KOMPETENZZENTRUM WasserBerlin

REPORT

Cicerostr. 24
D-10709 Berlin
Germany
Tel +49 (0)30 536 53 800
Fax +49 (0)30 536 53 888
www.kompetenz-wasser.de

Eco-engineered systems for removal of micropollutants from WWTP effluents – existing knowledge

Project acronym: EcoTreat 1

by

Daniel Wicke

Department “Surface Water”

KompetenzZentrum Wasser Berlin gGmbH, Cicerostr. 24, 10709 Berlin, Germany

Email: daniel.wicke@kompetenz-wasser.de, Tel. ++49 (0)30 536-53833

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Authors
Daniel Wicke

Quality Assurance
Pascale Rouault (KWB), Stellio Casas, Jeanne Serre, Sandrine Sourisseau (VERI), Christelle Pagotto (VEOLIA DT)

Publication / Dissemination approved by technical committee members

Bruno Tisserand, VERI
Boris David, DT
Isabelle Baudin-Bizien, VERI
Christelle Pagotto, DT
Sandrine Sourisseau, VERI
Sylvain Metton, MSE

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Abstract

This report summarizes relevant available knowledge on the removal of micropollutants from WWTP effluent in natural treatment systems such as constructed wetlands (polishing). Five studies were found investigating removal of various micropollutants in eight different full scale systems located in Spain, southern France, Korea and Sweden (all being different configurations of free water surface wetlands), demonstrating good removal (>80%) for more than 15 micropollutants compounds under summer conditions, e.g. diclofenac, ketoprofen, naproxen, ibuprofen, galaxolide, atenolol, ciprofloxacin, triclosan, glyphosate, ofloxacin and metoprolol. Hydraulic retention times (HRT) ranged from 0.25 to 30d. At HRT of 0.25d, only naproxen and atenolol were removed by >80% in summer, highlighting the importance of HRT for system performance. Another important factor influencing the removal is temperature and season with lower removal in winter. However, in warm climates (e.g. two studies in northern Spain and one study in southern France), reduction of removal efficiencies in winter is less pronounced with values for removal of the majority of investigated pharmaceuticals in winter still being >60%. In 4 FWS wetlands sampled during winter at sub-zero temperatures in Sweden, though, removal was mostly below 50%.

A variety of removal mechanisms simultaneously occur in natural treatment systems and are relevant to varying extent for each compound and system type. Important removal mechanisms are biodegradation (e.g. for naproxen, ibuprofen), photodegradation (e.g. for diclofenac, ketoprofen, sulfamethoxazole) and adsorption (e.g. for galaxolide, tonalide). The relevance of plant uptake and phytodegradation as removal mechanisms is not fully understood; however, a few studies demonstrate the translocation of pharmaceuticals (e.g. carbamazepine) to plant tissue. For biodegradation, redox conditions are an important parameter influencing microbial degradation pathways.

Design guidelines for eco-engineered treatment systems targeting the removal of micropollutants are not available to date. In addition, data necessary to dimension eco-engineered treatment systems that target the reduction of micropollutants in WWTP effluent (e.g. kinetic data such as removal rates and its dependence on temperature) is lacking. For the development of design guidelines for eco-engineered systems targeting the removal of micropollutants, removal rates for each system type and compound and their dependence from temperatures needs to be determined for all compounds of interest. Furthermore, more research is necessary for a deeper understanding of processes in eco-engineered systems, especially the relevance of the different removal mechanisms and conditions for removal for each individual micropollutant of interest.

Nevertheless, eco-engineered treatment systems are a promising technology for polishing of WWTP effluent, including further removal of micropollutants.

Acknowledgements

The EcoTreat project is a joint project by KWB and VERI/DT. Collation of data of selected micropollutants (properties and removal mechanisms) as mentioned in chapter 3.7 was mainly done by the working group of the EcoTreat project at VERI. Contribution towards Figure 7 of this report is greatly acknowledged.

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Chapter 1 Introduction

Effluent discharged by wastewater treatment plants (WWTP) can cause adverse effects in receiving surface waters due to elevated levels of nutrients and micropollutants. This is of concern as surface water is an important resource for drinking water as well as an ecological habitat. In recent years, micropollutants discharged by WWTP came into focus of interest as many of these pollutants (e.g. pharmaceuticals, biocides, personal care products) can only partially be removed during conventional wastewater treatment (see Chapter 2).

Strategies to further reduce the entry of micropollutants into surface waters include the additional treatment of secondary effluent of WWTP. In recent years, the focus of this strategy was on the development of technical treatment systems, mainly technologies based on ozonation and adsorption to activated carbon. However, these technologies are expensive regarding investment costs as well as operation and maintenance costs.

Natural treatment systems (e.g. constructed wetlands, treatment ponds or floating islands) could be a cost-efficient alternative to technical systems for further treatment of WWTP effluent, especially for smaller WWTP <10.000 PE. These passive treatment systems that are low in cost and easily operated and maintained take advantage of the degradation capabilities of natural systems, e.g. the high microbial activity in the root zone of reed as utilized in constructed wetlands or photodegradation in systems with open water surfaces. Constructed wetlands such as subsurface flow reed beds (also known as planted soil filters) or treatment ponds have been applied for many years for the treatment of primary wastewater at locations that are not connected to the sewer system (as reviewed by Sundaravadivel and Vigneswaran 2001). Other well established applications include the treatment of acid mine drainage (Sheoran and Sheoran 2006) and urban stormwater runoff (Mungasavalli and Viraraghavan 2006).

Promising studies demonstrate that constructed wetlands are also capable to reduce the concentration of pharmaceuticals, personal care products and pesticides in WWTP effluent (see Chapter 5). Additional benefits of eco-engineering systems include further nutrient reduction, ecological benefits (treatment systems as habitats and breeding grounds) as well as beneficial social aspects (e.g. increased public acceptance and potential recreational use of natural treatment systems).

The ECOTREAT project aims at the application and combination of eco-engineering systems for advanced treatment of wastewater effluent focusing on the reduction of micropollutants. Main goal is the development of design criteria for a treatment train consisting of different eco-engineered systems that reaches certain reductions for specified micropollutants. This report summarizes the main outcomes of a literature review that was conducted as part of the first phase of the EcoTreat project to get an overview about existing knowledge regarding the behaviour of micropollutants in eco-engineering systems and identify knowledge gaps. Additional benefits of these systems such as biodiversity contribution or ecosystem services were not included in the survey. At the beginning, the occurrence of micropollutants in WWTP effluent and prioritization efforts are presented (Chapter 2), followed by a chapter on main removal mechanisms in eco-engineered systems. Chapter 4 gives an overview of eco-engineered system types. In Chapter 5, results from existing studies for removal of micropollutants are presented with focus on full scale systems treating WWTP effluent. Chapter 6 gives conclusions and gaps of knowledge in regard to the objectives of the EcoTreat project.

Chapter 2

Micropollutants

The widespread occurrence of micropollutants such as pharmaceuticals (e.g. analgesics, antibiotics or psychiatric drugs), personal care products (e.g. synthetic musks such as galaxolide), and other organic trace pollutants in municipal wastewater has well been documented (e.g. reviews by Verlicchi et al. 2012 and Deblonde et al. 2011). With advances in chemical analysis of polar organic contaminants in water during the past 10-20 years, more and more groups of compounds were detected and came into focus as 'emerging pollutants' (e.g. corrosion inhibitors, surfactants, biocides; Reemtsma et al. 2006). In the following sections, an overview about occurrence and prioritization efforts for determination of most relevant micropollutants is given.

2.1 Occurrence

One important group of micropollutants which have obtained increasing attention over the past decade are pharmaceuticals. Pharmaceutical compounds are usually grouped into different classes based on their application. Important classes are

- analgesics and anti-inflammatories (e.g. diclofenac, naproxen)
- antibiotics (e.g. sulfamethoxazole)
- beta blocker (e.g. metoprolol)
- lipid regulators (e.g. bezafibrate) and
- psychiatric drugs such as anti-epileptics (e.g. carbamazepine).

In Table 1, the occurrence of pharmaceuticals often detected in WWTP effluent as published in 3 recent review studies (integrating results from >250 mostly European WWTP: Verlicchi et al. 2012, Deblonde et al. 2011 and Oulton et al. 2010) and 3 local studies in Berlin (Germany)(Miehe 2010), France (Seriki et al. 2012) and Switzerland (Kase et al. 2011) is summarized. It can be seen that the mean concentration of selected pharmaceuticals range between 0.1 and 4 µg/L, however single measurements can be as high as >50 µg/L (see e.g. Figure 1 for ibuprofen). Whereas some micropollutants exhibit high removal efficiencies in WWTP (e.g. paracetamol, ibuprofen), most compounds are only partially removed during wastewater treatment with some contaminants showing only very low removal (e.g. diclofenac, carbamazepine)(Table 1).

Concentrations of micropollutants in WWTP effluent can vary both between countries (e.g.: see differences of mean effluent concentrations of diclofenac and sulfamethoxazole in Berlin and France) and over time. Differences in effluent concentrations can also be attributed to differences in usages between countries (e.g. diclofenac: usage of 10 t in France versus 92 t in Germany; Table 1). Ranges for variability of micropollutant concentrations in secondary effluent is illustrated in Figure 1, showing concentration ranges of analgesic pharmaceuticals in effluent of 244 mostly European WWTP, ranging from low ng/L until >50µg/L.

Table 1: Pharmaceuticals in WWTP effluent and their removal – mean concentrations from review articles and local studies together with usage and removal data.

					Data from review articles			Local studies		
	Effluent conc [µg/L]	Usage [t] D	Usage [t] F	Removal in WWTP	Verlicchi et al. 2012	Deblonde et al. 2011	Oulton et al. 2010	Kase et al. 2011 (Swiss)	Miehe 2010 (4 Berlin WWTP)	Seriki et al. 2012 (5 French WWTP)
Analgesics	Diclofenac	92	9.9	0-38%	0.8	0.7	0.8	0.6	3.8 (0%)	0.7
	Ibuprofen	780		74-97%	3.6	3.5	3.3	0.4	0.07	
	Paracetamol	565	330	98-99%	0.9		0.5			0.6
	Naproxen	15		74-83%	1.0	0.9		0.46	0.3	
Antibiotics	Sulfamethoxazole	35	17	18-70%	0.3	0.26	0.18	0.24	1.0	0.08
	Clarithromycin	15		29-56%	0.29	0.15	0.39	0.28		1.0
	Erythromycin/H_2O	9		24-57%	0.73	0.24	0.29			0.43
	Ciprofloxacin	33		58-70%	0.86	0.23	0.3			
Beta blocker	Atenolol			38-57%	3.7	0.5		0.84		
	Metoprolol	153	8.8	24-56%	0.32	0.7		0.17		0.14
Lipid regulators	Bezafibrate	15	21	51-61%	0.9	0.8	1.5			0.23
	Gemfibrozil			42-54%	0.9	0.8	0.19			0.15
Antiepileptic	Carbamazepine	64	34	6-18%	1.0	0.77	0.44	0.48	2.3	2.42

Besides pharmaceuticals, other micropollutants are also of relevance in WWTP effluent. These include:

- personal care products (e.g. synthetic musk fragrances such as galaxolide; use in Europe (IFRA, 1998): galaxolide 1473 t),
- corrosion inhibitors (e.g. benzotriazole: high concentrations in WWTP effluent: 13.5 µg/L in Berlin; Miehe 2010)
- Contrast media (e.g. iopromide, high concentrations often >1µg/L, esp. in hospital influenced wastewater; low removal in WWTP, but low ecotoxicity)
- Estrogens (e.g. 17α-ethinylestradiol or EE2, low concentrations in low ng/L-range but very low effect concentrations (PNEC value: 0.01 ng/L; Bergmann et al. 2011)
- Pesticides (e.g. mecoprop, diazinon – in urban areas e.g. from wash-off of surfaces of domestic or public use, in rural areas from agricultural runoff)
- Phthalates (e.g. DEHP: high concentrations in WWTP effluent: e.g. 3.9 µg/L in review of Deblonde et al. 2011)
- Heavy metals (e.g. Zn and Cu; however, often only organic compounds are considered as micropollutants)

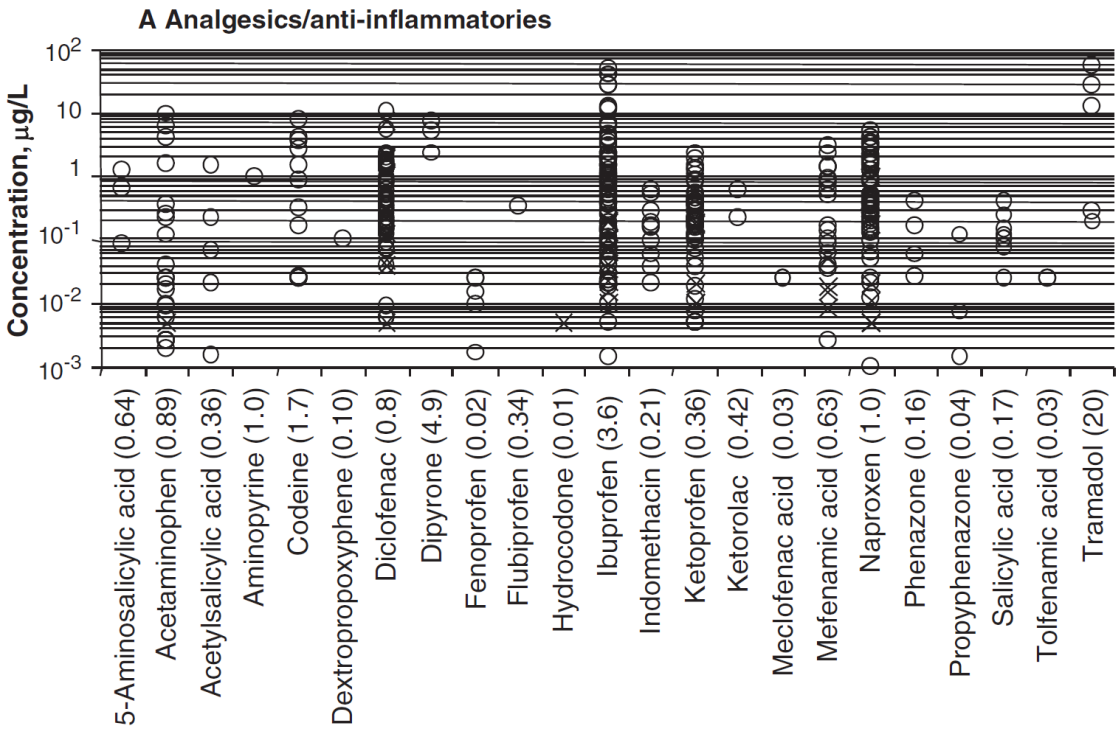

Figure 1: Concentration of selected analgesics/anti-inflammatories measured in the secondary effluent of 244 mostly European WWTP (from Verlicchi et al. 2012).

As WWTP effluent is usually discharged to receiving water bodies, micropollutants have also been detected in surface waters. Due to dilution effects, concentrations in surface waters are roughly about one order of magnitude below effluent concentrations (depending on mixing ratio). Concentrations in Swiss WWTP effluents and surface waters are exemplarily shown in Table 2.

Table 2: Average concentrations in WWTP effluent vs. surface water in Switzerland (from Micropoll database, Kase et al. 2011)

Compound		**WWTP Effluent** [µg/L]	**Surface water** [µg/L]
Diclofenac	Analgesic	1.2	0.15
Ibuprofen	Analgesic	1.4	0.04
Carbamazepine	Psychiatric drug	0.8	0.04
Atenolol	Beta blocker	1.2	0.28
Clarithromycin	Antibiotic	0.5	0.07
Sulfamethoxazole	Antibiotic	0.24	0.06
Mecoprop	Pesticide	0.42	0.045
Diazinon	Pesticide	0.17	0.015
Bisphenol A	Industrial chemical	0.84	0.33
Benzotriazole	Industrial chemical	17.3	3.0

2.2 Prioritization

The environmental risk posed by the presence of micropollutants in water is still under discussion. Toxicity studies have been performed for a variety of micropollutants, however usually in single-compound-single-organism studies that do not consider mixture effects. Furthermore, more toxicity studies exist on acute rather than chronic effects (Verlicchi et al. 2012).

