

# Assessment of Micropollutants from Municipal Wastewater- Combination of Exposure and Ecotoxicological Effect Data for Switzerland

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## 1. Introduction

Micropollutants (MPs) from municipal wastewater are frequently detected in surface waters and occur in ecotoxicologically relevant concentrations. Therefore a broadly accepted method for the assessment of MPs is needed. Here we propose a procedure for the assessment of MPs from municipal wastewater. The method suggested comprises (1) an approach for the identification of potentially polluted sites, (2) a compilation of a substance list with relevant MPs, (3) (eco)toxicologically based quality criteria, (4) a sampling strategy that considers the input-dynamics of chemicals and (5) a scheme to rate water quality with respect to MP contamination. In the proposed concept the assessment focuses upon those substances found repeatedly in municipal wastewaters (continuous inputs).

Additionally, we explain how the Environmental Quality Standard (EQS) proposals were derived in accordance with the Water Framework Directive (WFD), and the currently developed Technical Guidance Document for EQS (TGD for EQS). Based on the proposed EQS, we provide a Swiss-wide risk assessment for 6 selected MPs.

### 1.1 Background

MPs have been found in watercourses at concentrations that can damage the health of animals and plants (Chèvre et al., 2006; Escher et al., 2008; Nadzialik et al., 2010). MPs also pollute important drinking water sources such as lakes, large rivers and groundwater (AWEL, 2007, Loos et al., 2009). Studies have shown that in certain water bodies, including important drinking water sources such as Lake Constance, MPs from municipal wastewater are more numerous and are found at higher concentrations than MPs from agricultural sources (Singer et al., 2009). The assessment and reduction of pollution in surface waters constitutes an ongoing challenge for water protection authorities, especially because no generally applicable procedures are available for assessing water quality with respect to MPs. This project carried out within the Strategy Micropoll Project of the Federal Office for the Environment (FOEN) of Switzerland, developed a possible approach to address these

problems. The key points of the proposed approach are presented in this article. The assessment concept covers the following points:

- Identification of relevant substances: compilation of a list of MPs from municipal wastewater treatment plants (WWTP) that are important for Switzerland.
- Derivation of effect-based quality criteria for relevant substances.
- Survey using a sampling strategy that takes into consideration the input dynamics of the relevant substances.
- Procedure for assessing water quality with respect to MPs from municipal wastewater.

The assessment is based on an analysis and description of the sources and input pathways of MPs from municipal wastewater. Therefore it focuses on continuous inputs of MPs and the resulting chronic water pollution (Fig. 1).

<b>Input dynamics</b>	
<b>variable inputs</b> → <b>temporal dynamic pollution</b>	<b>continuous inputs</b> → <b>chronic pollution</b>
<b>Substances</b>	
<b>e.g. pesticides and veterinary pharmaceuticals, biocides in material protection</b>	<b>e.g. human pharmaceuticals, domestic chemicals, estrogens</b>
<b>Input pathway</b>	
<b>drained rainwater</b> <b>e.g. discharge from sealed areas, discharge from agricultural areas, combined sewer overflows</b>	<b>treated wastewater from municipal wastewater treatment plants</b>
<b>Quality Criterion</b>	
<b>Maximum Acceptable Concentration-Environmental Quality Standard, MAC-EQS</b>	<b>Annual Average-Environmental Quality Standard, AA-EQS</b>

Fig. 1. Overview of the pollution of surface water with MPs

The proposed approach is based on the chemical and physical surveys of nutrients of FOEN's Modular Stepwise Procedure (MSP) (Liechti, 2010). The following concept for the ecotoxicological assessment of micropollutants from municipal wastewater has been published in January 2011 as a joint report by Eawag and the Swiss Centre for Applied Ecotoxicology (Götz et al. 2011).

## 1.2 Sources

Thousands of different chemicals with various applications are in everyday use. The main sources for MPs discharged into surface waters via municipal wastewater can be categorized into substances with indoor applications and substances with applications outside of buildings.

Indoor applications:

- *Households* (e.g. dishwashing liquids, detergents, personal care products and pharmaceuticals)
- *Healthcare institutions* (e.g. pharmaceuticals, disinfectants and detergents)

- *Manufacturing and commercial enterprises* (e.g. industrial chemicals, production residues and corrosion protection agents), which are connected to the municipal sewage system. Pollutants from industrial and commercial sources are generally not comparable with those found in household wastewater.

Outdoor applications:

- Green spaces and parks in residential areas (e.g. biocides and pesticides).
- *Flat roofs and buildings envelopes and paints* (e.g. biocides and chemicals used in construction).

Depending on the sewage systems, substances from indoor and outdoor applications may have different input pathways into surface waters.

### 1.3 Input pathways

The most important input pathways for MPs from municipal wastewater are:

- with treated sewage from municipal sewage treatment plants
  - through combined sewer overflows during rain (combined systems)
  - through leakage in sewage systems
  - through rain water drains (separation systems)
- I. Many MPs found in surface waters originate from the urban drainage system (AFU St. Gallen, 2009; AWEL, 2003; AWEL, 2004; AWEL, 2005; CIPEL, 2008; Giger et al. ; 2006; Hollender et al. , 2007; IKS, 2006; Ort et al. , 2009; Singer et al. ,2008; Singer et al. , 2009; Singer et al. , 2010), are not or only poorly eliminated by municipal wastewater treatment plants and enter the surface water along with the treated sewage effluent. This is backed by the findings in EU-projects like Poseidon for similar MPs (Alder et al., 2006 in IWA, 2006). For such compounds, the concentrations measured in the water are usually well correlated with the proportion of the treated sewage effluent, especially for frequently and widely-used substances which are used indoors and hence enter the

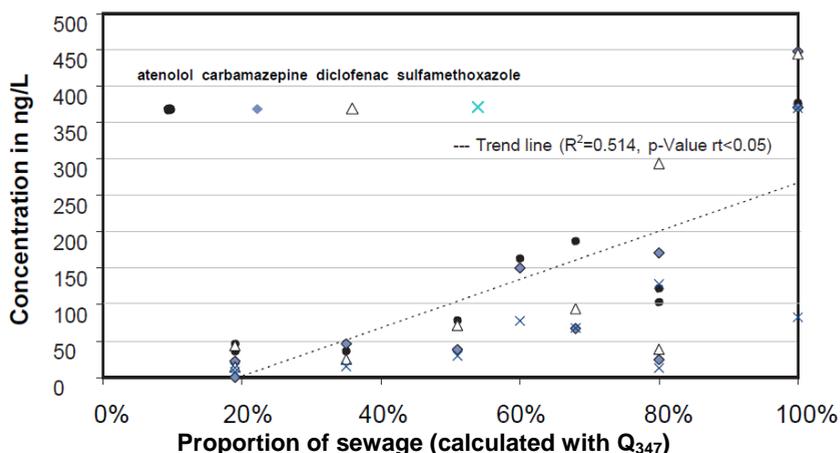


Fig. 2. Calculated concentrations of the drugs atenolol, carbamazepine, diclofenac and sulfamethoxazole with the proportion of sewage at minimum outflow ( $Q_{347}$ ) (s. section 1.3 b). Measurements are from 2007 and 2009/10.

surface waters mainly through wastewater treatment plants. This is shown in Figure 1 for the drugs atenolol (beta-blocker), carbamazepine (anticonvulsant), diclofenac (pain-killer) and sulfamethoxazole (antibiotic). The MPs shown are not eliminated by the wastewater treatment plant, continually enter the surface water and are mainly discharged via treated sewage from the municipal wastewater treatment plants.

