 - several smaller WWTP will be connected to these 16 regional WWTP
 - many of these 16 WWTP currently treat C + P
- many WWTP will not only be upgraded with oMP treatment but also to nitrify the effluent



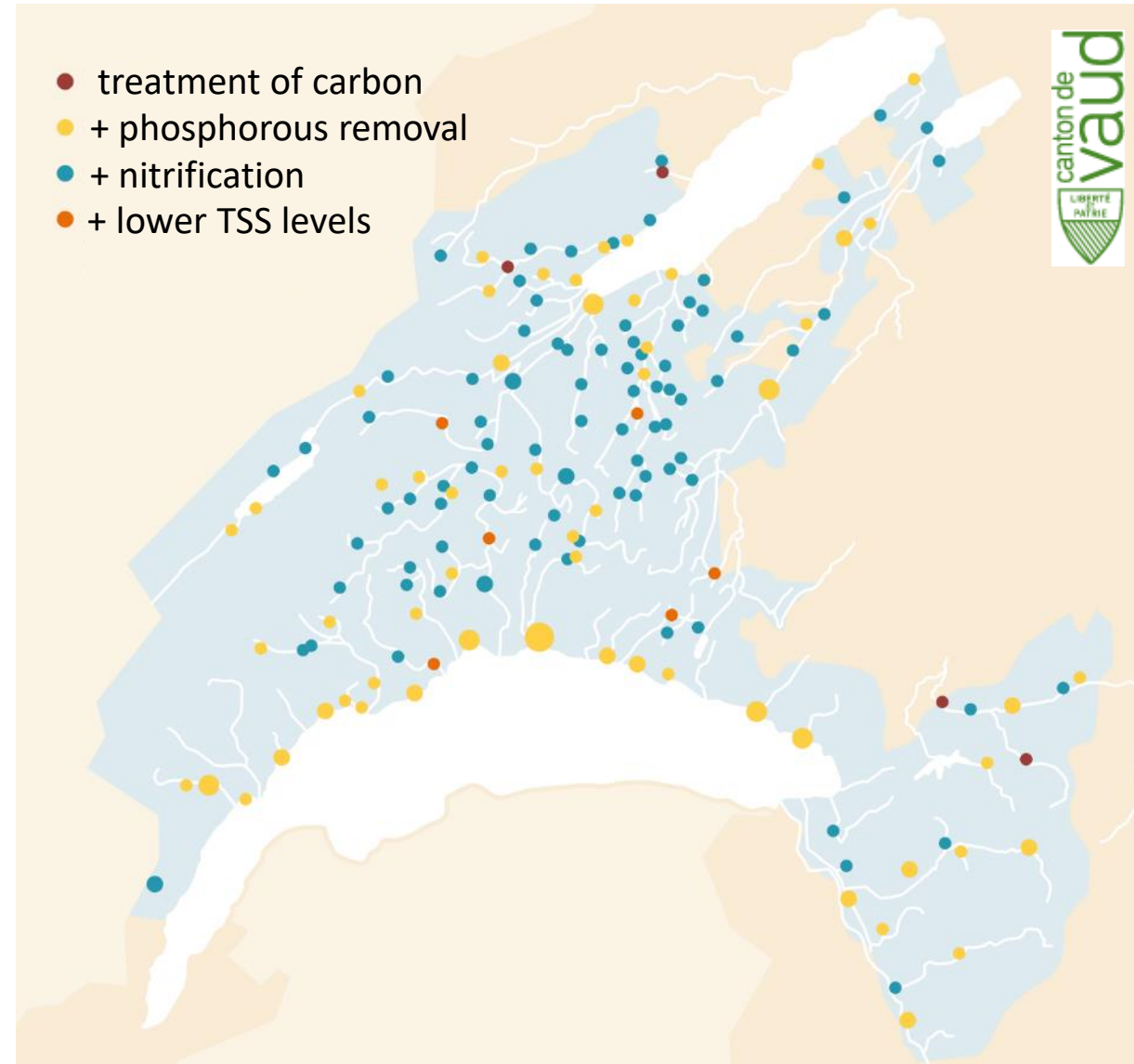
Cantonal Plan (Vaud)

- this plan will completely change the wastewater treatment in the region over the next 20 years

→ engineering challenges:
extension projects often only limited space available (especially in the vicinity of lakes)
few oMP treatment plants have been constructed so far

- communities have to be convinced to follow the planning of the Canton

→ political challenges



Modified Swiss legislation (OEaux-WPO 2016)



- over 100 communal WWTP will be equipped with an oMP treatment
 - Switzerland was the first country to impose such a legislation worldwide!
- Cantons decide based on criteria elaborated by the government which WWTP are concerned
- construction of the new oMP treatments are financed by a new tax which is payed by the WWTP without oMP treatment (9 CHF per inhabitant and year)
- substances for the monitoring of the removal of oMP are defined in a decree by the DETEC
 - substances may be changed if other substances are considered more adequate

Modified Swiss legislation (OEaux-WPO 2016)



- the 'old' legislation concerning industrial effluents remains valid
- furthermore, Cantons may oblige industries to further improve their wastewater pre-treatment to achieve the objectives stated by the modified legislation (OEaux-WPO):

- substances that enter waters as a result of human activities do not detrimentally affect the reproduction, development and health of sensitive plants, animals and microorganisms (f.)

¹ The water quality must be such that:

- a. no visible colonies of bacteria, fungi or protozoa and no unnatural proliferation of algae or higher water plants are formed in any waters;
- b. fish-spawning grounds are preserved;
- c. after application of appropriate treatment, the water complies with requirements of the legislation on foodstuffs;
- d. groundwater is not contaminated by infiltration of water;
- e. the hygiene requirements for bathing are met at sites where bathing is expressly permitted by the authorities or where a large number of people normally bathe and the authorities do not advise against it;
- f. substances that enter waters as a result of human activities do not detrimentally affect the reproduction, development and health of sensitive plants, animals and microorganisms.

WPO, Annex 2 Requirements on Water Quality, 11 General Requirements