One concept for prioritization of micropollutants is the assessment of their eco-toxicity in relation to occurrence. In this concept a concentration is defined, below which exposure to a substance is not expected to cause adverse effects by aquatic organism (Predicted No-Effect Concentration – PNEC). Different approaches exist how to determine the PNEC value for a specific compound (European_Commission 2003). In a common approach, the lowest known concentration resulting in an ecotoxic effect is determined from toxicity studies and divided by a safety factor to take into account the effect on other, potentially more sensitive aquatic species to those used in toxicity studies (Verlicchi et al. 2012). This safety factor typically varies between 10 (long-term toxicity data available for three species of three trophic levels) and 1.000 (at least one short-term test from each of three trophic levels) depending on the extent of studies and number of trophic levels investigated (European_Commission 2003). If for a specific micropollutant the measured environmental concentration (MEC) is higher than the PNEC, there is a high risk for eco-toxic effects on aquatic organisms and subsequent adverse effects on the ecosystem. Other criteria that can be taken into account for prioritization include the volume of production and the PBT (persistence, bioaccumulation, toxicity) criteria (European_Commission 2003).

In an extensive study by the IWW Water Centre, MEC/PNEC ratios were determined for 70 pharmaceuticals (Bergmann et al. 2011). MEC/PNEC ratios >1 were determined e.g.

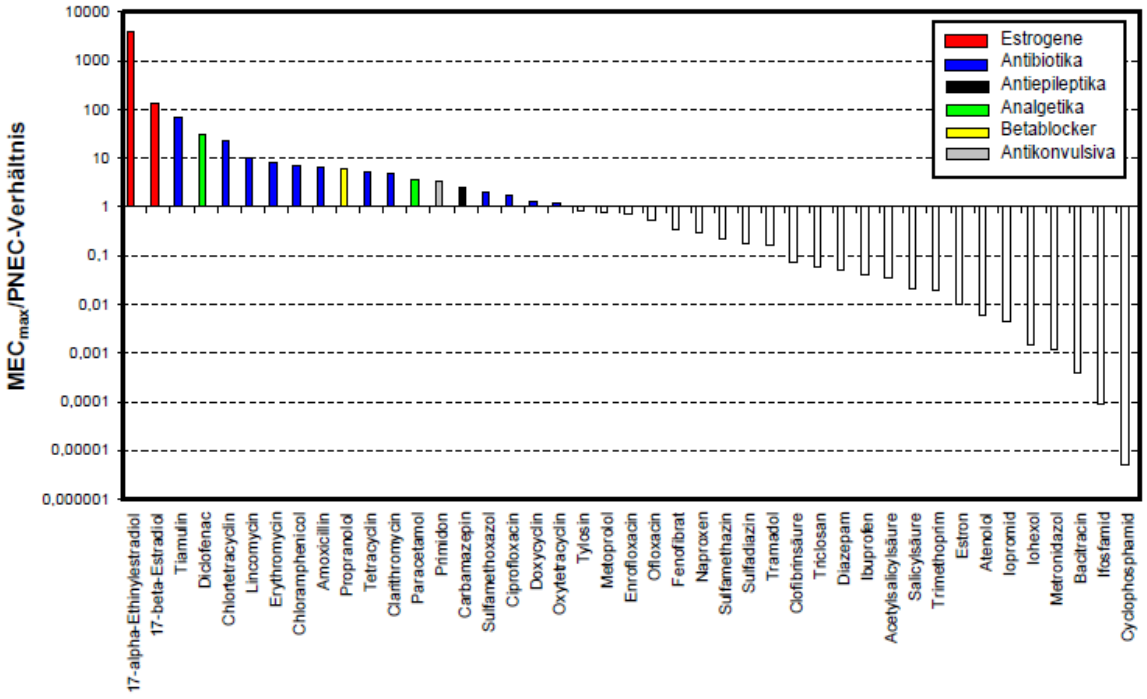

Figure 2: MEC/PNEC ratios for pharmaceuticals with good eco-toxic data basis (from Bergmann et al. 2011).

name	group	dw	gw	sw	MEC/PNEC-ratio	consumption [t]	consumption: evolution 2002-2009
17α-Ethinylestradiol	Estrogene	+	+	+	3800	< 5	?
Diclofenac	Analgetika	+	+++	+++	31,0	92	→
Amoxicillin	Antibiotika	<BG	++	++	6,4	142	↑
Clarithromycin	Antibiotika	<BG	+	++	4,9	15	↑↑
Carbamazepin	Antiepileptika	+	+++	+++	2,4	64	↓
Sulfamethoxazol	Antibiotika	+	++	+++	1,9	35	↓
Ciprofloxacin	Antibiotika	<BG	<BG	+	1,7	33	↑↑
Metoprolol	Betablocker	<BG	++	+++	0,8	153	↑
Naproxen	Analgetika	++	++	++	0,3	15	↑↑
Iomeprol	Kontrastmittel	+	+	+++	<<1	176	↑↑

dw: drinking water; gw: groundwater; sw: surface water; Iomeprol as indicator

Figure 3: Top 10 list of pharmaceuticals suggested by IWW for monitoring programmes in aquatic environment (Bergmann et al. 2011).

for 17α-ethinylestradiol, diclofenac and sulfamethoxazole (Figure 2). Further prioritization included the assessment of the evolution of consumption rates as well as occurrence in surface water, ground water and drinking water. Resulting list suggesting the top 10 compounds is shown in Figure 3.

A proposal for environmental quality standards (EQS) was derived by the Swiss Centre for Applied Ecotoxicology, giving concentrations for maximum acute concentrations (MAC-EQS) and average annual concentrations (AA-EQS, long-term effect) proposed for 44 pharmaceuticals, pesticides and industrial chemicals, e.g. giving maximum AA-EQS concentrations of 0.05 µg/L for diclofenac, 0.4 ng/L for ethinylestradiol and 0.02 µg/L for diuron (see Appendix D for complete list).

At EU level, the inclusion of diclofenac and the two hormones 17α-ethinylestradiol and 17ß-estradiol into the list of priority substances and setting of environmental quality standards (EQS) was proposed and intensively discussed. As in the new directive published in August 2013, the three substances were included into a new watchlist to gather more monitoring data to support future prioritisation. Other compounds such as pesticides (e.g. terbutryn or diuron) or industrial chemicals (e.g. nonylphenol, DEHP or PFOS) are already included in the EU priority list with environmental quality standards often <1 µg/L. This shows that micropollutants are also in focus on European level. Prioritization of micropollutants on EU level is pursued in several EU research projects, for example in the NORMAN network (working group 1).

Chapter 3

Mechanisms for removal of pollutants in eco-engineered systems

In natural treatment systems, physical, chemical and biological processes interact during attenuation of organic chemicals, including microbial biodegradation, sorption and sedimentation, photodegradation, plant uptake and metabolism, and volatilization (Figure 4). This chapter gives an overview of these mechanism and findings regarding their relevance in eco-engineered systems.

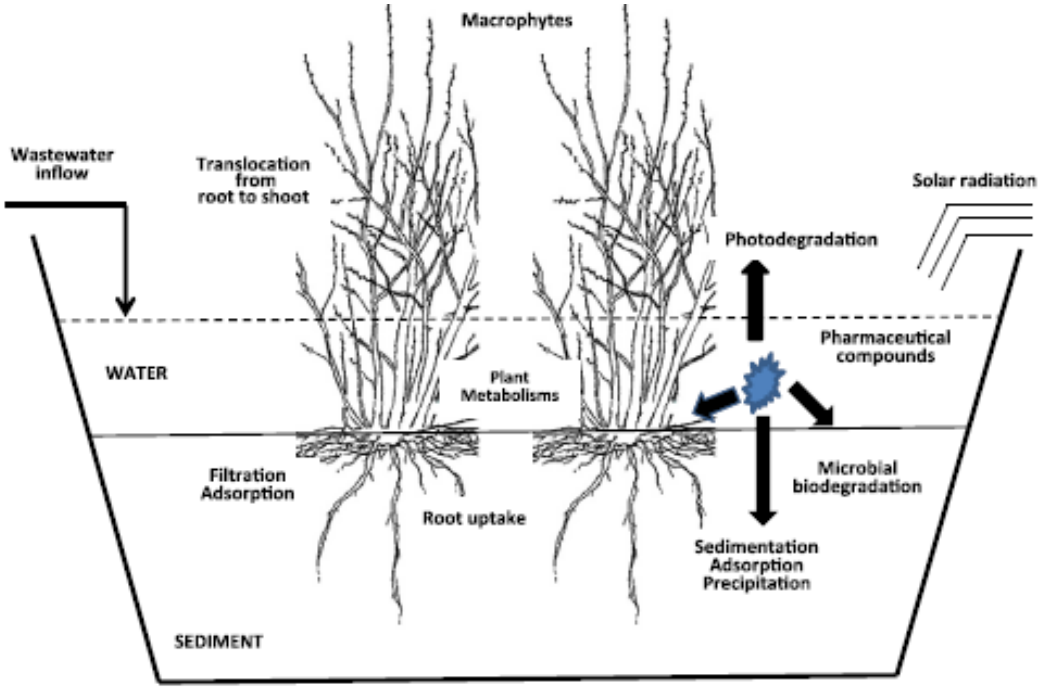

Figure 4: Removal mechanisms for micropollutants in natural treatment systems (from Zhang et al. 2013).

3.1 Biodegradation

Microbial biodegradation is an important removal mechanism in eco-engineered systems that takes place in microbial biofilms attached to surfaces of the system (e.g. roots or substrate of subsurface systems). During biodegradation, micropollutants may undergo i) mineralization, ii) transformation to more hydrophobic metabolites which partition onto the solid phase and iii) transformation into more hydrophilic metabolites that remain in the liquid phase (Zhang et al. 2013). Although metabolites of some micropollutants are known (e.g. Dihydroxy-carbamazepine or Hydroxy-ibuprofene), knowledge of metabolites during microbial degradation of micropollutants is still poorly understood for many compounds. However, knowledge of main metabolites is important as their eco-toxicity can also increase during biodegradation and toxicity studies need to include the investigation of metabolite toxicity. Assays determining the overall toxicity of water in contrast to single compound studies may help to assess the potential of increased ecotoxicity caused by metabolites.

Several factors influence microbial degradation in natural treatment systems:

- **Chemical structure** of the pollutant: the extent of microbial degradation of micropollutants within constructed wetlands is expected to strongly depend on the physico-chemical properties of the contaminant, and biodegradability (or recalcitrance) may often be explained by their chemical structure (e.g. functional groups)(Imfeld et al. 2009). Therefore, not every compound in natural treatment systems can be degraded. Examples for recalcitrant compounds with poor biodegradation are carbamazepine and the flame retardant TCEP.
- **Temperature**: as microbial metabolism depends on temperature, temperature plays an important role for biodegradation. Microorganisms living in constructed wetlands usually reach their optimal activity at warm temperatures (15-25°C), especially nitrifying and protein-degrading bacteria (Hijosa-Valsero et al. 2010). In contrast, decreasing temperature slows down microbial processes resulting in reduced biodegradation during winter, especially in moderate climates.
- **Redox-conditions**: the prevailing redox conditions influence, which microbial pathways can take place. High redox potentials induce aerobic metabolic pathways whereas low redox conditions favour anoxic or anaerobic pathways. For example, reductive dechlorination (relevant pathway for degradation of chlorinated micropollutants such as diclofenac, triclosan or chlorinated pesticides like lindane) requires anoxic or anaerobic conditions that prevail in subsurface wetlands (Matamoros et al. 2007). In a study on removal of pharmaceuticals in seven mesocosm-scale wetlands, aerobic pathways (high redox) were suggested for ibuprofen, diclofenac and salicylic acid, whereas degradation of galaxolide and tonalide was favoured at low redox conditions (Hijosa-Valsero et al. 2010).

  Table 3: Redox conditions reported for degradation of selected micropollutants and degradation rate constant k_{biol} for removal in WWTP (from Verlicchi et al. 2012).

aerobic degradation	**k_{biol}** [L/g/d]	**anoxic/anaerobic degradation**	**k_{biol}** [L/g/d]
Ibuprofen	1.5-35	sulfamethoxazole	0.3
naproxen	<0.2-9	naproxen	
17α-ethinylestradiol	0.4-20	chlorinated pesticides (e.g. lindane)	
salicylic acid		bisphenol A	
diuron		galaxolide, tonalide	
nonylphenol			

  For some compounds, both aerobic and anaerobic degradation has been reported (e.g. naproxen – see table Table 3).

- **Availability of surfaces** for biofilm growth: systems with larger surface areas (e.g. roots of floating islands) promote biofilm growth and hence the potential for microbial degradation.

Biodegradability can be quantified by the biodegradation rate constant k_{biol}. However, values for k_{biol} for micropollutants are scarce and the variability of reported values is high (see Table 3). Furthermore, results are only valid for the investigated system (mostly WWTP), as the extent of biodegradation depends on the prevailing conditions (e.g. redox – see above). Generally, biodegradation rates are higher for aerobic conditions, as the energy gain for bacteria is higher.

3.2 Photodegradation

Photodegradation, the degradation of contaminants by exposition to solar radiation, is an important and predominant removal mechanism for certain pharmaceuticals (e.g. diclofenac) and other micropollutants (e.g. triclosan) in the aquatic environment (Blough and Sulzberger 2003, Buser et al. 1998, Andreozzi et al. 2003). During photodegradation, aromatic rings, heteroatoms, and other functional groups absorb solar radiation which results in transformation of the compound into metabolites. In subsequent steps, metabolites can be further transformed by photolytic degradation into more biodegradable compounds (see Figure 5 for photodegradation pathway of ketoprofen and diclofenac).

The absorbance spectrum of a micropollutant and the quantum yield of photolysis in the water matrix are considered as important factors affecting photodegradation (Zhang et al. 2013). As the intensity of the sun varies during the year due to seasonal variation and cloud cover, the extent of potential photodegradation in eco-engineered systems also varies, especially for compounds with longer half-lives.

Photodegradation of micropollutants has been studied at different levels: determination of fundamental photochemistry in lab-scale experiments (e.g. determination of quantum yields and degradation products of single compounds in distilled water with lamp-based sun simulators or batch experiments with real waters such as surface waters or WWTP effluent exposed to sunlight), studies on the fate of micropollutants in surface waters and (to less extent) studies on micropollutant photodegradation in natural treatment systems (Boreen et al. 2003, Fatta-Kassinos et al. 2011).

Photolytic degradation of diclofenac was discovered by investigation of its fate in the Swiss lake Greifensee, resulting in lower diclofenac concentrations in summer than in winter, especially near the lake surface (Buser et al. 1998, Poiger et al. 2001). Subsequent laboratory experiments in lake water confirmed rapid photodegradation of diclofenac when exposed to sunlight (half-lives $t_{½}$=0.2–1.7 h; Poiger et al. 2001).