- II. Today, approximately 75% of urban areas in Switzerland are drained via combined sewer systems (Gujer, 2002). In combined systems, rain water flowing away from residential areas use the same drains as domestic wastewater. Heavy rainfall can cause an overload of sewage systems and treatment plants as their capacity is designed to contain two times the dry weather discharge. When this capacity is exceeded during heavy storms, untreated wastewater enters surface waters directly. In state of the art systems, an annual average of approximately 2.5% of wastewater enters surface waters via the discharge of sewage overflows due to heavy rainfall events. However, this amount can vary greatly, depending on the size and condition of the infrastructure. If a substance is not removed in the wastewater treatment plant and is continuously discharged into the water throughout the year, the proportion of a substance carried by sewage overflow roughly corresponds to the proportion of discharged untreated wastewater. This is, for example, the case with carbamazepine or the artificial sweeteners acesulfame and sucralose, which can therefore be used as tracers for treated wastewater (Fig. 3) (Bürge et al., 2009).

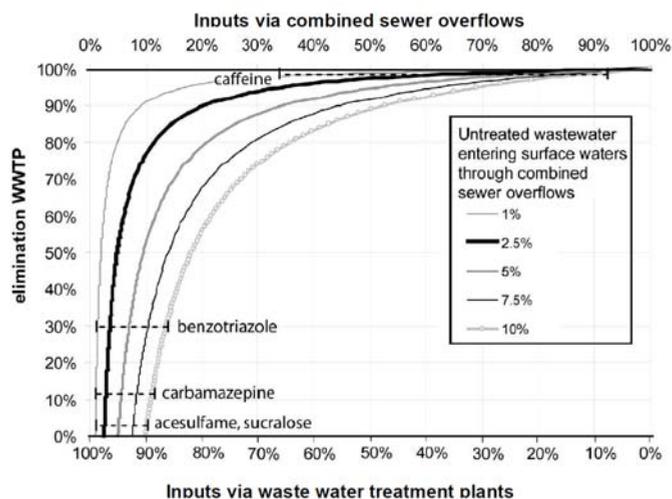


Fig. 3. Calculated proportion of MPs discharged via sewer overflows in combined systems, which is dependent on their elimination in the sewage treatment plant. In the Swiss Lowland, an average of 2.5% of untreated wastewater enters surface waters via the discharge from sewage drains. .

Substances that are predominantly removed by wastewater treatment plants, e.g. caffeine, are discharged into surface waters mainly via the combined sewage overflows and can therefore be used as tracers for the presence of untreated wastewater (Bürge et al., 2006; Wittmer et al., 2010). Inputs via combined sewage overflow also apply to

substances with external applications which are mobilized by rain and therefore primarily detected in municipal wastewater even if the combined sewage overflow is active. The Eawag-project REXPO (realistic exposure scenarios) demonstrated that up to 40% of the total amount of mecoprop detected in surface waters, enters through combined sewage overflows (Wittmer et al., 2010). Mecoprop is used as an herbicide in building envelopes and facades and flat roof protection, as well as in plant protection products.

- III. Due to leakages in the sewage system, raw wastewater can leach directly into soil, into surface waters and, indirectly into groundwater. It is, however, difficult to quantify losses due to leakages because they depend strongly on the state of local sewer systems (Rieckermann, 2006).
- IV. Inputs through rain water drains are not a part of municipal wastewater, but they contain a large number of substances that are similar to the substances found in municipal wastewater from combined systems (substances used outside of buildings). In separated sewer systems, partly polluted rainwater (from roofs, veneers and sealed areas) is transported directly into surface waters via rain water drains. Unlike in combined systems, MPs used outside of buildings flow directly into surface waters with rain water runoff. The advantage of the separating systems is, however, that no MPs from domestic wastewater can be released directly into surface waters, as is the case with the combined systems.

## 2 Micropollutants

### 2.1 Range of substances

In Switzerland, thousands of different chemicals are used in different applications and partly enter lakes and rivers. It is impossible to compile a complete list of these substances and their transformation products. In order to evaluate water quality, it is therefore necessary to focus on substances which are relevant to Switzerland's surface waters.

In order to identify substances relevant for Swiss surface waters, a large data set was evaluated: the results of various measurement campaigns in Swiss surface waters, studies on the behaviour of environmentally relevant substances, publicly available consumer data and various international substance lists (European-Commission, 2006; Freitas et al. , 2004; Hollender et al. , 2007; IKS, 2006; Keller & Balsiger 2007; Stamm et al., 2008; Stoob et al. , 2005). Based on these data as well as interviews with experts from research, industry, federal agencies and cantonal water protection departments, a list of 250 candidate substances was compiled.. For further prioritisation a procedure described in detail by (Götz et al. ,2010) was applied, which categorises chemicals according to their physico-chemical properties (distribution between water, air and particles), their biodegradability and their emission dynamics.

### 2.2 Swiss-specific MPs

A list of the main (Swiss-specific) MPs from municipal wastewater was selected from the categorised candidate substance list. The substances identified as Swiss- specific fulfill four criteria:

- a. The substance must demonstrably enter surface waters through municipal wastewater.
- b. The substance is approved for use in Switzerland by current legislation, i.e. is not prohibited.

- c. The substance has properties that indicate that it can be found with average to high probability in the water phase of surface waters.
- d. The substance meets at least one of the following three criteria:
- it has been shown to be widespread in surface waters (>20% of the measurements above the limit of quantification)
  - it has been measured in high concentrations in surface waters (>100 ng/L) and is common in municipal sewage treatment plant discharges (>20%);
  - it has high specific toxicity (e.g. by mutagenicity, carcinogenicity, hormone activity or immunotoxic effect) and as mentioned above meets the condition of relevant entry via municipal wastewater.

The criteria a-c must be fully met, while at least one of the three criteria of condition d) must be met. An example of a substance with a high specific toxicity is the synthetic estrogen ethinylestradiol, which exerts negative effects on the aquatic environment in concentrations below 1 ng/L (Parrot & Blunt, 2005; Wenzel et al. , 1999) .

The 47 Swiss-specific MPs for municipal wastewater selected using the above criteria are listed in Table 1a + 1b. The largest group of Swiss-specific MPs from municipal wastewater (22 MPs) are pharmaceuticals. The exposure relevance of pharmaceuticals and other listed

Name of substance	CAS	Group of substance	Surface water # Found / # Measurements	Surface water Average Concentration. (ng/L)	Surface water 90% percentile concentration. (ng/L)	WWTP effluent # Found / # Measurements	WWTP effluent Average Concentration. (ng/L)	WWTP effluent 90% percentile concentration. (ng/L)
Pharmaceuticals / Drugs								
Atenolol	29122-68-7	Beta-blocker	49 / 75	205	275	18 / 18	843	1160
Azithromycin	83905-01-5	Antibiotic	1 / 43	12	12	18 / 19	175	327
Bezafibrate	41859-67-0	Lipid-lowering drug	10 / 66	24	36	12 / 15	139	251
Carbamazepine	298-46-4	Anticonvulsant	112 / 509	13	43	78 / 78	482	790
<i>Carbamazepin-10,11 - Dihydro-10,11-Dihydroxy</i>	58955-93-4	Transformation product	4 / 4	490	1011	6 / 6	1551	1882
Clarithromycin	81103-11-9	Antibiotic	37 / 74	30	73	32 / 32	276	497
Diatrizoate (= amidotrizoic acids)	117-96-4	Contrast medium	15 / 53	206	482	7 / 10	598	1420
Diclofenac	15307-86-5	Analgesic	77 / 137	65	150	54 / 54	647	1170
Erythromycin <sup>1)</sup>	114-07-8	Antibiotic	6 / 28	25	44	17 / 17	42	75
Ethinylestradiol	57-63-6	Synthetic estrogen	4 / 99	5	10	6 / 27	2	3
Ibuprofen	15687-27-1	Analgesic	16 / 137	35	52	54 / 54	394	1439
Iomeprol	78649-41-9	Contrast medium	9 / 53	275	91	9 / 19	380	295
Iopamidol	62883-00-5	Contrast medium	14 / 53	92	51	15 / 19	377	880
Iopromid	73334-07-3	Contrast medium	21 / 53	96	65	13 / 19	876	2460
Mefenamic acids	61-68-7	Analgesic	7 / 28	7	14	10 / 10	870	1658
Metformin	657-24-9	Antidiabetic	13 / 13	713	3057	6 / 6	10347	13427
Metoprolol	37350-58-6	Beta-blocker	24 / 57	20	50	17 / 17	166	322
Naproxen	22204-53-1	Analgesic	22 / 137	37	82	38 / 39	462	678
Sotalol	3930-20-9	Beta-blocker	39 / 74	63	189	21 / 21	435	730
Sulfamethoxazole	723-46-6	Antibiotic	34 / 66	26	59	34 / 34	238	427
<i>N4-Acetylsulfamethoxazol</i>	21312-10-7	Transformation product	5 / 40	3	17	5 / 6	67	157
Trimethoprim	738-70-5	Antibiotic	26 / 74	13	36	42 / 45	100	163

Table 1a. Swiss-specific micropollutants from municipal wastewater: Compilation of analytical data from surface waters and wastewater treatment plant effluents. Data reported in (AFU St. Gallen, 2009; AWEL, 2003; AWEL, 2004; AWEL, 2005; CIPEL, 2008; Giger et al. ; 2006; Hollender et al. , 2007; IKS, 2006; Ort et al. , 2009; Singer et al. ,2008; Singer et al. , 2009; Singer et al. , 2010) and compiled in the Micropoll-database.

substances is also backed by findings of the EU (Loos et al. , 2009; Alder et al. ,2006 in IWA, 2006) and underlines the need for cross-border risk management. Pharmaceuticals entering surface waters via treated wastewater are generally biologically active substances, with the exception of x-ray contrast media for which only some metabolites and transformation products are discussed to have a biological effect. The second-largest group are 13 MPs with biocidal effect. These substances are used as active ingredients in plant protection products in agriculture or for protection of building materials. They are regularly detected in sewage treatment effluent.

Subsequently, hormone active substances and other substances with environmentally relevant properties are considered. As discussed in chapter 1.3 some MPs without currently-known effects, such as the artificial sweeteners acesulfame and sucralose were also considered as good tracer substances, indicating pollution through municipal wastewater due to their wide prevalence and high persistence in the environment.

Name of substance	CAS	Group of substance	Surface water # Found / # Measurements	Surface water Average Concentration: (ng/L)	Surface water 90% percentile concentration: (ng/L)	WWTP effluent # Found / # Measurements	WWTP effluent Average Concentration: (ng/L)	WWTP effluent 90% percentile concentration: (ng/L)
Substances with intended biocidal characteristics, which are subject to approval.								
2,4-D	94-75-7	Herbicide	16 / 125	67	53	4 / 6	13	25
Carbendazim	10605-21-7	Fungicide	37 / 73	16	34	17 / 30	81	170
Diazinon	333-41-5	Insecticide	367 / 1211	15	30	40 / 84	173	494
Diethyltoluamide (DEET)	134-62-3	Insecticide	236 / 331	135	120	11 / 55	593	817
Dimethoate	60-51-5	Insecticide	14 / 355	22	34	No data	No data	No data
Diuron	330-54-1	Herbicide	98 / 697	54	70	13 / 34	201	1379
Glyphosate <sup>3)</sup>	1071-83-6	Herbicide	64 / 162	373	637	No data	No data	No data
AMPA	1066-51-9	Transformation product	60 / 162	140	290	No data	No data	No data
Irgarol (Cybutryne)	28159-98-0	Herbicide	18 / 878	3	No data	9 / 29	30	58
Isoproturon	34123-59-6	Herbicide	211 / 1001	315	820	11 / 14	12	35
MCPA	94-74-6	Herbicide	56 / 137	40	111	6 / 6	25	44
Mecoprop-p	16484-77-8	Herbicide	100 / 188	45	74	26 / 29	424	765
Triclosan <sup>2)</sup>	3380-34-5	Microbiocide	3 / 12	20	31	6 / 6	116	224
Substances with an effect on the hormone balance (hormone active substances, which are not applied as pharmaceuticals/ drugs)								
Bisphenol A (BPA) <sup>4)</sup>	80-05-7	Additive	44 / 66	840	3440	22 / 25	331	679
Estradiol	50-28-2	Natural estrogens	17 / 92	2	3	18 / 28	3	5
Estrone	53-16-7	Natural estrogens	36 / 116	2	3	26 / 30	15	35
Nonylphenol <sup>3)</sup>	104-40-5	Additive	15 / 25	441	1100	7 / 7	267	353
Perfluorooctane sulfonate (PFOS) <sup>4)</sup>	1763-23-1	Tenside	No data	No data	No data	No data	No data	No data
Other substances with environmentally relevant properties <sup>***)</sup>								
Acesulfame	55589-62-3	Food additive	24 / 24	4010	6200	4 / 4	22500	30700
Benzothiazole <sup>4)</sup>	95-16-9	Additive	4 / 4	373	862	6 / 6	494	662
Benzotriazole	95-14-7	Corrosion preventative	366 / 382	1230	2990	41 / 41	12881	17300
EDTA <sup>**)</sup>	60-00-4	Complexing agent	202 / 248	2820	5380	10 / 10	20930	30290

Methylbenzotriazole	136-85-6	Corrosion preventative	303 / 331	249	516	30 / 30	1140	1950
NTA <sup>**)*)</sup>	139-13-9	Complexing agent	183 / 253	2890	5800	10 / 10	5370	6930
Sucralose	56038-13-2	Food additive	12 / 13	540	1039	6 / 6	4600	6523