In more direct experimental studies of the role of photodegradation, Matamoros et al. 2012 evaluated aquatic plants for removing polar micropollutants in a mesocosm experiment and found fast removal of diclofenac and triclosan in unplanted controls, whereas no removal was observed in covered controls, implying photodegradation as

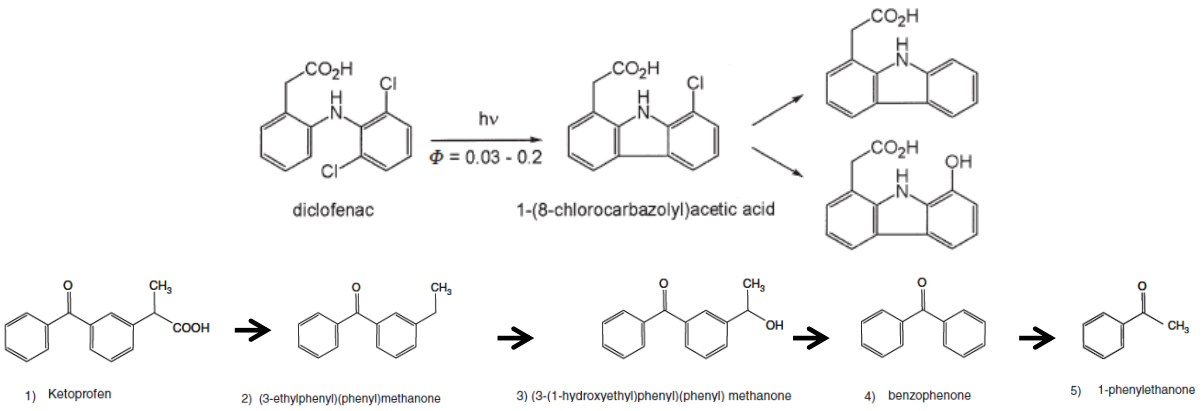

Figure 5: Photodegradation pathways for diclofenac (top, from Boreen et al. 2003) and ketoprofen (bottom, from Matamoros et al. 2009).

Table 4: Half-lives of selected pharmaceuticals, for which photodegradation is considered as a relevant mechanism.

Compound	$t_{½}$ [d]
Diclofenac	0.1 – 3
Sulfamethoxazole	0.1 – 2.4
Ketoprofen	< 0.1
EE2	4.4
Paracetamol	1.5 – 2.3
Triclosan	3
Lorazepam	< 1
Carbamazepine	0.3 – 88

most relevant removal mechanism. Similarly, photodegradation of diclofenac was shown by Zhang et al. 2012 in phytoremediation experiments at mesocosm scale as highest removal of diclofenac was shown in the unplanted controls.

Results of studies considered in this report are summarized in Appendix B. Selected pharmaceuticals with half-lives < 5d (relevant time-frame for eco-engineered systems) are listed in Table 4. At these time scales, photodegradation is a relevant removal mechanism for a number of compounds. Therefore, photolytic half-lives should be considered for the design of eco-engineered treatment systems. It has to be noted, though, that for some compounds (e.g. carbamazepine) results vary considerably. As for biodegradation, metabolites can be formed that could exhibit an increased ecotoxicity than the parent compound. This has been shown, for example, for triclosan photolysis that results in a (minor) formation of 2,8-dichlorodibenzo-p-dioxin, a potentially more harmful compound from environmental perspective (Boreen et al. 2003). This demonstrates the importance for more research that is necessary for identification of relevant metabolites formed by photodegradation of micropollutants under natural conditions.

3.3 Adsorption

Adsorption of dissolved organic contaminants to the substrate (soil, organic carbon, mineral surfaces and biofilms coating the gravel bed) can be a significant mechanism for their removal (Kadlec and Knight 1996). Furthermore, adsorption to suspended particles and subsequent sedimentation can also occur (see 3.6). As adsorption influences the distribution of substances between aqueous phase and solid surfaces, the fate of pharmaceuticals and other micropollutants in constructed wetlands can be strongly influenced by their adsorption (Bui and Choi 2010). Therefore, specific materials such as zeolites can be added to the substrate to increase the adsorption capacity of subsurface systems. The ability to estimate the adsorption of a pharmaceutical compound to solids is thus important for understanding its fate in eco-engineered treatment systems.

To evaluate the sorption behaviour of organic compounds in soils and sediments, the linear sorption coefficient (K_d) (L kg^{-1}) is often used to model sorption of contaminants in sediment and soils (Schwarzenbach et al. 2003). According to Ternes et al. 2004, log K_d < 2.7 implies poor capacity for sorption onto solids. However, since there are a

variety of mechanisms for sorption of pharmaceuticals onto both organic and inorganic solids in treatment processes, prediction of K_d is complex (Zhang et al. 2013). Additionally, the organic carbon partition coefficient (Koc) is also a reasonable parameter to use, and is defined as the ratio of contaminant mass adsorbed per unit weight of organic carbon in soil or sediment to the concentration in solution (Grathwohl 1990). Substances with Koc below 500-1000 L/Kg are generally unlikely to adsorb to sediment (SETAC, 1993). To avoid extensive testing of chemicals, a log Koc >= 3 can be used as a trigger value for sediment effect assessment (European_Commission 2003).

In studies on the fate of micropollutants in constructed wetlands, accumulation in substrate has not been found as a major pathway for most compounds, however some compounds were detected in sediment. In particular, hydrophobic fragrances with high log Kow values (e.g., galaxolide, tonalide; log Kow=5.7-5.9) were retained in CWs up to 25% by adsorption processes (Matamoros and Bayona 2006; Matamoros et al. 2008, Hijosa-Valsero et al. 2010). In addition, up to 20% of pesticides were found in the gravel bed of a pilot HSSF CW treating raw wastewater (injection experiment): pentachloro-phenol, pentachlorobenzene (~20%, log Kow=5.1), lindane (14%, log Kow=4.4) and chlopyriphos (7%, log Kow=5.0)(Matamoros et al. 2007).

No/minor accumulation (<3%) in wetland sediment was found for ibuprofen, naproxen, diclofenac, ketoprofen, carbamazepine, atenolol, sulfamethoxazole, triclosan, mecoprop, diuron, lindane, simazine and alachlor.

As adsorption is an exothermic process, it is favoured by low temperatures (unless biodegradation).

3.4 Plant uptake and phytodegradation

To date, only a few studies investigated the ability of plants to assimilate and translocate micropollutants, and available data on plant uptake is limited to only a few pharmaceutical compounds and plant species. Additionally, most studies on plant uptake of pharmaceuticals have been done in hydroponic solutions, rather in actual field-scale research, and the basic mechanisms involved in plant uptake of pharmaceuticals remain poorly understood (Redshaw et al. 2008).

Table 5: Removal of pharmaceuticals by plant uptake (for references more information see Appendix C).

Compound	Plant species	Time [d]	Removal [%]
Ibuprofen	Typha spp.	1	58
		2	81
		4	95
	Phragmitis australis	8	60
Naproxen	Scirpus validus	3	83
		7	86
		14	90
Carbamazepine	Typha sp.	7	52
	Scirpus (sedge)	3	53
Diclofenac	Phragmitis australis	8	18

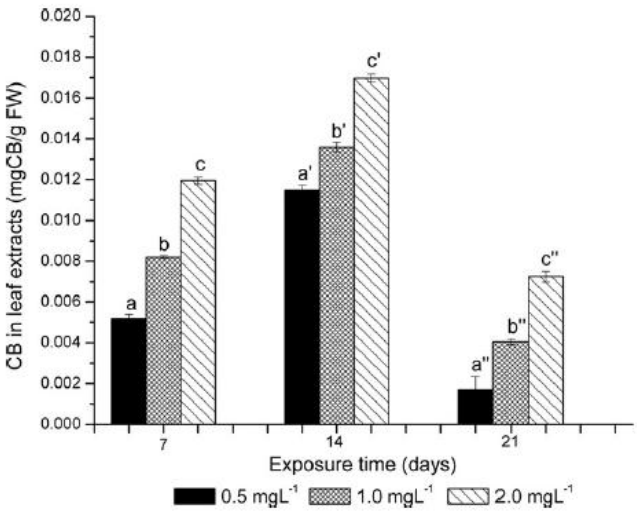

Figure 6: Carbamazepine in leaf extracts of *Typha* spp. after different exposure times as investigated in microcosm experiments (from Dordio et al. 2011).

Following plant uptake, organic pollutants may undergo partial or complete degradation, and plant enzymes may act on micropollutants and either mineralize them completely, or partially into stable intermediates that are stored in the plants (Zhang et al. 2013). Results of studies investigating uptake of pharmaceuticals in microcosm experiments with different plant species in hydroponic solutions (spiked nutrient solutions) are shown in Table 5. It can be seen that ibuprofen, naproxen and carbamazepine could be removed by >50% within a timeframe of 1-7 days under the conditions investigated. Especially the removal of carbamazepine is interesting, as carbamazepine is described as a recalcitrant compound with low removal in WWTP and constructed wetlands. Active uptake of carbamazepine by *Typha* spp. was demonstrated by Dordio et al. 2011 who detected carbamazepine in leaf extracts (Figure 6). In the same study, carbamazepine oxidation within plant tissue appears to be a possible route of metabolism.

It has to be noted, though that conditions of these studies often included high concentrations (e.g. 0.5 mg/L and higher) and substrate-less systems that likely behave differently in comparison to conditions in natural treatment systems (see Appendix C). More research is necessary to evaluate the relevance of micropollutant uptake by plants in full-scale wetland systems (including determination of most effective species) and phytodegradation mechanisms including metabolite formation.

3.5 Volatilization

Volatilization, the transition of a chemical compound from aqueous into the gas phase, is a relevant removal mechanism for volatile organic compounds (VOC) such as benzene. In constructed wetlands, volatilization can be enhanced through plants (phyto-volatilization), as has been shown, for example, in a study on treatment of groundwater contaminated with benzene and MTBE (Reiche et al. 2010).

However, as volatile compounds are usually removed during treatment in WWTP (e.g. stripped out during activated sludge treatment) or in the sewer network, volatilization as removal mechanism only plays a minor role for most micropollutants in WWTP effluent.

Nevertheless, for some semi-volatile compounds (e.g. nonylphenol), volatilization might contribute to reduction in systems with large air/water interfaces (open water surfaces) to a certain extent. However, no studies have been found on the extent of volatilization regarding the removal of micropollutants in WWTP effluent with natural treatment systems.

3.6 Sedimentation/filtration

Sedimentation and filtration are the main removal mechanisms for particles. For sedimentation, low flow conditions are required for removal of fine particles. In contrast to sedimentation, filtration is also relevant for removal of pathogens (e.g. in soil layer of subsurface wetlands). As particle separation processes are implemented at wastewater treatment plants (e.g. sedimentation in clarifier), suspended solid concentrations are already low (e.g. average TSS concentration in effluent of all Berlin WWTP: 5.1 mg/L; Uldack et al. 2013). Therefore, sedimentation and filtration are less relevant removal mechanisms for further removal of micropollutants in WWTP effluent. However, hydrophobic compounds that are adsorbed to particles that survived particle separation in WWTP could be further reduced by sedimentation and filtration processes in eco-engineered systems. Furthermore, production of organic particles in eco-engineered systems (and subsequent adsorption of hydrophobic contaminants) is also possible. Whereas ponds and free water surface (FWS) wetlands with low flow velocities are beneficial for sedimentation, removal of particles by filtration is relevant in subsurface systems (see Chapter 4).

3.7 Removal mechanisms of individual micropollutants

Due to differences in chemical structure and properties, micropollutants can be reduced with different removal mechanisms described above or combinations of these removal mechanisms. These can be derived from chemical properties (e.g. sorption coefficients) or literature data from investigations of individual mechanisms (e.g. photodegradation studies). By bringing all data together a matrix of compounds and removal mechanisms can be derived as exemplarily shown in Figure 7.

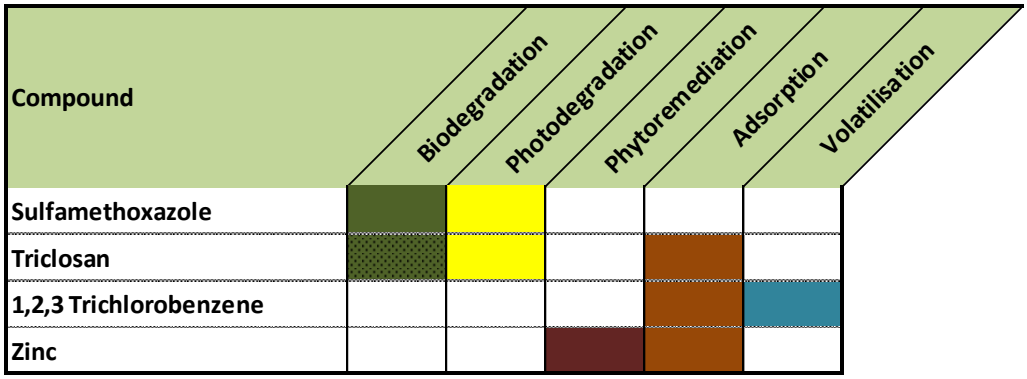

Figure 7: Removal mechanisms of selected micropollutants as derived from chemical properties and literature data.

Chapter 4

Eco-engineered systems

Ecological Engineering is the design of sustainable ecosystems consistent with ecological principles of natural, self-organizing, self-maintaining systems (Mitsch 2012). One of the main advantages of eco-engineered systems is that they are natural systems and thus not require chemicals, energy or high-tech infrastructure for operation. Furthermore, when these natural treatment systems are incorporated into a landscape or building design, they can provide added benefits as compared to a conventional treatment system.

In eco-engineered systems, contaminants are removed through natural processes including bacterial degradation, photolytic degradation, plant uptake chemical adsorption and sedimentation. The goal is to maximize the function of these processes within a limited area. Different systems that are based on the principles of ecological engineering have been developed, often including either submerged or emergent plants. However, to date these systems are not designed to remove micropollutants and rules are missing (including best choice of plant species for removal of micropollutants). In the next sections, main types of eco-engineered systems are introduced.

4.1 Constructed wetlands

The first experiments on the use of wetland plants to treat wastewaters were carried out in the early 1950s by Dr. Käthe Seidel in Germany (Seidel 1953). The first full scale systems were put in operation during the late 1960s and since then constructed wetland systems (also called treatment wetlands) have been spreading throughout the world (Vymazal 2007). Most constructed wetlands around the world are still primarily used to treat municipal and domestic wastewaters, e.g. in areas not connected to a sewer network. However, treatment of many types of agricultural wastewaters (e.g. reduction of nutrients), industrial wastewaters (e.g. acid mine drainage), stormwater runoff (reduction of particles and heavy metals) and landfill leachates has recently become also common.

Treatment wetlands can be constructed in a variety of hydrologic modes. The basic types of constructed wetland systems as classified by Kadlec and Knight (1996) are shown in Figure 8. Wetlands are distinguished according to the water flow regime as surface flow (or free water surface (FWS)) wetlands and horizontal (HF) or vertical flow

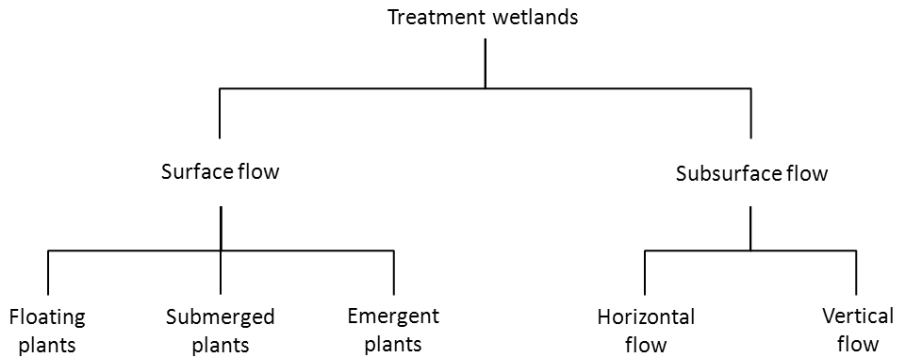

Figure 8: Constructed wetland types (from Kadlec and Knight 1996)

Figure 9: Example of constructed wetland (surface flow wetland in Berlin Hobrechtsfelde, photo taken by author).

(VF) subsurface flow wetlands. However, other classifications of natural treatment systems exist.

These three types of CWs may be combined with each other in hybrid constructed wetlands in order to exploit the specific advantages of the different systems, and are described more detailed in the following sections.