<sup>1)</sup> Erythromycin is quickly transformed into erythromycin-H<sub>2</sub>O. The quantitative analysis is problematic  
<sup>2)</sup> Triclosan adsorbs relatively strongly (>75% on sludge). The analysis of triclosan is difficult (Singer et al. 2002).  
<sup>3)</sup> For Nonylphenol (NP) only values measured since 2006 have been considered (Ban on certain products with NP from 1.8.2006, Chemrrv)  
<sup>4)</sup> Bisphenol A, PFOS and Benzothiazole are ubiquitous substances. The analysis is difficult due to blank values.  
<sup>5)</sup> Glyphosate is classified with the EPI-Suite (US-EPA, 2007), as «ready-biodegradable» and would not be considered in accordance with the procedure described above. Measurements show, however, that it occurs in the environment. Glyphosate is one of the best-selling pesticides in the world, frequently applied in residential areas and found in surface waters in the µg/L area (Battaglin et al. , 2005). These high concentrations are not so much explained by the environmental properties of Glyphosate . Due to the very high application a pseudo-persistence explain the high environmental relevance and is also indicated by the transformation product AMPA.  
<sup>6)</sup> EDTA and NTA are classified with the EPI-Suite ,(US-EPA, 2007) as «ready-biodegradable» and would not be considered in accordance with the procedure described above. Measurements of EDTA and NTA in surface waters show, however, that these substances get into surface waters, although the persistent criterion has not been met in accordance with the categorisation according to Götz (Götz et al. ,2010). Therefore the list has been expanded.  
<sup>7)</sup> An environmentally relevant property can also be, for example, a high persistence in addition to toxicity.  
 No data: No data available

Table 1b. Swiss-specific micropollutants from municipal wastewater: Compilation of analytical data from surface waters and wastewater treatment plant effluents. Data reported in (AFU St. Gallen, 2009; AWEL, 2003; AWEL, 2004; AWEL, 2005; CIPEL, 2008; Giger et al. ; 2006; Hollender et al. , 2007; IKSr, 2006; Ort et al. , 2009; Singer et al. ,2008; Singer et al. , 2009; Singer et al. , 2010) and compiled in the Micropoll-database.

### Locally-occurring MPs

Besides the above listed Swiss-specific MPs, additional water pollutants occurring only in certain regions can be of importance. Many substances have strong regional differences in consumption, have specific applications (for example, in industry and manufacturing) or are discharged only locally into a few surface water bodies. It should therefore be clarified during the water quality assessment whether other locally important pollutants are expected to be present in addition to the above Swiss-specific MPs.

## 3 Protection goals in the Swiss Water Protection Law and ecotoxicological effect assessment

### 3.1 Protection goals in the Swiss Water Protection Law

The Swiss Federal Water Protection Law (Swiss Federal Water Protection Law (GSchG), 2008) aims to protect waters from harmful effects. Harmful effects can be caused by pollutants which affect the structure or functioning of surface waters.

A good analysis of the protection goals can be found in (Häner et al. ,2010 and Junghans et al. ,2011). The purpose of the Swiss Water Protection Law of 1991 is to protect waters against harmful effects (Art. 1).

- to maintain the health of persons, animals and plants;
- to maintain the natural biotopes of indigenous fauna and flora; and
- to maintain waters suitable to sustain natural fish populations.

An additional important goal is to guarantee the supply and economic use of drinking water. Although this has to be considered when quality standards for surface waters are set, this protection goal will not be discussed any further in this document, whose primary focus is on chemical and ecotoxicological objectives.

Art. 6 of the Swiss Water Protection Law states that it is prohibited to introduce into a waterbody any substances which may pollute such waters, either directly or indirectly.

The Water Protection Law thus provides for comprehensive protection: Waterbodies are to be safeguarded against adverse impacts of all kind to ensure that they can serve a wide variety of functions. The Swiss Water Protection Law applies to all surface and subterranean waters (Art. 2 Swiss Water Protection Law). According to a declaration of the Federal Council (dated 29 April 1987, BBl 1987 II 1104) the protection extends to all natural and artificial public and private waters, including their sources.

Ecological goals for surface waters - and the associated water quality requirements - are specified in the Swiss Water Protection Ordinance:

Annex 1 Swiss Water Protection Ordinance defines ecological objectives for waterbodies. These objectives have to be taken into account for all measures taken under this ordinance (Art 1 Swiss Water Protection Ordinance). For surface waters it is required that pollutants which could enter the water as a result of human activities

- do not accumulate in plants, animals, micro-organisms, suspended matter or sediments
- do not have any harmful effects on the biocoenoses of plants, animals and micro-organisms and on the utilisation of the water
- do not interfere with the biological processes making possible the fulfilment of the basic physiological needs of plant and animal life, such as the metabolic processes, the reproductive processes and the olfactory orientation of animals.

Additionally, the Swiss Water Protection Ordinance also requires that pollutants which could enter the water as a result of human activities occur in a water body :

- at concentrations that are within the range of natural concentrations where they are already present naturally
- at near-zero concentrations where they are not naturally present.

The latter two requirements are based on relevant international agreements (such as the Convention for the Protection of the Aquatic Environment of the North-East Atlantic, OSPAR Convention), including those which aim to prevent and eliminate pollution of the aquatic environment by ceasing or phasing out discharges, emissions and losses of priority hazardous substances, with the ultimate aim of achieving concentrations in the aquatic environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. In general, the protection goals of the Swiss Water Protection Law and the EU Water Framework Directive (EU 2000, WFD, WRRL, RL 2000/60/EG) are quite similar.

### **3.2 Numerical requirements for water quality and effect-based Environmental Quality Standards (EQS)**

For MPs from municipal wastewater, to date, numerical requirements do not exist for most MPs in municipal wastewater, with the exception of pesticides (active substances in plant protection products and biocidal products) , which currently have a non-effect based limit of 0.1 µg/L (Water Protection Ordinance (GSchV, 2008)).

Effect-based numerical requirements for water quality are designated in conjunction with the EU WFD as Environmental Quality Standards (EQS). The aquatic environment can be affected by chemical pollution both in the short and long term, and therefore both acute- and chronic-effects data should be used as the basis for establishing the EQS. In order to ensure that the aquatic environment and human health are adequately protected, EQS expressed as an annual average value, should be established at a level providing protection against long-term exposure, and maximum allowable concentrations should be established to protect against short-term exposure (European Commission 2008).

In order to remain consistent with previous national and international Swiss-relevant publications , AA-EQS are used synonymously with Chronic Quality Criteria (AA-EQS =

CQK) and MAC-EQS are used synonymously with Acute Quality Criteria (MAC-EQS = AQK) respectively. AA-EQS must be derived as protection for the effects of long-term exposure and MAC-EQS against the effects of short-term exposure. To allow an overview about the general EQS situation, the main conclusions of The Society of Environmental Toxicology and Chemistry (SETAC) from recent workshops are listed.

**General situation of EQS setting/derivation (this paragraph is based on the workshop conclusions and recommendations of the SETAC concerning EQS derivation (Crane et al., 2010):**

Current practice is for each country to derive their own EQS on the same substances, often using methods that differ only slightly. (Crane et al., 2010). This is highly inefficient and a waste of resources. To improve the situation, it is recommended that the advantages and disadvantages of internationally sharing EQS data and adopting the same derivation strategies should be examined. This recommendation is based on the following considerations:

- e. Even after more than 30 years of work, most countries have developed fewer than 50 EQSs for the aquatic environment.
- f. Development of a single EQS usually requires at least 2 to 3 years and can cost US\$ 50K to US\$ 150K  $\approx$  112K Euro (exchange rate of January 2011) or more depending on data availability, levels of uncertainty that must be resolved, and any economic or social controversies about the substance.
- g. Most countries have similar priority substances.
- h. Duplication of work is wasteful; there is great potential for collaboration.
- i. Most EQS derivation procedures are similar, so there is potential for international harmonization.
- j. Pollution often straddles national borders.
- k. Industry and trade are multinational; that is, sources of pollution are international.

Currently in Europe, several multi-national meetings are scheduled, organized with the intention of harmonizing EQS derivation in different countries and EU member states. The EU Commission coordinates the work of Expert Group on Review (a sub group of Working Group E (WG E) which is tasked with the prioritization of substances and associated EQS derivation for candidate priority substances. The informal Multilateral Group (MG) promotes the exchange of knowledge between the European risk assessors working for the national authorities on Specific Pollutants. This leads to a combination of different national interests and stakeholder interests for the different chemical groups (e.g. plant protection products, biocides, pharmaceuticals, industrial chemicals). Both meetings are very important to reduce unnecessary effort and inefficiency in EQS derivation (see comments of Crane et al., 2010 above).

### **3.3 Derivation of effect based quality criteria**

The EQS-proposals presented here were derived according to the Technical Guidance Document for Deriving Environmental Quality Standards (European Commission, 2009), which is the current technical guidance document of the EU WFD. A short summary of the requirements and validity check of ecotoxicological effect data can be found in Matthiessen et al. (2009). The data used should:

- Be reliable and relevant (e.g., generated according to test guidelines or well documented in open accessible literature to achieve validity and relevance criteria)

- Have been assessed using proper statistical analysis methods
- Avoid unrealistically high test concentrations that may create artifacts
- Be based on experiments in which test concentrations were measured, with measured concentrations used to define endpoints if they differ from nominals by more than  $\pm 20\%$
- Be fully documented (e.g., conducted to Good Laboratory Practice (GLP))
- Have clear dose-response relationships

The EQS were derived by the Swiss Centre for Applied Ecotoxicology after an extensive review of existing ecotoxicological effect data, and adjustment using data sets of other EU member-states and the use of the current TGD for EQS. The resulting (sub)dossiers are commented on by external experts and checked for plausibility and validity in order to obtain independent multiple reviewed EQS-proposals of Swiss-specific MPs (Fig. 4). Additionally, there is active knowledge exchange with EU risk and hazard assessors to obtain a harmonized and balanced expert judgement for the hazard assessment of the priority substances. Two international working groups are very useful for this purpose: The first, EU Working Group E (WG E) on Chemical Aspects of the Water Framework Directive, is developing EQS-proposals for priority substances with member-states NGOs and stakeholder organizations involvement. The second, an informal Multilateral Group (MG) founded in 2006, in which Member States share their experiences and aim to develop common approaches to setting Specific Pollutant EQS values. In both groups some of the newly identified Swiss relevant MPs (table 1a, 1b) are currently assessed and it seems useful to start with similar or identical proposed EQS to allow a border crossing, harmonized risk management.

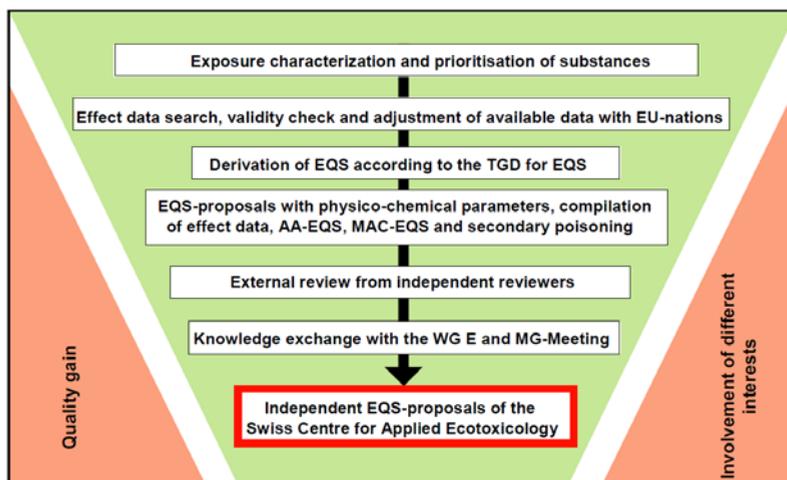


Fig. 4. Steps in the development of an EQS-proposal in Switzerland

For substances for which EQS exists or existed in EU member states, a comparison of the ecotoxicological effect data was made. These effect data were tested for validity (Klimisch et al., 1997; Matthiessen et al., 2009) and supplemented by valid up-to-date studies. Proposals for EQS are shown in Table 2. The proposed values are still provisional and will undergo an additional evaluation phase before being finalized. An overview of the currently proposed EQS- can be found at:

<http://www.oekotoxzentrum.ch/qualitaetskriterien>

As mentioned above, there are some substances for which EQS are being derived for both Switzerland and the EU. The quality criteria of 17-alpha-Ethinylestradiol, 17-beta-Estradiol, Diclofenac, Ibuprofen, PFOS and Cybutryne are currently discussed in the WG E.

Name of substance	CAS	MAC-EQS-proposal	AA-EQS-proposal
Drug / Pharmaceutical			
17-alpha-Ethinylestradiol	57-63-6	no quality criterion proposed	0.037 ng/L
Atenolol	29122-68-7	330 µg/L	150 µg/L
Azithromycin	83905-01-5	0.09 µg/L	0.09 µg/L*
Bezafibrate	41859-67-0	76 µg/L	0.46 µg/L*
Carbamazepine	298-46-4	2550 µg/L	0.5 µg/L
Clarithromycin	81103-11-9	0.11 µg/L	0.06 µg/L*
Diclofenac	15307-86-5, (15307-79-6)	700 µg/L	0.05 µg/L*
Ibuprofen	15687-27-1, (31121-93-4)	23 µg/L	0.3 µg/L*
Mefenamic Acid	61-68-7	40 µg/L	4 µg/L*
Metoprolol	37350-58-6	76 µg/L	64 µg/L
Naproxen	22204-53-1, (26159-34-2)	370 µg/L	1.7 µg/L(*)
Sulfamethoxazole	723-46-6	2.7 µg/L	0.6 µg/L
Trimethoprim	738-70-5	1100 µg/L	60 µg/L
Further substances with environmentally relevant properties			
Benzotriazole	95-14-7, (273-02-9)	120 µg/L	30 µg/L
Methylbenzotriazole	29878-31-7, 29385-43-1, (64665-57-2)	200 µg/L	75 µg/L
EDTA	60-00-4	12100 µg/L	2200 µg/L
NTA	139-13-9, (5064-31-3)	9800 µg/L	190 µg/L
* For these substances a secondary intoxication risk could exist that has not yet been considered numerically. at: <a href="http://www.oekotoxzentrum.ch/qualitaetskriterien">http://www.oekotoxzentrum.ch/qualitaetskriterien</a> the updated proposals are available			

Table 2. Proposals for quality criteria of selected Swiss-relevant substances derived according to the TGD for EQS and partly reviewed and verified by external experts.

#### 4. Assessment concept

Figure 4 shows an outline of the various steps of the assessment concept. The individual steps are detailed below.