4.1.1 Subsurface flow wetlands

In subsurface flow constructed wetlands (also called planted soil filters) water flows through a filter bed planted witch aquatic plants before being discharged. Two main types are distinguished based on flow modes: horizontal flow or vertical flow.

4.1.1.1 Horizontal flow

Horizontal subsurface flow wetlands (HSSF wetlands) consist of gravel or soil beds

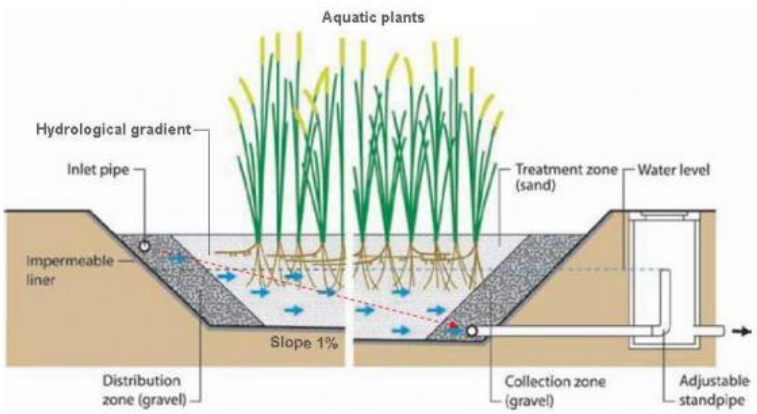

Figure 10: Schematic view of horizontal flow wetland (from Morel and Diener 2006)

planted with wetland vegetation (e.g. *Phragmitis australis*). The wastewater flows slowly through the porous media in a mostly horizontal path until it reaches the outlet zone where it is collected before leaving via level control system (Figure 10). The wastewater is intended to stay beneath the surface of the media and flows in and around the roots and rhizomes of the plants. During this passage the water will come into contact with a variety of aerobic, anoxic and anaerobic zones (mainly anoxic due to limited entry of oxygen into water). HSSF are commonly used for secondary treatment for single-family homes or small communities, however, there are many other applications to specialty wastewaters from industry (Kadlec and Knight 1996).

4.1.1.2 Vertical flow

In a vertical flow (VF) constructed wetland the wastewater is distributed over the surface and then drains vertically down through the filter layers towards a drainage system at the bottom (Figure 11). Typically, the water is applied intermittently (either by pump or self-acting syphon device) in short-term loading intervals (4 to 12 doses per day) and long resting periods during which the wastewater percolates through the unsaturated substrate, and the surface dries out. The intermittent batch loading enhances the oxygen transfer and leads to high aerobic degradation activities e.g. for oxidation of ammonia (Hoffmann et al. 2011), thus producing a nitrified effluent. However, it is also possible to operate VF wetlands with continuous flow and a constant water level above the bed. This variation of VF wetlands relies upon the opposite process: the use of overlying water blocks oxygen transport in order to create anaerobic conditions in the bottom bed sediments that fosters appropriate sulfur chemistry to immobilize metals and facilitate anaerobic degradation pathways (Kadlec and Knight 1996).

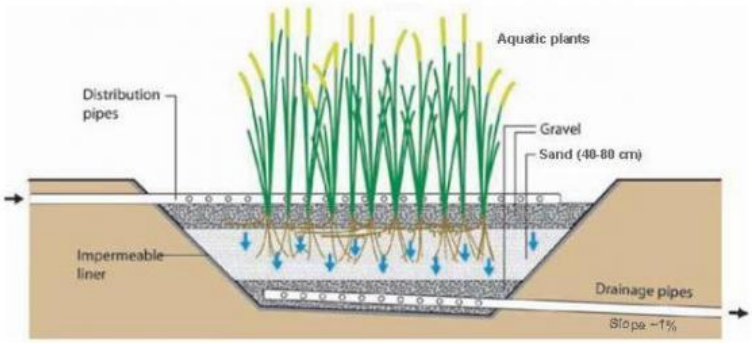

Figure 11: Schematic view of vertical flow wetland (from Morel and Diener 2006)

4.1.2 Surface flow or free water surface (FWS) wetlands

A typical free water surface (FWS) constructed wetland is a shallow sealed basin or sequence of basins, containing 20-30 cm of rooting soil, with a water depth of 20-40 cm (Figure 12).

One of their primary design purposes is to contact the wastewater with reactive biological surfaces (Kadlec and Knight 1996). Dense emergent vegetation covers significant fraction of the surface, usually more than 50% and is planted in a way that the flow is directed to proceed all parts of the wetland for high hydraulic efficiency (Vymazal 2007). The most commonly used species for FWS wetlands *Phragmitis* spp.

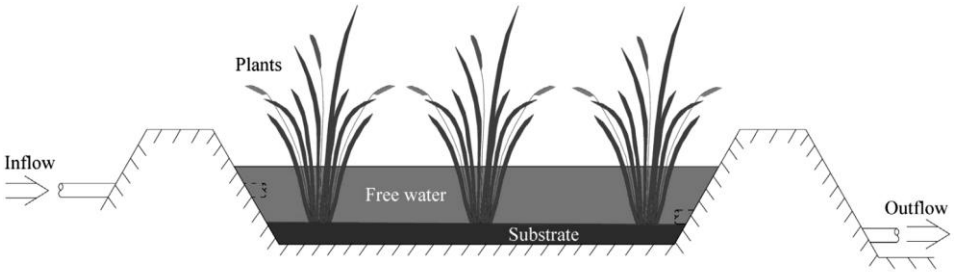

Figure 12: Schematic view of free water surface (FWS) constructed wetland (from Li et al. 2014).

(Common reed), *Typha* spp. (Cattail), *Scirpus* spp. (Bulrush) *Sagittaria* spp. (Arrowhead) (Vymazal 2007).

A special form of free water surface wetlands are long and narrow spiral or meander shaped wetlands that are planted at the banks. Main reason is to optimize flow conditions (e.g. reduction of preferential flows) and increase hydraulic efficiency. An example of a spiral-shaped wetland that is part of a series of wetlands constructed on a former sewage field in the northern part of Berlin can be seen in Figure 13.

Figure 13: Spiral-shaped FWS wetland in Berlin-Hobrechtsfelde – left: top view (source: Google Maps), right: outer part of spirale wetland (photo taken by author).

4.2 Treatment ponds

Treatment ponds were originally developed and are still mostly applied for treatment of raw wastewater (also named as wastewater stabilization ponds). The main difference to free water surface wetlands is the lack of vegetation and higher water depth. Three types are distinguished: anaerobic, facultative and aerobic ponds (Tilley et al. 2008). Anaerobic treatment ponds are deep ponds (2 to 5 m, typical HRT: 1-5d) devoid of dissolved oxygen, where sludge is deposited on the bottom and anaerobic bacteria break down the organic matter by anaerobic digestion (BOD removal), releasing methane and carbon dioxide. Facultative treatment ponds consist of large shallow ponds (depth of 1 to 2 m, typical HRT: 5-30d) with an upper aerobic layer (receiving oxygen from natural diffusion, wind mixing and algae-driven photosynthesis) and a deeper anoxic or anaerobic zone. Aerobic treatment ponds (or maturation or polishing ponds) are the shallowest of the ponds (typical HRT: 15-20d), usually constructed to a depth between 0.5 to 1.5 m to ensure that the sunlight penetrates the full depth (Tilley et al.

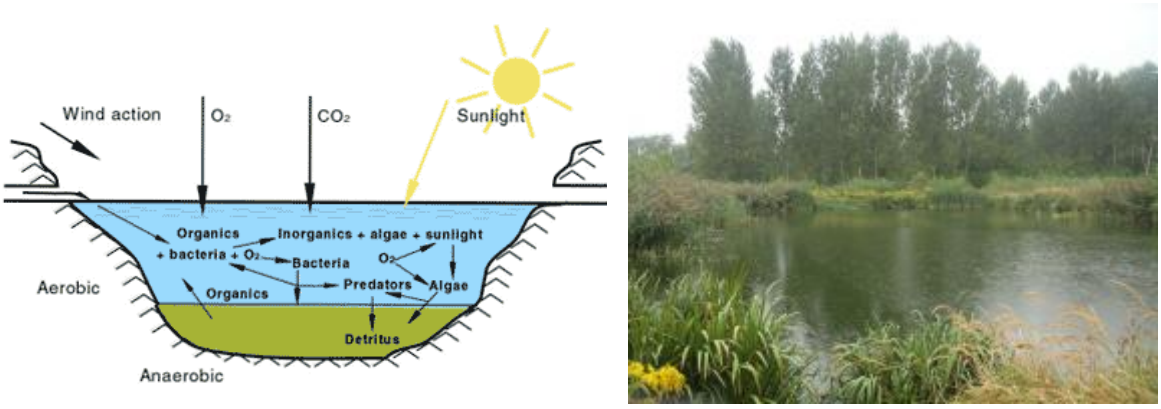

Figure 14: Schematic of facultative treatment pond (left, from Seriki et al. 2012) and example of polishing pond for further treatment of WWTP effluent in Hobrechtsfelde (taken by author).

2008). They are essentially designed for pathogen removal and retaining suspended stabilised solids.

For treatment of WWTP effluent, mainly shallower aerobic ponds are of relevance, as BOD is already removed in preceding WWTP. As treatment ponds are not planted and therefore have large open water surfaces, photodegradation and solar disinfection are important mechanism for removal of micropollutants and reduction of pathogens.

As with FWS wetlands, ponds can be designed in various shapes, also to optimize flow conditions (e.g. reduction of preferential flows) and increase hydraulic efficiency. Examples are meander-shaped ponds, in which the water is forced to follow a predefined path (see Figure 15).

Figure 15: Meander-shaped pond receiving effluent of WWTP Brunswick (from Abwasserverband_Braunschweig 2008).

4.3 Floating islands

Artificial floating islands as treatment systems are a quite recent development within the last 1-2 decades. Floating islands consist of emergent wetland vegetation growing on a mat or structure floating on the surface of a body of water (pond). Whereas the plant stems remain above the water level, their roots grow down through the buoyant structure and into the water column (Figure 16). In this way, the plants grow in a hydroponic manner, taking their nutrition directly from the water column which enhances potential rates of nutrient and element uptake into biomass. Beneath the floating mat, a hanging network of roots, rhizomes and attached biofilm is formed. This hanging root/biofilm network provides an active surface area for biochemical processes,

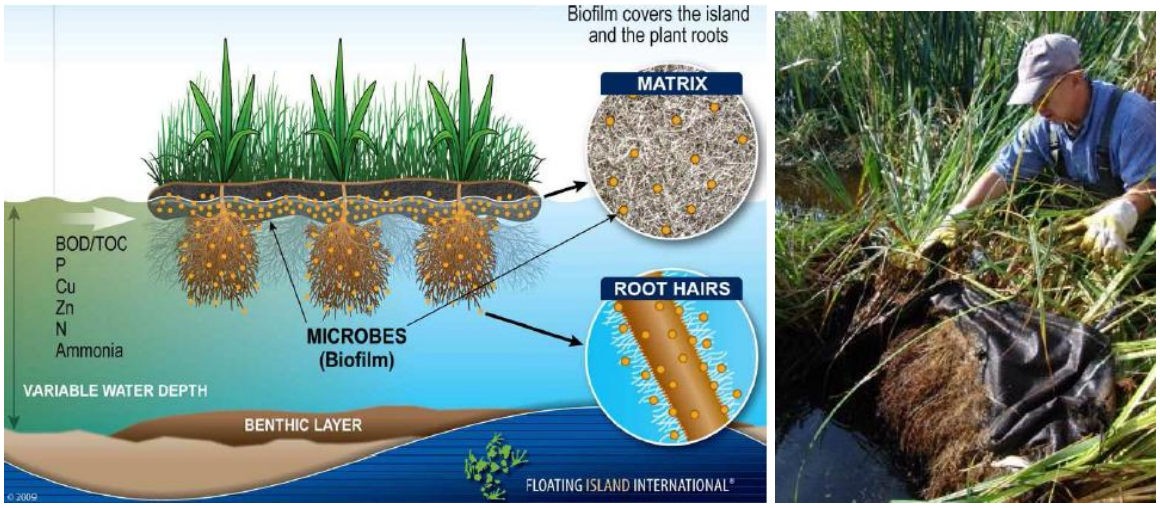

Figure 16: Left: Schematic view and principle of floating islands as water treatment system (from Biohaven 2011); Right; Floating island roots (from Barjenbruch and Rühmland 2009)

as well as physical processes such as filtering and entrapment. Thus, the general design objective of floating islands is to maximize the contact between the root/biofilm network and the polluted water passing through the system (Biohaven 2011).

Furthermore, the floating islands also reduce the open water surface area, which results in the reduction of the oxygen entry from the atmosphere as well as in shading of the water column preventing algal growth and oxygen entry from algae and aqueous plants. Thus, suboxic conditions are typical in ponds covered by floating island promoting anoxic and anaerobic degradation pathways.

4.4 Removal mechanisms in eco-engineered systems

Prevailing removal mechanisms in eco-engineered systems differ depending on system types and designs (Table 6). Whereas photodegradation only take place in systems with open water surfaces, adsorption processes require large surface areas acting as adsorption sites (e.g. in subsurface systems or root surfaces of floating islands). Similarly, microbial degradation is enhanced when large surface areas for biofilm growth are available. Table 6 gives an overview of prevailing removal mechanisms different eco-engineered system types.

Table 6: Main removal mechanisms in different types of natural treatment systems

Type	Subtype	redox conditions	Removal mechanisms: biodegra-dation	photodegra-dation	adsorption	sedimen-tation	filtration	Phyto-degradation	design considerations
Constructed wetlands	free water surface (FWS) wetlands (possible in different shapes, e.g. spiral or meander)	mainly **aerobic** with anoxic areas in substrate/soil	**(+)**	**+** (in open water areas)	–	**+**	–	**(+)** depending on planting)	- water depth: ~ 20-50 cm
	subsurface horizontal flow (HF) wetlands	mainly **anoxic,** but gradients of redox conditions present	**+**	–	**+**	–	**+**	**+**	- substrate depth usually 0.5-1m
	subsurface vertical flow (VF) wetlands	mainly **anoxic** with continuous flow, more oxic with intermittend flow	**+**	–	**+**	–	**+**	**+**	- substrate depth usually 0.5-1m
Treatment ponds	aerobic ponds (shallow: 0.5-1.5m), also in meander shape	mainly **aerobic** (O_2 from water surface and aquatic plants)	**(+)** (until now mainly applied for BOD reduction)	**+**	–	**+**	–	–	- water depth: 0.5-1.5 m
	facultative and anaerobic pond (up to 5m deep)	anoxic/anaerobic		**(+)** (only in upper layer)	–	**+**	–	–	- depth: 1-2.5m (facultative), 2-5m (anaerob)
Floating islands		mainly anoxic / anaerob conditions	**+**	–	**+**	**+**	**(+)** (through roots)	**+**	- water depth: ~ 1-2 m

Chapter 5

Existing experience on treatment performance of eco-engineered systems for removal of micropollutants

There are only few studies on the ability of eco-engineered systems to reduce the concentrations of organic micropollutants in WWTP effluent, mostly for pharmaceuticals and personal care products. Most investigations were done on constructed wetlands, as these eco-engineered systems are the most established system types, mainly applied for treatment of domestic wastewater, acid mine drainage, agricultural runoff, and more increasingly also stormwater (see Chapter 4). Often, systems were designed for removal of nutrients (ammonia, nitrate, phosphorous), with later investigations on the fate of micropollutants in these systems. In a review article, Haarstad et al. 2012 gives an overview on studies with information on the fate of heavy metals and organic pollutants (pesticides, industrial pollutants and pharmaceuticals) in treatment wetlands. The authors find that treatment wetlands are capable for reducing these contaminants with typical removal in the order of 30 to 60% for heavy metals, 50-100% for hydrophobic organic compounds, 40-99% for pesticides (but some compounds with much less removal) and performance of wetland systems of removing pharmaceuticals from wastewater being similar to that obtained in conventional activated sludge WWTP.