##### 4.1 Estimation of pollution from municipal wastewater

Assessing concentrations of MPs in surface waters is more time- and cost-intensive than other surface water monitoring, for example those relating to the nutrients (Liechti, 2010).

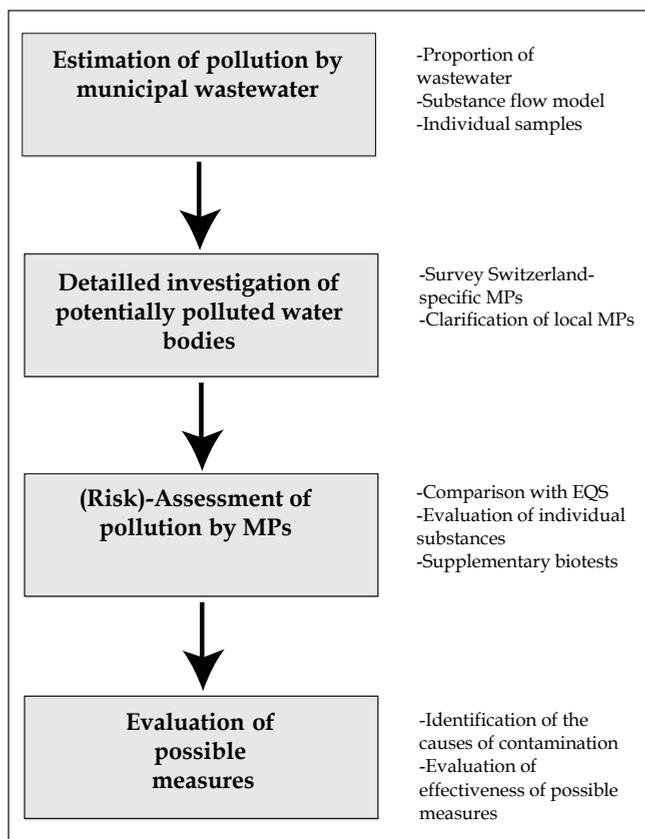


Fig. 5. Outline of the assessment concept

of water pollution. As a basis for assessing water quality using trace analysis methods, an outline should be compiled with regard to expected water pollution by MPs from municipal wastewater. For a first assessment the following methods should be taken into account:

- Identification of the proportion of wastewater in individual surface waters with minimum discharge ( $Q_{347}$ ): The ratio of wastewater can either (1) be estimated from the population connected to the surface waters via the urban sewer system or (2) be calculated from the measured wastewater discharges from municipal wastewater treatment plants. Detailed information can also be considered, such as discharges from

the combined sewage system during rain events, rain water drains in separated sewer systems, and discharges from industry and factories.

- Focusing measurement campaigns using grab samples: Grab samples are collected from specific locations (e.g. below the discharge point of larger wastewater treatment plants) and examined for substances of concern in urban drainage systems, e.g. a selection of the Swiss-specific compounds presented above. When identifying the potential for contamination by MPs in surface waters, specific data relating to the local drainage system should be considered, such as discharges from local point sources.

#### **4.2 Detailed investigation of potentially polluted water bodies**

After identification of the potential for contamination by MPs in surface waters, the identified water bodies have to be examined more closely. The list of Swiss-specific MPs can provide guidance for the selection of analytes as AA-EQS have already been derived (Table 2). It should be noted, however, that some substances, such as 17- $\alpha$ -ethinylestradiol, are difficult to measure due to the low concentrations at which they occur. Alternative strategies such as measurement of the estrogenicity of samples via integrative biotests or use of passive samplers are currently under development. This substance list can be expanded once more quality criteria have been derived or other substances with environmental relevant properties become known.

##### **Sampling**

The sampling strategy proposed here focuses on substances that tend to continuously enter surface waters. Studying MPs with complex input dynamics and various pathways requires a more complex sampling strategy, such as proposed for pesticides by Stamm and colleagues (Stamm et al. , 2006).

In order to measure or monitor the input of organic MPs into surface waters through treated wastewater, the following sampling strategy is recommended:

- Investigation of grab samples from surface waters at least four times a year or more (ideally twelve times a year or more depending on the input characteristics)
- Sampling during the week and not on holidays or weekends (particularly for smaller receiving streams or waste water treatment plants)

Additionally, composite samples from sewage treatment plant effluents can be analyzed. Concentrations in surface waters can then be estimated based on the dilution factor of wastewater in the receiving water body. The advantage of this approach is that most wastewater treatment plants routinely collect 24-hour composite samples of their effluents. This approach minimizes the risk of measurement artifacts associated with grab sampling, however, it ignores the input of MPs from other sources.

##### **Environmental concentration (EC)**

In order to assess the water body investigated, a statistical value must be calculated from the analytical data based on a standardised statistical procedure, e.g the environmental concentration (EC). The EC is a critical value. The assessment of the state of the investigated surface water body depends directly on the statistical procedure applied. The EC can be obtained from measured values as follows: arithmetical average value, geometrical average value, median or other percentiles (Liechti, 2010). In order to improve the comparability of the results of the surface water investigations, we suggest considering the 90th percentile for at least twelve samples (Liechti, 2010)

Since the survey of MPs is comparatively expensive, it might not be possible to get twelve measurements. In that case, the average value of the measurement of four seasonal samples normalised at base flow conditions ( $Q_{347}$  = the outflow daily average, which is achieved or exceeded on average on 95% of the days, i.e. on average 347 days per year) is proposed to be used as EC. If the difference between the smallest and the largest normalised concentration is higher than an order of magnitude, additional samples or aggregate samples should be taken into consideration.

### 4.3 Risk assessment of pollution by MPs

A risk assessment is generally made by comparing the environmental concentration (EC) with an EQS. For the evaluation of tested waters according to the above scheme relating to MPs, the EC obtained (90th. percentile, respectively average value) is used.

For continuous inputs of MPs via treated wastewater, the AA-EQS (chapter 3) is particularly relevant as this is how the biotic community can be protected from the consequences of long term exposure:

If the EC is higher than the AA-EQS a non-tolerable risk can be assumed for aquatic communities, as it is usually not known how long these excess concentrations have been in the water. Similar to the MSP, there is a proposed classification into five chemical status categories based on the following levels:

very good / good/moderate/insufficient/poor (see Table 3)

The chemical quality for long-term exposure (AA-EQS) has been achieved for the classifications 'very good' and 'good', and not achieved for the classifications 'moderate', 'insufficient' and 'poor'. The classifications and categories were determined according to Table 3. According to the wide concentration range found in different surface waters, a decadic categorisation scheme was proposed, which covered a large concentration spectrum.

The maximum acceptable concentration (MAC-EQS) aims to protect against possible effects from short-term concentration peaks (European Commission 2009). MAC-EQS can, on the other hand, be used when heavy rain events occur (e.g. storm water events) or when time-varied concentrations of chemicals are expected over a short period (e.g. seasonal applications or chemical accidents). If the short-term EC exceeds a MAC-EQS then a harmful effect on aquatic organisms is possible within the next 48 to 96 hours.

#### Mixture problems

The evaluation of the MP according to the quality classes (or 'categories') mentioned in Table 3 is based on the ecotoxicity of a single MP alone. Possible combination effects due to the occurrence of several MPs in the same water body are not taken into consideration in the current EQS approach. Since the problem of micropollutant mixtures is not currently recognized in the present single-substance based approach, classifications which include higher-level requirements than the proposed AA-EQS (Factor 10 and 100) are to be taken into account on a precautionary basis and are being proposed by other nations such as the Netherlands (negligible concentration) (van Vlaardingen & Verbruggen, 2007). These allow classification with stricter criteria than the suggested AA-EQS (e.g. AA-EQS/100). The "negligible concentration" (AA-EQS/100) should explicitly protect against potential mixture effects.

Several studies have shown that the consideration of mixture toxicity is an important issue in the context of MP (Kortenkamp et al. 2009 and references therein). It has been demonstrated that the use of NOEC as a toxicologically negligible concentration, which forms the basis for the derivation of the AA-EQS, may not be sufficiently protective when substances occur in complex mixtures. A study by (Junghans et al. 2004) demonstrated that 43 substances, each present at a concentration of as low as a tenth of their respective NOEC, still caused a significant biological effect. Indeed, another study (Baas and Kooijman 2010) demonstrated that, for some water samples, the AA-EQS is not protective when several MPs are present. Currently, several national and international activities are taking place concerning the assessment and regulation of mixture toxicity (e.g. Council of the European Union 2009). Nonetheless, the derivation of sound AA-EQS for single MPs and their degradation products is the basis for every assessment of the water quality and hence an important step to reach a good chemical status in surface waters.

Evaluation		Criterion/description		Compliance with quality criterion
very good		The environmental concentration (EC) is 100 times smaller than the quality criterion (AA-EQS)	$EC < 0.01 \times AA-EQS$	AA-EQS passed
		The environmental concentration (EC) is 10 times smaller than the quality criterion (AA-EQS)	$0.01 \times AA-EQS \leq EC < 0.1 \times AA-EQS$	
good		The environmental concentration (EC) is smaller than the quality criterion (AA-EQS)	$0.1 \times AA-EQS \leq EC < 1 \times AA-EQS$	
moderate		The environmental concentration (EC) is smaller than the doubled quality criterion (AA-EQS)	$1 \times AA-EQS \leq EC < 2 \times AA-EQS$	AA-EQS exceeded
insufficient		The environmental concentration (EC) is greater than the tenfold quality criterion (AA-EQS)	$2 \times AA-EQS \leq EC < 10 \times AA-EQS$	
poor		The environmental concentration (EC) is the same or greater than the tenfold quality criterion (AA-EQS)	$EC \geq 10 \times AA-EQS$	

Table 3. Evaluation of the chemical water quality for MPs from municipal wastewater (adapted from the Nutrients Module of the FOEN and the modular stepwise procedure) This classification system reflects the chemical quality and not the ecological quality.

An exceedance for one substance could mean that no good ecological status can be achieved in the context of the WFD, because very sensitive species are possibly impacted. A further evaluation of the context between the chemical and ecological status is currently in progress at the European (Environment Directorate-General of the European Commission, DGENV) and national level in the modular stepwise procedure framework (Modulstufenkonzept, MSP). Additional considerations of bioavailability, integrative biotest results and the use of effect directed analysis (EDA), passive sampling strategies and the identification of species

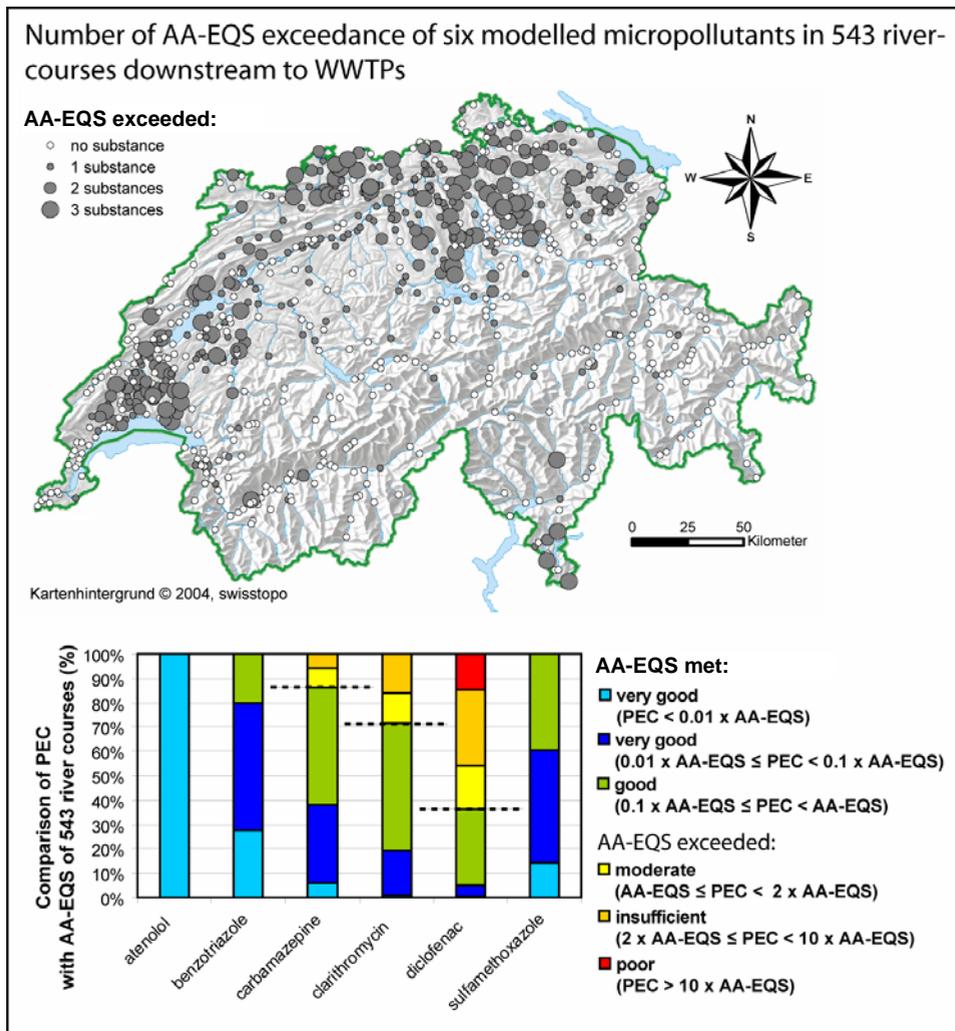


Fig. 5. Evaluation of 543 water sections downstream of sewage treatment plants concerning atenolol, benzotriazole, carbamazepine, clarithromycin, diclofenac und sulfamethoxazole. The environmental concentration (EC) of the MPs examined was calculated by means of the substance exposure model of Ort (Ort et al. , 2007) (PEC = predicted environmental concentration), assuming low flow ( $Q_{347}$ ) and compared with the chronic quality criteria. The risk assessment of sulfamethoxazole was made with a 5 times lower AA-EQS proposal of 0.12  $\mu\text{g/L}$  than in Table 2 and showed no exceedances.

at risk (SPEAR) seem to be case by case options to provide a more integrative assessment in the future.

During the evaluation of MPs according to the single substance based classifications set out above, it was noticed that the detection and quantification limit could influence the

outcome. Should the analytical limit of quantification for a substance be above a category limit, then a classification results as a minimum category. E.g. if a substance is not detectable and if the limit of quantification is between the AA-EQS/10 and the AA-EQS, then the minimum category can be designated "good+" since the actual exposure concentration can be designated as "good" or "very good".