This chapter concentrates on information regarding the removal of pharmaceuticals and other organic micropollutants from WWTP effluent. Some results from mesocosm experiments with raw wastewater as influent to the systems have also been included. Heavy metals were usually not in the focus of these studies that concentrate on the behaviour of organic micropollutants in constructed wetlands. A tabulated overview of removal efficiencies of individual contaminants from all considered studies has been compiled in Appendix A.

5.1 Constructed wetlands

5.1.1 Constructed wetlands as secondary treatment systems

Two very recent reviews of studies on constructed wetlands (CW) as alternative secondary wastewater treatment systems for removal of pharmaceuticals from wastewater were published by Li et al. 2014 and Zhang et al. 2013. Reviews included system of different sizes (from microcosm-scale to full scale), however, most studies were on mesocosm-scale systems (0.5-5m²). Horizontal subsurface flow constructed wetlands have been the most frequently employed constructed wetland system type, although vertical subsurface flow CWs and hybrid CWs have also shown good removal efficiencies for pharmaceuticals in some studies (Zhang et al. 2013). Furthermore, it is worthwhile noticing that CW systems treating raw wastewater can offer removal efficiencies for many pharmaceuticals as good or even better compared to conventional WWTP (Figure 17).

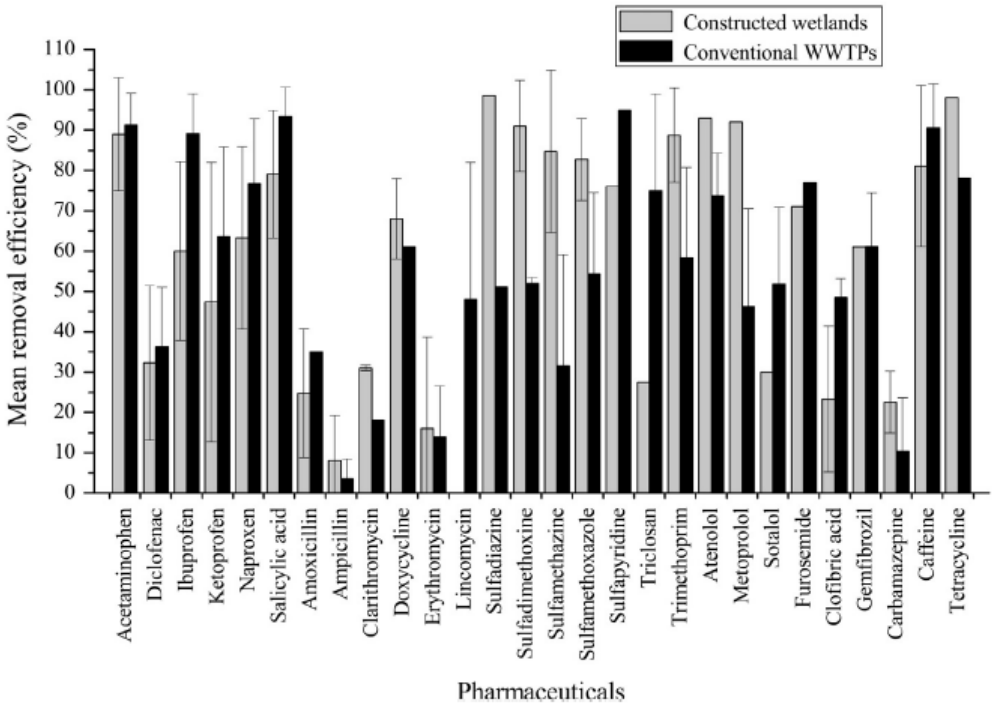

Figure 17: Comparison between mean removal efficiencies for pharmaceuticals in constructed wetlands and conventional WWTPs for raw wastewater (from Li et al. 2014).

5.1.2 Full scale systems as tertiary treatment

In the following subsections, five studies are presented that investigated full scale constructed wetland systems (all being FWS wetlands) regarding the behaviour of micropollutants (mainly pharmaceuticals) with one, the "Zone Libellule©" being a treatment train of five wetland systems in series.

5.1.2.1 Surface flow wetland Can Cabanyes

The Can Cabanyes surface flow constructed wetland (SFCW) is located in northeastern Spain and was created as part of a series of activities aimed at restoring a highly impacted fluvial peri-urban zone with a main objective to reduce ammonium concentrations (Llorens et al. 2009). It is a single cell system with an elongated shape and a surface area of 1 ha (maximum length and width of around 189 m and 53 m, respectively), with unplanted deep zones (water depth 1.5 m) and shallow zones (0.3-0.4 m) planted with *Phragmitis australis* and *Typha latifolia* (see Figure 18). It is in operation since 2003, treating approximately 100 m^3/d of secondary effluent from Granollers WWTP (0.4% of total discharge volume), operating with a high hydraulic retention time of 30 days and hydraulic loading rate of 1 cm/day.

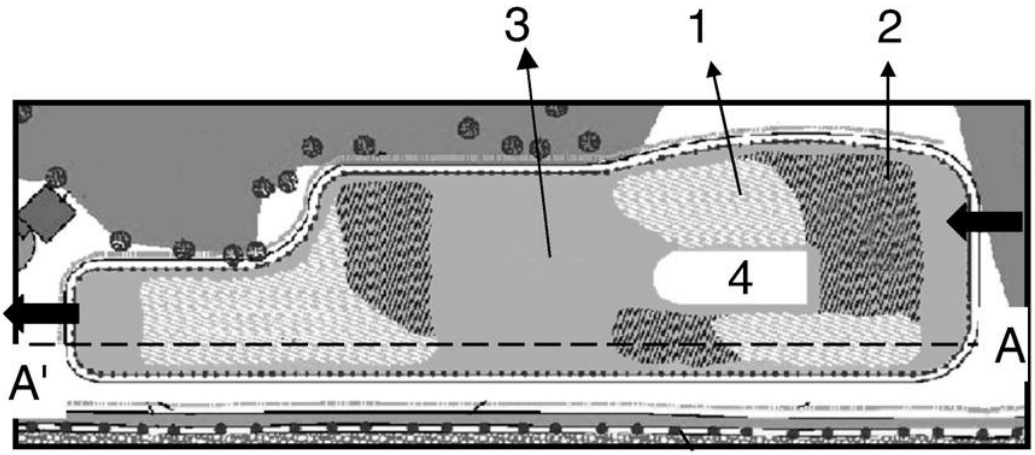

Figure 18: Schematic view of Can Cabanyes SF CW. (1) zone planted with *Phragmitis australis*; (2) zone planted with *Typha latifolia*; (3) deep zone free of macrophytes; (4) island (from Llorens et al. 2009)

Two sampling campaigns were performed in June 2005 (average air temperature of 20°C) and February 2006 (average air temperature of 7°C) for analysis of selected pharmaceuticals, personal care products and pesticides (Llorens et al. 2009, Matamoros et al. 2008). In another study of the same system, the removal efficiencies of benzotriazoles and benzothiazoles were investigated in 2006/2007, also in winter and summer (Matamoros et al. 2010).

Results of all three studies are summarized in Table 7. It can be seen that almost all contaminants (beside Carbamazepine) are moderately to very well reduced in summer.

Table 7: Inflow concentrations and removal of micropollutants in Can Cabanyes surface flow constructed wetland (HRT=30d) in summer and winter (values of reduction in Appendix A).

	Inflow concen-trations [µg/L]	Removal Summer	Removal winter
Diclofenac	1.3 ± 0.1	++	+
Naproxen	0.3 ± 0.1	++	o
Ketoprofen	2.1 ± 0.7	++	++
Ibuprofen	0.04 ± 0.03	++	++
Carbamazepine	0.4 ± 0.1	-	o
Galaxolide	2.9 ± 0.02	++	++
Tonalide	0.9 ± 0.1	++	++
Mecoprop	7.8 ± 3.2	+	++
MCPA	2.0 ± 1.5	++	+
Benzotriazole (BTri)	1.8 (s) - 4.5 (w)	o	--
Tolyltriazole	9.8 (w)-13.1 (s)	o	-
Benzothiazole (BT)	1.2 (w) - 1.5 (s)	+	--
MTBT	1.7 (w) - 0.6 (s)	o	-
OH-BT	0.5	o	--

removal: ++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

In winter, especially benzothiazoles and benzotriazoles were reduced to much lesser extent, whereas diclofenac, naproxen, and the pesticide MCPA only showed somewhat lower removal efficiencies (see Table 7 and Appendix A). This can be attributed to reduced solar radiation (decrease of photodegradation rates – relevant for diclofenac, naproxen and benzothiazoles) and water temperature (decrease of biodegradation kinetics) in winter. Nevertheless, high reductions for a number of compounds were observed also during cold season (e.g. ketoprofen, ibuprofen, diclofenac, galaxolide). It has to be noted though, that winters in northern Spain are still relatively mild with average minimum temperatures above 5°C (Llorens et al. 2009).

Main facts Can Cabanyes wetland

- System type: partially planted FWS wetland (1ha), treating WWTP effluent
- Location and climate: northern Spain, warm climate
- Long retention time of 30 days (inflow: 100 m^3/d)
- Good removal of most investigated micropollutants, especially in summer
- Also good removal in winter, beside benzothiazoles (BT) and benzotriazoles (BTri)

5.1.2.2 Polishing ponds and surface flow wetland at Empuriabrava

The Empuriabrava polishing ponds and surface flow constructed wetland (located in northeast Spain) receives the entire secondary effluent (mean flow rate: 3700 m^3/d) from the Empuriabrava WWTP that serves a mostly residential area with ca. 67000 inhabitants (Matamoros and Salvado 2012). Secondary effluent is first pumped into 2 parallel polishing ponds (surface area: 2 ha, depth: 1m, residence time: 4d) before entering the SFCW (Figure 19). The SFCW constitutes of three parallel cells (surface area 0.8 ha each; average water depth: 0.5 m) and a large shallow wetland in series (4.5 ha; average depth: 0.2 m) with a total HRT of around 8.5 days. The SFCW is sparsely planted with reed (*Phragmitis australis*) and bulrush (*Typha latifolia*) grouped in independent communities. The system is in operation since 1998 and was designed to reduce ammonium.

Four sampling campaigns were performed in July, November, March and May 2009/2010. Samples were analysed for 27 micropollutants (pharmaceuticals, personal care products, antiseptics, flame retardants, pesticides and plasticizers), of which 18 could be evaluated regarding their behaviour in the pond/SFCW-system. Results (from Matamoros and Salvado 2012) are summarized in Table 8 (see also Appendix A). In summer, most compounds are well reduced (> 70%) by the combined polishing ponds/SFCW system, with the exception of carbamazepine and TCEP. For carbamazepine and diazinone removal increased in winter, which could be an indication for adsorption as one relevant removal mechanism, as extent of adsorption increases with decreasing temperatures. For the other compounds, removal in winter was >60%, however, as for Can Cabanyes it has to be kept in mind that winters in northern Spain are still relatively mild with average minimum temperatures above 5°C.

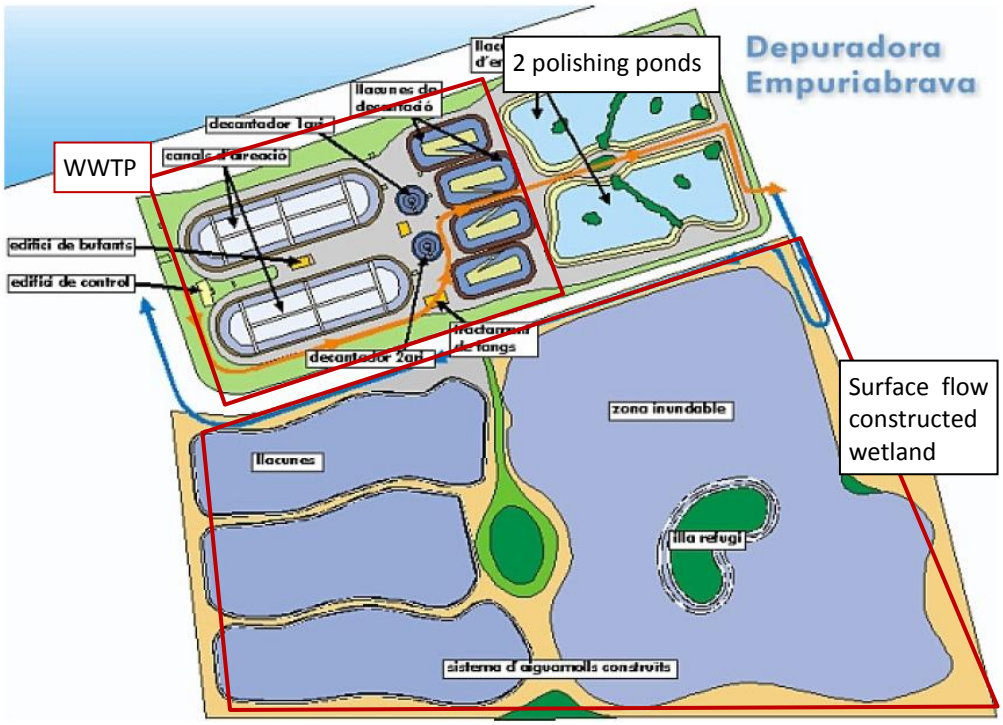

Figure 19: Empuriabrava WWTP with subsequent polishing ponds and surface flow constructed wetland (from Pallarès 2009)

In comparison with the Can Cabanyes Wetland (see 5.1.2.1), removal for the 8 compounds that were investigated in both studies (diclofenac, ketoprofen, naproxen, ibuprofen, carbamazepine, galaxolide, tonalide and MTBT) was similar at Empuriabrava,

Table 8: Inflow concentrations and removal of micropollutants in Empuriabrava polishing ponds (HRT=4d) and surface flow constructed wetland (HRT=8.5d) in summer and winter. Values of reduction can be found in Appendix A. (from Matamoros and Salvado 2012)

	Inflow concen-	Removal Summer	Removal winter
Diclofenac*	0.5 - 1.2	++	++
Ketoprofen*	0.4 - 0.9	++	++
Carbamazepine*	0.2 - 1.3	-	o
Naproxen*	0.4 - 0.6	++	+
Ibuprofen*	0.3 - 0.5	++	++
Cashmeran**	0.1 - 0.25	++	++
Galaxolide**	0.7 - 2.2	++	++
Tonalide**	0.25 - 0.7	++	+
Methyldihydrojasmonate**	0.45 - 0.65	+	+
Triclosan**	0.05 - 0.1	++	+
Oxybenzone**	0.05 - 0.5	++	o/+
Diazinon***	0.02 - 0.2	o	+
Terbutrin***	0.2 - 0.3	++	+
Tri(2-chloroethyl)phosphate (TCEP)	0.15 - 0.4	-	--
Benzothiazole, 2-methylthio- (MTBT)	0.05 - 0.2	+	+

* pharmaceuticals ** personal care products *** pesticides **** other
removal: ++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

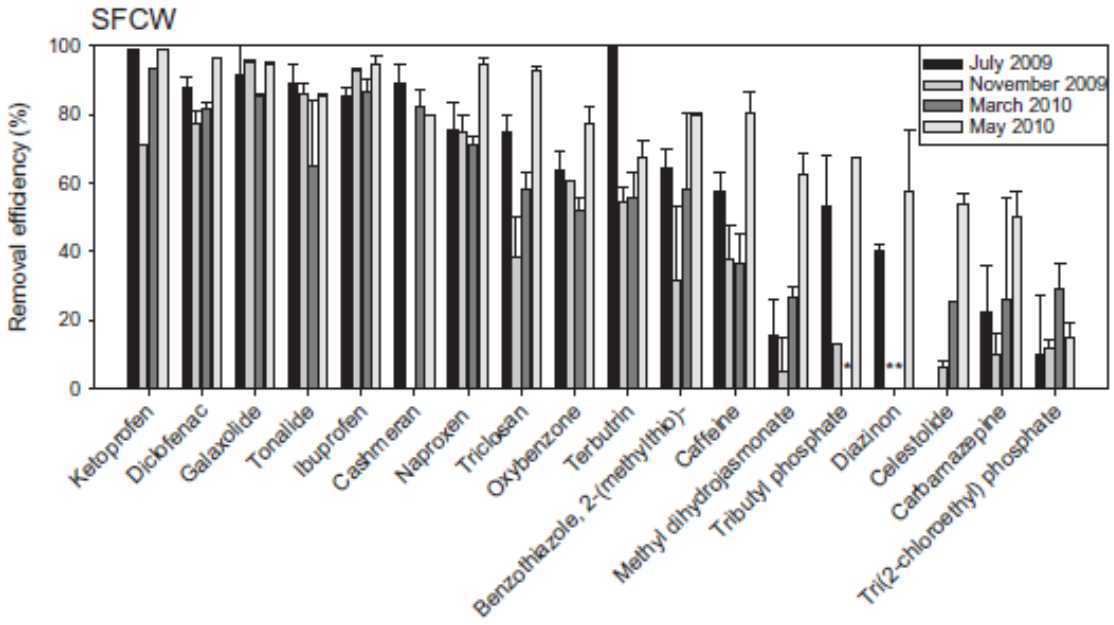

Figure 20: Seasonal removal efficiency of emerging pollutants in Empuriabrava surface flow constructed wetland (from Matamoros and Salvado 2012)

despite the much shorter residence time of 12.5 d (ponds+wetlands).