In the Swiss wide Risk Assessment for 6 substances all classes and colours were obtained. Signaling that the chosen classes are appropriate to identify accurately the risks and the safety for single substances.

In 14 % of the investigated cases 3 of 6 substances exceeded the AA-EQS, so there is the possibility for the occurrence of combination effects Further research is needed until other solutions for the mixture problematic are established. For known and monitored substances with a similar mode of action (e.g. specific estrogens, specific herbicides or specific pharmaceuticals like beta-blockers) the addition of risk quotients RQ ( $RQ = EC / AA-EQS$ ) seem useful to calculate a risk caused by mixture toxicity (Chèvre et al. 2008a, Chèvre et al. 2008b). But in most cases a large number of unknown substances occur and cause mixture effects, therefore the use of mode of action specific biotest monitoring or effect directed analysis (EDA) could lead to an estimation of mixture toxicity. In calculating risk quotients there is always the possibility of errors and deviations on the side of the analytics and the reliability of effect based quality criterion. More risk classes allow a better differentiation in a broader concentration range and, so they could help to avoid an overestimation of a identified risk and enable a better geographical resolution of hot spots or unpolluted areas.

### Precautionary target values

Some very exposure relevant and persistent MPs can potentially infiltrate into the ground water used for drinking water. Depending on how much effort is spent on eliminating these substances during drinking water treatment, this is reason for identifying and using a better classification system where chemicals occur above the AA-EQS level. The application of an effect based near-zero concentration and precautionary target values may be appropriate for reducing these concentrations in drinking water relevant water bodies. For surface waters, which are used as drinking water resources, precautionary target-values were proposed by the Waterworks Working Groups IAWD<sup>1</sup>, IAWR<sup>2</sup> and the RiWA-Maas<sup>3</sup>, who provide drinking water for 106 million people in 17 neighbouring countries (IAWD RIWA-Maas & IAWR, 2008). These values are proposed to be applied to evaluate surface waters used for drinking water, in addition to effect-based AA-EQS. The aim of these precautionary values is to achieve good drinking water quality using only natural preparatory methods for producing drinking water. Persistent substances, which are difficult to eliminate, even if they have no currently known effects, are generally undesirable in drinking water resources and should not exceed 1 µg/L (IAWD RIWA-Maas & IAWR, 2008). For biologically active substances, such as pharmaceuticals, a maximum concentration of 0.1 µg/L is proposed, unless toxicological findings necessitate a lower level (IAWD RIWA-Maas & IAWR, 2008).

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<sup>1</sup> IAWD = Internationale Arbeitsgemeinschaft der Wasserwerke im Donaeinzugsgebiet (International Waterworks Working Group for the Danube catchment area)

<sup>2</sup> IAWR = Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet (International Waterworks Working Group for the Rhine catchment area)

<sup>3</sup> RiWA = Vereniging van Rivierwaterbedrijven Maas (Waterworks Association)

#### 4.4 Hormone active effects

There is an urgent need to detect, assess, and reduce effects of hormonally active compounds and endocrine disrupters in aquatic systems, as reflected in national research programs like the Swiss NRP 50 "Endocrine Disruptors" and its consensus platforms (Schweizer Nationalfonds, FNSNF, 2007). As a medium-term measure, the EU strategy on endocrine disruptors (SEC, 2007) uses the Endocrine Disruptor Testing and Assessment (EDTA) Task Force of the Organisation for Economic Co-operation and Development (OECD) along with other research activities. In particular, the test methods of the OECD that are currently being validated or which have already been validated may contribute to a better understanding of the extent of endocrine disruption, especially if they are applied on environmental samples and in the context of risk-assessment strategies, for instance in waste water treatment. Further standardisation of such methods for regulative applications is recommended. (Kase et al., 2009).

In addition to the detection and evaluation of single substances with chemical analytics, the integrative effect detection using *in-vitro*-biotests is recommended for hormone active MPs. In particular, this is desirable for estrogen-receptor binding substances since their quality criteria are analytically difficult to monitor due to the low effect concentrations (< 1 ng/L). With *in vitro* testing the entire estrogen receptor binding potential of an environmental sample can be evaluated with a 17-beta-estradiol equivalent, for example, with the Yeast Estrogen Screen (YES Test) and various reporter gene systems with human cell lines (van der Linden et al. , 2008, Wilson et al. , 2004).

An evaluation of sensitive effect-based, easy-to-manage, economical and easy-to-interpret biotests for estrogenic effects for use by enforcement authorities or by private laboratories is also being sought in the ecotoxicology module of the MSP. A comparative assessment for the applicability of 15 (10 *in vitro* and 5 *in vivo*) biotest procedures for the detection of hormone-active and reproduction toxic effects were carried out on behalf of the Swiss Centre for Applied Ecotoxicology (Kase et al. , 2009). Some biotests are already quite advanced in the validation process of the OECD; others are also in the preparation phase for the ISO-level standardisation necessary for environmental sample testing so that probably within the next three to four years certified, standardised procedures for environmental sample testing can be expected.

#### 5. Swiss-wide situation analyses of selected MPs

Using the mass flow model developed and presented in (Ort et al. , 2007) and recent use data, a Switzerland-wide overview was produced for six MPs, for which AA-EQS were derived: atenolol, benzotriazole, carbamazepine, clarithromycin, diclofenac and sulfamethoxazole. It was thereby assumed that the substances observed enter the surface waters continuously via treated wastewater. For the six selected MPs, good prediction accuracy could be demonstrated (Ort et al. , 2007).

Figure 5 shows the expected Swiss-wide pollution of the water sections downstream of WWTPs at base flow conditions ( $Q_{347}$ ), based on predicted environmental concentrations (PEC) for six MPs. AA-EQS limits were not exceeded in any of the 543 sections modelled for atenolol, benzotriazole und sulfamethoxazole. The AA-EQS of carbamazepine, clarithromycin und diclofenac were exceeded in different quantities, mainly in the Swiss lowlands. In 14% of the water sections modelled, the EC of the three MPs lie above the AA-

EQS. These water sections could, for instance, be prioritised for more detailed studies. A procedure and further steps in line with the assessment concept detailed above should be checked and evaluated individually.

## 6. Discussion and outlook

The assessment concept presented here focuses mainly on the input of MPs via treated wastewater and shows possible methods to monitor and evaluate them. Certain aspects, e.g. the selection of relevant substances, can be used for other input pathways than input through wastewater treatment plants, namely the discharge of combined sewer overflows, leakages in the sewer system and, to a certain extent, to inputs through rainwater drains. The procedure presented permits an evaluation of single water sections for single MPs from municipal wastewater similar to the evaluation of other parameters such as nutrients or heavy metals which are regulated in the Water Protection Ordinance (GSchV, 2008). The input dynamics of MPs from municipal wastewater via combined sewer overflows or rain water drains cannot be compiled with the concept proposed. At best it can help determine fundamental contamination by these substances.

In further projects dynamic inputs, such as diffuse inputs of pesticides from agriculture or substances from street drainage systems, should be characterised and investigated.

## 7. Acknowledgements

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