Individual results for the removal of investigated micropollutants in the constructed wetland at all seasons are shown in Figure 20. It can be seen that in the wetland alone especially pharmaceuticals and personal care products can be reduced by >50% for most times of the year. Furthermore, the reduction of these compounds only varies moderately between different seasons (but, again, mild winters in north Spain). Some compounds though such as methyldihydrojasmonate, carbamazepine or TCEP (right side of Figure 20) can only be removed at lower extent in the wetland due to their chemical and physical properties. Compared to the ponds, the overall removal efficiency of emerging compounds in the SFCW system is significantly higher (61% of total removal on average) than in the pond system (51% on average), which could be attributed to the HRT in the CW being more than twice as high as in the pond as well as to the presence of plants (Matamoros and Salvado 2012).

Main facts Empuriabrava wetland

- System type: combination of polishing ponds (2 ha) and surface flow constructed wetland (7 ha)
- Location and climate: northern Spain, warm climate
- HRT: 4d in polishing ponds, 8.5d in wetland (total 12.5d)
- inflow: Ø 3700 m^3/d (entire WWTP discharge)
- Good removal of most investigated micropollutants beside TCEP and carbamazepine
- Also good removal in winter for most compounds
- Higher removal in wetland compared to ponds

5.1.2.3 Surface flow wetland at Damyang WWTP in Korea

These constructed wetlands consist of two ponds (120 m x 30 m x 0.13 m, each), one planted with *Typha* spp. and the other with *Acorus* spp., both fed with effluent of Damyang WWTP. The wetlands were designed to have a hydraulic retention time of only 6 h at a flow rate of 1800 m³/d (Park et al. 2009).

In 2007, two sampling campaigns in May (∅ temp.: 18°C, ∅ precipitation: 95 mm) and August (∅ temp.: 26°C, ∅ precipitation: 238 mm) were conducted (Park et al. 2009), no samples were taken during much colder winter months. Of 30 analyzed micropollutants (including pharmaceuticals, endocrine disruptors and personal care products), only 7

Table 9: Inflow concentrations and removal of micropollutants in Damyang surface flow consutructed wetland (HRT=0.25d) in May and August. Values of reduction in Appendix A.

	Inflow concentrations [µg/L]	Removal May	Removal August
Diclofenac	0.1 - 0.4	+	o/-
Naproxen	0.09 - 0.11	+	++
Carbamazepine	0.4 - 0.9	o	--
Sulfamethoxazole	0.04 - 0.06	-	o
Atenolol	0.04 - 0.22	++	++
Dilantin	0.07 - 0.14	--	-
TCEP	0.05	n.p.	--

removal: ++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

n.p. – not present in influent

showed concentrations >0.05 µg/L in the WWTP effluent (= influent to wetlands). Results are summarized in Table 9 (see also Appendix A). Although hydraulic retention time is with 0.25d very low, some micropollutants were well reduced. Best removal was reported for atenolol and naproxen (70-100%), moderate removal for diclofenac (40-80%) and sulfamethoxazole (30-55%) and low removal for TCEP and dilantin (antiepileptic drug). Carbamazepine showed varying reductions - whereas removal in May was almost 60%, no removal in August could be observed. It is also noticeable, that diclofenac is much less removed in August compared to May. Reason might be that precipitation is much higher in August which results in higher cloud cover and reduced sun light for photolytic degradation which is the main removal mechanism for diclofenac (see also chapter 3.2).

Main facts Damyang wetland South Korea

- System type: surface flow constructed wetland (0.7 ha) planted with Typha and Acorus spp.
- Moderate climate (cold winters, hot summers)
- HRT: 6 h; inflow: Ø 1800 m³/d
- Good to moderate removal of naproxen, atenolol and diclofenac at low HRT

5.1.2.4 Constructed wetland treatment train "Zone Libellule©"

The "Zone Libellule©" is a series of wetlands (total size: 0.7 ha) in Saint-Just (France), receiving effluent from the local WWTP (5,000 population equivalent) since 2009. At an average inflow of 440 m³/d, the hydraulic residence time of the whole system as calculated from results of three tracer experiments varies between 10 and 38 days (Schuemacher et al. 2013). The series of constructed wetlands consists of a treatment pond (area: 0.2 ha, depth: 1.5 m), a free water surface wetland planted with *Phragmitis australis* (0.1 ha, depth: 0.4 m), a meander (0.018 ha, depth: 0.2 m), a shallow pond with small islands to allow photodegradation called delta (0.15 ha, depth: 0.1 m) and a final pond (0.2 ha) that increases in depth from 0.1 to 0.8 m (∅ 0.66 m) for establishment of different plant varieties to increase O_2-concentration in the water (Figure 21). At the outlet the water flows through a sand filter planted with *Phragmitis australis* before discharged into a small river.

Figure 21: Schematic view of wetland series at Saint-Just (from Schuemacher et al. 2013).

The wetland system was investigated regarding the removal of a variety of >200 micro-pollutants (pharmaceuticals, alkylphenols, pesticides and phthalates) between April 2010 and February 2012 conducting an intensive sampling campaign that includes sampling of sub-systems in July 2011 and 5 samplings (inflow and outflow only) at varying seasons of the year.

Results for main compounds are summarized in Table 10. High inflow concentrations >1µg/L were measured for AMPA (main metabolite of glyphosate: 8.7 µg/L), 4-

Nonylphenoxyacetic acid (4-NP1EC, metabolite of nonylphenol: 1.8 µg/L) and the beta-blocker sotalol (1.3 µg/L). During summer, good removal efficiencies (>60%) were found

Table 10: Inflow concentrations and removal efficiencies for main micropollutants in wetland series "Zone Libellule©" (HRT=10-38d) in summer and winter (data from Schuemacher et al. 2013). Values of reduction can be found in Appendix A.

	Inflow concentrations* [µg/L]	Removal Summer (July)	Removal Winter (end Nov)
Diclofenac	0.86 ± 0.08	++	o
Naproxen	0.07 ± 0.01	++	o
Carbamazepine	0.77 ± 0.09	o	-
Ketoprofen	0.10 ± 0.02	++	++
Sulfamethoxazole	0.05 ± 0.02	o	--
Ciprofloxacin	0.87 ± 0.13	++	++
Erythromycin	0.11 ± 0.03	o-	-
Ofloxacin	0.19 ± 0.03	++	++
Norfloxacin	0.68 ± 0.10	++	++
Atenolol	0.1 ± 0.02	++	+
Metoprolol	0.08 ± 0.01	++	+
Sotalol	1.3 ± 0.18	o	-
AMPA	8.7 ± 1.9	+	o
Glyphosate	0.7 ± 0.23	++	-
Diazinon	0.04 ± 0.01	++	--
Diuron	0.22 ± 0.10	+	o
Terbutryn	0.03 ± 0.01	+	-
Nonylphenol	0.12 ± 0.02	-	--
4-NP1EC	1.8 ± 0.24	++	o

removal: ++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction
* for 6 week summer period in July/August (n=11), larger variations during year

for 14 of the 19 compounds listed in Table 10 of which the majority (11 compounds) was removed by >80%. Moderate removal (40-60%) was shown for carbamazepine, sulfamethoxazole, erythromycin and sotalol whereas nonylphenol was only removed at low extent (22% - see also Appendix A). In winter, removal remained very good (>80%) for 4 compounds (ketoprofen, ciprofloxacin, ofloxacin and norfloxacin), for all other compounds removal was decreased in winter (especially sulfamethoxazole, glyphosate, diazinon, terbutryn, diclofenac and naproxen). However, for half of the compounds in Table 10, removal in winter remains >50%.

Removal efficiencies for individual subsystems were also investigated during this study - results showed compound dependent behaviour. For example, ß-blockers (e.g. atenolol, metoprolol, sotalol) were mostly gradually removed in all sub-systems, whereas nonylphenol exhibited main removal only in the reed-planted FWS wetland (roselière). For the removal of diclofenac, AMPA or glyphosate the first sub-system (basin macro-

phytes), sub-system with longest residence time, played a major role. The system with least effect on removal of micropollutants was the meander, the system with shortest theoretical (and measured) residence time, indicating that residence time is a major parameter for removal of micropollutants in constructed wetland systems.

For investigation of sediment regarding accumulation of micropollutants 4 samples from first and last system were analyzed for 247 micropollutants. Concentrations > 100 ng/g were only found for 4 compounds in sediment of the first basin: the pesticide AMPA (2500 ng/g), the antibiotic ofloxacin (800 ng/g) and two nonylphenols (490 ng/g for 4-NP and 410 ng/g for the metabolite 4-NP1EC).

Main facts "Zone Libellule©" wetland series

- series of 5 FWS constructed wetlands of different design (total size: 0.7 ha) planted with variety of species
- Location and climate: southern France, warm climate
- HRT: 10-38 d; inflow: Ø 440 m³/d
- Good removal of majority of compounds in summer

5.1.2.5 Behaviour of four full scale wetlands in south Sweden in winter

In a study published by Breitholtz et al. 2012, incoming and outgoing waters from four Swedish free water surface wetlands, operated as final treatment steps of effluent from municipal WWTPs, were sampled under cold winter conditions (February 2010 with sub-zero temperatures on all sampling dates) and analyzed for levels of a set of 92 pharmaceuticals. It is the only study found investigating the removal of micropollutants in constructed wetlands under cold winter conditions of moderate climates. Details of the four FWS wetlands that are all planted with various plant species can be found in Table 11.

Sixty-five pharmaceuticals were detected in the range from 1 ng/L to 7.6 µg/L in incoming and outgoing waters. Average estimated removal rates of the four systems ranged from 42% to 52% (taking the average of all removal rates for all compounds per system). Considering the low temperatures, this is a quite remarkable extent. However,

Table 11: Details for four Swedish full scale FWS wetland systems (data from Breitholtz et al. 2012).

Name	**Inflow** [m³/d]	**Size** [ha]	**HRT** [d]	**Layout**
Eskilstuna	48.000	28	6-7	Five parallel basins followed by three parallel basins (mean depth: 1m, plant coverage ca. 20%)
Nynäshamn	5.500	28	10-14	Two inflow basins, two parallel CW basins (used alternatively), two serial basins, overland flow area
Oxelösund	4.000	24	6	One inlet basin, two parallel CW systems with each consisting of two basins, joint basin
Trosa	1.620	6	8	Overland flow area, collecting basin, three serial CW basins

Table 12: Inflow concentrations and removal efficiencies of selected micropollutants in four Swedish FWS wetlands during winter (data from Breitholtz et al. 2012).

	Inflow concen-	Eskilstuna **HRT=6-7d**	Nynashamn HRT=10-14d	Oxelösund HRT=6d	Trosa HRT=8d
Diclofenac	0.38-0.56	-	-	-	-
Naproxen	0.19-0.34	-	o	+	o
Ketoprofen	0.33-2.6	o	--	-	--
Ibuprofen	0.7-1.5	-	++	++	--
Carbamazepine	0.29-1.0	--	--	-	--
Sulfamethoxazole	0.05-0.14	--	--	--	--
Atenolol	1.1-2.0	-	o	o	o
Metoprolol	0.6-1.5	--	-	--	-

removal: ++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

removal rates of typical pharmaceuticals are much lower compared to studies in warm climates presented in 5.1.2.1 to 5.1.2.4 (see Table 12). It can be expected, though, that removal efficiencies in these systems are considerably higher in summer months due to higher temperatures for biodegradation processes and increased solar radiation improving photodegradation processes. Furthermore, for some compounds system-specific differences are noticeable (e.g. for ketoprofen, naproxen or ibuprofen; Table 12).

Ecotoxicological testing with a macro algae and crustacean in general showed that these treatment facilities release water with a relatively low toxic potential, comparable to water that has been treated with advanced tertiary treatments (Breitholtz et al. 2012).

Main facts Swedish FWS wetland systems

- 4 wetland systems with different combinations of FWS wetlands
- Location and climate: Sweden near Stockholm, cold-moderate climate
- HRT: 6-14d; inflow: Ø 1600-48000 m³/d
- Lower removal of main pharmaceuticals (e.g. diclofenac: ~30%, atenolol: ~50%), but sampling in winter at sub-zero temperatures (no results for summer)

5.1.3 Mesocosm scale studies

In mesocosm scale studies, different system types, design configurations and operation conditions can be investigated in a controlled manner. While no relevant mesocosm scale constructed wetland studies for the treatment of WWTP effluent were found, three studies investigated the removal of pharmaceuticals in CW systems receiving raw wastewater, including some evaluation of removal pathways and factors influencing removal. Main outcomes are summarized below, more details can also be found in Appendix A.

In a mesocosm scale horizontal SSF constructed wetland system planted with *Phragmitis australis* (two small parallel wetlands with low oxygen followed by larger wetland under oxic conditions) with an HRT of 3.5 d, all five investigated compounds (ibuprofen, naproxen, diclofenac, tonalide and bisphenol A) were removed by >95% (Ávila et al. 2010). From different behaviour in the subsystems the authors concluded that

- for ibuprofen, naproxen, diclofenac and bisphenol A biodegradation is main removal mechanism
- aerobic conditions enhance ibuprofen degradation
- naproxen, diclofenac and bisphenol A were degraded under anoxic/anaerobic conditions (reductive dehalogenation suggested as potential biodegradation mechanism for diclofenac)
- sorption on substrate postulated for tonalide and bisphenol A

Hijosa-Valsero et al. 2010 investigated in seven mesocosm-scale constructed wetlands the influence of different configurations (presence of plants, plant species chosen, surface vs. subsurface flow and presence of gravel bed) on the removal of 10 micropollutants (see also Appendix A, references [6] and [8]). Theoretical HRT values for the 7 all systems were between 2 and 6 days. It was found that the performance of the individual configurations was compound dependent:

- carbamazepine was much better removed with plant species (see also 3.4), presence of plants also contributed to removal of naproxen, ibuprofen, diclofenac, galaxolide, tonalide
- aerobic pathways (high redox) for ibuprofen, diclofenac, carbamazepine, salicylic acid
- low redox better for removal of galaxolide, tonalide, caffeine
- microbiological pathways probably main degradation route for PPCP inside CWs (because of linear correlations between temperature or redox potential)
- *Phragmitis australis* had a better performance compared to *Typha angustifolia* (at least during summer)

In a subsequent study of the same systems the medium-term behaviour during three years of operation was evaluated (ageing of the systems). It was shown that efficiency decreased throughout time and performance differences among CWs disappeared with the systems aging (Reyes-Contreras et al. 2012).

In a study by Rühmland et al. 2013, three pilot scale systems (a vertical subsurface flow constructed wetland with continuous flow and constant head planted with *Phragmitis australis*, an unplanted pond and a pond with floating islands – see 5.1.4.1) were investigated in summer regarding the fate of micropollutants. It was found that removal of diclofenac and sulfamethoxazole was system-dependent. Whereas diclofenac was better removed in the unplanted pond (by 80%, presumably by photodegradation), sulfamethoxazole was better removed in the VF constructed wetland (by 70%, under more anaerobic conditions)(Rühmland et al. 2013). Carbamazepine was not reduced, whereas metoprolol was well reduced in all three systems between 64 and 92%.

5.1.4 Other systems

5.1.4.1 Floating islands

Results for performance of floating islands regarding treatment of contaminants are scarce. Tanner and Headley 2008 investigated the removal of heavy metals (copper and zinc) and particulates by floating island mesocosm systems for treatment of stormwater. Results show that especially for particulates and copper, the planted floating islands showed greatest reductions compared to controls, reducing turbidity by 57-67% and copper concentrations by 65-75% after 7 days. For zinc, concentrations were reduced by less than 40%.

Regarding removal of pharmaceuticals, only one system was found investigating removal in a floating island system. Rühmland et al. 2013 studied three pilot-scale constructed wetland systems (surface area ~1500 m² each) in the northern part of Berlin (Hobrechtsfelde) treating WWTP effluent for removal of pharmaceuticals, of which one pond was partly covered (~2/3) with floating islands (hydraulic retention time ~3d). Results of a sampling campaign in summer 2012 show significant removal > 30% for 40 of 53 measured compounds. For example, diclofenac is reduced by 64% (compared to 20% in vertical flow constructed wetland and 86% in unplanted pond) and sulfamethoxazole by 60% (compared to 70% in vertical flow constructed wetland and 46% in unplanted pond, Rühmland et al. 2013). The low redox conditions in the floating island system (resulting from prevention of oxygen transfer from atmosphere) suggest anaerobic reduction mechanisms, e.g. reductive dehalogenation for diclofenac.

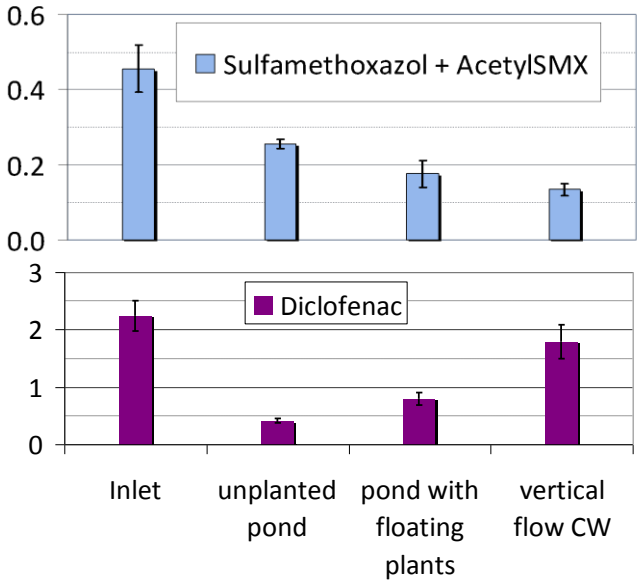

Figure 22: Removal of diclofenac and sulfamethoxazole in floating island pond compared to unplanted pond and VF CW (from Rühmland et al. 2013).

Chapter 6

Conclusions and gaps in knowledge

The review of literature shows a promising potential for removal of micropollutants in constructed wetlands. Removal efficiencies of micropollutants such as pharmaceuticals, personal care products or pesticides in full scale FWS constructed wetland systems treating WWTP effluent were high for the majority of investigated compounds, especially in summer. Compounds with lower removal include carbamazepine, the flame retardant TCEP, nonylphenol and sulfamethoxazole. For carbamazepine, however, reported removal efficiencies in natural treatment systems of 10-50% are still higher than in WWTP (<15%). However, results are somewhat inconclusive - whereas in two different full scale systems in northern Spain carbamazepine removal was higher in winter (up to 50%), its removal in a wetland system in southern France showed better removal in summer. Under cold winter conditions in northern Europe, carbamazepine was reduced only by 0-21%. Compounds that exhibited repeatedly high removal efficiencies at various hydraulic residence times (often also in winter) include naproxen, ibuprofen, atenolol and ketoprofen. Diclofenac, a compound with no or minor removal in WWTP, is also often well reduced in full scale FWS wetlands with open water surfaces at retention times of several days (besides winter conditions in northern Europe).

However, the number of studies is still limited and although all full scale systems were of similar type (free water surface wetlands), many differences occurred such as climates, plants, HRT, investigated compounds and design details, leading to varying results for a number of compounds and making general conclusions difficult.

Inflow concentrations often varied considerably and upper values reached values >1 µg/L for a number of compounds (e.g. diclofenac: 0.2 – 2.2 µg/L, naproxen: 0.07 [France] – 0.6 µg/L [Spain], ketoprofen: 0.1 [France] – 2.6 µg/L [Sweden], atenolol: 0.1 (France) – 2.0 [Sweden], sulfamethoxazole: 0.05 – 0.3 µg/L).

Temperature and season were repeatedly proved to be an important parameter for removal performance. As demonstrated in a study on Swedish wetlands, in winter (especially in moderate climate with sub-zero temperatures in winter) removal efficiencies could be much less, especially for compounds whose removal depends on microbial degradation, photodegradation (less daily sunshine and solar intensity in winter) and plant uptake. However, for compounds with good removal in summer and low to moderate removal in winter, the overall reduction during the year would still be >50%. Furthermore, if systems are built in warmer climates (e.g. southern France), their treatment performance will be less affected by the winter conditions and average yearly removal efficiencies >80% are likely to be possible for certain compounds.

A variety of removal mechanisms (e.g. photodegradation, biodegradation, adsorption, plant uptake) simultaneously occur in natural treatment systems and are relevant to varying extent for each compound. Although the relevance of potential removal mechanisms is only known for selected micropollutants (mostly pharmaceuticals), some experimental evidence is available indicating photodegradation (e.g. ketoprofen, diclofenac and sulfamethoxazole), biodegradation (e.g. ibuprofen, naproxen) and adsorption (e.g. galaxolide, tonalide) as relevant removal mechanisms for many

compounds. Especially photodegradation can be seen as relevant mechanism, as it is a mechanism playing only a minor role in WWTP, whereas biodegradation and adsorption are also relevant mechanisms in WWTP. Furthermore, for certain compounds with low biodegradation or adsorption potential (e.g. diclofenac), photodegradation in natural treatment systems seems to be a possible removal pathway as proven in a number of studies. However, the identification and ecotoxicological evaluation of potential metabolites formed by photolytic processes needs further attention. The extent of plant uptake and phytoremediation for removal of micropollutants is less understood, although uptake of carbamazepine and ibuprofen was repeatedly mentioned. More research is necessary to assess the removal potential for all micropollutants of interest and most relevant mechanisms and conditions (including metabolite formation and evaluation of metabolite toxicity).

Until now, systems are not designed for removal of micropollutants but mainly for reduction of nutrients. Due to the high number of micropollutants it is unlikely that one system type is able to reduce all micropollutants of interest to a high extent. Instead, combining a series of systems in a treatment train, each providing removal mechanisms and optimal conditions for a group of compounds, is likely to enhance micropollutant reduction in natural treatment systems considerably. Although information from existing studies gives indications regarding removal mechanisms and conditions for a few compounds, it is not known how to design either single systems or treatment trains consisting of several systems to achieve a certain level of removal for desired micropollutants. For the development of design guidelines for a treatment train of eco-engineered systems targeting the removal of micropollutants, removal rates for each system type and compound and their dependence from temperatures needs to be determined for all compounds of interest. Finally, management rules have to be adapted according to mechanisms involved in removal of micropollutants in these systems (e.g. plant uptake => regular weed cutting; sedimentation => regular removal of sediments).

Appendix A

Results ad details from experimental studies on removal of micropollutants in natural treatment systems

Compound	inflow concentration [µg/L]	reduction [%]		retention time [d]	system type	system size	plant species	inflow water type	country	comments	Refe-rence	removal mechanisms
Ibuprofen	0.5 - 3	15 - 85	- / ++	3 hours (?)	vertical flow reed bed	microcosm	reed (Phragmitis)	**WWTP effluent** (from demonstration plant with activated sludge)	UK	- 3 samplings - diclofenac, carbama-zepine and galaxolide were spiked - (probably) indoor	[1]	- galaxolide in secondary sludge (in pilot WWTP before reed beds)
Naproxen	0.9 - 1.8	10 - 85	-- / ++									
Diclofenac	0.7 - 3.2	60 - 90	+ / ++									
Galaxolide	0.5 - 1.7	40 - 65	o / +									
Carbamazepine	4.2 - 6.8	25	-									
Ibuprofen	0.04	96 ± 2	++	30 d (!)	surface flow constructed wetland	full scale (1 ha: 190 x 53 m) 100 m³/d	Phragmitis australis, Typha latifolia (~ 2/3 planted)	**WWTP effluent**	Spain	- only 0.4 % of WWTP (23700 m³/d, 154000 eq) effluent into wetland - data from sampling campaigns in winter (average min temp: 5°C) and summer (average temp 25°C) - also good removal of ammonium (especially in summer months) and coliforms (-2 log)	[2] [4] [10] (Btri, BT)	- galaxolide and tonalide associated with particles (others not) - photodegradation of benzothiazole mentioned
Naproxen	0.34	72 ± 28	+									
Diclofenac	1.25	85 ± 16	++									
Ketoprofen	2.1	98 ± 1	++									
Carbamazepine	0.37	39 ± 12	-									
Galaxolide	2.9	87 ± 2	++									
Tonalide	0,9	89 ± 1	++									
Mecoprop	7.8	85 ± 8	++									
MCPA	2.0	86 ± 10	++									
Benzotriazole	1.8 (s) - 4.5 (w)	0 (w) - 50 (s)	-- / o									
Tolyltriazole	9.8 (w)-13.1 (s)	39 (w) - 55 (s)	o									
Benzothiazole	1.2 (w) - 1.5 (s)	0 (w) - 80 (s)	-- / +									
OH-BT	1.7 (w) - 0.6 (s)	0 (w) - 40 (s)	-- / o									
MTBT	0.5	35 (w) - 58 (s)	- / o									

Sulfamethoxazole	0.04 - 0.06	30 - 55	- / o	6 h	surface flow constructed wetland	full scale (2x 120 x 30 m) 1800 m ³/d	Acorus followed by Typha	**WWTP effluent**	Korea	- 2 sampling campaigns in Mai and Agust, average temperatures 22-29 °C	[3]	- analysis of wetland soils and plants - no relationship between removal and log Kow and pKa - no/minor adsorption to soil - no/minor plant uptake - dehalogenation of triclosan and diclofenac under anoxic conditions proposed
Atenolol	0.04 - 0.22	95 - 100	++									
Carbamazepine	0.4 - 0.9	0 - 60	-- / o									
Dilantin	0.07 - 0.14	10 - 40	-- / -									
Diclofenac	0.1 - 0.4	40 - 80	o- / +									
Naproxen	0.09 - 0.11	72 - 85	+									
TCEP	0.05	10	--									
Triclosan	0.02 - 0.03	70 - 100	++									
Diclofenac	0.86 ± 0.08	51 (w) - 86 (s)	o / ++	10 - 38d for total system	treatment train of constructed wetlands	Full scale (0.7 ha for full system)	Variety of aquatic plants, including Phragmitis spp., Typha spp., Scirpus spp., Iris spp., Cares spp.	WWTP effluent	France (south)	- extensive report on several year investigation of wetland system - seasonal data (February, April, June, July, October and November), intensive sampling in July - 317 compounds analyzed in total (micropollutants and heavy metals - removal efficiencies during intensive sampling in July also for individual systems - investigation of sediment and plant tissue included in study	[13]	
Naproxen	0.07 ± 0.01	59 (w) - 98 (s)	o / ++									
Carbamazepine	0.77 ± 0.09	27 (w) - 47 (s)	- / o									
Ketoprofen	0.10 ± 0.02	97 (w,s)	++									
Sulfamethoxazole	0.05 ± 0.02	0 (w) - 51 (s)	-- / o									
Ciprofloxacin	0.87 ± 0.13	99 (w,s)	++									
Erythromycin	0.11 ± 0.03	20 (w) - 40 (s)	- / o									
Ofloxacin	0.19 ± 0.03	96 (w) - 99 (s)	++									
Norfloxacin	0.68 ± 0.10	99 (w,s)	++									
Atenolol	0.1 ± 0.02	72 (w) - 94 (s)	+ / ++									
Metoprolol	0.08 ± 0.01	67 (w) - 89 (s)	+ / ++									
Sotalol	1.3 ± 0.18	25(w) - 59 (s)	- / o									
AMPA	8.7 ± 1.9	49 (w) - 73 (s)	o / +									
Glyphosat	0.7 ± 0.23	31 (w) - 83 (s)	- / ++									
Diazinon	0.04 ± 0.01	17 (w) - 84 (s)	-- / ++									
Diuron	0.22 ± 0.10	43 (w) - 79 (s)	o / +									
Terbutryn	0.03 ± 0.01	25 (w) - 65 (s)	- / +									
Nonylphenol	0.12 ± 0.02	0 (w) - 22 (s)	-- / -									
4-NP1EC	1.8 ± 0.24	53 (w) - 84 (s)	o / ++									
Bisphenol A	0.01 ± 0.004	90 (w,s)	++									

Diclofenac	0.5 - 1.2	93 (86-98)	++	ponds: 4d SFCW: 8.5 d	2 parallel polishing ponds + surface flow constructed wetland (3 planted cells + shallow wetland)	full scale (ponds: 2 ha, SFCW: cells 0.8 ha + 4.5 ha polishing wetland) 3700 m³/d	Phragmitis australis, Typha latifolia in SFCW (sparsely planted)	**WWTP effluent**	Spain (north)	- seasonal data (March, May, July, November) for WWTP effluent and removal efficiencies - 27 compounds measured in total - removal efficiencies for pond and SFCW also separately - photodegradation: diclofenac, ketoprofen, triclosan	[5]	- galaxolide and tonalide better removed in wetland than in pond due to higher sorption capacity of wetland (log Kow>4) - triclosan, diclofenac and ketoprofen are photodegradable, therefore comparable or better removal in pond - ibuprofen, naproxen, oxybenzone mentioned as biodegradable compounds-> less affected by seasonality in wetland than pond
Ketoprofen	0.4 - 0.9	98 (91-99)	++								
Carbamazepine	0.2 - 1.3	43 (10-51)	-								
Naproxen	0.4 - 0.6	88 (72-96)	++								
Ibuprofen	0.3 - 0.5	92 (79-97)	++								
Cashmeran	0.1 - 0.25	80 (77-95)	+								
Galaxolide	0.7 - 2.2	95 (81-99)	++								
Tonalide	0.25 - 0.7	88 (62-97)	++								
Methy dihydrojasmonate	0.45 - 0.65	64 (41-81)	o								
Triclosan	0.05 - 0.1	86 (74-93)	++								
Oxybenzone	0.05 - 0.5	77 (42-94)	+								
Tri(2-chloroethyl)phosphate (TCEP)	0.15 - 0.4	27 (10-47)	-								
Diazinon	0.05 - 0.2	59 (10-82)	o								
Terbutrin	0.2 - 0.3	69 (52-73)	+								
Benzothiazole, 2-methylthio-	0.05 - 0.2	73 (52-87)	+								
Diclofenac	0.4 - 0.8	20 - 90	- / ++	theoretical HRT: 2-5 d (depending on system type)	different configurations: surface flow, subsurface flow	7 mesocosms (1 m²) (1 m x 0.8 m)	Phragmitis australis, Typha angustifolia (separately tested)	raw wastewater	Spain (north)	- winter (-3 - 18°C, av. 7°C) vs. summer (4 - 32°C, av. 20°C) - over 3 years in [8] - correlations between removal and redox, temp, oxygen (e.g. positive for CBZ, DCL, IBU and redox) - comparison of 7 different configurations (planted, unplanted, SSF, SF,…): removal varies	[6] [8]	- carbamazepine more easily removed with plant species - presence of plants contributed to removal of naproxen, ibuprofen, diclofenac, carbamazepine, galaxolide (GLX), tonalide (TON) - high oxygen aided diclofenac degradation, low O2 favoured GLX, TON, caffein removal - aerobic pathways (high redox) for ibuprofen, diclofenac, carbamazepine, salicylic acid - low redox better for degradation of galaxolide, tonalide, caffeine - generally, microbiological path-
Ibuprofen	8 - 24	40 - 96	o / ++								
Naproxen	1.3 - 3.5	27 - 83	- / ++								
Ketoprofen	0.3-1.7	20-90	- / ++								
Carbamazepine	0.5 - 1.5	20 - 60	- / o								
Caffeine	23 - 67	30 (w) - 95 (s)	- / ++								
Galaxolide	1.0 - 3.8	10 - 80	-- / +								
Tonalide	0.3 - 0.4	30 (w) - 70 (s)	- / +								
Methyl dihydrojasmonate (fragrance)	4 - 11	40 - 96	o / ++								

										depending on type		ways most probable degradation route for PPCP inside CWs
Carbamazepine	1000	88 - 97	++	0.5 - 7 d	batch experiments: no flow	microcosm CW (0.6 x 0.5 m)	Typha spp. with LECA as substrate	**WWTP effluent,** spiked (1 mg/L)	Portugal	- already high removal with substrate (LECA) alone - plants increase removal by 2-32% - comparison winter (av. 12°C) / summer (av. 26°C) included	[7]	- LECA mainly responsible for pharmaceutical removal (2%-32% increase by plants)
Ibuprofen	1000	82 - 96	++									
Clofibric acid	1000	48 - 75	o / ++									
Ibuprofen	132	98-99	++	3.5 d	subsurface flow CW	mesocosm 2x 0.65 m² (B1,B2 in parallel) + 1.65 m² (B3, in series)	Phragmitis australis	raw wastewater (Imhoff tank as primary treatment)	Spain	- high temperature (water temp: 22°C) - micropollutants spiked - first two parallel wetlands (B1+B2): anaerobic conditions, B3 aerobic conditions - anaerobic degra-dation of diclofenac and naproxen in B1/B2	[9]	- biodegradation for IB, NPX, DCF and BPA - aerobic conditions enhance IBU degradation; NPX, DCF, BPA degradation under anoxic/anaerobic conditions - sorption on substrate for tonalide and BPA - diclofenac can be degraded by reductive dehalogenation
Naproxen	36	99	++									
Diclofenac	3.2	99	++									
Tonalide	1.8	97-98	++									
Bisphenol A	1.5	85-99	++									
Bentotriazole	36	89-93	++	6 h	vertical subsurface flow CW	pilot wetland	?	raw wastewater	Denmark	- samples only in warm season	[10]	
Benzothiazole	1.1	83-90	++									
Simazine		25	-	5-6 d	horizontal subsurface flow wetland	pilot wetland (55 m²)	Phragmitis australis	raw wastewater (Imhoff tank as primary treatment)	Spain	- injection experiment (40L of 2.5 mg/L added to inlet of wetland), no continuous load - only minor accumu-lation in sediment (Pentachlorophenol 23%, Pentachloro-benzene 20%, Lindane 14%, all others <8%)	[11]	- gravel bed accumulation not a major pathway (highest for pentachlorophenol 23%, pentachlorobenzene 20%, lindane 14%, all others < 8%) - dehalogenation of chlorinated compounds PCP, lindane, pentachlorobenzen, endosulfan (anoxic conditions)
Alachlor		80	+									
Chlorpyriphos		83	++									
Pentachlorobenzene		99	++									
Pentachlorophenol		94	++									
Endosulfan		99	++									
Lindane		99	++									
Diuron		0	--									
Mecoprop		22	-									

Diclofenac	1.9	0-45	--/-	5-6 d	horizontal subsurface flow wetland	pilot wetland (55 m²)	Phragmitis australis	raw wastewater (Imhoff tank as primary treatment)	Spain	- shallow wetland more efficient	[12]	- low concentration in gravel bed (highest for galaxolide and tonalide - 25% of inflow in gravel, IBU<0.1%)
Ibuprofen	18	52-80	o/+									
Naproxen	1.6	75-94	+/++									
Ketoprofen	0.8	0-45	--/-									
Galaxolide	8	31-61	o									
Tonalide	5	32-65	o									

++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

References:

[1] Reif et al. 2011

[2] Llorens et al. 2009

[3] Park et al. 2009

[4] Matamoros et al. 2008

[5] Matamoros and Salvado 2012

[6] Hijosa-Valsero et al. 2010

[7] Dordio et al. 2010

[8] Reyes-Contreras et al. 2012

[9] Ávila et al. 2010

[10] Matamoros et al. 2010

[11] Matamoros et al. 2007

[12] Matamoros and Bayona 2006

[13] Schuemacher et al. 2013

Appendix B

Results and details from photodegradation studies

Compound	half live [d]	environment		comments	reference
Diclofenac	0,3 [s]- 5,0 [w]	lab study with compounds in distilled water	++ / o	- experimental determination (UV lamp irradiation) of quantum yields which were used to calculate half-life times at different latitudes/seasons (values for 50°N and summer [s] and winter [w]) - no reaction in dark control experiments	[1]
Sulfamethoxazole	0,4 [s] - 2,4 [w]		++ / +		
Carbamazepine	25 [s] - >100 [w]		--		
Propranolol	1,7 [s] - 16,8 [w]		+ / -		
Ofloxacin	1,8 [s] - 10,6 [w]		+ / -		
Gemfibrozil	0.63	lab study with river water	++	- 1 d = 24h irradiation - irridiation with xenon lamp (765 W/m², equivalent to midday midsummer in California) - concentrations: 1-2 µg/L, 20 mL volumes - temp: 20°C - no controls without radiation mentioned	[2]
Ibuprofen	0.63		++		
Ketoprofen	0.003		++		
Naproxen	0.06		++		
Propranolol	0.05		++		
EE2	0.1		++		
E2	0.08		++		
Estrone	0.1		++		
Diclofenac	0,01 - 0,07	spiked lake water exposed to sunlight	++	- investigations at Swiss lake (Greifensee) with >90% removal of diclofenac between inflow and outflow - lake water spiked with 1 µg/L, exposed under direct sunlight at noon in October (47 °N, Switzerland) - degradation products determined [4]	[3] [4]
Propranolol	0,25 - 0,33	spiked river water exposed to sunlight	++	- 1 d = 24h irradiation - high water temperatures (25-39°C) - concentrations: 100 µg/L - conducted in Japan (34° N) in May and August	[5]
Atenolol	3 - 30		o / --		
Acetaminophen	1,5 - 2,3		+		
Carbamazepine	4 - 88		--		

Ibuprofen	25 - 413		--		
Indomethacin	0,7 - 0,9		++		
Ibuprofen	14	spiked river water exposed to sunlight	--	- high concentrations (10-40 mg/L) - conducted in Spain (41°N) in May - sunlight radiation: up to 950 W/m² (daily average 270 w/m²) - quartz glass tubes (transparent to UV) - metabolites for Ketoprofen identified	[6]
Carbamazepine	2.8		+		
17a-ethinylestradiol	4.4		o		
Ketoprofen	0.002		++		
Sulfamethoxazole	0,04 - 0,07	lab study with spiked wastewater effluent	++	- using solar simulator at 765 W/m² (half-lives for mid-summer sunlit day) - effluent OM and nitrate enhance photodegradation - deoxygenated conditions enhanced photodegradation (factor 2 for SMX)	[7]
Trimethoprim	0,1 - 1		++		
Carbamazepine	0,25 - 2,3	lab study with synthetic field waters	++ / +	- using solar simulator with Xe lamp at 765 W/m² (half live of 1 d = 24h irradiation) - concentrations: 10 µM - higher NO3 and DOM concentrations enhance carbamazepine photolysis by factor of 3, but reduce SMX photolysis by factor of 2	[8]
Sulfamethoxazole	0,1 - 0,25		++		
Levofloxacin	0,01 - 0,05		++		
Atorvastatin	0,03 - 0,1		++		
Diclofenac	80% removal in 7 days	mesocosms	+	- phytoremediation experiment with diclofenac removal in unplanted control - nutrient solution spiked with 0,5 mg/L diclofenac	[9]
Diclofenac	3	mesocosms	+ / o	- 5L mesocosms, spiked with 10 µg/L under artificial light at 18°C - phytoremediation experiments that revealed photodegradation in unplanted controls	[10]
Triclosan	3		+ / o		
Lorazepam	<1	lab study with compounds in distilled water	++	- high concentration (10 mg/L) - irradiation with Xe lamp (55 W/m², 290-400 nm) - half-lives in summer sunny days (SSD) = 3.8 h lamp irridiation - influence of humic and fulvic acids invetsigated	[11]
Oxazepam	4		o		
Diazepam	7		-		
Alprazolam	228		--		

half lives: ++ < 1d; + 1-3d; o 3-7d; - 7-14d; -- >14d

[1] Andreozzi et al. 2003
[2] Lin and Reinhard 2005
[3] Buser et al. 1998
[4] Poiger et al. 2001
[5] Yamamoto et al. 2009
[6] Matamoros et al. 2009
[7] Ryan et al. 2011
[8] Lam and Mabury 2005
[9] Zhang et al. 2012
[10] Matamoros et al. 2012
[11] Calisto et al. 2011

Appendix C

Results and details from phytodegradation studies

Compound	reduction [%]	time [d]		plant species	comments	reference
Ibuprofen	58	1	o	Typha spp. (cattail)	- microcosm experiments conducted in Portugal (plants collected from streams) - Hoagland nutrient solution spiked with 20 µg/L ibuprofen - altered enzymatic activities in roots and leaves: indication for translocation of compound to aerial parts	[1]
	81	2	++			
	95	4	++			
Carbamazepine	52	7	o	Typha spp.	- conducted in Portugal (same authors as [1]) - probably in June - medium: aerated Hoagland nutrient solution spiked with 0,5 mg/L carbamazepine - detection of CB in leaf tissue	[2]
	65	14	+			
	81	21	++			
Diclofenac	18	8	--	Phragmitis australis	- high concentrations (0.1 mM: 15-32 mg/L) - lab experiments	[3]
Ibuprofen	60	8	+			
Acetpminophen	16	8	--			
Carbamazepine	53	3	o	Scirpus validus (sedge)	- high concentration (0.5 mg/L) - naproxen: only small (0.1-4%) uptake by plants (photodegradation observed) - carbamazepine: higher uptake by plants (>20%), no photodegradation observed - higher accumulation of carbamazepine in roots than in shoots	[4]
	56	7	o			
	58	14	o			
Naproxen	83	3	++			
	86	7	++			
	90	14	++			
Ibuprofen	40	14	o	Elodea canadensis	- 5L mesocosms, spiked with 10 µg/L under artificial light at 18°C - all small swimming or submerged aquatic plants - diclofenac, naproxen and triclosan also investigated: photodegradation found to be main mechanism (reduction 50-100%)	[5]
	10	7	--			
Caffeine	48	7	o	Lemna minor		
	38	7	-	Ceratophyllum		

++ 80-100%; + 60-80%; o 40-60; - 20-40; -- 0-20% reduction

[1] Dordio et al. (2011) [2] Dordio et al. (2011) [3] Kotyza et al. (2010) [4] Zhang et al. (2013) [5] Matamoros et al. (2012)

Appendix D

Micropollutant prioritization

Table 13: Proposal of environmental quality standards by Swiss Centre for Applied Ecotoxicology (from Kase et al. 2011 and Swiss_Centre_for_Applied_Ecotoxicology 2013)

Substance	CAS number	Acute quality criterium (MAC-EQS)	Chronic quality criterium (AA-EQS)
Pharmaceuticals and steroidal estrogens			
17-alpha-Ethinylestradiol	57-63-6	not proposed	0.037 ng/l
17-beta-Estradiol	50-28-2	not proposed	0.4 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	not proposed	0.05 µg/l*
Erythromycin	114-07-8	2.3 µg/l	0.04 µg/l
Estrone	53-16-7	not proposed	3.6 ng/l
Ibuprofen	15687-27-1	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	370 µg/l	1.7 µg/l(*)
Sulfamethazine	57-68-1	30 µg/l	30 µg/l
Sulfamethoxazole	723-46-6	2.7 µg/l	0.6 µg/l
Trimethoprim	738-70-5	1100 µg/l	60 µg/l
Pesticides			
Boscalid	188425-85-6	11.6 µg/l	11.6 µg/l
Carbendazim	10605-21-7	0.57 µg/l	0.34 µg/l
Cypermethrin	52315-07-8	$6*10^{-4}$ µg/l	$8*10^{-5}$ µg/l
2,4-D	94-75-7	1.3 µg/l	0.2 µg/l
Diethyltoluamid (DEET)	134-62-3	410 µg/l	41 µg/l
Diazinone	333-41-5	0.015 µg/l[#]	0.015 µg/l[#]
Dimethoate	60-51-5	0.977 µg/l	0.07 µg/l
Diuron	330-54-1	0.06 µg/l	0.02 µg/l
Ethofumesate	26225-79-6	26 µg/l	22 µg/l
Irgarol (Cyrbutryne)	28159-98-0	0.013 µg/l	0.0023 µg/l
Isoproturon	34123-59-6	1.2 µg/l	0.32 µg/l
MCPA	94-74-6	15.2 µg/l	1.34 µg/l
Mecoprop-P	16484-77-8	under reevaluation	under reevaluation

Metamitron	41394-05-2	39 µg/l	4.0 µg/l
Pirimicarb	23103-98-2	1.6 µg/l	0.09 µg/l
Tebuconazole	107534-96-3	1.4 µg/l	1.2 µg/l
Terbuthyazine	5915-41-3	1.28 µg/l	0.22 µg/l
Terbutryne	886-50-0	0.091 µg/l	0.065 µg/l
Triclosan	3380-34-5	0.02 µg/l[#]	0.02 µg/l[#]
Industrial chemicals			
Benzothiazole	95-16-9	246 µg/l	238 µg/l
Benzotriazole	95-14-7	120 µg/l	30 µg/l
Bisphenol A (BPA)	80-05-7	not proposed	1.5 µg/l
Methylbenzotriazole	29878-31-7	200 µg/l	75 µg/l
Nonylphenol	25154-52-3 and 84852-15-3	3270 ng/l	13 ng/l
Perfluorooctane sulfonate (PFOS)	1763-23-1	36 µg/l	230 ng/l* (based on direct aquatic long-term toxicity)
Complexing agents			
EDTA	60-00-4	12100 µg/l	2200 µg/l
NTA	139-13-9	9800 µg/l	190 µg/l

*Substances for which there may be a secondary intoxication risk that has not been numerically considered to date

[#]For some substances, the chronical (AA-EQS) and the acute quality criteria (MAC-EQS) are identical. This can be the case if the acute and chronic toxicity are not so different. Then, if a larger assessment factor is used for the calculation of the MAC-EQS than for the calculation of the AA-EQS (100 instead of 10), the MAC-EQS would be lower than the AA-EQS. In this case, the technical guidance document for deriving EQS specifies to raise the MAC-EQS to the AA-EQS.

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